Doctoral Thesis

Determination of biogenic and fossil matter in wastes, refuse-derived fuels and other plastic-containing mixtures – Potentials and limitations

submitted in satisfaction of the requirements for the degree of Doctor of Science of TU Wien, Faculty of Civil Engineering

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Dissertation

Bestimmung des biogenen und fossilen Anteils in Abfällen, Ersatzbrennstoffen und anderen Gemengen mit Kunststoffanteilen – Potentiale und Einschränkungen

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der Naturwissenschaften eingereicht an der Technischen Universität Wien, Fakultät für Bauingenieurwesen von

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Vienna, August 2018

Acknowledgments

First of all, I would like to thank my supervisor, Assoc. Prof. Dr. Johann Fellner, with a thank-you which should express my deepest appreciation and gratitude for his guidance and encouragements throughout the last five years. He offered inspiring ideas, space for my own initiatives and has always been available when help was needed. Without his belief in my abilities and his persistence, this thesis would never have been written. I sincerely hope that you are pleased with the ”gift”, in the end I do believe that it’s also a gift for myself.

I appreciate the contribution of Prof. Dr. Thomas Fruergaard Astrup and Prof. Dr.-Ing. Sabine Flamme as the co-supervisors of this thesis.

I want to express my gratitude to the helping hands in the laboratory and in the field, Philipp Aschenbrenner, Stefan Spacek and Manuel Hahn, who provided essential work and advice for the writing of this thesis. I always enjoyed working in the laboratory, escaping from the abstract office environment and immersing myself in hands-on activities.

Many thanks to my “buddy” and friend, Verena Trinkel, for scrutinizing my work and providing constructive inputs. You are missed! Thanks to Oliver Cencic for his efforts to meet my BIOMA-wishes and his patience in explaining the software, and to Christian Brandstätter for his support with statistics in R. My appreciation also goes to David Laner for his rare advice (for which I am entirely to blame), but which was always precisely what was needed to go forward. I also thank Jakob Lederer for giving me the opportunity to broaden my field of expertise and expand my future research work into foreign countries (inshallah). After five years in the same office, I hope your unique spirit and lightness has rubbed off on me at least to a small extent. Also thanks to Fritz and Dana, my other long-term office mates, and to Florian, my new neighbour, for a great place to work, inspiring talks and for disentangling my confused thoughts once in a while. To Florian I am additionally thankful for bringing me to the point to set a (joint) date for graduation. Thanks to Inge for her graphical support and prompt availability.

Many thanks also to all other colleagues accompanying me during my work at the institute. You all contributed to the pleasant working environment with your cheerful spirits and generous doses of laughter. During countless coffee and lunch breaks, conference visits, excursions and after-work beers you all did your bit to bring me forward in my professional and personal development and to deepen my critical scientific thinking. Moreover, I would like to mention Andi, Fritz, Hans, Dominik, Rainer, Emile,

Manuel, Sabine, Stefan and Alexej: it was my pleasure to refresh my mind between sessions of work by playing all of the table soccer games.

I want to thank Prof. Dr. Helmut Rechberger for the opportunity to carry out this thesis at the Institute for Water Quality and Resource Management and for his valuable contributions.

The thesis was conducted with the financial support offered by the Federal Ministry for Sustainability and Tourism and the Austrian Science Fund (FWF), project number TRP 285-N28, which is gratefully acknowledged. I am also grateful for the possibility to conduct parts of the work within the large-scale research initiative on anthropogenic resources (Christian Doppler Laboratory for Anthropogenic Resources). The financial support of this research initiative by the Federal Ministry for Digital and Economic Affairs and the National Foundation for Research, Technology and Development is gratefully acknowledged. Thanks to the Lions Club Wien St. Stephan for granting me additional financial support.

My gratitude further goes to the Waste-to-Energy plant operators in Austria for their part in providing data, supporting the work and putting up with my gnawing questions. Many thanks also to the operators of the RDF plants and engaged members of the paper & board plant for their support and assistance for drawing samples. Moreover, I gratefully acknowledge the contributions to this thesis from Sönke Szidat and Edith Vogel from the University of Bern by providing excellent work on radiocarbon analysis and by improving the paper through critical reviews.

I would like to dedicate this thesis to my grandfather, Martin Schwarzböck, who survived poverty, battlefields and the ever accelerating digital age society, and who is well on his way to reaching hundred years of age. I admire your tenaciousness and achievements in life. I sincerely thank you and also my mother, Lucia, and my father, Nikolaus, for believing in me and supporting my every step of the way in life. I am also grateful to my unique siblings, Tofana, Luise, Julia and Philipp, and also to my "step-siblings", Eva, Bernd and Christian; all of you have been there for me, encouraging me over the years and discussing with me my challenges in work. A heartfelt thanks to all my family and friends who enrich my life and who I believe have all contributed to me finishing this Ph.D. Finally, a special thanks to Adrian, who has been immensely supportive during all the ups and downs over the past years, enduring my stressed moments, late-night shifts and offering encouraging words whenever needed.

Abstract

Mixed combustible wastes and refuse-derived fuels (RDF) usually consist of both biogenic and fossil materials. To report climate-relevant CO_2-emissions or declare the share of renewable energy recovered in Waste-to-Energy (WtE) plants or in industrial processes, it is necessary to distinguish between the biogenic and fossil origins of the utilized waste components. In recent years different methods have been developed for this purpose. Standardized methods are: Manual Sorting (MS), the Selective Dissolution Method (SDM), the Radiocarbon Method (^{14}C-Method), and the **Balance Method** (**BM**). The BM is based on the evaluation of WtE plant operating data and is already applied in several WtE plants in Europe. The BM was further developed into the **adapted Balance Method** (**aBM**), which is applicable to waste samples and evaluates data on the elemental composition of the samples. The feasibility of the aBM in practice has, however, not been demonstrated yet.

The objective of the present thesis is to assess the BM and the aBM in terms of their feasibility, versatility, and reliability with respect to two major fields of application:

(A) Large-scale application of the **BM** to examine the eligibility of the method and to exploit further applications of BM-generated data. Operating data of 10 Austrian WtE plants are evaluated over a period of one year. Different parameters are derived: i.a. fossil CO_2-emission factors (EF), the ratio of biogenic energy from waste (q_B) or the plastic content ($x_{plastic}$).

(B) Characterization of artificially prepared RDF model mixtures as well as real RDF samples by means of the **aBM**. Performance data of the aBM are generated, indicating the validity of the method and providing the basis for standardization.

The results related to **(A)** show that with the aid of the **BM**, almost 90 % of the waste utilized in Austrian WtE plants annually could be characterized in terms of its composition. This represents a “sample size” which can hardly be achieved by any other method. Generated annual means for the WtE plants as well as monthly mean values at plant-level cover a wide range for all parameters considered. This indicates a strong variability of the waste composition, which is believed to be influenced by varying RDF demand of the cement industry, downtime periods of other WtE plants, or regional differences in waste collection. The observations clearly illustrate that the usage of an empirical value for EF or q_B for WtE plants is problematic and can easily lead to significant misestimations of relevant data (by up to 40 % at plant-level). Similarly, it can be assumed that data on the plastic content in mixed waste, generated by sorting campaigns, leads to distorted estimates. Detailed information on the share of plastics

in the feed of WtE plants, easily derived by applying the BM, represents valuable information when overall waste plastics generation and its utilization paths have to be assessed. Furthermore, the results reveal that temporally high-resolution data of the waste composition could be used to trace back insufficient mixing of the waste feed. In addition, the mandatory plausibility checks of the BM can support error detection in the operating data of WtE plants.

The investigations related to **(B)** represent the first in-depth assessment on the performance of the **aBM**. Based on the aBM-determined share of fossil carbon (x_F^{TC}), an absolute deviation from the reference value of below $\pm$ 3.6 % can be asserted. The comparison of aBM-generated values to results of MS and the SDM reveals that the aBM is the only method for which, independently of the RDF, low deviations and good correlations with the ^{14}C-Method are observed. A more extensive sample preparation is expected for the aBM compared to MS and the SDM. This is due to the aBM relying on elemental analysis where only a few centrigrams of sample can be measured. By means of a variance component analysis, it is shown that the drawing of test specimens from the analysis sample considerably affects the total variation of aBM-results. A usage of different grinding mechanisms can be recommended for the sample preparation to ensure a low heterogeneity of the test specimens. A further crucial factor for the application of the aBM is the choice of the necessary input values – the elemental composition of the water-and ash-free fossil and biogenic matter present in the RDF (TOX_F and TOX_B). These values are ideally generated specifically for an RDF by means of initial manual sorting and analyses. Thereby the highest accuracy of the aBM-results can be expected. However, the thesis shows that TOX_F and TOX_B values derived for 6 different RDFs are in a close range. This indicates that in future workload could be saved once a suitable data base about TOX_F and TOX_B values present in different types of RDFs is available. Finally, to conclude on the practicability of the aBM in comparison to standardized methods, the aBM presents itself as competitive with MS, the ^{14}C-method and also to the commonly applied SDM in terms of workload and costs.

The thesis shows that both the BM and the aBM are practicable methods to determine the fossil and biogenic fraction in mixed waste and RDFs. Both methods are competitive with other standardized determination methods such as the ^{14}C-method, MS, or the SDM. The BM stands out by virtue of its unique capability to deliver data at a high temporal resolution, data which can in future also be exploited for other purposes. The investigations into the performance of the aBM presented clearly illustrate that this method is fit for practical application and can support the formulation of a standard procedure. A transferability of the principle to environmental samples (e.g. mircoplastics content in water samples) is demonstrated and will be the subject of future investigations. Forthcoming research activities should further address the reproducibility of the aBM when applied by different laboratories and should push for a collection of data on the elemental composition of fossil and biogenic matter present in different RDF types.

Kurzfassung

Brennbare Abfälle und daraus produzierte Ersatzbrennstoffe (EBS) stellen zumeist ein Gemisch aus biogenen und fossilen Materialien dar. Um daher bei ihrer thermischen Verwertung die fossilen CO_2-Emissionen bzw. den Anteil erneuerbarer Energie auszuweisen, ist eine Unterscheidung zwischen fossilen und biogenen Abfallbestandteilen nötig. Zu diesem Zweck wurden verschiedene Bestimmungsmethoden entwickelt. Bereits standardisierte Methoden sind: Manuelle Sortierung (MS), die Selektive Lösemethode (SLM), die Radiokarbonmethode (^{14}C-Methode) und die **Bilanzenmethode** (**BM**). Die BM beruht auf der Auswertung von Betriebsdaten von Müllverbrennungsanlagen (MVA). Eine Weiterentwicklung der BM stellt die **adaptierte Bilanzenmethode** (**aBM**) dar. Diese basiert auf der Analyse der Elementarzusammensetzung von Abfallproben. Die praktische Anwendbarkeit der aBM wurde bisher noch nicht geprüft.

Das Ziel der Arbeit ist daher, die BM und die aBM in Bezug auf ihre Anwendbarkeit, Zuverlässigkeit und Flexibilität zu untersuchen, wobei zwei wesentliche Verwendungsbereiche unterschieden werden:

(A) Anwendung der **BM** auf nationaler Ebene um ihre Eignung im großen Maßstab und weiterführende Verwertungsmöglichkeiten der generierten Daten zu untersuchen. Betriebsdaten von 10 Österreichischen MVAn werden über ein Jahr gemäß BM ausgewertet und verschiedene Parameter generiert: u.a. fossile CO_2-Emissionsfaktoren (EF), biogene Heizwertanteile (q_B) und Kunststoffanteile.

(B) Charakterisierung von definierten Abfallgemischen und realen EBS Proben anhand der **aBM**. Leistungsmerkale der aBM werden generiert, die die Gültigkeit der Methode beschreiben und die als Basis für eine zukünftige Standardisierung dienen.

Ergebnisse betreffend **(A)** zeigen, dass fast 90 % des jährlich in österreichischen MVAn verwerteten Abfalls mittels **BM** charakterisiert werden konnte. Ein derart großer „Probenumfang“ ist mit keiner der anderen Bestimmungsmethoden möglich. Für alle betrachteten Parameter weisen die generierten Daten ausgeprägte Streubreiten auf, sowohl zwischen den einzelnen Anlagen als auch im Jahresverlauf. Dies weißt auf eine starke Variabilität der Abfallzusammensetzung hin, die unter anderem durch saisonabhängigen EBS Bedarf der Industrie, Stillstandszeiten anderer MVAn oder regionale Unterschiede im Abfallsammelsystem zu erklären ist. Die Beobachtungen zeigen somit, dass die Verwendung von allgemeinen Werten zu EF oder q_B zu wesentlichen Fehleinschätzungen führen kann. Ebenso können nur sporadisch durchführbare Sor-

tieranalysen den Kunststoffgehalt in Abfällen falsch beziffern. Detaillierte Informationen zu Kunststoffanteilen im Abfallinput von MVAn sind mittels BM einfach generierbar und stellen wesentliche Daten zur Erhebung der gesamten Kunststoffabfallmengen dar. Zusätzlich zeigen die Ergebnisse, dass mithilfe der BM durch zeitlich hoch aufgelöste Daten über die Abfallzusammensetzung, Perioden unzureichender Abfalldurchmischung detektiert werden können. Ein weiterer Zusatznutzen der BM besteht darin, dass durch die routinemäßig durchgeführten Plausibilitätstests Mess- bzw. Aufzeichnungsfehler der Anlagenbetriebsdaten aufgedeckt werden.

Die durchgeführten Arbeiten gemäß **(B)** stellen die ersten umfassenden Untersuchungen zur Anwendbarkeit der **aBM** dar. Es konnte dabei die Korrektheit der Methode nachgewiesen werden; beispielsweise lag die absolute Abweichung des fossilen Kohlenstoffanteils (x_F^{TC}) vom Referenzwert unter 3.6 %. Ein Vergleich der aBM-Ergebnisse mit jenen von MS und SLM zeigt, dass einzig die aBM für alle betrachteten EBS eine zufriedenstellende Übereinstimmung mit der ^{14}C-Methode liefert. Die Probenaufbereitung für die aBM ist verglichen mit MS und SLM als aufwändiger einzustufen, da die notwendige Elementaranalytik sehr geringe Probenmengen (wenige Zentrigramm) erfordert. Eine Varianzkomponentenanalyse zeigt, dass die Einwaage der Analyseprobe ein wesentlicher Faktor für die Streuung der Messwerte ist. Eine Anwendung unterschiedlicher Mahlprinzipien ist daher zu empfehlen um ausreichend homogene Analysenproben zu erhalten. Ein weiterer wichtiger Punkt für die Anwendung der aBM stellt die Wahl der Eingangswerte zur elementaren Zusammensetzung der fossilen und biogenen Materialien dar (TOX_F und TOX_B). Die Untersuchungen ergeben, dass EBS-spezifisch erhobene Daten zu TOX_F und TOX_B anhand von Sortierungen und Analysen zu hoher Genauigkeit der aBM-Ergebnisse führen. Gleichzeitig zeigt sich jedoch auch, dass die in der Arbeit erhobenen Werte zu TOX_F und TOX_B für 6 verschiedene EBS in einem engen Wertebereich liegen. Sobald eine geeignete Datenbasis verfügbar ist, kann daher Arbeitsaufwand eingespart werden. Die Untersuchungen zur Praktikabilität zeigen, dass die aBM durchaus eine Alternative zu bisher üblichen Methoden ist. Sowohl der Arbeitsaufwand als auch die Kosten sind mit denen der SLM vergleichbar.

Die Arbeit zeigt, dass die BM und die aBM praktikable Bestimmungsmethoden darstellen um den fossilen und biogen Anteil in Abfällen und EBS zu bestimmen. Beide Methoden sind konkurrenzfähig mit standardisierten Methoden. Die BM zeichnet sich im Speziellen durch die Bereitstellung von Daten mit hoher zeitliche Auflösung aus; Daten, die zukünftig auch für andere Zwecke verwertet werden könnten. Die präsentierten Ergebnisse zeigen, dass die aBM in der Praxis angewandt werden kann und ermöglichen die Ausarbeitung einer eigenen Norm. Eine Übertragbarkeit der Methodik auf Umweltproben (z.B. Mikroplastik in Gewässerproben) kann abgeleitet werden und wird Thema zukünftiger Untersuchungen sein. Weitere Forschungsaktivitäten sollten zudem die Reproduzierbarkeit der aBM bei Anwendung in unterschiedlichen Laboren behandeln und auf die Sammlung von Daten zur Elementarzusammensetzung von fossilen und biogenen Materialien in unterschiedlichen EBS abzielen.

Published articles and author's contribution

I Schwarzböck, T., Rechberger, H., Cencic, O., Fellner, J. 2016. **Determining national greenhouse gas emissions from waste-to-energy using the Balance Method**. *Waste Management*, 49, 263-271. DOI:10.1016/j.wasman.2016.01.025

II Schwarzböck, T., Rechberger, H., Cencic, O., Fellner, J. 2016. **Anteil erneuerbarer Energien und klimarelevante CO_2-Emissionen aus der thermischen Verwertung von Abfällen in Österreich** [Share of renewable energy and climate-relevant CO_2 emissions from thermal recovery of waste in Austria]. *Österreichische Wasser-und Abfallwirtschaft*, 68, 415-427. DOI:10.1007/s00506-016-0332-5

III Schwarzböck, T., Eygen, E.V., Rechberger, H., Fellner, J. 2017. **Determining the amount of waste plastics in the feed of Austrian waste-to-energy facilities**. *Waste Management & Research*, 35, 207-216. DOI:10.1177/0734242X16660372

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V Schwarzböck, T., Aschenbrenner, P., Spacek, S., Szidat, S., Rechberger, H., Fellner, J. 2018. **An alternative method to determine the share of fossil carbon in solid refuse-derived fuels – Validation and comparison with three standardized methods**. *Fuel*, 220, 916-930. DOI:10.1016/j.fuel.2017.12.076

VI Schwarzböck, T., Rechberger, H., Aschenbrenner, P., Spacek, S., Szidat, S., Fellner, J. 2018. **Klimarelevanz von Ersatzbrennstoffen – Anwendung und Vergleich verschiedener Bestimmungsmethoden** [Climate relevance of refuse-derived fuels – Application and comparison of different determination methods]. *Österreichische Wasser- und Abfallwirtschaft*, 70, 3-4, 179-193. DOI:10.1007/s00506-018-0466-8

VII Schwarzböck, T., Aschenbrenner, P., Mühlbacher, S., Szidat, S., Spacek, S., Fellner, J. 2018. **Determination of the climate relevance of refuse derived fuels – validity of literature-derived values in comparison to analysis-derived values**. *Detritus*, 02, 120-132. DOI:10.31025/2611-4135/2018.13649

Contribution:

I, II, II	responsible for research design, literature review, data evaluation and writing
IV, V, VI, VII	responsible for research design, literature review, experiment design, experimental work, data evaluation and writing

Related publications and conference contributions

1. Spacek, S., Mallow, O., Schwarzböck, T., Rechberger, H., Fellner, J. 2016. **Cost efficient Quantification of Microplastics**. European Conference on Plastics in Freshwater Environments, 21.-22.06.2016, Berlin, Germany.
2. Schwarzböck, T., Rechberger, H., Fellner, J. 2016. **The added-value of the Balance Method for Waste-to-Energy operators and national authorities**. in: Thomé-Kozmiensky, K.J. and Thiel, S. (Ed.), TK Verlag Karl Thomé-Kozmiensky, IRRC Waste-to-Energy, 05.-06.09.2016, Vienna, Austria.

Contribution:

Conference contribution 1	partly responsible for experiment design and data evaluation
Conference paper 2	responsible for research design, literature review, data evaluation and writing

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List of Abbreviations

%abs	Percent absolute
%rel	Percent relative
aBM	Adapted Balance Method
AMS	Accelerator mass spectrometry
$A_{plastic}$	Ash content of water-free synthetic polymers referred to total mass of the synthetic polymers
A_{waste}	Ash content in the water-free waste
BM	Balance Method
C&I	Commercial and industrial waste
$CHNSO$	Carbon, Hydrogen, Nitrogen, Sulphur, Oxygen
CO_2	Carbon dioxide
$C_{O_{2,B}}$	Carbon dioxide stemming from biogenic materials
$C_{O_{2,F}}$	Carbon dioxide stemming from fossil materials
CV	Coefficient of variation
CW	Commercial waste
C_{waste}	Carbon content in waste
$dev.^{14}C$	Mean deviation from result of ^{14}C-method
df	Degrees of freedom
Diff. between O_2-cons. & CO_2-prod.	Difference between O_2-consumption and CO_2-production during combustion
$d_{O_2-CO_{2,B}}$	Difference between O_2-consumption and CO_2-production during the combustion of biogenic material
$d_{O_2-CO_{2,F}}$	Difference between O_2-consumption and CO_2-production during the combustion of fossil material
$d_{O_2-CO_{2,waste}}$	Difference between O_2-consumption and CO_2-production during the combustion of waste
EF	Fossil CO_2-emission factor
EF_M	Fossil CO_2-emission factor related to unit of mass
EF_Q	Fossil CO_2-emission factor related to unit of energy
$F^{14}C_{bio}$	^{14}C-reference value in biogenic materials
FBC	Fluidized bed combustion
FT-IR	Fourier-transform infrared spectroscopy
GI	Grate incineration

HD-PE	High-density polyethylene
IPCC	Intergovernmental Panel on Climate Change
IW	Industrial waste
LHV_B	Lower heating value of biogenic matter present in the wet waste
LHV_F	Lower heating value of fossil matter present in the wet waste
LHV_{waste}	Lower heating value of wet waste
LSC	Liquid Scintillation counting
MC	Molar weight of carbon
M_{CO_2}	Molar weight of carbon dioxide
MM I	Artificially prepared RDF model mixture I
MM II	Artificially prepared RDF model mixture II
MS	Manual Sorting Method
MS	Mean sum of squares
MSW	Municipal solid waste
N	Number of samples
n	Number of repeated measurements
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
q_B	Share of energy stemming from biogenic sources
q_F	Share of energy stemming from fossil sources
RDF	Refuse-derived fuel
RSD	Relative standard deviation
SD	Standard deviation
SDM	Selective Dissolution Method
σ^2	Variance
SS	Sewage sludge
SS	Sum of Squares
TC_{waste}	Total carbon content in the water-free waste
TIC	Total inorganic carbon content in the water-free ash
TIX_{wf}	Total content of the respective element in water-free ash (with X beeing one of C, H, N, S, or O)
TOC	Total organic carbon on water-and-ash-free basis
TOC_B	Total organic carbon in the water-and-ash-free biogenic matter
TOC_F	Total organic carbon in the wwater-and-ash-free fossil matter
TOC_{waste}	Total organic carbon in the water-and-ash-free waste

TOH	Total organic hydrogen on water-and-ash-free basis
TOH_B	Total organic hydrogen in the water-and-ash-free biogenic matter
TOH_F	Total organic hydrogen in the water-and-ash-free fossil matter
TOH_{waste}	Total organic hydrogen in the water-and-ash-free waste
TON	Total organic nitrogen on water-and-ash-free basis
TON_B	Total organic nitrogen in the water-and-ash-free biogenic matter
TON_F	Total organic nitrogen in the water-and-ash-free fossil matter
TON_{waste}	Total organic nitrogen in the water-and-ash-free waste
TOO	Total organic oxygen on water-and-ash-free basis
TOO_B	Total organic oxygen in the water-and-ash-free biogenic matter
TOO_F	Total organic oxygen in the water-and-ash-free fossil matter
TOO_{waste}	Total organic oxygen in the water-and-ash-free waste
TOS	Total organic sulphur on water-and-ash-free basis
TOS_B	Total organic sulphur in the water-and-ash-free biogenic matter
TOS_F	Total organic sulphur in the water-and-ash-free fossil matter
TOS_{waste}	Total organic sulphur in the water-and-ash-free waste
TOX_B	Elemental composition of the water-and-ash-free biogenic matter (with X beeing one of C, H, N, S, or O)
TOX_F	Elemental composition of the water-and-ash-free fossil organic matter (with X beeing one of C, H, N, S, or O)
TOX_{RDF}	Elemental composition of the water-and-ash-free RDF (with X beeing one of C, H, N, S, or O)
TOX_{wood}	Elemental composition of the water-and-ash-free wood (with X beeing one of C, H, N, S, or O)
TX_{wf}	Total content of the respective element in water-free sample (with X beeing one of C, H, N, S, or O)
UCM	Ultracentrifugal mill
VCA	Variance component analysis
$V_{O_{2,B}}$	O_2-consumption of biogenic matter during combustion
$V_{O_{2,F}}$	O_2-consumption of fossil matter during combustion
$V_{O_{2,waste}}$	O_2-consumption of waste during combustion
waf	Water-and-ash-free
wf	Water-free
wt%	Weight percent
WtE	Waste-to-Energy
W_{waste}	Water content of waste
$x_{plastic}$	Plastic content (synthetic polymers) referred to wet waste
x_B	Mass fraction of water-and-ash-free biogenic matter referred to wet waste

$x_{B,waf}$	Mass fraction of water-and-ash-free biogenic matter referred to water-and-ash-free waste
$x_{B,wf}$	Mass fraction of water-and-ash-free biogenic matter referred to water-free waste
x_B^{TC}	Share of biogenic carbon referred to total carbon content
x_F	Mass fraction of water-and-ash-free fossil matter referred to wet waste
$x_{F,waf}$	Mass fraction of water-and-ash-free fossil matter referred to water-and-ash-free waste
$x_{F,waf,theory}$	Theoretical (true) value of the mass fraction of water-and-ash-free fossil matter referred to water-and-ash-free waste
$x_{F,wf}$	Mass fraction of water-and-ash-free fossil matter referred to water-free waste
$x_F^{CO_2}$	Share of fossil CO_2 related to the total CO_2 emitted during combustion
x_F^{TC}	Share of fossil carbon referred to total carbon content
$x_{F,^{14}C}^{TC}$	Share of fossil carbon as determined by the ^{14}C-method
$x_{F,aBM}^{TC}$	Share of fossil carbon as determined by the adapted Balance Method
$x_{F,theory}^{TC}$	Theoretical (true) value of the share of fossil carbon
x_I	Mass fraction of inert material referred to wet waste
$\overline{x}$	Mean value
x_W	Mass fraction of water referred to wet waste

1 Introduction

Waste materials are increasingly utilized in Waste-to-Energy plants (WtE plants) or in energy-intensive industrial processes as refuse-derived fuels (RDF). Thermal recovery in WtE plants and of RDF facilitates effective destruction of hazardous organic substances, reduction of waste volumes by one order of magnitude, and contributes positively to a low carbon energy supply. Together with century-long developments of thermal processes, which led to sophisticated air pollution technology, thermal recovery of waste has become an essential part of sustainable waste management. Innovations in metal recovery from residues of the waste incineration are leading to WtE becoming an important tool for material recovery[13–15]. The developments in WtE and RDF-utilization are supported by a number of initiatives and regulations at a national, supranational, and international level aiming at resource conservation, an efficient utilization of resources from waste materials or at combating climate change. Established policies include renewable energy targets (e.g. EU-Renewable Energy Directive 2009/28/EC[16], Renewable Obligation Certificates in the UK[17]), the diversion of waste from landfills and targets on recycling and recovery (e.g. EU-Landfill Directive[18], Waste Avoidance and Resource Recovery Strategy for New South Wales[19], EU-Waste Framework Directive 2008/98/EC[20], 2018 Circular Economy package of the EU[21], UK Producer Responsibility Obligation[22]) and incentives to reduce greenhouse gas emissions (e.g. EU-Directive on greenhouse gas emission trading 2009/29/EC[23], Chinas national emission trading System[24], Egyptian coal regulations[25]). The implementation of the Kyoto-protocol further stimulates the use of biomass-containing alternative fuels. In Austria the increased thermal utilization of waste has been facilitated by the Austrian landfill directive, which bans the disposal of waste with total organic carbon content larger than $50\,\mathrm{g\,kg^{-1}}$ or a lower calorific value above $6.6\,\mathrm{MJ\,kg_{waste}^{-1}}$[26,27]. This ban, which came into full effect in 2008, led to a strong increase in the share of thermally recovered municipal solid waste (MSW) in Austria. In 1999 around 17 % and in 2015 around 43 % of the total MSW generated in Austria was fed into WtE plants[28,29].

For the utilization in industrial processes (e.g. in cement or steel production processes), waste materials of high calorific value such as plastics, paper, cardboard or textiles present in MSW, commercial waste (CW) and industrial waste (IW) are separated in mechanical or mechanical-biological treatment plants. Thereby RDFs are produced with a heating value of up to $25\,\mathrm{MJ\,kg^{-1}}$[30,31]. The prime example amongst the industries utilizing RDFs is the cement industry, where in some plants the major part of the energy demand is already covered by RDFs. Substitution rates of conventional fuels of 80 % in Austria in 2017, 65 % in Germany in 2016, 60 % in Belgium in 2011, 54 % in Switzerland in 2014, and above 34 % within the European Union are reported[32–35]. In the course of this shift of waste treatment – from landfilling to thermal recovery – a drastic reduction of organic waste being landfilled could be documented. Significantly declining methane emissions from landfilling are reported (reduction by above 30 % from 1999 to 2015[36]). At the same time, an upward trend in carbon dioxide emissions from WtE is discernible. Carbon dioxide (CO_2) has a lower global warming potential than methane, but needs to be accounted for in greenhouse gas inventories, reduction commitments and emission trading schemes. The accounting needs to consider the biogenic-based (biomass) and the fossil-based materials which are typically both present in mixed waste (and particularly in MSW). CO_2-emissions stemming from fossil matter (like polymers produced out of crude oil) are accounted for as climate-relevant, whereas CO_2 from biogenic matter (such as paper, cardboard, natural textiles) are regarded as carbon neutral. Thus, plant operators need to assess the respective share of fossil CO_2 emitted through the thermal utilization of waste or RDF. The fossil CO_2 from waste fuels is usually expressed as a fossil CO_2-emission factor (EF). An EF relates the amount of emitted CO_2 to the waste mass or to the heating value of the waste. This allows the direct comparison of the climate-relevance of waste fuels with conventional fuels (for which the EF are known and fairly constant). Analogous to the share of fossil CO_2-emissions, the recovered energy during thermal treatment originates either from fossil energy carriers or from biomass (biogenic material) and is usually expressed as a percentage of the total energy content of the waste.

With respect to greenhouse gas emissions from waste, the biogenic carbon contained in waste can be of interest. The biogenic carbon content can also be translated into degradable organic carbon in waste. The degradable fraction of carbon is potentially available for degradation processes under anaerobic conditions as they typically prevail in landfills. Thus, information on the biogenic carbon in waste can support the estimation of landfill gas generation[37,38].

To distinguish between the fossil and biogenic share in waste mixtures, different approaches are possible, e.g. manual sorting of the waste mixture into fossil and biogenic components, chemical dissolution of biogenic components in a waste sample, determining fossil and modern carbon in a waste sample by means of radiocarbon analysis, or setting up mass and/or energy balances in WtE plants to calculate the respective mass shares. These approaches have been investigated[39–42] and, subsequently, three methods have been described in a standard for solid recovered fuels (EN 15440:2011)[43]: Manual Sorting (MS), the Selective Dissolution Method (SDM) and the Radiocarbon Method (^{14}C-method). The Balance Method (BM) has been elaborated for application in WtE plants[2,44,45] and has recently been described in the standard ISO 18466:2016[46]. Furthermore, an adapted version of the BM has been developed (adapted Balance Method), which is applicable to mixed solid waste and RDF samples[47]. The motivation for the development of the adapted version of the

BM arose from the need of RDF producers and cement plant operators to characterize the RDFs already before their combustion (which is not possible by applying the BM since it relies on operating data and is not applicable to cement plants). By utilizing commonly applied elementary analyses techniques, the principle of the BM could be transferred to an application in the laboratory. By applying the adapted Balance Method (aBM), a potential reduction in analysis costs compared to laboratory-based standardized methods was expected. Moreover, other benefits compared to standardized methods, such as increased reliability, robustness and accessibility of the method was suspected by the method developers. Preliminary investigations show promising results of the aBM, delivering accurate data when artificially prepared mixtures are tested[47,48]. However, only very simple material mixtures (two components at low grain sizes) have been assessed until now and no information on the applicability of the aBM when applied to real RDFs is available. Analytical characterization of RDFs in the laboratory can easily be impaired by sample handling (e.g. sample preparation techniques) as they are usually complex and heterogeneous mixtures. Thus, further performance data on the aBM need to be collected before an application in practice or a standardization of the method can be contemplated. Information on the performance (e.g. expected accuracy, precision, robustness) is a prerequisite necessary to fully validating the method. Furthermore, comparisons with standardized methods, also in terms of practicability (analysis duration, costs, etc.), provide valuable information which aids practitioners in choosing an appropriate method.

The principle of the BM and the aBM is not limited to the application to mixed waste or refuse-derived fuels, but could potentially be used for all mixtures whose constituents can theoretically be divided into mass fractions with distinct known elemental compositions (or other characteristics in which the mass fractions significantly differ). Thus, the application of the aBM to environmental samples for the purpose of detecting the plastic content has been identified as an additional potential field of application. This is due to the expectation that plastics in environmental samples differ in their composition compared to the biogenic matrix (biogenic matrix can be algae, cellulose, lignin, proteins, etc.). The transfer to this field is motivated by the fact that no harmonized method is available yet to quantify plastic pollution in the environment. In particular, microplastic quantification poses a challenge in terms of the application of analytical methods due to small particle sizes. Currently applied methods rely on classic light microscopy or a combination with FT-IR or Raman spectroscopy. These techniques are, however, limited to larger particles or only allow for particle counting rather than mass detection[49–51]. Thus, the aBM could support detection of plastic flows accumulating in the environment, an issue of increasing environmental, political, and public relevance.

2 Objectives

The thesis pursues the goal of assessing the aBM in depth for its applicability as an alternative method to determine the biomass content in solid waste and in plastic-containing mixtures. Performance data of the aBM are to be generated in order to provide practitioners with valuable information on the validity of the method and to create the basis for future standardization. The BM was recently standardized and is already applied in several WtE plants. Still, research questions remain concerning the versatility of BM-generated data for reporting and monitoring the waste composition and with respect to the usefulness for plant operators. Thus, the possibilities provided by the BM and by the aBM are to be exploited in detail within the thesis.

The thesis therefore addresses the following research questions:

(1) Is the BM eligible for nationwide application and which lessons can be learned by large-scale investigations?

(2) What is the added-value for plant operators by applying the BM? Are there further exploitation possibilities of BM-results and what are further development options of the method?

(3) How reliable is the aBM? – Does it deliver true values? How precise are the results?

(4) What are the potential effects of interferences impairing the aBM-results? Particularly with regards to sample preparation: Is there a critical sample preparation step? And with regard to the generation of the aBM-input parameter: Is it necessary to derive RDF-specific input-values?

(5) What is the performance of the aBM compared to standardized methods?

(6) Is the application of BM and aBM practicable? What are the benefits and drawbacks compared to standardized methods?

(7) What are the development options of the aBM in terms of potential applicability to other plastic-containing mixtures (other than waste and RDFs)?

In order to answer research questions (1) to (2), the BM is applied on a large scale. The operating data of 10 Austrian WtE plants are evaluated over a period of one year. Different parameters characterizing the waste are derived for each WtE plant, i.a. the mass share of fossil and biogenic materials in the waste, the share of fossil carbon and climate-relevant CO_2-emissions, fossil CO_2-emission factors, the ratio of biogenic energy from waste, or the plastic content in the waste. Experience acquired by this large-scale application are used to explore the potentials and limitations of the BM. The results are used to draw conclusions on temporal and spatial differences in waste composition, on the national greenhouse gases from WtE in Austria and on the amount of waste plastics thermally recovered in Austria.

To tackle the research questions (3) to (6) regarding the laboratory-based method (aBM), extensive investigations are conducted based on artificially prepared RDF model mixtures and on "real" RDF samples. RDF model mixtures are used to determine the trueness and precision of the aBM-results and to evaluate the influence of different sample preparation steps on the result. By applying the aBM to real RDF samples, the robustness of the required input data for a routine application of the aBM is assessed. Among other investigations, different options to derive necessary aBM-input data are explored in order to identify approaches to reduce the workload connected with the aBM. Moreover, comparisons of aBM-results to values obtained by standardized methods are conducted. This is to evaluate their congruence and to appraise the trueness of the aBM-data generated. Finally, the different determination methods are also compared in terms of practicability and feasibility for routine application.

By investigating an industrial effluent, first tests on applying the aBM to other plastic-containing materials are conducted (thereby answering research question (7)).

Table 2.1 presents an overview of the peer-reviewed papers and conference contributions where the investigation results are compiled. Four of the listed papers (*Paper I, II, III, and Conference paper 2*) deal with research questions regarding the BM, and five (*Paper IV, V, VI, VII, and Conference contribution 1*) of the manuscripts focus on the validation and development of the aBM.

Table 2.1: Papers which present findings consolidated within the present thesis, focusing either on the BM or on the aBM, and addressing different research questions (referring to the list above).

Paper	Reference	BM	aBM	Addressed research question
Paper I	Schwarzböck et al., 2016b[5]	✓		(1), (2)
Paper II	Schwarzböck et al., 2016c[6]	✓		(1), (2)
Paper III	Schwarzböck et al., 2017[1]	✓		(1), (2)
Paper IV	Schwarzböck et al., 2016a[3]		✓	(3), (4)
Paper V	Schwarzböck et al., 2018a[4]		✓	(3), (5)
Paper VI	Schwarzböck et al., 2018b[8]		✓	(6)
Paper VII	Schwarzböck et al., 2018c[12]		✓	(4)
Conference contribution 1	Spacek et al., 2016[9]		✓	(7)
Conference paper 2	Schwarzböck et al., 2016d[7]	✓		(2)

3 Scientific Background

3.1 Determining the biomass content in waste, refuse-derived fuels and plastic-containing mixtures

Characterizing solid waste and thereof derived materials in a reliable manner is always connected with a variety of challenges. The highly heterogeneous character and the variable and unknown composition of waste are typically the most decisive factors when it comes to the generation of valid characterization values. Sampling, sample preparation, and the analysis method itself can be regarded as most critical sources for errors introduced into the final analysis result[52–54]).

When it comes to determining the fossil and biogenic share in waste and RDF, the following most crucial factors influencing the reliability of generated data can be summarized:

(a) **Distinction between fossil and biogenic**: The distinction between materials which originate from fossil (e.g. crude oil) or from biogenic sources (e.g. from recently grown plants) is not straightforward as the waste materials are not labelled accordingly and the parameters "fossil" and "biogenic" are not determinable with common analytical methods. Thus, the carbon and energy content in the materials cannot be directly labelled as renewable or non-renewable.

(b) **Heterogeneity and complexity**: An increasing usage and development of highly compounded materials for packaging, construction, manufacturing, etc. can be observed. Thus, wastes are not only increasing in mass flow, but also in heterogeneity and complexity[15].

(c) **Limited suitability of existing data**: There are already data collected by different institutions regarding the composition of commingled waste (e.g. by conducting sorting analyses). However, the distinction between fossil and biogenic is typically not ascribed particular importance during sorting campaigns, but the focus is rather on the determination of the share of different aggregated waste fractions (such as biowaste, hygienic products, composite materials, fine fraction, etc.). Thus, when existing data on the fractional composition of waste are used to estimate the "pure" fossil or biogenic share, assumptions are necessary to assign fossil or biogenic shares for each sorted compound. This is particularly crucial as commingled waste often contains a high fraction of mixed compounds which contain both fossil and biogenic materials. Considerable shares of fine particles (below ~ 20 mm) and of composite materials can easily falsify the results when inaccurate assumptions are made (e.g. reported shares of fines range between 9 and 25 wt% and of composites and miscellaneous combustible between 2 and 20 wt% in MSW in Europe[55–61]. Similarly, textiles can either be of natural or synthetic origin, which is hardly visually or analytically distinguishable.

(d) **Sampling**: Representative sampling of commingled waste and thereof derived fuels is particularly challenging due to the highly heterogeneous character of these materials. Many investigations and regulations deal with this topic and try to give guidance (e.g. in Standards EN 14899:2005, ASTM D6009-12, DIN 5438:2015, DS 3077:2013[62–65] or other guiding documents[66–68] and research activities[52,69–72]). Sampling in a less heterogeneous medium, e.g. flue gas of WtE plants, represents a viable alternative[41,73].

(e) **Temporal variation of waste composition**: High temporal variations in waste composition have to be expected due to changing consumption behaviors, seasonal fluctuations in waste production, changing collection systems, etc.[14,44,45,74,75]. Thus, regular investigations and sampling over a longer time period can be required to cover the whole spectrum.

(f) **Regional differences**: Differences in waste composition may also occur due to diverse regional conditions. Composition of MSW, CW and IW and thereof-derived RDF depend generally on the waste collection and sorting schemes, local industries and waste handling practices. Thus, derived values on the waste composition might not be transferable between different regions[74,76–80].

(g) **Behaviour during sample preparation and analysis**: For most analytical methods a small grain size of the sample is required, hence, the samples need to undergo certain comminution steps. Different compounds in solid wastes are strongly heterogeneous with respect to their physical properties and texture and thus may behave differently when it comes to sample comminution. For example, organic matter might be fractionated due to electrostatic effects of cellulose fibers[81], or volatile organic substances might dissipate due to elevated temperatures in the milling chamber[82]. Hence, the sample preparation needs careful attention in order to ensure correct and reproducible analysis results. This is particularly valid when only very small test specimens are required for the analysis (e.g. only a few milligrams)[81,82]. Depending on the composition of the waste sample, an appropriate sample preparation which does not impair the analysis result is required.

(h) **Dependency on water and ash content**: Most characterizing parameters generally depend on the respective water and ash content of the waste and its constituents, e.g. heating value, share of biogenic materials (which are assumed to have a higher ash and water content than fossil materials). The knowledge of the water and ash content is crucial when generating and reporting these parameters.

(i) **Variety of parameters of interest**: For an estimate on the fossil CO_2-emissions, it is required to not only know the mass share of fossil materials, but to consider information on the share of fossil carbon. Analogously, the biogenic share

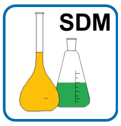
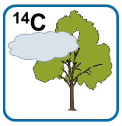
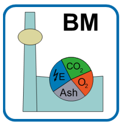
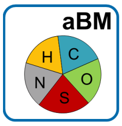
> of the recovered energy needs to be defined, which requires the heating value to be known. Thus, different parameters might need to be assessed, which usually increases the necessary analysis efforts. Table 3.1 lists the most relevant parameters when it comes to the share of fossil and biogenic matter, giving also indications whether they are directly derivable by means of the different determination methods.

All determination methods which aim at estimating the fossil or biogenic share in mixed wastes or RDF generally have to deal with the aspects mentioned. Different approaches of the determination methods available try to overcome certain challenges. Table 3.1 summarizes the principles and characteristics of the different methods, particularly the standardized methods as well as the alternative methods investigated within this thesis: Manual Sorting (MS), the Selective Dissolution Method (SDM), the Radiocarbon Method (^{14}C-Method), the Balance Method (BM) and the adapted Balance Method (aBM). Only the ^{14}C-Method and the BM can avoid the necessity of taking solid (heterogeneous) waste samples – either by taking samples in the flue gas (^{14}C-Method) or by evaluating operating data (BM) ("post-combustion" analysis). When analyses are to be conducted before the thermal utilization (e.g. for characterization of RDFs prior to distribution), MS, the SDM, the ^{14}C-Method, and the aBM can be applied as they rely on an analysis of waste samples in the laboratory ("pre-combustion"). Apart from sampling requirements, the different principles of the methods involve certain methodological and parametrical limitations. For example, MS depends on a person's subjective appraisal when sorting fossil and biogenic materials, certain constituents might be unselectively dissolved when the SDM is applied, and the BM requires all necessary operating data to be available at a certain timely resolution and precision.

Furthermore, certain parameters of interest cannot be directly derived by MS, the SDM, or the ^{14}C-Method. As seen from Table 3.1, only the BM and the aBM can provide all key parameters without additional data or analyses required: including the biogenic and fossil mass share, the fossil carbon share and CO_2-emissions, and the ratio of biogenic energy. A simplified conversion from the biogenic carbon share to the share of biogenic energy (for example for ^{14}C-results) could be contemplated. This could be done by considering a stable ratio between the lower heating value and the carbon content in biomass and in the fossil fraction present in waste; for example, suggested by Fichtner (2007)[41].

Until now the ^{14}C-method has been regarded as the most reliable method due to its analytical accuracy and well-established procedure to detect the ^{14}C in CO_2 of any source[17,42,83]. However, high costs often limit its application in practice.

Table 3.1: Overview of methods to determine the fossil and biogenic share in mixed waste and RDF.

	 **Manual Sorting (MS)**	 **Selective Dissolution Method (SDM)**	 **Radiocarbon Method (¹⁴C-method)**	 **Balance Method (BM)**	 **Adapted Balance Method (aBM)**
Standardized	✓ EN 15440:2011	✓ EN 15440:2011	✓ EN 15440:2011 ASTM D6866	✓ ISO 18466:2016	-
Principle	manual sorting into fossil and biogenic compounds	chemical dissolution of biogenic materials	different ratio of ^{14}C-isotopes in biogenic and fossil fractions	reconciliation of mass-, and energy-balance equations derived from operating data of WtE plants	reconciliation of mass-balance equations for TOC, TOH, TON, TOS, and TOO
Analysis of	solid sample “pre-combustion”	solid sample “pre-combustion”	solid sample or flue gas sample “pre-combustion” or “post-combustion”	operating data “post-combustion”	solid sample “pre-combustion”
Necessary data/analyses	mass share of compounds, biogenic share in each sorted compound, water content	mass & ash content of dissolution residue, ash content, water content	abundance of ^{14}C in sample, $F^{14}C_{\text{bio}}$ reference value	TOX_B, TOX_F, flue gas volume, CO_2-conc. flue gas, O_2-conc. flue gas, steam production, mass of residues, boiler efficiency	TOX_B, TOX_F, TOX_{RDF}, ash content, water content
Additional data/analyses to provide parameters	Carbon and energy content of fossil and biogenic matter in sorted compounds	Carbon and energy content of sample and dissolution residue	Energy content of fossil and biogenic matter		
Parameters determinable:					
mass share (x_F, x_B)	✓	✓	-	✓	✓
carbon share (x_F^{TC}, x_B^{TC}, CO_{2F}, CO_{2B})	(✓)	(✓)	✓	✓	✓
ratio of energy (q_B, q_F)	(✓)	(✓)	(✓)	✓	✓

3.2 Balance Method

The Balance Method relies on the distinctly different elemental composition of fossil and biogenic organic matter (where fossil in this context is understood as materials produced out of crude oil, natural gas or coal). The difference is particularly significant when the elemental composition is related to the water-and-ash-free matter. Thus, the Balance Method considers the total organic carbon (TOC), total organic hydrogen (TOH), total organic oxygen (TOO), total organic nitrogen (TON), and total organic sulphur (TOS). As depicted in Figure 4.4 and Figure 4.2, the main constituent of fossil matter are TOC and TOH (TOC: 430 – 920 mg/kg, TOH: 40 – 140 mg/kg). These components are lower in biogenic matter (TOC: 460 – 520 mg/kg, TOH: 62 – 82 mg/kg), in which TOO represents a main component (with 350 – 470 mg/kg). The elemental composition of fossil and biogenic matter on water-and-ash-free basis – abbreviated in the following as TOX_F and TOX_B – represents the basic input parameter for both the BM and aBM. Based on TOX_F and TOX_B, theoretical balance equations are set up by virtually dividing the waste into four mass fractions: inert (x_I), fossil organic matter (x_F), biogenic matter (x_B), and water (x_W). Figure 3.1 and Figure 3.2 show the simplified balance equations for the BM and the aBM. The BM utilizes five mass balances and one energy balance, each describing a certain waste characteristic (e.g. content of organic carbon, heating value, ash content). The aBM is based on six mass balances related to the elemental composition of the waste. Each balance equation encompasses a theoretically derived term (left side of equations) that has to be attuned to analysis data (right side of the equations). The analysis data are derived from routinely recorded operating data of the WtE plant (BM) or by elemental analyses and ash content determination (aBM). All input data need to be considered together with a corresponding uncertainty. The unknown variables of interest x_F and x_B (BM) or $x_{F,waf}$ and $x_{B,waf}$ (aBM) are contained in the equations. The BM equations additionally consider the water content (x_W) and the ash content (x_I), as the mass fractions refer to the wet waste. This is unlike to the equations of the aBM, where the mass fractions $x_{F,waf}$ and $x_{B,waf}$ refer to water-and-ash-free waste/RDF sample. The set of balance equations is overdetermined (more equations than unknowns). By considering a corresponding uncertainty for all input data, a data reconciliation algorithm based on non-linear optimization can be applied. During data reconciliation, the uncertainties of TOX_F, TOX_B, and of coefficients on the left side are narrowed and the derived values are used to calculate the unknown mass fractions x_F, x_B, x_W (BM), and $x_{F,waf}$ and $x_{B,waf}$ (aBM), including their uncertainties. A detailed mathematical description of the BM is provided in Fellner et al. (2007)[2] and in the Standard ISO 18466:2016[46]. The principle of the aBM is described in Fellner et al. (2011)[47].

The validity of the BM-results have been confirmed already by means of comparative analyses and sensitivity analysis[2,44,45,74]. Excellent agreements and comparable uncertainty ranges between results of the ^{14}C-method and BM-results at WtE plants in Switzerland and Denmark have been reported. The maximum error of the BM-result is observed as being below 8 %rel[47,74].

Mass balance	$x_F +$	$x_B + x_I +$	x_W	=	1	
Ash balance		x_I		=	A_{waste}	Mass of incineration residues
Carbon balance	$TOC_F * x_F +$	$TOC_B * x_B$		=	C_{waste}	Calculated from CO_2-conc. in flue gas
Energy balance	$LHV_F * x_F +$	$LHV_B * x_B$	$- 2.45 * x_W$	=	LHV_{waste}	Calculated from steam production
O_2-consumption	$V_{O_{2,F}} * x_F +$	$V_{O_{2,B}} * x_B$		=	$V_{O_{2,waste}}$	Calculated from O_2-conc. in flue gas
Diff. between O_2-cons. & CO_2-prod.	$d_{O_2-CO_{2,F}} * x_F +$	$d_{O_2-CO_{2,B}} * x_B$		=	$d_{O_2-CO_{2,waste}}$	Calculated from O_2-and CO_2-conc. in flue gas

⇓ ⇓ Coefficients derivable from elemental composition of fossil and biogenic matter (TOX_F and TOX_B)

⇓ Parameters derivable from operating data of WtE plant

Note: LHV represents the lower heating value which can be derived from the elemental composition using empirical equations, e.g. according to Boie, or Dulong, given e.g. in Kost (2001) or Garcés et al. (2016)[55,84].

Figure 3.1: Balance equations of the Balance Method (simplified). x_F and x_B represent the mass fractions of water-and-ash-free fossil and biogenic matter referred to wet waste.

Mass balance	$x_{F,waf}$ +	$x_{B,waf}$	=	1	
Carbon balance	$TOC_F * x_{F,waf}$ +	$TOC_B * x_{B,waf}$	=	TOC_{waste}	Total organic carbon in waste/RDF sample
Hydrogen balance	$TOH_F * x_{F,waf}$ +	$TOH_B * x_{B,waf}$	=	TOH_{waste}	Total organic hydrogen in waste/RDF sample
Oxygen balance	$TOO_F * x_{F,waf}$ +	$TOO_B * x_{B,waf}$	=	TOO_{waste}	Total organic oxygen in waste/RDF sample
Nitrogen balance	$TON_F * x_{F,waf}$ +	$TON_B * x_{B,waf}$	=	TON_{waste}	Total organic nitrogen in waste/RDF sample
Sulphur balance	$TOS_F * x_{F,waf}$ +	$TOS_B * x_{B,waf}$	=	TOS_{waste}	Total organic sulphur in waste/RDF sample

⇓ ⇓ Coefficients derivable from elemental composition of fossil and biogenic matter (TOX_F and TOX_B)

⇓ TOX_{waste} derivable from elemental analysis and ash content determination (Eq. 3.1)

Figure 3.2: Balance equations of the adapted Balance Method (simplified), $x_{F,waf}$ and $x_{B,waf}$ represent the mass fractions of water-and-ash-free fossil and biogenic matter referred to water-and-ash-free waste/RDF sample.

Within the BM and aBM-calculations all data on the elemental composition need to be considered on a water-and-ash-free reference base. This is required to define TOX_F and TOX_B, which are distinct in their differences and which are independent of the water and ash content of the compounds present in fossil and biogenic matter. Moreover, the ash balance can be considered for the calculations. For the aBM, also TOX_{waste} needs to be considered on a water-and-ash-free reference base, which is calculated according to Eq. 3.1.

$$TOX_{waste} = \frac{TX_{wf} - TIX_{wf} * A_{waste}}{1 - A_{waste}} \tag{3.1}$$

whereby TOX_{waste} represents the total organic content of the respective element (with X being one of C, H, N, S, or O) in the water-and-ash-free sample in g $\text{kg}^{-1}_{\text{waf}}$, TX_{wf} the total content of the respective element in the water-free (dry) sample in g $\text{kg}^{-1}_{\text{wf}}$, TIX_{wf} the total inorganic content of the respective element in the water-free ash in g $\text{kg}^{-1}_{\text{wf}}$, and A_{waste} the ash content in the water-free sample in kg $\text{kg}^{-1}_{\text{wf}}$.

Eq. 3.2 to Eq. 3.11 provide the calculations which are necessary to derive different parameters once x_F and x_B, and $x_{F,waf}$ and $x_{B,waf}$, respectively, are determined by data reconciliation based on the equations in Figure 3.1 and Figure 3.2.

The **fossil mass fraction** on a water-free basis ($x_{F,wf}$) can be determined by Eq.(3.2) and Eq.(3.3):

$$x_{F,wf} = \frac{x_F}{1 - x_W} \tag{3.2}$$

$$x_{F,wf} = x_{F,waf} * (1 - A_{waste}) \tag{3.3}$$

Analogously the **biogenic mass fraction** ($x_{B,wf}$) is calculated by Eq.(3.4) andEq.(3.5):

$$x_{B,wf} = \frac{x_B}{1 - x_W} \tag{3.4}$$

$$x_{B,wf} = x_{B,waf} * (1 - A_{waste}) \tag{3.5}$$

whereby $x_{F,wf}$ and $x_{B,wf}$ represent the mass fraction of water-and-ash-free fossil and biogenic matter referred to water-free sample in kg $\text{kg}^{-1}_{\text{wf}}$, x_F and x_B are the mass fraction of water-and-ash-free fossil and biogenic matter referred to wet waste in kg kg^{-1}, $x_{F,waf}$ and $x_{B,waf}$ are the mass fraction of water-and-ash-free fossil and biogenic matter referred to water-and-ash-free sample in kg $\text{kg}^{-1}_{\text{waf}}$, x_W mass fraction of total water referred to wet waste in kg kg^{-1}, and A_{waste} the ash content in the water-free sample in kg $\text{kg}^{-1}_{\text{wf}}$.

As the synthetic polymers are considered to be produced out of crude oil, the fossil fraction (x_F) also represents the **share of plastics** in the waste. By considering typical values for the ash content of plastics (representing the content of inorganic additives and fillers) the fraction of plastics ($x_{plastic}$) in the waste feed can be estimated according to Eq.(3.6):

$$x_{plastic} = \frac{x_F}{1 - A_{plastic}} \tag{3.6}$$

whereby $x_{plastic}$ represents the share of water-free synthetic polymers referred to the wet waste in kg kg^{-1}, x_F is the mass fraction of water-and-ash-free fossil matter referred to wet waste kg kg^{-1}, and $A_{plastic}$ represents the ash content of the water-free synthetic polymers referred to total mass of the synthetic polymers in kg kg^{-1}.

An average value for $A_{plastic}$ of 0.09 ± 0.04 kg kg^{-1} plastics is considered in the thesis based on the national material flow studies of Bogucka & Brunner (2007) and Fehringer & Brunner (1997)[85,86].

Inserting $x_{F,waf}$ and $x_{B,waf}$ into the carbon balance (Figure 3.2), allows the **share of fossil carbon** to be determined (x_F^{TC}):

$$x_F^{TC} = \frac{(x_{F,waf} * TOC_F) * (1 - A) + A * TIC}{TC_{waste}} \tag{3.7}$$

whereby x_F^{TC} represents the fraction of fossil carbon related to the total carbon in $\mathrm{kg\,kg^{-1}}$, TOC_F represents the total organic carbon in the water-and-ash-free fossil matter in $\mathrm{g\,kg^{-1}_{waf}}$, TIC represents the total inorganic carbon in the water-free ash in $\mathrm{g\,kg^{-1}_{wf}}$, and TC_{waste} the total carbon content in the water-free sample in $\mathrm{g\,kg^{-1}_{wf}}$. The share of biogenic carbon x_B^{TC} is then defined as:

$$x_B^{TC} = 1 - x_F^{TC} \tag{3.8}$$

When the heating value is determined via empirical equations utilizing the elemental composition, e.g. equations according to Boie or Dulong[55,84], the **ratio of energy originating from biogenic sources** can also be derived:

$$q_B = \frac{LHV_B * x_B}{LHV_B * x_B + LHV_F * x_F} \tag{3.9}$$

whereby q_B represents the share of energy content stemming from biogenic sources in $\mathrm{MJ\,MJ^{-1}}$, LHV_B and LHV_F is the lower heating value of the biogenic matter and the fossil matter present in the wet sample in $\mathrm{MJ\,kg^{-1}}$, and x_B and x_F represent the mass fractions of water-and-ash-free biogenic and fossil matter referred to the wet sample in $\mathrm{kg\,kg^{-1}}$.

Fossil CO_2-emission factors (EF) can be derived, expressing the mass of climate-relevant CO_2 (CO_{2F}) emitted per unit mass or unit energy content:

$$EF_M = TC_{waste} * x_F^{TC} * \frac{M_{CO_2}}{M_C} * (1 - W_{waste}) \tag{3.10}$$

$$EF_Q = \frac{TC_{waste} * x_F^{TC} * \frac{M_{CO_2}}{M_C} * (1 - W_{waste})}{LHV_{waste}} \tag{3.11}$$

whereby EF_M is the fossil CO_2-emission factor per unit mass in $\mathrm{kg_{CO_2,F}\,t^{-1}}$, EF_Q is the fossil CO_2-emission factor per unit energy content in $\mathrm{kg_{CO_2,F}\,GJ^{-1}}$, and LHV_{waste} is the lower heating value of the wet waste in $\mathrm{GJ\,t^{-1}}$, and M_{CO_2} and M_C are the molar weights of CO_2 and carbon, respectively in $\mathrm{g\,mol^{-1}}$.

4 Materials and Methods

4.1 Determination of the elemental composition of fossil and biogenic matter

As described in section 3.2, the BM as well as the aBM require information on the elemental composition of the water-and-ash-free organic fossil and of the water-and-ash-free biogenic matter present in the waste-mixture (TOX_F, TOX_B). The following options to determine TOX_F and TOX_B are applied:

(a) Collection of necessary information from literature and statistical data (used for the application of the BM to WtE plant operating data)

(b) Determination by manual sorting together with elemental analyses and ash content determination of the sorted compounds (done for the investigations of the aBM)

(c) Combination of **(a)** and **(b)** (done for the investigations of the aBM and application of the aBM to real RDFs)

Option (a) is chosen for the application of the BM at WtE plants in Austria. Information on TOX_F and TOX_B in MSW and CW are based on collected data by Fellner et al. (2007)[2] and are amended with more previously reported figures. Data on the composition of mixed waste (MSW and CW) are derived from sorting campaigns carried out in Austria[58,59,87–89]. Extensive investigations on the characterization of mixed MSW carried out by Kost (2001)[55] deliver data on the elemental composition of different waste fractions. Additionally, consumption data of polymers are considered[90]. It is assumed that there is a typical composition of fossil and biogenic matter in mixed waste in Austria utilized in WtE plants. Figure 4.1 shows that biogenic matter in mixed waste is basically composed out of paper, cardboard, hygienic articles, wood, kitchen waste, garden waste, and natural fibers (textiles). Figure 4.3 depicts the fractional composition of fossil organic matter (waste plastics) derived in mixed waste in Austria. Polyethylene and polypropylene (PE and PP) constitute the main compounds amongst the polymer types (around 60 wt%). The relative shares of the waste fractions in fossil and in biogenic matter are combined with data on the elemental composition of the different fractions (content of carbon, hydrogen, oxygen, nitrogen, sulphur and chlorine) (Figure 4.2 and Figure 4.4). This allows the ranges for the elemental composition of the fossil and the biogenic matter to be derived. Thereto Monte Carlo simulations have been applied. Eq.(4.1) and Eq.(4.2) present exemplary the equations for the derivation of the carbon content in fossil and in biogenic matter.

$$TOC_{F_i} = \frac{\sum_{k=1}^{k=n} TOC_{F_i}^k * f_{F_i}^k}{\sum_{j=1}^{k=n} f_{F_i}^k} \tag{4.1}$$

$$TOX_{B_i} = \frac{\sum_{k=1}^{k=n} TOC_{B_i}^k * f_{B_i}^k}{\sum_{j=1}^{k=n} f_{B_i}^k} \tag{4.2}$$

whereby, TOC_{F_i} represents the total organic carbon in the water-and-ash-free fossil matter for simulation run i in $\mathrm{g\,kg_{waf}^{-1}}$, $TOC_{F_i}^k$ represents the total organic carbon in the water-and-ash-free fossil compound k for simulation run i in $\mathrm{g\,kg_{waf}^{-1}}$, and $f_{F_i}^k$ the relative share of the water-and-ash-freee fossil compound k in the total water-and-ash-free fossil matter (e.g. share of polyethylene, polypropylene, polystyrol, etc.) for simulation run i in $\mathrm{kg_{waf}\,kg_{waf}^{-1}}$. With the same procedure for biogenic matter, whereby TOC_{B_i} represents the total organic carbon in the water-and-ash-free biogenic matter for simulation run i in $\mathrm{g\,kg_{waf}^{-1}}$, $TOC_{B_i}^k$ represents the total organic carbon in the water-and-ash-free biogenic compound k for simulation run i in $\mathrm{g\,kg_{waf}^{-1}}$, and $f_{B_i}^k$ the relative share of the water-and-ash-free biogenic compound k in the total water-and-ash-free biogenic matter (e.g. wood, paper, kitchen waste, etc.) for simulation run i in $\mathrm{kg_{waf}\,kg_{waf}^{-1}}$.

Option (b) is chosen to determine TOX_F and TOX_B for the artificially prepared RDF model mixtures, which are investigated to determine the trueness and repeatability of the aBM. The exact share of each compound in the RDF model mixtures is known because it is mixed correspondingly and the elemental composition of each compound is determined by analyses and by applying Eq.(4.1). Thus, as for option **(a)**, information on the relative shares of the single compounds in the fossil or biogenic matter are combined with the respective TOC-, TOH-, TOO-, TON- and TOS-content of the different fossil or biogenic compounds (which are analytically derived). Eq.(4.1) and Eq.(4.2) are applied without simulation runs i, deriving TOX_F and TOX_B in the RDF model mixtures.

Option (c), where analysis data are combined with literature values to derive TOX_F and TOX_B, is applied for the investigations with real RDF samples. The procedure is defined after in depth-investigations comparing the validity of literature-derived data with analysis-derived data (investigations described in *Paper VII*).

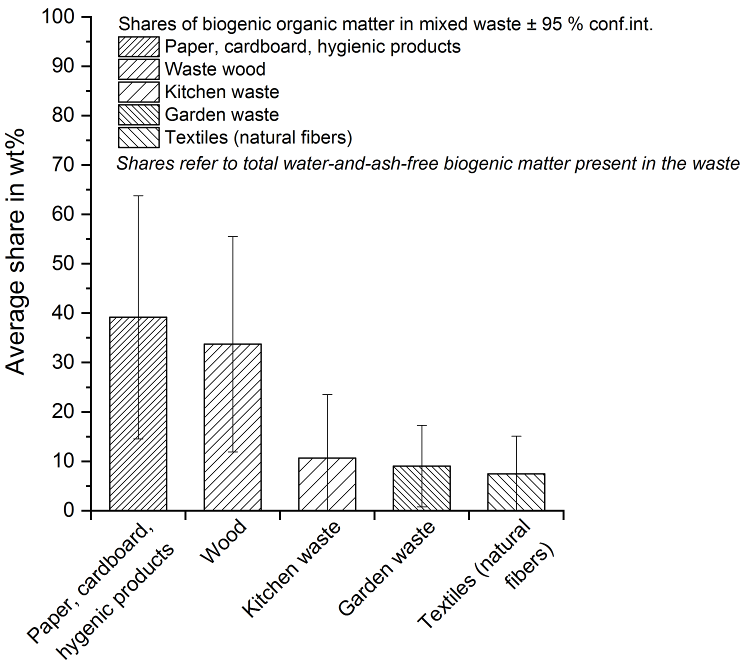


Figure 4.1: Shares of different biogenic compounds present in mixed waste (MSW and CW) in Europe (referred to water-and-ash-free biogenic matter) (based on Figure 3 in *Paper III*[1]).

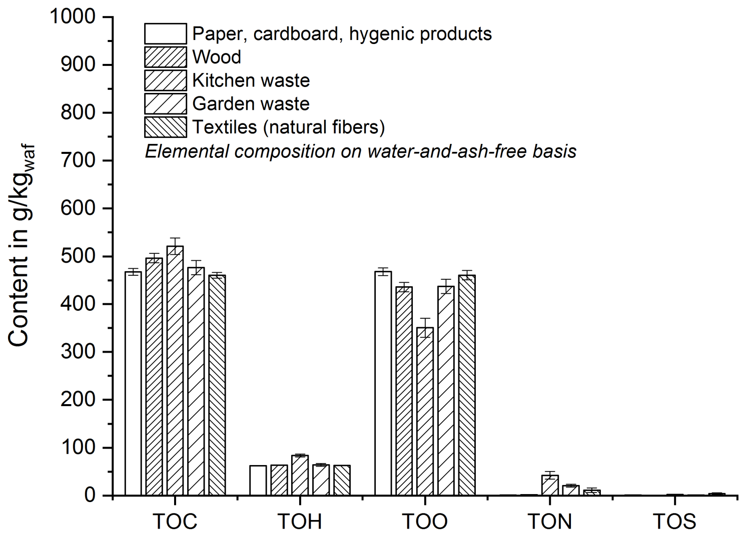


Figure 4.2: Elemental composition of different biogenic compounds (on water-and-ash-free basis) (based on Figure 3 in *Paper III*[1]).

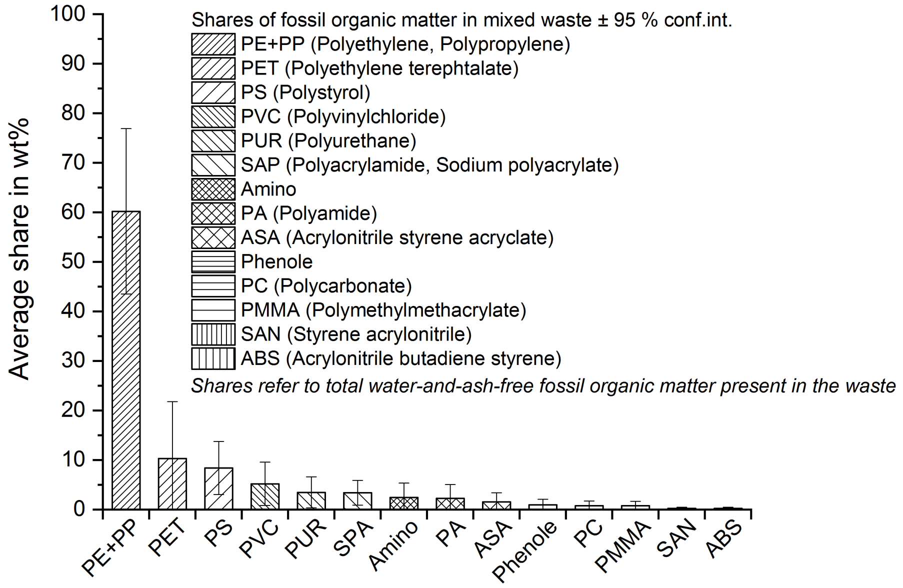


Figure 4.3: Shares of different fossil compounds present in mixed waste (MSW & CW) in Europe (referred to water-and-ash-free fossil organic matter) (based on Figure 4 in *Paper III*[1]).

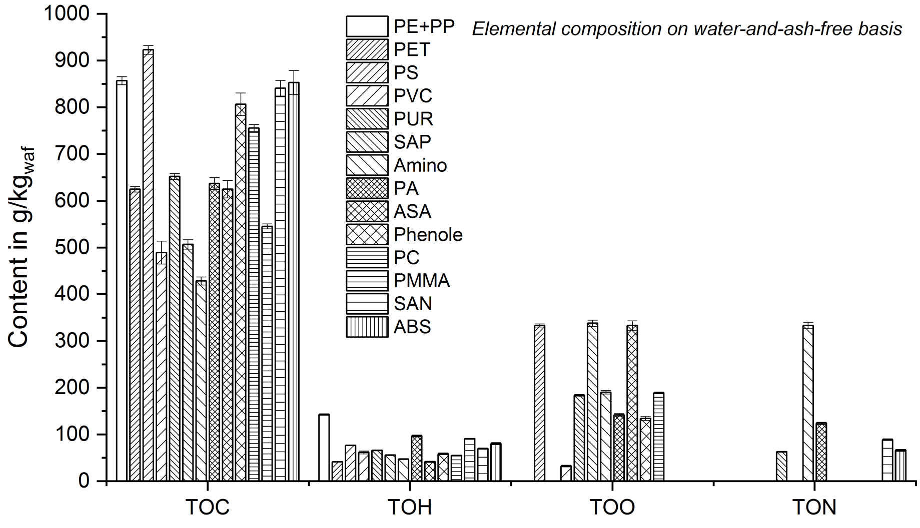


Figure 4.4: Elemental composition of different fossil polymers (on water-and-ash-free basis).

4.2 Evaluation of operating data of WtE plants – investigations addressing the Balance Method (*Paper I – III*)

The BM is applied to operating data of 10 out of 13 WtE plants in Austria for a period of one year. A range of parameters is derived characterizing the waste feed in terms of climate-relevance, renewable energy content, plastic content. Also general physical properties like heating value, water and ash content are appraised. Operating data as hourly mean values are evaluated, generating monthly and annual mean values of the BM-output parameters per WtE plant. Thereby, conclusions can be drawn on the temporal variability of the waste feed per plant and differences between plants. The nationwide application provides for the first time the possibility to assess the total annual fossil CO_2-emissions from WtE in Austria. Additionally, the general applicability of the BM on a large-scale, the usability of the WtE plant data for the BM, and the possibilities and added-value for plant operators by applying the BM are assessed.

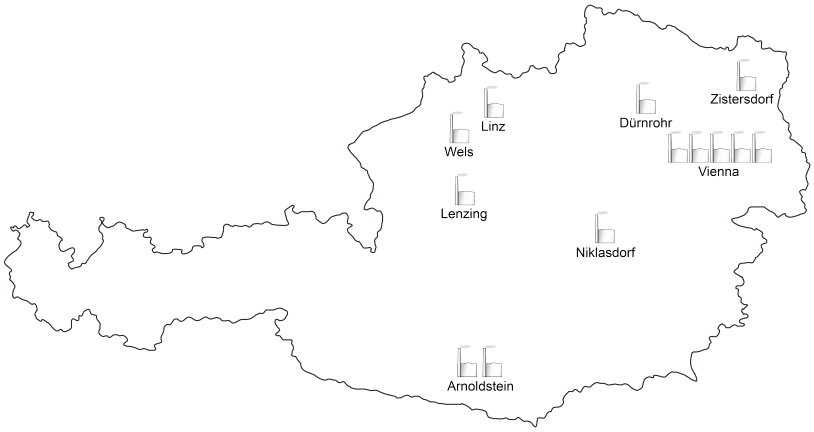


Figure 4.5: Locations of WtE plants in Austria.

4.2.1 WtE plants investigated

In the respective year (the year 2014), a total capacity of around 2.76 Mio. tons in 13 WtE plants was available in Austria to recover energy from MSW, CW, IW, sewage sludge (SS) and hazardous waste. The locations of the WtE plants in Austria are shown in Figure 4.5 and Table 4.1 gives information on the combustion technology and on the types of waste utilized in the different WtE plants. Around 2.3 Mio tons of waste can be considered within the study which corresponds to around 88 % of the overall waste fed into the Austrian WtE plants in 2014. Two plants (K, L) cannot be considered due a lack of data or insufficient data quality. One plant (M) was not in operation in 2014 and thus, no waste has been utilized within the study period in this plant. Data of ten WtE plants are evaluated, six of them are using grate incineration (GI), four are equipped with a fluidized bed combustion system (FBC).

Table 4.1: Waste-to-Energy plants in Austria in 2014 including information on the combustion technology and waste types utilized (based on Table 2 in *Paper II* [6]).

WtE plant	Combustion technology	Waste types utilized (qualitative information)	Considered in the study
A	Grate incineration	mainly MSW	✓
B	Grate incineration	MSW, CW & IW	✓
C	Stationary fluidized bed combustion	RDF, SS	✓
D	Stationary fluidized bed combustion	RDF, SS	✓
E	Circulating fluidized bed combustion	RDF, SS	✓
F	Grate incineration	mainly CW & IW	✓
G	Stationary fluidized bed combustion	RDF, minor amounts of SS	✓
H	Grate incineration	MSW, CW, minor amounts of IW and SS	✓
I	Grate incineration	mainly MSW	✓
J	Grate incineration	MSW, CW, minor amounts of SS	✓
K	Stationary fluidized bed combustion and rotary kiln combustion	hazardous and non-hazardous waste, IW and industrial sludge, SS	no
L	Stationary fluidized bed combustion and rotary kiln combustion	hazardous and non-hazardous waste, IW and industrial sludge, SS	no
M	Grate incineration	MSW, CW & IW	no[a]
	Total capacity		~2.76 Mio tons
	Total amount of waste utilized in 2014		~2.6 Mio tons
	Total amount of waste characterized within the study		~2.3 Mio tons

[a] Plant M was not in operation during the study period (2014)

4.2.2 Plausibility tests of the WtE plant operating data

Besides the elemental composition of fossil and biogenic matter (TOX_F, TOX_B) present in the waste feed, WtE operating data are used as input parameter for the BM. The data are inserted into the right side of the balance equations in Figure 3.1. Ideally, the operating data are used as hourly mean values. Prior to the evaluation by means of the BM, selected operating data need to be checked for errors in measurement. This is required due to the high sensitivity of the BM-results to certain input data. CO_2- and O_2-concentrations in the dry flue gas, for example, strongly affect different balances (carbon balance, O_2-consumption as well as the difference between O_2-consumption and CO_2-production) and thus, should not contain systematic errors. The plausibility of the data is checked relying on chemical-physical correlations between the heating value, the flue gas volume and flue gas composition. In particular, the following coherence between the WtE operating data is assumed and tested before the BM-evaluation is conducted:

(1) Opposed development of the O_2-concentration and the CO_2-concentration in the flue gas (this is assumed due to the fact that a higher carbon content theoretically results in a higher O_2-consumption and vice versa).

(2) Sum of O_2- and CO_2-concentration in the flue gas ranges between 15 and 21 vol% (conditioned by O_2-content in the combustion air).

(3) Correlation between the heating value of the waste and the O_2-consumption during combustion (based on the theoretical consideration that during combustion of organic matter the consumption of 1 mole O_2 corresponds to an energy equivalent of 360 to 400 kJ) (Fellner et al., 2007[2]).

(4) Correlation between heating value and carbon content in the waste (based on the theoretical consideration that the combustion of 1 g of organic carbon produces an amount of heat between 34 and 44 kJ) (Fellner et al., 2007[2]).

(5) Correlation between O_2-consumption and carbon content in the waste

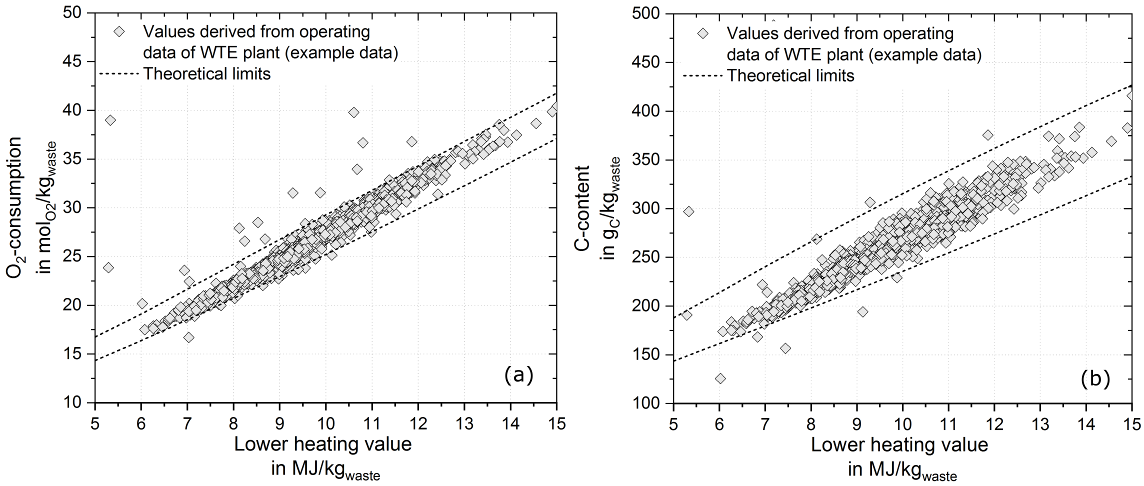


Figure 4.6: Example of expected correlation between (a) lower heating value of the waste and O_2-consumption during combustion and between (b) lower heating value and carbon content of the waste (based on Fellner et al., 2007[2]).

If the expectations according to (1) or (2) are not fulfilled or if the data are not in the expected ranges according to (3) or (4) (example data are shown in Figure 4.6), then errors in the measurements or data transmission need to be suspected. Additional investigations are necessary to detect the reasons for the implausible data observed. Information on the measurement points, measurement methods, frequency and type of test measurements can help to clarify incoherent data. Condition (5) (example data are shown in Figure 4.7) is finally used to only consider data which are within the expected range. Figure 4.6, and Figure 4.7 provide examples of correlation graphs which are used to exclude data from being considered in the BM.

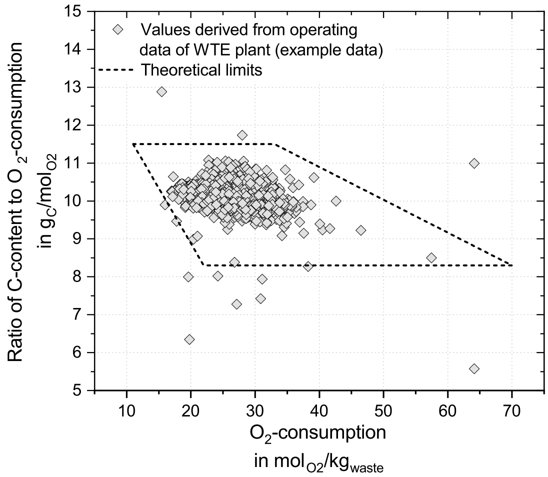


Figure 4.7: Example of expected correlation between O_2-consumption during combustion and carbon content of the waste (based on Fellner et al., 2007[2]).

4.3 Evaluation of elemental composition data of wastes and plastic-containing mixtures – investigations addressing the adapted Balance Method (*Paper IV – VII*)

As for the BM, the aBM requires data on the elemental composition of water-and-ash-free fossil and biogenic matter (TOX_F and TOX_B) present in the material (waste, RDF, or other plastic-containing mixture) to be analyzed. These data are attuned to the analytically-determined elemental composition of the respective material (TOX_{waste}).

Until now, the aBM has been tested with artificially prepared 2-component mixtures, where an impairment of the results by sample milling was eliminated (mixing at small grain sizes)[47,48]. In order to generate more practical performance data, also with more complex mixtures and with real RDF samples, and to assess the applicability of the aBM, the following aspects are examined within this thesis:

- Trueness/accuracy of the mean: by comparing aBM results to theoretical values of artificially prepared RDF model mixtures and to ^{14}C-method-results of real RDF samples
- Repeatability/precision: by evaluating the dispersion of results around the mean, based on tests with artificially prepared mixtures and real RDF samples
- Robustness of the aBM and effects of potential interference:
  - by evaluating the influence of sample preparation and different material matrices on the aBM-result
  - by assessing the usability of different generated input parameters for the aBM

- Comparability to standardized methods: in terms of trueness, repeatability, and practicability

Furthermore, first investigations on the potential applicability to other plastic-containing mixtures with other matrices (industrial effluent sample) are conducted. Table 4.2 summarizes the aspects which are investigated by means of testing different materials (artificially prepared RDF model mixtures, real RDF samples, industrial effluent sample).

Table 4.2: Materials investigated within the thesis in order to examine performance aspects of the aBM.

Material investigated	Description	Examined aspects of the aBM	Reference to Paper No.	Section in this thesis
RDF model mixture I	artificially prepared mixture	trueness repeatability/precision influence of sample preparation and matrices on the aBM-result	*IV*	5.2.1, 5.2.4
RDF model mixture II	artificially prepared mixture			
RDF 1	residues of a paper and board recycling plant (paper reject)	trueness (matching with results of the ^{14}C-method) repeatability/precision comparison to standardized methods robustness of the aBM-input values (TOX_F, TOX_B) practical applicability (in comparison to standardized methods)	*V, VI*	5.2.1, 5.2.4, 5.2.2, 5.2.5
RDF 2	light weight fraction of RDF production plant A (CW & IW)			
RDF 3	light weight fraction of RDF production plant A (MSW, CW & IW)			
RDF 4	light weight fraction of RDF production plant B	repeatability/precision comparison to standardized methods robustness of the aBM-input values (TOX_F, TOX_B) practical applicability (in comparison to standardized methods)	*VI, VII*	5.2.4, 5.2.5
RDF 5	light weight fraction of RDF production plant B			
RDF 6	light weight fraction of RDF production plant B			
Industrial effluent	particulate matter in the effluent of a plastic producer	further development options	*Conference contribution 1*	5.3

4.3.1 Artificially prepared RDF model mixtures

Investigations conducted

In a first step to validate the aBM, the method is tested on artificially prepared RDF model mixtures. Thereby the trueness and repeatability of the aBM-results are estimated. As the aBM-analyses require the RDF samples to be finely comminuted (at least below 0.5 mm), the influence of different sample preparation steps on the final result is investigated to identify approaches for optimization. Thereto a hierarchical experimental set-up is chosen and a nested variance component analysis is conducted (as described in 4.3.5).

Preparation of RDF model mixtures and sample preparation

Two predefined material mixtures with different composition and different heterogeneity are prepared out of paper, cardboard, polyethylene (HD-PE), polyethylenterephthalat (PET), and polystyrene (PS). The mixtures are prepared by mixing the respective materials after being shredded down to a grain size of around 4 mm. The composition of the two mixtures are presented in Table 4.3. Paper and cardboard are considered to be biogenic matter, whereas HD-PE, PET and PS represent fossil materials (produced out of crude oil). Elemental analyses (carbon content) of each compound are used together with the composition to determine the theoretical share of fossil carbon in the RDF model mixtures ($x^{TC}_{F,theory}$). $x^{TC}_{F,theory}$ is subsequently compared to the results found by applying the aBM.

Table 4.3: Composition of the RDF model mixtures (based on Table 1 in *Paper IV* [3]).

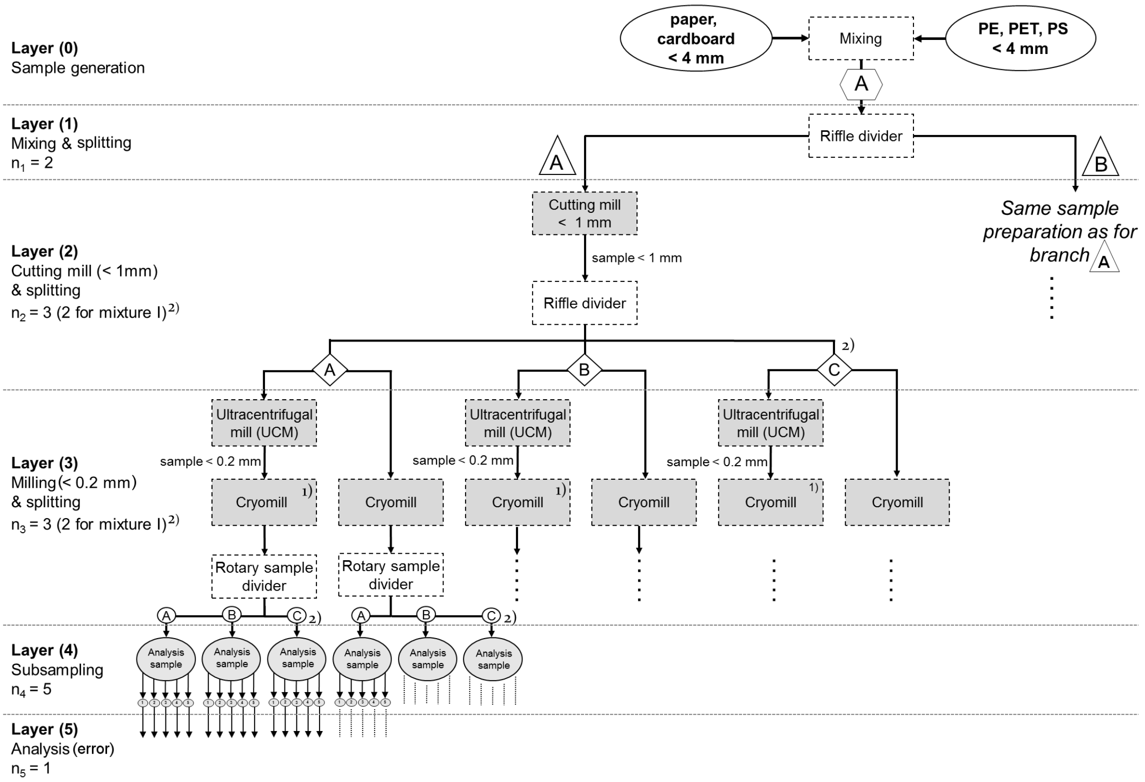
	Biogenic materials		Fossil materials			Theoretical value	
	Paper (wf)	Cardboard (wf)	HD-PE (wf)	PET (wf)	PS (wf)	Fossil mass fraction $x_{F,waf,theory}$	Share of fossil carbon $x^{TC}_{F,theory}$
				in wt%			
RDF model mixture I	79.4	-	20.6	-	-	24.5	38.7
RDF model mixture II	26.4	34.3	18.8	10.3	10.2	44.1	59.3

The RDF model mixtures undergo the sample comminution and partitioning steps as outlined in 4.8. At each layer of conditioning replicate samples are produced, creating a hierarchical structure of the experimental set-up. After being ground to particle size of <1 mm by a cutting mill and split by a riffle divider, the mixtures are further comminuted applying two different mills:

(1) An ultracentrifugal mill (UCM, Retsch ZM 200), which is a high speed rotor mill generating materials of defined particle dimensions (controlled by a sieve)

(2) A Cryomill (Retsch) configured as a cryogenic ball mill with the milling bin being cooled by liquid nitrogen. The cooling is intended to embrittle elastic particles and thereby support their crushing. The Cryomill has no provisions to control the generated particle size.

The performances of the two different mills (UCM, Cryomill, and a combination of both) are compared to evaluate the effect on aBM results and to derive recommendations for optimizing the comminution procedure when applying the aBM.



n_1, n_2, n_3, n_4, n_5.............number of replications at Layer (1), (2), (3), (4), and (5)

¹⁾ The Cryomill-milling step after UCM-milling is only done for mixture II (not for mixture I)

²⁾ For mixture I only two replications are done at each layer (no C-branches at Layer (2) and Layer (3) are produced)

Figure 4.8: Scheme of the sample comminution and partitioning steps applied to RDF model mixtures (based on Figure 3 in *Paper IV* [3]).

4.3.2 Samples of "real" refuse-derived fuels

Investigations conducted

After investigating the general validity of the aBM by tests with artificially prepared RDFs, the method is also tested with real RDFs which are generated in industry or in waste splitting plants. Six different RDFs are sampled at different plants. They are prepared based on findings from the investigation with RDF model mixtures, and analyzed by means of the aBM. Additionally, they are sorted into different fractions, and RDF-specific input values for TOX_F and TOX_B are generated. This allows the robustness of TOX_F and TOX_B for RDF and the general validity of literature-derived values to be appraised. Standardized methods are applied to the RDF samples in order to compare the results to the results of the aBM. Finally, the trueness of the aBM results is appraised by matching the aBM results with results obtained by the most reliable standardized method (^{14}C-method).

Refuse-derived fuels and sample preparation

Six different RDFs are sampled stemming from three different plants, namely

- 1 Paper reject from a paper and board recycling plant
- 2 RDFs from waste splitting plant A (input material is either mainly CW and IW or a mix of MSW and CW & IW)
- 3 RDFs from waste splitting plant B (input material is mainly CW and IW)

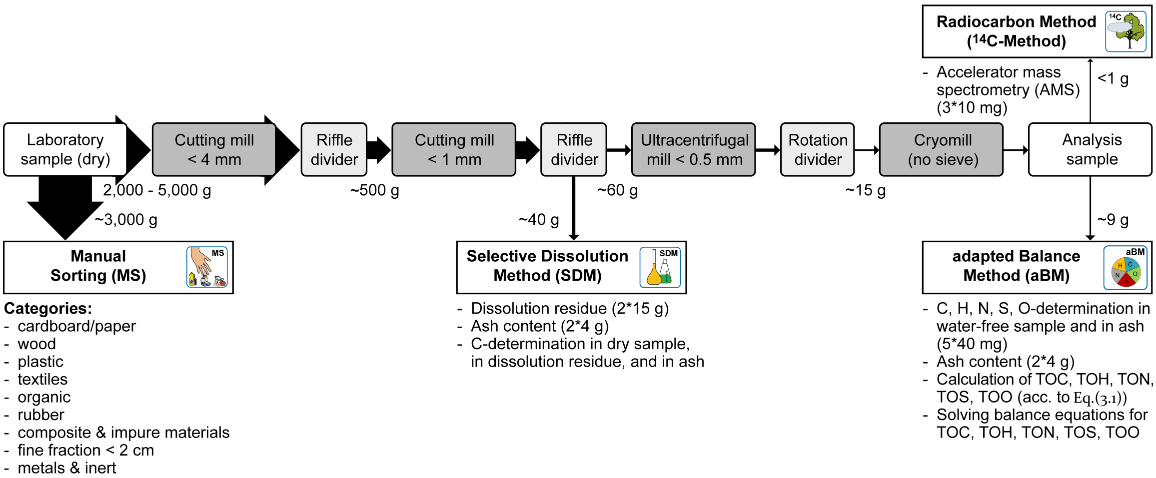


Figure 4.9: Procedure for sample preparation and analysis of real RDF samples (based on Figure 2 in *Paper V* [4]).

2 to 15 samples per RDF are taken, each of them comprising 5 to 10 kg. The RDFs are

prepared in the laboratory following the procedure in Figure 4.9. Besides the aBM, standardized methods are applied to the RDFs (MS, SDM, ^{14}C-method). However, the number of samples investigated per RDF is limited due to budgetary and time constraints and the RDF from plant B could only be investigated by means of the aBM and MS.

4.3.3 Investigations of other plastic-containing mixtures: The example of microplastic in an industrial effluent (*Conference contribution 1*)

First investigations on the application of the aBM to environmental samples are conducted. Thereto samples of particulate matter from an effluent of a plastic producer are analysed. Solid samples of each 100 to 200 g are collected by using nets with 0.25 mm mesh size.

As addressed in section 4.1, an application of the aBM requires data for TOX_F and TOX_B to be initially defined. For samples with unknown composition, like the collected particulate matter, the acquisition of these data require some additional analyses and assumptions. In the case of the samples collected, TOX_F data can be assumed to follow the types and share of the plastic produced at the collection site. PE/PP plastic pellets, obtained from the producer, are therefore used to derive TOX_F, whereas, for deriving TOX_B it is assumed that the biomass is composed out of algae and wood. Additional algae samples are collected at the effluent and are also analysed for their elemental composition and ash content (the samples are collected at a site without plastic contamination). The same analyses are conducted for wood pieces which are sorted out of additionally collected samples. By assuming the ratio of algae and wood to be 8:1, TOX_B is derived.

Table 4.4: Approaches to prepare samples and to define TOX_F and TOX_B for the application of the aBM to particulate matter from an effluent of a plastic producer.

	Prepared sample mass	Considerations to determine TOX_F	Considerations to determine TOX_B	Sample preparation steps	
Approach I	~ 5 g	- on-site produced plastic pellets (PE/PP)	- algae samples collected on-site - wood pieces sorted out of samples - ratio of algae:wood assumed as 8:1		UCM milling (<0.5 mm)
Approach II	~ 5 g	- on-site produced plastic pellets (PE/PP)	- wood pieces sorted out of samples	treatment with H_2O_2	UCM milling (<0.5 mm)

The preparation of the effluent samples follows two different approaches, as outlined in Table 4.4. Approach I generally follows the procedure as developed for RDF samples. However, no cutting mill is necessary due to the small sample and particle sizes. UCM is used for comminuting to grain sizes <0.5 mm. Approach II was developed as an attempt to reduce uncertainties introduced by the assumptions on the biomass composition and to reduce the heterogeneity of the biomass. The samples are treated with 30 % H_2O_2, thereby oxidizing a large part of the biogenic matrix (in the present case algae). The oxidation residue is then mainly composed out of mineral matter, plastics and hardwood. Thus, when applying the aBM to the residue, TOX_B can be replaced by TOX_{wood} – the elemental composition of wood on a water-and-ash-free basis.

The same set of aBM balance equations as given in Figure 3.2 can be used to determine the unknown mass fractions of water-and-ash-free plastic and water-and-ash-free biomass, respectively. For deriving the plastic content on a dry basis, the inert matter and inorganic additives in plastic need to be considered. For approach II, additionally the mass of oxidation loss needs to be taken into account to calculate the plastic content in the original sample. Details of the further developed aBM applicable to particulate matter in water samples are described in the Austrian patent A 50072/2017[91].

4.3.4 Determining trueness and precision of the adapted Balance Method

In order to assess the performance of the aBM in terms of accuracy, the trueness and the precision of the method are estimated based on the investigations with RDF model mixtures and with real RDFs. The parameter x_F^{TC} is used to exploit the performance of the aBM. This parameter is chosen because it is determinable by means of all methods mentioned (MS, SDM, ^{14}C-method, aBM – although by MS and SDM only with additional analysis/data) and because x_F^{TC} allows the ^{14}C-method to be used as a provisional reference method. Moreover, x_F^{TC} represents the share of fossil CO_2-emissions – information which is pressumably most relevant for industrial plants utilizing RDFs.

Trueness is understood as equivalent to the accuracy of the mean and refers to the systematic error of an analysis method. Thus, it gives information on the closeness of the measured value from a reference value[10,92]. Within the thesis, the trueness of the aBM is assessed by comparing analysis results of the RDF model mixtures to the theoretical (true) value. For the “real” RDFs, the true value is not known, thus a provisional reference value is used, namely the results of the $_{14}$C-method. The deviations of the aBM-value from the reference value are calculated per sample. By considering a normal distribution of the deviations, the overall closeness (trueness) for the RDF model mixtures and for the RDFs investigated is estimated based on a 95 %-confidence interval.

The **precision** represents the random error of an analysis method and describes the variability of the analysis results when repeated measurements are conducted (under defined conditions)[92]. Within the thesis, measurements which are conducted under the same conditions (same measurement device, same observer, repetition over a short period of time) are used to estimate the precision under repeatability conditions. In this case, the term repeatability can also be used to describe the variability of the analysis results. A high degree of repeatability is achieved when the dispersion around the mean is low. Thus, repeatability can be described by the variance (σ^2) or the standard deviation (SD) of repeated measurement results[10].

Table 4.5: Calculations of simple analysis of variances (according to Hartung et al.,2009[10]).

Source of variation	Mean sum of squares (MS) as estimate of variance (σ^2)	Sum of Squares (SS)	Degrees of freedom (*df*)
Variation between samples	$MS_{between} = \frac{SS_{between}}{df}$	$SS_{between} = \sum_{i=1}^{N} (\overline{x}_i - \overline{x})^2$	$N - 1$
Variation within samples	$MS_{within} = \frac{SS_{within}}{df}$	$SS_{within} = \sum_{i=1}^{N} \sum_{j=1}^{n} (x_{ij} - \overline{x}_i)^2$	$N * n - n$
Total	$MS_{tot} = \frac{SS_{tot}}{df}$	$SS_{tot} = \sum_{i=1}^{N} \sum_{j=1}^{n} (x_{ij} - \overline{x})^2$	$N * n - 1$

x_{ij} ...aBM-result of j-measurement of sample i
$\overline{x}_i$ ...mean aBM-results for sample i
$\overline{x}$ ...mean of $\overline{x}_i$
N ...number of samples
n ...number of repeated measurements

To estimate the repeatability of the aBM based on RDF model mixtures and RDFs, five to eight repetitions per analysis sample are considered. The repetitions represent measurements of the elemental composition (elementary analysis). For each measurement result an evaluation by means of the aBM is conducted. Thus, the repeatability evaluation is based on five to eight aBM-results per sample (n), from which a mean per sample is calculated ($\overline{x}_i$). In order to differentiate whether or not a variation is caused by differences *between* the samples of each RDF or by differences due to effects of analysis and aBM-calculations (variation *within* samples), a simple analysis of variance is conducted. The respective equations are provided in Table 4.5, based on Hartung et al. (2009)[10]. MS in Table 4.5 is an estimate for the variance (σ^2), thus the standard deviation (SD) and relative standard deviation can be calculated by Eq.(4.3) and Eq.(4.4). SD determined *within* the samples is assumed to represent the variation caused by the procedure of the aBM (analysis, aBM-evaluations), excluding the sampling and sample preparation effects. It is used as an estimate for the precision (repeatability) of the aBM-results per RDF model mixture or per RDF within the thesis.

$$SD = \sqrt{MS} \tag{4.3}$$

$$RSD = \frac{SD}{\overline{x}} \tag{4.4}$$

From the variance analysis it can be further concluded whether or not the variation between the RDF samples is significantly greater than the variation caused by the repeated measurements. Therefore an F-test is conducted by comparing the ratio of $MS_{between}$ and MS_{within} to the respective F-value.

4.3.5 Nested variance component analysis

A nested variances model with nested structure is used to determine the relative importance of the different sources of variation during the sample preparation procedure. The variance component analysis (VCA) assumes that the variance of the overall result reflects the sum of the variances of all influencing factors. Five different layers of sample preparation steps are defined as influencing factors within the thesis. These layers result from the hierarchical sample comminution and partitioning scheme selected, as presented in Figure 4.8. Replicate samples are produced after each preparation step. A nested design of the VCA is chosen based on Hartung et al. (2009)[10] and Sokal & Rohlf (2012)[11] as this design can account for the hierarchy of the layers (which are thus not independent from each other). The following layers are defined:

Layer (1) “Mixing & splitting”
Layer (2) “Cutting mill ($<$ 1 mm) & splitting”
Layer (3) “Milling ($<$ 0.2 mm) & splitting”
Layer (4) “Subsampling for analysis”
Layer (5) “Analysis (error)”

Layer (2) is nested within Layer (1), Layer (3) is nested within Layer (2), etc. The number of groups per layer is determined by the number of replications produced by sample splitting after each preparation step. Mean values are calculated at each layer and the variance components are calculated based on the calculations given in Table 4.6. Mean sum of squares (MS) are computed for each layer by summarizing the squared deviation between replications and the group means of the layer, and relating it to the respective degree of freedom (df). The added variance component among the groups of a layer is estimated by comparing the MS between the groups of the respective layer with the MS between the groups of the subsequent layer. Thus, it is assumed that the variation increases from one layer to the other. The sum of squares for each layer adds up to the total sum of squares. By computing F-values according to Table 4.6, it can be tested whether the MS of a layer is larger than it would be expected to be by chance based on the observed variation among the samples of the subjacent layer. If the F-value is below a chosen significance level of 0.05, it is assumed that the differences among samples at the respective layer are significant and that there is thus a significant influence on the final result.

Table 4.6: Calculations of nested variance component analysis (according to Hartung et al., 2009[10] and Sokal & Rohlf, 2012[11] and based on Table 2 in *Paper IV*[3]).

Source of variation	Variance component	Mean Sum of Squares (MS)	Sum of Squares (SS)	F_s
Layer (1)	$\sigma_1^2 = \frac{MS_1 - MS_2}{n_2 * n_3 * n_4 * n_5}$	$MS_1 = \frac{SS_1}{n_1 - 1}$	$SS_1 = \sum_i^{n_1} n_2 * n_3 * n_4 * (\overline{x}_{n_i} - \overline{x})^2$	$\frac{MS_1}{MS_2}$
Layer (2)	$\sigma_2^2 = \frac{MS_2 - MS_3}{n_3 * n_4 * n_5}$	$MS_2 = \frac{SS_2}{n_1 * (n_2 - 1)}$	$SS_2 = \sum_i^{n_1} \sum_j^{n_2} n_3 * n_4 * (\overline{x}_{n_i n_j} - \overline{x}_{n_i})^2$	$\frac{MS_2}{MS_3}$
Layer (3)	$\sigma_3^2 = \frac{MS_3 - MS_4}{n_4 * n_5}$	$MS_3 = \frac{SS_3}{n_1 * n_2 * (n_3 - 1)}$	$SS_3 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} n_4 * (\overline{x}_{n_i n_j n_k} - \overline{x}_{n_i n_j})^2$	$\frac{MS_3}{MS_4}$
Layer (4)	$\sigma_4^2 = \frac{MS_4 - MS_5}{n_5}$	$MS_4 = \frac{SS_4}{n_1 * n_2 * n_3 * (n_4 - 1)}$	$SS_4 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{x}_{n_i n_j n_k n_l} - \overline{x}_{n_i n_j n_k})^2$	$\frac{MS_4}{MS_5}$
Layer (5)	$\sigma_5^2 = MS_5$	$MS_5 = (\epsilon * \overline{x})^2$		
Total	$\sigma_{tot}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2$	$MS_{tot} = \frac{SS_{tot}}{n_1 * n_2 * n_3 * n_4 * n_5 - 1}$	$SS_{tot} = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{x} - \overline{x}_{n_i n_j n_k n_l})^2 = SS_1 + SS_2 + SS_3 + SS_4$	

$\overline{x}$	...total mean
$\overline{x}_{n_i}$	...mean of i-th group at Layer (1)
$\overline{x}_{n_i n_j}$	...mean of j-th group at Layer (2) within the i-th group of Layer(1)
$\overline{x}_{n_i n_j n_k}$	...mean of k-th group at Layer (3) within j-th group of Layer (2) within i-th group of Layer (1)
$\overline{x}_{n_i n_j n_k n_l}$	...l-th analysis result at Layer (4) within k-th group at Layer (3) within j-th group of Layer (2) within i-th group of Layer (1)
n_1, n_2, n_3, n_4, n_5	...number of replications at Layer (1), (2), (3), (4), (5)
ϵ	...error for analysis estimated based on CHNSO device specifications (0.9%)

5 Results and Discussion

5.1 Application of the Balance Method to Austrian WtE plants

5.1.1 Fossil CO_2-emissions from WtE plants (*Paper I*)

The reporting of fossil CO_2-emissions from WtE can be necessary due to obligations within the framework of greenhouse gas inventories, emission trading schemes, or also to monitor the emissions after changes in waste management systems (e.g. shift from landfilling to WtE or diverting plastics to material recycling). In particular, for the latter frequently available information can also be beneficial to check the effect of waste management measures.

The carbon intensity of waste fuels can be expressed as fossil CO_2-emission factors (EF). EF relating the fossil CO_2-emissions to the waste mass (EF_M) or to the energy content of the waste (EF_Q) are determined for each WtE plant on a monthly and annual basis. As an example, the EF_Q per month for six (out of ten) WtE plants are presented in Figure 5.1 together with the mean monthly values of all ten plants. Distinct variations are observable over time (plant-specific and of the total monthly mean) as well as between the plants. It can be presumed that the wide range of monthly emission factors (between 25 ± 2 and $62 \pm 3\,\mathrm{kg_{CO_2,F}\,GJ^{-1}}$) reflects the regional variation in waste feed composition and the shares of different waste types utilized (MSW, IW, CW). The waste types are expected to vary due to different characteristics of the respective regions of Austria where the WtE plants are located and where different waste collection schemes and different sectors of industries and businesses are established. For example, WtE plant F shows the highest EF_M and EF_Q, which might be due to predominantly CW and IW being recovered in this plant. The lowest EFs are found for WtE plant C, fed with RDF from MSW and sewage sludge (sewage sludge is regarded as biogenic). However, the available data do not allow a clear correlation between waste types and EFs (no detailed information on the type of waste feed per plant is available to the author). High temporal variations of the monthly EFs per plant indicate that a considerable variability in terms of fossil content can be expected throughout the year (relative standard deviations RSD of up to 23 % for EF_M and up to 17 % for EF_Q; Table 5.1). When GI and FBC plants are regarded separately, the monthly variability in waste composition are more pronounced for FBC plants (EF_Q: RSD of 10–17 % for FBC plants and 4–13 % for GI plants). This is somewhat unexpected considering that the waste fed into FBC plants is usually mechanically pretreated and thus typically more homogeneous than the waste fed into GI plants.

It is assumed that the operation of mechanical pretreatment plants, which supply WtE plants and the industry with RDF, is affected by seasonal demand of (plastic-dominated) RDF by industry, resulting in variations in the plastic content in the WtE feed of FBC plants. For example, differences in cement production between summer and winter can reach up to 100 %[93], causing the demand for RDF by this industry to supposedly also vary seasonally. Furthermore, downtime periods of surrounding plants or changing shares of sewage sludge (which is fed into FBC rather than GI plants) are assumed to cause the share of energy from biomass to fluctuate, particularly in plants with a low total capacity.

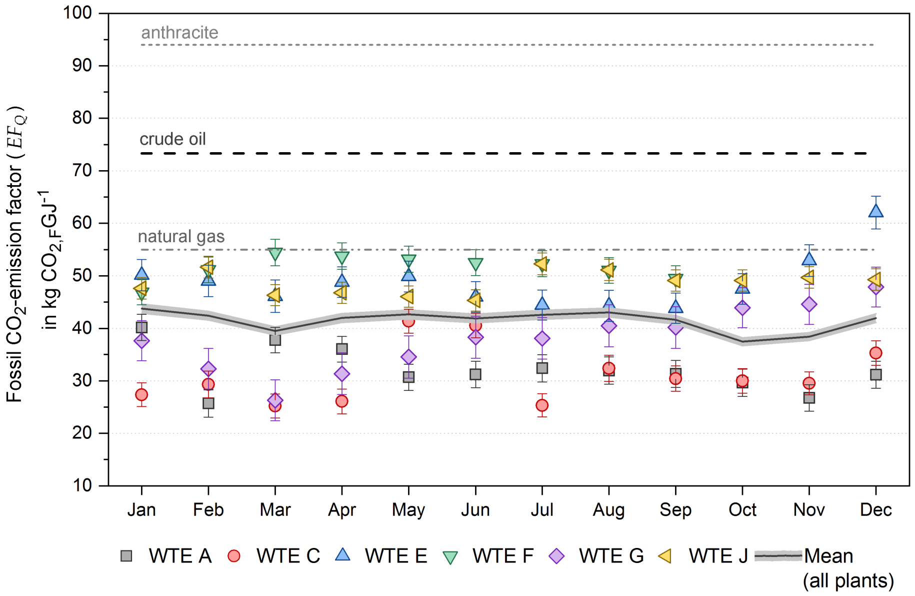


Figure 5.1: Fossil CO_2-emission factors determined for six (out of ten) WtE plants investigated in Austria as monthly mean values for the year 2014; together with the monthly mean over all ten WtE plants investigated (based on Figure 5 and Figure 6 in *Paper I*[5]).

Thus, different factors (waste types, season, business activities, total throughput, availability of other plants, etc.) lead to the phenomenon that the monthly variations per plant, expressed as RSD, can reach the same level of magnitude as the RSD between the annual values of all Austrian plants. The observations clearly indicate that a generally valid fossil CO_2-emission factor for WtE plants can hardly be defined, neither at a national nor regional level. The usage of generic EFs as provided in the literature (e.g. by IPCC or the German Environment Agency[94,95]) can easily lead to significant over- or underestimations when it comes to reporting the climate-relevant CO_2-emissions from thermal utilization of waste. This is particularly true when single plants or short time periods are considered. In the case presented, significantly false estimates can be anticipated when using an EF_Q of 43.9 $\mathrm{kg}_{CO_2,F}\ \mathrm{GJ}^{-1}$, a value provided by the German Environment Agency (2015)[95]; false estimates amount to up to 40 %rel on a plant-specific level – with respect to the annual mean – or even 75 %rel – with

Table 5.1: Fossil CO_2-emission factors determined for ten WtE plants in Austria for the year 2014. (based on Figure 7 in *Paper I*[5]).

	EF_M Fossil CO_2-emission factor (mass-based)		EF_Q Fossil CO_2-emission factor (energy-based)	
WtE plant	annual mean[a] in $kg_{CO_2,F}\,t^{-1}$	RSD in %rel	annual mean[a] in $kg_{CO_2,F}\,GJ^{-1}$	RSD in %rel
A (GI)	318 ± 24	23 %	32.2 ± 2.4	13 %
B (GI)	424 ± 23	11 %	41.5 ± 2.2	4 %
C (FBC)	255 ± 18	23 %	31.6 ± 2.2	17 %
D (FBC)	366 ± 35	15 %	39.4 ± 3.7	14 %
E (FBC)	472 ± 28	10 %	49.0 ± 2.8	10 %
F (GI)	548 ± 27	5 %	51.5 ± 2.5	5 %
G (FBC)	347 ± 34	22 %	38.0 ± 3.7	16 %
H (GI)	354 ± 32	10 %	35.4 ± 3.2	6 %
I (GI)	488 ± 28	10 %	48.0 ± 4.8	9 %
J (GI)	496 ± 17	7 %	48.7 ± 1.6	5 %
GI-plants	419 ± 19[a]	6 %	42.7 ± 1.9[a]	7 %
FBC-plants	390 ± 21[a]	11 %	42.3 ± 2.3[a]	11 %
All plants	409 ± 18[a]	7 % / 23 %[b]	42.6 ± 1.9[a]	5 % / 17 %[b]

RSD ...relative standard deviation referring to monthly mean values

[a] weighted mean according to waste throughput (for EF_M) or to energy content (for EF_Q)

[b] RSD referring to *annual* mean values

respect to the monthly means.

Moreover, it has been observed (Table 5.1) that the relative variations of EF_Q are lower than the respective relative variations of EF_M (for six out of ten WtE plants A, B, C, G, H, J). This can be explained by the fact that EF_M is strongly dependent on the total carbon content, and the water and ash content of the waste. EF_Q is determined mainly by the different shares of fossil and biogenic materials and is to a large extent independent of the ash content or the total carbon content. Thus, EF_Q is considered to be more conclusive as it also better allows the energetic substitution of conventional fuels by waste fuels to be represented. The fact that the BM can easily deliver both parameters, EF_M and EF_Q, can contribute to the avoidance of misinterpretations of data and allows easy comparison with conventional fuels.

The significant variation in EF for WtE plants found is also in line with data reported by Obermoser et al. (2009)[45], who analysed data of 11 different WtE plants in Austria, Germany, Belgium and Switzerland and found EF between 30 and 67 $kg_{CO_2,F}\,GJ^{-1}$.

In terms of climate-relevance, the fossil carbon (CO_2) in the waste is relevant when the waste is thermally recovered. In the case that the waste does *not* undergo a treatment and is disposed of on a landfill, the *biogenic* organic carbon contained in the waste becomes relevant for greenhouse gas emissions. This is due to the biogenic carbon representing the fraction of carbon which can potentially be degraded in landfills. Degradable organic carbon is the main parameter affecting the methane (CH_4) emissions from solid waste disposal, emissions for which the global warming potential is around 25 times higher than for CO_2 [36,37]. Information on the biogenic carbon contained in mixed waste can also be provided by the BM. Results within the work present on this parameter are, however, not presented in order to limit the extent of the thesis and because landfilling of waste with a high carbon content is no longer an option in Austria due to the landfill directive implemented [26,27]. However, landfilling of untreated waste is still common in many regions outside of Europe as well as in several European countries. Thus, information on potential landfill gas production can be relevant for waste management decisions also due to greenhouse gas reduction targets (e.g. within the Kyoto-protocol). The utilization of BM data for this purpose can ease and improve currently proposed methodologies. Currently, default values on the degradable carbon in waste or the conduction of sampling campaigns and analyses are being proposed to estimate the CH_4-emission potential from solid waste disposal (e.g. by IPCC or UNFCCC [37,96]).

5.1.2 Ratio of energy from biogenic sources in the WtE plant feed (*Paper II*)

Analogously to the fossil CO_2-emissions, the plant-specific ratio of energy from biogenic sources (q_B) in the waste feed of the WtE plant are determined by the BM. This information is useful for plant operators to report the electricity that is recovered from renewable sources, which is relevant for energy labeling and subsidies for renewable electricity production (e.g. EU directives 2003/54/EG and 2009/28/EG, US National Energy information System, UK Renewables Obligation Certificates and Austrian Directive on elecricity labelling [16,17,97–99]). Similar to the temporal variations observed for the fossil CO_2-emissions, q_B is also prone to vary throughout the year and particularly for certain WtE plants (Figure 5.2). The ratio of energy stemming from biogenic sources ranges in average from 39.0 ± 2.2 to 51.1 ± 2.2 % per month (when monthly means over all ten plants are calculated). The relative plant-wise variation of the monthly mean values is found to be between 4 and 17 % (expressed as RSD in Table 5.2). For some plants (predominantly FBC plants), this variation is almost as distinct as the variation between the plants on an annual basis (which is 19 %, see Table 5.2). Plant-specific annual values of 35.7 ± 2.4 to 61.2 ± 2.7 % of energy originating from biogenic sources are found.

Thus, also in the case of reporting the share of renewable energy from waste in WtE plants, the differences between the plants need to be considered as well as changes over time.

Table 5.2: Ratio of energy originating from biogenic sources (q_B) determined for ten WtE plants in Austria for the year 2014.

	q_B Share of energy from biogenic sources	
WtE plant	annual mean in MJ MJ^{-1} as %rel	RSD in %rel
A (GI)	60.3 ± 2.8	9 %
B (GI)	48.5 ± 2.4	4 %
C (FBC)	61.2 ± 2.7	11 %
D (FBC)	50.9 ± 4.4	14 %
E (FBC)	38.9 ± 3.1	16 %
F (GI)	35.7 ± 2.4	8 %
G (FBC)	53.1 ± 4.4	15 %
H (GI)	56.3 ± 3.7	5 %
I (GI)	42.0 ± 3.0	13 %
J (GI)	39.3 ± 2.3	8 %
GI-plants	47.2 ± 2.2[a]	6 %
FBC-plants	46.9 ± 2.7[a]	12 %
All plants	48.4 ± 2.2[a]	7 % / 19 %[b]

RSD ...relative standard deviation referring to monthly mean values
[a] weighted mean according to energy content
[b] RSD referring to *annual* mean values

Considering a standard value of 50 % for q_B, suggested by the German Environment Agency[95], annual over- or underestimations of up to 40 %rel need to be anticipated at a plant level. Other literature sources provide values for the biogenic carbon content of 42 to 62 %[94,100,101]. These would translate to around 38 to 57 % of biogenic energy (by considering a stable ratio between the heating value and carbon content, as suggested by Fichtner, 2007[41]). Based on the investigations presented, the usage of these values would also result in significant false estimates for some WtE plants. If WtE plant operators are granted higher feed-in tariffs for renewable energies, these false estimates of the share of biogenic energy recovery can easily lead to distortions of monetary flows.

A possible limitation of generating data by means of BM with high accuracy arises when the boiler efficiency changes significantly over time. However, regular determination of the current boiler efficiency, which can be done based on plant operation data (by energy balances), could ensure the reliability of the BM-data.

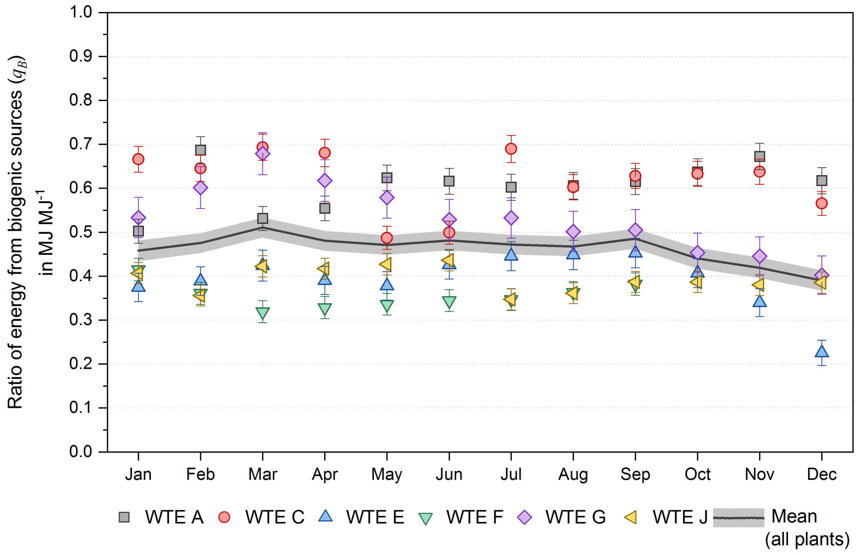


Figure 5.2: Ratio of energy originating from biogenic sources for six (out of ten) WtE plants investigated in Austria as monthly mean values for the year 2014; together with the monthly mean over all ten WtE plants investigated (based on Figure 6 in *Paper II*[6]).

5.1.3 Content of plastics in the WtE plant feed (*Paper III*)

Measures in waste management systems increasingly focus on resource efficiency and redirecting waste flows back into the production process. For example, the European Commission is particularly pushing increased recycling rates for packaging waste, including plastics[21]. In order to understand the current situation, the recycling potential and the effects of the respective recycling measures, detailed knowledge of relevant plastic flows is needed. For plastics only limited data is available on post-consumer plastics flows through society. Among the post-consumer plastic waste streams, plastics in commingled waste (MSW, CW and IW) represent a major flow but until now the data has only been estimated based on sorting campaigns[102]. These campaigns are not only time- and cost-intensive but also deliver information of limited significance and at a very low frequency (at best once a year).

The BM has been identified as a possible alternative approach. The information generated by the BM on the share of fossil mass in commingled waste can be used as a basis to also derive the plastics content in the waste streams entering WtE plants. This is because plastics in these waste streams are mainly produced from fossil sources (based on figures from European bioplastics e.V.[103] and PlasticsEurope[104], it is estimated that the share of biopolymers is below 0.5 %). Thus, information generated by the BM is utilized together with literature information on the average ash content in plastics (see Eq. 3.6) to collect data on plastic streams which are thermally recovered in Austria.

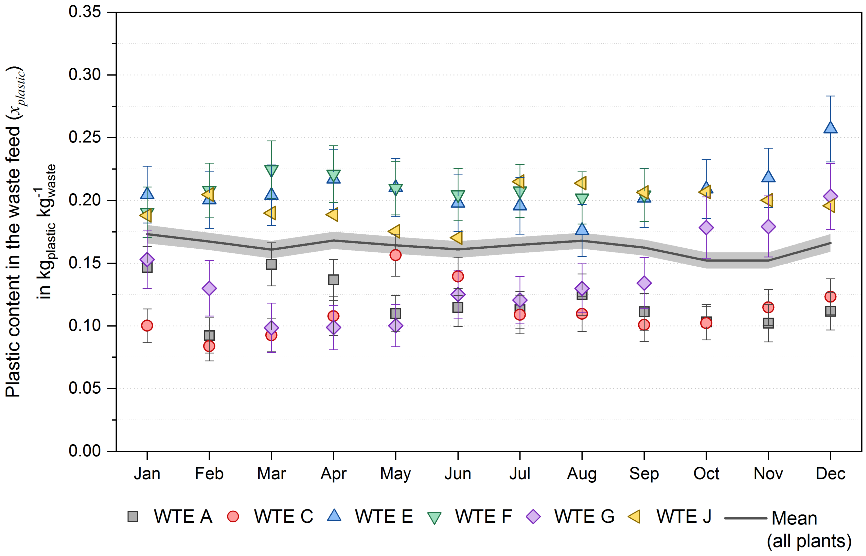


Figure 5.3: Content of plastics in the waste feed of six (out of ten) WtE plants investigated in Austria as monthly mean values for the year 2014; together with the monthly mean over all ten WtE plants investigated; plastics content refers to waste feed exclusive sewage sludge (based on Figure 5 and 6 in *Paper III*[1]).

On average 16.5 ± 1.8 wt% of the waste fed into WtE plants in Austria is identified as being plastic waste (based on 10 WtE plants investigated and disregarding the amount of sewage sludge utilized in some plants) (Table 5.3). The plastic content found is considerably above findings from previous sorting campaigns conducted for MSW in Austria (8 to 13 wt%[58,59,105]). Differences can be attributed to the following reasons:

(i) Previous sorting campaigns were only conducted within a limited time frame.

(ii) Previous sorting campaigns were not conducted with the aim of concluding on the plastic content, thus the plastic content determined might not include significant amounts of plastic present in composite and mixed fractions (such as fine fraction, hygienic articles, etc.).

(iii) Previous sorting campaigns were only conducted with MSW; CW and IW, which might include a considerable share of plastics, was not considered.

In total, the thesis reveals that about 385 kt of waste plastics were thermally recovered in Austrian WtE plants in 2014. This represents about 45 $kg_{plastic}\ cap^{-1}\ yr^{-1}$. In addition, the cement industry uses about 210 kt of waste plastics (corresponding to 25 $kg_{plastic}\ cap^{-1}\ yr^{-1}$) as alternative fuel (based on data given in Mauschitz, 2015[106]). Due to this significant amount of waste plastics utilized in industry, changing fuel demands, e.g. by cement plants in winter time, are also assumed to result in fluctuations of high-calorific waste (plastics) ending up in WtE plants. These seasonal dependencies are assumed to be one reason why the variation in plastics content is

Table 5.3: Content of plastics in the waste feed determined for ten WtE plants in Austria for the year 2014 (based on Figure 8 in *Paper III*[1]).

	$x_{plastic}$ Plastic content referred to waste feed (exkl. sewage sludge)	
WtE plant	annual mean in $kg_{plastic}\ kg_{waste}^{-1}$ as %rel	RSD in %rel
A (GI)	11.8 ± 1.5	15 %
B (GI)	15.9 ± 1.7	11 %
C (FBC)	11.2 ± 1.4	18 %
D (FBC)	17.4 ± 2.5	13 %
E (FBC)	20.9 ± 2.3	9 %
F (GI)	20.7 ± 2.1	5 %
G (FBC)	13.6 ± 2.0	25 %
H (GI)	13.8 ± 1.9	10 %
I (GI)	18.3 ± 2.5	11 %
J (GI)	19.6 ± 2.0	7 %
GI-plants	16.1 ± 0.8[a]	7 %
FBC-plants	17.3 ± 1.0[a]	11 %
All plants	16.5 ± 1.8[a]	4 % / 22 %[b]

RSD ...relative standard deviation referring to monthly mean values
[a] weighted mean according to waste throughput
[b] RSD referring to *annual* mean values

observed to be particularly high for FBC plants (Table 5.3). For at least two FBC plants, which are known to also receive RDFs from mechanical treatment plants, an increase in plastics content in winter time can be observed (WtE plant E and G) in Figure 5.3. In the period November to February up to 28 % higher plastic contents are found in comparison to the period May to August. A variation in the plastic content of 25 % is found for WtE plant G, indicating strongly varying waste composition in this plant, even disregarding varying amounts of sewage sludge.

The data generated once more demonstrate that valuable information on the composition of commingled waste can be provided when applying the BM. The information can be of interest for decision makers and plant operators for different reasons, i.a.:

(i) They support the analysis of national and regional plastics flows, thereby enabling the analyses of waste plastic generation over time,
(ii) they allow the performance of different waste plastic collection schemes to be

evaluated (e.g. separate collection vs. commingled collection),

(iii) the overall potential of plastic recycling becomes evident and the effects of measures to redirect plastic flows can be monitored.

5.1.4 Benefits for plant operators and potential for process control in WtE plants (*Conference paper 2*)

As demonstrated in previous sections, information on the temporal development of waste composition in terms of fossil and biogenic share can be provided when applying the BM in WtE plants. This section presents additional benefits which have been identified for plant operators when utilizing data generated by the BM:

(1) Conducted plausibility test of BM can help to improve recorded operating data (by detecting errors).

(2) Detailed information provided by the BM could potentially be used, e.g. to assess the mixing of the waste in the waste bunker. This can help to improve the bunker waste mixing and thereby ensure a more stable operation of the WtE plant.

Detection of errors in the plant operating data recorded

As described in section 4.2.2, the application of the BM requires the WtE plant operating data to be checked for consistency and plausibility. This is to avoid errors in the BM output data due to their sensitivity to certain input data. Besides excluding implausible data for the BM evaluation, the plausibility checks serve to detect errors in the recorded data which otherwise would probably remain unnoticed. The thesis shows that the data provided of all WtE plants investigated contain certain inconsistencies, of which the most important are:

- errors in the data documentation (e.g. wet flue gas volume specified as dry flue gas volume)
- errors in data conversion (e.g. relation of flue gas volume to a certain oxygen content)
- errors in O_2 or CO_2 measurements (e.g. due to missing control measurements and calibration avtivities)
- systematic over- or underestimations of flue gas volumes

An example is shown in Figure 5.4, where a large share of the data points displayed are outside the theoretically plausible band and a potential overestimation of the flue gas volume of around 20 % can be observed. After investigations of the plant operator and control measurements, the implausible data could be attributed to a significant amount of leak air entering the plant (located between the measuring points for flue

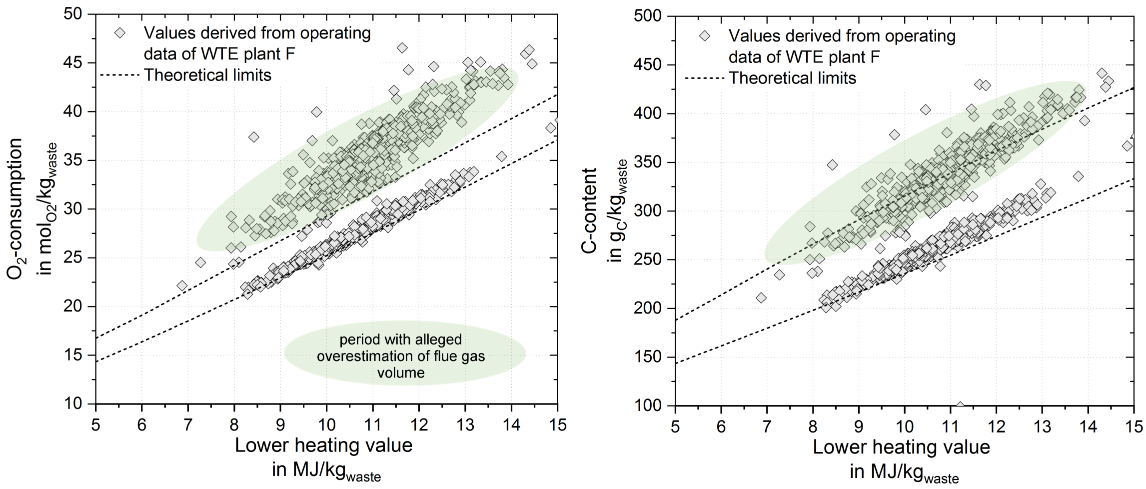


Figure 5.4: Results of plausibility checks (correlation between lower calorific value and O_2-consumption and carbon content of the waste, respectively) for the operating data of WtE plant F (data points represent 6-hourly averages).

gas volume and for the O_2- and CO_2- concentration of the flue gas). Consequently, corrections of the data can be done, also for other detected data errors (e.g. of O_2-measurements after conducting control measurements). Finally, almost 97 % of the operating data of the WtE plants investigated can be considered within the thesis (the number refers to the share of waste mass combusted during the recording of plausible operating data) (Table 5.4). For seven out of ten plants, the share of data classified as plausible is even above 98 %.

Table 5.4: Share of operating data classified as plausible after plausibility checks and data error rectifications, given in wt% of total waste feed (based on Table 2 in *Paper I* [5]).

WtE plant	A	B	C	D[b]	E	F	G	H	I	J	**Total**
	Share of plausible data in wt%[a]										
	98.3	99.3	95.8	84.4	99.5	99.5	98.3	99.0	82.8	99.7	**96.7**

[a] Expressed as share of waste mass combusted during the record of plausible operating data (related to total waste feed) in wt% relative

[b] Seven months have been evaluated for WtE plant D (twelve months for the other plants)

Thus, the BM provides the possibility to identify and rectify unrecognized data errors, thereby confirming the reliability of the measurements at the WtE plant. This can be useful for WtE plant operators as they, for example, use the measured flue gas flow to determine the air ingress and calculate the efficiency of the plant. In some EU member states information on plant efficiency is used to pay emission taxes. Thus, errors in the flue gas measurements can result in false estimates on plant efficiency, incorrect tax payments, or biased conclusions on the air ingress into the plant.

The experiences from large-scale application of the BM also demonstrate that valid operating data are crucial for reliable results. This also implies that additional calibration efforts and control measurements might be required when the BM is to be employed, particularly when a routine application of the method is intended. These additional controls of measuring devices add further reliability to reported values by plant operators.

Improvement of plant operation by information on waste mixing

A further potential of the BM which has been identified in the frame of this thesis, is the provision of information on the waste composition at a high temporal resolution (down to hourly mean values or even more detailed, depending on the availability of operating data). Utilizing this “realtime” data, short time fluctuations of plant operation (e.g. of the steam production) can be traced back to highly inhomogeneous waste composition and thus, to insufficient mixing of the waste feed. An example is shown in Figure 5.5, where hourly means for steam production, consumption of auxiliary fuel oil as well as the water content of the waste feed and the ratio between fossil matter and biogenic matter are presented for a period of 10 days for one plant. Data on steam production and auxiliary fuel oil represent recorded operating data, whereas the water content and ratio between fossil and biogenic matter represent results of the BM.

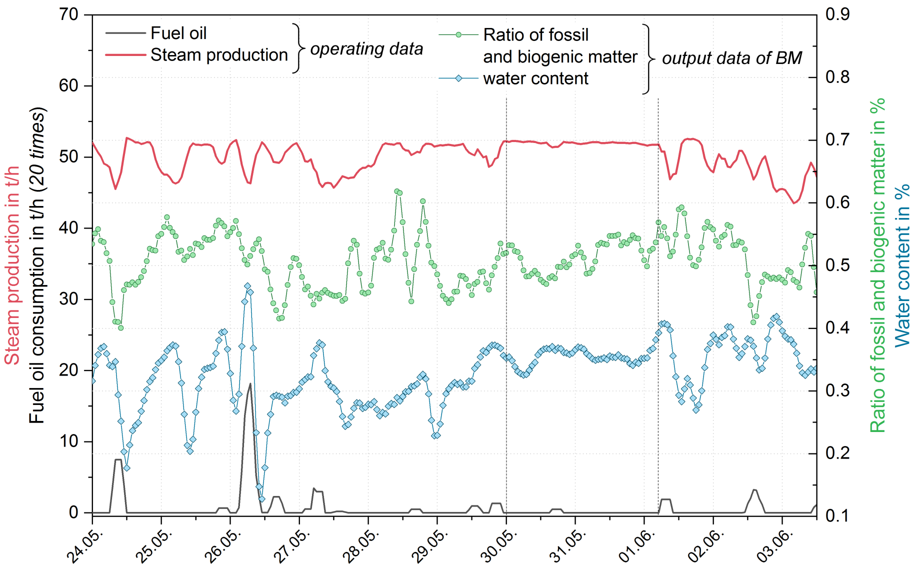


Figure 5.5: Hourly averages for steam production, fuel oil consumption, water content and ratio between fossil and biogenic matter in the waste feed of plant B for a period of 10 days (based on Figure 9 in *Conference paper 2* [7]).

The temporal trend of these four parameters clearly indicates that within the time period of May 30th until June 1st the plant yielded the most constant and thus also the highest rate of steam production, which was also associated with the highest rate of waste throughput (16.2 t h^{-1}). During these two days the water content as well as the ratio of fossil and biogenic matter in the waste feed exhibited comparatively small variations, indicating perfectly adequate mixing of the waste prior to its combustion. In contrast, the time periods before May 30th and also after June 1st were characterized by significant changes in waste composition. These large variations in waste composition are most probably a consequence of insufficient mixing of the waste received, which goes along with varying and thus also reduced steam (energy) production of the plant. Furthermore, the consumption of auxiliary fuels (40 vs. 1.8 kg h^{-1}) increased and waste throughput decreased (14 vs. 16.2 t h^{-1}) during the times of highly variable waste composition. The lower steam production and the higher fuel oil consumption during times of insufficient waste mixing can also be translated into economic terms. Income losses due to lower energy output, additional costs for auxiliary fuels and reduced waste throughput of almost 12,000 € could be estimated for the 10-day period considered. The utilization of high-frequency BM-data at the WtE plant could provide a possibility to control the mixing of the waste in the receiving bunker. Insufficient mixing could be detected by monitoring parameters such as the ratio between fossil and biogenic matter or the water content.

5.2 Application and validation of the adapted Balance Method to characterize refuse-derived fuels

5.2.1 Trueness and repeatability of the adapted Balance Method (*Paper IV & V*)

Trueness of the aBM

The agreement of aBM-results with the theoretical composition of the RDF model mixtures is assessed to draw conclusions on the trueness of the aBM-results. The determined share of fossil carbon (x_F^{TC}) is compared with the theoretical value of the two RDF model mixtures ($x_{F,theory}^{TC}$). Figure 5.6 (a) presents the frequencies across the samples of mixture I and mixture II with respect to the absolute deviation from the theoretical value. The aBM-values for the RDF model mixtures appear to be in good agreement with the theoretical values. No indication of differences between deviations from the theoretical value of mixture I and of mixture II can be found, although the mean deviation shows a slight overestimation of x_F^{TC} (+1.4 %abs). Data of both data sets are combined and fitted to a normal distribution function (shown as theoretical density in Figure 5.6 (a)). Based on the assumption of normally distributed data, there is a probability of 95 % that the pooled data are within 3.0 %abs (6.7 %rel) of the theoretical x_F^{TC}-value. This finding is regarded as an estimate for the trueness

Table 5.5: Estimates on the trueness of the aBM-results based on RDF model mixtures for the parameter x_F^{TC} (share of fossil carbon) (based on Table 3 in *Paper IV* [3]).

	RDF model mixture I	RDF model mixture II
	Paper:PE	Paper:Cardboard:PE:PET:PS
Theoretical fossil carbon fraction $x_{F,theory}^{TC}$ in wt% $\pm SD$	38.7 ± 0.7	59.3 ± 1.6
Share of fossil carbon determined by aBM $x_{F,aBM}^{TC}$ in wt% (arithmetic mean $\pm SD$)	40.9 ± 1.9	60.3 ± 1.7
Mean deviation of aBM-value from theoretical value in %abs $(x_{F,aBM}^{TC} - x_{F,theory}^{TC})$	+2.2 %	+1.0 %
2-tailed t-test for differences from 0	$(***)$	$(***)$
Variation of the deviation from theoretical value (SD of $(x_{F,aBM,i}^{TC} - x_{F,theory}^{TC})$)	3.0 %abs / 7.7 %rel	2.0 %abs / 3.3 %rel
Deviation of aBM-value from theoretical value at a probability of 95 % (based on a normal distribution function, see Figure 5.6)	3.0 %abs (6.7 %rel)	
Number of samples	$N = 16$	$N = 36$

Significance codes for t-test: $p < 0.001$ $(***)$; $p < 0.01$ $(**)$; $p < 0.05$ $(*)$; $p < 0.1$ ( ); $p > 0.1$ $(-)$ with $(***)$ being highly significant

of the aBM within the thesis. The mean deviation of the aBM-calculated share of fossil carbon ($x_{F,aBM}^{TC}$) in the RDF model mixtures from the theoretical value ($x_{F,theory}^{TC}$) is found to be +2.2 %abs for RDF model mixture I, and +1.0 %abs for RDF model mixture II (+5.7 %rel, and +1.7 %rel, respectively) (Table 5.5).

The trueness of the results for the RDF samples investigated can hardly be evaluated due to the unknown theoretical (true) value. However, the ^{14}C-method is used as a provisional reference method, since this method has the highest analytical accuracy amongst the available methods [42,83]. Comparing the mean share of fossil carbon (x_F^{TC}) determined by the aBM and by the ^{14}C-method for three different RDFs, no significant differences are found between the two methods (based on statistical tests). On average the aBM-values are 0.6 %abs above the ^{14}C-values (Figure 5.6 (b)). Mean deviations between the two methods of −0.9 %abs (RDF 3) to +1.9 %abs (RDF 2) are found, which corresponds to relative deviations between −1.1 %rel and +2.3 %rel (Table 5.6). For RDF 1 and RDF 3 the deviations are clearly within the uncertainties of the ^{14}C-method.

The deviations from the reference value can be observed to vary amongst the single RDF samples between 2.8 %abs and 6.8 %abs. The highest variation found for RDF 1

Table 5.6: Estimates on the trueness of the aBM based on RDF samples and on the comparison with ^{14}C-method for the parameter x_F^{TC} (share of fossil carbon). (based on data presented in *Paper V* [4]).

	RDF 1	RDF 2	RDF 3
Share of fossil carbon determined by ^{14}C-method $x^{TC}_{F,^{14}C}$ in wt% $\pm SD$	55.6 ± 0.5	82.6 ± 0.4	81.3 ± 0.4
Share of fossil carbon determined by aBM $x^{TC}_{F,aBM}$ in wt% (arithmetic mean $\pm$ SD)	56.4 ± 0.7	84.5 ± 1.0	80.4 ± 0.8
Mean deviation of aBM-value from ^{14}C-value in %abs $(x^{TC}_{F,aBM} - x^{TC}_{F,^{14}C})$	$+0.8\,\%$	$+1.9\,\%$	$-0.9\,\%$
2-tailed t-test for differences from 0	( )	$(*)$	( )
Variation of the deviation from ^{14}C-value (SD of $(x^{TC}_{F,aBM,i} - x^{TC}_{F,^{14}C})$)	6.8 %abs / 12.2 %rel	4.8 %abs / 5.8 %rel	2.8 %abs / 3.5 %rel
Deviation of aBM-value from ^{14}C-method at a probability of 95 % (based on a normal distribution function, see Figure 5.6 (b))	3.6 %abs (6.1 %rel)		
Number of samples	$N = 8$	$N = 4$	$N = 4$

Significance codes for t-test: $p < 0.001$ $(***)$; $p < 0.01$ $(**)$; $p < 0.05$ $(*)$; $p < 0.1$ ( ); $p > 0.1$ $(-)$ with $(***)$ being highly significant

indicates that the composition of this RDF varies distinctly and the trueness of the aBM-results can also differ depending on the samples.

Fitting the deviations of all three RDFs to a normal distribution function (Figure 5.6 (b) delivers an agreement of the aBM-data with the ^{14}C-method data within 3.6 %abs (6.1 %rel) (based on a probability of 95 %). This indicates a high degree of trueness of the aBM, also when applied to real RDFs.

Repeatability of the aBM

In a second step, the repeatability (precision) of the aBM is estimated by evaluating the variation of the observations for the RDF model mixtures as well as for the RDF samples. Thereto the standard deviation caused by the variation of the measurement repetitions per sample is determined based on a simple analysis of variance (equations provided in Table 4.5).

Results are presented in Figure 5.7, where a part of the total variance is attributed to the

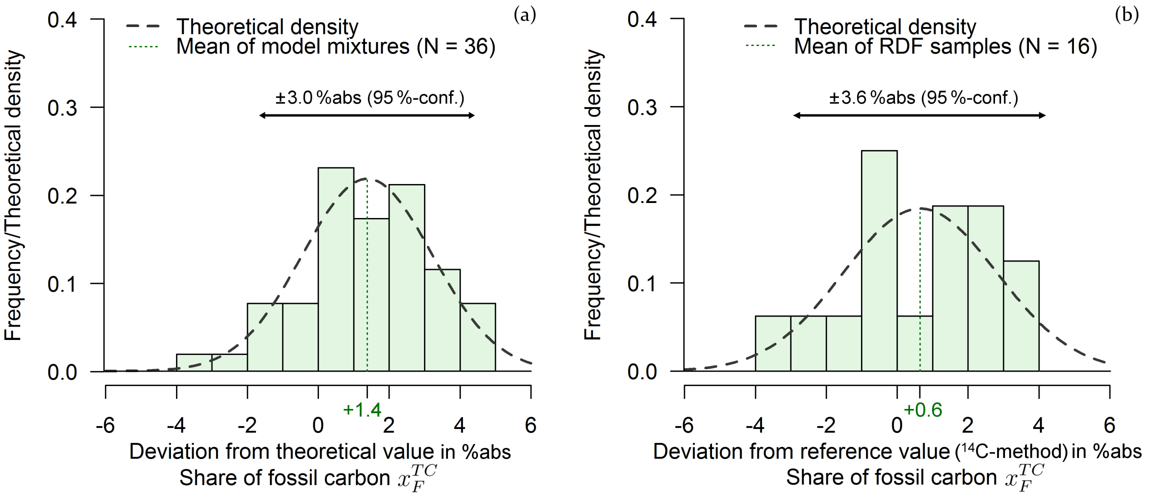


Figure 5.6: Relative frequency histogram and fitted normal density curve for the absolute deviation of the aBM-results (a) from the theoretical value found for RDF model mixtures and (b) from the reference value (results of ^{14}C-analysis) found for real RDF samples, based on the parameter x_F^{TC} (share of fossil carbon).

differences *between* the samples and one part is assumed to be caused by the analyses conducted and the aBM-evaluation (*within* the samples). The latter is regarded as an indicator for the repeatbiltiy (precision) of the aBM.

The standard deviation resulting from variation within the sample measurements of the RDF model mixtures is determined as being 1.9 %abs and 1.1 %abs for the data sets of model mixture I and model mixture II, respectively (when x_F^{TC} is considered). This means that relatively, the x_F^{TC} sample values of the RDF model mixtures are scattered between ± 2 %rel and ± 5 %rel around their mean (RSD as presented in Figure 5.7).

For the RDFs investigated (RDF 1, RDF 2, RDF 3, RDF 4, RDF 5, RDF 6), the standard deviations determined within the RDF samples for the aBM-calculated x_F^{TC} range from 0.6 %abs to 2.0 %abs. RSD between ± 0.9 %rel and ± 2.3 %rel are therefore determined expressing the dispersion around the mean, which is caused by the necessary analyses of the aBM. These data represent the repeatability (precision) determined within the thesis and will be compared to one of other methods (see section 5.2.3).

For all materials considered (RDF model mixtures and real RDF samples), the variance between the samples is significantly greater than the variance caused by the repeated measurements (based on a 95 %-confidence interval). This indicates that sampling and sample preparation adds more to variance of the aBM-results than the conducting of the aBM analyses and its calculations. Thus, sampling and sample preparation can be confirmed as crucial steps to arrive at a representative result on the RDF composition. The effects of the different sample preparation steps on the aBM results are addressed in section 5.2.4.

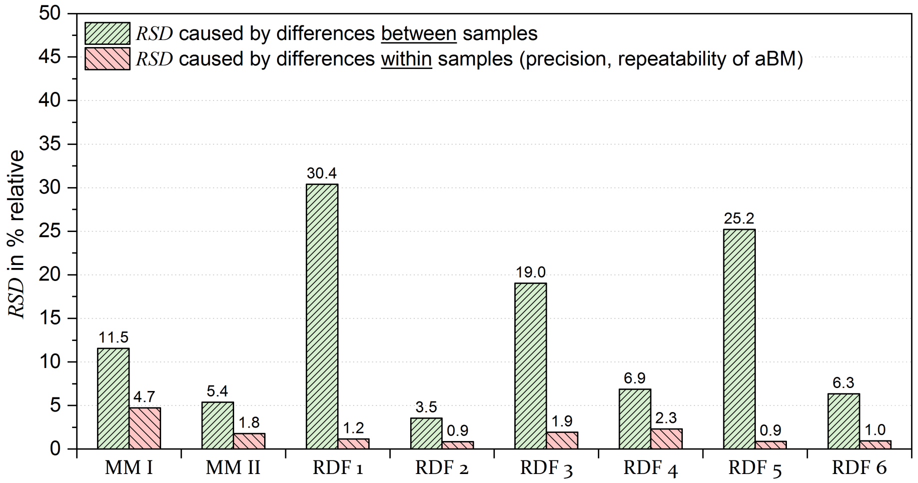


Figure 5.7: Relative standard deviation (RSD) ascribed to differences between the samples and to differences within samples (representing the determined repeatability of the aBM within the thesis); results from variance analysis according to Table 4.5 and based on the parameter x_F^{TC}.

5.2.2 Comparison of the aBM-results to results from standardized methods (*Paper V*)

Comparisons of aBM-results to ^{14}C-method results have already been described in the previous section. In order to also consider the performance of other standardized methods (SDM and MS), this section presents the direct comparisons and correlations between the aBM, the SDM, MS, and the ^{14}C-method based on the RDFs investigated. Results of three RDFs investigated are presented in terms of the share of fossil carbon x_F^{TC} determined.

Figure 5.8 shows that the share of fossil carbon in the RDFs is determined in the range of 51.8 to 84.5 % within the thesis. The lowest shares are found for RDF 1, which stems from the reject stream of a paper and board recycling plant and for which around 37 wt% of the mass are found to be represented by paper and cardboard (based on sorting results).

Visible from Figure 5.8 and pointed out already in the previous section (Table 5.6), an excellent agreement between the ^{14}C-method and the aBM is discernable for the RDF samples investigated. Also exemplary results for single sorted RDF fractions, such as paper/cardboard, plastics and composites, are consistent between the ^{14}C-method and the aBM (examples are presented in Figure 5.8). However, the fossil share in textiles appears to be underrated by the aBM compared to the ^{14}C-method. The apparent underrating is to some extent reflected in the aBM-results for RDF 2: RDF 2 is found to contain a significant amount of textiles (~23 wt% based on sorting results) and a slightly higher deviation (1.9 %abs) of the aBM from the ^{14}C-method-results is found compared to the other RDFs.

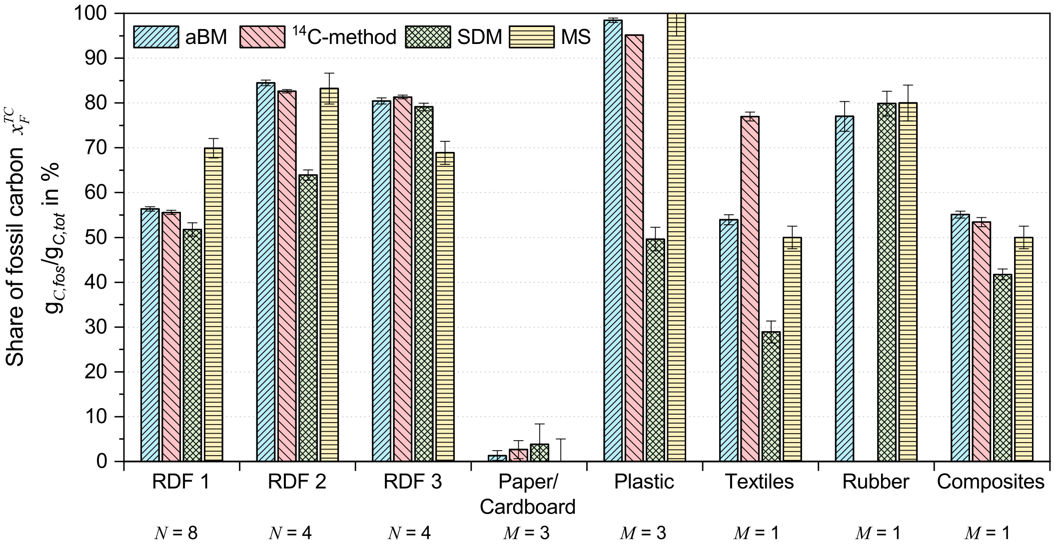


Figure 5.8: Average share of fossil carbon determined by different methods for RDF and sorted RDF-fractions; N = number of RDF samples; M = number of samples stemming from different RDFs (based on data presented in *Paper VI* [8]).

When results of the SDM are considered, an underestimation by trend of the fossil share of carbon can be observed. Significantly lower SDM-results compared to the ^{14}C-method and aBM are determined for RDF 2 (−18.7 wt% absolute), RDF 1 (−3.8 wt% absolute), particularly for the sorted plastics fraction, textiles and composites (up to −50 wt% absolute) (Table 5.7 and Figure 5.8). This suggests the presence of considerable amounts of chemically dissolvable materials, which are of fossil origin. For example, not only are significant shares of textiles found in RDF 2, but also foamed polymers within the plastics fraction of RDF 2. Both materials potentially comprise polymers containing amino-groups. When treated with concentrated sulphuric acid, these polymers are dissolved almost entirely and are therefore wrongly accounted for as biogenic.

Comparing results of MS to ^{14}C-method- and aBM-results, significant differences are found for RDF 1 and allegedly also for RDF 3 (although no significance test could be done for this RDF due to limited sample size) (Table 5.7). No clear trend on under- or overestimations is discernable. The apparently false estimates can be attributed to different methodological factors of MS:

(i) High shares of fine fraction, textiles or composite materials can easily falsify the fossil mass share. These fractions are usually a mix of biogenic and fossil materials; the actual ratio between biogenic and fossil can, however, vary between different wastes and RDFs. When considering a global fossil share in the mixed fractions (e.g. 50 wt% are suggested for the fine fraction and in textiles in EN 15440:2011[43]), distortions of the overall result can easily occur.

Table 5.7: Share of fossil carbon (x_F^{TC}) determined for three different RDFs; results of four different methods are presented, together with the deviations from results of the ^{14}C-method (based on Tables 6, 7, and 8 in *Paper IV* [4]).

	Share of fossil carbon x_F^{TC}								
Method	RDF 1			RDF 2			RDF 3		
	$mean \pm SD$	$dev.^{14}C$	$Sign.$	$mean \pm SD$	$dev.^{14}C$	$Sign.$	$mean \pm SD$	$dev.^{14}C$	$Sign.$
	wt%	wt%abs		wt%	wt%abs		wt%	wt%abs	
^{14}C-method	55.6 ± 0.5	-		82.6 ± 0.4	-		81.3 ± 0.4	-	
aBM	56.4 ± 0.7	+0.8	(−)	84.5 ± 1.0	+1.9	(−)	80.4 ± 0.8	−0.9	(−)
SDM	51.8 ± 1.5	−3.8	(∗ ∗ ∗)	63.9 ± 1.2	−18.7	(∗∗)	79.1 ± 0.8	−2.2	(−)
MS	69.9 ± 1.6	+14.3	(∗ ∗ ∗)	83.2 ± 3.9	+1.2[a]	n.a.	68.9 ± 2.6	−6.0[a]	n.a.

Significance codes for t-test: $p < 0.001$ (∗ ∗ ∗); $p < 0.01$ (∗∗); $p < 0.05$ (∗); $p < 0.1$ ( ); $p > 0.1$ (−)

$dev.^{14}C$ mean deviation from result of the ^{14}C-method as absolute percentage (minus = result is lower than result of the ^{14}C-method)

SD represents the analytical uncertainty (derived per method as described in section 2.5 of paper V and considering the number of samples N given in Figure 5.8)

[a] MS: $dev.^{14}C$ refers to another ^{14}C-method-mean value than presented here (as only two MS samples can be compared)

(ii) For estimating the share of fossil carbon by means of MS, information on the carbon content in the sorted fractions is necessary. By relying on carbon contents reported in the literature, further systematic uncertainties might be introduced into the result. For example, within the thesis the carbon content in biogenic materials derived for RDF 1 from the literature is found to be almost 9 %abs below the analytically derived value.

(iii) Finally, sorting inaccuracies are easily introduced into the results by human subjectivity while sorting as well as by practical limitations of the method. When sorting RDF 1, for example, shares of small cardboard particles or cellulose fibers which are attached to bigger plastic particles can hardly be separated.

The results show that

- for none of the RDFs investigated a consistent relationship between the four compared methods observable.
- the aBM is the only method for which low deviations and good correlations with the results of the ^{14}C-Method could be observed for all RDFs investigated.
- the most significant inaccuracies of the methods are assumed to be caused by high shares of textiles and foamed plastics (particularly relevant for SDM and aBM) as well as considerable shares of fine fraction and composites in the RDFs (affecting mainly MS-results).

5.2.3 Comparison of trueness and precision for different determination methods in previous studies

In order to put the aBM-results within the thesis into perspective, Table 5.8 contrasts results on trueness and precision with findings from previous studies and with the results of standardized methods. For the aBM, the mean deviations from the reference value found (as presented in Table 5.8) are comparable – yet in a slightly higher range – to reported figures in Fellner et al. (2011)[47] and in Schnöller et al. (2014)[107] (deviations of below 1.1 %abs from reference x_F^{TC}-value are reported, compared to a deviation below 2.2 %abs within this thesis). However, the present thesis constitutes the first aBM-investigation with more complex mixtures and, in particular, also with reals RDFs. Thus, slightly higher inaccuracies are somewhat expected when compared to the aBM-performance based on simple artificial RDFs (two-component mixtures which were mixed at low grain sizes are examined in Fellner et al., 2011 and in Schnöller et al., 2014[47,107]).

The trueness of the aBM also appears competitive with results reported for standardized methods. For example, Ariyaratne et al. (2014)[109] applied the SDM and ^{14}C-method to 5-component artificial RDFs (wood, paper, plastics) and noted significantly higher deviations from the theoretical value for both methods (up to 12 %abs for the SDM and 13 %abs for the ^{14}C-method). Also Muir et al. (2015)[73] found distinct differences between the theoretical and the determined value when SDM is applied to RDFs (up to 26 %abs deviation). Within the present thesis, deviations of 12 %abs (at 95 % conf.) from the reference value are found for the SDM-results, which is significantly higher than deviations found for the aBM (with deviations of 3 %abs at 95 % conf.) (Table 5.8). Cuperus et al. (2005) tested 53 different pure materials, from which single materials revealed an SDM error of up to 100 %abs[40]. All the findings clearly show the high dependence of SDM's reliability on the presence of certain materials in the sample. Significant analytical inaccuracies of SDM are also evident when comparing results of different laboratories, as done by Muir et al., 2015 (absolute differences of up to 19 %abs based on the share of biogenic energy)[73]. A recent interlaboratory comparison further showed that from the SDM-values generated by 12 laboratories only 30 to 70 % were within the tolerance limits of two standard deviations (based on the share of biogenic carbon)[112]. Regarding the repeatability of the SDM, however, standard deviations are reported which are in the range of the aBM (SDM: ± 1 to ± 5 %abs, ± 0.1 to ± 7 %rel; aBM: ± 0.6 to ± 3 %abs, ± 0.9 to ± 8 %rel) (Table 5.8).

As for the ^{14}C-method, collected findings from the literature show that results for this method can vary by up to ±5 %abs when applied to WtE flue gas samples or to RDFs (repeatability in Table 5.8). The uncertainty of Liquid Scintillation counting (LSC) is even above that of Accelerator mass spectrometry (AMS) (±14 %abs are reported for LSC by Muir et al., 2015, compared to below ±1 %abs for AMS)[73]. The reliability of ^{14}C-results is mainly determined by the choice of the $F^{14}C_{\mathrm{bio}}$ reference value, which

Table 5.8: Comparison of determination methods in terms of trueness and repeatability based on results in previous studies and within the present thesis.

Method	Deviation from reference value (Trueness[1])	Precision (Repeatability)	Parameter	Type of samples	Reference
aBM	<1.1 %abs	<±5 %rel	x_F	artificial RDF (2-components)	Fellner et al. (2011)[47]
	<1 %abs <2 %rel	±2.5–3.1 %abs ±6–8 %rel	x_F^{TC}	artificial RDF (2-components)	Schnöller et al. (2014)[107]
	<2.2 %abs (mean) 3.0 %abs (95%)	±1.1–2.0 %abs ±1.8–4.8 %rel	x_F^{TC}	artificial RDFs (2- and 5-components)	this thesis
	0.8–2 %abs (mean)[2] <3.6 % abs (95%)[2]	±0.6–2.0 %abs ±0.9–2.3 %rel	x_F^{TC}	6 different RDFs (for trueness only 3 RDFs)	this thesis
SDM	0–100 %abs	1.4 %abs	x_B	53 different waste compounds	Cuperus et al. (2005)[40]
		±3.6 %abs ±6.6 %rel	x_F^{TC}	reassampled SRF from MSW	QUOVADIS (2007)[68]
		±0.1–2.4 %rel	x_B	RDF from MSW	Severin et al. (2010)[108]
	1.7–12 %abs 15 %rel (mean)		x_F^{TC}	artificial RDF (5-components)	Ariyaratne et al. (2014)[109]
	2.3 %abs 5.7 %rel	±2 %abs ±4.4 %rel	x_F^{TC}	artificial RDF (2-components)	Schnöller et al. (2014)[107]
	2–19 %abs (mean)[2] 12.1 %abs (95%)[2]	±1–5 %abs ±1–13 %rel	x_F^{TC}	3 different RDFs	this thesis
	1–26 %abs (mean)[2]	7–19 %abs[3] 9–33 %rel[3]	q_B	RDF (3 different size fractions)	Muir et al. (2015)[73]
^{14}C-method (AMS)	1.8–7.5 %rel		x_B^{TC}	flue gas of artificial RDF (2-components)	Fichtner (2007)[41]
		±3 %rel	x_B^{TC}	>100 products	Fichtner (2007)[41]
		±3–4 %abs	x_F^{TC}	flue gas at 3 WtE plants	Mohn et al. (2008)
		±3–4 %abs (95 %)	x_F^{TC}	flue gas at WtE plant	Palstra & Meijer (2010)[42]
		±1.6 %abs ±3.0 %rel	x_F^{TC}	flue gas at WtE plant	Calcagnile et al. (2011)[110]
		3.6–5.0 %abs	x_F^{TC}	flue gas at 5 WtE plants	Mohn et al. (2012)[77]
		±0.7–4.5 %abs	x_B^{TC}	biogas samples	Palstra & Meijer (2014)[111]
	0.0–13 %abs 25 %rel (mean)		x_F^{TC}	artificial RDF (5-components)	Ariyaratne et al. (2014)[109]
	6.8 %abs 16.8 %rel	±1.1 %abs	x_F^{TC}	artificial RDF (2-components)	Schnöller et al. (2014)[107]
		±0.2–0.3 %abs	x_B^{TC}	RDF (3 different size fractions)	Muir et al. (2015)[73]
		±0.2 %abs	x_F^{TC}	flue gas at WtE plant	Muir et al. (2015)[73]
		±0.5–1.8 %abs	x_F^{TC}	3 different RDFs	this thesis
^{14}C-method (LSC)		±5.0 %abs (95 %)	x_B^{TC}	flue gas at WtE plant	Larsen et al. (2013)[74]
		±8–14 %abs	x_B^{TC}	RDF (3 different size fractions)	Muir et al. (2015)[73]
		±10–14 %abs	x_F^{TC}	flue gas at WtE plant	Muir et al. (2015)[73]
MS	1–14 %abs (mean)[2]		x_F^{TC}	3 different RDFs	this thesis
		±3.7 %abs	q_B	MSW (3 samples)	Muir et al. (2015)[73]

[1] Trueness is synonymous with accuracy of the mean

[2] taking ^{14}C-result as reference value

[3] variation between results from two different laboratories (representing the reproducibility)

depends on the growing years of the biomass.

For MS, only limited information on the performance is available, which is most probably due to the restricted practicability of the method. For example, analysis replications of the same sample are hardly feasible and results can often not be validated.

Taking the performance indicators presented in Table 5.8 into account, the thesis results clearly show that the aBM is competitive with the standardized methods.

5.2.4 Robustness of the adapted Balance Method (*Paper IV & VII*)

Different effects of potential interferences on the aBM are investigated with the aim of providing indications on the robustness of the method and to identifying approaches for optimization.

Effects of sample preparation

The effects of two different mills are comparatively assessed, as well as the contribution of each sample preparation step on the total variance of the aBM-results. The trueness and precision of RDF model mixture samples prepared by UCM, Cryomill or a combination of both as a finishing comminution step is evaluated.

Results show that the share of fossil carbon of samples comminuted by the Cryomill is overrestimated by trend (+3.3 and +1.9 %abs) (Table 5.9) and the deviations from the theoretical value for Cryomill-finished samples is significantly different from zero (for both mixtures). For UCM-comminuted samples this deviation is less significant and an overestimation of x_F^{TC} is less distinct (+0.2 to +1.1 %abs). This indicates that the trueness of the results after Cryomill-milling might be impaired by this comminution step. A t-test also reveals that there are significant differences in means between samples with different finishing both when mixture I and mixture II is considered.

Significant differences in the variation of the results are also observed when comparing samples of mixture I processed with different mills (UCM or Cryomill) (indicated by the significance code of the Levene test in Table 5.9). When mixture II is considered, the difference in standard deviation observed for samples with different final comminution is not significant.

The diverse variances for samples with different final preparation steps are attributed to unequal grain size distributions within the analysis samples. When applying the UCM, cellulose fibers of paper and cardboard material in the mixtures are not completely destroyed and tend to agglomerate to particles larger than the desired 0.2 mm (visual observation and confirmed by sieve analysis). In contrast, the Cryomill crushes fibers to a large degree, but does not allow samples of defined particle size to be

Table 5.9: Results of aBM for two RDF model mixtures with different mills applied as final comminution step for the parameter x_F^{TC} (share of fossil carbon) (based on Table 3 in *Paper IV* [4]).

	RDF model mixture I Paper:PE		RDF model mixture II Paper:Cardboard:PE:PET:PS	
	UCM-finished samples	Cryomill-finished samples	UCM+Cryomill-finished samples	Cryomill-finished samples
Theoretical fossil carbon fraction $x^{TC}_{F,theory}$ in wt% waf ± SD	38.7 ± 0.7		59.3 ± 1.6	
Share of fossil carbon determined by aBM $x^{TC}_{F,aBM}$ in wt% for samples with different finishing (arithmetic mean ± SD)	39.8 ± 2.1	42.0 ± 0.7	59.5 ± 1.6	61.2 ± 1.3
Result of 2-tailed t-test for *differences in mean* between samples with different finishing	$(*)$		$(**)$	
Result of Levene test for *differences in variation* between samples with different finishing	$(*)$		$(-)$	
Mean deviation of aBM-value from theoretical value %abs $x^{TC}_{F,aBM} - x^{TC}_{F,theory}$)	+1.1 %	+3.3 %	+0.2 %	+1.9 %
2-tailed t-test for differences from 0	( )	$(**)$	$(-)$	$(***)$
Number of samples	$N = 8$	$N = 8$	$N = 18$	$N = 18$

Significance codes for t-test: $p < 0.001$ $(***)$; $p < 0.01$ $(**)$; $p < 0.05$ $(*)$; $p < 0.1$ ( ); $p > 0.1$ $(-)$ with $(***)$ being highly significant generated. Although the milling bin of the Cryomill is cooled with liquid nitrogen (−196 °C) to enhance crushing of elastic particles (rather than plating them), sieve analysis for samples milled only via Cryomill show an accumulation of plastics in the larger grained fraction of the samples (sieving results are presented in the supplementary material of *Paper IV*).

In order to assess the impact of the single sample preparation steps on the variation (precision) of the aBM-results, a variance component analysis (VCA) as a nested design is conducted based on equations in Table 4.6. Looking at the results in Figure 5.9, the samples milled by UCM clearly show the highest overall variance. The last milling step (Layer (3)) as well as the subsampling Layer (4) add the most to the overall variance. This is also observed for Cryomill-samples of mixture I and mixture II. Thus, these two layers appear the most crucial when it comes to sample preparation. Statistical tests also indicate that there is a significant difference among the samples after the last milling and splitting step and also after the subsampling for analysis (confidence level of 95 %). The subsampling represents the drawing of small specimens (4 to 40 mg in this thesis) from the analysis sample to be fed into the elemental analyzer. High variances for this layer indicate that the particle size is still not fine enough to reduce the error from subsampling. An alternative to further milling could be an increase in the specimens to reduce this error and to control this step by appropriate homogenization and the sampling tool (e.g. according to EN 15442:2011[113] the width and length of the sampling tool should exceed the grain size by at least a factor of ten).

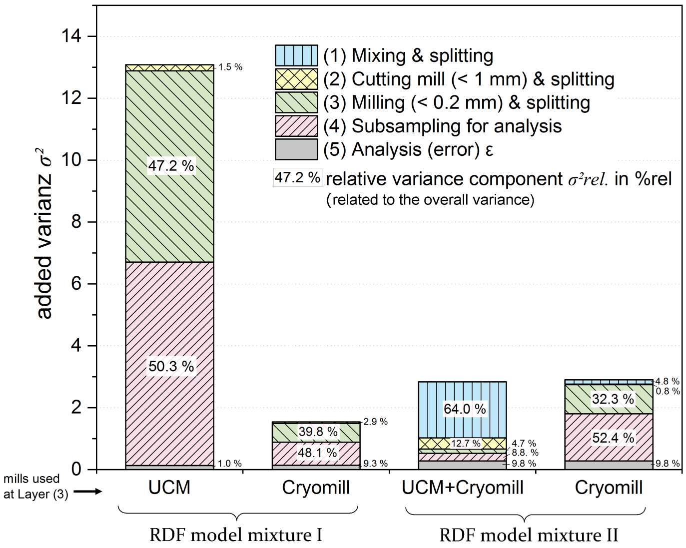


Figure 5.9: Variance components describing the share of fossil carbon x_F^{TC} determined by the aBM for RDF model mixture I and RDF model mixture II; results of nested variance component analysis for different steps of sample preparation are presented (according to Table 4.6) (based on Table 4 and 5 in *Paper IV*[3]).

For RDF model mixture I, the added variance from Layer (4) is lower for Cryomill-samples than for UCM-samples. It is assumed that these findings result from better fiber destruction by the Cryomill, which facilitates representative subsampling for final analysis. Likewise, with regards to mixture II, the significantly lower added variance from Layer (4) for UCM+Cryomill-samples compared to Cryomill-samples indicates that more homogenous samples are produced when both mills are applied. Thus, the application of both mills leads to a small variation of replicate measurements. It is assumed that the different grinding mechanisms of both mills destroy cellulose fibers (mainly by the Cryomill) as well as plastic particles (mainly by the UCM) to a large extent. The influence of the matrices on the variation of the results is also confirmed when Cryomill-samples of mixture I and Cryomill-samples of mixture II are compared. It is apparent that the added variation from milling and especially from subsampling is higher for mixture II than for mixture I. This demonstrates that the destruction of plastic particles is crucial when they are represented at a high share (in mixture II almost 40 % by weight).

Unexpectedly, a dominant influence of the first mixing and splitting step for UCM+Cryomill samples (a relative importance of Layer (1) of 64 %) is observed. This high variation caused by Layer (1) suggests that the mixing and first splitting (done at 4 mm grain size) did not lead to two equally divided parts. However, this finding is not confirmed by the results of the Cryomill-samples of mixture II. It is expected that this error could easily be reduced by thorough homogenization of the sample before being split or by a further particle size reduction (e.g. by cutting mill) before the next splitting to reduce demixing effects.

A proper homogenization of the sample before analysis and a suitable method of drawing representative specimens from the analysis sample are essential. Both are obviously linked to the grain size and grain size distribution of the analysis sample. Subsampling for elemental analysis requires high experimental control and a sufficient number of replications is indispensable, particularly when more complex mixtures are analysed.

Robustness of the aBM-input parameter

The application of the BM as well as the aBM requires information on the elemental composition of biogenic and fossil organic matter (on a water-and-ash-free basis) present in the material to be analyzed (TOX_F, TOX_B). This information is not only essential for the application but also apparently determines the aBM and BM results and can require considerable workload to be done before valid BM- and aBM-results can be delivered.

Previous investigations in Fellner et al. (2011)[47] show that for the aBM a relative error of 1 % of TOX_F and TOX_B can lead to a systematic error of the share of fossil carbon

Table 5.10: Elemental composition of water-and-ash-free fossil organic matter (TOX_F) present in MSW and RDFs (based on Figure 6 and 7 in *Paper VII*[12]).

in g kg^{-1}_{waf}	TOC		TOH		TOO		TON		TOS	
	$mean$	SD	$mean$	SD	$mean$	SD	$mean$	SD	$mean$	SD
MSW Austria[a]	777	16	112	11	61	13	13.9	5.6	3.0	0.3
RDF Austria[b]	769	20	109	7	88	22	13.0	5.4	3.0	1.1
RDF 1	782	8	119	4	31	8	4.7	1.0	5.8	1.4
RDF 2	726	8	99	1	143	5	23.3	1.8	4.0	0.5
RDF 3	777	8	115	3	108	9	3.3	0.5	3.6	0.5
RDF 4	773	10	111	3	92	11	4.0	0.7	9.2	1.4
RDF 5	780	6	117	1	85	4	3.6	0.5	5.1	1.2
RDF 6	785	6	111	1	94	4	9.1	0.5	11.5	1.3
RDF 1 to RDF 6:										
$mean$	771	18[c]	112	6[c]	92	29[c]	8.5	6.2[c]	6.5	2.5[c]
CV	3 %		6 %		40 %		97 %		48 %	
RDF 3 to RDF 6:										
$mean$	779	5[c]	113	3[c]	95	9[c]	5.0	2.7[c]	7.3	3.6[c]
CV	1 %		3 %		10 %		55 %		50 %	

[a] used within this thesis for BM application (based on existing sorting campaigns, reported elemental compositions and regional consumption data – see section 4.1)

[b] Source: Fellner et al. (2011)[47]

[c] 95 %-confidence interval

of up to 0.7 %rel (with the most decisive parameters being TOC_B, TOO_B, TOC_F and TOH_F). For the BM an error of up to 2.2 %rel must be assumed due to a 1 % relative error of carbon content in fossil matter (with TOC_F being the most decisive parameter before TOH_B)[2]. Relative errors of the BM-result (biogenic carbon) of around 2.5 % and 5 % are found by Larsen et al (2013) when varying TOX_F and TOX_B input values, respectively[74].

Within the thesis, different options have been chosen to derive TOX_F and TOX_B (see section 4.1). For the BM previous data collections by Fellner et al. (2007)[2] are relied on with amendments based on more recent reported sorting results. No further investigations have been conducted regarding the input values for the BM within this thesis. The derived elemental composition (with a 95 %-confidence interval) which is utilized in the present investigations for the BM is presented in Table 5.10 and Table 5.11.

Table 5.11: Elemental composition of water-and-ash-free biogenic matter (TOX_B) present in MSW and RDFs (based on Figure 6 and 7 in *Paper VII*[12]).

in g kg$^{-1}_{\mathrm{waf}}$	TOC		TOH		TOO		TON		TOS	
	$mean$	SD	$mean$	SD	$mean$	SD	$mean$	SD	$mean$	SD
MSW Austria[a]	483	4	65	12	443	68	7.0	2.5	1.1	0.2
RDF Austria[b]	479	7	63	1	452	5	3.7	0.8	1.1	0.2
RDF 1	477	5	63	1	451	9	1.9	0.1	2.4	0.3
RDF 2	463	9	64	1	478	9	7.8	0.7	4.1	0.5
RDF 3	470	10	65	2	482	10	2.7	0.5	2.0	0.5
RDF 4	482	2	66	1	458	7	4.2	0.5	4.2	1.3
RDF 5	475	4	65	1	474	7	4.4	0.5	4.7	1.1
RDF 6	467	2	64	1	512[c]	7	3.6	0.5	6.5	1.5
RDF 1 to RDF 6:										
$mean$	472	6[d]	65	1[d]	476	17[d]	4.1	1.6[d]	4.0	1.3[d]
CV	2 %		2%		5%		50 %		41 %	
RDF 3 to RDF 6:										
$mean$	474	7[d]	65	1[d]	481	22[d]	3.7	0.7[d]	4.3	1.8[d]
CV	1%		1%		5%		20 %		42 %	

[a] used within this thesis for BM application (based on existing sorting campaigns, reported elemental compositions and regional consumption data – see section 4.1)

[b] Source: Fellner et al. (2011)[47]

[c] most probably a slight overestimation of the oxygen content occured

[d] 95 %-confidence interval

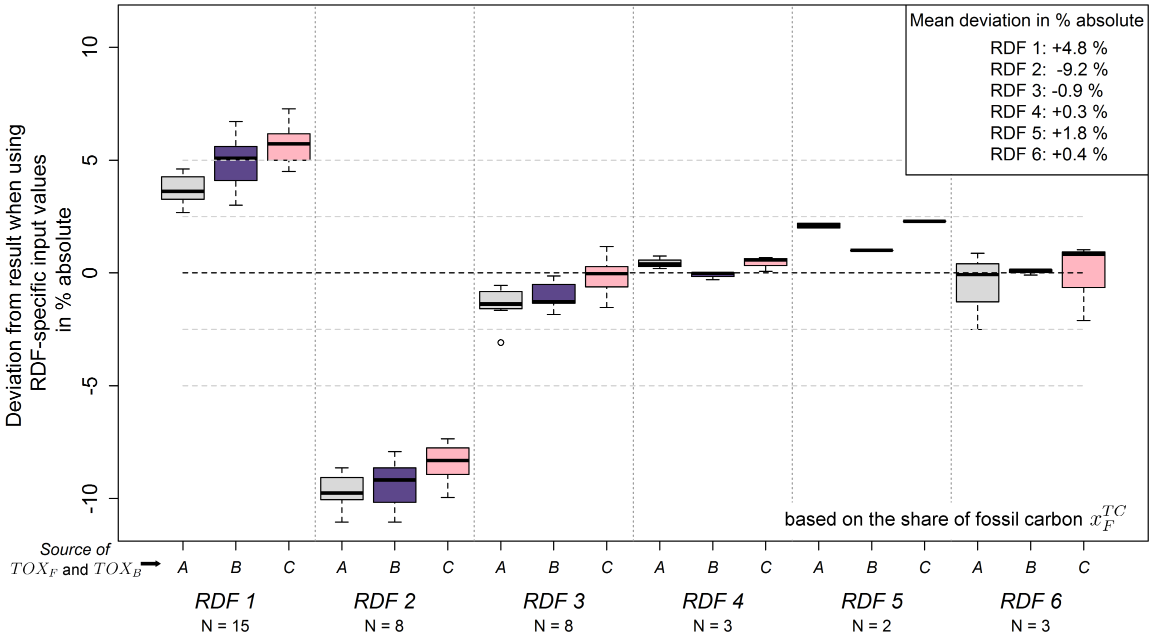
For the aBM, input values used within the thesis are generated RDF-wise (for six different RDFs). This is to extend the currently sparsely available database and to draw conclusions on the robustness of generated and previously collected data for TOX_F and TOX_B (e.g. in Fellner et al, 2011[47]).

In *Paper VII*[12], different procedures to derive TOX_F and TOX_B are compared, using either literature values or own analyses. These investigations revealed that the most accurate aBM results (<2 %rel) are expected when RDF-specific sortings and elemental analyses of sorted compounds are combined with information from the literature. Literature values for the elemental composition of fossil and biogenic matter in mixed compounds are used (mixed compounds represent a mixture of biogenic and fossil matter, e.g. composites, textiles, fine fraction).

The data generated on TOX_F and TOX_B for the RDFs investigated are listed in Table 5.10 and in Table 5.11. Amongst the six RDFs (RDF 1 to RDF 6), the TOC and TOH show a variability with a coefficient of variation (CV) below 6 %rel (in fossil organic matter) and below 2 %rel (in biogenic matter). Disregarding TON and TOS (negligible influence on aBM results and high analytical uncertainties), the most variable value is the TOO in the fossil organic matter, which varies by around 40 %rel considering all RDFs investigated. This indicates a high dependence of the TOO content on the polymer types present in the RDF. A higher TOO content found in the fossil organic matter of RDF 2 signals higher shares of polyamide, polyethylene terephthalate, or polyurethane. In contrast, RDF 1 can be assumed to contain high shares of polyethylene and polypropylene, which are characterized by a low or even zero oxygen content (and higher carbon and hydrogen content) compared to other polymers.

A close range of values for both TOX_F and TOX_B can be observed when only 4 RDFs (RDF 3 to RDF 6) are considered. These RDFs are all produced out of predominantly CW and IW (production at two different RDF plants in Austria). With regard to TOC, TOH and TOO, the variation between values of these allegedly similar RDFs is below 10 %rel, with the CV for TOC and TOH even being below 3 %rel. These low variations indicate that there might be typical values for TOX_F and TOX_B present in certain RDF types. Figure 5.10 presents the deviations of aBM-results when using different TOX_F and TOX_B input values (A: only from literature, B: mean of 6 RDFs within the thesis, C: mean of 4 RDFs within the thesis). Deviations for x_F^{TC} of up to 10 %abs are observed when aBM-results are compared to results using RDF-specific input values. However, when only RDF 3 to RDF 6 are regarded, the deviation is significantly lower, with below 2.5 %abs. This substantiates the suggestion that a collection of RDF-specific data could be used as a basis for future aBM-applications without the need for extensive sorting and analyses to initially derive TOX_F and TOX_B.

The thesis also shows that the composition of biogenic matter tends to less variability compared to the composition of the fossil matter. This confirms that TOX_B is insensitive to changing shares of different biogenic compounds (e.g. different shares of wood, paper or natural textiles). When fossil matter is considered, the universal appli-



A, B, C represent sources of TOX_F and TOX_B: A = RDF in Austria (from Fellner et al., 2011), B = Mean of 6 RDFs in the thesis (as presented in Table 5.10 and Table 5.11), C = Mean of 4 RDFs in the thesis (as presented in Table 5.10 and Table 5.11)

Figure 5.10: Comparison of aBM-results when using different TOX_F and TOX_B input values – absolute deviations refer to deviation from the aBM-results using RDF-specific input values.

cability of TOX_F-values for RDFs appears limited mainly by the presence of different shares of polymers with high oxygen contents (like PA, PET, PUR).

5.2.5 Practicability of the adapted Balance Method (*Paper VI*)

The choice of a determination method not only depends on its accuracy and precision, but clearly also on its practicability. Therefore, the different determination methods are compared in terms of costs, availability and analysis duration (Table 5.12). All details provided in Table 5.12 refer to the determination of the share of fossil carbon (x_F^{TC}) in one RDF sample. The estimated workload for sample preparation, analysis and calculation ranges from 4 to 6 hours (SDM, ^{14}C-method, aBM) to up to above 60 hours for MS. For the SDM, the ^{14}C-method and the aBM more than half of the workload needs to be anticipated for sample preparation (for the aBM even two thirds). This is due to the small specimens used for the analyses, requiring the sample to be comminuted down to small grain sizes (at least down to below 0.5 mm for the aBM). As expected, the workload for MS is dominated by the sorting activities, which, however strongly depend on the person's performance and on the amount, composition and structure of the sample to be sorted. Besides the amount of work to be done, the duration until an analysis result is available also depends on waiting and reaction times (particularly for the SDM, the ^{14}C-method and the aBM). Thus, the total duration per analysis method is estimated for MS to be around 8 days, for the SDM to be 4 to 5 days (incl. combustion, dissolution, and oxidation reactions), for the ^{14}C-method to be more than 20 days (incl. graphitization reactions), and for the aBM to be around 3 days (incl. combustion, waiting times during CHNSO-analyses).

At an initial application of a respective method to a certain RDF or if high accuracies or precisions are demanded, additional analysis might be necessary. For example, the determination of the carbon content in sorted compounds of MS can be done in order to increase the accuracy. Verifying the $F^{14}C_{bio}$ reference value for the application of the ^{14}C-method also requires additional analytical efforts. Regarding the aBM, the necessity of initial sorting and analysis campaigns to derive the necessary aBM-input parameter (TOX_F and TOX_B) has been discussed already in section 5.2.4. A close range of values found within the thesis indicates potentials to save workload with regards to initially determining TOX_F and TOX_B.

Comparing the availability of the methods discussed, the applicability of the ^{14}C-method is limited by the availability of only a few laboratories which offer the expertise and are equipped with the highly-specialized instruments for the necessary analyses. In comparison, laboratory equipment necessary to conduct the analyses for the SDM and the aBM are available at most analytical laboratories. If only the fossil/biogenic mass share is to be determined, then the SDM is performable in every wet-chemical laboratory, and MS would only require equipment for weighing and drying.

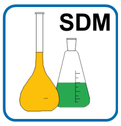
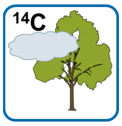
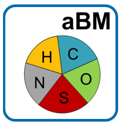
The connected workload and availability of the methods is also reflected in the analysis costs. Highest costs per sample need to be expected for analysis by means of the ^{14}C-method and MS (350 € to above 700 € per sample). Whereas, the costs for the SDM and aBM are estimated to be by a factor 2 to 8 below the one of the ^{14}C-method.

5.3 Determination of (micro)plastic content in an industrial effluent (*Conference paper 1*)

The content of plastics in the samples of particulate matter collected at an effluent of a plastic producer are determined by the aBM as given in Figure 5.11. Between 10 ± 3 and 23 ± 2 wt% of plastic material is detected in the samples. Three of the samples underwent an oxidative treatment with H_2O_2 (following Approach II in Table 4.4). Thereby, the uncertainty of the results could be reduced due to the elemental composition of the biomass in the oxidation residue being more distinct.

The figures presented represent the first test results when the aBM is applied to other plastic-containing mixtures besides RDF. The general transferability of the methodology is thereby confirmed. A series of research questions remain, which are addressed in upcoming research work, including:

Table 5.12: Comparison of determination methods in terms of workload, estimated time, availability, and expected costs (information provided refer to the determination of the share of fossil carbon in RDF (based on Table 5 in *Paper VI* [8]).

	 Manual Sorting (MS)	 Selective Dissolution Method (SDM)	 Radiocarbon Method (^{14}C-method)	 Adapted Balance Method (aBM)
Sample preparation	Drying	Drying, milling, splitting, up to <1 mm	Drying, milling, splitting, up to <0.2 mm or finer	Drying, milling, splitting, up to <0.5 mm or finer
Workload for sample preparation	~ 0.5 h	~ 2 h	~ 3.5 h	~ 3.5 h
optional (e.g. at initial application)[1]	+ ~ 18 h (milling for C-analysis of sorted compounds)		+ ~ 3.5 h (milling of sorted biogenic compounds)	+ ~ 18 h (milling for CHNSO-analysis of sorted compounds)
Analysis & calculations	Sorting	Determining dissolution residue, ignition residue, C-content	Graphitization, AMS-analysis	Determining CHNSO-content, ignition residue
Workload for analysis	> 60 h[2]	~ 1.7 h	~ 2.5 h	~ 2 h
optional (e.g. at initial application)[1]	+ ~ 3 to 6 h (determining C-content and sorting precision of sorted compounds)		+ ~ 20 h (sorting and verifying of $F^{14}C_{bio}$ reference value)	+ ~ 25 h (sorting and determining CHNSO-content in sorted compounds)
Duration until analysis result	~ 8 d	4 – 5 d	> 20 d	~ 3 d
optional (e.g. at initial application)[1]	+ ~ 2.5 d (determining C-content and sorting precision of sorted compounds)			+ ~ 10 d (determining CHNSO-content in sorted compounds)
Availability	✓✓ no special equipment necessary Optional: Determination of C-content in most analytical laboratories available	✓ Determination of C-content in most analytical laboratories available; for mass shares no special equipment necessary	(✓) Highly specialized equipment necessary; 64 laboratories in Europe (134 worldwide)[3]	✓ Determination of C-content in most analytical laboratories available; O-content rarer
Analysis costs (per sample, excl. sample preparation)	> 700 €	80 – 150 €	360 – 650 €	80 – 150 €

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[1] MS: for determining the share of fossil carbon, information on the carbon-content in the sorted compounds is necessary. This information can either be determined RDF-specific or derived from the literature; aBM: at an initial application of the aBM, it might be necessary to initially derive the RDF-specific elemental composition of fossil and biogenic matter present in the RDF. This can be done by sorting or deriving necessary information from suitable data bases; the latter significantly reduces this initial workload.

[2] considering sorting of 30 kg RDF and a workload of two hours minimum for the sorting of 1 kg RDF.

[3] http://www.radiocarbon.org/Info/lablist.html (updated in October 2017) [114]

- Can the suitability of the procedure developed and the trueness of the data generated be confirmed (i.a. conduction of spiking tests, comparison to ^{14}C-method)?
- Which procedure can be applied when the elemental composition of the fossil fraction is unknown (unknown polymer mixture)?
- How to deal with polymers in the fossil fraction which are dissolved during oxidative treatment (e.g. aged plastics, polyamide, polyurethane)
- How to deal with low sample volumes and which sampling procedure is suitable?

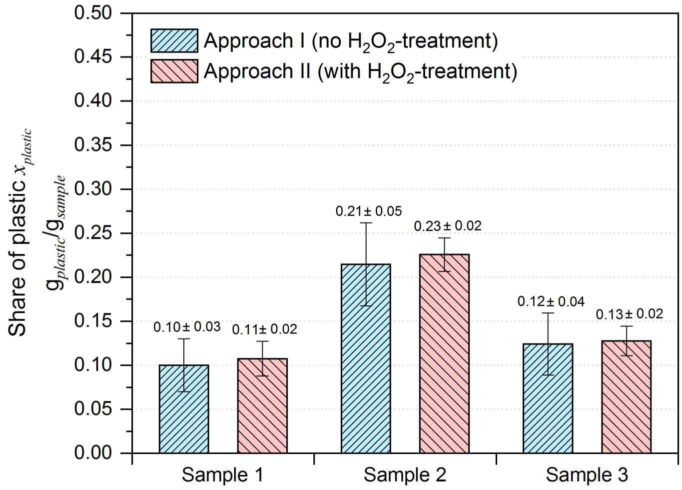

Figure 5.11: Plastic content determined by applying the aBM to samples of particulate matter collected at an effluent of a plastic producer (based on the poster presented as *Conference contribution 1*[9]).

Note: Slight differences to the values presented in *Conference contribution 1* are due to ongoing evaluations and developments

6 Conclusions and Outlook

6.1 Potentials and limitations of the Balance Method ("post-combustion")

The investigations represent the first evaluation of the share of biogenic and fossil matter in the waste feed of WtE plants on a national basis (considering 88 % by weight of the waste fed into WtE plants in Austria). Plant-wise it was possible to generate monthly information on the climate-relevant CO_2-emissions, the share of energy from biogenic sources as well as the plastic content – information which has not been available before in this detail. This already signals that the application of the BM offers possibilities which can hardly be provided by other determination methods at reasonable cost. The BM can "analyse" almost the total waste feed plant-wise and provides data of high temporal resolution (if required down to hourly values). Considering that the composition of waste is typically very heterogeneous and can vary easily depending on time and region, the consideration of large sample sizes and regular, plant-specific analyses are crucial if reliable data on waste characteristics are to be generated. The high resolution which is offered by the BM might not be necessary for certain tasks (e.g. for reporting the annual fossil CO_2-emissions for the national emission inventory), but detailed data can give insights into seasonal dependencies and can support the control and monitoring of waste management measures (e.g. change of collection systems).

Detailed data on the plastic content in the feed of WtE plants, which can be easily derived when the BM is applied, represent valuable information on post-consumer plastic flows, which are of importance for decision makers and plant operators. The overall potential for plastic recycling becomes evident in view of the fact that waste plastics in commingled waste represents a major plastic flow in Austria and Europe. Thus, the data generated, particularly that obtained during continuous assessment, supports the monitoring of measures to increasingly redirect plastics back into the production process (as stipulated e.g., by the circular economy package of the European Commission[21]).

The thesis further demonstrates that detailed plant-specific data (as provided by the BM) can potentially support WtE plant operators to optimize the plant performance. Through the provision of a variety of parameters, thereby characterizing the waste feed at a high temporal resolution, the application of the BM in WtE plants could be used to trace back highly inhomogeneous, insufficiently mixed waste at the feeder. A sufficient mixing of the waste in the bunker could be controlled by using online-data on the ratio between fossil and biogenic matter or the water content, both output parameters of the BM. Thereby it is expected that a more stable operation of the WtE plant could be achieved, improving in turn the plant's energy-efficiency. Trials at WtE plants confirming the possible usability of such BM-data are, however, pending.

Another benefit of the BM which has been demonstrated through the investigations presented is the confirmation of the validity of WtE operating data. The plausibility of certain recorded data at the plant is checked routinely by the BM. Within the thesis, particularly measurements and conversion calculations of the flue gas volume and its composition appear prone to error, which could however usually be rectified. Correct flue gas measurements allow for valid estimates of the plant efficiency to be reported by the operator, which in turn contributes to the avoidance of incorrect tax payments. Limitations of the BM could arise if the necessary operating data are not recorded at the WtE plant (e.g. CO_2-measurements in the flue gas) or are available at insufficient resolution or accuracy. In such cases additional calibration efforts and measurements are required.

Applying the BM at WtE plants can also contribute to the avoidance of economically relevant distortions plant-wise when the ratio of biogenic energy produced is to be reported. The thesis demonstrates that the reliance on literature values or on single short-term determinations can easily lead to under- or overestimations of the renewable electricity production and thus to falsified feed-in revenues.

6.2 Potentials and limitations of the adapted Balance Method ("pre-combustion")

When it comes to analysing the fossil or biogenic share in RDFs *prior* to their combustion, the necessity of taking samples is hardly avoidable. This is particularly relevant when the designated usage of the RDFs is in industrial plants, such as cement or steel works. These industries are required to report their fossil CO_2-emissions and are also included in the CO_2-emission trading scheme. Thus, false estimates of the climate-relevant CO_2-emissions derived from the literature or from unreliable data can again lead to distorted payments. To characterize RDFs and monitor the carbon-footprint of producing industries, reliable and cost-efficient determination methods are demanded by both the RDF producer and the industries utilizing the RDF. The aBM has been developed with the aim to provide a method covering these needs after all of the standardized methods have been identified as having significant limitations in their applicability. The thesis represents the first in-depth investigation regarding the performance of the aBM. The accuracy of the aBM is confirmed, data on the precision are generated and direct comparisons to standardized methods prove the competitiveness of the aBM. In particular, the aBM appears more versatile than the widely used SDM and MS when considerable shares of certain compounds are present in the RDF (e.g. textiles, foamed plastics, fine fraction, composites). In particular, the SDM shows significant limitations when, for example, amino-based polymers, rubber, or wool are present in the RDF. Underestimations of the share of fossil carbon of up to 19 % absolute by the SDM are detected within the thesis. The aBM turned out to be the only method (amongst the three methods applied) for which low deviations and good correlations with the results of the references method (^{14}C-Method) could be observed for all RDFs investigated. On a 95 %-confidence interval the aBM-results for x_F^{TC} are determined to be within $\pm$ 3.6 %abs from the ^{14}C-method (SDM results $\pm$ 12.1 %abs). Slightly elevated inaccuracies of the aBM however, are also revealed for RDFs which contain high shares of textiles. A share of textiles of around 23 % by weight in one of the RDF investigated led to an absolute deviation from the ^{14}C-method, with an increase of around 1 %abs (based on x_F^{TC}). This added inaccuracy is expected to result from the elemental composition of synthetic and natural textiles being in a relatively close range, making it more difficult for the aBM to distinguish between fossil and biogenic matter.

Another factor potentially influencing the robustness of the aBM is the sample preparation. Compared to the standardized methods, a more extensive sample preparation can be necessary for the aBM and also for the ^{14}C-method than required by the SDM or MS. In the case of the aBM this is due to the method relying on elemental analyses. Instruments to measure the elemental composition typically require only very small test specimens (a few centigrams), which calls for the analysis sample to be milled down to small grain sizes to ensure representativeness. For the aBM it has been detected that the precision can be improved by adding another grinding step after the sample is at a grain size of <0.5 mm (for example, further grinding to <0.2 mm). In particular, the destruction of plastics and paper fibers is identified as being crucial and the usage of different grinding mechanisms during sample preparation can be recommended based on the results. A combination of a high speed rotor mill and a ball mill can be suggested as a finishing step. By appropriate sample preparation, the variance added by the subsampling step for elemental analysis can be controlled and reduced. Together with a sufficient number of replications (at least five can be recommended) highly precise results can be achieved (based on the determination of the parameter x_F^{TC} precisions of $\pm$ 1 to 5 %rel being found).

The input values TOX_F and TOX_B – the water-and-ash-free elemental composition of the fossil and biogenic organic matter present in the RDF – play a decisive role in obtaining accurate aBM results. These data need to be defined before the application of the aBM. Within the thesis, TOX_F and TOX_B are generated RDF-wise for six different RDFs stemming from Austrian splitting facilities for MSW and C&I. Extensive sortings and analyses are conducted to derive TOX_F and TOX_B for each RDF. Detailed investigations showed that the most accurate aBM results are expected when TOX_F and TOX_B are derived based on own analysis data in combination with information from the literature (<2 % relative). However, comparing the six generated datasets for TOX_F and TOX_B show that they are in a close range and are also in a similar range with values collected in previous studies (e.g. Fellner et al., 2011[47]). Thus, it is expected that workload could be saved when access to already existing data is provided. However, a varying composition of the plastics present in different RDFs must be expected (which is reflected mainly by the varying TOO-content). A distinction between RDFs of different origin can be regarded as valid. For example, RDFs produced out of MSW typically contain elevated shares of plastics with higher TOO-content (like PA, PET, or PUR), whereas plastics in RDF produced out of C&I waste are dominated by PE and PP. Other consumption behaviours, offered products or packaging regulations could influence the composition of plastics in waste in different countries.

The choice of a procedure to derive the necessary aBM-input parameters, TOX_F and TOX_B, can impair the practicability of the aBM compared to other methods (SDM, ^{14}C-method), particularly when an unknown RDF is to be characterized for the first time. However, besides a potentially higher workload during an initial application of the aBM, a routine application is regarded as highly practicable. Laboratory equipment necessary to conduct the analyses for the aBM (elemental composition, ash content) are available at most analytical laboratories and the analysis results are available within an estimated three days, independent of which parameter is of interest ($x_{F,wf}$, x_F^{TC}, q_B, etc). Thus, the aBM can be regarded as the most versatile method available. In terms of duration and costs, the aBM and SDM are expected to be at similar levels. However, in general the appropriateness of a determination method depends on the boundary conditions and analytical tasks. When only the share of fossil or biogenic mass is demanded, and a significant distortion of the results by certain materials in the RDF can be excluded, then SDM could be more practical than other methods. Provided there is enough monetary resources and a very high analytical precision is demanded, the ^{14}C-method could be feasible. The ^{14}C-method's analyses, however, can only be conducted by a very limited number of laboratories.

Based on the good performance of the aBM (both in terms of trueness and precision), an application also for other purposes and to other sample matrices can be contemplated. First results for an application to solid samples taken from an industrial effluent show that the method can be further developed and altered in its analytical procedure. In particular, the quantification of plastic constituents in environmental samples is still connected with a variety of challenges and is becoming an important field of research and development.

6.3 Concluding remarks and outlook

The thesis demonstrates that both BM and aBM are applicable and versatile methods to deliver valuable information which are relevant for plant operators, authorities, industrial stakeholders, decision makers as well as the scientific community. Both methods are competitive with other standardized determination methods such as the ^{14}C-method, the SDM, and MS. The BM stands out by virtue of its unique capability to deliver data on a very high temporal resolution, data which can in future be exploited also for other purposes than reporting the fossil and biogenic share in the waste. Further developments of the BM could involve an extension of the plausibility checks in order validate recorded WTE plant data and detect drifts of measurement devices already at an early stage. The presented investigations on the performance of the aBM make this method fit for pratical application and provide the basis for formulating a standard procedure for RDF characterization. Subsequent steps to demonstrate that the aBM performance is not limited to the laboratory that developed the method should involve multiple laboratories and operators who conduct aBM determinations from the same analysis samples (e.g. round-robin tests).

In the context of recycling and material recovery, both methods represent viable tools for quantifying the share of plastics in mixed waste. This will become particularly more relevant once the higher recycling targets for plastic packaging are implemented in the European Union[21]. Recycling and sorting plants will need to verify the “purity” of the plastic streams. The aBM could support such verification processes. Considering that TOX_F differentiates between plastic types, the aBM could even be considered for the purpose of determining the share of unwanted plastics at the input of plastic-recycling plants. For example, the balance equations could be extended in order to also differentiate between polyolefines (having a very distinct TOX-composition without any oxygen) and other plastics (which do contain oxygen). This differentiation is relevant when polyolefines (with the most important being PE and PP) are used for material recovery. Even a further development of the BM in order to provide information on the mass shares on a fractional basis (e.g. paper, wood, textiles, polyolefines, other plastics, biogenic waste) in WtE plants can be contemplated. Thereto, the balance equations could be adapted to consider more characteristics of the waste fractions and of the resulting combustion residues (e.g. connecting the nitrogen concentration to NO_x-concentration in the flue gas). The data provided could then substitute laborious and only sporadically conducted sorting campaigns.

The detection of plastic and microplastic in environmental samples by means of the aBM is already underway and will be intensified in future. This is particularly relevant as no standard procedure to detect plastic contamination in water or other environmental compartments is available yet, which poses a variety of challenges. The topic of plastic pollution is of increasing concern all around the globe. Thus, future tests on the feasibility of the aBM for the purpose of quantifying (micro)plastic contamination will not be limited to industrial effluents, but will be extended to other matrix within which further tests will be conducted including, for example, compost samples.

In the context of greenhouse gas emissions, the BM and aBM could also support the estimation of methane production during anaerobic degradation of waste (e.g. in landfills). This could be done by quantifying the biogenic carbon which can be translated into degradable organic carbon. Calculation methodologies, e.g. as suggested by IPCC[37] or the UNFCC[96], could be improved by considering waste-specific data on the degradable organic carbon instead of relying on a default value. Thus, future prospects for utilization of the BM and the aBM also include support for decisions on waste management strategies, help in reaching conclusions on avoided greenhouse gas emissions after diverting selected waste materials from landfills and in providing estimations on landfill gas yield.

The need for information on landfill gas generation, fossil CO_2-emissions from thermal recovery of waste as well as on the plastic recovery potential will, in particular, increase in the emerging market economies. For example, WtE in China is rapidly increasing and, concurrently, an emission trading scheme was implemented in 2017[24,115]. Greenhouse gas reduction targets or severe problems in managing increasing amounts of waste in other countries, e.g. Indonesia, India or Egypt, strongly underline the need for a shift in their waste management systems and for an increased use of RDF in industry[25,116–118]. Thus, the transfer of the BM and aBM to countries outside of Europe will also be subject to future investigations. For example, data on TOX_F and TOX_B in waste and RDF will be collected in different countries. An appropriate database including typical values for different RDF types and origins should be set-up to even increase the practicability of the method.

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Appendix

Paper I

Determining national greenhouse gas emissions from waste-to-energy using the Balance Method

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Waste Management, 2016, 49, 263-271

DOI: 10.1016/j.wasman.2016.01.025

Waste Management 49 (2016) 263–271

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Determining national greenhouse gas emissions from waste-to-energy using the Balance Method

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ARTICLE INFO

Article history:
Received 19 November 2015
Revised 20 January 2016
Accepted 23 January 2016
Available online 1 February 2016

Keywords:
Greenhouse gas emissions
Waste-to-energy
Balance Method
Renewable energy content
Biomass content
CO_2 emission factor

ABSTRACT

Different directives of the European Union require operators of waste-to-energy (WTE) plants to report the amount of electricity that is produced from biomass in the waste feed, as well as the amount of fossil CO_2 emissions generated by the combustion of fossil waste materials. This paper describes the application of the Balance Method for determining the overall amount of fossil and thus climate relevant CO_2 emissions from waste incineration in Austria. The results of 10 Austrian WTE plants (annual waste throughput of around 2,300 kt) demonstrate large seasonal variations in the specific fossil CO_2 emissions of the plants as well as large differences between the facilities (annual means range from 32 ± 2 to 51 ± 3 kg $CO_{2,foss}$/GJ heating value). An overall amount of around 924 kt/yr of fossil CO_2 for all 10 WTE plants is determined. In comparison biogenic (climate neutral) CO_2 emissions amount to 1,187 kt/yr, which corresponds to 56% of the total CO_2 emissions from waste incineration. The total energy input via waste feed to the 10 facilities is about 22,500 TJ/yr, of which around 48% can be assigned to biogenic and thus renewable sources.

1. Introduction

In many affluent countries waste has become an important resource for energy production. For the European Union it is estimated that almost 78,000 kt of waste are annually utilized in waste-to-energy (WTE) plants, thereby generating 112,000 TJ of electricity and 280,000 TJ of heat (CEWEP, 2014). The biomass share of waste thermally utilized is usually accounted for as renewable energy and thus not included in national CO_2 inventories. However, as mixed waste (municipal solid waste MSW, commercial waste CW and industrial waste IW) is highly heterogeneous with respect to its composition and may significantly vary over time, the determination of the biomass content and thus the share of renewables in the feed of WTE plants constitutes a significant challenge.

In recent years different methods, including manual sorting (QUOVADIS, 2007; van Dijk et al., 2002), selective dissolution (Cuperus et al., 2005; van Dijk et al., 2002), the radiocarbon method (Mohn et al., 2008) and the Balance Method (Fellner et al., 2007) have been developed to determine the biomass content of waste, and thus the fraction of renewable energy and fossil CO_2 emissions produced by WTE plants. The Balance Method is in the last stage of standardization, whereas the other three methods are already specified in the European Standard EN 15440 and in the ASTM standard D6866 as application for solid recovered fuels (CEN/TC343, 2011; ASTM, 2012). A detailed description of these standardized methods is additionally given in Staber et al. (2008). Until now all of these methods have also been applied to different WTE plants (Fellner et al., 2011b; Jones et al., 2013; Mohn et al., 2008; Palstra and Meijer, 2010) and different wastes (Fellner et al., 2011a; Larsen et al., 2013; Muir et al., 2015; Saiz-Rodríguez et al., 2014) aiming at, on the one hand, the determination of characteristic values for the biomass content and fossil CO_2 emissions per unit of waste (mass or energy content) and on the other hand, at a comparison of the different analysis methods. With respect to the latter, results of the different studies indicate that methods requiring waste feed sampling (e.g. sorting analysis or selective dissolution method) are much more vulnerable to waste heterogeneity and temporal changes in waste composition as quantities of manageable waste samples (at maximum a few tons) are very small in comparison to the total amount thermally utilized. The Balance Method as well as the radiocarbon method largely avoid problems associated with waste heterogeneity as the measurements or sampling takes place in the highly homogeneous flue gas. Compared to the other methods, these two methods have additionally been proven to be practical for a continuous monitoring of the biomass content in the feed of WTE plants which

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http://dx.doi.org/10.1016/j.wasman.2016.01.025
0956-053X/

provides the possibility to investigate temporal differences with a much higher resolution than, for example, with the selective dissolution method (Palstra and Meijer, 2010; Fellner et al., 2011b; Mohn et al., 2012). A further advantage of the Balance Method is that it is based on routinely recorded operating data of WTE plants which usually avoids the need for additional sampling and measurement efforts.

Recent research (e.g. from Fellner et al., 2011b; Fuglsang et al., 2014; Larsen and Astrup, 2011; Mohn et al., 2012; Obermoser et al., 2009) on the composition of wastes furthermore suggests that there is no typical biomass content in terms of mass, energy or carbon. Monthly variations in fossil CO_2 emissions for one particular plant (expressed as % fossil CO_2 relative to total CO_2 emissions) could be in the range of 20% (Fuglsang et al., 2014) or even higher (Fellner et al., 2011b). Also for specific types of wastes (such as MSW, CW or IW), no typical biomass contents are observable. Jones et al. (2013), for instance, investigated the fraction of fossil carbon in mixed waste containing different shares of MSW and IW. They report large variations in the composition of the different waste mixtures. However, no significant correlation between the share of MSW or IW and the content of fossil carbon was detected. Based on their results, it could at best be speculated that higher shares of IW are associated with slightly larger fossil carbon contents. Mohn et al. (2012), however, observed a contrary pattern. Their application of the radiocarbon method to five Swiss waste incinerators over a time period of several months indicates significant variations in the waste composition, with a slight tendency of lower fossil carbon contents at higher shares of industrial waste. Horttanainen et al. (2013) and Larsen and Astrup (2011) conclude that the type of source separation of household waste significantly influences the fossil carbon ratio and thus the emission factors (after investigating different scenarios). This suggests that regional variations of waste compositions also strongly depend on the collection scheme.

Recent analyses of the waste feed conducted at five different WTE plants in Denmark reveal once more no identifiable correlation between the content of fossil carbon and the waste types received at the plants (Fuglsang et al., 2014). Moreover, their results, provided as fossil CO_2 emissions as a percentage of total CO_2 emissions, varied significantly between the different plants, ranging from 52% to 78% (based on weekly measurements via the radiocarbon method).

Hence, all investigations demonstrate a highly heterogeneous and varying composition of the waste feed in WTE plants, making it questionable to simply translate plant or waste specific results to other facilities. Yet such extrapolation using either data once determined for one specific plant or default values for fossil CO_2 from waste combustion (e.g. from IPCC) are used in practice to derive emission data from WTE facilities for national CO_2 inventories. These practices can easily lead to considerable over- or underestimations of greenhouse gas emissions from waste incineration. Obermoser et al. (2009) mention a possible miscalculation by a factor of 2 when generic emission factors are used. In countries where WTE plants already participate in the CO_2 emission trading scheme according to the European Directive 2009/29/EC (European Parliament, 2009b), such as Denmark and Sweden, this factor directly affects the required emission certificates and thus financial burdens for the plant operator (Pacher et al., 2007). Additional financial distortions may arise in case that the share of “green” electricity produced by WTE plants (e.g. according to the European Directive 2009/28/EC by the European Parliament, 2009a) is miscalculated, as “green” electricity is subsidized in many European countries. According to findings from Obermoser et al. (2009) incorrect money transaction associated with over- or underestimation of the biomass content in the feed of Austrian WTE plants could be in the range of millions of Euros per year. These limitations of using generic emission factors illustrate the need for a reliable and cost efficient method which accounts for variations in waste composition.

The objective of the presented study is to determine the total fossil and thus climate relevant CO_2 emissions from waste incineration in Austria over a period of one year. Ideally all WTE plants in Austria are considered and plant-specific emission factors are to be determined and compared. For these tasks only the Balance Method appears applicable as it allows representative sampling, long-term monitoring and reliable results (<4% relative uncertainty) and can deliver results at the given budget constraint (compared to the radiocarbon method with significant analysis costs) (Staber et al., 2008).

In the meantime, the results of the analysis presented have been incorporated into the national greenhouse gas inventory of Austria.

2. Materials and methods

2.1. Balance Method

The Balance Method, applied within the present study, relies on the distinct chemical composition of biogenic and fossil organic matter and the significant differences between the two materials. Theoretical data on the chemical composition of moisture- and ash free biogenic and fossil organic matter are combined with routinely measured operating data of the incineration plant. In principle the method is based on five mass balances and one energy balance, whereby each balance describes a certain waste characteristic (e.g. content of organic carbon, heating value, ash content) (Fig. 1 – right side). For setting up the theoretical balances, the waste is virtually divided into four fractions: inert (m_I), biogenic and fossil organic materials (m_B, m_F) and water (m_W). Inert materials include all incombustible solid residues like glass, stones, ashes or other inorganic matter from biowaste and plastics (e.g. kaolin in paper). Biogenic and fossil organic material groups refer only to the moisture-and-ash-free organic matter (see Fig. 1 – left side). As the qualitative composition of organic materials in the waste is usually well known (e.g. biogenic matter encompasses paper, wood, kitchen waste, etc., and fossil organic matter includes PP, PE, PET, PVC, etc.), the content of C, H, O, N and S as mass fraction of total mass of moisture-and-ash-free biogenic material (m_B) and of total mass of moisture-and-ash-free fossil organic materials (m_F) is derivable (Fellner et al., 2007). From this theoretical chemical composition the coefficients at the left side of the equations can be determined according to Fellner et al. (2007).

Each balance equation encompasses a theoretically derived term (left side of equations) that has to be attuned to data determined from routinely recorded operating data of the WTE plant (right side of equations). A simplified structure of the set of equations is illustrated in Fig. 1 (right side). A detailed mathematical description of each equation is given in Fellner et al. (2007). Required input data for the Balance Method include besides information about the chemical composition of moisture-and-ash-free biogenic and fossil organic matter, information about the quantity of fuels incinerated (waste mass and auxiliary fuels), the amount of solid residues and steam produced as well as data on the volume and composition (O_2 and CO_2 content) of the dry flue gas (see also supplementary information). Further, uncertainties for each input parameter need to be defined.

Because the system of equations (set of constraints) used within the Balance Method is over-determined (6 equations for 4 unknowns), data reconciliation can be performed to improve the accuracy of the results. In particular, non-linear data reconciliation according to Narasimhan and Jordache (2000) is conducted (for

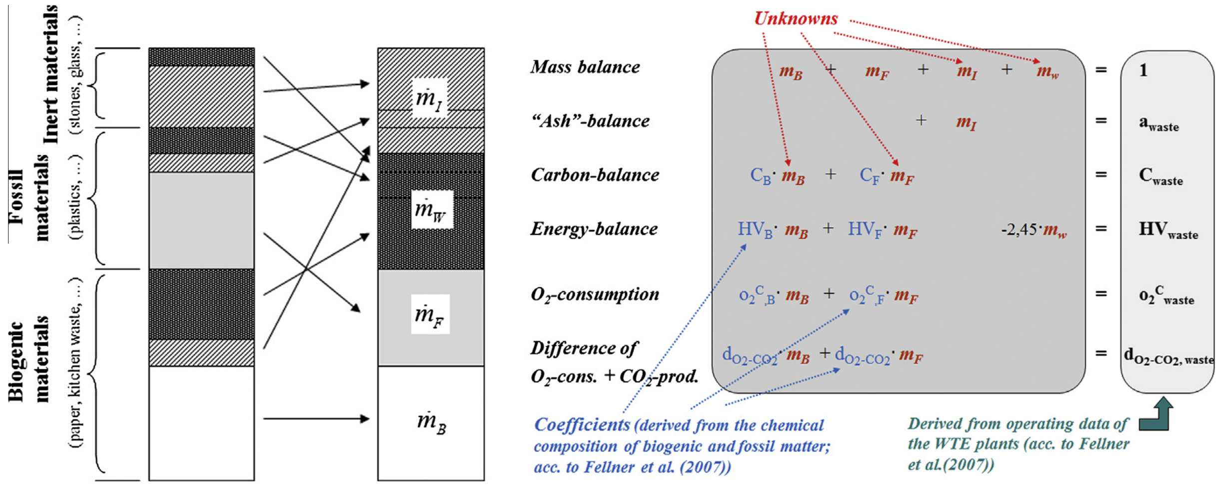

Fig. 1. Left side: split-up of waste fractions into the four "material groups" (m_B, m_F, m_W, and m_I); Right side: simplified set of equations of the Balance Method (Fellner et al., 2006).

details please refer to Fellner et al., 2007 and Rechberger et al., 2007). The improved values for the elemental composition (C, H, O, N, S) of moisture-and-ash-free biogenic and fossil organic matter and for parameters derived from operating data are used to calculate the unknown fractions (m_B, m_F, m_W, and m_I) including their uncertainties. Inserting these results into the carbon balance and considering the ratio of molar mass of carbon dioxide and carbon allows the amount of fossil CO_2 emissions to be determined. For calculating the share of energy from biogenic matter, the results for m_B and m_F are inserted into the energy balance equation (for details please refer to Fellner et al., 2007).

2.2. Application of the Balance Method to waste-to-energy plants in Austria

The Balance Method is applied to all Austrian WTE plants, with the exception of three facilities; two only combust hazardous waste and do not provide all operating data necessary for applying the Balance Method, and one facility was under reconstruction in 2014, the year the analysis was being conducted. Thus altogether the waste feed from 10 waste incineration plants can be included in the study and around 91% of the waste incinerated in Austria in 2014 is characterized with respect to its biogenic and fossil carbon content as well as in terms of its share of renewable (biogenic) energy. Based on the information on the composition of the waste feed of each plant and their respective annual waste throughput, the total fossil CO_2 emissions as well as the total amount of renewable energy from WTE in Austria are determined.

Table 1 gives an overview of the 10 Austrian waste incineration plants that are investigated. The annual throughput of these facilities amounts to about 2300 kt of waste per year. The WTE plants utilize different types of combustion technologies (grate incineration or fluidized bed combustion) and mainly incinerate municipal solid waste (MSW), commercial and industrial waste (CW&IW), sewage sludge (SS) and refuse derived fuels (RDF) (see Table 1), whereby the share of the different waste types may significantly vary during the one-year period investigated (2014).

The procedure for the application of the Balance Method to the operating data of the WTE plants is schematically illustrated in Fig. 2.

A list of the input parameter required together with their necessary temporal resolution and precision is defined and transmitted to the plant operators. The specific requirements for the different parameters basically depend on the sensitivity of the final results to the respective parameters (Fellner et al., 2007). CO_2 and O_2 concentrations in the dry flue gas, for example, strongly affect different balances (carbon balance, O_2 consumption as well as the difference between O_2 consumption and CO_2 production) and thus need to be available at a high temporal resolution (like hourly mean values) and high accuracy, whereas the mass of solid residues have a low impact on the output and might also be derived from long-term experiences (Fellner et al., 2007). After the collection and transmission of the operating data by the plant operators, the data are checked for their plausibility. Thereto, existing correlations between the flue gas and steam production are used (e.g. during the combustion of organic matter the consumption of 1 mole of O_2 corresponds to an energy equivalent of 360–400 kJ; and the combustion of 1 g of organic carbon produces an amount of heat ranging from 34 up to a maximum of 44 kJ) (Fellner et al., 2007). Only data which are within the expected theoretical limits are subsequently evaluated by means of the Balance Method. Additional information from the operator on experiences with the measurement methods, on calibration practices or the combustion process might be necessary to find the cause for implausible data sets. Once a plausible data set is obtained, it is imported into the software BIOMA, which has particularly been developed for the application of the Balance Method in WTE plants (http://iwr.tuwien.ac.at/ressourcen/downloads/bioma.html). It allows the

Table 1
Overview of waste-to-energy plants in Austria.

WTE plant	Combustion technology	Waste incinerated (qualitative information)
A	Grate incinerator (GI)	MSW
B	Grate incinerator (GI)	MSW and CW&IW
C	Stationary fluidized bed combustion (FBC)	RDF and SS
D	Stationary fluidized bed combustion (FBC)	RDF and SS
E	Circulating fluidized bed combustion (FBC)	RDF and SS
F	Grate incinerator (GI)	CW&IW
G	Stationary fluidized bed combustion (FBC)	RDF
H	Grate incinerator (GI)	MSW and CW&IW and minor amounts of SS
I	Grate incinerator (GI)	MSW
J	Grate incinerator (GI)	MSW and CW&IW and minor amounts of SS

MSW – municipal solid waste, CW&IW – commercial and industrial waste, SS – sewage sludge, RDF – refuse derived fuels.

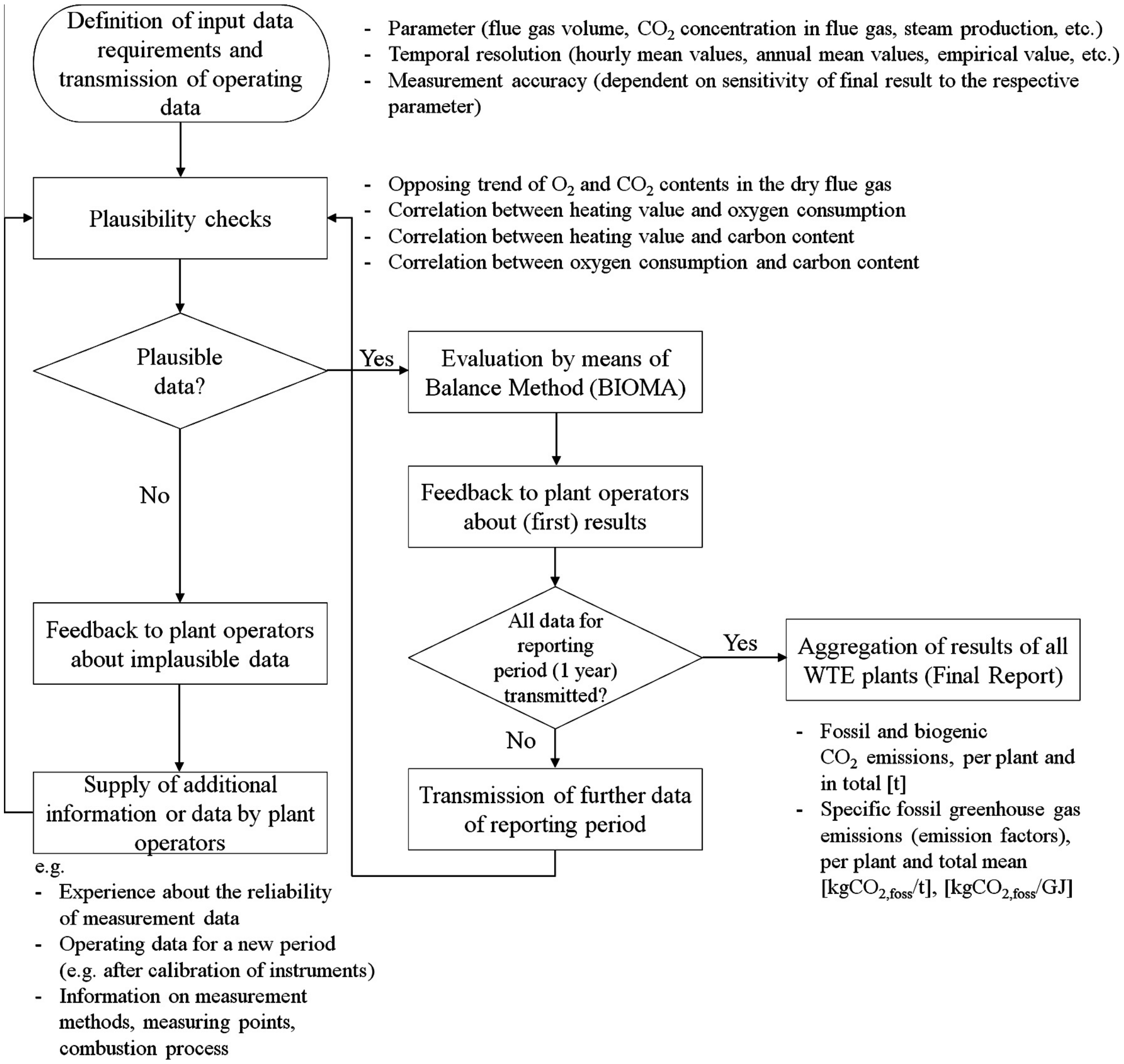

Fig. 2. Procedure for the analysis of the operating data of the WTE plants using the Balance Method (software BIOMA).

biogenic and fossil mass fraction in the waste feed and the amount of biogenic and fossil CO_2 emissions to be determined for any time period required. In addition, other parameters of interest for operators of WTE plants, such as the lower calorific value of the waste, its water content or its total carbon content can be calculated and automatically displayed by the BIOMA interface. For the presented study monthly results as well as annual results on fossil CO_2 emissions and emission factors (emissions per unit of mass or unit of energy) are generated for each plant. Thereto the input data are aggregated to monthly and annual values before being evaluated by means of the Balance Method. Finally, the annual results for all plants are aggregated in order to determine the total amount of national greenhouse gases from WTE plants in Austria in 2014. The total emission factors (for all plants) are estimated by weighting the annual emission factor per plant by the total waste feed (for the mass related emission factor) or by the respective energy input of the waste (for the energy related emission factor). The overall renewable share of the energy in the waste feed is calculated by relating the sum of energy input from biogenic sources to the total energy input by waste and auxiliary fuels.

In order to aggregate the uncertainties for each plant to an overall uncertainty (all plants are considered together) the following procedure is chosen:

First the uncertainties for each plant (for annual results) are split into two parts. One part origins from the "uncertain assumption" concerning the composition of moisture-and-ash-free biogenic and fossil organic matter, whereas the other part results from the uncertainties of the plant operating data. In a second step the latter is aggregated by error propagation (random effects on the overall uncertainty). The other part of the uncertainty, which results from the uncertain chemical composition of the biogenic and fossil organic matter, is simply added up for each plant (systematic effects on the overall uncertainty). Finally the so aggregated "composition based" uncertainty and the "operation data based" uncertainty are added to arrive at the overall uncertainty for the sum of all plants investigated (an example for the splitting is provided in Table 3 of the Supplementary information). The "composition based" uncertainty of the results is determined by solving the set of balances under the assumption that operating data of the plant are applied without uncertainty.

3. Results and discussion

The Balance Method is applied to 10 WTE plants for a period of 12 months (the year 2014). As for one facility (plant D) the required operating data are incomplete or connected with measurement errors, the analysis period for this particular plant has to be reduced to 7 months.

An important step prior to determining the waste composition with regards to biomass and fossil organic matter via the Balance Method is the plausibility test of the operating data (as indicated in Fig. 2). Results of these plausibility checks are summarized in the following section.

3.1. Plausibility checks on operating data

For the plausibility tests, operating data (hourly values) are aggregated to 6-h averages (in order to account for the fact that there is obviously a temporal difference between certain input and output flows of the facility), which are subsequently tested for their correlation between O_2 consumption, carbon content and the lower calorific value of the waste. In Figs. 3 and 4 results of the plausibility tests for plant G are summarized. From the correlation in Fig. 3 it can be expected that there are no significant systematic under- or overestimations of the CO_2 and O_2 measurements or of the measured flue gas volume. As the calculation of the lower calorific value of the waste does not account for possible changes of the boiler efficiency over time, only the correlation in Fig. 4 between O_2 consumption and carbon content is used to decide on the plausibility of data points. It can be seen that the vast majority (more than 90%) of the 6-h averages are within the defined limits for plausible data pairs and can thus be used for the analysis in accordance with the Balance Method. However, in order to end up with a high share of plausible values, additional data or information on the measured data or the combustion process had to be requested from the operators in all cases within this study as data were either scattered outside the expected range or other errors in measurements (e.g., no opposite trend of O_2 and CO_2 data), data conversion or data transfer were evident. Additional to the plausibility checks, results of calibration measurements at the WTE plants are used (if available) to confirm the validity of the operating data. This is particularly crucial for the measurements of the O_2 and CO_2 content in the flue gas, to which the final outcome of the Balance Method is highly sensitive.

Table 2 summarizes the share of plausible operating data for all 10 WTE plants analyzed. With the exception of plant D and I, all facilities are characterized by a high ratio (well above 95%) of plausible operating data. The lower share of plausible operating data for plant D and I can be explained by instable CO_2 measurements in plant D and by a lower temporal resolution of measurement data in plant I (daily mean values instead of hourly mean values). In total over 96% of the waste (thus almost 2200 kt of waste out of 2300 kt of waste throughput in the 10 plants) is analyzed in the study, a sample that can hardly be achieved by any other determination method.

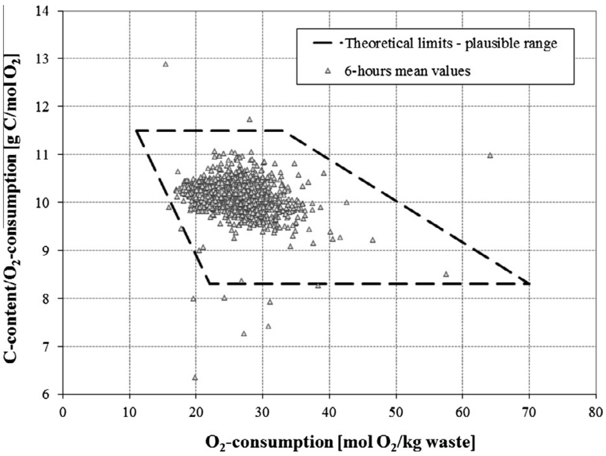

Fig. 4. Results of plausibility checks (correlation between O_2 consumption and carbon content) of the operating data of WTE plant G on a 6-hourly basis.

3.2. Fossil CO_2 emissions from Austrian WTE plants

In the end all plausible operating data are used to analyze the waste composition and to determine the amount of fossil CO_2 emissions as well as the share of energy from biogenic sources by means of the Balance Method (Fellner et al., 2007). In Figs. 5–7, results for the different plants are summarized and compared. Besides monthly data, annual averages are given.

Fig. 5 shows the specific fossil CO_2 emissions per ton of waste on a monthly basis for all 10 WTE plants, divided into fluidized bed combustion (FBC) plants (upper part) and grate incinerators (GI) in the lower part of the figure. The FBC plants predominantly utilize refuse derived fuels (RDF) and sewage sludge (SS), whereas the grate incinerators are generally fed with municipal solid waste and commercial and industrial waste. The monthly averages for the specific CO_2 emissions of the different WTE plants (FBC and GI) range from 189 ± 17 to 598 ± 31 kg fossil CO_2 emitted per ton of waste. This wide range of emission factors for different plants reflects wide regional variation in waste feed composition, which is understandable in light of the fact that the plants presented in Fig. 5 are situated in different federal states of Austria, which are characterized by different waste collection schemes (e.g. separate

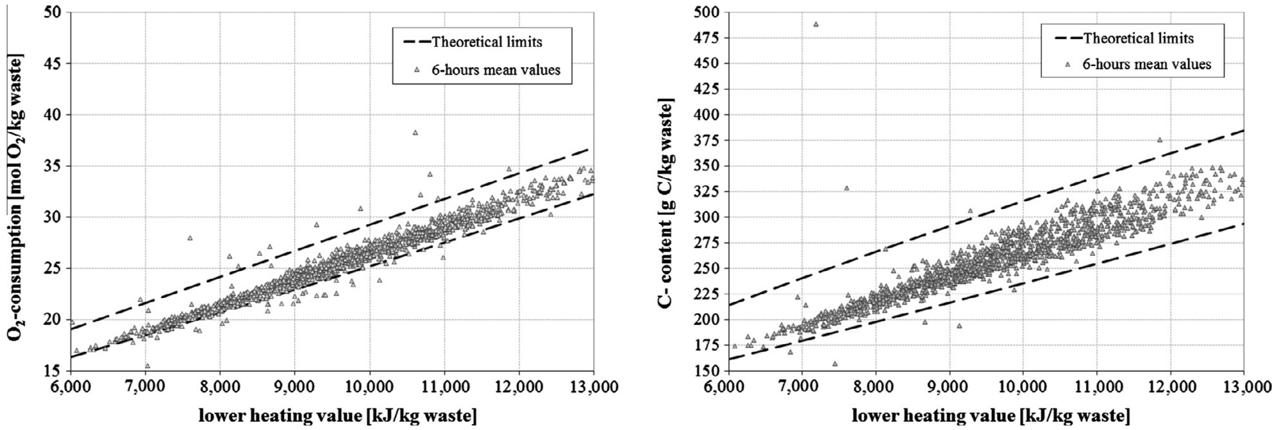

Fig. 3. Results of plausibility checks (correlation between lower calorific value and O_2 consumption and carbon content, respectively) of the operating data of WTE plant G on a 6-hourly basis.

Table 2
Share of plausible operating data (given in % of total waste mass combusted).

WTE plant	A	B	C	D[b]	E	F	G	H	I	J	**Total**
Share of plausible data[a]	98.3%	99.3%	95.8%	84.4%	99.5%	99.5%	98.3%	99.0%	82.8%	99.7%	**96.7%**

[a] Expressed as waste mass combusted during the record of plausible operating data referred to the total waste throughput.

[b] Only a period of 7 months has been evaluated.

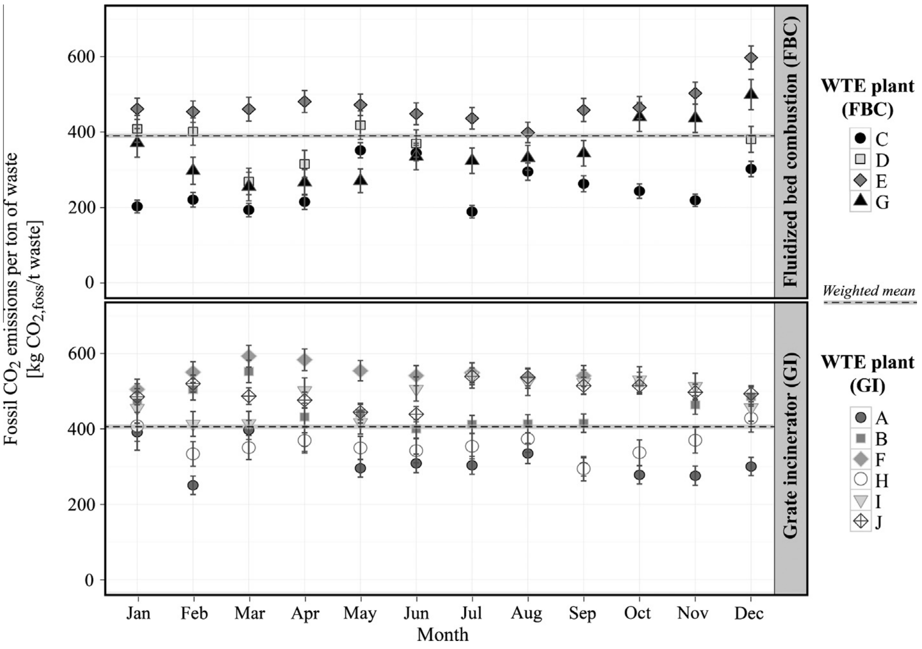

Fig. 5. Monthly averages (incl. standard deviation) and weighted (based on waste flows for each plant) annual means of fossil CO_2 emissions (given in kg CO_2 per ton of waste) of 10 (out of 13) WTE plants in Austria in 2014; upper part: fluidized bed combustion plants (treating RDF + SS); lower part: grate incinerators (treating MSW + CW&IW).

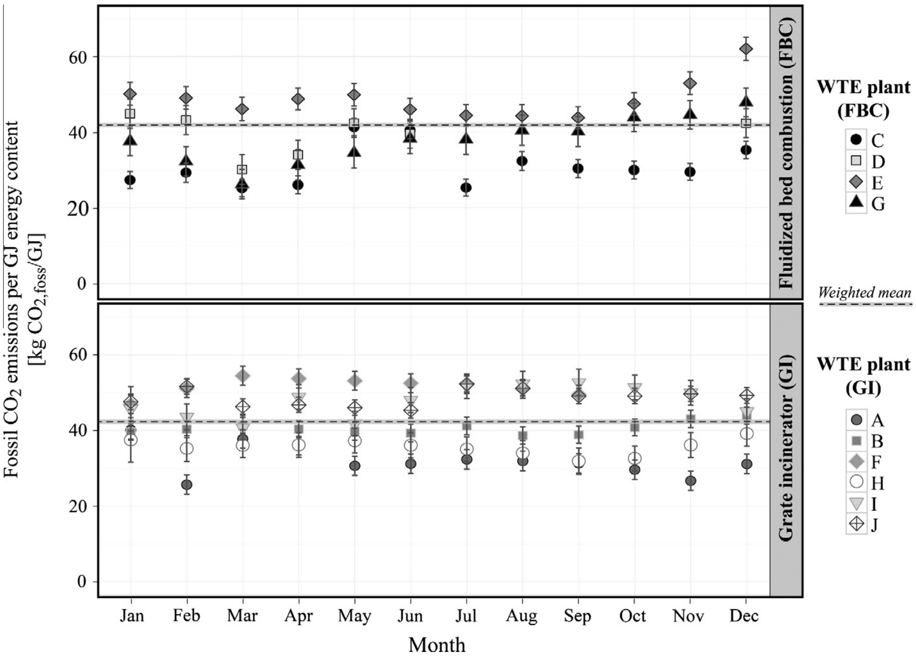

Fig. 6. Monthly averages (incl. standard deviation) and weighted (based on energy content of the waste for each plant) annual means of fossil CO_2 emissions (given in kg CO_2 per GJ heating value of the waste) of 10 (out of 13) WTE plants in Austria in 2014; upper part: fluidized bed combustion plants (treating RDF + SS); lower part: grate incinerators (treating MSW + CW&IW).

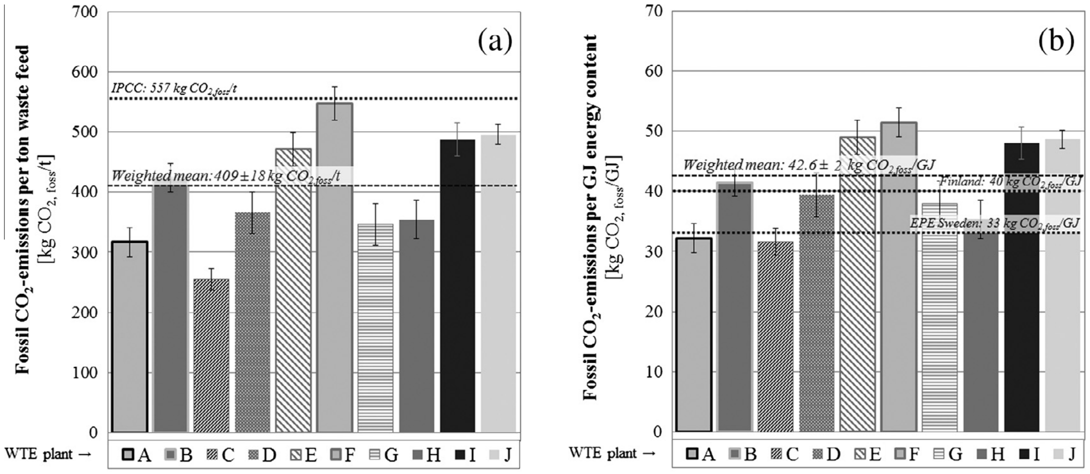

Fig. 7. Annual averages (with standard deviation) of fossil CO_2 emissions from 10 (out of 13) WTE plants in Austria, including weighted mean values: (a) related to total waste feed; (b) related to energy content of waste and standard values for fossil CO_2 emissions from waste incineration according to IPCC (2000), EPA Sweden (Olofsson, 2004), and Anderson et al. (2011) for Finland. For plant D the annual mean value given is based on the analysis of the waste feed over a period of 7 months only.

collection of either all packaging plastics or just PET bottles; separate collection or joint collection of biowaste; the latter is practiced in some urban centers) and since different types of industry and businesses are found throughout the region. No quantitative information about the ratios of different waste types utilized is available to the authors for the WTE plants investigated. However, the highest specific fossil CO_2 emissions are found for WTE plant F, which treats almost exclusively commercial and industrial waste. This suggests that diverse ratios of commercial and industrial and municipal solid waste may cause significantly different CO_2 emission factors. However, the available data does not suggest a correlation between waste types (household waste and commercial waste) and emission factors, which confirms observations of Larsen et al. (2013). They concluded, based on their investigations, that a considerable variability in terms of biomass content was observable for each waste type and that the difference in biogenic carbon for the different waste types was not significant considering a 95% confidence interval.

Furthermore, temporal variations of specific CO_2 emissions are obvious from Fig. 5. For instance, the monthly emission factors for WTE plant G range from 255 ± 38 to 499 ± 40 kg $CO_{2,foss}$ per ton of waste input (which corresponds to a standard deviation of the monthly values of 22%), thereby highlighting that a reliable analysis of the waste composition requires methods that characterize the waste feed over longer time periods, as already indicated by other studies (Fellner et al., 2011b; Fuglsang et al., 2014; Obermoser et al., 2009).

When comparing the weighted (based on the waste flows of each plant) annual mean values for GI plants (419 ± 19 kg $CO_{2,foss}$/ton waste) and for FBC plants (390 ± 21 kg $CO_{2,foss}$/ton waste), there tends to be lower emission factors observable for FBC plants (significant differences at a confidence level of 95% using rank sum test). This trend is ascribed to the higher share of sewage sludge (up to 20% of total waste) incinerated in FBC plants, which reduces the fossil carbon content in the waste (carbon from sewage sludge is regarded as biogenic). However, the monthly variations in waste composition for both types of incineration technology are on a similar level, with a standard deviation from the annual mean of 21–26% (no indication of significant differences in variances at a confidence level of 95% using the Levene's test). This indicates that the feed of both plants is prone to changing composition despite the fact that pretreated and thus more homogenous waste material is fed into FBC plants which would imply lower variations than in GI plants.

Monthly averages of fossil CO_2 emissions related to the energy content of the waste feed (lower heating value) are summarized in Fig. 6. The monthly values range from 25 ± 2 to 62 ± 3 kg fossil CO_2 per GJ and thus cover the whole range of emission factors determined by Obermoser et al. (2009), who compared data of 11 WTE plants in different European countries (revealing a range of 30–67 kg fossil CO_2 per GJ). The difference between results for FBC plants (weighted mean of 42 ± 2 kg $CO_{2,foss}$/GJ) and GI plants (weighted mean of 43 ± 2 kg $CO_{2,foss}$/GJ) is less pronounced for the energy related emission factors compared to the specific fossil emissions based on the waste mass.

Annual averages for the specific CO_2 emissions per ton of waste and per GJ energy content of the waste are presented in Fig. 7(a) and (b) for all 10 plants investigated. Again a high variation of the results for the different plants can be identified, ranging from 255 ± 18 (WTE plant C) to 548 ± 27 (WTE plant F) kg $CO_{2,foss}$ per ton of waste and from 32 ± 2 (WTE plant A and WTE plant C) to 52 ± 3 (WTE plant F) kg $CO_{2,foss}$ per GJ of energy input from waste.

Comparing the variations among the values in Fig. 7(a) and (b), it is evident that specific fossil CO_2 emissions per energy input are scattered less (with 17% standard deviation) in comparison to specific fossil CO_2 emissions that are related to the waste mass (with 23% standard deviation). This observation is explained by the fact that variations of the energy related emission factor reflect only differing ratios between biogenic and fossil organic matter in the waste feed. Changes in the total content of organic matter, which obviously influence specific CO_2 emissions, are to a large extent already reflected by the calorific value of the waste. Hence, variations in the total organic matter content of the waste hardly change the energy related emission factor. The waste mass related emission factor however has to account for both, varying contents of total organic matter and changing ratios of biogenic and fossil organic matter. Hence, it is concluded that the energy related emission factor (in kg $CO_{2,foss}$ per GJ) represents the more reliable indicator for waste characterization, since its variability is lower by definition.

When considering a default standard emission factor provided by the Intergovernmental Panel on Climate Change (IPCC) of 557 kg fossil CO_2 per ton of waste (IPCC, 2000), the fossil CO_2 emissions would be significantly overestimated for almost all WTE plants investigated (up to 100%). Emission factors reported for Germany with 354 (Hoffmann et al., 2010) or 382 kg fossil CO_2 per ton of combusted waste (ITAD, 2013) are closer to the value found within this study for Austria (409 ± 18 kg$CO_{2,foss}$/t). Whereas the

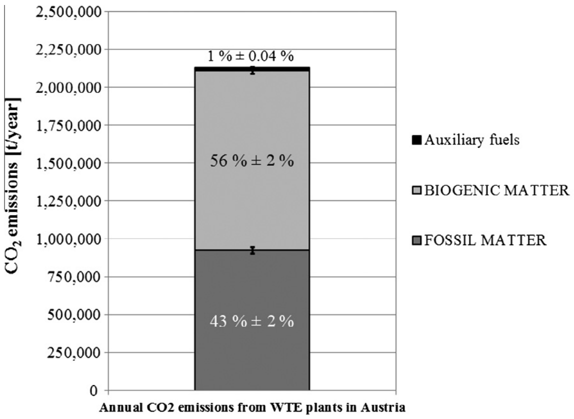

Fig. 8. Annual CO_2 emissions from 10 (out of 13) WTE plants in Austria with an annual waste throughput of about 2,300 kt.

EpE (2008) in France estimates even lower specific fossil CO_2 emissions from waste incinerators, with only 293 kg fossil CO_2 per ton of household and non-hazardous industrial waste.

The annual waste throughput of all plants amounts to around 2300 kt (2110 kt of solid waste and 150 kt of sewage sludge), with an average lower calorific value of the solid waste (excl. sewage sludge) combusted of 10,400 ± 70 MJ/kg waste. Thus, the overall amount of energy input to the 10 facilities in 2014 is about 22,500 TJ per year (21,950 TJ/yr stem from MSW, CW&IW and RDF; 250 TJ/yr from SS and 300 TJ/yr from auxiliary fuels), resulting in average energy specific greenhouse gas emissions from Austria's WTE plants of approximately 43 ± 2 kg $CO_{2,foss}$/GJ (Fig. 7b). Comparing this finding once more with emission factors reported from other European countries, the deviation appears lower than for the mass-related emission factor. For example, the Swedish EPA (Olofsson, 2004) suggests an emission factor of 33 kg $CO_{2,foss}$/GJ for waste incinerators. For waste incineration in Finland a default factor of 40 kg $CO_{2,foss}$/GJ has been estimated by Anderson et al. (2011) and Denmark has implemented a generic emission factor of 37 kg $CO_{2,foss}$/GJ (Danish Energy Agency, 2013).

The presented study shows that from the overall amount of energy input to the 10 WTE facilities in Austria, 47.7 ± 2% stem from biogenic material.

Based on the evaluations for the year 2014, the total annual CO_2 emissions from WTE plants in Austria can be estimated to 2130 ± 35 kt. In Fig. 8 these emissions are divided according to their climate relevance, with 43 ± 2% originating from the combustion of fossil matter (924 ± 22 kt fossil CO_2), 56 ± 2% originating from the combustion of biomass (1187 ± 25 kt biogenic CO_2) and around 1% can be assigned to the utilization of auxiliary fuels such as fuel oil and natural gas (20 kt ± 1 kt fossil CO_2).

4. Conclusions

The evaluation of the waste composition of 10 WTE plants in Austria (with a total annual waste throughput of around 2300 kt of waste) via the Balance Method reveals that there are significant differences regarding the specific fossil CO_2 emissions between the facilities. Annual energy specific greenhouse gas emissions for Austria's WTE plants range from 32 ± 2 to 52 ± 3 kg fossil CO_2 per GJ of energy input from waste. The average fossil CO_2 emission factor amounts to 43 ± 2 kg fossil CO_2 per GJ, which is higher than values suggested for other European countries, like Sweden, Denmark or Finland (Anderson et al., 2011; Danish Energy Agency, 2013; Olofsson, 2004).

In addition to regional differences, large temporal variations regarding the composition of the waste (biogenic, fossil) can be observed for at least some of the plants analyzed (when monthly mean values are regarded). It is assumed that these variations are not only caused by a changing composition of the different wastes combusted, but also by changing shares of the different types of waste (municipal solid waste, commercial waste, refuse derived fuels, sewage sludge).

The results further indicate that the usage of generic emission factors (e.g. 557 $kgCO_{2,foss}$/t waste as default given by the IPCC (2000)) can result in considerable overestimations (or in some cases possibly underestimations) of fossil CO_2 emissions (as also demonstrated in other studies (Fellner et al., 2011b; Fuglsang et al., 2014; Obermoser et al., 2009). Thus, a plant-specific and continuous evaluation of the waste composition is highly recommended as it constitutes the only reliable means for quantifying fossil CO_2 emissions or green electricity production from WTE plants.

By means of the Balance Method the waste composition can be evaluated for any time period required. The method allows both trends and the variability in the composition of the waste feed to be identified. In addition, the Balance Method delivers statistically valid results with specified uncertainties and requires no additional sampling or measurements (except in those cases in which the CO_2 measurement of the flue gas needs to be implemented), which results in virtually no additional costs for the plant operator who wants to analyze the biomass content in the waste feed. The plausibility checks done with the software BIOMA can help to discover systematic measurement errors or faulty data documentation. However, valid operating data are crucial for reliable results and additional calibration efforts and control measurements might be required, especially when a routine application of the Balance Method is intended.

The produced results represent the first comprehensive evaluation of climate relevant CO_2 emissions from all WTE plants on a national basis and have directly been incorporated into the greenhouse gas inventory of Austria.

Acknowledgments

The authors would like to acknowledge the funding of the present study which was provided by the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management. In addition we thank the operators of the waste-to-energy plants for their cooperation.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.01.025.

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DETERMINING NATIONAL GREENHOUSE GAS EMISSIONS FROM WASTE-TO-ENERGY USING THE BALANCE METHOD

Supplementary Material

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A) Summary of input data required for the Balance Method

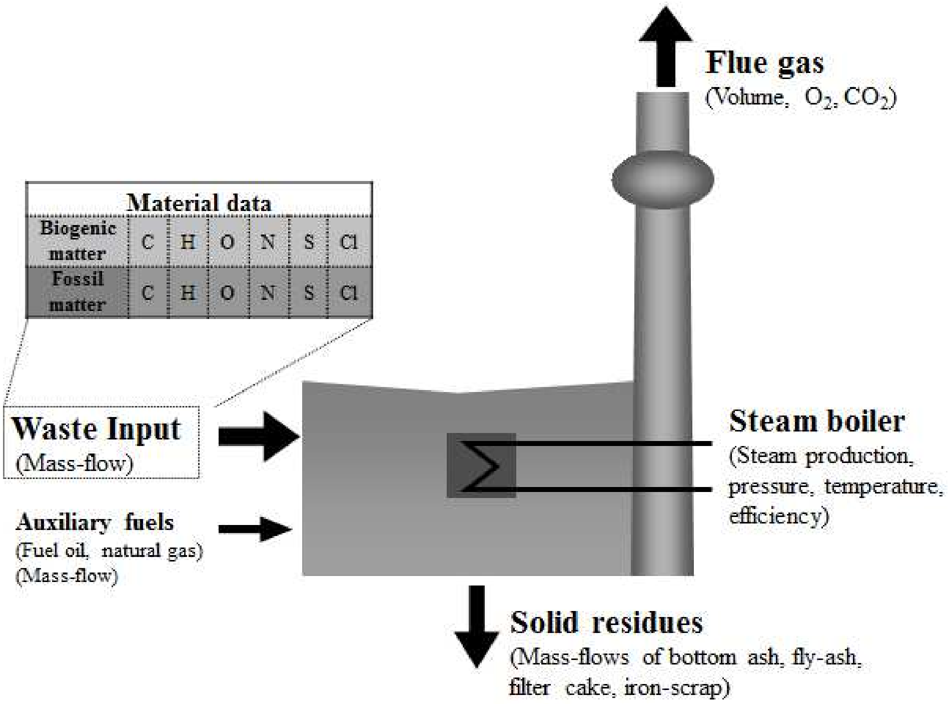

Figure 1: Required input data for the Balance Method

B) Elemental composition of moisture-and-ash-free biogenic and fossil organic matter used for the Balance Method

In principle the Balance Method is based on the distinct chemical composition of moisture-and-ash-free (maaf) biogenic and fossil organic matter and on the differences in the composition of both materials. As qualitative information (IUT&SDAG, 2014; Nelles, M., 1998; PlasticsEurope, 2010; Schneider, F. & Lebersorger, S., 2011; TBHauer, 1999 & 2002) about the different biogenic and fossil materials present in mixed waste is available plausible ranges for the chemical composition can easily be derived.

Biogenic matter in waste is basically composed of the following materials paper, cardboard, hygienic articles, wood, kitchen waste, garden waste and textiles (natural fibers), whereas fossil organic matter (plastics) in mixed wastes may include the whole range of different polymers produced (e.g. polyethylene PE, polypropylene PP, PVC, polystyrene PS, polyamide PA).

Combining contents of C, H, O, N, S and Cl in each biogenic or fossil compound (such as wood, paper or PE) with information about their relative shares (referred to the total amount of moisture-and-ash-free biogenic and fossil organic matter, respectively) allows calculating ranges for the elemental composition (content of C, H, O, N, S and Cl) of maaf biogenic and fossil organic matter.

In Figure 2 the data used for determining the elemental composition of maaf biogenic matter present in mixed wastes as well as the range for the elemental composition of biogenic matter (indicated by red bars in the right side of the Figure 2, which denote the likely range for the elemental composition) are given. A comparison of the elemental composition of different biogenic compounds present in waste (right side of Figure 2) demonstrates that they only slightly differ in their C, H and O-contents. This finding indicates that almost indispensable of the mixture of biogenic compounds (e.g. wood, paper, garden waste), elemental composition of maaf biogenic matter in wastes may only vary in a narrow range (see Figure 2 – right side and Table 1)

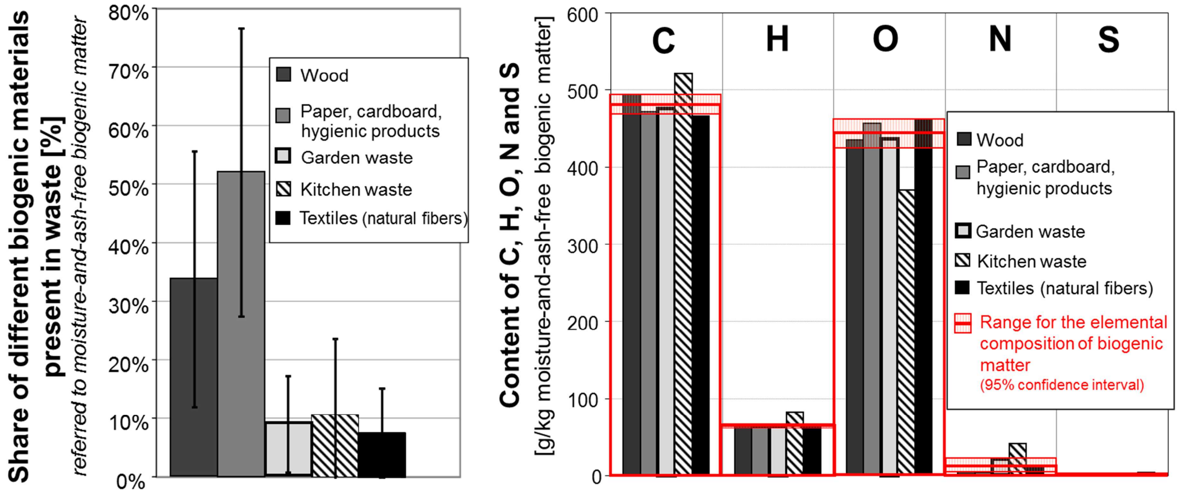

Figure 2 **Left side: Possible ratios of different biogenic compounds (e.g. wood, paper, …) present in mixed wastes (referred to maaf biogenic matter); right side: elemental composition (content of C, H, O, N and S) of different biogenic materials present in mixed waste, including an estimate for the range of the elemental composition (indicated red) of biogenic matter present in mixed waste (referred to maaf biogenic matter) - (Schwarzböck et al., 2016)**

Figure 3 illustrates the assumed composition of waste plastics (with respect to polymers) present in commingled waste. The composition (including the potential range for the different polymers - indicated by the black errors bars) has been derived from polymer consumption statistics (PlasticsEurope, 2010) taking the life time of plastics in different applications as wells as the potential collection and disposal routes into account. In addition data of detailed sorting campaigns conducted in Austria have been considered (Nelles, 1998; TBHauer, 1999, 2002).

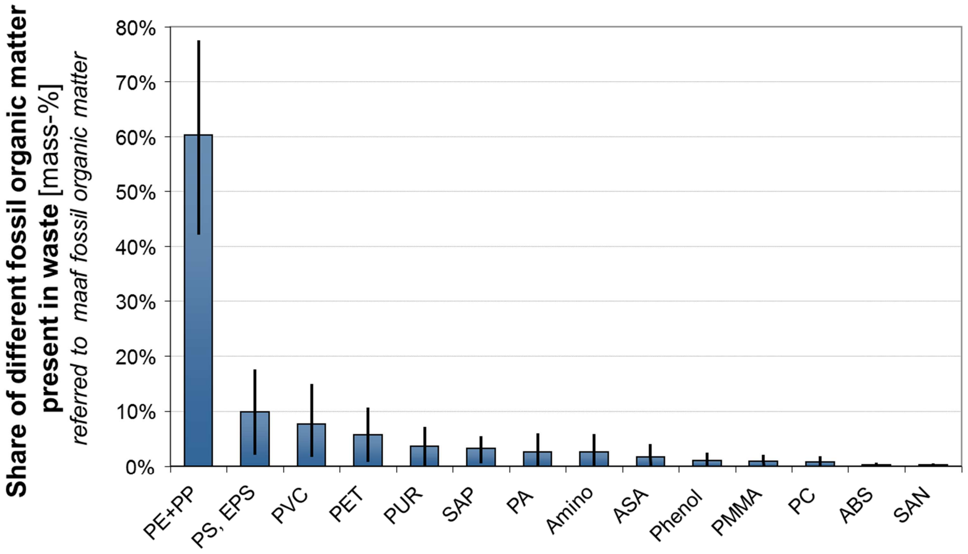

Figure 3 Possible ratios of different plastics (fossil organic) materials (e.g. PE, PVC, PET, paper, …) present in mixed wastes (referred to maaf fossil organic matter) – no differentiation between polyethylene PE and polypropylene PP was made since their elemental composition is identical (Schwarzböck et al., 2016)

In analogy to the biogenic matter, combining the data given in Figure 3 with the elemental composition of each polymer allows calculating the most likely C, H, O, S, N and Cl-contents of maaf fossil organic matter present in mixed wastes (see Table 1).

Table 1 Elemental composition of maaf biogenic and fossil organic matter present in commingled wastes (Schwarzböck et al., 2016)

Moisture- and ash-free		biogenic matter		fossil matter	
content of	unit	av	+/- *)	av	+/- *)
C	g/kg	483	*9*	777	*32*
H	g/kg	65	*2.4*	112	*11*
O	g/kg	443	*14*	61	*26*
N#)	g/kg	7	*5*	14	*11*
S#)	g/kg	1.1	*0.5*	3	*1*
Cl#)	g/kg	-	-	32	*24*

**) 95% confidence interval*

#) Contents of N, S and Cl are of minor significance for the results of the Balance Method (see (Fellner et al., 2007)

C) Elemental composition of auxiliary fuels (natural gas and crude oil) as used for the Balance Method

Table 2: Elemental composition of natural gas and crude oil as used for the Balance Method

Moisture- and ash-free	Crude oil		Natural gas	
content of	av	+/-	av	+/-
C	850 g/kg	*1 %*	0.536 kg/Nm³	*1 %*
H	150 g/kg	*1 %*	0.179 kg/Nm³	*1 %*
CH_4	-	-	0.9 Nm³/Nm³	*1 %*
LHV	43,150 kJ/kg	*1 %*	35,838 kJ/Nm³	*1 %*

D) Splitting of plant-specific uncertainty for overall uncertainty

Table 3: Splitting of uncertainty for the emission factor per plant into a "composition based" uncertainty (from the composition of moisture-and-ash-free biogenic and fossil organic matter) and an uncertainty resulting from the uncertainties of the plant operating data

WTE plant	Total uncertainty of annual value for the energy based emission factor[a] [kg CO_2/GJ]	Share of "composition based" uncertainty, in [%] based on total uncertainty[b]	Share of uncertainty from plant operating data, in [%] based on total uncertainty
A	2.42	64 % (1.55)	36 % (0.87)
B	2.22	70 % (1.55)	30 % (0.67)
C	2.22	70 % (1.55)	30 % (0.67)
D	3.70	42 % (1.55)	58 % (2.15)
E	2.82	55 % (1.55)	45 % (1.27)
F	2.45	63 % (1.55)	37 % (0.91)
G	3.75	41 % (1.55)	59 % (2.20)
H	3.16	49 % (1.55)	51 % (1.61)
I	2.74	57 % (1.55)	43 % (1.19)
J	2.21	70 % (1.55)	30 % (0.66)
Total uncertainty (for all plants)	1.55 + mean(0.87+0.67+0.67+2.15+1.27+0.91+2.20+1.61+1.19+0.66)/sqrt(10)		

[a] Determined by data reconciliation within the software BIOMA

[b] Determined by solving the set of balances under the assumption that operating data of the plant are applied without uncertainty.

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Paper II

Anteil erneuerbarer Energien und klimarelevante CO_2-Emissionen aus der thermischen Verwertung von Abfällen in Österreich

[Share of renewable energy and climate-relevant CO_2 emissions from thermal recovery of waste in Austria]

Therese Schwarzböck, Helmut Rechberger, Oliver Cencic and Johann Fellner

Österreichische Wasser-und Abfallwirtschaft, 2016, 68, 415-427

DOI: 10.1007/s00506-016-0332-5

Österr Wasser- und Abfallw 2016 · 68:415–427
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Anteil erneuerbarer Energien und klimarelevante CO_2-Emissionen aus der thermischen Verwertung von Abfällen in Österreich

Therese Schwarzböck · Helmut Rechberger · Oliver Cencic · Johann Fellner

Zusammenfassung Da brennbare Abfälle zumeist ein Gemisch aus biogenen (z. B. Papier, Holz, Küchenabfälle) und fossilen Materialien (Kunststoffe) darstellen, entstehen bei ihrer thermischen Verwertung sowohl klimaneutrale als auch klimarelevante CO_2-Emissionen. Analog verhält es sich auch bei der erzeugten Energie (Strom), die entsprechend dem jeweiligen Biomassegehalt des Abfalls zum Teil als erneuerbar eingestuft wird und als solche auch auszuweisen ist. Im Zuge der vorliegenden Studie wurden erstmals auf nationaler Basis die fossilen und biogenen Anteile in thermisch verwerteten Abfällen bestimmt. Die methodische Grundlage dabei bildet die von der Technischen Universität Wien auf europäischer Ebene patentierte Bilanzenmethode. Das Verfahren beruht auf einem mathematischen Abgleich von Materialdaten (z. B. mittlere stoffliche Zusammensetzung biogener und fossiler Materialen) mit messbaren Betriebsgrößen der Verbrennungsanlage (z. B. Reingasmenge, O_2- und CO_2-Konzentration im Reingas, Dampfmenge). Aufgrund einer Anlagenertüchtigung und teils fehlender CO_2-Messungen konnten 10 von 13 Abfallverbrennungsanlagen und damit rund 88 % des in österreichischen Müllverbrennungsanlagen verwerteten Abfalls für die Auswertung berücksichtigt werden (rund 2,3 Mio. Tonnen). Die Ergebnisse zeigen eine große Streuung der biogenen Heizwertanteile der Anlagen (im Jahresmittel stammen zwischen 35,7 ± 2,4 % und 61,2 ± 2,7 % der eingesetzten Energie aus biogenen Quellen). Auch eine starke zeitliche Variation der Abfallzusammensetzung auf Basis von Monatsmittelwerten ist deutlich erkennbar. Folglich lässt sich für Abfallverbrennungsanlagen kein allgemein gültiger Heizwertanteil oder Emissionsfaktor ableiten und eine anlagenspezifische Auswertung über einen längeren Zeitraum (wie es mit der Bilanzenmethode relativ einfach möglich ist) erscheint zielführend für eine zuverlässige Ausweisung des erneuerbaren Energieanteils oder der fossilen CO_2-Emissionen. Die eingesetzten Energien aus fossilen und biogenen Abfallbestandteilen (für die 10 betrachteten Anlagen) liegen im Jahr 2014 bei rund 11.450 ± 120 TJ und 10.730 ± 110 TJ. Es ergeben sich gesamt rund 1060 ± 24 kt klimarelevantes CO_2, das aus den thermischen Abfallverwertungsanlagen in Österreich im Jahr 2014 emittiert wurde (mit Hochrechnung auf alle 13 Anlagen).

Share of renewable energy and climate-relevant CO_2 emissions from Waste-to-Energy plants in Austria

Abstract Since combustible wastes usually consist of biogenic (e.g. paper, wood, food waste) and fossil organic matter (plastics), their thermal recovery results in climate neutral and climate relevant CO_2 emissions. Moreover, the fraction of biogenic materials in the waste feed is relevant for the amount of renewable energy produced. The latter has to be reported and might be subsidized according to national laws (e.g. based on European directive 2009/28/EG). The present study represents the first comprehensive evaluation of the share of biogenic and fossil materials in the waste feed of waste-to-energy (WTE) plants on a national basis. The Balance Method, which is patented on a European level by TU Wien, was applied to 10 out of 13 Austrian WTE plants (around 2.3 Mio tons of waste corresponding to around 88 % of the overall waste feed in Austrian WTE plants). The method is based on the mathematical reconciliation of the material properties (e.g. mean chemical composition of biogenic and fossil materials) and routinely recorded operating data of WTE plants (e.g. flue gas volume, CO_2 and O_2-content in the dry flue gas, steam production). The results demonstrate large variations for the share of energy from biogenic sources in the different WTE plants, ranging from 35.7 ± 2.4 % to 61.2 ± 2.7 % (based on annual averages). Additionally, for several WTE plants large temporal variations can be observed based on monthly mean values. Thus, a plant-specific and continuous evaluation of the waste composition in WTE plants (which the Balance Method allows to do at reasonable efforts) can be recommended for a reliable reporting of the renewable share of energy or fossil CO_2 emissions from waste incineration. The energy input which stems from fossil and biogenic sources can be estimated to 11,450 ± 120 TJ and 10,730 ± 110 TJ, respectively for the year 2014 (for the 10 WTE plants). In total 1060 ± 24 kt fossil CO_2 emissions from the thermal recovery of waste in Austria's WTE plants in 2014 could be determined (estimation for all 13 WTE plants).

1 Einleitung und Zielsetzung

Nach Inkrafttreten der Deponieverordnung in Österreich, die seit 2004 bzw. in einzelnen Bundesländern seit 2009 das Deponieren von unbehandeltem Restmüll und Rückständen aus der kommunalen Abwasserreinigung untersagt, ist ein deutlicher Anstieg der thermisch verwerteten Abfälle zu verzeichnen (von 14,5 auf 36,4 %;

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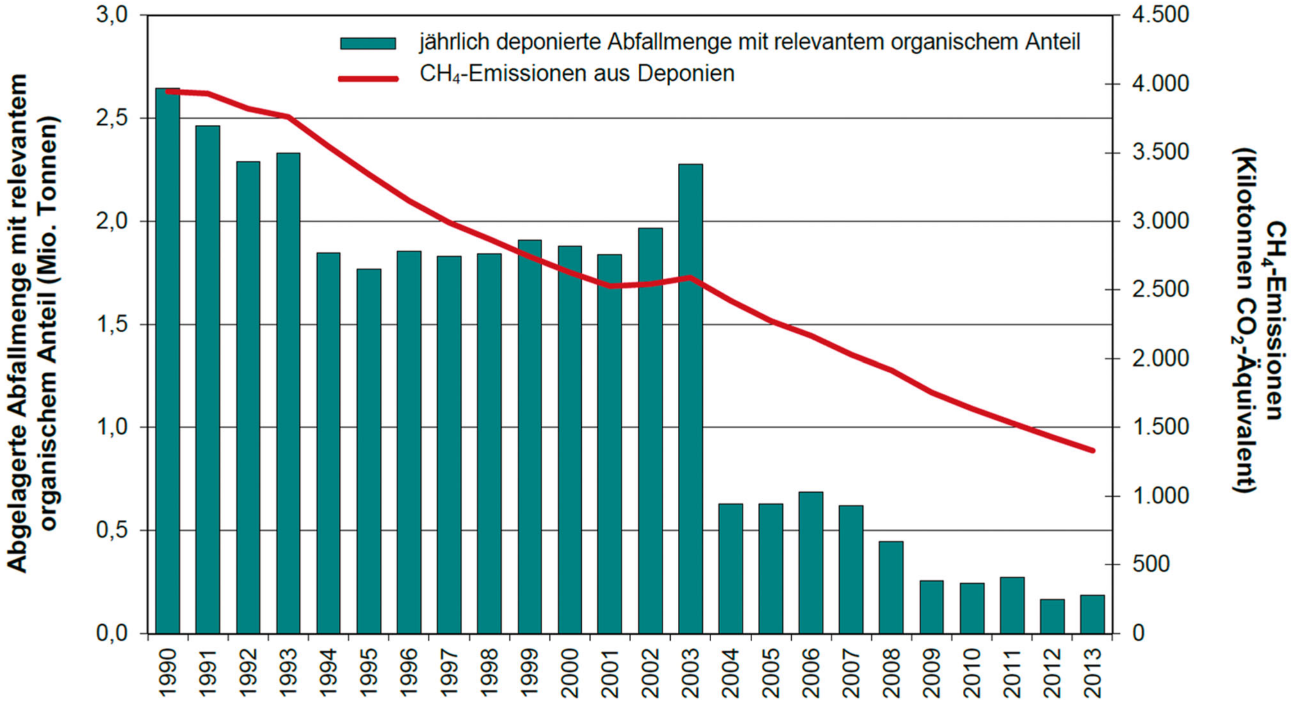

Abb. 1 Methan-Emissionen aus Deponien und jährlich deponierte Abfälle mit relevantem organischen Anteil (Umweltbundesamt 2015b)

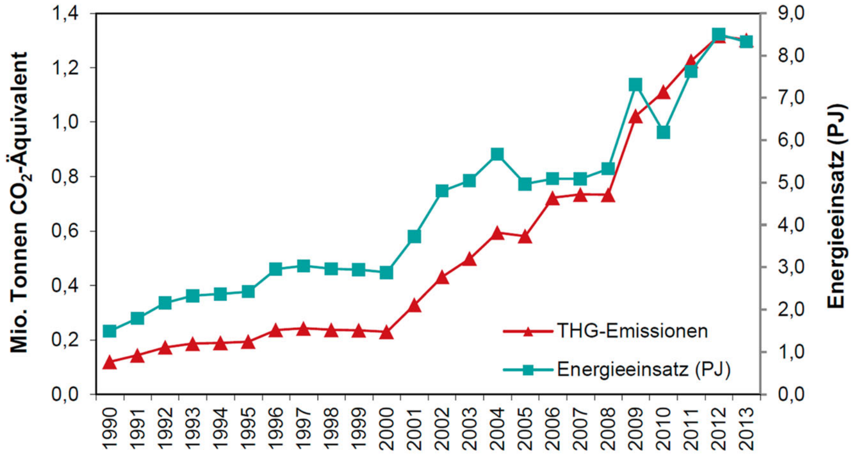

Abb. 2 Treibhausgasemissionen der Abfallverbrennung und eingesetzte Energie aus Abfällen (Umweltbundesamt 2015b)

BAWP 2011). Im Jahr 2000 standen in Österreich fünf Abfallverbrennungsanlagen zur thermischen Behandlung von Siedlungs- und Gewerbemüll, Industrieabfälle und Klärschlamm mit einer Kapazität von rund 730.000 Tonnen pro Jahr zur Verfügung (Stubenvoll et al. 2002). Mittlerweile sind 11 Anlagen mit einer Gesamtkapazität von rund 2.600.000 Tonnen pro Jahr in Betrieb (exklusive der 2 Anlagen zur Behandlung von gefährlichen Abfällen). Diese Entwicklung führte zu einer drastischen Reduktion der deponierten Mengen an biologisch abbaubaren Abfällen und damit verbunden auch zu einem Rückgang aktueller und insbesondere zukünftiger Methanemissionen von Deponien (siehe Abb. 1). Durch den Anstieg der verbrannten Abfallmengen gelangt jedoch mehr CO_2 in die Atmosphäre. Laut Klimaschutzbericht hat sich seit 2014 die emittierte Menge an treibhausrelevantem CO_2 aus der thermischen Verwertung nahezu verdoppelt (auf rund 1,3 Mio. Tonnen $CO_{2,equ}$; siehe Abb. 2) (Umweltbundesamt 2015b). Obgleich CO_2 weitaus weniger klimawirksam ist als Methan, ist es in der Klimabilanz Österreichs selbstverständlich zu berücksichtigen. Allerdings wird bei der Abfallverbrennung sowohl treibhausrelevantes (aus Kunststoffen stammend) als auch treibhausneutrales CO_2 (aus biogenen Quellen wie Holz, Papier, Küchen- und Gartenabfälle) freigesetzt. Eine Abschätzung beider CO_2-Anteile (biogen und fossil) ist daher notwendig. Analog zur Klimarelevanz stammt die bei der thermischen Verwertung erzeugte Energie aus Abfällen von verschiedenen Primärenergieträgern (biogen und fossil). Die Zusammensetzung eingesetzter Abfälle ist daher auch aus energiepolitischer Sicht von Interesse. Einerseits wird die Einspeisung von Strom aus erneuerbaren Energien gefördert (2009/28/EG) und andererseits sind die Stromlieferanten verpflichtet, den Primärenergieträgeranteil auszuweisen (Bundeskanzleramt 2011).

Die Quantifizierung der Anteile der „grünen" und fossilen Energie bzw. des klimaneutralen und klimarelevanten Kohlenstoffdioxidausstoßes ist aufgrund der variablen Zusammensetzung thermisch verwerteter Abfälle und der zahlreichen Fraktionen im Müll, die Verbunde aus unterschiedlichen Werkstoffen darstellen, schwierig. Bisherige Methoden, den Anteil fossiler CO_2-Emissionen zu bestimmen, basieren vorwiegend auf Sortieranalysen, welche jedoch mit großer Unsicherheit behaftet sind (Fellner et al. 2007; Fichtner 2007; Severin et al. 2010). Restfeinfraktionen (die bis zu 30 % betragen) können nicht mehr den Attributen „fossil" oder „biogen" zugeordnet werden. Zudem geben Verfahren, die auf einer punktuellen Analyse beruhen, selbst bei repräsentativ gezogenen Proben des Abfallinputs nur eine Momentaufnahme der Zusammensetzung zum Zeitpunkt der Probenahme wieder (wie beispielsweise die selektive Lösemethode) (Cuperus et al. 2005; van Dijk und Steketee 2002). Eine weitere gängige Methode zu Bestimmung der CO_2-Emissionen aus der Abfallverbrennung ist die Verwendung von sogenannten Emissionsfaktoren, die die fossile CO_2-Menge pro Tonne Abfall bzw. pro GJ Energieinhalt des Abfalls angeben. Diese Emissionsfaktoren beruhen zumeist auf Ergebnissen von Sortieranalysen und werden üblicherweise als typischer Emissionswert für verschiedene Brennstoffe (z. B. Steinkohle, Diesel, Braunkohle) angegeben. Jüngere Untersuchungen belegen allerdings, dass allgemeine Emissionsfaktoren für die Abfallverbrennung nur sehr bedingt Gültigkeit haben, da die Zusammensetzung des Abfalls sowohl zeitlich als auch regional sehr stark variieren kann (Fuglsang et al. 2014; Obermoser et al. 2009). Ein an der Technischen Universität Wien entwickeltes Verfahren ist die sogenannte Bilanzenmethode. Diese beruht auf einem mathematischen Modell, das vorhandene Betriebsparameter der Müllverbrennungsanlagen und Informationen über die chemische Zusammensetzung der biogenen und fossilen Abfallanteile verwendet. Dadurch lassen sich zeitliche Veränderungen der Zusammensetzung des Abfalls (Unterscheidung zwischen biogen und fossil) beobachten (Fellner et al. 2007).

Ziel der vorliegenden Studie ist es, die Zusammensetzung des Abfallinputs aller österreichischen Abfallverbrennungsanlagen zu analysieren und zu vergleichen. Da aufwendige Probenahmen und Sortierungen vermieden werden sollen (sehr kosten- und zeitintensiv), wurde die Bilanzenmethode als relativ einfaches und kostengünstiges Tool zur Bestimmung des biogenen und fossilen Brennstoffanteils eingesetzt.

Folgende Kennwerte (pro Anlage und gesamt für die thermische Verwertung von Abfällen in Österreich) für ein Kalenderjahr (2014) gilt es zu generieren:

- Erneuerbarer Energieanteil (Energieanteil aus Biomasse).
- Fossiler Kohlenstoffanteil und Ableitung von fossilen CO_2-Emissionsfaktoren: spezifische klimarelevante CO_2-Emissionen bezogen auf Abfallinput (kg $CO_{2,foss}$ pro Tonne Abfallinput) bzw. bezogen auf den Heizwert des Abfalls (kg $CO_{2,foss}$ pro GJ Heizwert des Abfalls.
- Klimarelevante Gesamt-CO_2-Emissionen aus der thermischen Verwertung von Abfällen in Österreich.

2 Methodik

2.1 Bilanzenmethode zur Bestimmung des fossilen/biogenen Anteils im Input der Abfallverbrennungsanlagen

Die methodische Grundlage für die Ermittlung der fossilen und biogenen Anteile im Input der Abfallverbrennungsanlagen bildet die am 30.3.2005 zum österreichischen Patent angemeldete und in der Zwischenzeit (26.12.2012) auf europäischer Ebene patentierte Bilanzenmethode („Verfahren zur Ermittlung der Anteile biogener und fossiler Energieträger sowie biogener und fossiler Kohlendioxidemissionen"). Das Verfahren beruht auf einem mathematischen Abgleich von Materialdaten (z. B. mittlere stoffliche Zusammensetzung biogener und fossiler Materialen) mit messbaren Betriebsgrößen der Verbrennungsanlage (z. B. Reingasmenge, O_2- und CO_2-Konzentration des Reingases und Dampfmenge). Dazu werden insgesamt sechs Bilanzgleichungen herangezogen (Abb. 3):

- Massenbilanz,
- Aschenbilanz,
- Kohlenstoffbilanz,
- Energiebilanz,
- Sauerstoffverbrauchsbilanz und
- Differenz aus Sauerstoffverbrauch und Kohlendioxidproduktion.

Jede der Gleichungen charakterisiert eine bestimmte Abfalleigenschaft (zum Beispiel Aschegehalt, Kohlenstoffgehalt, Heizwert). Für die Erstellung der Bilanzgleichungen werden die Materialien des Abfallinputs gedanklich in vier Stoffgruppen unterteilt: inerte (m_I), biogene (m_B) und fossile (m_F) Materialien sowie Wasser (m_W). Die inerte Stoffgruppe beinhaltet dabei per Definition die Trockenmasse aller nicht brennbaren Abfallbestandteile, wie beispielsweise Steine, Glas, Aschen oder anorganische Anteile in Bioabfällen bzw. Kunststoffen (zum Beispiel Kaolin in Papier bzw. anorganische Additive in Kunststoffen). In den biogenen und fossilen Stoffgruppen m_B und m_F ist jeweils nur die wasser- und aschefreie organische Substanz subsumiert (siehe Abb. 4).

Die Unbekannten des Gleichungssystems sind die Massenanteile an inerten, biogenen und fossilen Stoffen sowie Wasser (m_I, m_B, m_F und m_w) (siehe Abb. 3). Die Koeffizienten der Unbekannten auf der linken Seite der Gleichungen (z. B. Heizwert biogen HW_B, Kohlenstoffgehalt biogen c_B, $d_{O2\text{-}CO2,B}$, $O_2{}^c{}_{,B}$ etc.) lassen sich aus der chemischen Zusammensetzung der biogenen und fossilen Materialien berechnen. Daten hierfür können aus der Literatur entnommen oder durch Laboranalysen bestimmt werden. Die in dieser Studie verwendeten Eingangsdaten zur chemischen Zusammensetzung des biogenen und fossilen Materials auf wasser- und aschefreier Basis sind in Tab. 1 angegeben und stammen aus Ergebnissen bestehender Abfallsortieranalysen, nationalen Produktions- und Einsatzdaten von Polymeren sowie Ergebnissen von Monte-Carlo-Simulationen (Fellner et al. 2007; Schwarzböck et al. 2016c).

Um einen möglichen Einfluss anorganischer Reaktionen (zum Bespiel Kalkbrennen bzw. Oxidation von Metallen) auf die einzelnen Bilanzen zu berücksichtigen, wurden folgende Prozesse in den oben angeführten Gleichungen inkludiert:

- etwa 25 g $CaCO_3$/kg Abfall werden zu CaO und CO_2 dissoziert. Dies entspricht rund 50 % der gesamten Karbonatmenge im Abfallinput (Priester et al. 1996),
- Oxidation von Aluminium in einem Ausmaß von rund 0,75 g Al/kg Abfall (berechnet nach Skutan and Brunner 2006 sowie Mitterbauer et al. 2009), und
- Oxidation von Eisen im Ausmaß von rund 4 g Fe/kg Abfall (nach AGW 1992).

Das Gleichungssystem der Bilanzenmethode besteht aus 6 Gleichungen und 4 Unbekannten. Für jeden Eingabewert wird eine entsprechende Unsicherheit angegeben. Es handelt sich somit um

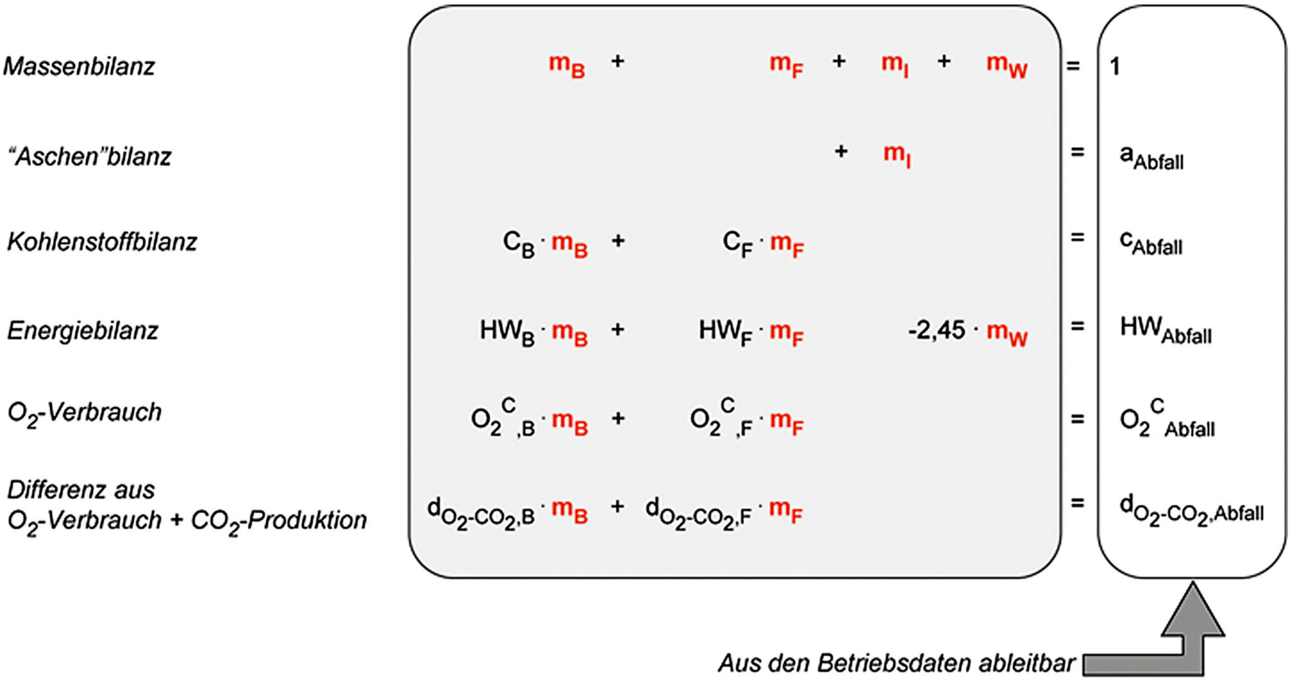

Abb. 3 Gleichungssystem der Bilanzenmethode (vereinfachte Darstellung); mit c_B, c_F … Kohlenstoffgehalt im biogenen bzw. fossilen Abfallanteil, HW_B, HW_F … Heizwert des biogenen bzw. fossilen Abfallanteils, $O_2{}^C{}_{,B}$, $O_2{}^C{}_{,F}$ … Sauerstoffverbrauch des biogenen bzw. fossilen Abfallanteils, m_B, m_F … Massenanteile des biogenen bzw. fossilen Materials auf wasser- und aschefreier Basis, m_I, m_W … Inertanteil bzw. Wasseranteil des Abfalls (Fellner et al. 2006a)

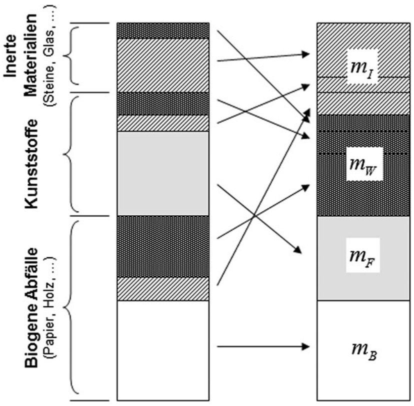

Abb. 4 Unterteilung des Abfalls in Stoffgruppen (basierend auf Fellner et al. 2007)

ein überbestimmtes System, das mithilfe nichtlinearer Ausgleichsrechnung zu lösen ist. Konkret wird dazu die Methode der schrittweisen linearen Ausgleichsrechnung angewandt. Ausgabewerte sind die berechneten Massenanteile m_B, m_F, m_W, m_I sowie die zugehörigen Unsicherheitsbereiche.

Eine detaillierte Beschreibung der einzelnen Gleichungen der Bilanzenmethode ist dem österreichischen Patent A539/2005 („Verfahren zur Ermittlung der Anteile biogener und fossiler Energieträger sowie biogener und fossiler Kohlendioxidemissionen") bzw. der europäischen Patentanmeldung (Fellner et al. 2006b) zu entnehmen. Die Methode wird ebenfalls in Fellner et al. (2007) im Detail beschrieben. Die Gültigkeit der Bilanzenmethode wurde in verschiedenen Studien anhand von Vergleichsanalysen mit anderen Methoden und Sensitivitätsanalysen bestätigt (Larsen et al. 2013; Mohn et al. 2008; Obermoser et al. 2009; Rechberger et al. 2014). Eine Routineanwendung erfolgt bereits in mehr als 15 europäischen Müllverbrennungsanlagen zur Stromkennzeichnung oder zur Ausweisung der Treibhausgasemissionen.

2.2 Abfallverbrennungsanlagen in Österreich

Im Jahr 2014 standen in Österreich 13 Abfallverbrennungsanlagen für die Behandlung von Siedlungsabfällen, Gewerbe- und Industrieabfällen, Klärschlamm und gefährlichen Abfällen mit einer Gesamtkapazität von rund 2,75 Mio Tonnen zur Verfügung (Tab. 2). Davon konnten 10 Anlagen für die Auswertungen herangezogen werden. Eine Anlage war im Berichtsjahr nicht in Betrieb, während bei weiteren zwei Anlagen, die vorwiegend gefährliche Abfälle behandeln, die Auswertung aufgrund der Datenlage (keine CO_2-Messungen oder unzureichende Datenqualität) nicht möglich war. Damit konnten rund 88 % des thermisch verwerteten Abfalls in Österreichs Müllverbrennungsanlagen im Jahr 2014 für die Auswertung berücksichtigt werden (rund 2,3 Mio. Tonnen von ca. 2,6 Mio Tonnen Abfall inklusive Klärschlamm).

Die untersuchten Anlagen umfassen demnach 6 Anlagen mit Rostfeuerung sowie 4 Anlagen mit Wirbelschichtfeuerung, wobei überwiegend Restmüll, Gewerbe- und Industrieabfall sowie Klärschlamm und Ersatzbrennstoffe eingesetzt werden (Tab. 2).

2.3 Notwendige Betriebsdaten für die Anwendung der Bilanzenmethode

Für die Anwendung der Bilanzenmethode nach der Beschreibung in Kapitel 2.1 sind neben Informationen zur chemischen Zusammensetzung der biogenen und fossilen Materialien, Reingasparameter, Input- und Outputströme und die Dampfparameter der Müllverbrennungsanlagen notwendig. Tab. 3 listet die nötigen Betriebsdaten auf, die idealerweise als Stundenmittelwerte in die Berechnungen gemäß Bilanzenmethode eingehen.

Tab. 1 Chemische Zusammensetzung des biogenen und fossilen Materials in Mischabfällen (Fellner et al. 2007; Schwarzböck et al. 2016c)

Wasser- und aschefrei		Biogenes Material[a]		Fossiles Material[a]	
Gehalt an	Einheit	MW	±[b]	MW	±[b]
C	g/kg	483	9	777	32
H	g/kg	65	2.4	112	11
O	g/kg	443	14	61	26
N[c]	g/kg	7	5	14	11
S[c]	g/kg	1.1	0.5	3	1
Cl[c]	g/kg	–[d]	–	32	24

[a] Kleine Unterschiede der Werte im Vergleich zu Werten in Fellner et al. (2007) sind auf eine Erweiterung der Datenbasis zurückzuführen
[b] 95 % Vertrauensintervall
[c] Der Gehalt an N, S und Cl ist für die Ergebnisse der Bilanzenmethode von untergeordneter Bedeutung (Fellner et al. 2007)
[d] Cl-Gehalt < 5 g/kg

2.4 Plausibilitätsprüfungen der Betriebsdaten

Vor der eigentlichen Berechnung mittels Bilanzenmethode werden die Betriebsdaten durch Plausibilitätsprüfungen auf mögliche Messfehler untersucht. Dafür werden folgende chemisch-physikalische Beziehungen zwischen dem Heizwert und der Reingasmenge sowie dessen Zusammensetzung herangezogen: Jedes Mol verbrauchter Sauerstoff geht mit einer Energiefreisetzung von 360 bis 400 kJ einher (basierend auf theoretischen Berechnungen des unteren Heizwertes und des Sauerstoffverbrauchs für „extreme" Abfallzusammensetzungen – entweder nur biogen oder nur fossil zusammen mit inertem Material und Wasser). Es ergeben sich ähnliche Zusammenhänge für den Kohlenstoffgehalt. Hier werden durch die Verbrennung von einem Gramm organischen Kohlenstoffs 34 bis maximal 44 kJ an Wärme freigesetzt (Fellner et al. 2007).

Folgende Zusammenhänge in den Betriebsdaten werden vor der Auswertung mit der Bilanzenmethode überprüft:

1. Gegengleicher Verlauf der O_2- und CO_2-Konzentrationen im Reingas,
2. Summe der O_2- und CO_2-Konzentrationen im Reingas im Bereich zwischen 15 und 21 %,
3. Korrelationen zwischen dem Heizwert des Brennstoffs und dem Sauerstoffverbrauch während der Verbrennung,
4. Korrelationen zwischen dem Heizwert und dem Kohlenstoffgehalt des Brennstoffs,
5. Korrelationen zwischen dem Sauerstoffverbrauch und dem Kohlenstoffgehalt des Brennstoffs.

Sind die erwarteten Zusammenhänge gemäß Überprüfung 1) und 2) nicht erkennbar oder liegen die Daten nicht wie erwartet in den definierten Wertebereichen gemäß Überprüfung 3), 4) und/oder 5), müssen Mess- oder Datenübertragungsfehler vermutet werden. Ein besonderes Augenmerk ist dabei auf die Messungen der O_2- und CO_2-Konzentration im Reingas zu legen, da sich die Auswertung der Bilanzenmethode sehr stark auf diese Messungen stützt und sich Fehlmessungen dementsprechend stark auf das Ergebnis auswirken (siehe dazu auch Sensitivitätsanalysen in Fellner et al. 2007). Zusatzangaben zu beispielsweise den Messstellen, Messmethoden, Überprüfungsmessungen oder gegebenenfalls weitere Datensätze können zur Klärung der unplausiblen[1] Daten oder teilweise auch zur Korrektur von systematischen Fehlern herangezogen werden.

Die Überprüfung der Daten gemäß Punkt 5) ist schlussendlich die ausschlaggebende für den etwaigen Ausschluss von Datensätzen. Eine beispielhafte Darstellung der untersuchten Korrelation bietet Abb. 5. Alle Daten, die innerhalb des definierten Wertebereichs liegen (plausible Datensätze[1]), werden für die Auswertung mittels Bilanzenmethode herangezogen.

3 Ergebnisse und Diskussion

3.1 Plausibilitätsprüfung

Die Plausibilitätsprüfung wird basierend auf gleitenden 6-Stunden-Mittelwerten der notwendigen Betriebsparameter durchgeführt. In Abb. 5 sind exemplarisch die Ergebnisse einer Anlage (Anlage E) dargestellt. 90 % der Werte in Abb. 5 liegen im definierten Wertebereich. Bei nahezu allen Anlagen (bei 8 von 10) liegt der Anteil der Abfallmenge bei plausiblen Betriebsdaten über 95 % (Tab. 4). Die etwas niedrigere Plausibilitätsrate für die Anlagen D und I ist auf instabile CO_2-Messungen sowie teils auf geringere zeitliche Auflösung der ausgewerteten Betriebsdaten (Tagesmittelwerte statt Stundenmittelwerte) zurückzuführen. Insgesamt können über 96 % der verbrannten Abfallmenge im Jahr 2014 in die Auswertung miteinbezogen werden (rund 2,2 Mio Tonnen von 2,3 Mio Tonnen Abfall).

Bei der Mehrzahl der Anlagen waren als Resultat der Plausibilitätsprüfungen Rückfragen an den Betreiber nötig, da sich einzelne Parameter als nicht stimmig darstellten. Grund dafür waren häufig Fehler in der Dokumentation oder auch Messfehler. Die gröbsten und häufigsten Fehler in den übermittelten Betriebsdaten lassen sich für vorliegende Untersuchung wie folgt zusammenfassen:

- Feuchte Reingasmengen als trocken angegeben.
- Umrechnung der Reingasmengen von Ist-O_2-Gehalt auf 11 % O_2-Gehalt nicht nachvollziehbar oder nicht ausgewiesen.
- Systematische Über- oder Unterschätzung der Reingasmengen.
- Keine Informationen über Messprinzip der O_2- und CO_2-Messungen (trocken oder feucht).

3.2 Biogener Heizwertanteil

Anhand der berechneten Massenanteile der wasser- und aschefreien biogenen und fossilen Abfallfraktion im Input der Abfallverbrennungsanlagen (m_B und m_F aus Abb. 3) und der jeweiligen Kohlenstoffgehalte (C_B und C_F in Abb. 3) lassen sich gemäß Fragestellung die fossilen Kohlenstoffanteile (entspricht den Anteilen der biogenen CO_2-Emissionen) ableiten. Weiters kann mittels des

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[1] Die Bezeichnung unplausibel bedeutet, dass die Messdaten bestimmte Korrelationen nicht ausreichend genau erfüllen. Es ist jedoch gleichzeitig festzuhalten, dass sich diese Wertung lediglich auf die Anwendung der Daten im Rahmen der Bilanzenmethode bezieht.

Tab. 2 Übersicht über die österreichischen Abfallverbrennungsanlagen im Jahr 2014 mit jeweiliger Feuerungstechnologie und verbrannten Abfallarten

Anlage	Feuerungstechnologie	Verbrannter Abfall (qualitative Angabe)
A	Rostfeuerung (RF)	Siedlungsabfälle und ähnliche Gewerbeabfälle
B	Rostfeuerung (RF)	Siedlungsabfälle und ähnliche Gewerbeabfälle
C	Stationäre Wirbelschichtfeuerung (WS)	Fraktionen aus Siedlungs- und Gewerbeabfallsplitting, Klärschlamm
D	Wirbelschichtfeuerung (WS)	Fraktionen aus Siedlungs- und Gewerbeabfallsplitting, Klärschlamm
E	Zirkulierende Wirbelschichtfeuerung (WS)	Fraktionen aus Siedlungs- und Gewerbeabfallsplitting, Klärschlamm
F	Rostfeuerung (RF)	Gewerbeabfälle, Industrieabfälle, Siedlungsabfälle
G	Stationäre Wirbelschichtfeuerung (WS)	Fraktionen aus Siedlungs- und Gewerbeabfallsplitting, geringe Anteile Klärschlamm
H	Rostfeuerung (RF)	Siedlungsabfälle und ähnliche Gewerbeabfälle, geringe Anteile Industrieabfälle und Klärschlamm
I	Rostfeuerung (RF)	Überwiegend Siedlungsabfälle
J	Rostfeuerung (RF)	Siedlungsabfälle und ähnliche Gewerbeabfälle, geringe Anteile Klärschlamm
K[a]	Stationäre Wirbelschichtfeuerung und Drehrohrofen (WS+DRO)	Gefährliche und nicht gefährliche Abfälle, Industrieschlämme, Klärschlamm
L[a]	Stationäre Wirbelschichtfeuerung und Drehrohrofen (WS+DRO)	Gefährliche und nicht gefährliche Abfälle, Industrieschlämme, Klärschlamm
M[a]	Rostfeuerung (RF)	Siedlungsabfälle und ähnliche Gewerbeabfälle

[a] Anlagen K, L und M konnten in der vorliegenden Auswertung nicht berücksichtigt werden, wobei Anlage M im Jahr 2014 nicht in Betrieb war und demnach im Berichtsjahr keinen Abfall verwertet hat

Tab. 3 Benötigte Stundenmittelwert-Betriebsdaten der Müllverbrennungsanlagen für die Anwendung der Bilanzenmethode

Betriebsparameter	Einheit
Verbrannte Abfallmenge	[t/h]
Verbrannte Klärschlammmenge	[t/h]
Zusatzbrennstoffe (Öl und/oder Gas)	[t/h] bzw. [m^3/h]
Rückstandsmengen (Schlacke, Asche)	[t/h][a]
Reingasmenge trocken	[Nm^3/h]
O_2- und CO_2-Konzentration im trockenen Reingas	[Vol-%]
Dampfproduktion	[t/h]
Dampftemperatur und Dampfdruck	[°C] und [bar]
Speisewassertemperatur	[°C]
Wirkungsgrad des Dampfkessels	[-]

[a] Daten für die Rückstände sind auch in Form von Monatsmittelwerten ausreichend

berechneten biogenen Massenanteils m_B (wasser- und aschefrei) sowie des Heizwertes des biogenen Abfallanteils HW_B (abgeleitet aus der chemischen Zusammensetzung der wasser- und aschefreien biogenen Materialien), der erneuerbare (biogene) Anteil der eingesetzten Energie aus Abfällen berechnet werden. Diese biogenen Heizwertanteile sind in Abb. 6 als Monatsmittelwerte pro untersuchter Anlage dargestellt, aufgeteilt in Anlagen mit Rostfeuerung (RF) und Anlagen mit Wirbelschichttechnologie (WS). Die RF-Anlagen verwerten vorwiegend Siedlungsabfälle und ähnliche Gewerbeabfälle (ausgenommen Anlage F, die überwiegend mit Gewerbe- und Industrieabfällen gefahren wird), während der Input in die WS-Anlagen im Wesentlichen aus aufbereiteten Siedlungs- und Gewerbeabfällen und Klärschlamm besteht. Die genaue quantitative Zusammensetzung des Abfallinputs der Anlagen (Anteil an den jeweiligen Abfallarten) ist den AutorInnen nicht bekannt.

Aus Abb. 6 zeigt sich jedoch, dass der biogene Anteil am Heizwert (bezogen auf den Heizwert des gesamten Abfalls inklusive Klärschlamm) starken Schwankungen unterliegt und im Monatsmittel ein Minimum von 22,5 ± 2,9 % (MVA E) und ein Maximum von 69,3 ± 3,0 % (MVA C) erreicht. Im Jahresmittel liegen die Werte zwischen 35,7 ± 2,4 % (MVA F) und 61,2 ± 2,7 % (MVA C). Diese große Bandbreite (es ergibt sich eine mittlere Streuung der Jahresmittelwerte über alle Anlagen von ± 10 %abs und ± 21 %rel) weist auf eine regional stark schwankende Abfallzusammensetzung hin, da die Müllverbrennungsanlagen in verschiedenen Regionen Österreichs angesiedelt sind. Neben dem Einfluss unterschiedlicher Sammelsysteme in den Bundesländern kann zusätzlich davon ausgegangen werden, dass die Anteile der jeweilig eingesetzten Abfallarten (Siedlungsabfälle, Gewerbeabfälle, Industrieabfälle etc.) die Ergebnisse der Auswertung mitbestimmen, da unterschiedliche Industriebranchen und Betriebe in den Regionen angesiedelt sind.

Weiters sind starke zeitliche Schwankungen der biogenen Heizwertanteile zu verzeichnen. Beispielsweise stammen, basierend auf den Monatsmittelwerten, in MVA E zwischen 22,5 % und 45,2 % der Energie aus biogenen Quellen (das entspricht einer mittleren relativen Streuung von 16 %) (Abb. 6). Bei der Hälfte der Anlagen ergibt sich eine mittlere relative Streuung der berechneten Heizwertanteile von über 10 %, wobei dies vorwiegend bei den Wirbelschichtanlagen zu beobachten ist. Diese stärkere zeitliche Variabilität der Abfallzusammensetzung in den Wirbelschichtöfen im Vergleich zu den Rostfeuerungsanlagen ist unerwartet, da in Wirbelschichtöfen vorwiegend vorsortierte bzw. aufbereitete Abfälle mit geringerer Korngröße eingebracht werden, und daher grundsätzlich von einem homogeneren Brennstoff in diesen Anlagen ausgegangen werden kann. Es wird daher angenommen, dass der teils saisonabhängige Bedarf an Ersatzbrennstoffen (in Form von aufbereitetem Abfall) in der Industrie die Be-

Tab. 4 Als plausibel eingestufte Betriebsdaten der einzelnen Anlagen für das Kalenderjahr 2014 (angegeben als verbrannte Abfallmenge bei plausiblen Betriebsdaten bezogen auf die gesamte Menge an verbranntem Abfall)

Anlage	A	B	C	D^{a}	E	F	G	H	I	J	*Gesamt*
Plausible „Abfallmenge"	98,3%	99,3%	95,8%	84,4%	99,5%	99,5%	98,3%	99,0%	82,8%	99,7%	*96,7%*

^{a}Auswertung für nur 7 Monate

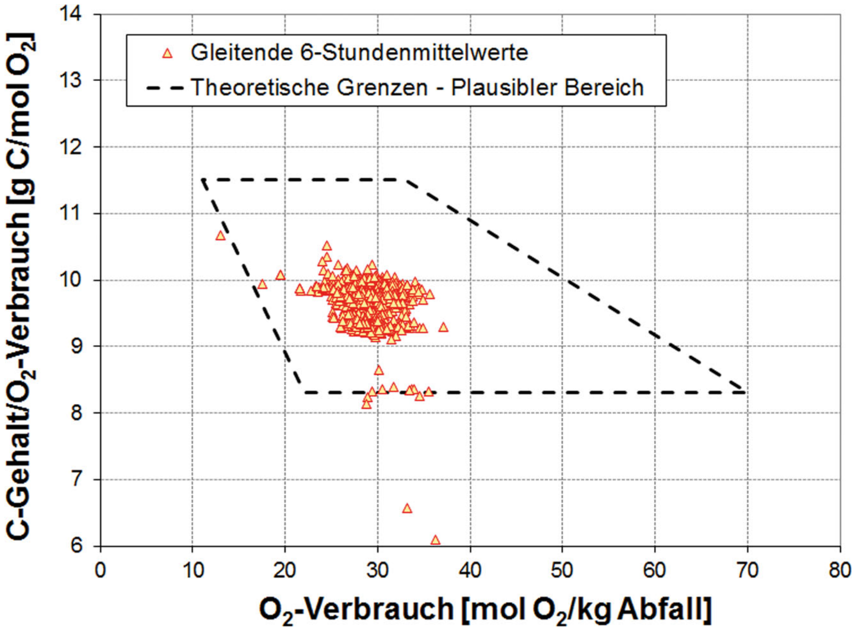


Abb. 5 Resultate der Plausibilitätsprüfung der Abfallverbrennungsanlage E (Korrelation zwischen Sauerstoffverbrauch und Kohlenstoffgehalt)

wirtschaftung und den Betrieb von mechanischen Abfallaufbereitungsanlagen mitbestimmt. Beispielsweise wurden im Jahr 2014 laut Verein der österreichischen Zementindustrie rund 300.000 t Kunststoff-Abfälle in österreichischen Zementwerken als Ersatzbrennstoffe eingesetzt (VÖZ 2015). Bei einer Gesamtkapazität der Wirbelschichtöfen in Österreich von rund 650.000 t Abfällen pro Jahr (exklusive Klärschlamm), ergibt sich bereits bei einem Zementproduktionsrückgang von 20 % pro Monat ein Anstieg der Kunststoffabfälle (und damit der Abfälle fossilen Ursprungs), die in Wirbelschichtöfen verwertet werden, von knapp 10 % (unter der Annahme, dass der schwankende Bedarf der Zementindustrie nur durch die Verbrennung in den Wirbelschichtanlagen ausgeglichen wird). Zahlen des Vereins Deutscher Zementwerke zeigen sogar Unterschiede in der Zementproduktion zwischen Winter- und Sommermonaten von über 100 % (VDZ 2016). MVA G und MVA E der vorliegenden Studie zeigen einen deutlichen Abwärtstrend des biogenen Heizwertanteils gegen Ende des Jahres 2014 (Abb. 6). Soweit den AutorInnen bekannt ist, werden in diesen Anlagen Fraktionen von mechanischen Abfallaufbereitungsanlagen verwertet, die auch Ersatzbrennstoffe für Zementwerke bereitstellen. Für die anderen Anlagen wird erwartet, dass andere Einflussfaktoren, wie Stillstandzeiten benachbarter Anlagen (für Revision oder Erneuerung) einen stärkeren Effekt auf die Zusammensetzung des Abfalls haben.

Eine quartalsmäßige Darstellung des biogenen Heizwertanteils in Abb. 7 lässt gesamt keinen deutlichen saisonalen Trend erkennen, weder für die Rostfeuerungsanlagen mit vorwiegend Siedlungs- und Gewerbeabfällen, noch für die Anlagen mit Wirbelschichtöfen. Einzig im 4. Quartal 2014 zeigt sich ein geringerer biogener Anteil der eingesetzten Energie für WS-Anlagen (41 % im Vergleich zu 47 bis 50 % in den anderen Quartalen). Aus Abb. 7 ist zudem erkennbar, dass die mittlere absolute Streuung zwischen den WS-Anlagen in den Winterquartalen (1. und 4. Quartal) mit 25 bis 30 %abs deutlich höher ist als im 2. und 3. Quartal des Jahres 2014 (16 bis 20 %abs; dargestellt als Fehlerbalken in Abb. 7). Das deutet wiederum auf eine stärkere (qualitative) Variation des Abfallinputs dieser Anlagen in den Wintermonaten hin.

Im Mittel über alle betrachteten Anlagen stammen rund 48 ± 2 % der über Abfälle eingesetzten Energie aus biogenen Quellen (gewichteter Jahresmittelwert) (Abb. 7).

Das Umweltbundesamt in Deutschland gibt als Standardwert einen biogenen Heizwertanteil von 50 % an (Icha 2015). Obwohl dieser Schätzwert innerhalb der Unsicherheit des in dieser Studie bestimmten Gesamtmittelwertes liegt, können sich bei Anwendung dieses Richtwertes anlagenspezifisch sehr hohe Über- oder Unterschätzungen (bis 32 %rel bezogen auf Jahresmittelwert, bis 60 %rel bezogen auf Monatsmittelwerte) des erneuerbaren Energieanteils ergeben. Bei höheren Einspeisetarifen für „grünen" Strom kann das leicht zu finanziellen Verzerrungen führen (z. B. ungerechtfertigt getätigte Fördergeldzahlungen).

Die Ausführungen zu den zeitlichen Schwankungen sowie Streuungen zwischen den Anlagen bezüglich biogener Heizwertanteile sind im Wesentlichen auch auf die Ergebnisse der biogenen Kohlenstoffanteile übertragbar, da der Heizwert wesentlich vom Kohlenstoffgehalt des Abfalls bestimmt wird. Die biogenen Kohlenstoffanteile liegen jedoch im Vergleich zu den biogenen Heizwertanteilen rund 7 bis 9 %abs höher. Diese Differenz der Kohlenstoff- und Heizwertanteile ist einerseits auf die Bedeutung der chemischen Zusammensetzung der biogenen und fossilen Materialien für den Heizwert (neben dem Kohlenstoffgehalt spielen beispielsweise auch der Wasserstoff- und Sauerstoffgehalt eine wichtige Rolle) zurückzuführen, insbesondere jedoch ist der Heizwert im Vergleich zum Kohlenstoffgehalt vom Wassergehalt des Materials abhängig. Da der Wassergehalt üblicherweise in biogenen Materialien (Küchenabfälle, Grünschnitt, etc.) höher liegt als in fossilen, liegt der Anteil für den biogenen Kohlenstoff stets deutlich über dem biomassebürtigen Heizwertanteil.

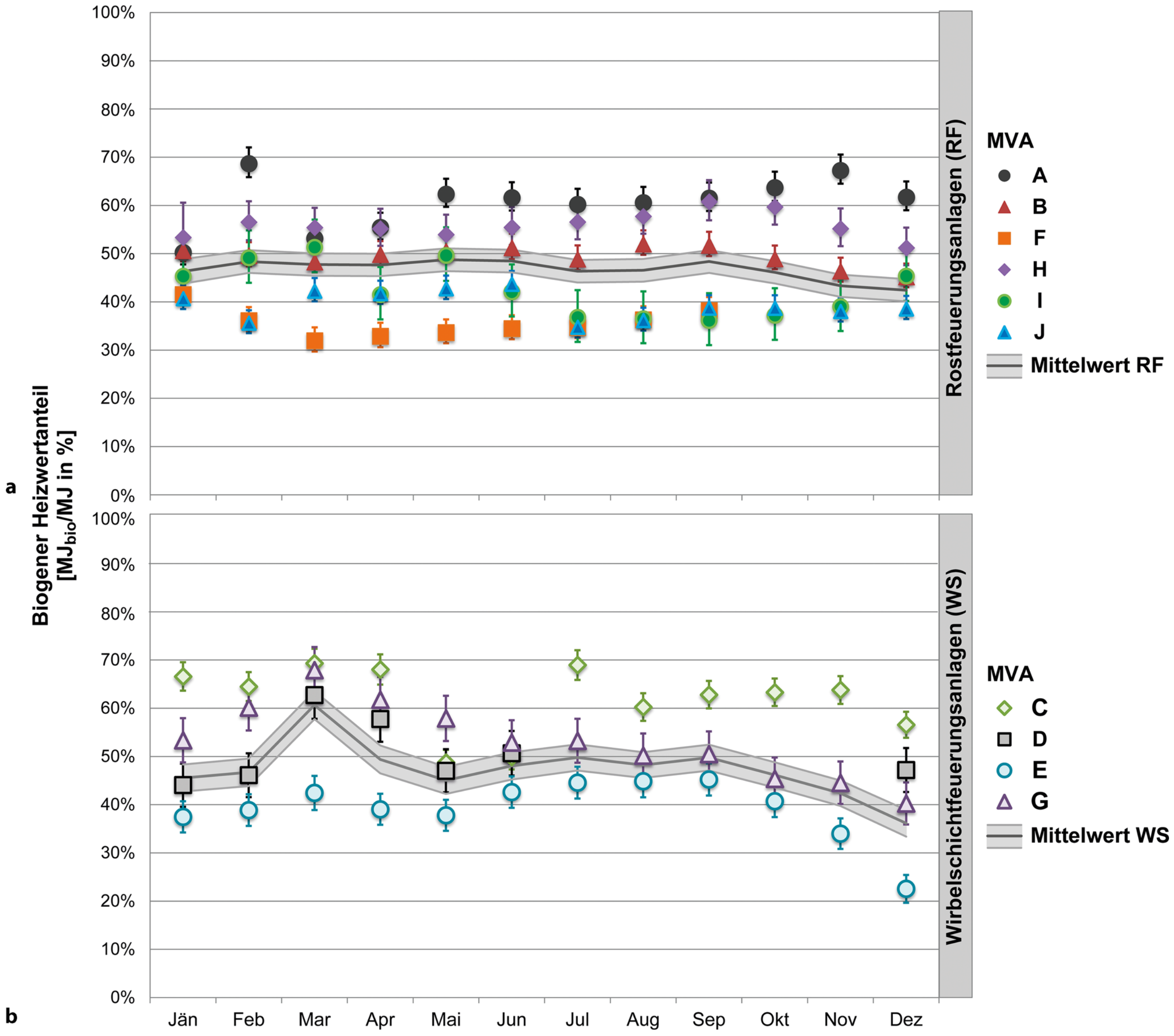


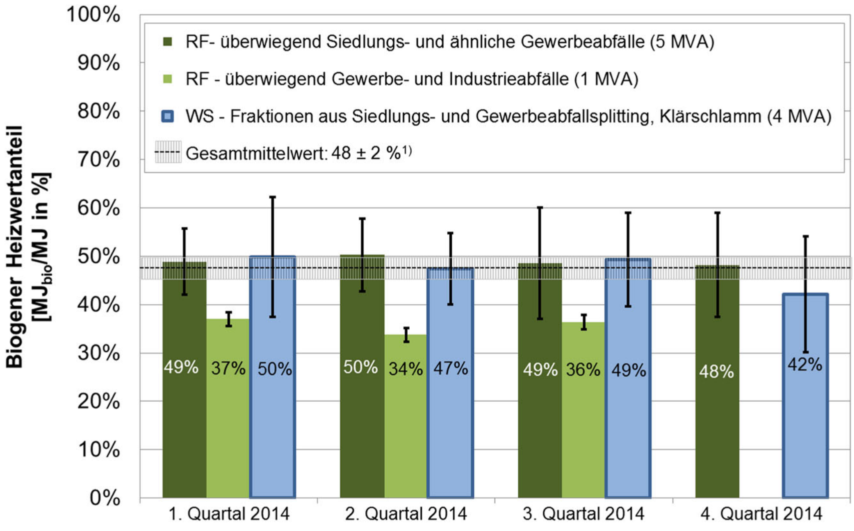
Abb. 6 Biogener Heizwertanteil der Müllverbrennungsanlagen (MVA) mit Rostfeuerung (**a**) und mit Wirbelschicht (**b**); gewichtete Monatsmittelwerte mit Standardunsicherheit (der ausgewiesene biogene Heizwertanteil bezieht sich nur auf den Abfallinput, Zusatzbrennstoffe sind hier nicht berücksichtigt)

Die eingesetzte Energie aus Abfällen (für die 10 betrachteten Anlagen) liegt im Kalenderjahr 2014 bei rund 22.500 TJ. Davon stammen im Mittel 47,7 ± 1,0 % aus biogenen Abfallbestandteilen (Papier, Küchenabfälle, Holz, Klärschlamm etc.), 50,9 ± 1,0 % aus Abfällen fossilen Ursprungs (Kunststoffe) und 1,4 ± 1,0 % aus Zusatzbrennstoffen (Erdgas, Erdöl).

3.3 Fossile CO_2-Emissionsfaktoren

Aus dem berechneten Massenanteil der wasser- und aschefreien fossilen Abfallfraktion im Input der Abfallverbrennungsanlagen (m_F in Abb. 3), dem Kohlenstoffgehalt im fossilen Material (c_F in Abb. 3) lässt sich der fossile Kohlenstoffgehalt des Abfalls pro Anlage ableiten. Mithilfe der molaren Massen von Kohlenstoff und Sauerstoff sowie der eingesetzten Abfallmenge bzw. Energiemenge aus Abfall (abgeleitet aus Abfallmenge und Heizwert) können daraus die spezifischen fossilen CO_2-Emissionen bezogen auf Abfall- oder Energieinput berechnet werden.

Tab. 5 listet die fossilen CO_2-Emissionsfaktoren bezogen auf den Energieinhalt der Abfälle als Monats- und Jahresmittelwerte pro Anlage sowie als Gesamtmonatsmittelwert und Gesamtjahresmittelwert über alle betrachteten Anlagen. Es zeigt sich, wie schon bei den biogenen Heizwertanteilen (Kapitel 3.2), eine große zeitliche Schwankung der ermittelten Emissionsfaktoren im Bereich von 4 bis 17 %rel pro Anlage bezogen auf den jeweiligen Mittelwert (mit einem Minimalwert von 25 ± 2 kg $CO_{2,foss}$/GJ für Anlage C im März und Maximalwert von 62 ± 3 kg $CO_{2,foss}$/GJ für Anlage E im Dezember). Die Schwankungen liegen dabei tendenziell wieder für die Wirbelschichtanlagen (MVA C, D, E, G) auf einem höheren Niveau im Vergleich zu den Anlagen mit Rostfeuerung (MVA A, B, F, H, I, J). Im Jahresmittel variieren die spezifischen fossilen CO_2-Emissio-



¹⁾ gewichteter Mittelwert ± Standardunsicherheit

Abb. 7 Biogener Heizwertanteil für Müllverbrennungsanlagen (MVA) mit unterschiedlichem Abfallinput (qualitativ); gewichtete Quartalsmittelwerte mit mittlerer Streuung zwischen den Anlagen (Fehlerbalken); RF: Rostfeuerung, WS: Wirbelschichtfeuerung; die vergleichsweise geringen Unsicherheiten für die Kategorie „RF – überwiegend Gewerbe- und Industrieabfälle" beruhen darauf, dass in dieser Kategorie lediglich eine Anlage vertreten ist; (der ausgewiesene biogene Heizwertanteil bezieht sich nur auf den Abfallinput, Zusatzbrennstoffe sind hier nicht berücksichtigt)

nen zwischen 32 ± 2 und 51 ± 2 kg $CO_{2,foss}$/GJ. Damit ergibt sich eine mittlere Streuung über alle Anlagen von ± 18 %rel bezogen auf den Gesamtmittelwert. Das bedeutet, dass die zeitliche Variation der Abfallzusammensetzung einer Anlage teilweise ein annähernd so großes Ausmaß annehmen kann wie die Unterschiedlichkeit der Abfallzusammensetzung zwischen den einzelnen Anlagen. Obwohl keine genauen Angaben dazu verfügbar sind, ist dennoch anzunehmen, dass die Abfallart (Anteile an Rest-, Gewerbe- oder Industrieabfällen bzw. aufbereitete Abfallfraktionen) einen wesentlichen Beitrag zu den zeitlichen Schwankungen leistet.

Den höchsten Anteil an fossilen CO_2-Emissionen (und damit CO_2 aus erdölbasierten Kunststoffen) liefert die Abfallverbrennungsanlage F, welche fast ausschließlich Gewerbe- und Industrieabfälle verwertet. Der fossile Emissionsfaktor für diese Anlage liegt demnach bei 51,5 kg $CO_{2,foss}$/GJ und damit 21 % über dem Gesamtmittelwert. Ein klarer Zusammenhang zwischen dem Anteil an Industrie- oder Gewerbeabfällen zu Siedlungsabfällen und dem fossilen Kohlenstoffanteil im Abfall konnte jedoch auch in anderen Studien nicht erkannt werden, wobei durchaus große Variationen bei verschiedenen Szenarien zur Zusammensetzung und Sammelsystemen berichtet werden (Fuglsang et al. 2014; Horttanainen et al. 2013; Jones et al. 2013; Larsen und Astrup 2011; Larsen et al. 2013).

Im Gesamtmittel über alle hier betrachteten Anlagen in Österreich können 42,6 ± 2 kg emittiertes fossiles CO_2 pro GJ Energieinhalt des Abfalls abgeschätzt werden. Im Vergleich dazu gibt das Umweltbundesamt einen Emissionsfaktor von 43,9 kg fossiles CO_2 pro GJ an (Umweltbundesamt 2015a). Dieser liegt damit innerhalb des Unsicherheitsbereiches des hier ermittelten Kennwertes. Die Gültigkeit eines für die Abfallverbrennung allgemein festgelegten Emissionsfaktors ist allerdings auf Basis der erhobenen Daten infrage zu stellen, da es für einzelne Anlagen zu einer signifikanten Überschätzung oder auch Unterschätzung der fossilen CO_2-Emissionen kommen kann (bis zu 40 % bezogen auf den Jahresmittelwert; bei Monatsmittelwerten sogar bis zu 75 %). Diese Fehlschätzung kann durch Verwendung eines hier ermittelten Mittelwertes (beispielsweise mit Einteilung der Anlagen nach Abfallart wie in Abb. 7 für die Heizwertanteile dargestellt) nur unwesentlich verringert werden (mit Über- bzw. Unterschätzungen des Jahresmittelwertes von bis zu 30 % und des Monatsmittelwertes bis zu 60 %). Eine sehr große Bandbreite an fossilen Emissionsfaktoren für 11 verschiedene Abfallverbrennungsanlagen in Österreich, Deutschland, Belgien und der Schweiz wurde auch in Obermoser et al. (2009) gefunden, mit Werten zwischen 30 und 67 kg $CO_{2,foss}$/GJ. Es kann daher nicht von einem allgemeingültigen Emissionsfaktor für Abfallverbrennungsanlagen ausgegangen werden, weder auf nationaler noch auf regionaler Ebene.

In Tab. 6 sind die berechneten fossilen CO_2-Emissionen bezogen auf die Menge an durchgesetztem Abfall als Jahresmittelwerte dargestellt. Die Emissionsfaktoren bewegen sich zwischen 255 ± 18 und 548 ± 27 kg fossiles CO_2 pro Tonne Abfall. Damit würde der abgeschätzte Emissionsfaktor des IPCC (2000) für Siedlungsabfälle von 557 kg $CO_{2,foss}$/t Abfall durchwegs eine Überschätzung des fossilen Kohlenstoffs im Abfallinput österreichischer Müllverbrennungsanlagen ergeben (bis über 100 % des Jahresmittelwertes). Die Variationskoeffizienten (die relative Streuung der Werte gemessen am Mittelwert) liegen für diesen massebezogenen Emissionsfaktor deutlich über denen der energiebezogenen Emissionsfaktoren in Tab. 5. Dies kann dadurch erklärt werden, dass variierende Gesamtkohlenstoffgehalte bzw. Heizwerte des Abfalls Auswirkungen auf die massebezogenen Emissionsfaktoren haben. Unterschiede der spezifischen Emissionen bezogen auf den Energieinhalt sind jedoch fast ausschließlich auf unterschiedliche Anteile von biogenen und fossilen Materialien im Abfall zurückzuführen und großteils unabhängig vom Aschegehalt des Abfalls.

3.4 Gesamte klimarelevante CO_2-Emissionen aus der thermischen Verwertung von Abfällen in Österreich

Abb. 8 präsentiert die gesamten jährlichen fossilen CO_2-Emissionen aus der Abfallverbrennung in Österreich, basierend auf der Auswertung für 2014. Für die 10 untersuchten Anlagen (MVA A bis MVA J) ergeben sich klimarelevante CO_2-Emissionen von 924 ± 22 kt pro Jahr. Dies entspricht rund 44 % der CO_2-Emissionen aus der Verbrennung von Abfällen. Zusätzlich wurde die Menge an emittiertem fossilen CO_2 der nicht in die Untersuchung einbezogenen Anlagen (MVA K, L) mit 135 ± 10 kt für das Jahr 2014 abgeschätzt. Diese Abschätzung basiert auf dem Abfalldurchsatz der Anlagen, dem mittleren Heizwert

Tab. 5 Spezifische fossile CO_2-Emissionen (Fossiler CO_2-Emissionsfaktor) pro Müllverbrennungsanlage bezogen auf den jeweiligen Energieinhalt der Abfälle (gewichtete Monatsmittelwerte und Jahresmittelwerte für 2014 mit Standardunsicherheit sowie Variationskoeffizienten zur Darstellung der mittleren monatlichen Schwankungsbreite in %)

	A [kg $CO_{2,foss}$/GJ Heizwert]	B	C	D	E	F	G	H	I	J	*MW*
Jän	40,2	40,4	27,4	44,9	50,1	46,9	37,6	37,5	45,7	47,6	*43,8*
Feb	25,7	41,1	29,3	43,2	49,0	51,2	32,3	35,2	43,6	51,6	*42,4*
Mar	37,8	41,8	*25,2*	30,1	46,1	54,5	26,3	36,1	40,8	46,3	*39,5*
Apr	36,0	41,2	26,1	34,0	48,8	53,7	31,4	36,2	48,9	46,8	*42,0*
Mai	30,7	40,3	41,4	42,4	49,9	53,2	34,5	37,3	41,8	46,1	*42,7*
Jun	31,2	40,0	40,5	39,6	46,0	52,5	38,3	36,1	48,0	45,3	*41,9*
Jul	32,4	41,6	25,3	n.a.	44,4	52,3	38,1	35,1	51,7	52,3	*42,6*
Aug	31,9	39,5	32,4	n.a.	44,3	51,0	40,5	34,1	52,4	51,1	*43,0*
Sep	31,3	39,7	30,4	n.a.	43,8	49,5	40,2	31,9	52,7	49,1	*41,6*
Okt	29,6	41,6	30,0	n.a.	47,5	n.a.	43,9	32,6	51,4	49,1	*37,5*
Nov	26,7	44,0	29,5	n.a.	52,9	n.a.	44,6	36,2	50,0	49,7	*38,5*
Dez	31,2	44,9	35,3	42,4	*62,1*	n.a.	47,9	39,2	45,1	49,3	*41,9*
MW	*32,2 ± 2*	*41,5 ± 2*	*31,6 ± 2*	*39,4 ± 4*	*49,0 ± 3*	*51,5 ± 2*	*38,0 ± 4*	*35,4 ± 3*	*48,0 ± 5*	*48,7 ± 2*	*42,6 ± 2*
VarK	13 %	4 %	17%	14 %	10 %	5 %	16 %	6 %	9 %	5 %	5 %

MW Gewichteter Mittelwert (gewichtet mit Energieinhalt der verwerteten Abfälle) mit Standardunsicherheit, *MVA* Müllverbrennungsanlage, *VarK* Variationskoeffizient (Streuung der Monatsmittelwerte bezogen auf den Jahresmittelwert) in [%rel], *n.a.* Werte nicht verfügbar

Tab. 6 Spezifische fossile CO_2-Emissionen (Fossiler CO_2-Emissionsfaktor) pro Müllverbrennungsanlage bezogen auf den jeweiligen Abfallinput (gewichtete Jahresmittelwerte für 2014 mit Standardunsicherheit sowie Variationskoeffizienten zur Darstellung der mittleren monatlichen Schwankungsbreite in %)

	A [kg $CO_{2,foss}$/t Abfall]	B	C	D	E	F	G	H	I	J	*MW*
MW	*318 ± 24*	*424 ± 23*	*255 ± 18*	*366 ± 35*	*472 ± 28*	*548 ± 27*	*347 ± 34*	*354 ± 32*	*488 ± 28*	*496 ± 17*	*409 ± 18*
VarK	23 %	11 %	23%	15 %	10 %	5 %	22 %	10 %	10 %	7 %	23 %

MW Gewichteter Mittelwert (gewichtet mit Energieinhalt der verwerteten Abfälle) mit Standardunsicherheit, *MVA* Müllverbrennungsanlage, *VarK* Variationskoeffizient (Streuung der Monatsmittelwerte bezogen auf den Jahresmittelwert) in [% rel]

(Böhmer et al. 2007) und einer Abschätzung des fossilen Kohlenstoffanteils von rund 90 %. Damit ergeben sich gesamt rund 1.060 ± 24 kt klimarelevantes CO_2, das aus den thermischen Abfallverwertungsanlagen in Österreich im Jahr 2014 emittiert wurde.

Aus Abb. 8 ist zu erkennen, dass die einzelnen Anlagen, je nach Kohlenstoffanteil (rechte Säule in Abb. 8) und jeweiligem Durchsatz (nicht dargestellt) unterschiedlich viel fossiles CO_2 emittieren. Beispielsweise stammen 50 % der klimarelevanten CO_2-Emissionen der 10 untersuchten Abfallverbrennungsanlagen aus dem Abfalleinsatz von nur 3 der MVA (MVA E, H und J).

Gemessen an den gesamten Treibhausgasemissionen Österreichs im Jahr 2014 (76.200 kt) (Umweltbundesamt 2015c) stammen damit 1,4 % aus der Verbrennung von Kunststoffen in den Müllverbrennungsanlagen. Der Anteil der Abfallverbrennung innerhalb des Sektors der Abfallwirtschaft kann anhand der erhobenen Daten mit rund 38 % abgeschätzt werden (bezogen auf 2.900 kt Treibhausgasemissionen im Sektor Abfallwirtschaft, Umweltbundesamt 2015c). Damit liegt dieser Wert unter dem angegebenen Wert des Umweltbundesamtes von 43,5 % für das Jahr 2013 (die Deponierung macht laut Klimaschutzbericht 44,6 % der Treibhausgasemissionen im Sektor Abfallwirtschaft aus und ist damit zusammen mit der Abfallverbrennung der dominierende Faktor innerhalb dieses Sektors) (Umweltbundesamt 2015b).

4 Schlussfolgerungen

Die präsentierten Ergebnisse wurden im Zuge einer erstmals auf nationaler Basis durchgeführten Untersuchung zu den fossilen und biogenen Anteilen in Abfällen für die thermische Verwertung generiert. Es konnten mit vergleichsweise wenig Aufwand (keine Probenahmen, Messungen oder Analysen) Kennwerte wie der erneuerbare Anteil der eingesetzten Energie (biogener Heizwertanteil) oder die spezifischen fossilen CO_2-Emissionen (Emissionsfaktoren) abgeschätzt werden.

Die Anwendung der Bilanzenmethode auf die Betriebsdaten von 10 Abfallverbrennungsanlagen in Österreich (von gesamt 13 Anlagen in Österreich) für das Kalenderjahr 2014 zeigt signifikante Unterschiede zwischen den ermittelten Werten pro Anlage. Beispielsweise variiert der mittlere biogene Heizwertanteil im Jahr zwischen 35,7 ± 2,4 % (MVA F) und 61,2 ± 2,7 % (MVA C). Dies legt nahe, dass regionale Abfallwirtschaftspraktiken und Sammelsysteme erheblichen Einfluss auf die Zusammensetzung des thermisch verwerteten Abfalls haben. Weiters wird angenommen, dass Anteile der jeweils eingesetzten Abfallarten (Siedlungsabfälle, Gewerbeabfälle, Industrieabfälle etc.) den biogenen bzw. fossilen Anteil im Abfall in relevantem Ausmaß mitbestimmen. Den AutorInnen liegen zu den verbrannten Abfallarten keine quantitativen Angaben vor, jedoch

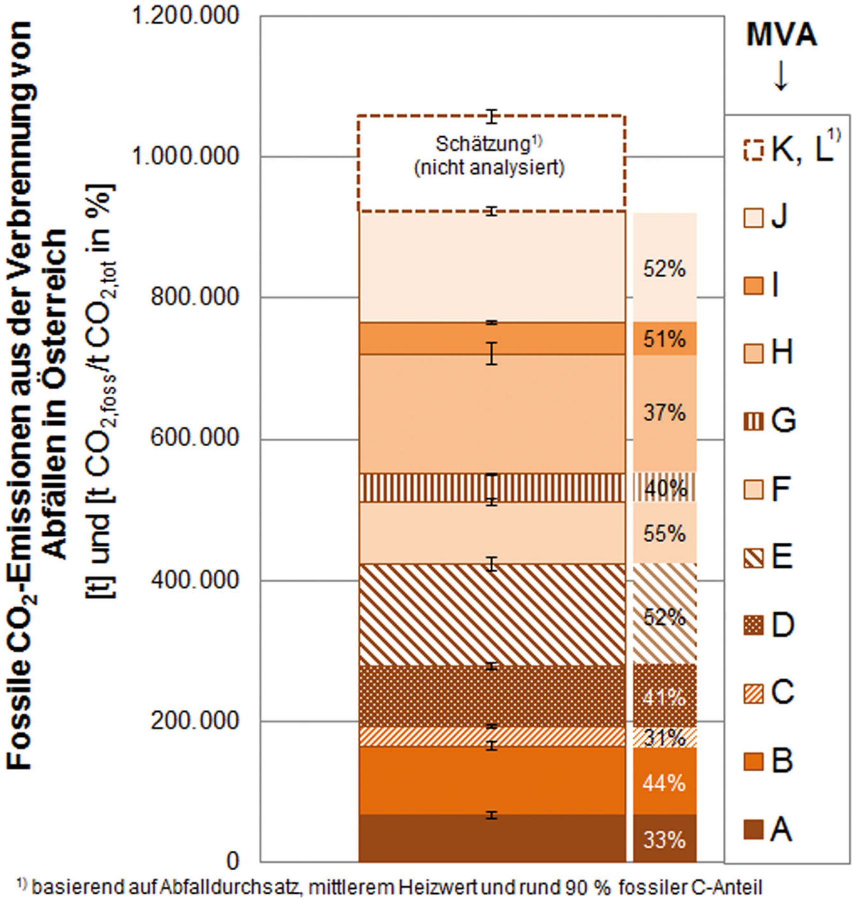


Abb. 8 Fossile CO_2-Emissionen aus der Verbrennung von Abfällen für die Müllverbrennungsanlagen in Österreich sowie der jeweilige prozentuale Anteil der fossilen CO_2-Emissionen an den gesamten CO_2-Emissionen aus der Verbrennung pro Anlage (entspricht dem fossilen Kohlenstoffanteil pro Anlage)

konnte für die Anlage F, die vorwiegend Gewerbe- und Industrieabfälle einsetzt, der im Mittel geringste biogene Anteil verzeichnet werden. Zudem legen große Schwankungen der Monatsmittelwerte einiger Anlagen (bis 16 %rel pro Anlage) nahe, dass die eingesetzten Abfallarten auch zeitlich stark variieren. Da insbesondere die Monatsmittelwerte der Anlagen mit Wirbelschichtfeuerung stark streuen, wird davon ausgegangen, dass dies zum Teil auf saisonale Änderungen im Ersatzbrennstoffbedarf (z. B. verursacht durch Zementproduktion) zurückzuführen ist.

Es konnten fossile CO_2-Emissionsfaktoren von 32 ± 2 kg $CO_{2,foss}$/GJ (MVA C) bis 51 ± 2 kg $CO_{2,foss}$/GJ (MVA F) bestimmt werden (im Jahresmittel). Der Mittelwert über alle Anlagen ergibt sich zu 42,6 ± 2 kg $CO_{2,foss}$/GJ, welcher nur leicht unter dem Richtwert des Umweltbundesamt (2015a) von 43,8 kg $CO_{2,foss}$/GJ liegt, jedoch über dem der in Schweden (32 kg $CO_{2,foss}$/GJ), Dänemark (37 kg $CO_{2,foss}$/GJ) oder Finnland (40 kg $CO_{2,foss}$/GJ) vorgeschlagenen Werte (Anderson et al. 2011; Danish Energy Agency 2013; Olofsson 2004; Umweltbundesamt 2015a).

Auch in Bezug auf die Emissionsfaktoren sind klarerweise die starken Variationen zwischen den Anlagen sowie die zeitlichen Schwankungen zu beobachten. Es kann also bei Anwendung eines allgemeinen Emissionsfaktors (wie beispielsweise in IPCC 2000 oder Umweltbundesamt 2015a angegeben) sehr leicht zu Über- oder Unterschätzungen pro Anlage kommen. Bei Verwendung des Richtwertes des Umweltbundesamts (2015a) von 43,8 kg $CO_{2,foss}$/GJ kommt es basierend auf den vorliegenden Auswertungen zu Fehleinschätzungen der fossilen CO_2-Emissionen pro Anlage von bis zu 40 % bezogen auf den Jahresmittelwert und bei Monatsmittelwerten sogar bis zu 75 %. Der abgeschätzte Emissionsfaktor des IPCC (2000) für Siedlungsabfälle von 557 kg $CO_{2,foss}$/t Abfall ergibt durchwegs eine Überschätzung des fossilen Kohlenstoffs im Abfallinput österreichischer Müllverbrennungsanlagen (bis über 100 % des Jahresmittelwertes).

Die Auswertungen zeigen, dass eine zuverlässige Aussage über den erneuerbaren Energieanteil im Abfall oder den Anteil der klimarelevanten CO_2-Emissionen aus der Abfallverbrennung nur anlagenspezifisch sinnvoll ist. Die großen zeitlichen Schwankungen pro Anlage belegen zudem, dass nur eine Überwachung über einen längeren Zeitraum, vor allem bei Anlagen mit stark variierenden Inputströmen, zielführend für die Ausweisung des erneuerbaren Energieanteils oder die Treibhausgasinventuren ist. Diese Beobachtungen bestätigen die Ergebnisse anderer Studien (Fellner et al. 2011; Fuglsang et al. 2014; Obermoser et al. 2009). Ungerechtfertigt getätigte Fördergeldzahlungen und Verzerrungen der Treibhausgasinventur könnten durch eine Auswertung im fortlaufenden Betrieb verhindert werden. Die Bilanzenmethode bietet eine Möglichkeit diese veränderliche Zusammensetzung des Abfalls laufend aufzuzeichnen.

Die Bilanzenmethode stellt sich als kostengünstiges, verlässliches Verfahren dar, das statistisch fundierte Ergebnisse liefert und für dessen Anwendung üblicherweise keine zusätzliche Messtechnik erforderlich ist (eventuell mit Ausnahme der CO_2-Messungen im Reingas). Ein zusätzlicher Nutzen für die Anlagenbetreiber entsteht, indem durch die Plausibilitätsuntersuchungen der Betriebsdaten mögliche systematische Fehlmessungen oder Fehldokumentationen aufgedeckt werden können. Valide Messwerte (insbesondere der CO_2- und O_2-Konzentration im Reingas) sind jedoch Voraussetzung für belastbare Ergebnisse, sodass regelmäßige Kontroll- und Kalibrierungsmessungen speziell bei einer Routineanwendung unabdingbar sind.

Die Methode könnte außerdem als Monitoring-Instrument zur Überwachung der Menge an thermisch verwerteten Kunststoffen (ableitbar aus dem fossilen Abfallanteil) eingesetzt werden, was verlässlichere Werte bieten würde als Sortieranalysen (Schwarzböck et al. 2016c). Beispielsweise könnten die Auswirkungen von höheren/geringeren Kunststoffrecyclingraten auf die Entwicklung der klimarelevanten CO_2-Emissionen aus der Abfallverbrennung beobachtet werden. Dies ist natürlich nur in Zusammenhang mit der Entwicklung in anderen Sektoren (Industrie, Energie) sinnvoll. Dementsprechend müssen die klimarelevanten CO_2-Emissionen aus der thermischen Abfallverwertung, obgleich der Anteil an den nationalen Treibhausgasemissionen nur marginal erscheinen mag (1,4 %), immer gemeinsam mit alternativen Szenarien der Abfallbewirtschaftung (Deponierung, Recycling) und Energieversorgung (fossile Energieträger) hinsichtlich der Erreichung der österreichischen Klimaziele beurteilt werden.

Da es die Methode zudem erlaubt, auch andere Kennwerte des Abfalls im fortlaufenden Betrieb der Abfallverbrennungsanlagen zu erfassen (z. B. den Wassergehalt, Heizwert), wird momentan untersucht, inwiefern das Verfahren, neben der Ausweisung des biogenen und fossilen Anteils im Abfall, zusätzlich zur Prozessoptimierung herangezogen werden kann. Beispielsweise könnte die Durchmischung des Abfalls besser überwacht werden, wodurch eventuell ein geringerer Restsauerstoffgehalt zu einem höheren Wirkungsgrad des Kessels führen würde (Riber et al. 2013). Auch gibt es erste Überlegungen dazu, wie die Bilanzenmethode zur Maximierung der Dampfproduktion eingesetzt werden kann (Schwarzböck et al. 2016b).

Danksagung

Die AutorInnen danken dem Ministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft für die Finanzierung der Studie und der Umweltbundesamt GmbH sowie den Betreibern der österreichischen Abfallverbrennungsanlagen für die gute Kooperation. Zusätzlicher Dank an Inge Hengl für die Unterstützung bei der grafischen Gestaltung.

Open access funding provided by TU Wien (TUW).

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Paper III

Determining the amount of waste plastics in the feed of Austrian waste-to-energy facilities

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Waste Management & Research 2017, 35, 207-216

DOI: 10.1177/0734242X16660372

Original Article

WM&R

Waste Management & Research
2017, Vol. 35(2) 207–216

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Determining the amount of waste plastics in the feed of Austrian waste-to-energy facilities

Therese Schwarzböck[1], Emile Van Eygen[2], Helmut Rechberger[1] and Johann Fellner[2]

Abstract

Although thermal recovery of waste plastics is widely practiced in many European countries, reliable information on the amount of waste plastics in the feed of waste-to-energy plants is rare. In most cases the amount of plastics present in commingled waste, such as municipal solid waste, commercial, or industrial waste, is estimated based on a few waste sorting campaigns, which are of limited significance with regard to the characterisation of plastic flows. In the present study, an alternative approach, the so-called Balance Method, is used to determine the total amount of plastics thermally recovered in Austria's waste incineration facilities in 2014. The results indicate that the plastics content in the waste feed may vary considerably among different plants but also over time. Monthly averages determined range between 8 and 26 wt% of waste plastics. The study reveals an average waste plastics content in the feed of Austria's waste-to-energy plants of 16.5 wt%, which is considerably above findings from sorting campaigns conducted in Austria. In total, about 385 kt of waste plastics were thermally recovered in all Austrian waste-to-energy plants in 2014, which equals to 45 kg plastics cap^{-1}. In addition, the amount of plastics co-combusted in industrial plants yields a total thermal utilisation rate of 70 kg cap^{-1} a^{-1} for Austria. This is significantly above published rates, for example, in Germany reported rates for 2013 are in the range of only 40 kg of waste plastics combusted per capita.

Keywords

Plastics waste generation, plastic content, thermal utilisation, waste-to-energy, waste incineration, Balance Method, municipal solid waste

Introduction

Consumption of plastics and thus also the generation of waste plastics has increased tremendously during the last decades. Whereas at the beginning of the 1980s global consumption of plastics amounted to about 65 m t, in 2014 worldwide production has increased to more than 300 m t (PlasticsEurope, 2015). A significant share of plastics (more than one-third) is used in short-life products, such as packaging (PlasticsEurope, 2015). These plastics almost directly contribute to present waste generation, whereas plastics used in other sectors, such as the building and construction sector (e.g. pipes, flooring) or the automotive sector, will become wastes with a delay of some years to decades.

To deal with the increasing waste plastics quantities, appropriate waste management systems have to be set up, as the European Commission is pushing for increased recycling rates, among others, for various materials in packaging waste including plastics (European Commission, 2015). However, there is a need for detailed knowledge on the current situation of material flows and stocks to understand what potential for recycling is available. For metals, this kind of information is quite well established, but for plastics, only limited data is available on the flows through society (Van Eygen et al., submitted). A challenge therefore still remains in accurately recording the plastics flows in waste production and waste treatment.

Many affluent countries have introduced separate collection of certain plastic wastes (with special focus on packaging plastics) in recent years. The aim is, on the one hand, to reduce the quantity of mixed household wastes and, on the other hand, to generate post-consumer waste streams that contain one type of polymer only. The latter is understood to be a prerequisite for high-quality recycling of plastics waste.

The amount of plastics waste separately collected is typically recorded quite accurately, owing to its economic value

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and its positive image for the plastics industry, as recycling separately collected post-consumer plastics may at least partly allow closing material cycles and is thus considered an important process for the plastics industry to contribute to resource conservation. There is for instance a 40% to 90% reduction in energy consumption by producing recycled plastic compared with producing plastic from virgin materials (oil and gas) (Association of Cities and Regions for Recycling, 2004).

Whereas, the amount of plastics recycled after separate collection can be monitored quite easily (it equals the total output of recycling facilities for plastic waste plus all plastic waste exported for recycling, whereby for the latter a realistic material recovery rate has to be assumed), the quantification of the total plastic waste generated at a regional or nationwide level is rather difficult. This is because the vast majority of plastics is collected in waste streams, such as municipal solid waste (MSW), commercial waste (CW) or industrial waste (IW), where they are commingled with various other materials.

Thus, total plastic waste generation P_{tot} is usually estimated as:

$$P_{tot} = \sum_{i=1}^{n} W_i \cdot c_{pi} \tag{1}$$

where statistics on the generation of different wastes W_i are combined with data on the waste composition, in particular the content of plastics c_{pi}. Information on the latter is either close to 100% for separately collected waste plastics, derived from literature (e.g. plastics content in end-of-life vehicles), or can be based on sorting analyses for different mixed waste types. These latter analyses are at most conducted once a year, but owing to the fact that waste composition may show significant variations even over time periods of a few days (Morf and Brunner, 1998; Obermoser et al., 2009), a few single sorting campaigns are not sufficient to calculate a reliable annual average plastic content. In addition, some types of waste streams, such as IW, but also CW, may show distinctly different compositions with respect to their contents of plastics, depending on the activities of the respective companies generating the waste. Furthermore, the plastic content of wastes determined via sorting analyses may be of limited significance even for the respective waste sample analysed: (1) owing to the lack of visual recognisability of different materials (e.g. synthetic versus biogenic fibres) and (2) owing to the fact that waste sorting analyses are typically aimed at determining the content of different aggregated waste fractions (such as biowaste, hygienic products, composite materials, etc.) that do not necessarily contain only plastics or are free of plastics (Dahlén and Lagerkvist, 2008). Thus, results of sorting analyses further require the determination/assignment of average plastic contents to the single waste fractions sorted out.

All these limitations demonstrate that figures for total quantities of plastic wastes generated are associated with significant uncertainties. Hence, also data on the recycling or thermal recovery quota of plastic waste, as published for different European countries (e.g. BIO Intelligence Service, 2013; Bogucka et al., 2008; PlasticsEurope, 2015) are rather unclear.

Therefore, a significant share of waste plastics is collected via ‘mixed’ wastes (MSW, CW, and IW), and plastic contents of these waste are relatively uncertain. The aim of the current study is thus to determine the total amount of waste plastics present in these wastes. The investigations are conducted for Austria for the year 2014. Austria is chosen as a case study, as there is a landfill ban for wastes with more than 50 g organic carbon per kilogram dry waste, meaning that mixed wastes containing even minor amounts of plastics are to be diverted into thermal treatment plants. For the determination of the plastics content in the incinerated commingled wastes, an alternative approach to sorting analyses, the so-called Balance Method (according to Fellner et al., 2007), is applied. This method was originally developed to evaluate the ratio of energy from biogenic and thus renewables sources in the feed of waste-to-energy (WtE) plants, but also allows calculating the content of plastics (fossil material) in the waste feed.

Materials and methods

Balance Method

The Balance Method, applied in the present study to determine the content of plastics in mixed wastes, combines data on the elemental composition of moisture- and ash-free (maaf) biogenic and fossil organic matter with routinely measured operating data of the WtE plant. In principle, the method utilises one energy balance and five mass balances, whereby each balance describes a certain waste characteristic (e.g. content of organic carbon, lower calorific value, ash content). Each balance equation encompasses a theoretically derived term (left side of equations) that has to be attuned to measured data of the incineration plant (right side of equations). A simplified structure of the set of equations is illustrated in Figure 1. A detailed mathematical description of each equation is given in Fellner et al. (2007).

For setting up the six balance equations, the waste mass is virtually divided into four ‘material groups’: inert (m_I), biogenic and fossil organic materials (m_B, m_F), and water (m_W) (Figure 2). Inert materials include all incombustible solid residues like glass, stones, ashes, or other inorganic matter from biowaste and plastics (e.g. kaolin in paper or inorganic additives in plastics). Biogenic and fossil organic material groups refer only to the maaf organic matter (see Figure 2). As the qualitative composition of organic materials in mixed wastes is usually well known (e.g. biogenic matter encompasses paper, wood, kitchen waste, etc. and fossil organic matter includes polymers, such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinylchloride (PVC), etc.) the content of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine of the maaf biogenic and fossil organic materials (m_B and m_F) can be derived. The quantitative shares of the different compounds in the biogenic fraction are of minor significance for the determination of the chemical composition, as the elemental composition of the

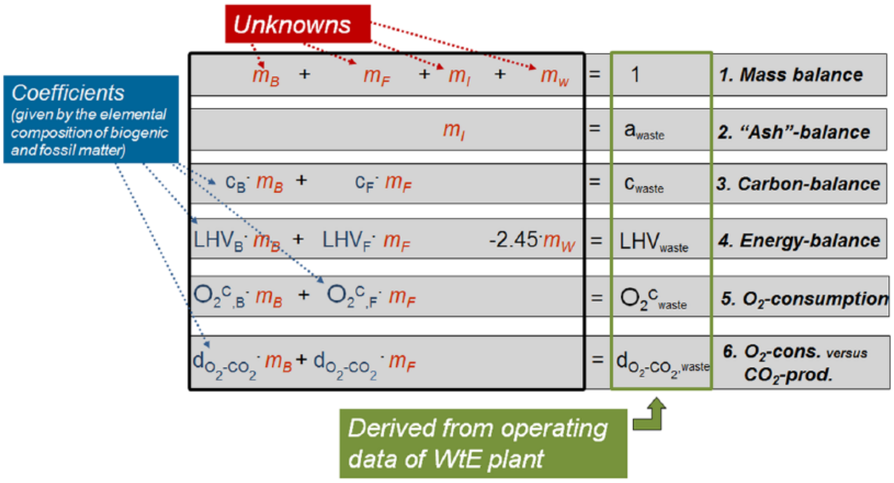


Figure 1. Simplified set of equations used by the Balance Method (based on Staber et al., 2008); the left side of the equations represent the theoretical balance (utilising information on the elemental composition of biogenic and fossil organic matter) that has to be attuned to the different waste characteristics derived from operation data of the WtE plant (right side of the equations).
WtE: waste-to-energy.

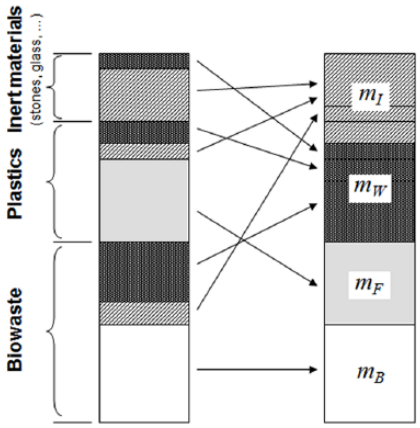


Figure 2. Split-up of waste fractions into the four 'material groups' (m_B, m_F, m_W, and m_I), which represent the unknowns in the set of six equations (based on Fellner et al., 2007).

different biogenic materials present in waste is quite similar and differs only slightly (see Figure 3(b)).

The input data required for the Balance Method comprise information on the elemental composition of maaf biogenic and fossil organic matter present in the waste feed, information on the quantity of fuels incinerated (waste mass and auxiliary fuels), the amount of solid residues and steam produced, as well as data on the volume and composition (O_2 and CO_2 content) of the dry flue gas (a graphical overview of the required input data is presented in the supplementary material Figure A.1, available online). For each parameter a respective uncertainty is specified.

Because the system of equations (set of constraints) used within the Balance Method is over-determined (six equations for four unknowns), data reconciliation has to be performed to eliminate data contradiction and to improve the accuracy of the results. The reconciled values are subsequently used to compute the unknown quantities (m_B, m_F, m_W, and m_I) including their uncertainties.

The fossil mass fraction m_F represents the content of synthetic polymers in the waste feed of the plant. By considering typical values for the ash content of plastics a_p (representing the content of inorganic additives and fillers) the fraction of plastics c_P in the waste feed can easily be determined according to:

$$c_P = \frac{m_F}{\left(1-a_p\right)} \qquad (2)$$

Based on national material flow studies focusing on Austrian plastics production and consumption (Bogucka and Brunner, 2007; Fehringer and Brunner, 1997), the average content of inorganic additives and fillers a_p is estimated to 90 ±40 g kg^{-1} plastics, which is used in the present study.

Prior to solving the set of equations for calculating the mass fraction m_F, the input data (operating data of the WtE plant) are checked regarding their plausibility. Thereto, existing correlations between the flue gas and its composition and the steam production are used (e.g. during the combustion of organic matter the consumption of 1 mole of oxygen gas corresponds to an energy generation of 360 to 400 kJ; and the combustion of 1 g organic carbon produces a heat amount of 34 up to a maximum of 44 kJ) (for details see Fellner et al., 2007). The calculations according to the Balance Method are only performed with plausible data, whereby the temporal resolution of the data used is preferably in the range of hourly averages for most input data.

The analysis algorithm of the Balance Method, including the plausibility check of the input data, has been implemented into the software BIOMA (http://iwr.tuwien.ac.at/ressourcen/downloads/bioma.html), which allows determining the composition of the waste feed with respect to its content of biomass and fossil organic matter. In the frame of the presented study, all analyses according to the Balance Method have been conducted using BIOMA.

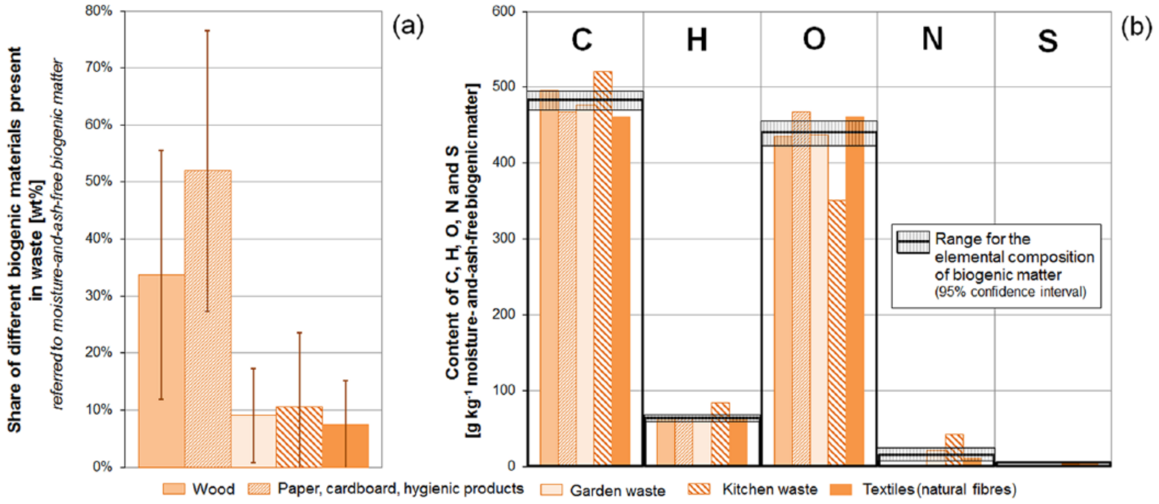


Figure 3. (a) Possible ratios of different biogenic compounds (e.g. wood, paper, etc.) present in mixed wastes (referred to maaf biogenic matter); (b) elemental composition (content of carbon, hydrogen, oxygen, nitrogen, and sulphur) of different biogenic materials present in mixed waste, including an estimate for the range of the elemental composition (indicated as hatched area) of biogenic matter present in mixed waste (referred to maaf biogenic matter).

Elemental composition of biogenic and fossil organic matter used for the Balance Method

In principle, the Balance Method is based on the distinct chemical composition (content of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine) of maaf biogenic and fossil organic matter and on the differences in the composition of the two materials. As at least qualitative information on the different biogenic and fossil materials present in mixed waste is available (from literature or sorting analyses), plausible ranges for the chemical composition can be derived.

Biogenic matter in waste is basically composed of paper, cardboard, hygienic articles, wood, kitchen waste, garden waste, and textiles (natural fibres) (Figure 3(a)), whereas fossil organic matter (plastics) in mixed wastes may include the whole range of different polymers produced (e.g. PE, PP, PET, PVC, polystyrene PS, polyamide PA) (Figure 4).

Combining contents of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine in each maaf biogenic or fossil compound (such as wood, paper, or PE) with information on their relative shares (referred to the total amount of maaf biogenic and fossil organic matter, respectively), allows calculating ranges for the elemental composition (content of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine) of maaf biogenic and fossil organic matter (see Figure 3(b)). In practise, this has been accomplished by applying the Monte Carlo simulation to the following equations, which are exemplary given for carbon:

$$C_{Bi} = \frac{\sum_{k=1}^{k=n} C_{Bki} \cdot f_{Bki}}{\sum_{j=1}^{k=n} f_{Bki}} \tag{3}$$

$$C_{Fi} = \frac{\sum_{k=1}^{k=n} C_{Fki} \cdot f_{Fki}}{\sum_{j=1}^{k=n} f_{Fki}} \tag{4}$$

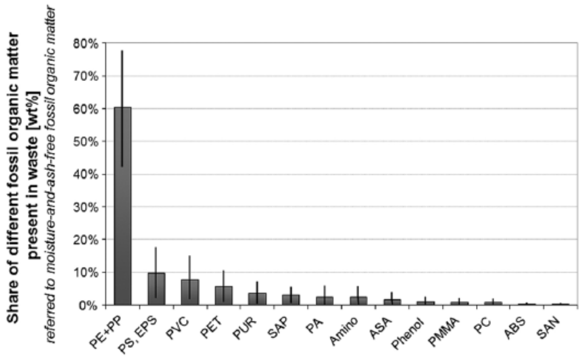


Figure 4. Possible ratios of different plastics (fossil organic) materials (e.g. PE, PVC, PET, etc.) present in mixed wastes (referred to maaf fossil organic matter) – no differentiation between PE and PP was made since their elemental composition is identical.

ABS: acrylonitrile butadiene styrene; ASA: acrylonitrile styrene acrylate; EPS: expanded polystyrene; PA: polyamide; PC: polycarbonate; PE: polyethylene; PET: polyethylene terephtalate; PMMA: Poly(methyl methacrylate); PP: polypropylene; PS: polystyrene; PUR: polyurethane; PVC: polyvinyl chloride; SAN: styrene acrylonitrile; SAP: superabsorbent polymers.

where C_{Bi}, C_{Fi} is the carbon content in maaf biogenic matter (*fossil organic matter*) present in mixed wastes for simulation run i; C_{Bki}, C_{Fki} is the carbon content in maaf biogenic matter (*fossil organic matter*) of compound k (e.g. wood, kitchen waste) for simulation run i, and f_{Bki}, f_{Fki} is the relative share of maaf biogenic compound k (e.g. wood, kitchen waste) referred to total maaf biogenic matter (*fossil organic matter*) present in mixed wastes for simulation run i.

In Figure 3 the data used for determining the elemental composition of maaf biogenic matter present in mixed wastes are given. The respective results of the Monte Carlo simulation are indicated by hatched areas in Figure 3(b) and denote the likely range for the elemental composition. A comparison of the different biogenic compounds present in mixed wastes (wood, paper,

Table 1. Elemental composition of maaf biogenic and fossil organic matter present in commingled wastes.

Moisture- and ash-free		Biogenic matter[a]		Fossil matter[a]	
Content of	Unit	Average	SD[b]	Average	SD[b]
C	$g\,kg^{-1}$	483	9	777	32
H	$g\,kg^{-1}$	65	2.4	112	11
O	$g\,kg^{-1}$	443	14	61	26
N[c]	$g\,kg^{-1}$	7	5	14	11
S[c]	$g\,kg^{-1}$	1.1	0.5	3	1
Cl[c]	$g\,kg^{-1}$	–[d]	–	32	24

[a] Minor differences in the elemental composition compared with values given in Fellner et al. (2007) are owing to an updated database, which considers recent results of waste composition studies.
[b] 95% confidence interval.
[c] Contents of N, S and Cl are of minor significance for the results of the Balance Method (see Fellner et al., 2007).
[d] Cl-content $<5\,g\,kg^{-1}$. (Kost, 2001; LfU, 2003).
SD: standard deviation; C: carbon; H: hydrogen; O: oxygen; N: nitrogen; S: sulphur; Cl: chlorine.

Table 2. Overview of the investigated WtE plants in Austria.

WtE plant	Combustion technology	Waste incinerated (qualitative information)
A	Grate incinerator	MSW
B	Grate incinerator	MSW and CW&IW
C	Stationary fluidised bed combustion	RDF and SS
D	Stationary fluidised bed combustion	RDF and SS
E	Circulating fluidised bed combustion	RDF and SS
F	Grate incinerator	CW&IW, and minor amounts of MSW
G	Stationary fluidised bed combustion	RDF, and minor amounts of SS
H	Grate incinerator	MSW, CW&IW, and minor amounts of SS
I	Grate incinerator	MSW
J	Grate incinerator	MSW, CW&IW, and minor amounts of SS

CW&IW: commercial and industrial waste; MSW: municipal solid waste; RDF: refuse derived fuels; SS: sewage sludge; WtE: waste-to-energy.

garden waste, etc.) demonstrates that they only differ slightly in their elemental composition (particularly in their carbon, hydrogen, and oxygen contents). This finding indicates that the elemental composition of maaf biogenic matter in wastes may vary almost independently from the shares of the biogenic compounds. A probable range for the elemental composition of maaf biogenic organic matter can be derived (see Table 1).

Figure 4 illustrates the assumed composition of waste plastics (with respect to polymers) present in commingled waste. The composition (including the potential range for the different polymers – indicated by the black errors bars) has been derived from polymer consumption statistics (PlasticsEurope, 2010), taking into account the life time of plastics in different applications as well as the potential collection and disposal routes. In addition, data from detailed sorting campaigns conducted in Austria have been considered (Nelles, 1998; TBHauer, 1999, 2002).

In analogy to the biogenic matter, combining the data given in Figure 4 with the elemental composition of each polymer allows calculating the most likely carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine content of maaf fossil organic matter present in mixed wastes. Thereto the Monte Carlo simulation (using equation (4)) has been applied. Using the final result of these simulations, a probable range for the elemental composition of maaf biogenic and fossil organic matter is summarised in Table 1.

Investigated WtE plants in Austria

The feed of 10 Austrian WtE plants, which represent 91% of the waste incinerated in Austria in 2014, has been investigated with respect to its plastic content. Three facilities could not be included in the study as they did not provide all operating data required for the Balance Method or were under reconstruction in the respective time period.

Table 2 gives an overview of the 10 Austrian waste incineration plants investigated. The overall capacity of these facilities amounts to about 2.3mt of waste per year (BMLFUW, 2011). The WtE plants utilise different types of combustion technologies (grate incineration or fluidised bed combustion) and mainly incinerate MSW, CW and IW, sewage sludge, and refuse derived fuels (see Table 2), whereby the share of the different wastes may vary significantly during the investigated time period of one year.

The Balance Method is applied to the operating data of the 10 WtE plants for a period of 12 months. As for one facility (WtE plant D) the required operating data are incomplete or connected with significant measurement errors, the analysis for this particular plant is reduced to 7 months where reasonable (plausible) operating data are available. The procedure for the application of the Balance Method to the operating data of the WtE plants is described in detail in Schwarzböck et al. (2016). Based on the

Table 3. Share of plausible operating data (given in % of total waste mass combusted) for the WtE plants over a period of 12 months.

WtE plant	A	B	C	D[b]	E	F	G	H	I	J	**Total**
Share of plausible data[a]	98.3	99.3	95.8	84.4	99.5	99.5	98.3	99.0	82.8	99.7	**96.7**

[a]Expressed as waste mass combusted during the record of plausible operating data referred to in the total waste throughput in per cent.
[b]Only a period of 7 months has been evaluated.
WtE: waste-to-energy.

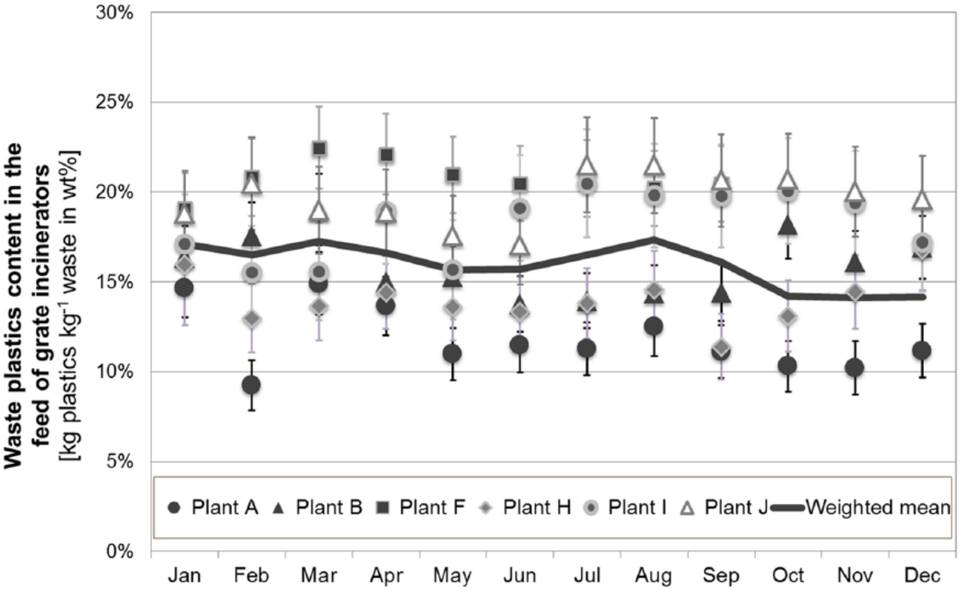


Figure 5. Monthly averages (with standard deviation) of waste plastics content (given in kilograms of waste plastic per kilogram of waste) in the feed of grate incinerators (GI) in Austria, which all mainly utilise MSW, CW, and IW; the monthly mean for all plants (continuous line) accounts for the plastics content and the respective waste mass combusted in each plant.

calculated composition of the waste feed of each plant (using the Balance Method) and their respective annual waste throughput the total amount of waste plastics thermally recovered in 2014 in Austria is determined within the study. The annual average waste plastics content (over all 10 plants) is estimated by summing up the absolute plastics content for all plants (found by applying the calculated plastic content to the actual waste feed) and by relating it to the total amount of waste incinerated in all 10 WtE plants in 2014. To obtain monthly averages considering all 10 plants, the plastics contents per plant are weighted by the monthly waste feed.

Results and discussion

Plausibility checks on operating data

An important step prior to determining the waste composition with regards to biomass and fossil organic matter via the Balance Method is the test for plausibility of the operating data. For these tests, operating data are checked for their correlation between flue gas data (expressed as carbon content and oxygen consumption of the waste) and heat production of the plant (in particular lower calorific value of the waste) (example graphs are presented in the supplementary material in Figure B.2 and B.3, available online). The correlation between O_2 consumption and carbon content is used to finally decide on the plausibility of data points (for details on the plausibility tests see Fellner et al., 2007). Table 3 summarises the share of plausible operating data for all 10 WtE plants that were analysed. With the exception of two plants, all facilities are characterised by a very high share (well above 95%) of plausible operating data. Instable CO_2 measurements or a lower temporal resolution of the measurements lead to a slightly lower share of plausible operation data for plant D and I, however still above 82% of the data can be used for the analysis. In other words, in total over 96% of the waste feed (thus, almost 2.2m t out of 2.3m t of waste throughput) can be analysed in the study; a sample that can hardly be achieved by any other determination method (such as sorting analysis).

Content of plastics in the feed of Austrian WtE plants

The plausible operating data are subsequently used to analyse the waste composition using the Balance Method. Based thereon the amount of plastics in the waste feed is estimated (according to equation (2)). Figures 5 and 6 summarise and compare the results for the different plants as monthly and as annual averages.

Figure 5 shows the content of waste plastics in the feed of the six WtE plants with grate incineration (GI) that predominantly utilise MSW, CW, and IW. Monthly results for the different WtE plants range from 9 to 23 wt% plastics. This rather large range of

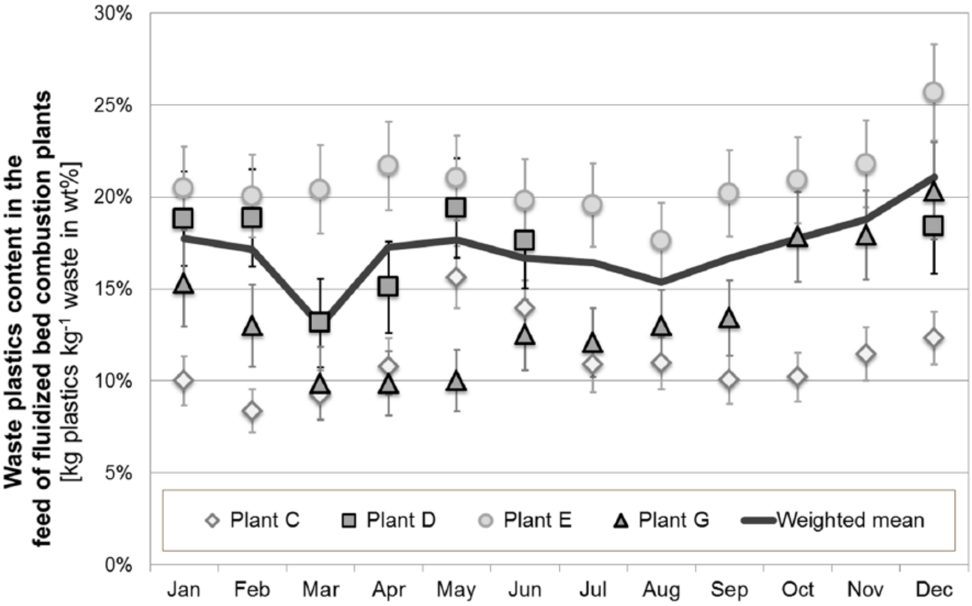


Figure 6. Monthly averages (with standard deviation) of waste plastics content (given in kilograms of waste plastics per kilogram of waste) in the feed of fluidised bed combustion (FBC) plants in Austria, which all mainly utilise refuse derived fuels and sewage sludge; the monthly mean for all plants (continuous line) accounts for the plastics content and the respective waste mass combusted in each plant.

plastics content for different plants indicates a regional dependence of the waste feed composition, as almost all plants presented in Figure 5 are situated in different federal states of Austria, which are characterised by different waste collection schemes (e.g. separate collection of either all packaging plastics or just PET bottles). In addition, diverse ratios of commercial, industrial, and MSW may cause significantly different plastic contents in the waste feed. The highest waste plastics contents are observed for plant F, which almost exclusively combusts CW and IW.

Furthermore, temporal variations of waste plastics contents are obvious from Figure 5 as well. For instance, the monthly averages for plant H range from 11 wt% (September) to 17 wt% (December), thereby highlighting that a reliable analysis of the waste composition requires methods that characterise the waste feed over longer time periods, as also concluded in other studies (Fellner et al., 2011; Fuglsang et al., 2014; Obermoser et al., 2009). The annual average waste plastics content in the feed of all Austrian grate incinerators amounts to 16.1 ±1.1 wt%.

For fluidised bed combustion (FBC) plants, observed variations in waste composition (with respect to the contents of waste plastics) are even more pronounced than for grate incinerators (monthly averages for the plastics content in the waste feed range between 8 and 26 wt% – see Figure 6). This finding is somehow unexpected, as the waste utilised at these plants is pre-treated (mechanical separation), which should typically result in more homogenous fuels. However, to the knowledge of the authors, the operation of mechanical treatment plants and also the management of their outputs are both strongly influenced by the fuel demand of the Austrian cement industry, which also utilises significant amounts of refuse derived fuels (RDF). In winter times, cement production in Austria and thus also the demand for high calorific RDF is reduced, which might result in higher amounts of waste plastics being fed into FBC plants. This trend is definitely observable at plant E and plant G, which receive RDF from mechanical waste treatment plants, which also provide fuels for cement kilns. The fuel input into the other FBC plants (C and D) is less influenced by the demand of cement kilns and thus show a less pronounced seasonal trend. For those plants, other factors are expected to have a more dominant influence on the observed trend in waste plastics content in 2014, such as temporary shutdowns (for the revision or renewal) of neighbouring waste combustion plants.

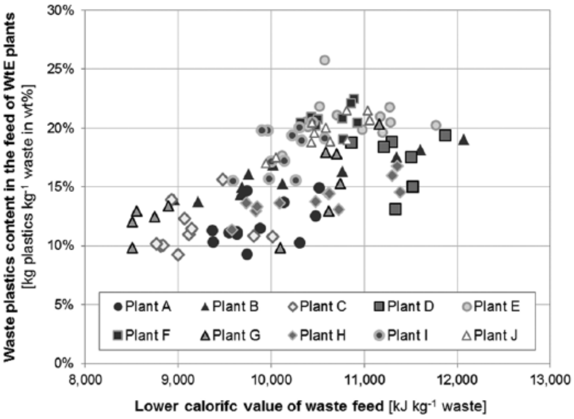
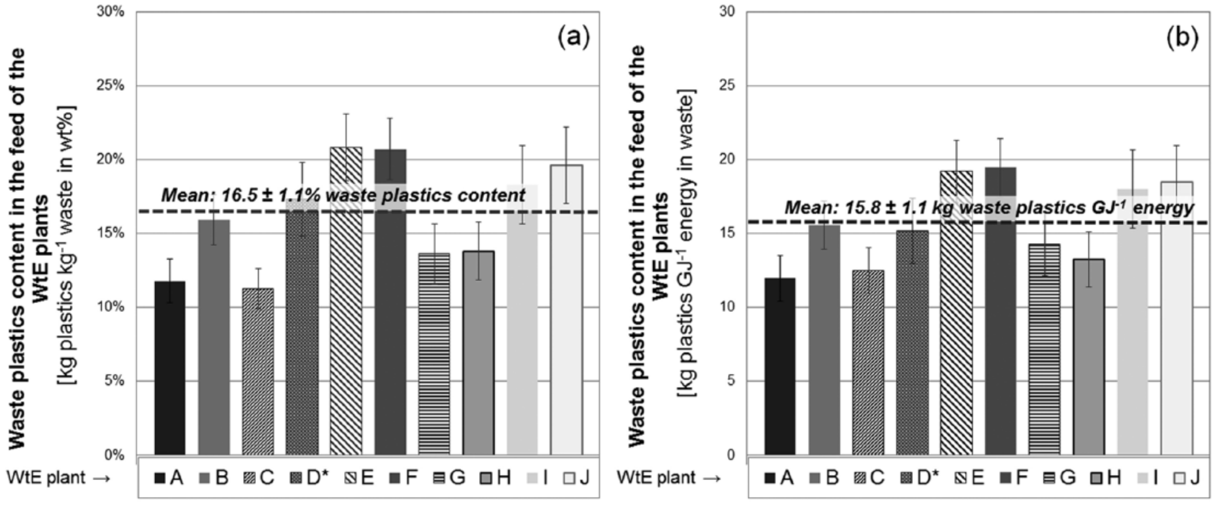


Figure 7. Waste plastics content versus lower calorific value of the waste feed (excluding sewage sludge) for the 10 WtE plants investigated (monthly averages).
WtE: waste-to-energy.

The annual average plastics content in the feed of Austrian fluidised bed combustion plants amounts to 17.3 ±1.2 wt% and is thus slightly above the average content for waste treated in grate incinerators.

When relating the plastics content to the calorific value of the waste (see Figure 7), it becomes evident that an increased energy content of the waste usually goes along with higher contents of



* for WtE plant D only a period of 7 months has been evaluated

Figure 8. Annual averages (with standard deviation) of waste plastics content in Austrian WtE plants: (a) related to total waste input (in kilograms of plastics per kilogram of waste); (b) related to the calorific value of the solid waste (in kilograms of plastics per GJ of energy content of the waste exclusive sewage sludge).
WtE: waste-to-energy.

plastics. For some WtE plants (e.g. plant B, plant G, plant H, and plant J), a distinct correlation between plastics content and lower calorific value of the waste feed is evident (coefficient of determination higher than 0.6 – not shown in Figure 7); whereas for others, only a general tendency towards more waste plastics in wastes with higher energy contents is observable. For the latter plants it is assumed that other factors, such as the water or ash content of the waste feed, vary more and are hence dominating the calorific value of the waste input.

Annual averages for the plastics contents per kilogram waste and per GJ energy content are presented in Figure 8(a) and (b) for all 10 plants analysed. Again, a high variation of the results for the different plants can be identified, ranging from 11.2 ±1.7 wt% (WtE plant C) to 20.9 ±2.3 wt% (WtE plant E) for the waste mass-related plastics content. The average percentage of plastics in the feed of all Austrian WtE plants amounts to 16.5 ±1.1 wt% (Figure 8(a)).

Calculating energy-related plastics contents (Figure 8(b)), given in kilograms of plastics per GJ calorific value of the waste feed, shows that variations between the input of the different plants are less pronounced. The smallest value of 12.0 kg plastics GJ^{-1} is observed at plant A, whereas plant F shows the highest amount of plastics utilised per unit of energy content (19.5 kg plastics GJ^{-1}). The smaller variation of energy-related plastics contents in comparison with the mass-related contents is explained by the fact that variations of the former reflect differing ratios between biogenic and fossil organic matter (plastics) only. Changes in water or ash content, which may obviously also influence the content of plastics, are to some extent already represented by the calorific value of the waste.

Hence, it may be concluded that information on the calorific value of the waste allows better estimates for its content of waste plastics, although possible ranges are still large.

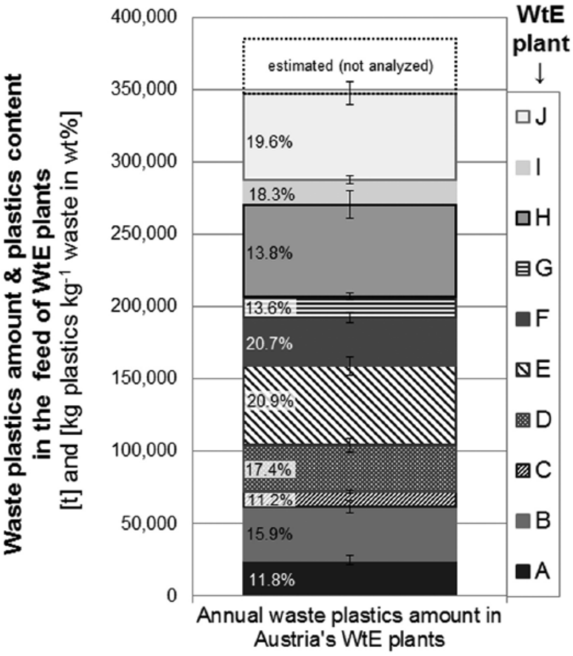


Figure 9. Annual amount of waste plastics in the feed of 10 Austrian WtE plants with an annual waste throughput of approximately 2.3 m t (including 0.15 m t of sewage sludge).

Total amount of waste plastics thermally utilised in Austria

In Figure 9 the annual flows of waste plastics into all 10 WtE plants are summarised. In total, about 347 ±24 kt of plastics have been thermally utilised in Austria's waste incineration plants in 2014, neglecting the input into three plants with an annual total waste throughput of about 230 kt (not investigated). Including the waste feed of these three plants into our analysis (assuming an average plastics content of 16.5 ±2.7 wt% in their feed) increases

(+38 ±6 kt) the overall amount of waste plastics thermally utilised in Austria to about 385 ±25 kt. Almost 50% of this amount is fed into only three plants (E, H, and J).

The overall energy input via waste plastics into all waste incineration plants totals approximately 14,400 ±900 TJ a^{-1} (assuming an average lower calorific value of waste plastics of 37.5 MJ kg^{-1}, according to Kost, 2001), which equals around 11% of Austria's coal consumption of 130,000 TJ a^{-1} in 2013 (BMWFW, 2015).

Conclusions

The evaluation of the waste composition of 10 WtE plants in Austria (with a total annual capacity of 2.3 m t of waste) via the Balance Method revealed that there are significant differences regarding the plastics content in the waste feed of the different plants. In addition to regional differences, significant temporal variations of the plastics content are observable also at some of the plants analysed. It is assumed that these variations are caused by changing shares of the different types of waste (MSW, CW, IW, RDF), but also by a changing composition of the different wastes combusted. For instance, the plastics content in RDFs utilised in FBC plants may be influenced by the seasonal fuel demand of Austria's cement kilns, which is definitely lower in winter times. Hence, more plastics may be fed into FBC plants in winter times.

In general, the share of plastics (annual averages) in the waste feed ranges from 11 ±2 to 21 ±3 wt% for the different plants, with an average plastics content of 16.5 wt%. This value is significantly higher than the figures reported by waste sorting studies (8–13 wt%) done in Austria (BMLFUW, 2011; IUT&SDAG, 2014; Schneider and Lebersorger, 2011), which however all focused on MSW and did not account for the plastics present in composites or other mixed material fractions, such as hygienic products. Whereas, the monthly averages of the plastics content determined for plant A (9–15 wt%) are in the range of the results of sorting campaigns, the outcomes for plant I, which also utilises only MSW, indicate a significantly higher plastics content (16–20 wt%). Hence, it can be concluded that there is no typical plastics content in MSW. Furthermore, sorting campaigns most likely tend to underestimate the content of plastics in waste, since even in comparison with results of plant A (waste feed with comparatively low plastics content), sorting analyses generally claim lower contents of plastics in MSW.

The results of the study further indicate a higher monthly variation of the waste plastics content in the feed of FBC plants in comparison with those of GI plants. This might be attributed to the fact that the former are very often designed for specific (industrial) waste streams and that they also compete with industrial co-combustion of wastes (e.g. cement kilns), thereby being exposed to changing fuel demand, which may result in a changing composition of RDFs.

In total about 385 kt of waste plastics have been utilised in Austria's WtE facilities in 2014, which represents about 45 kg plastics cap^{-1} a^{-1}. In addition, the cement industry uses about 210 kt of waste plastics (corresponding to 25 kg cap^{-1} a^{-1}) as an alternative fuel (based on data given in Mauschitz, 2015). Results of sorting campaigns (BMLFUW, 2011; IUT&SDAG, 2014; Schneider and Lebersorger, 2011) would reveal a much lower per capita combustion rate of plastics in Austria of 21 to 35 kg plastics cap^{-1} a^{-1} for 2014. In comparison, PlasticsEurope reports 20 kg cap^{-1} a^{-1} of plastics, which were thermally recovered in Europe in 2014 (EU-28 plus Switzerland and Norway) (PlasticsEurope, 2015). This can be easily explained by the fact that within the EU about 40% to 50% of collected waste plastics still ends up at landfills (European Commission, 2015; PlasticsEurope, 2015), whereas in Austria plastic waste is banned from landfilling. However unexpectedly, lower energetic utilisation rates of waste plastics, compared with values determined for Austria, are also reported for Germany, which shows a comparable share of MSW thermally treated (Austria: 37%; Germany: 35% according to Eurostat, 2015). From the figures for 2013 given in Lindner and Hoffmann (2015), per capita incineration rates of 25 kg plastics per year in German WtE plants can be derived, and an additional amount of 15 kg cap^{-1} a^{-1} enters industrial co-combustion plants. Considering the overall waste feed of 21.9 m t in 2013 (Confederation of European Waste-to-Energy-Plants, 2013), the average content of plastics in the feed of German WtE plants amounts to only about 10 wt%. This is in the range of results obtained by sorting analyses in Austria (8–13 wt% based on BMLFUW, 2011; IUT&SDAG, 2014; Schneider and Lebersorger, 2011), but is far below the values determined in the present study.

Based on these comparisons of the determined figures with literature values, it can be speculated that plastic flows entering waste incineration facilities are underestimated if they are solely based on results from sorting analyses. Sorting campaigns usually focus on the composition of MSW only and additionally disregard plastics contained in composite material fractions. The herein presented approach (country-wide application of the Balance Method), considers all waste plastics, independent of their compound or combination with other materials. This benefit, together with a very high share of characterised waste in the feed of the WtE facilities (around 91%), the method has to be regarded as the most reliable of all available tools to determine the overall plastics flows that are thermally utilised via waste combustion. Once, the input parameters are collected, the Balance Method allows assessment of the waste composition for any time period of interest (ranging from years to hours) without sampling or supplementary analyses. Only in the case that the WtE plant does not provide CO_2 measurements for the flue gas, a CO_2 analyser needs to be installed.

The results of the study are directly incorporated into the national analyses of plastics flows and thus contribute to a better understanding of the recycling potentials of waste plastics in Austria (see Van Eygen et al., submitted).

Acknowledgements

The authors would like to thank the operators of the WtE plants for their cooperation.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: Part of the presented work was conducted thanks to funds by the Austrian Science Fund (FWF), project number TRP 285-N28. Further, the work was partly supported by a large-scale research initiative on anthropogenic resources (Christian Doppler Laboratory for Anthropogenic Resources). The financial support of this research initiative by the Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development is gratefully acknowledged. Moreover, the authors would like to acknowledge the financial support by the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management.

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Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities

Supplementary Material

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A) Summary of the operating data of Waste to Energy plants required as input parameter for the Balance Method

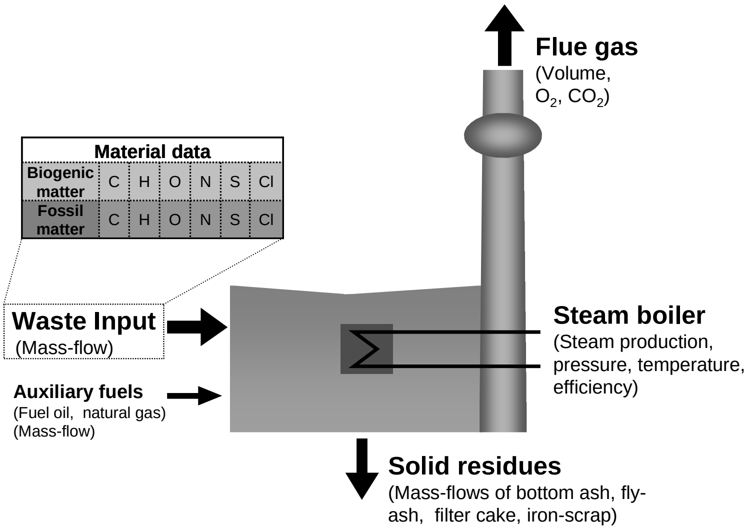

Figure A.1. Required input data for the Balance Method.

B) Examples of plausibility graphs for the Balance Method

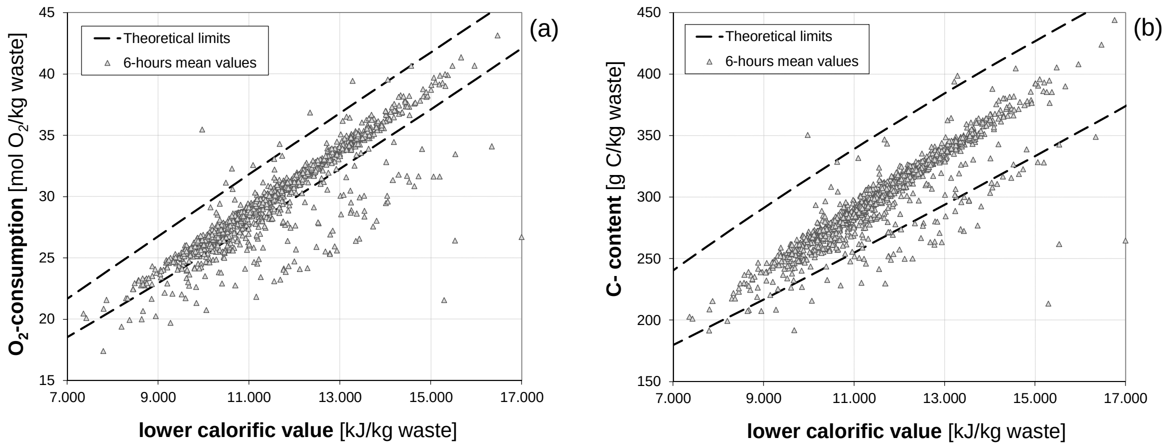

Figure B.2. Results of plausibility checks for operating data of WtE plant B on a 6-hourly basis: (a) Correlation between lower calorific value and O_2 consumption and (b) Correlation between lower calorific value and C content of the waste.

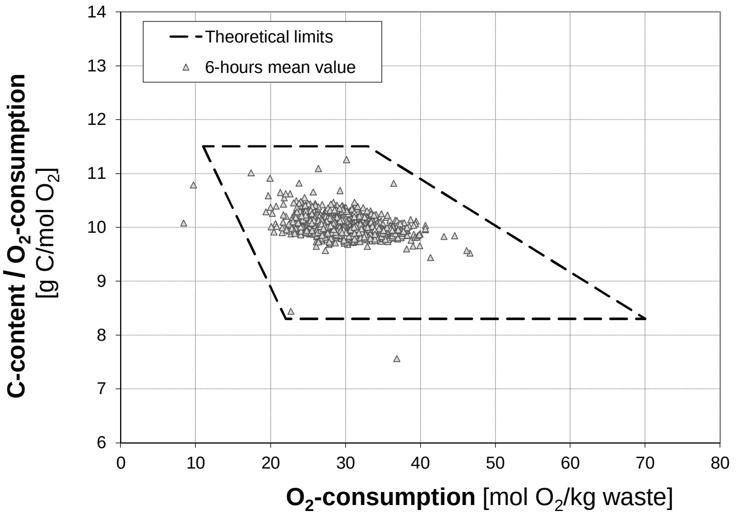

Figure B.3. Results of plausibility checks for the operating data of WtE plant B on a 6-hourly basis: correlation between O_2 consumption and C content of the waste.

Paper IV

Effects of sample preparation on the accuracy of biomass content determination for refuse derived fuels

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Christian Brandstätter and Johann Fellner

Fuel Processing Technology, 2016, 153, 101-110

DOI: 10.1016/j.fuproc.2016.07.001

Fuel Processing Technology 153 (2016) 101–110

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Effects of sample preparation on the accuracy of biomass content determination for refuse-derived fuels

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A R T I C L E I N F O

Article history:
Received 5 April 2016
Received in revised form 29 June 2016
Accepted 1 July 2016
Available online 4 August 2016

Keywords:
Biomass content
Refuse-derived fuels
adapted Balance Method
Sample preparation
Variance component analysis

A B S T R A C T

A reliable and practical method for characterizing refuse-derived fuels (RDF) with respect to greenhouse gas-relevance (or biomass content) is required by industries and waste management companies. As RDF usually consist of a variety of materials with different physical properties, sampling and sample preparation may represent crucial steps with regard to reliable analysis results. This is particularly valid for analytical methods, which rely on only small test specimens (centigrams), such as the adapted Balance Method (aBM). The aBM was recently developed by the authors and is based on elemental analyses (CHNSO). The investigations focus on elaborating an appropriate sample preparation for the aBM. To this end, two RDF model mixtures are generated out of paper, cardboard and different plastics, and comminuted down to a grain of size of <0.2 mm using two differing mills as finishing step. The results of the aBM (applied for 52 samples) show that the performance of the method in terms of trueness and variation is competitive relative to standardized methods. Deviations between the determined value and the theoretical biogenic mass fraction are below 4.5%rel (at a probability of 95%). Furthermore, the standard deviation for both mixtures is below ± 3.0%rel. A nested variance component analysis indicates that the last milling step and the step of drawing the test specimens for analysis contribute most to the observed variability. A consecutive application of two types of mills as a finishing step prior to analysis is proposed in order to facilitate a sufficient grinding of plastics as well as of cellulose fibers.

1. Introduction

Energy recovery from wastes and refuse-derived fuels (RDF) has become of increasing importance for energy-intensive industry branches such as cement manufacturing. In Austria this development has been strongly facilitated by the implementation of the landfill directive in 2009, which bans the disposal of waste with a total organic carbon content larger than 50 g/kg or a lower calorific value above 6.6 MJ/kg waste [1]. Thus, materials of high calorific value present in wastes such as plastics, paper, cardboard or textiles are separated in mechanical-biological pre-treatment plants and are subsequently utilized as RDF in industrial plants, thereby substituting conventional fuels. According to the Association of Austrian Cement Industry, the share of refuse-derived fuels in the European cement industry reached a level of 34% by 2012 [2]. In Austria in 2014 already 75.5% of the energy required in cement works stem from secondary fuels [2]. These fuels are, on the one hand, associated with several benefits for the operators: they are usually cheaper, domestically available, and usually less CO_2 intensive than conventional fuels (e.g. coal) [3,4]. However, their utilization goes along with various challenges. Probably the biggest challenge for producers and operators is the heterogeneity of the fuel, which requires reliable, practical and cost effective methods to characterize their quality and thus the environmental aspects associated with their thermal utilization. Besides the compulsory parameters according to EN 15359:2011 [5] (calorific value, content of chlorine and heavy metals), other specifications like, phosphorous content or the biomass content are becoming of increasing importance with respect to the quality and economic value of solid recovered fuels (SRF, which are RDFs produced in accordance with European Standards). The European Recovered Fuel Organization, for example, addresses the significance of determining

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Abbreviations: A, ash content; aBM, adapted Balance Method; CV, coefficient of variation (related to the mean); HD-PE, high-density polyethylene; MS, mean sum of squares; n, number of analyses; N, number of analysis samples; PET, polyethylene terephthalate; PS, polystyrene foam; RDF, refuse-derived fuel; RSD, relative standard deviation (related to the mean); SD, standard deviation; SRF, solid recovered fuel; SS, sum of squares; TIX_{wf}, total inorganic content of the respective element in the water-free ignition residue; TOC, total organic carbon; TOH, total organic hydrogen; TON, total organic nitrogen; TOO, total organic oxygen; TOS, total organic sulfur; TOCl, total organic sulfur; TOX_{waf}, total organic content of the respective element in the water-and-ash-free sample; TX_{wf}, total content of the respective element in the water-free sample; UCM, ultra-centrifugal mill; VCA, variance component analysis; waf, water-and-ash-free; wf, water-free; wt%, percentage by weight; x_B, biogenic matter; $x_{B,aBM}$, biogenic mass fraction determined by the adapted Balance Method; $x_{B,Theory}$, theoretical biogenic mass fraction; x_F, fossil matter; σ^2rel., relative variance component (related to the overall variance); σ^2, variance component.

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http://dx.doi.org/10.1016/j.fuproc.2016.07.001

the biomass content in SRF for the sake of reducing greenhouse gas emissions through the substitution of fossil fuels [6].

Both producers and users of RDF are interested in reliable and cost-effective methods for characterizing the fuel in terms of greenhouse gas-relevance. Until now, three methods to determine the biomass content in SRF have been described in the standard EN 15440:2011 [7], namely the manual sorting method, the selective dissolution method, and the radiocarbon method. All three methods are commonly applied (for example [8–12]). In addition to the standardized methods, the Balance Method has been developed and implemented in various waste-to-energy plants in recent years and is currently in the last stage of standardization [13–16]. This method combines standard data on the chemical composition of biogenic and fossil organic matter with routinely measured operating data from waste-to-energy plants and has been demonstrated as a reliable method with very low costs in comparison to alternative methods [16,17]. However, the Balance Method does not allow a characterization of the fuel before its utilization as it employs post-combustion data. Hence, the authors have developed a laboratory-based analysis method – the so-called adapted Balance Method (aBM) – which shows promising results [18,19]. Analyses of defined mixtures of biogenic (like cardboard and wood) and fossil materials (like polyethylene and polystyrene) revealed deviations from the theoretical value of below 1% when the materials were mixed after milling [20]. When materials were mixed prior to the sample preparation, results of the aBM differ by <5% (relative) from the known composition of a two-component mixture consisting of paper and polyethylene [19].

However, waste materials are typically strongly heterogeneous with respect to their physical properties and texture and thus, different steps during sampling, sample processing, and analysis can be critical factors for a reliable analysis result [21]. Due to different material characteristics, the components of the mixture may behave differently when it comes to comminution or sample size reduction. Hence, besides sampling, the sample preparation needs careful attention in order to ensure correct and reproducible analysis results. This is particularly valid when only very small test specimens are required for the analysis. For example, the adapted Balance Method (which relies on the elemental analysis) or the radiocarbon method depends on the analysis of only a few milligrams or centigrams per measurement.

Hence, the aim of the investigations presented in this paper is to elaborate an appropriate sample preparation procedure in order for the adapted Balance Method (aBM) to achieve highly reproducible results. In particular, the following aspects are addressed:

- Determination of the reliability of the aBM in terms of accuracy and precision (by means of predefined RDF model mixtures)
- Evaluation of the influence of different sample preparation steps on the final result of the aBM (hierarchical experimental set-up)
- Identification at which layer of the analysis procedure (different sample conditioning steps and chemical analysis) most of the efforts should be concentrated in order to avoid/minimize potential errors
- Identification of approaches for optimizing the conditioning procedure (comparison of different milling strategies).

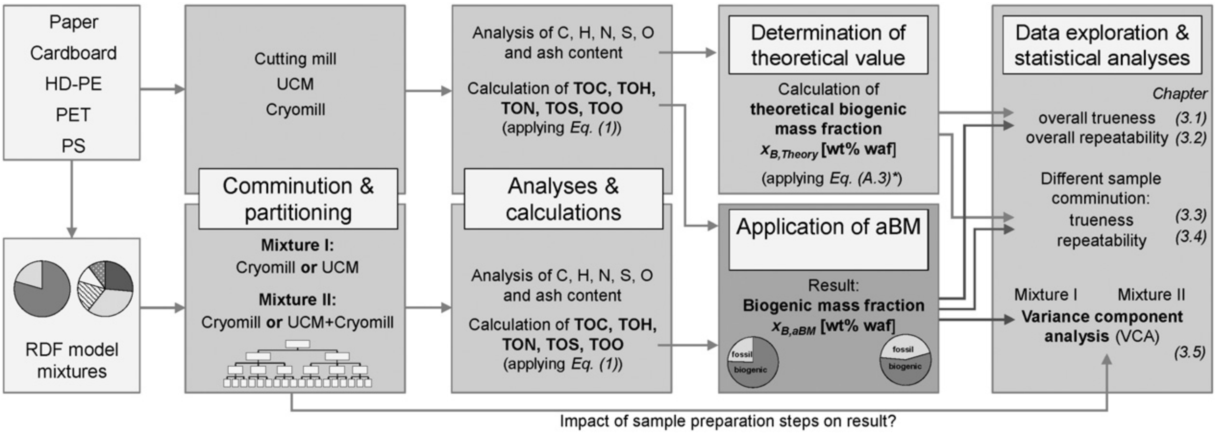
2. Materials and methods

Within the framework of the present study the biomass content of two predefined material mixtures with different composition and different heterogeneity is determined using the adapted Balance Method (aBM) (Fig. 1). Mixture I consists of paper and polyethylene, whereas mixture II is made out of paper, cardboard, polyethylene, polyethylene terephthalate and polystyrene. A special focus is given to the effects of the sample preparation on the final analysis results, different comminution steps are applied and evaluated using various statistical methods, such as the variance component analysis (VCA). For the latter in particular, a hierarchical experimental set-up is chosen, meaning that after each conditioning step replicate samples are produced.

2.1. Determination of the biomass content using the adapted Balance Method

The adapted Balance Method (aBM) relies on the distinctly different chemical composition of water-and-ash-free biogenic and fossil organic matter, where fossil in this context is understood as materials produced out of crude oil, natural gas or coal.

The necessary input data for the calculation are derived from elemental analyses (CHNSO). Additional data on the chemical composition of the water-and-ash-free biogenic and fossil matter are required, which can be derived from literature or from separate analyses of pure biogenic and fossil organic matter present in the fuel (see [18]). Mass balance equations are set up for carbon, hydrogen, nitrogen, sulfur and oxygen. Each balance equation contains the two unknown mass fractions of fossil and biogenic matter (x_B and x_F). As an example, the two pie charts on the left in Fig. 2 show the elemental composition of water-and-ash-free biogenic and fossil matter present in municipal solid waste (total organic carbon TOC, total organic hydrogen TOH, total organic nitrogen TON, total organic sulfur TOS, total organic oxygen TOO and total organic sulfur TOCl) (data as given in [17]). By multiplying these compositional data by the respective mass fractions of waf biogenic organic matter (x_B) and fossil organic matter (x_F), the composition of the material mixture (or RDF) is obtained (pie chart on the



* Eq. (A.3) can be found in the supplementary information

Fig. 1. Schematic illustration of the procedure chosen for the investigations conducted: application of the adapted Balance Method (aBM) to two different predefined RDF model mixtures and evaluation of the impact of different comminution steps on the final results.

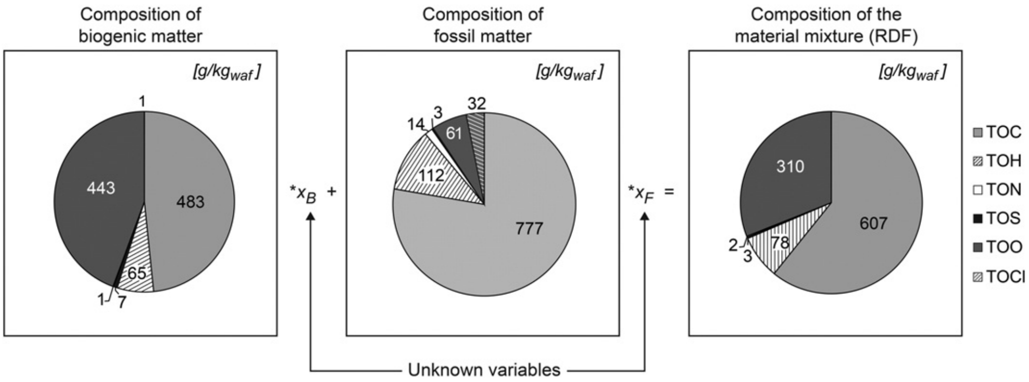


Fig. 2. Schematic illustration of the adapted Balance Method, showing the relation between the chemical composition of biogenic and fossil organic matter and the material mixture (all on a water-and-ash-free basis - waf); for each element (TOC, TOH, TON, TOS, TOO, TOCl; presented data are for municipal solid waste given in [17]) a balance equation is set up to determine the unknown variables: mass fraction of biogenic matter x_B [wt% waf] and mass fraction of fossil matter x_F [wt% waf].

right in Fig. 2). The set of five balance equations is overdetermined (more equations than unknowns), thus a data reconciliation algorithm based on non-linear optimization can be applied to reveal the quantity of the unknown mass fractions (biogenic x_B, fossil x_F). The basic balance equations of the adapted Balance Method are provided in the Supplementary material section C.; further details are given in [18].

2.2. RDF model mixtures

For the preparation of the two predefined RDF model mixtures, the following biogenic and fossil materials are used:

Biogenic materials:

- cardboard: packaging, double walled
- paper: 80 g/m^2, Antalis Austria GmbH and 150 g/m^2, Inkjet Paper, Canon

Fossil materials:

- high-density polyethylene (HD-PE): laboratory grade HD-PE bottles, 250 ml, SciLabware
- polyethylene terephthalate (PET): cleaned PET-bottles without label, 237 ml, SPAR AG
- extruded polystyrene foam (PS): insulation boards, Austrotherm GmbH.

All chosen materials are usually represented in RDF made out of municipal solid waste and commercial waste in a high proportion [22–24] and are characterized by different physical behaviors (e.g. thermal stability, density). Paper and cardboard are considered to be biogenic matter, whereas HD-PE, PET and PS represent fossil materials (produced out of crude oil). All materials are shredded down to a grain size of <4 mm by a cutting mill (Retsch SM 2000). Two material mixtures of different composition regarding the biomass content are prepared out of the <4 mm materials. The respective amounts of the different materials are weighed with an electronic balance (Sartorius Extended, Sartorius Mechatronics) and filled into a 60 l container. The mixtures are thoroughly mixed by shaking the container in circular motions for about 10 min.

Based on the share of the biogenic and fossil materials and their ash content (as determined by analyses), the theoretical biomass fraction for the mixtures is calculated on a water-free (wf) and water-and-ash-free (waf) reference basis (equations are given in the Supplementary material, Eqs. A.1 to A.4). Table 1 summarizes the respective shares of the used materials and the theoretical biogenic mass fraction of both mixtures. The biogenic mass fraction on a water-and-ash-free basis $x_{B,Theory}$ of mixture I is 75.5 wt% waf and mixture II holds 55.9 wt% waf (calculation available in Supplementary material - Eq. A.3).

2.3. Sample comminution and partitioning

For the CHNSO elemental analysis a final sample size of only a few centigrams is required. Thus, different sample preparation steps (comminution, partitioning) are necessary. The sample preparation is carried out in accordance with the Norm EN 15413:2011 [25].

The material mixtures undergo the sample comminution and segregation steps as outlined in Fig. 3. At each layer of conditioning replicate samples are produced. The first splitting of the mixture takes place at a grain size of <4 mm by using a riffle divider (Rational Kornservice 5 l with 18 splits at 19.1 mm each) resulting in two divided parts with each around 300 or 600 g. Afterwards the grain size is reduced to <1 mm using a cutting mill (Retsch SM 2000). The thereby observed sample loss is below 7 g (~1.8 wt% of the initial mass).

Once the <1 mm sample is obtained, two different mills are used to further reduce the particle size - a high-speed rotor mill (UCM, ultra-centrifugal mill, Retsch ZM 200) or a cryogenic mixer mill (Cryomill, Retsch). Both mills are commonly applied to reduce the particle size of waste samples (e.g.: [26–28], [29] – plastic, [30] – polymers). The Cryomill is preferably used for materials with a high share of plastics because the milling bin is cooled by liquid nitrogen in order to embrittle the material and thereby support the crushing of elastic particles (rather than plating them). However, the Cryomill has no provisions to generate samples of defined particle sizes, while the particle size of

Table 1
Composition of the RDF model mixtures.

	Biogenic materials		Fossil materials			Theoretical biogenic mass fraction in the mixture $x_{B,Theory}$	
	Paper wf [wt%]	Cardboard wf [wt%]	HD-PE wf [wt%]	PET wf [wt%]	PS wf [wt%]	wf [wt%]	waf [wt%]
Mixture I (600 g)	79.4	–	20.6	–	–	79.4	**75.5**
Mixture II (1200 g)	26.4	34.3	18.8	10.3	10.2	60.7	**55.9**

wf = water-free.
waf = water-and-ash-free.
wt% = wt% percentage by weight (ratio of mass to total mass).

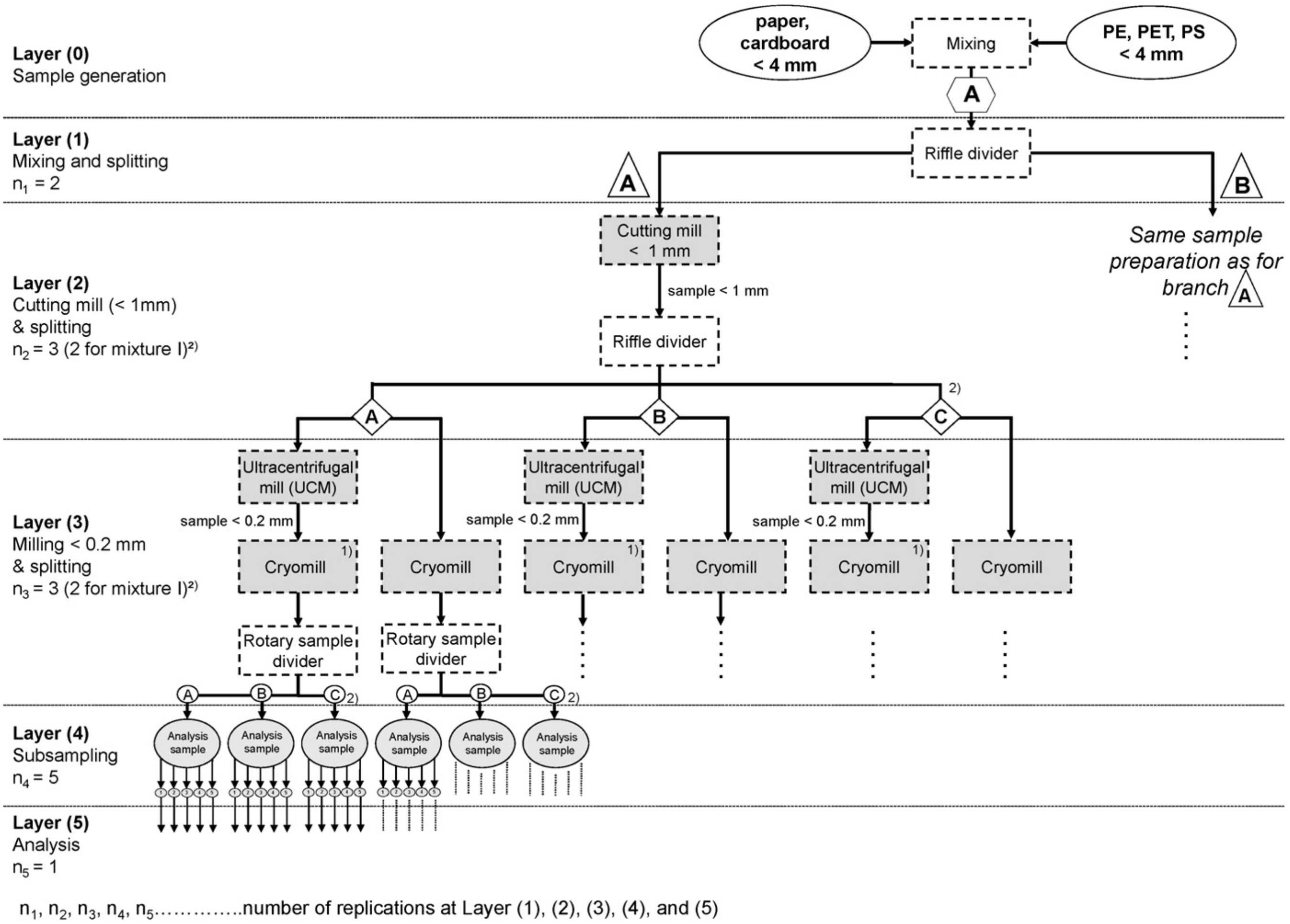


Fig. 3. Scheme of the sample conditioning (comminution and partitioning steps); note that the divided samples at each layer are illustrated in different shapes 1) The Cryomill-milling step after UCM-milling is only done for mixture II (not for mixture I); 2) For mixture I only two replications are done at each layer (no C-branches at Layer (2) and Layer (3) are produced).

comminuted materials via UCM is controlled by screens of defined dimensions. The performances of the two different mills are compared within this study to identify approaches for optimizing the conditioning procedure in terms of trueness and precision of the final results.

For mixture I (two-component mixture) the <1 mm fraction is milled down to <0.2 mm using either the ultra-centrifugal mill (UCM) or the Cryomill. The chosen test set-up for mixture II (five-component mixture) is partly based on results for mixture I (e.g. better performance of the Cryomill in terms of variance and trueness; see Sections 3.3 and 3.4). Thus, this mill is also used to comminute one half of mixture II. However, the other half of the samples are milled by the UCM and subsequently crushed into fine powder by the Cryomill prior to analysis (see Fig. 2 Layer (3)). Thus, two different milling procedures for each mixture are applied. The material losses from UCM-milling amount to 5.3 wt% on average, whereas the Cryomill causes lower losses in the range of 1.1 wt%. In order to receive replicate samples on Layer (3), a rotary sample divider (Retsch PT 100) is used, resulting in two (mixture I) or three (mixture II) analysis samples. All devices are cleaned carefully before each sample processing.

The splitting steps at each layer of comminution finally result in 16 analysis samples of mixture I (8 UCM-samples, 8 Cryomill-samples) and 36 samples of mixtures II (18 UCM + Cryomill samples, 18 Cryomill-samples), each of them holding 11 to 16 g.

The "pure" biogenic and fossil materials (paper, cardboard, HD-PE, PET, PS) are also comminuted down to <0.2 mm and subsequently their ash content and elementary composition (C, H, N, S, O) is determined in analogy to the material mixtures (see Section 2.4). Finally, the data obtained by the analyses of the single biogenic and fossil materials are aggregated to the elementary composition of waf biogenic and fossil organic matter present in mixture I and mixture II (see Supplementary material Table D.3), which serve as input data for the aBM.

2.4. Chemical analyses

2.4.1. Water content and ash content

For each analysis sample (Layer (4)) the water content and ash content is analyzed in duplicate and in accordance with EN 15414-3:2011 [31] and EN 15403:2011 [32]. To this end, 4 g material of each sample are dried at 105 °C for 24 h before being combusted at 350 °C in a muffle furnace for 1 h and at 550 °C for 4 h under air injection. All weights of the sample (before drying, after drying, after ignition) are recorded (using a mechanical balance 2432, Sartorius Mechatronics) in order to calculate the water and ash content.

2.4.2. Elemental analysis

The water-free (dried at 105 °C for 24 h) analysis samples (Layer (4)) are analyzed for the elemental composition (content of C, H, N and S) using an Elementar Macro instrument (Elementar Analysensysteme GmbH, Hanau, Germany). At a combustion temperature of 1150 °C, the total carbon TC, total hydrogen TH, total nitrogen TN, and total sulfur TS content are determined according to DIN 51732:2014 [33]. Five measurements per sample are carried out, each of them comprising 40 mg of sample material.

The total oxygen content TO is determined using an Elementar Vario EL instrument (Elementar Analysensysteme GmbH, Hanau, Germany). The analysis is based on the pyrolysis of the sample at 1150 °C and the conversion of all oxygen into CO. Compared to the CHNS-analysis, for each O-measurement only 4 mg of sample mass can be analyzed (due to limitations of the analyzer, allowing maximum 2 mg oxygen absolute). Due to the smaller sample size for oxygen analysis, seven measurements per sample are carried out. The uncertainties given by the device specifications are 0.5%rel for the CHNS-combustion analysis and 0.2%abs for the O-analyzer.

In addition, the ignition residue of each test sample treated in the muffle oven is analyzed for its elemental composition to appraise the total inorganic content of carbon, hydrogen, nitrogen, sulfur and oxygen. The values measured are converted according to Eq. (1) in order to receive the elemental composition of the analysis sample on a water-and-ash-free reference base.

$$\mathrm{TOX_{waf}} = (\mathrm{TX_{wf}} - \mathrm{TIX_{wf}} * \mathrm{A})/(1-\mathrm{A}) \tag{1}$$

whereby $\mathrm{TOX_{waf}}$ [g/kg] represents the total organic content of the respective element (C, H, N, S, O) in the water-and-ash-free sample, $\mathrm{TX_{wf}}$ [g/kg] the total content of the respective element in the water-free sample as measured, $\mathrm{TIX_{wf}}$ [g/kg] the total inorganic content of the respective element in the water-free ignition residue as measured, and A [kg/kg] the ash content (see also [19]). The thereby obtained values for total organic carbon TOC, total organic hydrogen TOH, total organic nitrogen TON, total organic sulfur TOS, and total organic oxygen TOO represent the main input parameter required for the adapted Balance Method (values are given in Supplementary material Table D.4). In addition, the contents of TOC, TOH, TON, TOS and TOO for the biogenic and fossil organic matter present in the mixture are required as input data for the aBM (see Supplementary material: Eqs. (B.1) and (B.2) and Table D.3).

2.5. Statistical tests

Statistical tests are carried out in order to evaluate differences between data sets regarding their central tendencies (means) and variances. All tests are carried out using the program R (Version 3.0.2) [34] or DataLab (Version 3.530) [35]. In particular, the following tests are applied:

- Shapiro test: test for normal distribution (required to decide which subsequent statistical test, e.g. *t*-test, Kruskal-Wallis test, is applied)
- Levene test: test for homogeneity of variances (required to decide which subsequent statistical test, e.g. *t*-test, Welch-Test, is applied)
- *t*-Test and paired *t*-test: test for differences in means; applied when there is no indication that the data are not normally distributed and the variances are assumed to be equal
- Welch-Test: test for differences in means from two populations; applied when there is evidence that the variances of the data-sets are unequal
- Kruskal-Wallis test: test for differences in multiple means (non-parametric test); applied when there is evidence that the variances of the data-sets are unequal and the data are not normally distributed.

For all statistical tests a level of significance of 0.05 is used.

The overall trueness of the investigations achieved is estimated by applying statistical tests to the relative deviation from the theoretical value of all samples analyzed (52 in total).

2.6. Nested variance component analysis

Critical factors for a reliable determination of the biomass content in heterogeneous wastes and RDF include sampling, sample preparation and the chemical analysis itself. All steps are associated with errors and contribute to the variation observed for the final results. The total variance of replicate samples can be used to estimate the overall quality of the whole analysis (including sample conditioning). However, to find the cause for the scattered analyses data, the hierarchy of the variation's sources has to be investigated [36]. For this purpose analysis variances models with nested structure can be used as they allow the relative importance of the different sources of variation to be determined [37].

The variance component analysis (VCA) assumes that the variance of the results reflects the sum of the variances of all influencing factors and allows the total variation measured to be attributed to the single processing steps. A nested VCA, based on Hartung (1991) [38] and Sokal & Rohlf (2012) [37] is deployed for evaluating the random variation added by the four defined layers of sample preparation steps and the analysis itself. To do so, replicate samples are produced after each preparation step (see Fig. 3) and mean values are calculated at each layer.

Input of the variance component analysis (VCA) are the results after applying the adapted Balance Method, namely the parameter “Biogenic mass fraction” $x_{B,aBM}$, for each measurement conducted (five calculated values per sample).

As outlined in Fig. 3 and Table 2, altogether five layers of sample preparation and analysis are defined, namely (1) “Mixing and splitting”, (2) “Cutting mill (<1 mm) & splitting”, (3) “Milling (<0.2 mm) & splitting”, (4) “Subsampling for analysis”, and (5) “Analysis (error)”, with the second layer nested within the first, the third layer nested within the second etc. The number of groups per layer is determined by the number of replications produced by sample splitting after each preparation step. For example, Layer “Mixing and splitting” only contains two groups as the sample is split into two parts after being mixed, whereas Layer (2) “Cutting mill (<1 mm) & splitting” includes six subgroups (samples A and B of Layer (1) are each split into three parts: A, B, C) – see Fig. 3; note that the divided samples of each layer are illustrated in different shapes.

The variance components per layer are calculated as summarized in Table 2. The variation caused by a layer (e.g. variance component of Layer (1) σ_1^2) is estimated by summarizing the squared deviation between replications (e.g. $\overline{x}_{n_i}$ group means of Layer (1) for A and B) and the group means of the layer (e.g. $\overline{x}$ the total mean for A) and multiplying it by the sample size (replications) of the underlying layers. The computed sum of squares (SS) is divided by the degrees of freedom (represented by the denominator in the MS-equations in Table 2) to obtain the mean sum of squares (MS) per layer. The added variance component among the groups of a layer is estimated by comparing the MS between the groups of the respective layer (see Table 2; e.g. $\mathrm{MS_1}$ represents the mean sum of squares for groups of Layer (1), namely A and B in Fig. 3) with the MS between the groups of the subsequent layer (e.g. $\mathrm{MS_2}$ as MS of groups of Layer (2), namely A, B, C in Fig. 3).

Negative estimators for σ^2 can occur when the variation at one layer decreases more strongly than expected by the variation of the subjacent layer (e.g. $\mathrm{MS_2} > \mathrm{MS_1}$). Here, negative estimates are considered to be zero. The variation of the last layer reflects the variation within the measurements. As this layer contains both, the variation caused by drawing the five test specimens from the analysis sample and the variation of the analysis itself, two different factors are distinguished (Layer (4) and Layer (5)). Systematic errors from CHNSO-analysis are ruled out as regular calibrations and daily offset corrections are carried out. Thus the analysis error σ_5^2 is derived from the given device specifications (error term ε of Layer (5)). Layer (4) then accounts for the variance caused by “Subsampling for analysis” (σ_4^2).

The sum of squares for each layer add up to the total sum of squares SS_{tot}, which would also be obtained if the sum of squares of the entire data set is calculated.

The results are presented as variance components (σ^2) and their relative importance (σ^2 rel.) expressed as proportions of the sum of variance components. Furthermore, the coefficient of variation (CV) is determined for each layer, relating the variance component to the mean of the respective data set.

In order to test for significant differences between samples after each preparation step, F-values ($\mathrm{F_s}$) can be computed as given in Table 2. The MS of each layer is related to the MS immediately beneath it. It can be tested whether the variation among the samples at a layer is higher

Table 2
Calculation of variance components at five layers (after [37,38]).

Source of variation	Variance component	Mean sum of squares (MS)	Sum of squares (SS)	F_s
Layer (1) Mixing & splitting	$\sigma_1^2 = \frac{MS_1 - MS_2}{n_2 * n_3 * n_4 * n_5}$	$MS_1 = \frac{SS_1}{n_1 - 1}$	$SS_1 = \sum_i^{n_1} n_2 * n_3 * n_4 (\overline{x}_{n_i} - \overline{x})^2$	$\frac{MS_1}{MS_2}$
Layer (2) Cutting mill (<1 mm) & splitting	$\sigma_2^2 = \frac{MS_2 - MS_3}{n_3 * n_4 * n_5}$	$MS_2 = \frac{SS_2}{n_1 * (n_2 - 1)}$	$SS_2 = \sum_i^{n_1} \sum_j^{n_2} n_3 * n_4 (\overline{x}_{n_i n_j} - \overline{x}_{n_i})^2$	$\frac{MS_2}{MS_3}$
Layer (3) Milling (<0.2 mm) & splitting	$\sigma_3^2 = \frac{MS_3 - MS_4}{n_4 * n_5}$	$MS_3 = \frac{SS_3}{n_1 * n_2 * (n_3 - 1)}$	$SS_3 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} n_4 (\overline{x}_{n_i n_j n_k} - \overline{x}_{n_i n_j})^2$	$\frac{MS_3}{MS_4}$
Layer (4) Subsampling for analysis	$\sigma_4^2 = \frac{MS_4 - MS_5}{n_5}$	$MS_4 = \frac{SS_4}{n_1 * n_2 * n_3 * (n_4 - 1)}$	$SS_4 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{x}_{n_i n_j n_k n_l} - \overline{x}_{n_i n_j n_k})^2$	$\frac{MS_4}{MS_5}$
Layer (5) Analysis (error)	$\sigma_5^2 = MS_5$	$MS_5 = (\varepsilon * \overline{x})^2$		
Total	$\sigma_{tot}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2$	$MS_{tot} = \frac{SS_{tot}}{n_1 * n_2 * n_3 * n_4 * n_5 - 1}$	$SS_{tot} = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{\chi} - \overline{\chi} n_i n_j n_k n_l)^2 = SS_1 + SS_2 + SS_3 + SS_4$	

$\overline{x}$ = total mean.
$\overline{x}_{n_i}$ = mean of *i*-th group at Layer (1).
$\overline{x}_{n_i n_j}$ = mean of *j*-th group at Layer (2) (within *i*-th group of Layer (1)).
$\overline{x}_{n_i n_j n_k}$ = mean of *k*-th group at Layer (3) (within *j*-th group of Layer (2) within *i*-th group of Layer (1)).
$\overline{x}_{n_i n_j n_k n_l}$ = *l*-th analysis result at Layer (4) (within *k*-th group of Layer (3) within *j*-th group of Layer (2) within *i*-th group of Layer (1)).
n_1, n_2, n_3, n_4, n_5 = number of replications at Layers (1), (2), (3), (4), and (5).
ε = error for analysis estimated based on CHNSO device specification (0.9%).

than that to be expected on the basis of the observed variation among the samples of the subjacent layer. If the tested MS of a layer is larger than it is expected to be by chance (the case if the F_s-value is below the defined level of significance of 0.05), one can conclude that the differences among samples at the respective layer are significant [37].

3. Results and discussion

3.1. Overall assessment of the trueness of the biogenic mass fraction

The biomass content (biogenic mass fraction) of the prepared RDF model mixtures is determined by deploying the adapted Balance Method based on elemental analysis. The theoretical (true) value $x_{B,Theory}$ is determined from the predefined composition of the mixtures (see Table 1 and Supplementary material Eq. A.3).

The calculated biogenic mass fractions $x_{B,aBM}$ of mixture I and mixture II based on results per sample are presented in Fig. 4. The calculated values appear to be in good agreement with the theoretical values. No indication of differences between deviations from the theoretical value of mixture I and of mixture II can be found and the assumption that the data of both mixtures are normally distributed cannot be rejected (on a confidence level of 95%). Thus, the data of both data sets are combined and fitted to a normal distribution function, as shown in Fig. 4 b). Based on the assumption of normally distributed data, there is a probability of 95% that the pooled data are within 4.5%rel from the theoretical value. Moreover, it can be concluded that the results are underestimated by trend (around 0.6%rel) as the mean deviation in Fig. 4 b) is slightly below zero.

3.2. Overall assessment of the variation (repeatability) of the biogenic mass fraction

The variation of the observations for the biogenic mass fraction $x_{B,aBM}$ and thus the reproducibility of the whole method (sample preparation, chemical analysis and calculations according to the aBM) is estimated by calculating the standard deviation over the sample means. The maximum standard deviation found for the data sets of mixture I and mixture II is 1.7%abs (1.6%abs for mixture I and 1.7%abs for mixture II). This means that the sample values are scattered below ±3.0%rel around their mean.

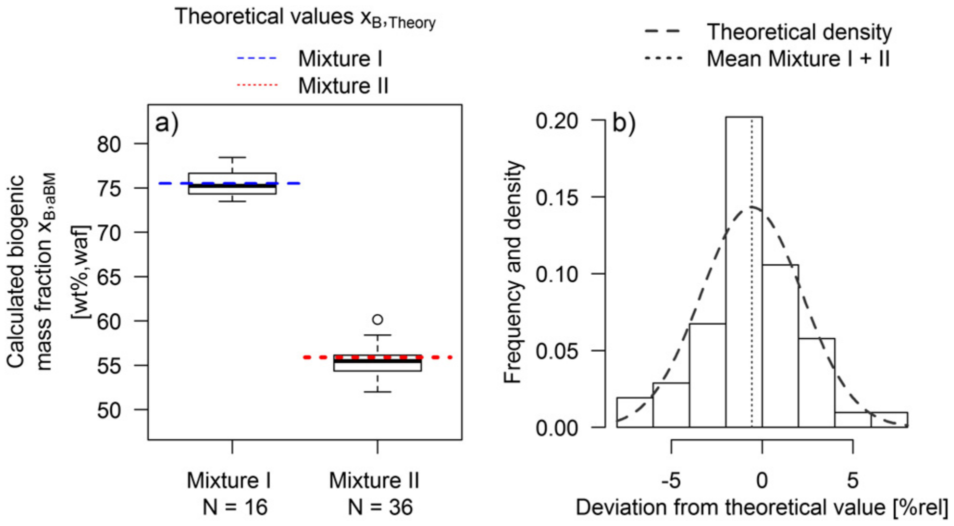


Fig. 4. a) Biogenic mass fraction $x_{B,aBM}$ of all samples (N…number of analysis samples) analyzed on a water-and-ash-free (waf) basis (for mixture I and mixture II) compared to the theoretical biogenic mass fraction $x_{B,Theory}$ of both mixtures; the outlier visible for mixture II may indicate improper homogenization but is not expected to cause an overestimation of the mean and is therefore retained; b) Relative frequency histogram and fitted normal density curve of the relative deviation from the theoretical value for results of mixture I and mixture II together.

3.3. Impact of different sample comminution on the trueness of the biogenic mass fraction

Table 3 summarizes the overall results for both RDF model mixtures. Besides the means and uncertainties of the biogenic mass fractions $x_{B,aBM}$ for each mixture, mean values (incl. standard deviation) for samples with a similar final conditioning step are also given. The calculated mean biogenic fraction on a water-and-ash-free basis (waf) for mixture I is 75.5 ± 1.6 wt% waf (with a theoretical value $x_{B,Theory}$ of 75.5 wt% waf) and for mixture II 55.4 ± 1.7 wt% waf (with a theoretical value $x_{B,Theory}$ of 55.9 wt% waf). Thus, a high accuracy of the mean (trueness) could be achieved. However small but significant differences between data sets can be observed when comparing results of samples finished with different mills (for both mixtures). This is not only the case for the aBM-output parameter "Biogenic mass fraction", but also for the aBM-input parameter TOC, TOH, and ash content (not presented here). The biogenic fraction for samples finally comminuted by a Cryomill solely appears underestimated by trend (−1.1 to −2.3%rel). Whereas, the samples treated with UCM show on average a 0.7 to 1.2%rel higher biomass content compared to the theoretical value. According to a *t*-test, only the deviations of Cryomill-finished samples are significantly different from zero (Table 3). It must be noted that the small sample size for the data sets of mixture I can easily influence the outcome of the significance test. However, the results clearly indicate that the sample preparation chosen may slightly change the sample composition (e.g. by thermal stress).

The mean deviation from the theoretical biogenic mass fraction (calculated as relative standard deviation) is lower for samples of mixture I (1.0–1.7%rel) compared to samples of mixture II (3.0–3.4%rel). This may partly be attributed to the lower biomass content of mixture II (absolute deviation is related to a lower mean), but also indicates that a higher complexity in terms of composition of the material mixture is more susceptible to changes in composition during sample preparation (mixture II contains a more heterogeneous material).

3.4. Variations in the biogenic mass fraction for different sample comminution

Significant differences in the variation of the results are observed when comparing samples of mixture I processed with different mills (Table 3). The standard deviation based on the mean values range from 0.7%abs (0.9%rel) for Cryomill-finished samples to 1.7%abs (2.2%rel) for UCM-finished samples. When mixture II is considered, the difference in standard deviation observed for samples with different final comminution is not significant, with 1.6%abs (2.8%rel) for samples with UCM + Cryomill conditioning and 1.4%abs (2.6%rel) for solely Cryomill-finished samples.

The diverse variances for samples with different final preparation steps are attributed to unequal grain size distributions within the analysis samples. When applying the UCM, cellulose fibers of paper and cardboard material in the mixtures are not completely destroyed and tend to agglomerate to particles larger than the desired 0.2 mm (visual observation and confirmed by sieve analysis conducted – see Supplementary material section E.). In contrast, the Cryomill crushes fibers to a large degree, but does not allow samples of defined particle size to be generated. Although the milling bin of the Cryomill is cooled with liquid nitrogen (−196 °C) to enhance crushing of elastic particles (rather than plating them), sieve analysis for samples milled via Cryomill show an accumulation of plastics in the larger grained fraction of the samples (see Supplementary material section E.; TOC and TOH increase with particle sizes and TOO decreases with particle size).

Comparing the results of the chemical analysis with the respective biomass content calculated via aBM demonstrates the distinct dependency of the biomass content on the elementary content of TOC, TOH and TOO (see Supplementary material: Fig. F.1 and F.2). Higher contents of organic carbon and organic hydrogen and lower contents of organic oxygen inevitably result in lower contents of biogenic matter and vice versa.

3.5. Assessing the impact of each preparation step on the variance of the biogenic mass fraction

In order to assess the impact of each preparation step on the variation observed for the final results, a variance component analysis (VCA) as a nested design is conducted based on equations in Table 2. Tables 4 and 5 present the results of the VCA for the parameter "Biogenic mass fraction" $x_{B,aBM}$ for mixture I and mixture II. Therein, variance components (σ^2), their relative importance (σ^2 rel.) as a percentage of total variation, the coefficient of variation (CV) as well as the results of the significance tests (*p*-values) are summarized.

Looking at the results for mixture I, the last milling step Layer (3) adds the most to the overall variance for UCM-samples as well as for

Table 3
Biogenic mass fractions determined by the adapted Balance Method $x_{B,aBM}$ compared to the theoretical biogenic mass fraction $x_{B,Theory}$ of both RDF model mixtures (given as mean value over results of the respective samples).

	Mixture I Paper:PE		Mixture II Paper:cardboard:PE:PET:PS	
	UCM-finished samples	Cryomill-finished samples	UCM + Cryomill-finished samples	Cryomill-finished samples
Theoretical biogenic mass fraction $x_{B,Theory}$ [wt% waf] ± SD	75.5 ± 0.3		55.9 ± 0.4	
Calculated biogenic mass fraction $x_{B,aBM}$ [wt% waf] (arithmetic mean ± SD)	75.5 ± 1.6		55.4 ± 1.7	
Calculated biogenic mass fraction $x_{B,aBM}$ [wt% waf] for samples with different finishing (arithmetic mean ± SD)	76.4 ± 1.7	74.7 ± 0.7	56.3 ± 1.6	54.6 ± 1.4
Result of 2-tailed *t*-test for differences in means / Levene test for differences in SD between samples with different finishing	*** / *		** / -	
Deviation of calculated value from theoretical value [%rel] $(x_{B,aBM} - x_{B,Theory})/x_{B,Theory}$ / results of 2-tailed *t*-test for differences from 0	+1.2% /	−1.1% / **	+0.7% / -	−2.3% / ***
Mean deviation of calculated value from theoretical value as RSD [%rel] = SD of $(x_{B,aBM,i} - x_{B,Theory})$	1.7%	1.0%	3.0%	3.4%
Number of samples	$N = 8$	$N = 8$	$N = 18$	$N = 18$

waf = water-and-ash-free.
$x_{B,aBM}$ = biogenic mass fraction on water-and-ash-free basis, determined by the adapted Balance Method (aBM).
$x_{B,aBM,i}$ = biogenic mass fraction on water-and-ash-free basis, determined for sample *i* by the aBM.
$x_{B,Theory}$ = biogenic mass fraction on water-and-ash-free basis, theoretical value based on the preset composition.
S D= standard deviation based on sample results.
RSD = relative standard deviation (SD related to the mean $x_{B,aBM}$).
N = number of samples (with 5 analyses for each sample).
Significance codes for t-test and Levene test -p > 0.1; 0.1 ≥ p > 0.05; * 0.05 ≥ p > 0.01; ** 0.01 ≥ p > 0.001; *** 0.001 ≥ p.

Cryomill-samples (relative variance components for Layer (3) 48.6% UCM-samples; 50.9% for Cryomill-samples). The p-values, with well below 0.05, indicate that there is a significant difference among the samples after the last milling and splitting step (confidence level of 95%).

The first mixing and milling steps Layer (1) and Layer (2) appear to not add significant variation to the final result (with p-values well above 0.05). The variance components, being zero (or negative) for these layers, could be caused by an insufficient number of replicates, leading to strong effects on the subsequent layers which might overlie the variance of Layer (1) and Layer (2).

The variance component of Layer (4) of the Cryomill-samples suggests that the results after the subsampling step do not differ significantly from each other (p-value > 0.05) and the added variance from this layer is significantly lower for Cryomill-samples (0.12) than for UCM-samples (4.03). It is expected that these findings result from better fiber destruction by the Cryomill, which facilitates representative subsampling for final analysis. Finally, Layer (5), which represents the analysis itself, shows a distinctly higher relative importance for the Cryomill-samples compared to UCM-samples (38.5% and 5.4%, respectively). However, the absolute variance component is more or less equal (0.45 and 0.47, respectively).

The visually observed phenomenon of fiber agglomerations after UCM-milling is assumed to add heterogeneity to the analysis samples, which is reflected in the results of the VCA. Table 4 shows that the overall variance is higher for UCM-samples (3.9%) compared to Cryomill-samples (1.4%). This is consistent with the findings in previous sections where the variance of the sample means is compared (see Section 3.4 and Table 3).

The results of the VCA for the conditioning and analysis of the five-component mixture II are summarized in Table 5. In comparison to the results for mixture I, the results are more complex and hence more difficult to interpret. The overall variance, expressed as a coefficient of variation (CV), is slightly higher for Cryomill-samples (3.1%) compared to samples prepared with UCM + Cryomill (2.9%). Comparing the variance of the single layers for the UCM + Cryomill-samples, there is a strong indication for an added variance component for each preparation step (p-values < 0.05). This means that in general all preparation steps cause “significant” changes in the sample composition with regard to the biomass content. Unexpectedly, a dominant influence of the first mixing and splitting step for UCM + Cryomill-samples (a relative importance of Layer (1) of 63.5%) is observed. This high variation caused by Layer (1) suggests that the mixing and first splitting (done at 4 mm grain size) did not lead to two equally divided parts. This could be caused by insufficient homogenization before the splitting or demixing effects due to insufficient particle size reduction. However, this finding is not confirmed by the results of the Cryomill-samples, where the first layer only adds a low variance component (with 6.6% related to the overall variation). In general, for the Cryomill-samples the first two preparation steps (Layer (1) and Layer (2)) did seemingly not lead to significant differences in sample results (p-values > 0.05).

Nevertheless, the initial mixing and splitting may represent a sensitive step for sample preparation, especially when more complex mixtures are concerned, but no distinct conclusions can be drawn as only two replications have been done at this layer.

For both mixtures a significant share of the overall variation originates from Layer (4), which represents the subsampling step where small specimens are drawn from the analysis sample to be fed into the elemental analyzer. The significantly lower absolute magnitude of the variance component of Layer (4) for UCM + Cryomill-samples (0.28) compared to Cryomill-samples (1.61) indicates that more homogenous samples are produced when both mills are applied. The lower variance component for UCM + Cryomill-samples is also evident when the respective variance components of Layer (3) are compared (0.13 for UCM + Cryomill-samples and 0.96 for Cryomill-samples). Thus, the application of both mills leads to a small variation of replicate measurements. It is assumed that the different grinding mechanisms of both mills destroy cellulose fibers (mainly by the Cryomill) as well as plastic particles (mainly by the UCM) to a large extent.

Comparing the variance components σ^2 of Cryomill-samples of mixture I to Cryomill-samples of mixture II (thus only comparing results for the two mixtures generated via the same sample preparation), it is apparent that the added variation from milling and especially from subsampling is higher for mixture II, which contains a higher fraction of fossil materials. This indicates once more that a proper destruction of plastic particles is crucial, in particular if they represent a high share in the mixture. Moreover, this outcome demonstrates that for mixtures that are more complex, subsampling for elemental analysis requires high experimental control and a sufficient number of replications is indispensable. A proper homogenization of the sample before analysis and a suitable method of drawing representative specimens from the analysis sample are essential. Both are obviously linked to the grain size and grain size distribution of the analysis sample.

Overall, the coefficients of variation (CV) of both mixtures are below 3% for all layers, which is regarded as a promising result and shows the general suitability of the sample preparation method applied in conjunction with the aBM.

Table 4
Results of the nested variance component analysis for the biogenic mass fraction $x_{B,aBM}$ of RDF model mixture I (obtained by the aBM).

	Source of variation (Layer)	Mixture I Paper: PE (79.4 wt%: 20.6 wt%, wf)									
		Parameter: Biogenic mass fraction $x_{B,aBM}$									
		UCM-finished samples					Cryomill-finished samples				
		σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value	σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value
				$n = 40$					$n = 40$		
(1)	Mixing & splitting	0[a]	0.0%	0.0%	0.02	0.896	0[a]	0.0%	0.0%	0.15	0.736
(2)	Cutting mill (<1 mm) & splitting	0[a]	0.0%	0.0%	0.90	0.475	0[a]	0.0%	0.0%	0.75	0.530
(3)	Milling (<0.2 mm) & splitting	4.26	48.6%	2.7%	5.74	0.001	0.60	50.9%	1.0%	6.17	0.001
(4)	Subsampling for analysis	4.03	46.0%	2.6%	9.57	0.000	0.12	10.6%	0.5%	1.27	0.233
(5)	Analysis (error) ε	0.47	5.4%	0.9%			0.45	38.5%	0.9%		
	Total	8.76	100.0%	3.9%			1.17	100.0%	1.4%		

σ^2 = variance component.
σ^2 rel. = relative variance component (related to the overall variance).
CV = coefficient of variation (related to the mean).
n = number of analyses (16 samples with 5 analyses each).
ε = error for analysis derived from device specification of CHNSO-analyzer (0.9%).
wf = water-free.

[a] Negative estimates for variance components are assumed to be zero.

Table 5
Results of the nested variance component analysis for the biogenic mass fraction $x_{B,aBM}$ of RDF model mixture II (obtained by the aBM).

	Source of variation (Layer)	Mixture II Paper: cardboard: PE: PET: PS (26.4 wt%: 34.3 wt%: 18.8 wt%: 10.3 wt%: 10.2 wt%, wf)									
		Parameter: biogenic mass fraction $x_{B,aBM}$									
		UCM + Cryomill-finished samples					Cryomill-finished samples				
		σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value	σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value
				$n = 90$					$n = 90$		
(1)	Mixing & splitting	1.79	63.5%	2.3%	13.30	0.022	0.20	6.6%	0.8%	2.24	0.209
(2)	Cutting mill (<1 mm) & splitting	0.36	12.6%	1.0%	5.44	0.010	0.05	1.6%	0.4%	1.11	0.397
(3)	Milling (<0.2 mm) & splitting	0.13	4.7%	0.6%	2.22	0.019	0.96	31.2%	1.7%	3.57	0.000
(4)	Subsampling for analysis	0.28	9.8%	0.9%	2.05	0.001	1.61	52.2%	2.2%	7.2	0.000
(5)	Analysis (error) ε	0.26	9.3%	0.9%			0.26	8.4%	0.9%		
	Total	2.82	100.0%	2.9%			3.08	100.0%	3.1%		

σ^2 = variance component.
σ^2 rel = relative variance component (related to the overall variation).
CV = coefficient of variation (related to the mean).
n = number of analyses (36 samples with 5 analyses each).
ε = error for analysis derived from device specification of CHNSO-analyzer (0.9%).
wf = water-free.

3.6. Comparison of the aBM results to findings in other studies

Previous studies conducted by Fellner et al. (2011) [18] and Schnöller et al. (2014) [19] applying the aBM on 2-component mixtures revealed deviations from the theoretical value of <1%abs and 5%rel respectively. Thus, the found accuracy of the mean of the present study (4.5%rel deviation at a probability of 95%) is in a similar range of previous results and is competitive to results reported for standardized methods. For example, Ariyaratne et al. (2014), who analyzed the biomass content of predefined material mixtures (wood, paper, plastics) using the selective dissolution and the radiocarbon method (both methods described in EN 15440:2011), noted significantly higher deviations from the theoretical value (up to 7 and 16%, respectively) [39].

With respect to the repeatability, the obtained results indicate slightly lower variations (± 3%rel) compared to values in the literature (< ± 5%rel [18] and 4–5%rel [19]). In Schnöller et al. (2014), however, smaller test specimens were used (20 mg instead of 40 mg) and oxygen measurements were not considered [19]. The higher standard deviation in results for smaller test specimens supports the finding that the subsampling and analysis practice impair the variation of the aBM results.

Reported relative standard deviations of the biomass content for (real) refuse-derived fuels characterized by the selective dissolution method vary by ± 1.2% [8], below ± 2.5% [40], or ± 6.7% [9]. For the radiocarbon method Larsen et al. (2013) note a relative uncertainty in the range of 7 to 10% at a confidence interval of 95% when flue gas samples from a stack of a waste incineration plant are analyzed [15]. The results presented herein for the aBM are therefore clearly compatible and within the range of standardized methods for determining the biomass content of wastes.

4. Conclusions

The investigations conducted on two refuse-derived fuel (RDF) model mixtures (2-component and 5-component mixtures with 75.5 and 55.9% biogenic content, respectively) demonstrate the feasibility of the adapted Balance Method (aBM) for determining the biogenic mass fraction in heterogeneous material mixtures. At a probability of 95%, the calculated values deviate <4.5%rel from the preset (theoretical) biogenic mass fraction of the model mixtures, thereby demonstrating the trueness of the results.

In addition, a high level of repeatability for the analysis (including the sample preparation) is also proven as the relative standard deviation for the biogenic mass fraction of all samples analyzed is below ± 3.0%.

A small but significant effect of the sample preparation method chosen on the trueness and on the variation of the final results is observed when comparing samples comminuted with different mills. The biogenic mass fraction tends to be underestimated when the Cryomill is applied (up to minus 2.3% rel). The significant difference in standard deviation when different mills are compared is explained by the higher heterogeneity of the UCM-finished samples, which may be attributed to the agglomeration of fibers to bigger particles than the desired grain size of 0.2 mm.

The nested variance component analysis (VCA), which was already applied in previous studies for heavy metal data in waste incineration residues [36] or for metal flows in a mechanical-biological treatment plant [41], proves to be an appropriate tool to account for the complexity of the experiment and extract relevant information from it. For instance, it is shown that for both model mixtures the last milling step and the step of drawing the test specimens for analysis ("Subsampling for analysis") strongly affect the total variation observed for the biogenic mass fraction. This finding indicates that these particular steps require the greatest experimental control. Both are obviously linked to the grain size and grain size distribution of the analysis sample.

The lowest added variation due to milling and subsequent sampling for analysis is observed when the final preparation consists of a milling step by means of an UCM followed by a grinding process via Cryomill. This confirms findings from Smidt et al. (2008), who concluded on an improvement of reproducibility of analysis results for municipal solid waste when two mills with different working principles are applied in association [27].

In general, the choice of appropriate conditioning steps for the adapted Balance Method, should be based on the expected qualitative composition of the waste or RDF to be analyzed (for example, a rough approximation of the share of plastics and paper by visual inspection) together with the desired precision of the final result. Material mixtures with a high fraction of paper or cardboard primarily call for an adequate destruction of cellulose fibers (which, for example, a Cryomill is capable of) to avoid particle agglomeration. A further milling step (utilizing, for example, an UCM) to ensure a certain grain size for plastics might be practical when a high precision (error < 3%rel) is desired and the effort demanded is justifiable. When RDF with a rather high content of plastics are to be characterized, the precision is expected to be mainly influenced by the proper and assured crushing of the plastic particles.

As the performance of the mills applied appears limited, a combination of both types of milling processes (high-speed rotor mill, mixer mill) is proposed in order to facilitate a sufficient grinding of plastics and cellulose fibers to a grain size below 0.2 mm.

Acknowledgements

The authors would like to acknowledge the funding of the present study, which was provided by the Federal Ministry for Transport, Innovation and Technology (bmvit) and the Austrian Science Fund (FWF): [TRP 285-N28]. In addition, we would like to thank our laboratory team, particularly Stefan Spacek, for their support and laboratory analyses as well as Inge Hengl for graphical support.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2016.07.001.

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Effects of sample preparation on the accuracy of biomass content determination for refuse-derived fuels

Appendix A. Supplementary material

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A. Calculation of theoretical biogenic mass fractions on water-and ash-free basis (waf) in the model mixtures ($x_{B,Theory}$)

1. Water- and ash-free <u>mass</u> of materials mixed (paper, cardboard, HD-PE, PET, PS) $M_{i,waf}$

$$M_{i,waf} = M_{i,ar} * (1 - W_i) * (1 - A_i) \qquad \text{(A.1)}$$

$M_{i,waf}$	water- and ash-free mass of material i [g_{waf}]
$M_{i,ar}$	mass “as received” of material i (incl. water and ash) [g]
W_i	water content of material i [kg/kg]
A_i	ash content of material i [kg/kg_{wf}]

2. Theoretical biogenic mass fraction of the model mixture $x_{B,Theory}$

$$m_{B,i,waf} = M_{i,waf} / M_{waf} \qquad \text{(A.2)}$$

$$x_{B,waf} = \sum_{i=1}^{n} m_{B,i,waf} = x_{B,Theory} \qquad \text{(A.3)}$$

$$x_{F,waf} = \sum_{i=1}^{m} m_{F,i,waf} \qquad \text{(A.4)}$$

$m_{B,i,waf}$ ..	mass fraction of water-and ash-free biogenic material i based on the total water-and ash-free matter of the model mixture [kg_{waf}/kg_{waf}]
M_{waf}	total water-and ash-free matter of the model mixture [g_{waf}]
$x_{B,waf}$	water-and ash-free biogenic mass fraction of the model mixture [kg_{waf}/kg_{waf}]
$x_{F,waf}$	water-and ash-free fossil mass fraction of the model mixture [kg_{waf}/kg_{waf}]
n	number of biogenic materials in the model mixture
m	number of fossil materials in the model mixture

B. Calculation of the chemical composition of the water-and-ash-free (waf) biogenic and fossil matter in the model mixtures (*TOX_B, TOX_F*)

$$TOX_B = \sum_{i=1}^{n} (M_{B,i,waf}/M_{B,waf}) * TOX_i \tag{B.1}$$

$$TOX_F = \sum_{i=1}^{m} (M_{F,i,waf}/M_{F,waf}) * TOX_i \tag{B.2}$$

TOX_B ...... total organic content of the respective element (C, H, N, S, O) of the water- and ash-free biogenic matter [g/kg$_{\text{waf}}$]

TOX_F ...... total organic content of the respective element (C, H, N, S, O) of the water- and ash-free fossil matter [g/kg$_{\text{waf}}$]

$M_{B,i,waf}$ ... water- and ash-free mass of biogenic material i [g$_{\text{waf}}$]

$M_{F,i,waf}$ ... water- and ash-free mass of fossil material i [g$_{\text{waf}}$]

$M_{B,waf}$ .... total water-and ash-free biogenic matter of the model mixture [g$_{\text{waf}}$]

$M_{F,waf}$ .... total water-and ash-free fossil matter of the model mixture [g$_{\text{waf}}$]

TOX_i .... total organic content of the respective element (C, H, N, S, O) in the water- and ash-free material i [g/kg$_{\text{waf}}$]

n .... number of biogenic materials in the model mixture
m .... number of fossil materials in the model mixture

C. Balance equations of the adapted Balance Method (Fellner et al, 2011)

Carbon balance

$$x_B * TOC_B + x_F * TOC_F = TOC_{mixture} \tag{C.1}$$

Hydrogen balance

$$x_B * TOH_B + x_F * TOH_F = TOH_{mixture} \tag{C.2}$$

Nitrogen balance

$$x_B * TON_B + x_F * TON_F = TON_{mixture} \tag{C.3}$$

Sulfur balance

$$x_B * TOS_B + x_F * TOS_F = TOS_{mixture} \tag{C.4}$$

Oxygen balance

$$x_B * TOO_B + x_F * TOO_F = TOO_{mixture} \tag{C.5}$$

x_B .... water- and ash-free biogenic mass fraction of the mixture [wt%]
x_F .... water- and ash-free fossil mass fraction of the mixture [wt%]

In addition to the five substance balance equations the following condition needs to be fulfilled:

$$x_{B,wf} + x_{F,wf} + A = 1 \tag{C.6}$$

A .... ash content in the mixture [wt%]

$x_{B,wf}$ ...... water-free biogenic mass fraction of the mixture as determined by the adapted Balance Method [wt%]

$x_{F,wf}$ .... water-free fossil mass fraction of the mixture as determined by the adapted Balance Method [wt%]

D. Chemical composition of used materials, of RDF model mixtures and of fossil and biogenic matter present in the RDF model mixtures

Table D.1 Chemical composition of the water-and-ash free (waf) materials in RDF model mixture I TOX_i

	TOC	TOH	TOO	TON	TOS	Ash	Share m_i
	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	wt%	wt%$_{waf}$
Paper*	446 ± 5	61 ± 0.5	528 ± 9	1.5 ± 0.5	2 ± 0.5	20 ± 0.8	75.5
HD-PE	868 ± 2	148 ± 1	3 ± 0.5	1.5 ± 0.5	3 ± 0.5	0.1 ± 0.04	24.5

* Different types of paper were used in mixture I and mixture II

Table D.2 Chemical composition of the water-and-ash free (waf) materials in RDF model mixture II; TOX_i

	TOC	TOH	TOO	TON	TOS	Ash	Share m_i
	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	wt%	wt%$_{waf}$
Paper*	421 ± 2	61 ± 0.5	541 ± 3	3 ± 0.5	3 ± 1	19 ± 0.5	23.1
Cardboard	459 ± 2	63 ± 0.3	470 ± 6	4 ± 0.5	2 ± 0.3	15 ± 0.3	32.7
HD-PE	868 ± 1	146 ± 0.3	3 ± 1	1 ± 0.3	2 ± 0.3	0.02 ± 0.01	21.2
PET	628 ± 1	41 ± 0.3	323 ± 6	1 ± 0.3	2 ± 0.3	0.03 ± 0.001	11.5
PS	916 ± 3	76 ± 0.3	11 ± 2	1 ± 0.3	2 ± 0.3	0.15 ± 0.04	11.5

* Different types of paper were used in mixture I and mixture II

Table D.3 Chemical composition of the water-and-ash-free (waf) biogenic and fossil matter present in RDF model mixture I and mixture II; TOX_B and TOX_F

		TOC	TOH	TOO	TON	TOS
		g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$
Mixture I	**Biogenic**	446 ± 5	61 ± 0.5	528 ± 9	1.5 ± 0.5	2 ± 0.5
	Fossil	868 ± 2	148 ± 1	3 ± 0.5	1.5 ± 0.5	3 ± 0.5
Mixture II	**Biogenic**	443 ± 1	62 ± 0.5	499 ± 3	3 ± 0.5	3 ± 0.3
	Fossil	818 ± 1	100 ± 0.2	89 ± 2	1 ± 0.3	2 ± 0.3

Table D.4 Average chemical composition of the water-and-ash free (waf) mixture I and mixture II; $TOX_{mixture}$

	TOC	TOH	TOO	TON	TOS	Ash	N
	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	wt%	-
Mixture I	551 ± 8	82 ± 2	399 ± 13	1 ± 0.6	2 ± 0.5	16 ± 0.4	16
Mixture II	616 ± 5	77 ± 1	323 ± 9	1 ± 0.3	2 ± 0.5	10 ± 0.6	36

N..............number of samples (with 5 analyses for each sample)

TOC.........Total organic carbon, TOH .... Total organic hydrogen, TOO......... Total organic oxygen
TON.........Total organic nitrogen, TOS...... Total organic sulfur
waf...........water- and ash-free
wt%..........percentage by weight (ratio of mass to total waf mass)

E. Sieve analysis

Sieves with a mesh size of 0.5 mm, 0.25 mm, 0.125 mm, and 0.063 mm are used (Retsch, sieve diameter 200 mm). The sieve stack is shaken at a mechanical vibration table for about 10 min.

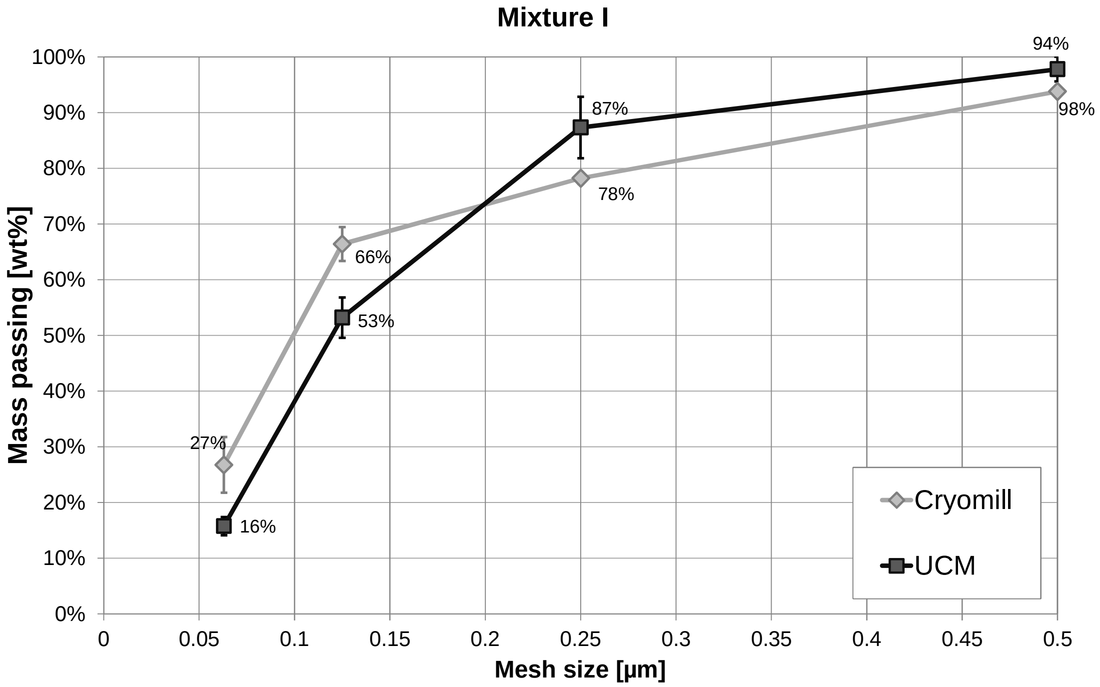

Fig. E.1 Results of grain size analysis for RDF model mixture I (samples finished with Cryomill and samples finished with ultra-centrifugal mill UCM), means and standard deviation after six analysis are presented (with each 6 - 10 g of sieved material)

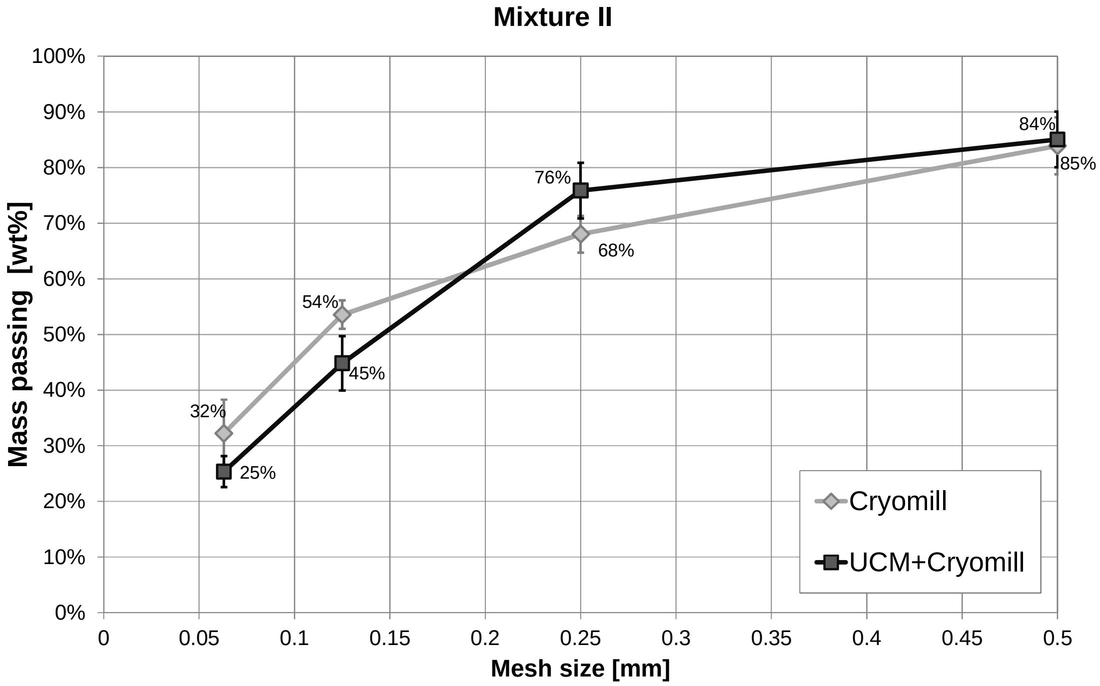

Fig. E.2 Results of grain size analysis for RDF model mixture II (samples finished with Cryomill and samples finished with ultra-centrifugal mill UCM + Cryomill), means and standard deviation after three analysis are presented (with each 20 - 23 g of sieved material)

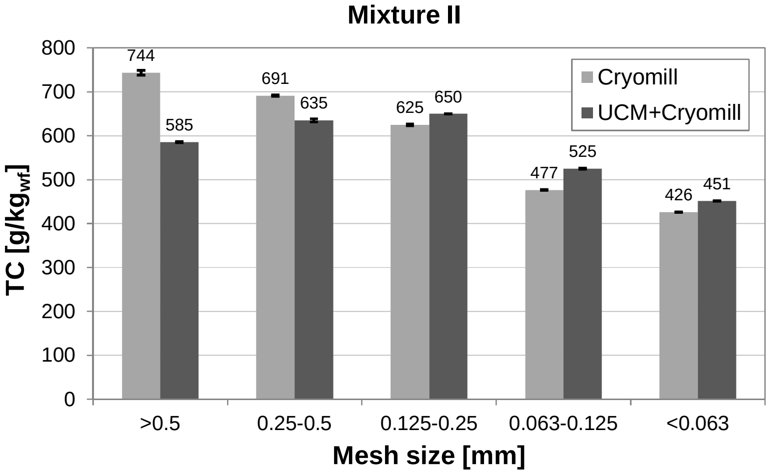

Fig. E.3 Total carbon content (TC) of the different sieve fractions of the water-free (wf) model mixture II (samples finished with Cryomill and finished with ultra-centrifugal mill UCM + Cryomill)

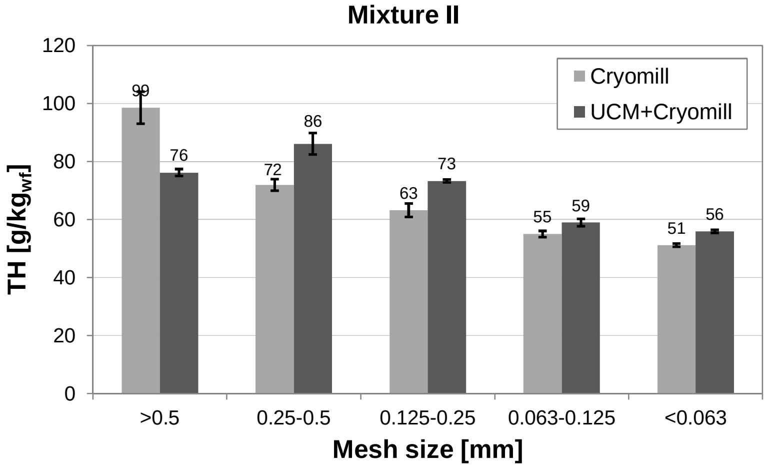

Fig. E.4 Total hydrogen content (TH) of the different sieve fractions of the water-free (wf) model mixture II (samples finished with Cryomill and finished with ultra-centrifugal mill UCM + Cryomill)

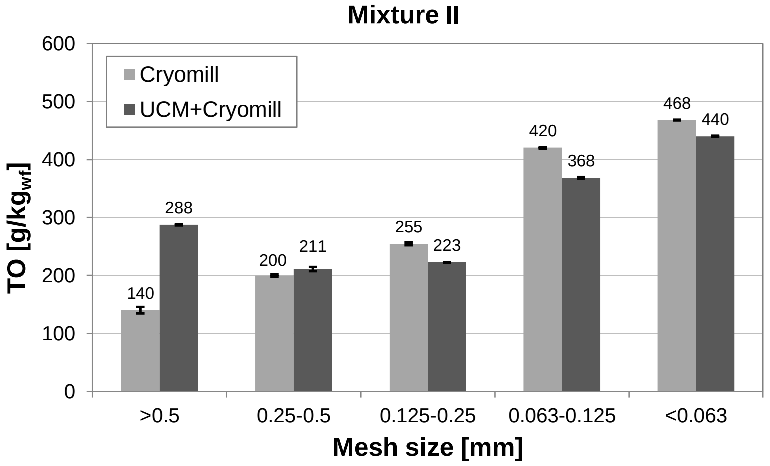

Fig. E.5 Total oxygen content (TO) of the different sieve fractions of the water-free (wf) model mixture II (samples finished with Cryomill and finished with ultra-centrifugal mill UCM + Cryomill)

In Cryomill-samples the TOC and TOH are significantly increasing with particle sizes and TOO is decreasing with particle size. This indicates an accumulation of plastics in the larger grained fraction of the sample.

F. TOC, TOH and calculated biogenic mass fraction $x_{B,aBM}$ of RDF model mixture I and mixture II

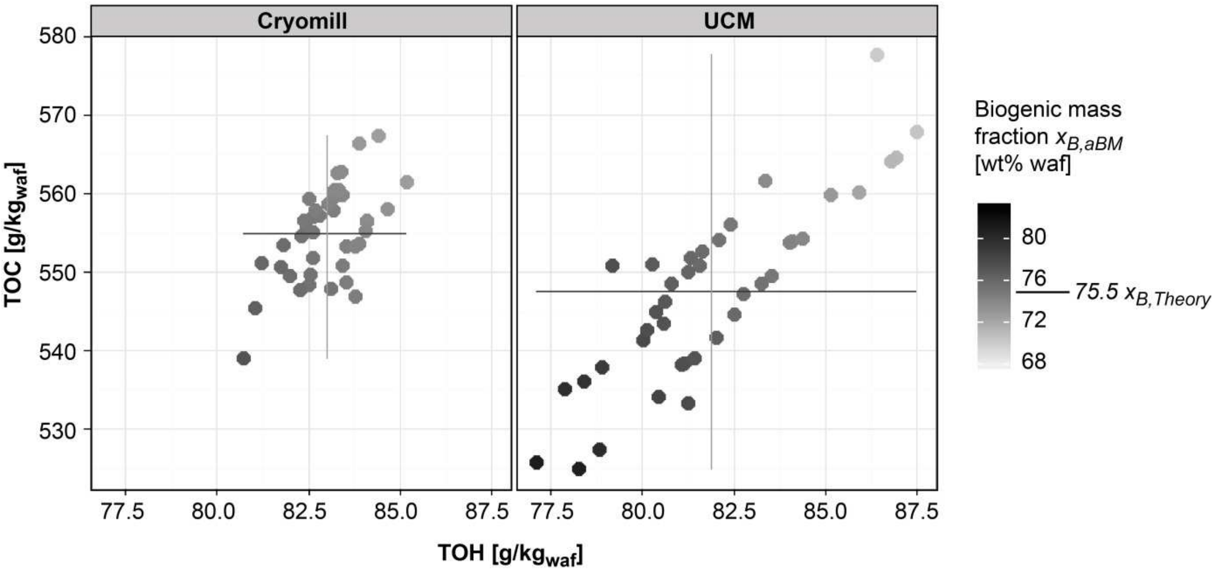

Fig. F.1 Analysis results for total organic carbon (TOC) and total organic hydrogen (TOH) for samples of RDF model mixture I, divided according to the final milling process (Cryomill or UCM), including the corresponding biogenic mass fraction (as calculated by means of the adapted Balance Method), the brighter the colour the lower the biogenic mass fraction (the whole range of colours shown equals ± 10 % of theoretical value of 75.5 m% waf); straight lines indicate the means and range of TOC and TOH

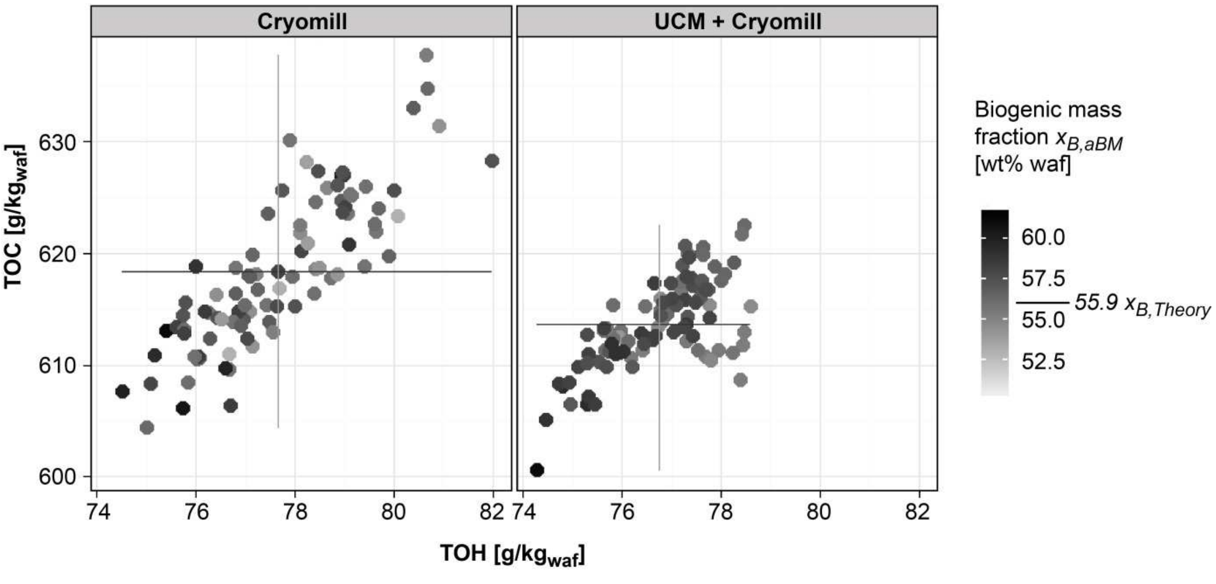

Fig. F.2 Analysis results for total organic carbon (TOC) and total organic hydrogen (TOH) for samples of RDF model mixture II, divided according to the final milling process (Cryomill or UCM), including the corresponding biogenic mass fraction (as calculated by means of the adapted Balance Method), the brighter the colour the lower the biogenic mass fraction (the whole range of colours shown equals± 10 % of theoretical value of 55.9 m% waf); straight lines indicate the means and range of TOC and TOH

Paper V

An alternative method to determine the share of fossil carbon in solid refuse-derived fuels – Validation and comparison with three standardized methods

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Fuel, 2018, 220, 916-930

DOI: 10.1016/j.fuel.2017.12.076

Fuel 220 (2018) 916–930

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

An alternative method to determine the share of fossil carbon in solid refuse-derived fuels – Validation and comparison with three standardized methods

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ARTICLE INFO

Keywords:
Fossil carbon
Biomass content
Refuse-derived fuels
Balance Method
Radiocarbon Method
Selective Dissolution Method

ABSTRACT

Today different types of wastes are used as refuse-derived fuels (RDF) either in waste-to-energy plants or as fuel substitutes in energy-intensive industrial processes. In order to quantify their greenhouse-gas relevance (fossil carbon content), reliable and practical analytical methods are required, which allow differentiation between biogenic and fossil organic carbon. In the present paper, an alternative method to determine the fossil share in RDFs is examined and validated. The so-called “adapted Balance Method” (aBM) is applied to three different RDFs and the results are compared to three standardized methods, namely the Radiocarbon Method (^{14}C-Method), the Selective Dissolution Method (SDM), and the Manual Sorting Method (MS). The aBM is based on the distinctly different elemental composition of water-and-ash-free biogenic and of fossil matter (TOX_{BIO} and TOX_{FOS}). Within the study, these compositional data are derived by manual sorting of the RDFs. The results show that the values obtained by the aBM are in excellent agreement with the results of the ^{14}C-Method (considered as reference method). Mean deviations between the two methods of −0.9 to +1.9% absolute for the share of fossil carbon are found which are statistically insignificant. High trueness and reliability of the aBM can be expected, independent of the RDF type. In contrast, the reliability of the other standardized methods (SDM and MS) appears to strongly depend on the type and composition of the RDF. The results further indicate that the generation of RDF-specific data on TOX_{FOS} is important for the aBM if significant shares of polymers with comparably high oxygen content might be present in the RDF and if low uncertainties of the results (<3% relative) are required. The findings demonstrate that the alternative method has advantages compared to standardized methods with respect to reliability and/or costs.

1. Introduction

The utilization of waste materials as a secondary energy resource is increasing throughout most of the world. Today many wastes and waste fractions are used for energetic applications, a practice supported by national governments and the European Commission [1]. Policies on waste management and emission reductions as well as on the energy market have been established. The implementation of the Kyoto-protocol further stimulates the use of biomass-containing alternative fuels (e.g. Renewable Energy Directive [2], Directive on greenhouse gas emission trading [3], Landfill Directive [4], Chinas national emission trading System [5], Egyptian coal regulations [6]). Refuse-derived fuels (RDF) are being used in both, waste-to-energy plants and as a fuel substitute in energy-intensive industries. RDF in industrial processes are

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Abbreviations: A, ash content; aBM, adapted Balance Method; BM, Balance Method; C&I, commercial & industrial waste; MS, Manual Sorting method; MSW, municipal solid waste; n, number of samples; RDF, refuse-derived fuel; R^2, correlation coefficient; SD, standard deviation; SDM, Selective Dissolution Method; SRF, solid recovered fuel; *TC*, total carbon in the water-free sample; TH, total hydrogen in the water-free sample; TIX_{wf}, total inorganic content of the respective element in the water-free ash; TN, total nitrogen in water-free sample; *TO*, total oxygen in the water-free sample; *TOC*, total organic carbon; *TOH*, total organic hydrogen; *TON*, total organic nitrogen; *TOO*, total organic oxygen; *TOS*, total organic sulphur; TOX_{BIO}, total organic content of the respective element in the water-and-ash-free biogenic matter; TOX_{FOS}, total organic content of the respective element in the water-and-ash-free fossil matter; TOX_{RDF}, total organic content of the respective element in the water-and-ash-free RDF; TS, total sulphur in the water-free sample; TX_{wf}, total content of the respective element in the water-free sample; waf, water-and-ash-free; wf, water-free; wt%, percentage by weight; $x_{B,waf}$, biogenic mass fraction on water-and-ash-free basis; $x_{B,wf}$, biogenic mass fraction on water-free basis; $x_{B,TC}$, share of biogenic carbon; $x_{F,waf}$, fossil mass fraction on water-and-ash-free basis; $x_{F,wf}$, fossil mass fraction on water-free basis; $x_{F,TC}$, share of fossil carbon; ^{14}C-Method, Radiocarbon Method; %abs, absolute percentage; %rel, relative percentage

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https://doi.org/10.1016/j.fuel.2017.12.076
Received 17 August 2017; Received in revised form 15 December 2017; Accepted 18 December 2017

utilized to save costs for fuels, to reduce natural resource consumption and to lower the amount of greenhouse gas emissions associated with the production process [7–9]. Due to the CO_2 emission trading scheme in place in Europe [10], lowering fossil CO_2 emissions by utilizing biomass-containing RDFs is of economic relevance for cement manufacturers. CO_2 emissions stemming from the biogenic matter are regarded as carbon neutral, whereas CO_2 from fossil matter is climate-relevant.

The prime example for the utilization of RDFs is the cement industry, which represents one of the most material-, energy-, and CO_2-intensive industries [11,12]. Within the European Union, more than 34% of thermal energy demand in the production process of cement plants is already provided by RDFs [13]. In some European countries the substitution rate of primary energy carriers has already reached a level of above 50% – e.g. Austria 76.1% (2015) [13], Germany 64.6% (2015) [14], Belgium 60% (2011) [15], Switzerland 53.7% (2014) [16].

Compared to fossil fuels, RDFs exhibit a much broader variation in composition, which strongly depends on the waste utilized for RDF production. Variations can easily appear due to different types of commercial and industrial waste, municipal solid waste, waste collection scheme, or seasonal variations in waste generation. In order to check the quality of solid RDFs with respect to their composition (e.g. calorific value, biomass content, heavy metal contents) and their associated environmental impacts, reliable and practical methods are required. Both, waste management companies generating RDFs and industries utilizing these fuels require tools for reporting and documentation purposes. With respect to the determination of the climate-relevant share in solid RDFs, three methods are described in the standard EN 15440:2011: the Manual Sorting method (MS), the Selective Dissolution Method (SDM), and the Radiocarbon Method (^{14}C-Method) [17]. Furthermore, the Balance Method (BM) has recently been published in the Standard ISO 18466:2016 [18] and has also been recognized by the United Nations Framework Convention on Climate Change (UNFCC) as an approved methodology to determine the fraction of fossil carbon in waste [19]. Table 1 summarizes the available methods with respect to their applicability to solid RDF samples ("prior combustion") and/or to gaseous samples ("post-combustion"). Possible outcomes (parameter) of the methods are listed.

Only the BM and ^{14}C-Method are applicable for a "post-combustion" analysis in the flue gas, whose representative sampling is considerably easier compared to the solid waste material, as the latter is much more heterogeneous. The BM is able to monitor the fossil share in the input of waste-to-energy plants in real-time [20–22]. This is possible by using operating data of the waste-to-energy plant, usually making additional sampling and analysis campaigns redundant. Yet, characterizing the waste and RDFs *prior* to combustion requires solid samples to be analyzed. This is possible by means of the MS, SDM, and ^{14}C-Method and by means of a recently adapted version of the BM (adapted Balance Method). The adapted Balance Method (aBM), which relies on the analysis of the elementary composition of the RDF in the laboratory, has recently been successfully applied to artificially produced RDFs [23,24]. Some methodological and economic benefits compared to the laboratory-based standardized methods (SDM, MS, ^{14}C-Method) have been identified so far; i.a.:

- In contrast to SDM and MS, the uncertainties of the aBM results are statistically derived. They are propagated from the uncertainties of the input parameters [24]. By comparison, the methodological constraints of the SDM (unselective dissolution) can lead to significant inaccuracies which are difficult to detect and quantify [1,25]. As MS is greatly affected by the knowledge of the sorting person and available facts about the waste compounds, the uncertainties of this method can hardly be calculated [26,27]. Despite the high analytical precision of the ^{14}C-Method, uncertainties for this method are introduced by the choice of a ^{14}C-reference value [28,29].
- The aBM is far less time- and cost-intensive than MS or the ^{14}C-Method. The ^{14}C-Method can only be employed by a limited number of laboratories which are equipped with the appropriate instruments (around 64 laboratories in Europe) [30]. Costs for aBM and SDM are expected in a similarly lower range than MS and ^{14}C-Method [24,30].
- High trueness and precision of the aBM was found recently when defined mixtures of biogenic (e.g. cardboard, paper) and fossil materials (plastics) were investigated (deviations from the theoretical value below 4.5%rel; precision of ±3%rel) [23]. This is better than reported for SDM and MS [27,31,32].
- Contrary to most standardized methods, the aBM can provide a range of parameters with reference to the fossil/biogenic content in RDFs, including the key parameters identified in Table 1. Different parameters may be required depending on the interested party (RDF producer, RDF user, authority, etc.) or the reporting obligations (CO_2-emissions, energy produced, etc.). Thus, when choosing a method one needs to be aware of the potential parametrical limitations of these methods. For example, the ^{14}C-Method does not provide information on the biogenic or fossil mass share in the RDF, whereas from sorting (MS) the share of fossil carbon cannot directly be derived. After sorting, additional information or analyses on the carbon content of the different RDF compounds are necessary. The same applies also to the share of biogenic energy, which is only directly derivable from aBM results.

Table 1
Available methods to determine the fossil share in solid refuse-derived fuels; indicating possible output parameter of the methods and the applicability prior to combustion or as a post-combustion method (measurement in the flue gas).

Method applicable	Parameter			
	Fossil/ biogenic **mass** share in wt%	Fossil/biogenic - share of **carbon** in wt% - share of **CO_2-emissions** in wt% - CO_2-emission factor	Ratio of **energy** from fossil/ biogenic sources in %	**Plastic** content in wt%
prior-combustion	MS, SDM, aBM	(MS)[3], SDM[1], ^{14}C-Method[2], aBM	(MS)[3], SDM[1], ^{14}C-Method[2], aBM	MS, SDM, aBM
post-combustion	BM	^{14}C-Method[2], BM	^{14}C-Method[2], BM	BM

aBM – adapted Balance Method, BM – Balance Method (ISO 18466:2016), SDM – Selective Dissolution Method (EN 15440:2011), MS – Manual Sorting (EN 15440:2011), ^{14}C-Method – Radiocarbon Method (EN 15440:2011).

[1] SDM: Carbon/energy-based parameters (share of carbon, CO_2-emission factors, ratio of energy) can only be derived when the carbon/energy content is known in the RDF and in the dissolution residue.

[2] ^{14}C-Method: Energy-based parameters (ratio of energy, energy-related CO_2-emission factor) can only be derived when the energy content is known in the fossil and biogenic matter.

[3] MS: Carbon/energy-based parameters (share of carbon, CO_2-emission factors, ratio of energy) can only be derived when the carbon/energy content is known in the fossil and biogenic matter in each compound.

Finally, during a recent interlaboratory comparison, the SDM was applied to determine the ratio of biogenic carbon in RDF samples (output of mechanical biological plant). The results showed that from the values generated by 12 laboratories only 30–70% were within the tolerance limits of two standard deviations [33]. This rather poor result again indicates that routinely applied methods can be unsatisfactory and that the development of alternative approaches is justified.

The objective of the study presented is to examine the aBM as an alternative method for determining the fossil carbon (and mass) share in solid RDFs. Following the promising results with artificially produced

RDFs [23,24], the validation of the method is to be complemented by investigations with real RDF samples. In particular, the study (1) compares results obtained by the aBM with results when standardized methods are applied, (2) appraises the trueness of the aBM results by matching them with ^{14}C-Method analysis results, (3) examines the robustness of the aBM and of the aBM input parameter, and (4) assesses the applicability of the method compared to standardized methods.

To do so, the method is applied to three different RDFs which are drawn from different plants and are produced from different types of waste. The results obtained are compared to results of the standardized methods, particularly the ^{14}C-Method, SDM, and MS, which are all described in EN 15440:2011. The ^{14}C-Method is regarded as the method with the lowest uncertainty when determining the fossil content in mixed wastes and is used as reference method within this study.

2. Materials and methods

2.1. Adapted Balance Method (aBM)

The aBM relies on the distinctly different elemental composition of biogenic and fossil organic matter on a water-and-ash-free basis (where fossil is understood as materials produced out of crude oil, natural gas or coal).

The necessary input data for the aBM comprise:

(1) data on the chemical composition of the water-and-ash-free RDF (TOX_{RDF}) under investigation (example shown in Fig. 1 – bar chart on the right side). These data are derived from elemental analyses together with ash content determination.

(2) data on the elemental composition of the water-and-ash-free biogenic and fossil organic matter present in the RDF (TOX_{BIO}, TOX_{FOS}) (examples shown in Fig. 1 – bar charts on the left). These data can be collected from literature or from manual sorting together with elemental analyses and ash content determinations for each sorted compound (applying Eq. (3)).

Uncertainties in TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are propagated from the elemental analyses (at least triplicate) and ash content determination (duplicate). By means of balance equations TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are related by the respective mass shares of water-and-ash-free biogenic matter ($\boldsymbol{x_{B,waf}}$) and water-and-ash-free fossil matter ($\boldsymbol{x_{F,waf}}$). $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ are the unknown variables to be determined (illustrated in Fig. 1). The aBM sets up mass balance equations for total organic carbon (*TOC*), total organic hydrogen (*TOH*), total organic nitrogen (*TON*), total organic sulfur (*TOS*), and total organic oxygen (*TOO*). Each balance equation contains the two unknown mass shares $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$. In addition, the sum of $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ is per definition equal to 1. The set of six balance equations (for *TOC*, *TOH*, *TON*, *TOS*, *TOO,* sum of $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$) is overdetermined (more equations than unknowns). A data reconciliation algorithm based on non-linear optimization can be applied to reveal the quantity of the unknown mass fractions (biogenic $\boldsymbol{x_{B,waf}}$, fossil $\boldsymbol{x_{F,waf}}$). During data reconciliation, the uncertainties in TOX_{RDF}, TOX_{BIO}, and TOX_{FOS} are narrowed and the derived values are used to calculate $\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$ including their uncertainties. Algorithm and further details on the aBM are provided in Fellner et al. (2011) [24]. The fossil mass fraction on a dry basis ($\boldsymbol{x_{F,wf}}$) is determined by considering the ash content (*A*) in the RDF:

$$x_{F,wf} = x_{F,waf} * (1-A) \tag{1}$$

whereby $\boldsymbol{x_{F,wf}}$ represents the fossil mass fraction on a dry basis in kg/kg, $\boldsymbol{x_{F,waf}}$ the fossil mass fraction on a water-and-ash free basis in kg/kg and *A* the ash content in kg/kg.

Inserting the results ($\boldsymbol{x_{B,waf}}$ and $\boldsymbol{x_{F,waf}}$) into the *TOC* balance, allows the fraction of fossil carbon as a percentage of the total carbon to be determined ($\boldsymbol{x_{F,TC}}$):

$$x_{F,TC} = ((x_{F,waf} * TOC_{FOS}) * (1-A) + A * TIC)/TC_{RDF,wf} \tag{2}$$

whereby TOC_{FOS} represents the total organic carbon in the water- and ash-free fossil matter in g/kg$_{waf}$ (e.g. from Fig. 1), *TIC* represents the total inorganic carbon in the water-free ash in g/kg$_{wf}$, and $TC_{RDF,wf}$ the total carbon content in the water-free RDF in g/kg$_{wf}$.

If required, the fossil carbon content of the RDF can easily be transferred to fossil carbon dioxide emissions ($CO_{2,fos}$) by considering the respective molar weights (of carbon and of carbon dioxide). In addition to fossil carbon and $CO_{2,fos}$, the ratio of energy originating from biogenic sources can also be derived. To do so, the heating value of the RDF and of the biogenic matter present in the RDF has to be determined via empirical equations (e.g. after Boie, 1957 or Dulong [34,35]) which use the elemental composition of the fuel.

Finally, fossil CO_2-emission factors (*EF*) can be derived, expressing the mass of climate-relevant CO_2 emitted per unit mass or unit energy content of the RDF:

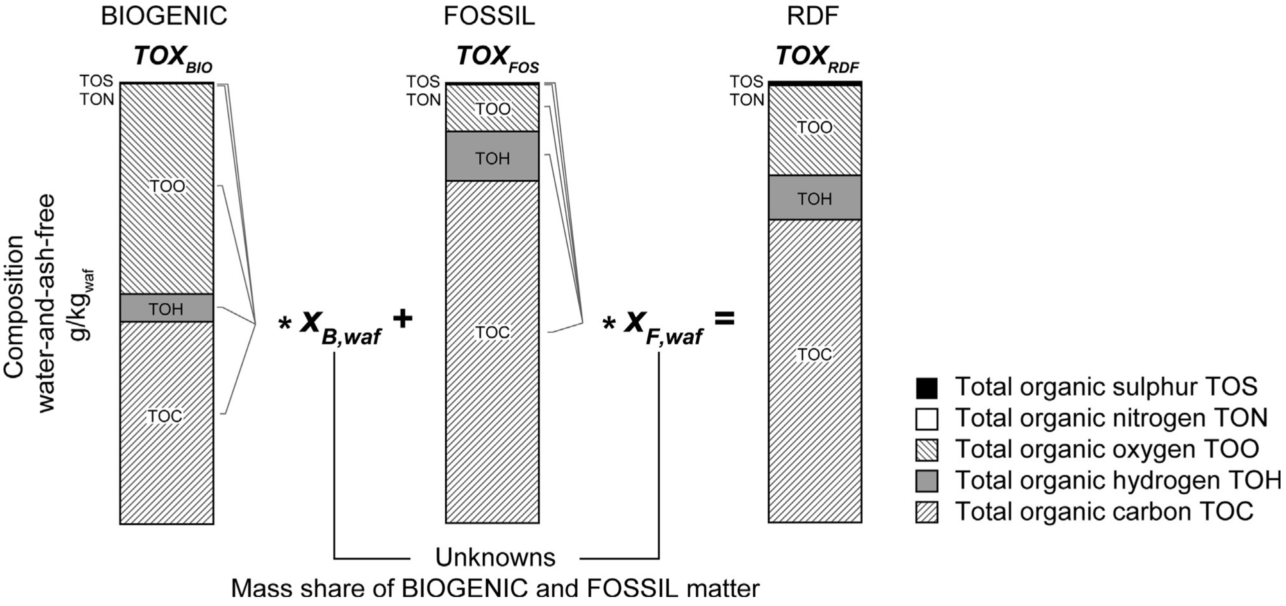

Fig. 1. Schematic illustration of the adapted Balance Method, showing the relation between the elemental composition (on water-and-ash-free reference base) of biogenic organic matter (TOX_{BIO}), fossil organic matter (TOX_{FOS}), and organic matter in the RDF (TOX_{RDF}).

Table 2
Description of refuse-derived fuels investigated and number of samples investigated per method.

	Origin	Remarks on visual appearance	Number of samples investigated[1]			
			^{14}C-Method	aBM	SDM	MS
Paper Reject	Residues discharged after the first process steps of shredding, dissolution, and screening of a recycling paper & board factory	No defined particle size; predominantly cardboard & packaging plastics; partly agglomerated (partly-dissolved cardboard pieces & cellulose fibers attached to plastics); similar appearance of samples	8	15	15	15
RDF C&I	RDF prepared from commercial & industrial waste (light weight fraction, PVC removal)	Particle size: < 50 mm slight differences between samples observable (e.g. different shares of aluminum compounds, plastic threads, paper scraps)	4	8	5	5
RDF MSW + C&I	RDF prepared from pre-processed municipal solid waste and commercial & industrial waste (light weight fraction)	Particle size: < 50 mm differences between samples observable (e.g. different shares and types of foamed plastics, fabrics, plastic threads)	4	8	5	6

RDF – refuse-derived fuel, C&I – commercial and industrial waste, MSW – municipal solid waste.

[1] Samples of 5–10 kg are drawn daily over a period of 7–15 days (see details in Supplementary material).

$$EF \text{ per unit mass in } \mathrm{kg_{CO_{2,fos}}/t_{RDF}} = TC_{RDF,wf} * x_{F,TC} * M_{CO2}/M_C \tag{3}$$

$$EF \text{ per unit energy in } \mathrm{kg_{CO_{2,fos}}/GJ_{RDF}} = (TC_{RDF,wf} * x_{F,TC} * M_{CO2}/M_C)/LHV_{RDF} \tag{4}$$

whereby LHV_{RDF} is the lower heating value of the RDF in GJ/t and M_{CO2} and M_C are the molar weights of CO_2 and carbon respectively in g/mol.

2.2. Samples and sample preparation

Three different types of solid RDFs are investigated in the study presented:

- Residues of a pulp and paper factory (**Paper Reject**)
- RDF prepared from commercial & industrial waste (**RDF C&I**)
- RDF prepared from pre-processed municipal solid waste and commercial & industrial waste (**RDF MSW + C&I**)

Details on the RDF types are provided in Table 2. Samples are drawn over a period of 15 days (Paper Reject) and 8 days (RDF C&I and RDF MSW + C&I). Each sample comprises 5–10 kg of dry matter (which corresponds to around 60 L). Samples of all three RDFs are analyzed by means of the ^{14}C-Method, aBM, SDM, and MS. Due to time and budget constraints, only the aBM could be applied to all drawn samples. The presented comparisons between methods are all based on the same respective samples (e.g. the same 8 Paper Reject samples are considered when ^{14}C-method is compared to aBM).

For the elemental analysis (necessary to determine the elemental composition of the RDF samples TOX_{RDF}) a final sample size of only a few centigrams is required (10–40 mg for single determination). Thus, an elaborate sample preparation procedure (comminution, reduction) is necessary to ensure reliable analytical results. The procedure of sample preparation applied within the study is shown in Fig. 2. It is carried out in agreement with EN 15413:2011 and based on findings in previous works of the authors [23].

Around 4 kg per sample are milled down to a grain size of < 4 mm by means of a cutting mill (Essa CM 1000). The sample < 4 mm is reduced to around 500 g using a riffle divider and further milled down to < 1 mm (by cutting mill Retsch SM 2000). After another splitting step using a riffle divider, one part of the 1 mm sample is set aside to apply the Selective Dissolution Method (Section 2.5.1). Another part (around 60 g) is further treated with an ultra-centrifugal mill (Retsch ZM 200) to receive a sample with a final grain size of < 0.5 mm. A rotary divider (Retsch, PT 100) is applied and, finally, 15 g are comminuted by a cryogenic mixer mill (Cryomill, Retsch) whose milling bin is cooled by liquid nitrogen. This final preparation step is done in order to facilitate the proper grinding of the cellulose fibers present in the sample. Despite the lack of a Cryomill sieve, a further grain size reduction (down to < 0.2 mm) can be expected by the last milling step (confirmed in [23]). The finely ground analysis sample is used for analyses necessary for the aBM and the ^{14}C-Method.

2.3. Determination of the elemental composition of biogenic and fossil organic matter present in RDF (Manual Sorting)

In order to examine the robustness and validity of input parameters of the adapted Balance Method, new input data on the elemental composition of the water-and-ash-free biogenic and fossil matter (TOX_{BIO} and TOX_{FOS}) are generated from the samples investigated. This is done by sorting samples of all three RDF types and analyzing the biogenic and fossil matter in the RDFs. The so generated data for the RDFs can then be compared with each other and to literature-derived values (e.g. [24]). This is to appraise the variability and universality of the aBM-input parameter (TOX_{BIO} and TOX_{FOS}).

Around 4 kg per RDF are sorted into 9 categories: *cardboard/paper*, *wood*, *plastic*, *textiles*, *organic*, *rubber*, *composite & impure materials*, *fine fraction < 2 cm, metals & inert*. In order to estimate TOX_{BIO} and TOX_{FOS} present in the RDF, a rough mass share of biogenic and fossil matter is appraised for each sorted compound. The organic parts in *cardboard/paper, wood*, and *organic* are generally regarded as biogenic, and *plastics* are expected to be produced from fossil sources. Yet, some "contaminations" are expected in these constituents due to e.g. partly-dissolved paper fibers attached to plastics or undetectable impregnated cardboard. For the other compounds, the appraisal on the biogenic and fossil share is even more challenging, particularly for *textiles* (mix of natural and synthetic fibers), *rubber* (mix of natural and synthetic rubber), *composite & impure materials* (mix of cardboard, different polymers, etc.), and the *fine fraction < 2 cm* (mix of generally all compounds mentioned).

Thus, the appraisal on the rough mass share of biogenic and fossil matter in the sorted compounds is carried out by

(1) a preliminary evaluation by means of the aBM, using analyses of the sorted compounds (TOC, TOH, TOO, TON, and TOS determined according to Eq. (3)) and literature data for TOX_{BIO} and TOX_{FOS} as input values,
(2) applying the Selective Dissolution Method (see Section 2.5.1) for selected compounds, and by
(3) conducting Radiocarbon analyses (see Section 2.5.2) for selected compounds

For (1), the following assumptions are made:

- Natural *textiles* are mainly composed of cellulose (90 wt%) and wool (10 wt%) (based on Kost, 2001 [34]).
- Synthetic *textiles* are composed of polyamide (30 wt%), polyester (49 wt%), polyacrylonitrile (15 wt%) and polypropylene (6 wt%) (based on Kost, 2001 [34]).
- Compounds of *rubber* and *organic* are negligible (shares of below 1 wt% are found in the RDFs by manual sorting).
- *Composite & impure materials* mainly contain cardboard and plastics, whereby the elemental composition of these compounds is assumed to correspond to the average elemental composition found for paper

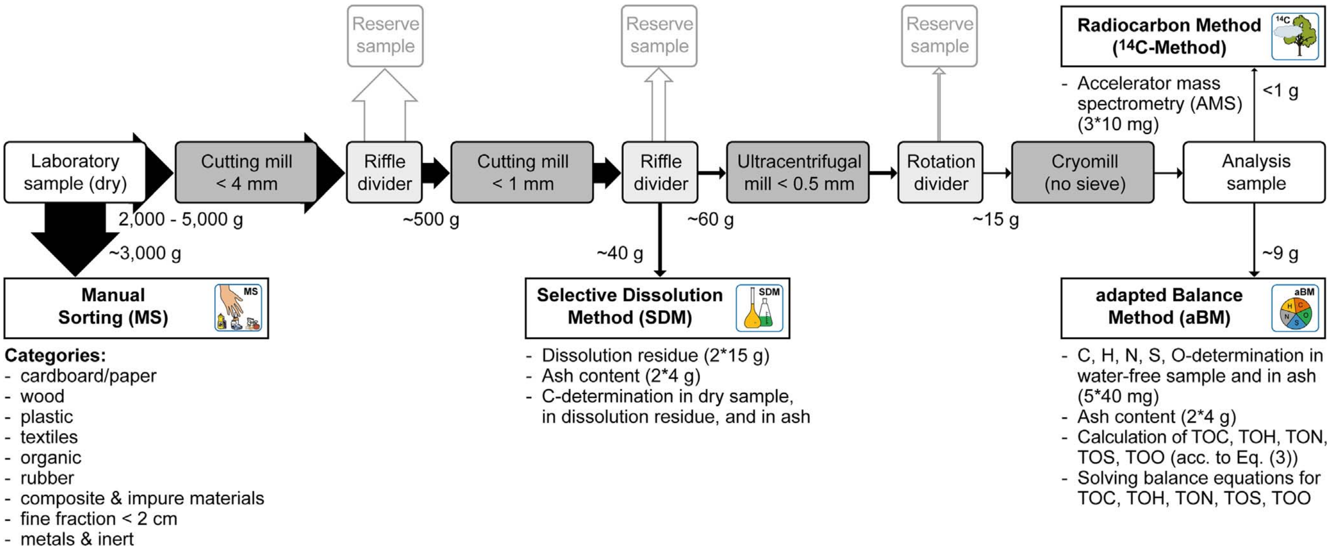

Fig. 2. Sample preparation procedure and analysis methods applied (it has to be noticed that the four analysis methods have not been applied to all RDF samples taken).

and mixed plastics in municipal solid waste in Kost (2001) [34] (values are provided in Supplementary material Table D.2).

- *Metals & inert* compounds are sorted at 100% sorting precision, thus they are not relevant for the investigations and are not further considered.

Additional sortings of the *fine fraction < 2 cm* are conducted in order to appraise the rough composition of this compound. In total around 400 g of the fine fraction of Paper Reject (from different samples) and around 140 g of RDF C&I and RDF MSW + C&I (from different samples) are sorted into the same categories as for the primary sorting. It is assumed that the average sorting results of the *fine fraction < 2 cm* apply to the fine fractions of all samples of the same RDF. An overall composition of the RDFs in terms of compounds is calculated, taking the results of the primary sorting and the fine fraction sorting into account (the sorting results are provided in the Supplementary material Table C.1).

Table 3 provides the biogenic mass share considered in each sorted compound. These shares are used together with values for *TOX* of each compound (*TOC*, *TOH*, *TOO*, *TON*, and *TOS*) to appraise typical ranges for TOX_{BIO} and TOX_{FOS} in the three RDF types. *TOX* values are used from own analyses results for *cardboard/paper*, *wood* and *plastic*; values for natural and synthetic textiles as well as for cardboard/paper and plastics in the composite compounds are based on Kost (2001) [34] (values in Supplementary material Table D.2). This procedure for deriving ranges for TOX_{BIO} and TOX_{FOS} is confirmed to be appropriate in Schwarzböck et al. (2017) [36].

The definition of TOX_{BIO} and TOX_{FOS} for each RDF is generally required for the application of aBM but needs to be determined only once for each type of RDF and can then be utilized for this type of RDF, unless major changes in the composition of biogenic and fossil organic matter are expected (e.g. change of waste collection scheme for certain plastics).

2.4. Chemical analyses

2.4.1. Water content and ash content

The water content of each laboratory sample is determined by drying the unprepared sample at 105 °C for at least 24 h (start of drying directly after the delivery to the laboratory). For each analysis sample the ash content is analyzed in duplicate and in accordance with EN 15403:2011 [37]. To this end, 4 g material of each sample are dried at 105 °C for 24 h before being combusted at 350 °C in a muffle furnace for one hour and at 550 °C for four hours under air injection. All weights of the sample (before drying, after drying, after ignition) are recorded (Sartorius Entris) in order to calculate the ash content.

2.4.2. Elemental analysis and determination of TOX_{RDF} (for the adapted Balance Method)

The water-free (dried at 105 °C for 24 h) analysis samples are analyzed for the elemental composition using an Elementar Vario Macro instrument (Elementar Analysensysteme GmbH, Langenselbold,

Table 3
Appraised biogenic share in the different sorted compounds of the RDFs.

	Compound	Biogenic share in wt%,wf			
		Paper Reject	RDF C&I	RDF MSW + C&I	acc. to EN 15440:2011[1]
1	*Cardboard/paper*	93	93	92	100
2	*Wood*	99	99	99	100
3	*Plastic*	5	4	8	0
4	*Textiles*	65	45	45	50
5	*Organic*	disregarded (< 1 wt%)	disregarded (< 1 wt%)	disregarded (< 1 wt%)	100
6	*Rubber*	disregarded (< 1 wt%)	disregarded (< 1 wt%)	disregarded (< 1 wt%)	80
7	*Composite and impure materials*	34	58	46	–
8	*Fine fraction < 2 cm*	60	45	38	50
9	*Metals & inert*	0	0	0	0

RDF – refuse-derived fuel, C&I – commercial and industrial waste, MSW – municipal solid waste, wt%,wf – weight percent on water-free basis.

[1] Information given in EN 15440:2011 on the biogenic shares is relevant for Manual Sorting (MS) only and is not considered for the adapted Balance Method (aBM).

Germany). At a combustion temperature of 1150 °C, the total carbon *TC*, total hydrogen *TH*, total nitrogen *TN*, and total sulfur *TS* content is determined according to DIN 51732:2014 [38]. Five measurements per sample are carried out, each of them comprising around 40 mg of sample material.

The total oxygen content *TO* is determined using an Elementar Vario EL instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). The analysis is based on the pyrolysis of the sample at 1150 °C and the conversion of all oxygen into carbon monoxide. For the analysis of *TO*, sample specimens of only 4 mg are used and 7 measurements per sample are conducted (due to limitations of the analyzer, allowing maximum 2 mg oxygen absolute).

Each analytical sequence is accompanied by verification samples and blanks to assure accuracy of the measurement result and to control disturbed baselines. Calibration correction factors are determined with set control limits of 5% (for C, N, S) or 10% (for H, O) (according to DIN 51732:2014 and manufacturer information; see also Supplementary material Table K.1 and Table K.2).

Each RDF-analysis sample is analyzed. In addition, the ignition residue of each test sample treated in the muffle oven is analyzed for its elemental composition to appraise the total inorganic content of carbon *TIC*, hydrogen *TIH*, nitrogen *TIN*, sulfur *TIS* and oxygen *TIO*. The values measured are converted according to Eq. (3) in order to determine the elemental composition on a water-and-ash-free reference basis.

$$TOX_{RDF} = (TX_{wf} - TIX_{wf} * A)/(1-A) \quad (5)$$

whereby TOX_{RDF} represents the total organic content of the respective element (*X…C, H, N, S, O*) in the water-and-ash-free sample in g/kg$_{\mathrm{waf}}$, TX_{wf} the total content of the respective element in the water-free sample in g/kg$_{\mathrm{wf}}$, TIX_{wf} the total inorganic content of the respective element in the water-free ash in g/kg$_{\mathrm{wf}}$, and *A* the ash content on a water-free basis in kg/kg$_{\mathrm{wf}}$. The values obtained thereby for total organic carbon *TOC*, total organic hydrogen *TOH*, total organic nitrogen *TON*, total organic sulfur *TOS*, and total organic oxygen *TOO* are summarized as TOX_{RDF}. They represent the input data required for the adapted Balance Method (additionally to TOX_{BIO}, TOX_{FOS}; see Section 2.3) (results for TOX_{RDF} are given in Supplementary material Table D.1).

2.5. Application of other methods (alternatively to adapted Balance Method)

In order to compare the results obtained by the aBM to results of standardized methods, the Selective Dissolution Method (SDM) and the Radiocarbon Method (^{14}C-Method) are applied according to Standard EN 15440:2011 [17]. Additionally, the sorting results can be used to derive the fossil mass fraction based on the Manual Sorting method (MS) (also described in EN 15440:2011).

2.5.1. Selective Dissolution Method (SDM)

The Selective Dissolution Method (SDM) relies on the assumption that biogenic components will selectively dissolve and oxidize when concentrated sulphuric acid and hydrogen peroxide are applied. The fossil components are expected to remain in the dissolution residue.

Various materials do not entirely act in accordance with this assumption of selective dissolution and can introduce errors to the results of the SDM [1,17,25,39]. For example, polymers originating from fossil fuel containing amino groups are almost entirely dissolved (up to 100%) when applying the SDM (e.g. nylon or polyurethane). For viscose and wool, both in large parts biomass, the biogenic content is reported to be underestimated by SDM up to 40%. Other polymers which originate from biomass but are re-engineered at molecular level (e.g. rubber) can be non-selectively dissolved in the range of 15–100% [1]. Thus, when high (unknown) shares of materials are present which do not react according to the assumptions of the SDM, the reliability of the results of the SDM is rather limited.

For the investigations presented, the SDM is applied as described in EN 15440:2011. Threefold test portions are used (15 g; double determination) in order to account for the rather heterogeneous samples (particles sizes of < 1 mm are used as stipulated in EN 15440:2011). The carbon content is determined in the < 1 mm sample, in the dissolution residue, and in the ignition residue using an Elementar Vario Macro instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). Equations are provided in EN 15440:2011 and in Supplementary material B.

In total, 25 samples are analyzed according to the SDM (15 Paper Reject-, 5 RDF C&I-, 5 RDF MSW + C&I-samples).

The uncertainty of the results is estimated from the duplicate determination (repeatability) and from values for the reproducibility of the method given in Table F.1.4 in EN 15440:2011.

2.5.2. Radiocarbon Method (^{14}C-Method)

The Radiocarbon Method (^{14}C-Method) is based on different ratios of carbon isotopes ^{14}C and ^{12}C in biogenic and fossil materials. F^{14}C is defined as ^{14}C/^{12}C ratio of a sample related to the level of this isotopic ratio for the reference year 1950 [40]. Consequently, biogenic materials show a value of ∼1, whereas ^{14}C is extinct in fossil materials corresponding to an F^{14}C value of 0. In order to determine the fraction of biogenic carbon, it is necessary to know the F^{14}C values in the sample and in pure biogenic materials present in the waste (i.e. the F^{14}C reference value). The latter depends on the type of biomass and on the period of growth, and dominates the uncertainty of the method. This is due to the changing radiocarbon content in the atmosphere in the past century caused by nuclear weapon tests [28,29,39,41]. However, the ^{14}C-Method is regarded as a reliable method for the determination of the biomass content in secondary fuels as it has the lowest analytical uncertainty (accelerator mass spectrometry AMS < 3–7% relative [29,42–44]). Liquid Scintillation Counting (LSC) can also be applied to analyze the ^{14}C content [25,41].

Within the study presented, radiocarbon analyses according to EN 15440:2011 using AMS are conducted ([45]) for the finely ground analysis samples (see Section 2.2). A triplicate determination with each 10 mg is chosen. In total, 16 samples are analyzed (8 Paper Reject-, 4 RDF C&I-, 4 RDF MSW + C&I-samples). F^{14}C reference values applied within the study are provided in Table 5. F^{14}C reference values for the ^{14}C content of pure biogenic matter in RDF C&I and RDF MSW + C&I are estimated according to Mohn et al. (2008) [29] (see Table 4). Approximate shares of cardboard, wood, textiles, and fresh biomass (< 0.5 wt%) in the biogenic fraction are used from sorting results and their respective biogenic shares (given in Table 3) are considered. ^{14}C analyses of pure cardboard/paper sorted out of the Paper Reject samples are used to derive the F^{14}C reference value for this RDF type. Thereby, the uncertainty of the F^{14}C reference value for ^{14}C-Method could be reduced as the cardboard/paper represents the major constituent in the biogenic matter of Paper Reject (around 92 wt%). A F^{14}C

Table 4
^{14}C content (given as mean and standard uncertainty) of biomass compounds used as reference value within the study ([29], value for Cardboard/paper in Paper Reject analytically determined).

^{14}C content F^{14}C$_{\mathrm{bio}}$ [pMC]	Cardboard/paper	Wood	Textiles	Fresh biomass
Paper Reject	1.076 ± 0.020	1.150 ± 0.098	1.058 ± 0.036	1.015 ± 0.015
RDF C&I, RDF MSW + C&I	1.101 ± 0.024	1.150 ± 0.098	1.058 ± 0.036	1.015 ± 0.015

Table 5
^{14}C content (given as mean and standard uncertainty) of biomass in RDFs used as reference value within the study (calculated according to [29] and based on own analyses for Paper Reject).

	Paper Reject	RDF C&I	RDF MSW + C&I
^{14}C content $F^{14}C_{bio}$ [pMC]	1.080 ± 0.024	1.101 ± 0.038	1.088 ± 0.038

reference value of 1.080 ± 0.024 is determined for Paper Reject, indicating that the wood used for the cardboard/paper in this RDF has grown in more recent years than calculations by Mohn et al. (2008) [28] and Fellner et al. (2009) [29] would suggest. Equations to calculate the share of fossil carbon ($x_{F,TC}$) are provided in Mohn et al. (2008), in EN 15440:2011 and in Supplementary material B.

The uncertainty of the radiocarbon analysis results mainly from the ^{14}C reference value chosen (estimated as 3%rel). The heterogeneity of the rather small test specimens of only 10 mg accounts for 2–3%rel uncertainty (determined by triplicate determination).

Analyses by means of ^{14}C-Method reveal information on the fossil or biogenic carbon found in the RDF ($x_{F,TC}$, $x_{B,TC}$), while no information on the biogenic or fossil mass fraction ($x_{F,wf}$, $x_{B,wf}$) is ascertainable with this method. In order to still be able to compare the mass-related parameter to results of other methods as well, a conversion factor (derived from aBM results) is used within this study. An uncertainty of the conversion factor of 3%rel is considered.

2.5.3. Manual sorting (MS)

The samples are sorted into 9 categories (same sorting as described in Section 2.3): *cardboard/paper*, *wood*, *plastic*, *textiles*, *organic*, *rubber*, *composite & impure materials*, *fine fraction < 2 cm*, *metals & inert*. The *fine fraction < 2 cm* is represented by 24 wt% (RDF MSW + C&I) to 65 wt% (Paper Reject) of the total mass.

A biogenic share is assigned to each sorted compound according to EN 15440:2011 (values given in Table 3). The fossil mass fraction in the RDF can thereby be estimated. For the appraisal of the fossil carbon share in the samples, the carbon content of the fossil and biogenic matter in each compound is required. Within this study, values published in Kost (2001) [34] are used together with theoretical considerations (e.g. chemical structure of cellulose, polyethylene).

Due to the usually small or compressed constituent particles in RDF, a visual recognition is challenging and manual sorting is only attainable with great effort. At the same time, the uncertainty can hardly be quantified; also due to the strong dependence on a person's subjective categorization of particles. Within the study, the uncertainty of the manual sorting is estimated based on evaluations by aBM, by SDM, and ^{14}C-Method applied to selected sorted compounds (see Table 3 and Supplementary material B).

2.6. Statistical tests

Statistical tests are carried out in order to evaluate differences between data sets regarding their central tendencies (means) and variances. All tests are carried out using the program R (Version 3.0.2) [46] or DataLab (Version 3.530) [47]. In particular, the following tests are applied:

- Shapiro test: Test for normal distribution (required to decide which subsequent statistical test, e.g. t-Test, Wilcoxon rank sum test, is to be applied)
- 2-sample F-test: Test for homogeneity of variances between data sets; applied when there is no evidence that the data sets are not normally distributed
- Levene test: Test for homogeneity of variances between data sets; applied when there is evidence that the data sets are not normally distributed
- Paired *t*-test: Test for differences in means; applied when there is no indication that the differences between the data sets are not normally distributed
- Wilcoxon rank sum test (non-parametric test): Test for differences in means; applied when there is evidence that the differences between the data sets are not normally distributed

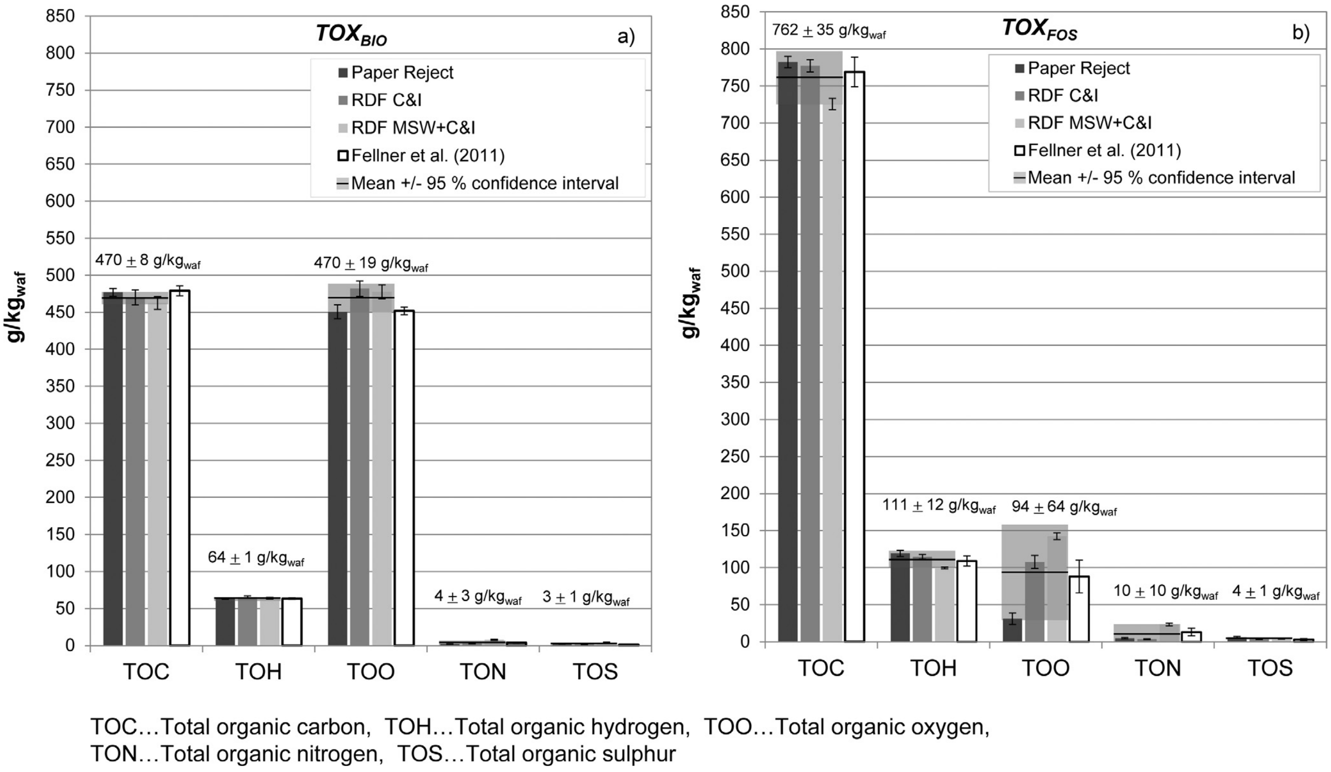

Fig. 3. Elemental composition of water-and-ash-free biogenic and fossil organic matter (TOX_{BIO}, TOX_{FOS}) present in RDFs investigated and compared to generic values given in Fellner et al. (2011) [24]. Values given indicate the means and 95% confidence intervals, taking data sets of the RDFs investigated into account.

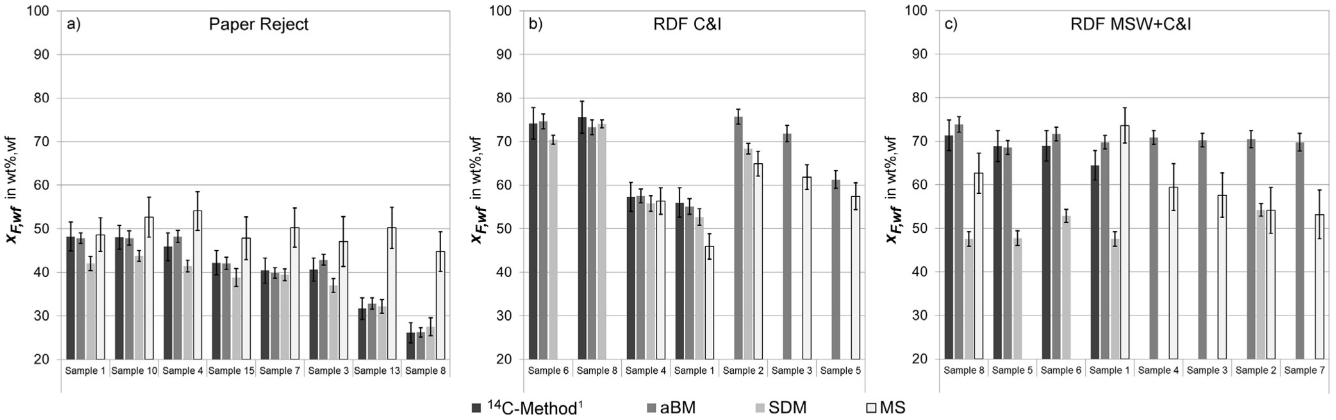

Fig. 4. Fossil mass fraction on water-free basis $x_{F,wf}$ determined for three RDF types by means of four different methods; error bars represent ± one standard deviation (note: not all samples could be analyzed by all methods due to time and budget constraints, see Table 2).

^{1}^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

For all statistical tests a level of significance of 0.05 is used.

3. Results and discussion

3.1. Elemental composition of biogenic and fossil organic matter (TOX_{BIO}, TOX_{FOS})

The aBM requires data on TOX_{RDF} and on TOX_{BIO} and TOX_{FOS} present in the RDF sample. Within this study, TOX_{BIO}, TOX_{FOS} are determined by manual sorting and elemental analyses for each RDF type (see Section 2.3). Fig. 3 shows that the results obtained for the different RDFs are in a close range. They are similar to values given in Fellner et al. (2011) [24], where typical values for RDF processed from household and commercial waste are collected. *TOC* and *TOH* show a small variability with coefficient of variation < 10%rel (in fossil organic matter) and < 2%rel (in biogenic organic matter). The deviation from the literature values is below 2%rel for *TOC* and *TOH*. The most variable value is the *TOO* in the fossil organic matter, which varies by around 60%rel (deviation from literature values of 7%rel). This indicates a high dependence of the *TOO* content on the present polymer type in the RDF. A higher *TOO* content found in the fossil organic matter of RDF MSW + C&I signals higher shares of polyamide, polyethylene terephthalate, or polyurethane. In contrast, the Paper Reject can be estimated to contain high shares of polyethylene and polypropylene, which are characterized by a low or even zero oxygen content (and higher carbon and hydrogen content) compared to other polymers.

The composition of the biogenic matter tends to less variability compared to the composition of the fossil matter. The values derived for *TOC*, *TOH*, and *TOO* vary only by up to 4%rel (coefficient of variation) and deviate from the literature values below 4%rel. This confirms findings in Schwarzböck et al. (2017) [48] that the elemental composition of water-and-ash-free biogenic matter in wastes is almost independent of the shares of the different biogenic compounds (e.g. wood, paper, food waste, textiles). A probable range for the elemental composition of water-and-ash-free biogenic organic matter can thus be easily derived, also without extensive sorting analyses. Recent investigations even indicate that there are typical values for TOX_{BIO} and TOX_{FOS} depending on the RDF type [36]. Thus, the initial workload for sorting analyses could be saved at all, once there is a database available.

3.2. Fossil mass fraction and share of fossil carbon in the RDF samples determined by different methods

3.2.1. Comparison in terms of variance and differences between methods

The fossil mass fraction ($x_{F,wf}$) and the share of fossil carbon ($x_{F,TC}$) in the RDF samples is calculated by means of aBM and three standardized methods as described in Sections 2.1 and 2.5. Generally, the carbon-related figure ($x_{F,TC}$) – unlike the mass-related parameter ($x_{F,wf}$) – is less dependent on the ash content in the RDF and is directly related to the heating value. As visible from Fig. 6 to Fig. 8, $x_{F,TC}$ is at least 6% abs higher than $x_{F,wf}$ due to the higher carbon content in fossil matter compared to biogenic matter. Assuming that all carbon (*TC*) in the RDF is oxidized to carbon dioxide (CO_2) during the combustion, $x_{F,TC}$ also

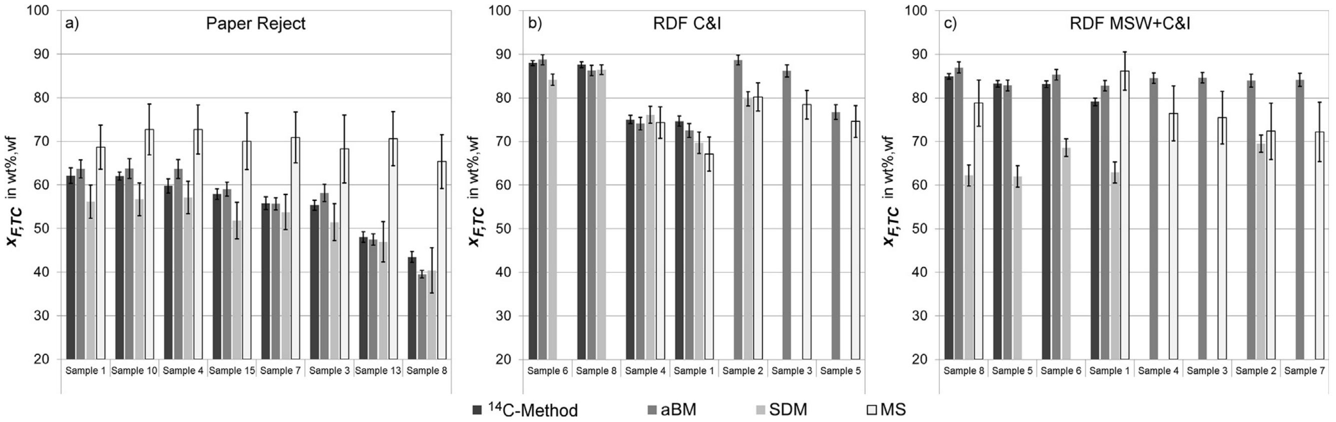

Fig. 5. Share of fossil carbon $x_{F,TC}$ determined for three RDF types by means of four different methods; error bars represent ± one standard deviation (note: not all samples could be analyzed by all methods due to time and budget constraints, see Table 2).

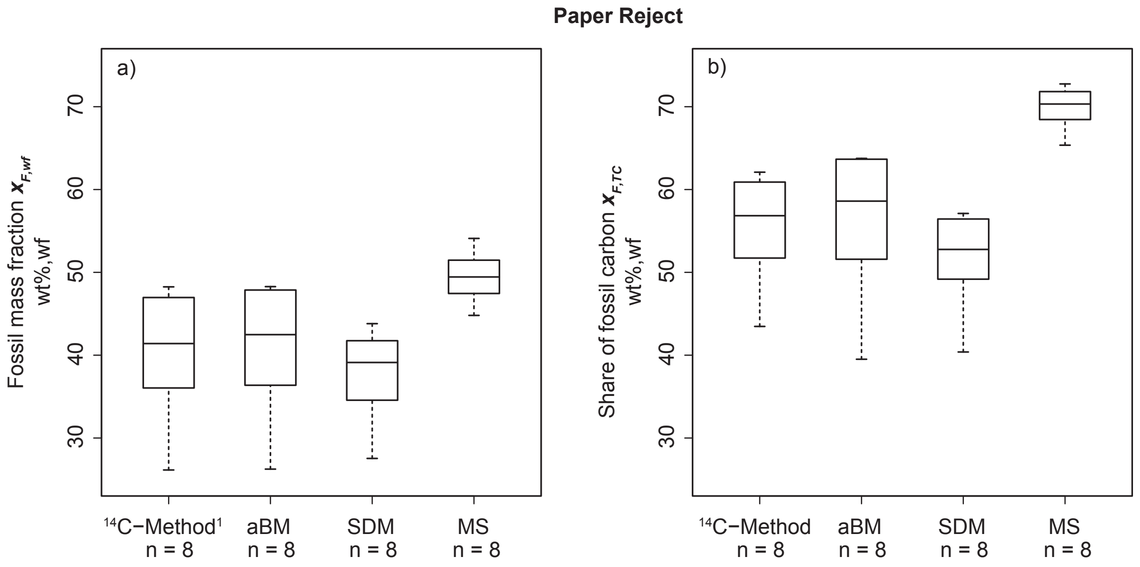

Fig. 6. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in Paper Reject determined by four different methods.
^{1} ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

represents the share of fossil CO_2 related to the total CO_2 emitted during incineration.

Paper Reject (Fig. 4a), Fig. 5a), and Fig. 6):

In the Paper Reject samples, the aBM reveals fractions of fossil matter $x_{F,wf}$ (represented mainly by plastics) between 26 and 48 wt% and shares of fossil carbon $x_{F,TC}$ between 39 and 64 wt%. An average ash content of 7 wt% in the Paper Reject results in $x_{F,TC}$ being 12 to 18%abs above $x_{F,wf}$ (Fig. 4 and Fig. 5).

The aBM delivers results in a similar range as the ^{14}C-Method ($x_{F,wf}$ 26–48 wt% and $x_{F,TC}$ 43–62 wt%). The **variance** between the samples for the aBM and ^{14}C-Method cannot be observed to be significantly different (based on a 2-sample F-test). Standard deviations of 8.7%abs are found for $x_{F,TC}$-values generated by aBM and 6.7%abs for values of ^{14}C-Method, indicating a similar dispersion of the method's results (visible from Fig. 6).

Fig. 6 shows that the results for SDM applied to Paper Reject are in a slightly smaller range than for the ^{14}C-Method and aBM (standard deviation of 5.7%abs for SDM). A significant difference in variance of the SDM-sample results compared to ^{14}C-Method and aBM can, however, not be observed (based on 2-sample F-tests). Different findings for Paper Reject samples evaluated based on MS: Significantly smaller dispersion is found (standard deviation $x_{F,TC}$ of 2.5%abs) compared to ^{14}C-Method-, aBM-, and SDM-results. It is assumed that differences in the composition of the samples are barely detectable by MS.

Comparing the mean values obtained – $x_{F,wf}$ and $x_{F,TC}$ – by aBM and ^{14}C-Method for Paper Reject, no significant **differences** are found between the two methods (based on statistical tests, indicated in Table 6 by significance codes). The deviations in results of the aBM and the ^{14}C-Method are in the range of −3.9 to +4.0 wt%abs ($x_{F,TC}$). Mean deviations of +0.6 wt%abs for $x_{F,wf}$ and +0.8 wt%abs for $x_{F,TC}$ are found (Table 6). The ranges of uncertainty of the two approaches overlap each other for all 8 samples compared, with the exception of two samples when $x_{F,TC}$ is regarded (Sample 4 and Sample 8 in Fig. 5a)).

Based on statistical tests, the results of SDM compared to aBM and ^{14}C-Method differ significantly. With a deviation between −6.1 wt%abs and −1.2 wt%abs ($x_{F,TC}$) from ^{14}C-Method, the SDM appears to underrate the fossil share in the Paper Reject by trend. The ranges of uncertainty between SDM and ^{14}C-Method overlap for 5 of 8 samples (Fig. 5a)). This could be explained by the fact that glue residues which are found in the samples might represent soluble polymers (e.g. based on amino groups) and are misleadingly declared biogenic by the SDM (but actually are of fossil origin). A mean deviation of −2.6 wt%abs ($x_{F,wf}$) and −3.8 wt%abs ($x_{F,TC}$), however, can be regarded as in rather good agreement with the ^{14}C-Method when the uncertainties of the methods and results found in other studies are taken into consideration [31,33]. For example, Muir et al. (2015) [25] reported 30–35 wt%abs underestimation by

Table 6
Results for Paper Reject: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	40.4 ± 1.0[1]	–		55.6 ± 0.5	–	
aBM	41.0 ± 0.5	+0.6	(–)	56.4 ± 0.7	+0.8	(–)
SDM	37.8 ± 0.6	−2.6	(*)	51.8 ± 1.5	−3.8	(***)
MS	49.5 ± 1.3	+9.1	(***)	69.9 ± 1.6	+14.3	(***)

Significance codes: (–) p > .1; () p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 6), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.

[1] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

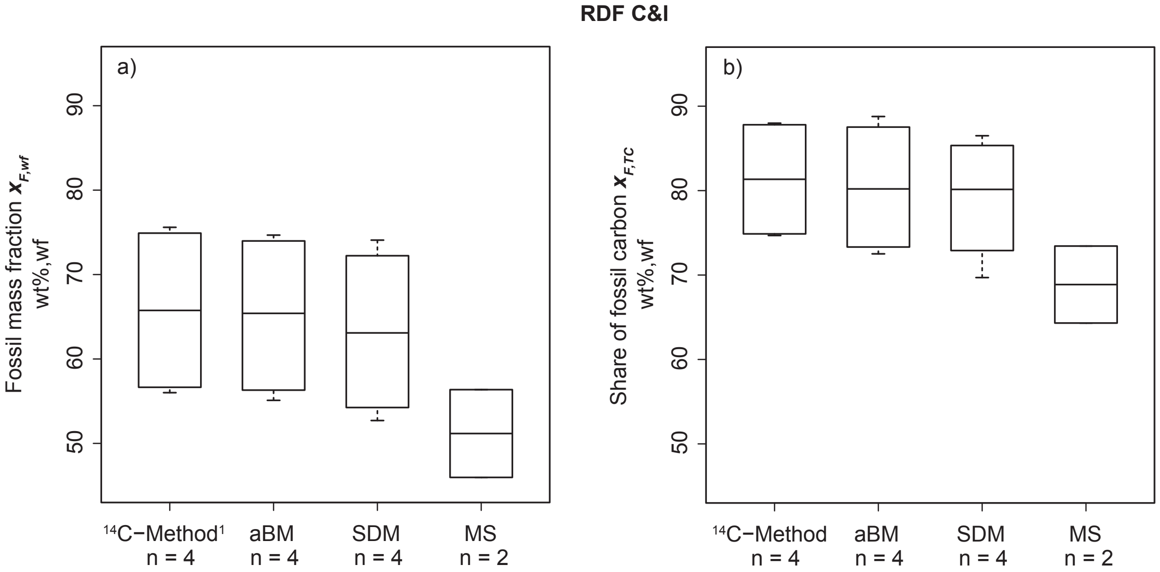

Fig. 7. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in RDF C&I determined by four different methods.
$^{1\,14}$C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

SDM compared to ^{14}C-Method when investigating the fossil energy share in MSW samples.

MS appears to significantly overestimate the fossil mass fraction $x_{F,wf}$ in the Paper Reject samples. Results of 0.4–19 wt%abs above ^{14}C-Method (mean deviation of +9.1 wt%abs) are found. The uncertainty ranges overlap each other for 4 of 8 samples (Fig. 4a)). Even higher differences between the MS results and the other methods can be observed when $x_{F,TC}$ is considered (Fig. 5a)). A mean deviation of +14.3 wt%abs compared to ^{14}C-results (and aBM results) is detected (see Table 6). A statistical test confirms a significant difference between the MS and ^{14}C-Method for Paper Reject samples (paired 2 sample *t*-test; significance indicated by codes in Table 6). This overestimation of the fossil fraction by MS can be ascribed to the following three factors: (1) The sorting category *fine fraction < 2 cm* is found to represent almost 65 wt% in the Paper Reject samples. According to EN 15440:2011, the fossil share in this category can be estimated to be 50 wt%. Based on further sorting and analyses (see Section 2.3), however, only 40 wt% of the *fine fraction < 2 cm* is estimated to actually be of fossil origin. This implies an approximately 5–6%abs systematic overestimation when adhering to the assumptions in EN 15440:2011. (2) The fact that the mass-based parameter ($x_{F,wf}$) is in better agreement with the other methods than the carbon-based figure ($x_{F,TC}$) indicates that inaccuracies are introduced by the utilization of literature values to derive the fossil carbon content from the manual sorting results (Supplementary material B). The carbon content considered in biogenic matter (TOC_{BIO}) as estimated from literature values is found to be almost 9%abs (90 $gC_{bio}/kg_{waf,bio}$) lower (allegedly underestimated) than the TOC_{BIO} determined by analyses. Together with the inaccuracy from (1), this coincides with the mean deviation of MS results from ^{14}C-Method results (+14 wt%abs). (3) Partly-dissolved cardboard pieces and cellulose fibers attached to plastics lead to difficulties in manually separating these materials. This factor presumably contributed to an overestimation of the plastics compound during sorting. Only extensive additional investigations can provide estimates on this error. Appraisals within this study reveal that the sorted plastics compound contains around 5 wt% of biogenic particles (Table 3).

It can be estimated from the aBM results that the fossil mass fraction in the reject of the paper and board factory considered is around 38%wt (on a dry basis) and can vary ±7 wt%abs. The share of fossil carbon is expected to be 54 wt% with a variability of ±8 wt%abs (standard deviation between sample results). Thus, around 54 wt% of the CO_2 emissions originating from the combustion of the Paper Reject would need to be counted as climate-relevant. These results are derived from aBM analyses of all 15 Paper Reject samples (only 8 are shown in Fig. 4a) and Fig. 5a) as for the other 7 no other method than aBM is applied; results of all samples are provided in the Supplementary material Table H.1).

RDF C&I (Fig. 4b), Fig. 5b), and Fig. 7):

When RDF C&I samples are considered, ^{14}C-Method, aBM and SDM all show a similar dispersion of the sample results (Fig. 7). A standard deviation between the samples of around 10 wt%abs for $x_{F,wf}$ and around 8 wt%abs for $x_{F,TC}$ is found (based on same 4 samples, shown in Fig. 4b) and Fig. 5b)). No significant differences in variance between the four methods can be found.

Low deviations between results of different methods for $x_{F,wf}$ and for $x_{F,TC}$ are found when RDF C&I samples are regarded. The differences in means between the methods are not found to be significant based on statistical tests. Comparing aBM with ^{14}C-Method, the mean deviation of the share of fossil carbon $x_{F,TC}$ is −0.9 wt%abs, which can be counted as good agreement between these methods (Table 7). As seen from Fig. 4b) and Fig. 5b), the range of uncertainty overlaps for all RDF C&I samples when aBM and ^{14}C-Method are considered.

Slight underestimations by SDM of $x_{F,wf}$ and $x_{F,TC}$ are observed when comparing the figures to ^{14}C-Method results (mean deviation −2.6 wt%abs for $x_{F,wf}$ and −2.2 wt%abs for $x_{F,TC}$ – Table 7). However, statistical tests do only indicate a fairly significant difference for $x_{F,wf}$ and the ranges of uncertainty overlap for all 4 samples ($x_{F,wf}$). This is regarded as rather good agreement.

As there are only 2 MS values available for RDF C&I to be compared to the ^{14}C-Method, no clear statement on an over-underestimation can be provided. Contrary to the findings for Paper Reject, the carbon content considered in the biogenic matter and fossil matter (TOC_{BIO}, TOC_{FOS}) which is necessary to derive $x_{F,TC}$ from $x_{F,wf}$ does affect the observed difference to ^{14}C-Method results only marginally (deviation from ^{14}C-Method of around −6 wt%abs for both parameters).

When all 8 samples of RDF C&I are considered (Fig. 4b) and Fig. 5b)), the aBM delivers fossil mass fractions of 55–76 wt% with a standard deviation of 8 wt%abs between the samples. Thus, it can be expected that the composition of this RDF can vary considerably with time and

Table 7
Results for RDF C&I: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	65.8 ± 1.8[2]	–		81.3 ± 0.4	–	
aBM	65.2 ± 1.1	−0.6	(–)	80.4 ± 0.8	−0.9	(–)
SDM	63.2 ± 0.7	−2.6	(*)	79.1 ± 0.8	−2.2	(–)
MS[1]	51.2 ± 3.6	−5.5	(n.a.)	68.9 ± 2.6	−6.0	(n.a.)

Significance codes: (–) p > .1; ( ) p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 7), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.

[1] MS: Dev.^{14}C refers to another ^{14}C-Method-mean value than presented here (as only two MS samples can be compared).

[2] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

representative analyses results require high experimental control (e.g. concerning samples sizes).

RDF MSW + C&I (Fig. 4c), Fig. 5c), and Fig. 8):

The different methods deliver a broad range of results for samples of RDF MSW + C&I (sample results presented in Fig. 4c) and Fig. 5c)). As already observed for Paper Reject and RDF C&I, there is good agreement between the results of aBM and ^{14}C-Method for RDF MSW + C&I samples (uncertainty ranges overlap for 3 of 4 samples; Fig. 4c) and Fig. 5c)). A mean deviation of $x_{F,wf}$ between aBM and ^{14}C-Method of +2.6 wt%abs is determined. Regarding $x_{F,TC}$, the deviation between these two methods is on average +1.9 wt%abs. The deviation is slightly higher compared to results of the other RDFs but no significant differences are found between aBM and ^{14}C-Method (Table 8).

Different observations are made when results of SDM are compared to ^{14}C-Method and aBM. As also observed for Paper Reject, the SDM constitutes a significantly lower $x_{F,wf}$ and $x_{F,TC}$. With a mean difference of −19.5 wt%abs for $x_{F,wf}$ and −18.7 wt%abs for $x_{F,TC}$, the deviation from ^{14}C-Method is even more distinctive for the RDF MSW + C&I samples than for the Paper Reject samples. It can be assumed that the RDF MSW + C&I samples contain significant shares of fossil materials which are dissolved when sulphuric acid is applied. For example, foamed plastics which are used in mattresses, furniture, building insulation, the automobile industry, etc., could be detected visually in all of the RDF MSW + C&I samples. These polymers, such as polyurethane, usually contain amino groups and are easily dissolved (almost entirely according to Cuperus et al., 2005 [1]). Additionally, an average share of 23 wt% of textiles is found in the RDF MSW + C&I samples. Textiles are expected to contain dissolvable fossil polymers (such as polyamide or nylon) and therefore introduce systematic errors into the results of the SDM.

For the 2 RDF MSW + C&I samples, where MS results can be compared to ^{14}C-Method results, very good agreement between MS and ^{14}C-Method is found. Yet, the very limited sample size makes is difficult to make out a clear trend.

3.2.2. Correlation of aBM results with results of standardized methods

In order to evaluate the agreement of the aBM results with the results of the standardized methods, a simple linear regression is performed. Fig. 9 shows the correlation curves for the share of fossil carbon ($x_{F,TC}$), divided according the method applied. The linear regression confirms that the values obtained by the aBM are in excellent agreement with the values of the **^{14}C-Method**. A correlation coefficient R^2 of 0.98 is found when all investigated samples are regarded as one dataset. A separate consideration of the RDFs (presented in the Supplementary material Fig. I.1) reveals that there is a strong relationship of aBM

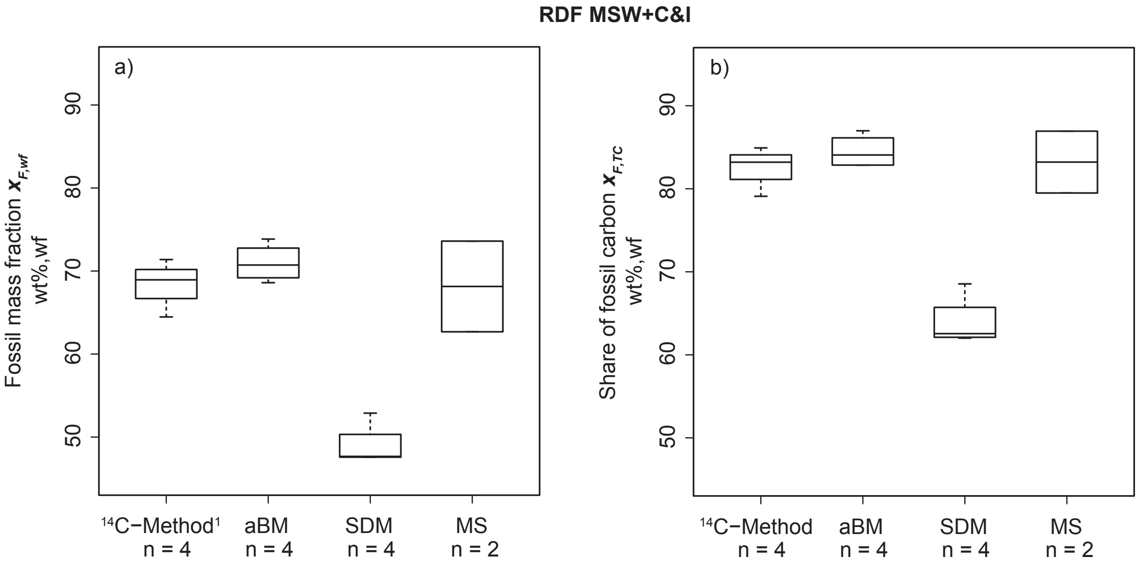

Fig. 8. Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$) in RDF MSW + C&I determined by four different methods.
[1] ^{14}C-Method: $x_{F,wf}$ is estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results.

Table 8
Results for RDF MSW + C&I: Fossil mass fraction ($x_{F,wf}$) and share of fossil carbon ($x_{F,TC}$); means of different methods and deviations from results of ^{14}C-Method.

Method	Fossil mass fraction $x_{F,wf}$			Share of fossil carbon $x_{F,TC}$		
	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.	Mean ± SD wt%,wf	Dev.^{14}C wt%abs,wf	Sign.
^{14}C-Method	68.4 ± 1.7	–		82.6 ± 0.4	–	
aBM	71.0 ± 1.4	+2.6	(–)	84.5 ± 1.0	+1.9	(–)
SDM	48.9 ± 0.8	−19.5	(**)	63.9 ± 1.2	−18.7	(**)
MS[1]	68.1 ± 3.4	−0.2	(n.a.)	83.2 ± 3.9	+1.2	(n.a.)

Significance codes: (–) p > .1; () p < .1; (*) .05 ≥ p > .01; (**) .01 ≥ p > .001; (***) .001 ≥ p with (***) indicating the highest significance.
SD – Standard deviation, representing the analytical uncertainty (derived per method as described in Section 2.5 and considering the number of samples n given in Fig. 8), wt%,wf – weight percent on water-free basis, Dev.^{14}C – Mean deviation from result of ^{14}C-Method as absolute percentage (negative = result is lower than result of ^{14}C-Method), Sign. – Significance level for Dev.^{14}C.

[1] MS: Dev.^{14}C refers to another ^{14}C-Method-mean value than presented here (as only two MS samples can be compared).

results with ^{14}C-Method values for Paper Reject and for RDF C&I. The correlation for RDF MSW + C&I-samples is found to be moderate, with a correlation coefficient of 0.53. The linear regression line is, however, for this RDF also close to the ideal correlation with a low intercept (6.93) and a slope of almost 1 (0.90).

The **SDM** results for all investigated samples in Fig. 9 can be regarded as in relatively good agreement with the aBM figures, with a correlation coefficient R^2 of 0.79. Yet, it can already be seen that the regression line is skewed by RDF MSW + C&I samples in the upper range of the graph. This leads to an overall slope of 0.69, which is clearly below the ideal correlation (1). For RDF MSW + C&I there is no detectable linear relationship of aBM results with SDM results ($R^2 < 0.1$). The regression line of aBM versus MS is rather weak, with a high absolute intercept and a slope different from 1 despite the moderate correlation coefficient of 0.64 (graph shown in Supplementary material Fig. I.1). Thus, for RDF MSW + C&I a reliable determination of the fossil content by means of the available methods appears the most challenging. It is expected that especially the composition of the fossil fraction (plastics and synthetic fibers) is the most decisive factor for the inaccuracies of the determination methods. The fact that there is no clear correlation between results of aBM and SDM indicates that the error due to non-selective dissolution of certain materials by SDM is not consistent with the samples considered. This implies that the content of dissolvable fossil polymers (foamed plastics, synthetic fibers) differs from one sample to the other.

SDM results can be considered to have a clear relationship to aBM results for the other RDFs (Paper Reject and RDF C&I). Correlation coefficients of 0.80 (Paper Reject) and 0.72 (RDF C&I) are determined (see Supplementary material Fig. I.1). However, in all cases, the slope deviates from the ideal correlation more than for ^{14}C-Method results. Thus, the relationship between the results of aBM and ^{14}C-Method is stronger than the one observed between the results of aBM and SDM.

A significant deviation from aBM is also noticeable when **MS** results are considered. A correlation coefficient of 0.52 is found when all RDFs are considered. The lowest correlation is found for Paper Reject with R^2 being only 0.22. The correlation between MS and aBM can only be considered as acceptable for one RDF (RDF C&I). A correlation coefficient of 0.78 indicates a good relationship for this RDF; the regression curve is found with a slope 0.74 (ideal = 1) and an intercept of 15.46 (ideal = 0). The regression line for RDF C&I is within a narrow range when ^{14}C-Method, SDM and MS are compared to aBM, meaning similar results are found with all methods. Yet, the relationship between ^{14}C-Method results and aBM is the most obvious ($R^2 = 0.99$, low intercept, slope almost 1). For Paper Reject and RDF MSW + C&I the linear

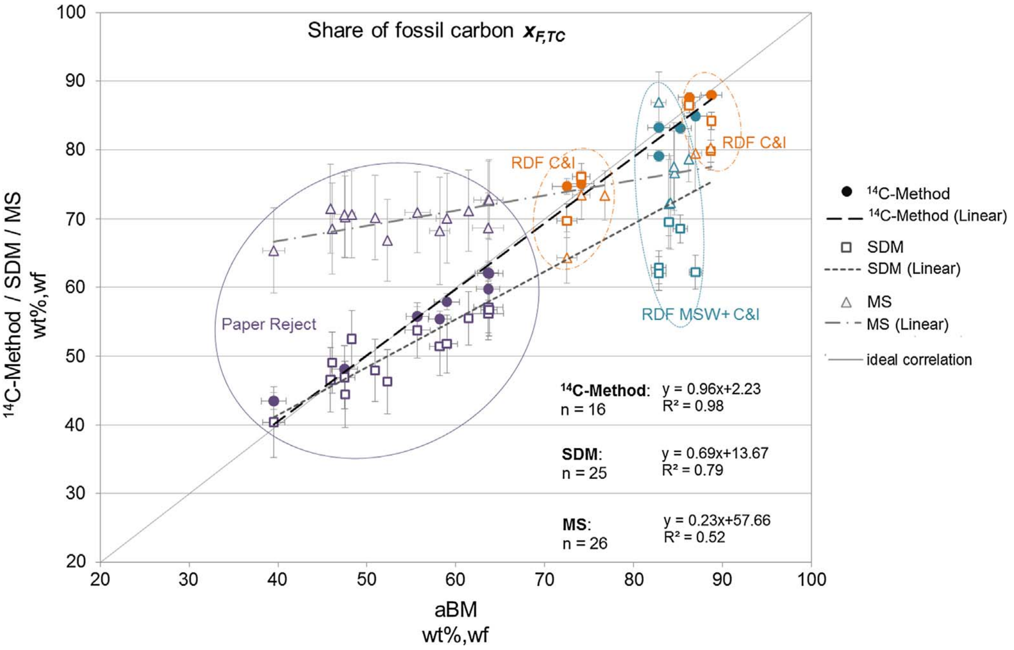

Fig. 9. Share of fossil carbon $x_{F,TC}$: Correlations of values obtained by aBM with values from standardized methods (^{14}C-Method, SDM, MS); results of all RDF samples investigated are considered.

regression between MS and aBM is rather poor, with slope and intercept far off the ideal curve. The high intercept for the MS regression curve of RDF MSW + C&I, together with a relatively clear relationship ($R^2 = 0.64$), indicates that there is a systematic underestimation of the fossil carbon content by MS when compared to aBM results. This is in agreement with findings in van Dijk & Steketee (2002) [49] where on average almost 20 wt% of biomass are found in the sorted fossil fraction of 10 different RDFs.

Concluding from the separate regression curves per RDF, it has to be considered that especially for RDF C&I and RDF MSW + C&I, only a very limited number of data points are compared (between 4 and 6), which are all in a similar range (between 60 and 90% of fossil carbon). Thus, the findings are regarded as qualitative, rather than quantitative trends.

3.3. Fossil CO_2-emissions from RDF

The elemental composition of the RDF (C, H, N, S, O), which is determined when applying the aBM, can be used to estimate the heating value of the RDF by means of empirical equations. This can be regarded as an advantage of the aBM over the standardized methods as no additional analyses to derive the heating value are necessary. CO_2-emission factors (specific fossil CO_2-emissions) related to the energy content of the RDF can easily be derived and are presented in Table 9 for each RDF investigated. Table 9 additionally provides the specific fossil CO_2-emissions related to the mass, which is derivable from the share of fossil carbon and the total carbon content in the RDF.

The results show that the fossil CO_2 emitted per GJ of heating value ranges from 48 to 71 kg. The fossil CO_2-emission factor related to the mass reveal that 650–1,800 kg fossil CO_2 are emitted per ton of RDF. The lowest fossil CO_2-emission factor is found for Paper Reject, which holds significantly higher water content (around 42 wt%) compared to the other RDFs. The slightly lower water content for RDF C&I (around 5 wt%) compared to RDF MSW + C&I (around 10 wt%) leads to a difference in heating value of around 3 MJ/kg between the two RDFs. Thus, this difference in heating value explains the slightly lower energy-based CO_2-emission factor for RDF C&I compared to RDF MSW + C&I. The difference between these two RDFs is less pronounced and even shows an adverse tendency when the mass-related CO_2-emission factor is regarded. Thus, a distinction between these RDFs is not possible in terms of climate relevance when merely the mass-related emission factor is determined.

4. Conclusions

The study shows that the values obtained by the adapted Balance Method (aBM) are in excellent agreement with the results of the Radiocarbon Method (^{14}C-Method). Mean deviations of –0.9 to + 1.9% abs for the share of fossil carbon are found which are statistically insignificant. Thus, the aBM is the only method for which low deviations and good correlations with the results of ^{14}C-Method could be observed for all RDFs investigated. This confirms recent validation results of the aBM [23] (considering that the ^{14}C-Method has the highest analytical precision and lowest uncertainty amongst the available standardized methods for determining the fossil content in RDFs). For the other two methods – Selective Dissolution Method (SDM) and Manual Sorting (MS) – the results of at least one type of RDF are in a range far off the values of the ^{14}C-Method. The reliability of these standardized methods appears to strongly depend on the composition of the RDF analyzed. High trueness and reliability of the aBM results is expected, independent of the RDF type.

Table 9
Fossil CO_2-emission factors determined for the RDFs based on the adapted Balance Method.

	CO_2-Emission factor ($kgCO_{2,fos}$/GJ[1])	CO_2-Emission factor ($kgCO_{2,fos}$/t)	Water content (wt%)	Lower heating value[1] (MJ/kg)
Paper Reject	48 ± 3	650 ± 20	42.0 ± 3.8	13.5 ± 0.3
RDF C&I	66 ± 3	1,800 ± 20	5.1 ± 0.2	27.0 ± 0.9
RDF MSW + C&I	71 ± 3	1,700 ± 20	10.4 ± 0.4	24.1 ± 0.8

[1] The lower heating value is estimated by means of the empirical equation of Boie in Kost (2001) [34].

By applying the SDM, underestimations (although not consistent between the samples) of the fossil carbon share ($\boldsymbol{x_{F,TC}}$) are expected, depending on the RDF type (within this study between − 19 and − 2% abs). In contrast, the results of MS when applied according to EN 15440:2011 tends to overestimate the share of fossil carbon (within this study up to + 14%abs). Furthermore, significant limitations regarding the reliability of SDM and MS results are indicated for certain types of RDFs. Errors are especially introduced into SDM results for the RDF produced out of pre-processed municipal solid waste and commercial and industrial waste (RDF MSW + C&I). Significant shares of fossil materials which dissolve during selective dissolution are thus misleadingly accounted for as biogenic matter. Besides the fact that the results of manual sorting are prone to human error, MS does not appear practical, particularly for RDF with a high share of "mixed" compounds (mix of biogenic and fossil constituents). The biogenic share in mixed compounds such as the fine fraction, textiles, and rubber apparently yields false estimates when using the defined values given in the standard EN 15440:2011.

A critical factor for the application of the aBM is the choice of the necessary input values − the water-and-ash-free elemental composition of the biogenic and the fossil organic matter (TOX_{BIO} and TOX_{FOS}). These values are ideally generated specifically for an RDF by means of initial manual sorting and analyses. However, the study shows that the TOX_{BIO} and TOX_{FOS} values derived for 3 different RDFs are in a close range and similar to values collected in Fellner et al. (2011) [24], as typical values for RDFs processed from household and commercial waste. Considering also the recent findings in Schwarzböck et al. (2017) [36], where TOX_{BIO} and TOX_{FOS} are appraised for 6 different RDFs, it can be assumed that TOX_{BIO} can easily be derived, also without extensive sorting analyses. For the determination of TOX_{FOS}, the oxygen content (*TOO*) appears to be the parameter which varies the most between different RDFs. Thus, the presence of polymers with comparably high oxygen contents (e.g. polyamide, polyethylene terephthalate, or polyurethane) might limit the universal applicability of TOX_{FOS} values from the literature. The share of these polymers, however, is typically low for RDF produced out of commercial and industrial waste [36,48,50,51]. The generation of RDF-specific input values for the aBM is regarded as important when no information on the origin of the RDF is available or when a low uncertainty of the results (< 3% rel.) is required. Workload could be saved once a database is established where data about different types of RDFs are collected (e.g. on a national basis).

Concerning the viability and costs, the aBM is regarded as competitive with the SDM (which is the method currently most often applied). When the fossil or biogenic content in RDFs is to be determined routinely, the aBM might even be superior to the SDM (faster, less chemicals needed). The ^{14}C-Method provides reliable results, but compared to the aBM generates significantly higher costs and can only be conducted by a limited number of laboratories [52]. Additionally, the choice of the necessary ^{14}C-reference value can be challenging when the age of the biomass is unknown [29,28]. MS is hardly feasible for routine application due to the high workload involved. Within this study, significant inaccuracies are also identified when MS is applied. This confirms that the aBM is the more cost-efficient and reliable approach compared to MS.

The study demonstrates that the developed method is a valid alternative to standardized methods for determining the fossil and biogenic share in solid RDFs. This confirms and rounds up the previous findings when defined RDF mixtures were investigated by the authors [23,24]. The mass share as well as the share of fossil carbon (which also corresponds to the share of fossil CO_2-emissions from RDF utilization) can readily be derived by analyses of the elemental composition of the RDF and a set of balance equations. Furthermore, the aBM can be applied to determine different other parameters, such as the share of renewable energy or fossil CO_2-emission factors, all of which can be derived without additional analyses required.

Further investigations will focus on possible simplifications of the method, in particular regarding the generation of the necessary input data (TOX_{BIO} and TOX_{FOS}).

Acknowledgements

The authors would like to acknowledge the funding of the present study, which was provided by the Austrian Science Fund (FWF), project number TRP 285-N28. We thank the RDF-plant operators and paper & board plant operators for their support and assistance for drawing samples. Thanks to the laboratory team of TU Wien for their contributions as well as Inge Hengl for graphical support. In addition, we are grateful for the assistance of Edith Vogel during ^{14}C-analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.12.076.

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A novel method to determine the share of fossil carbon in solid refuse-derived fuels – validation and comparison with three standardized methods

Supplementary Material

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A. Balance equations of the adapted Balance Method (Fellner et al, 2011) [24]

Carbon balance

$$x_{B,waf} * TOC_{BIO} + x_{F,waf} * TOC_{FOS} = TOC_{RDF} \tag{A.1}$$

Hydrogen balance

$$x_{B,waf} * TOH_{BIO} + x_{F,waf} * TOH_{FOS} = TOH_{RDF} \tag{A.2}$$

Nitrogen balance

$$x_{B,waf} * TON_{BIO} + x_{F,waf} * TON_{FOS} = TON_{RDF} \tag{A.3}$$

Sulphur balance

$$x_{B,waf} * TOS_{BIO} + x_{F,waf} * TOS_{FOS} = TOS_{RDF} \tag{A.4}$$

Oxygen balance

$$x_{B,waf} * TOO_{BIO} + x_{F,waf} * TOO_{FOS} = TOO_{RDF} \tag{A.5}$$

$x_{B,waf}$ ..... water- and ash-free biogenic mass fraction in wt%
$x_{F,waf}$ ..... water- and ash-free fossil mass fraction in wt%

In addition to the five substance balance equations the following condition needs to be fulfilled:

$$x_{B,wf} + x_{F,wf} + A = 1 \tag{A.6}$$

A .... ash content in the mixture in wt%
$x_{B,wf}$ ...... water-free biogenic mass fraction of the mixture as determined by the adapted Balance Method in wt%
$x_{F,wf}$ .... water-free fossil mass fraction of the mixture as determined by the adapted Balance Method in wt%

B. Calculations to determine the fossil mass share $x_{F,wf}$ and share of fossil carbon $x_{F,TC}$ by means of SDM, ^{14}C-Method and MS

Selective Dissolution Method (EN 15440:2011) [17]:

$$x_{\mathrm{B}} = \left[1 - \left\{\frac{m_{\mathrm{residue}} - m_{\mathrm{residue\text{-}ash}}}{m_{\mathrm{SRF}}} + \frac{A_{\mathrm{SFR}}}{100}\right\}\right] \cdot 100 \qquad \text{(B.1)}$$

x_B ....Biomass content on a dry basis in wt%

$m_{residue}$ ....Remaining dry mass after the test portion has been dissolved in g

$m_{residue-ash}$.Mass of ash of dissolution residue (including filter), burned according to EN 15403 in g

m_{SRF} ....mass of dry test portion used for dissolution in g

A_{SRF}.............Ash content of sample according EN 15403 in wt% = *A* in the presented study

$$x_{\mathrm{NB}} = 100 - x_{\mathrm{B}} - A_{\mathrm{SRF}} \qquad \text{(B.2)}$$

x_{NB} ....Non-biomass on a dry basis in wt% = $\boldsymbol{x_{F,wf}}$ in the presented study

$$x_{\mathrm{B}}^{\mathrm{TC}} = 100 - \left(\frac{A_{\mathrm{SRF}} \cdot C_{\mathrm{ash}} + x_{\mathrm{residue}} \cdot C_{\mathrm{residue}}}{C_{\mathrm{tot}}}\right) \qquad \text{(B.3)}$$

x_B^{TC} ....Biomass content expressed as a percentage by total carbon content in %

C_{ash} ....Total carbon content of the ash fraction in wt%

$x_{residue}$ ....Amount of dissolution residue in wt%

$C_{residue}$ ....Total carbon content of the non-biomass (fossil) fraction in wt%

C_{tot}..............Total carbon content of the sample in wt%

with

$$x_{F,TC} = 100 - \ x_B^{TC} \qquad \text{(B.4)}$$

$x_{F,TC}$ .... Share of fossil carbon in wt% = $\boldsymbol{x_{F,TC}}$ in the presented study

Radiocarbonmethod (Mohn et al., 2008) [29]:

$$\%\mathrm{BioC} = 100\% - \%\mathrm{FosC} = (f_{\mathrm{M,sample}}/f_{\mathrm{M,bio}}) * 100\% \qquad \text{(B.5)}$$

$\%BioC$ ....Share of biogenic carbon in %

$\%FosC$.......Share of fossil carbon [%] = $\boldsymbol{x_{F,TC}}$ in the presented study

$f_{M,sample}$ ....Fraction of modern carbon in the sample

$f_{M,bio}$ ....Fraction of modern carbon in the pure biogenic fraction of the sample = F^{14}C$_{\mathrm{bio}}$ in presented study (Table 5)

$$f_{\mathrm{M,bio}} = \sum \alpha_{\text{waste fraction}} \times f_{\text{M,bio,waste fraction}} \qquad \text{(B.6)}$$

$\alpha_{waste\ fraction}$ .... Share of compounds in biomass in wt%

$f_{M,bio,waste\ fraction}$... Fraction of modern carbon in the respective biomass compound = F^{14}C$_{\mathrm{bio}}$ in biomass compounds (Table 4)

Manual Sorting (EN 15440:2011) [17]:

$$x_{\mathrm{NB}} = \left\{ \frac{\varepsilon_{\mathrm{NB}} \cdot \sum_{i}^{n} x_i^{\mathrm{NB}} + (1 - \varepsilon_{\mathrm{B}}) \cdot \sum_{i}^{n} x_i^{\mathrm{B}} + \varepsilon_{\mathrm{NB}}^{\mathrm{inert}} \cdot \sum_{i}^{n} x_i^{\mathrm{inert}}}{n} \right\} \cdot 100\,\% \qquad \text{(B.7)}$$

x_{NB} ....Non-biomass on a dry basis in wt% = $\boldsymbol{x_{F,wf}}$ in the presented study

ε_{NB} ....Sorting precision of the sorted non-biomass (fossil) fraction on a dry and ash-free basis in wt%

ε_{B} ....Sorting precision of the sorted biomass fraction on a dry and ash-free basis in wt%

ε_{NB}^{inert} ....Sorting precision of the sorted non-biomass (fossil) content of the inert matter in wt%

x_i^{NB} ....Content component i in the non-biomass (fossil) category on a dry basis in wt%

x_i^{B} ....Content component i in the biomass category on a dry basis in wt%

x_i^{inert} ....Content component i in the ash matter category on a dry basis in wt%

Note: EN 15440:2011 suggests sorting precisions to be determined by applying SDM to the sorted compounds. However, particularly in the case of the fossil (plastic) fraction and textiles, the SDM results are considered not applicable to estimate the sorting precisions within this study (due to apparent significant underestimations of the fossil fraction – see Table E.1). Further, it is found that a compound-specific uncertainty appears justified (instead of considering a sorting precision for the fossil fraction as a whole as stipulated in the standard). Thus, the sorting precision in the study is not known for MS based on the stipulation in the standard. Only evaluations by aBM, SDM, and ^{14}C-Method lead to viable estimates on the sorting precision and the biomass content in the mixed components. This however, is considered as not feasible in practical applications and is therefore not considered in Eq. (B.2) (it would lead to differences of the $\boldsymbol{x_{F,wf}}$ results of below 2%absolut). Instead a sorting precision of 100 % in Eq.(B.2) is assumed (this appears justified as the sorting was conducted very meticulously) and an uncertainty of the result is estimated. The estimate on the uncertainty is calculated based on evaluations by aBM, SDM and ^{14}C-Method, applied to selected sorted components, particularly to mixed components such as composite and textiles (described in section 2.3, results in Table 3). A weighted sorting precision is calculated (considering component specific evaluation results) according to the following equation:

$$\varepsilon_{MS} = \sum_{i=1}^{n} (x_i^{B,real} - x_i^{B,norm}) * x_i \qquad \text{(B.8)}$$

ε_{MS} ....Weighted sorting precision in wt%

$x_i^{B,real}$ ....Biogenic share in sorted component i acc. to own evaluations (Table 3) in wt%

$x_i^{B,norm}$ ....Biogenic share in sorted component i according EN 15440:2011 in wt%

x_i................Mass share of sorted component i in wt%

It is assumed that the real biogenic share is within 95 % of ± ε_{MS}. Thus, an uncertainty for MS s_{MS} of one standard deviation is considered as:

$$s_{MS} = \frac{\varepsilon_{MS}}{1.96} \qquad \text{(B.9)}$$

The determination of the **share of fossil carbon $x_{F,TC}$** by MS is not described in EN 15440:2011. In order to calculate the share of fossil carbon, the following equation is applied:

$$x_{F,TC} = \sum_{i=1}^{n} x_{i,waf} * x_i^F * TOC_i^{FOS} \Big/ TOC_{RDF} \qquad \text{(B.10)}$$

$x_{F,TC}$	Share of fossil carbon in %
$x_{i,waf}$	Mass share of sorted component i, water-and ash-free in wt% waf
x_i^F	Fossil share in sorted component i, water-and ash-free, calculated from $x_i^{B,norm}$ and ash content of component i in wt% waf
TOC_i^{FOS}	Total organic carbon in fossil share of component i in g/kg$_{waf}$, values published in Kost (2001) [34] for mixed plastics and shares in textiles are used; together with chemical structure of polyamide, polyester, polyacrylonitrile, and polypropylene.
TOC_i^{BIO}	Total organic carbon in biogenic share of component i in g/kg$_{waf}$, values published in Kost (2001) [34] for mixed paper, wood, wool, and shares in textiles are used; together with chemical structure of cellulose.
TOC_{RDF}	Total organic carbon in RDF in g/kg = $TOC_i^{BIO} + TOC_i^{FOS}$

C. RDF sorting results

Table C.1: Sorting results of the investigated RDFs (mass shares of compounds on a water-free basis)

Compound	Paper Reject wt%, wf		RDF C&I wt%, wf		RDF MSW+C&I wt%, wf	
		incl. sorting of fine fraction		incl. sorting of fine fraction		incl. sorting of fine fraction
Cardboard/paper	5.9 %	37.4 %	2.8 %	6.9 %	4.1 %	5.1 %
Wood	1.6 %	2.5 %	0.1 %	0.2 %	2.2 %	1.9 %
Plastic	20.4 %	41.0 %	32.5 %	49.6 %	47.1 %	56.5 %
Textiles	1.1 %	1.1 %	0.7 %	1.4 %	12.1 %	22.6 %
Organic	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %
Rubber	0.7 %	0.7 %	0.1 %	0.4 %	0.8 %	0.9 %
Composite & impure materials	3.0 %	15.0 %	21.8 %	40.7 %	8.4 %	11.7 %
Fine fraction < 2 cm	65.1 %	-	41.3 %	-	24.1 %	-
Metals & inert[1]	2.2 %	2.3 %	0.7 %	0.8 %	1.2 %	1.3 %
Sum	100 %	100 %	100 %	100 %	100 %	100 %
Total sorted	41.9 kg		3.6 kg		4.0 kg	

[1] Metals and inert materials are not further considered in the study (these compounds are neither of fossil nor of biogenic origin)

D. Elemental composition of RDFs investigated (*TOX_{RDF}*) and of sorted compounds

Table D.1: Average elemental composition of the water-and-ash free (waf) RDFs (TOX_{RDF})

	n	TOC	TOH	TOO	TON	TOS	Ash
		g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	wt%
		Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Paper Reject	15	614 ± 22	87 ± 4	298 ± 29	3.0 ± 0.8	2.5 ± 0.1	7.2 ± 0.1
RDF C&I	8	691 ± 27	101 ± 6	205 ± 27	3.8 ± 1.4	4.3 ± 0.8	9.1 ± 0.2
RDF MSW+C&I	8	674 ± 7	93 ± 2	234 ± 7	18.9 ± 3.6	5.6 ± 0.7	8.7 ± 0.2

n ..... number of samples (with 5 elemental analyses for each sample; duplicate ash content determination)
SD .. standard deviation propagated from the elemental analyses and ash content determination

Table D.2: Average elemental composition of the water-and-ash free (waf) sorted compounds (*TOX*); mean values disregarding the RDF type

	n	TOC	TOH	TOO	TON	TOS	Ash
		g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	g/kg_{waf}	wt%
		Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Cardboard/paper	13	473 ± 6	65 ± 1	488 ± 7	2.0 ± 0.3	2.5 ± 0.2	12.1 ± 1.5
Paper mixed[1]		467 ± 6	65 ± 1	443 ± 9	2.0 ± 1.0	1.0 ± 0.5	
Wood	3	494 ± 4	63 ± 1	475 ± 2	8.9 ± 0.3	3.5 ± 0.8	1.3 ± 0.1
Plastic	16	762 ± 3	110 ± 2	100 ± 3	9.4 ± 0.8	5.5 ± 0.2	4.2 ± 0.3
Mixed plastic[1]		790 ± 29	130 ± 9	30 ± 32	2.0 ± 2.0	1.0 ± 2.0	
Textiles[2]	7	562 ± 2	70 ± 1	399 ± 6	15.9 ± 0.9	7.4 ± 0.5	8.3 ± 0.4
Synthetic textiles[3]		677 ± 34	70 ± 4	206 ± 10	47.2 ± 2.0	0.1 ± 0.1	
Natural textiles[4]		448 ± 22	62 ± 3	467 ± 23	16.3 ± 0.8	7.2 ± 0.4	
Rubber	1	714 ± 10	85 ± 2	n.a.	16.0 ± 1.2	31.8 ± 2.6	15.9 ± 0.3
Composite & impure materials	8	646 ± 32	96 ± 5	284 ± 10	2.1 ± 0.1	8.9 ± 1.1	15.2 ± 4.1

n ..... number of samples (with 5 elemental analyses for each sample; duplicate ash content determination)
SD .. standard deviation propagated from the elemental analyses and ash content determination

[1] source: Kost (2001) [34]; used for cardboard/paper and plastics in composite compounds to derive TOX_{BIO} and TOX_{FOS}; also used for MS to derive the share of fossil carbon

[2] not used to generate TOX_{BIO} and TOX_{FOS} within the study, instead values for synthetic and natural textiles are used as listed in this table

[3] considering the theoretical composition of polymers in textiles; shares of different polymers in textiles based on Kost (2001) [34] (polyamide 30 wt%, polyester 49 wt%, polyacrylonitrile 15 wt% and polypropylene 6 wt%)

4 considering the theoretical composition of cellulose (cotton); composition of wool according to Kost (2001) [36]; shares of cellulose and wool based on Kost (2001) [34] (cellulose 90 wt%, wool 10 wt%)

E. Elemental composition of water-and-ash-free biogenic and fossil organic matter present in the RDFs investigated (TOX_{BIO} and TOX_{FOS})

Table E.1: Elemental composition of water-and-ash-free biogenic organic matter (TOX_{BIO}) present in RDFs investigated

	TOC	TOH	TOO	TON	TOS
	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Paper Reject	477 ± 5	63 ± 1	451 ± 9	1.9 ± 0.1	2.4 ± 0.3
RDF C&I	470 ± 7	65 ± 2	482 ± 10	2.7 ± 0.5	2.0 ± 0.5
RDF MSW+C&I	463 ± 8	64 ± 1	478 ± 9	7.8 ± 0.7	4.1 ± 0.5
MEAN	**470 ± 8**	**64 ± 1**	**470 ± 19**	**4 ± 3**	**3 ± 1**

Table E.2: Elemental composition of water-and-ash-free fossil organic matter (TOX_{FOS}) present in RDFs investigated

	TOC	TOH	TOO	TON	TOS
	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$	g/kg$_{waf}$
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Paper Reject	782 ± 8	119 ± 4	31 ± 8	4.7 ± 1.0	5.8 ± 1.4
RDF C&I	777 ± 8	115 ± 3	108 ± 9	3.3 ± 0.5	3.6 ± 0.5
RDF MSW+C&I	726 ± 8	99 ± 1	143 ± 5	23.3 ± 1.8	4.0 ± 0.5
MEAN	**762 ± 35**	**111 ± 12**	**94 ± 64**	**10 ± 10**	**4 ± 1**

F. Share of fossil carbon ($x_{F,TC}$) in sorted compounds of RDFs, determined by different methods

Table F.1: Share of fossil carbon ($x_{F,TC}$) determined for different sorted RDF compounds by means of different methods; mean values disregarding the RDF type

	aBM		^{14}C-Method		SDM	
	gC$_{fos}$/gC$_{wf}$ in %		gC$_{fos}$/gC$_{wf}$ in %		gC$_{fos}$/gC$_{wf}$ in %	
	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD
Cardboard/paper	13	1.3 ± 1.1	3	2.6 ± 1.9	2	3.9 ± 3.0
Wood	3	2.7 ± 1.5	-	-	2	0.4 ± 0.4
Plastic	16	98.5 ± 0.5	2	95.1 ± 0.4	4	49.6 ± 2.6
Textiles	7	39.2 ± 1.1	1	77.0 ± 0.9	4	32.0 ± 2.4
Rubber	1	77.0 ± 3.3	-	-	1	79.9 ± 2.8
Composite	8	64.4 ± 0.8	2	53.4 ± 1.5	8	54.8 ± 1.2

aBM ....adapted Balance Method ^{14}C-Method ......Radiocarbon Method
SDM ....Selective Dissolution Method
n ....number of samples analyzed
SD ....standard deviation (aBM: propagated from the uncertainties of the input parameter *TOX*, TOX_{BIO}, TOX_{FOS}; ^{14}C-Method: propagated from triplicate determination and an estimated uncertainty of the ^{14}C reference value of 3 %rel; SDM: propagated from duplicate determination and reproducibility values provided in EN 15440:2011)

G. Fossil mass share ($x_{F,wf}$) for all RDF samples investigated determined by different methods

aBM .... adapted Balance Method
^{14}C-Method ... Radiocarbon Method
SDM.............. Selective Dissolution Method
MS .... Manual Sorting
SD................. standard deviation (aBM: propagated from the uncertainties of the input parameter *TOX*, TOX_{BIO}, TOX_{FOS}; ^{14}C-Method: propagated from triplicate determination and an estimated uncertainty of the ^{14}C reference value of 3 %rel; SDM: propagated from duplicate determination and reproducibility values provided in EN 15440:2011; MS: estimated from selective dissolution of sorted compounds according to EN 15440:2011)

Table G.1: Fossil mass fraction ($x_{F,wf}$) determined for Paper Reject samples by means of different methods

	Ash content	aBM	^{14}C-Method*	SDM	MS
	g/g$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	6.9 ± 0.1	47.8 ± 1.2	48.2 ± 3.3	42.1 ± 1.6	48.6 ± 3 .6
Sample 2	6.5 ± 0.1	37.3 ± 1.2	-	34.4 ± 1.5	46.6 ± 4.4
Sample 3	6.1 ± 0.1	42.9 ± 1.3	40.6 ± 2.7	37.0 ± 1.6	47.1 ± 5 .7
Sample 4	6.0 ± 0.1	48.3 ± 1.4	45.9 ± 3.2	41.4 ± 1.3	54.1 ± 4 .4
Sample 5	6.2 ± 0.1	36.2 ± 1.2	-	35.4 ± 1.5	50.7 ± 4.7
Sample 6	8.3 ± 0.2	44.9 ± 1.7	-	43.0 ± 1.3	49.8 ± 4.5
Sample 7	7.7 ± 0.2	39.9 ± 1.2	40.4 ± 2.9	39.5 ± 1.4	50.3 ± 4 .5
Sample 8	7.0 ± 0.1	26.2 ± 1.1	26.1 ± 2.3	27.5 ± 2.0	44.8 ± 4 .6
Sample 9	7.6 ± 0.2	32.6 ± 1.3	-	31.0 ± 1.6	49.4 ± 4.6
Sample 10	7.2 ± 0.1	47.9 ± 1.6	48.0 ± 2.7	43.8 ± 1.3	52.7 ± 4 .6
Sample 11	8.5 ± 0.2	31.1 ± 1.4	-	31.9 ± 1.6	46.2 ± 4.9
Sample 12	7.4 ± 0.1	31.4 ± 1.2	-	32.6 ± 1.5	50.6 ± 4.9
Sample 13	6.8 ± 0.1	32.9 ± 1.3	31.7 ± 2.5	32.1 ± 1.6	50.2 ± 4 .7
Sample 14	7.2 ± 0.1	33.5 ± 1.2	-	37.4 ± 1.5	49.5 ± 4.8
Sample 15	9.2 ± 0.2	42.1 ± 1.4	42.2 ± 2.8	38.8 ± 2.1	47.8 ± 4 .9
MEAN	**7.2 ± 0.05**	**38.3 ± 0.3**	**40.4 ± 1.0**	**36.5 ± 0.4**	**49 .2 ± 1.2**

Table G.2: Fossil mass fraction ($x_{F,wf}$) determined for RDF C&I samples by means of different methods

	Ash content	aBM	^{14}C-Method*	SDM	MS
	g/g$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	10.3 ± 0.2	55.1 ± 1.8	56.0 ± 3.4	52.7 ± 1.9	46.0 ± 3.0
Sample 2	8.2 ± 0.2	75.7 ± 1.6	-	68.4 ± 1.2	64.9 ± 2.8
Sample 3	9.1 ± 0.2	71.9 ± 1.9	-	-	61.9 ± 2.9
Sample 4	9.1 ± 0.2	57.5 ± 1.6	57.3 ± 3.3	55.8 ± 1.8	56.4 ± 3 .0
Sample 5	7.9 ± 0.2	61.3 ± 2.0	-	-	57.5 ± 3.0
Sample 6	9.7 ± 0.2	74.7 ± 1.7	74.2 ± 3.6	70.4 ± 1.0	-
Sample 7	11.0 ± 0.2	63.0 ± 2.0	-	-	-
Sample 8	7.4 ± 0.1	73.3 ± 1.7	75.6 ± 3.6	74.1 ± 0.9	-
MEAN	**9.1 ± 0.1**	**66.6 ± 0.6**	**65.8 ± 1.8**	**64.3 ± 0.6**	**57.3 ± 1.3**

* ^{14}C-Method: $x_{F,wf}$ estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results; considering 3 %rel uncertainty of the conversion factor (this is done because $x_{F,wf}$ is not ascertainable directly by ^{14}C-Method).

Table G.3: Fossil mass fraction ($x_{F,wf}$) determined for RDF MSW+C&I samples by means of different methods

	Ash content	aBM	^{14}C-Method*	SDM	MS
	g/g$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %	gC$_{fos}$/gC$_{wf}$ in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	7.5 ± 0.1	69.8 ± 1.6	64.5 ± 3.4	47.6 ± 1.7	73.6 ± 4 .1
Sample 2	8.3 ± 0.2	70.5 ± 2.0	-	54.2 ± 1.4	54.1 ± 5.2
Sample 3	9.5 ± 0.2	70.3 ± 1.6	-	-	57.6 ± 5.1
Sample 4	8.6 ± 0.2	70.9 ± 1.6	-	-	59.5 ± 5.4
Sample 5	9.0 ± 0.2	68.6 ± 1.6	68.9 ± 3.5	47.8 ± 1.7	-
Sample 6	8.7 ± 0.2	71.7 ± 1.6	69.0 ± 3.5	52.9 ± 1.5	-
Sample 7	9.5 ± 0.2	69.7 ± 2.0	-	-	53.2 ± 5.6
Sample 8	8.7 ± 0.2	73.9 ± 1.8	71.4 ± 3.5	47.6 ± 1.7	62.7 ± 4 .6
MEAN	**8.5 ± 0.1**	**70.7 ± 0.6**	**68.4 ± 1.7**	**50.0 ± 0.7**	**60.1 ± 2.0**

* ^{14}C-Method: $x_{F,wf}$ estimated based on $x_{F,TC}$ using a conversion factor determined by aBM results; considering 3 %rel uncertainty of the conversion factor (this is done because $x_{F,wf}$ is not ascertainable directly by ^{14}C-Method).

H. Share of fossil carbon ($x_{F,TC}$) for all RDF samples investigated determined by different methods

aBM	adapted Balance Method
^{14}C-Method ...	Radiocarbon Method
SDM..............	Selective Dissolution Method
MS	Manual Sorting
SD.................	standard deviation (aBM: propagated from the uncertainties of the input parameter *TOX, TOX_{BIO}, TOX_{FOS}*; ^{14}C-Method: propagated from triplicate determination and an estimated uncertainty of the ^{14}C reference value of 3 %rel; SDM: propagated from duplicate determination, elemental analyses and reproducibility values provided in EN 15440:2011; MS: estimated from selective dissolution of sorted compounds according to EN 15440:2011 and considering +5 % from carbon content estimates)

Table H.1: Share of fossil carbon ($x_{F,TC}$) determined for Paper Reject samples by means of different methods

	aBM	^{14}C-Method	SDM	MS
	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	63.7 ± 1.2	62.1 ± 1.8	56.2 ± 3.8	68.7 ± 5.0
Sample 2	52.3 ± 1.4	-	46.3 ± 4.7	66.8 ± 6.0
Sample 3	58.2 ± 1.3	55.4 ± 1.2	51.4 ± 4.2	68.2 ± 7.8
Sample 4	63.7 ± 1.3	59.8 ± 1.6	57.1 ± 3.7	72.7 ± 5.6
Sample 5	50.9 ± 1.3	-	47.9 ± 4.5	70.1 ± 6.2
Sample 6	61.5 ± 1.6	-	55.5 ± 3.9	71.1 ± 5.9
Sample 7	55.7 ± 1.3	55.8 ± 1.4	53.8 ± 4.0	70.9 ± 5.9
Sample 8	39.5 ± 1.4	43.5 ± 1.2	40.4 ± 5.2	65.4 ± 6.2
Sample 9	47.6 ± 1.4	-	44.4 ± 4.8	70.2 ± 6.0
Sample 10	63.8 ± 1.5	62.0 ± 0.9	56.7 ± 3.8	72.7 ± 5.8
Sample 11	46.1 ± 1.7	-	49.1 ± 4.4	68.5 ± 6.6
Sample 12	45.9 ± 1.4	-	46.6 ± 4.7	71.5 ± 6.5
Sample 13	47.5 ± 1.5	48.1 ± 1.2	46.9 ± 4.6	70.6 ± 6.2
Sample 14	48.3 ± 1.4	-	52.5 ± 4.1	70.6 ± 6.3
Sample 15	59.0 ± 1.4	57.9 ± 1.2	51.8 ± 4.2	70.1 ± 6.5
MEAN	**53.6 ± 0.4**	**55.6 ± 0.5**	**50.4 ± 1.1**	**69.9 ± 1.6**

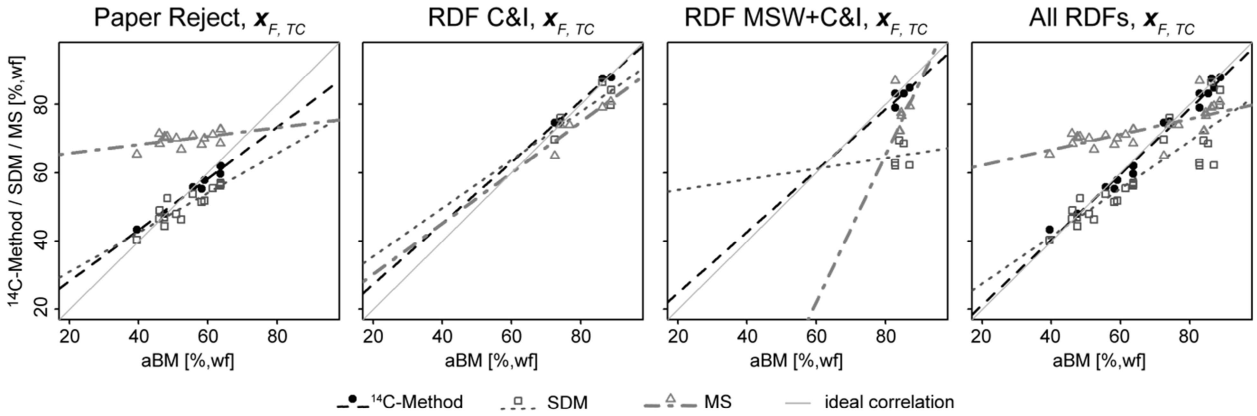
Table H.2: Share of fossil carbon ($x_{F,TC}$) determined for RDF C&I samples by means of different methods

	aBM	^{14}C-Method	SDM	MS
	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	72.5 ± 1.6	74.7 ± 1.1	69.7 ± 2.4	64.3.0 ± 3.7
Sample 2	88.7 ± 1.1	-	79.8 ± 1.6	80.3 ± 3.2
Sample 3	86.2 ± 1.4	-	-	78.7 ± 3.3
Sample 4	74.1 ± 1.4	75.1 ± 1.0	76.1 ± 1.9	73.4 ± 3.6
Sample 5	76.8 ± 1.7	-	-	73.4 ± 3.6
Sample 6	88.8 ± 1.1	88.0 ± 0.5	84.2 ± 1.3	-
Sample 7	80.1 ± 1.6	-	-	-
Sample 8	86.3 ± 1.2	87.6 ± 0.7	86.5 ± 1.1	-
MEAN	**81.7 ± 0.5**	**81.3 ± 0.4**	**79.3 ± 0.7**	**74.0 ± 1.6**

Table H.3: Share of fossil carbon ($\boldsymbol{x_{F,TC}}$) determined for RDF MSW+C&I samples by means of different methods

	aBM	^{14}C-Method	SDM	MS
	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %	gC_{fos}/gC_{wf} in %
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Sample 1	82.8 ± 1.2	79.1 ± 0.8	62.9 ± 2.4	86.9 ± 4.4
Sample 2	84.0 ± 1.5	-	69.5 ± 2.0	72.1 ± 6.4
Sample 3	84.6 ± 1.2	-	-	76.7 ± 6.1
Sample 4	84.6 ± 1.2	-	-	77.5 ± 6.4
Sample 5	82.9 ± 1.2	83.2 ± 0.8	62.0 ± 2.5	-
Sample 6	85.3 ± 1.2	83.2 ± 0.8	68.5 ± 2.0	-
Sample 7	84.2 ± 1.5	-	-	72.3 ± 6.8
Sample 8	87.0 ± 1.3	84.9 ± 0.7	62.2 ± 2.4	79.5 ± 5.3
MEAN	**84.4 ± 0.5**	**82.6 ± 0.4**	**65.0 ± 1.0**	**77.5 ± 2.4**

I. Correlation of aBM results with results of standardized methods (separately for the different RDFs)



^{14}C-Method: n = 8 y = 0.75x+13.19 R² = 0.97
SDM: n = 15 y = 0.58x+19.56 R² = 0.80
MS: n = 15 y = 0.12x+63.21 R² = 0.22

^{14}C-Method: n = 4 y = 0.89x+9.44 R² = 0.99
SDM: n = 5 y = 0.70x+21.49 R² = 0.72
MS: n = 5 y = 0.74x+15.46 R² = 0.78

^{14}C-Method: n = 4 y = 0.90x+6.93 R² = 0.53
SDM: n = 5 y = 0.15x+51.86 R² = 0.01
MS: n = 6 y = 2.15x-107.13 R² = 0.64

^{14}C-Method: n = 16 y = 0.96x+2.26 R² = 0.98
SDM: n = 25 y = 0.69x+13.67 R² = 0.79
MS: n =26 y = 0.23x+57.66 R² = 0.52

Figure I.1: Share of fossil carbon $x_{F,TC}$: Correlations of values obtained by aBM with values from standardized methods (^{14}C-Method, SDM, MS); results of all RDF samples investigated are considered.

J. Details on sampling period and number of RDF samples investigated per method

Table J.1: Sampling period and number of RDF samples investigated per method

	Sampling period	**Number of samples drawn**[1]	**Number of samples analyzed**			
			^{14}C-Method	**aBM**	**SDM**	**MS**
Paper Reject	06.05.2015-21.05.2015	15 (at ~10 kg dry each[2])	8	15	15	15
RDF C&I	20.04.2016-29.04.2016	8 (at ~5 kg dry each[2])	4	8	5	5
RDF MSW+C&I	20.04.2016-29.04.2016	8 (at ~5 kg dry each[2])	4	8	5	6

RDF......refuse-derived fuel C&I....... commercial and industrial waste MSW....... municipal solid waste

[1] Daily grab samples

[2] One sample corresponds to around 60 liters

K. Calibration verification of used elemental analysis instruments

Table K.1: Calibration correction factors for the elemental analysis instrument Elementar Vario Macro; determined for days when measurements of the investigated RDFs are conducted using standard reference materials. Control limits of 0.95 to 1.05 (for C, N, S) and 0.90 to 1.1 (for H) are considered (acc. to manufacturer recommendations)[1].

Measurement date	**Sample**	**Daily correction factor**				**Used standard material**[2]
		C	**H**	**N**	**S**	
20.07.2015	Paper Reject	0.9995	0.9980	1.0005	1.0082	Sulfanilamide
21.07.2015	Sorted cardboard, composite, textiles, wood	1.0108	1.0417	1.0098	1.0470	Sulfanilamide
22.07.2015	Sorted cardboard, composite, textiles, wood	1.0007	1.0405	0.9910	1.0170	Sulfanilamide
06.10.2015	Paper Reject	1.0218	1.0085	1.0043	1.0139	Sulfanilamide
08.10.2015	Paper Reject	1.0091	1.0146	1.0066	1.0091	Sulfanilamide
09.10.2015	Paper Reject	1.0075	1.0122	0.9991	1.0075	Sulfanilamide
13.10.2015	dissolution residue	1.0017	1.0226	-	-	Polyethylene
14.10.2015	dissolution residue	1.0014	1.0285	-	-	Polyethylene
15.10.2015	dissolution residue	1.0036	1.0318	-	-	Polyethylene
09.12.2015	ignition residue	0.9574	1.0320	1.0099	0.9450	Sulfanilamide
09.12.2015	ignition residue	0.9846	1.1009	1.0535	0.9114	Sulfanilamide
09.12.2015	ignition residue	0.9580	1.0480	0.9954	0.9178	Sulfanilamide
18.12.2015	Sorted plastics	1.0014	1.0574	-	-	Polyethylene
18.12.2015	Sorted plastics	1.0031	1.0779	-	-	Polyethylene
18.12.2015	Sorted plastics	1.0014	1.0728	-	-	Polyethylene
23.12.2015	Sorted cardboard, composite, textiles, wood	0.9952	1.0635	0.9996	0.9793	Sulfanilamide
28.12.2015	Sorted cardboard, composite, textiles, wood	0.9894	1.0801	1.0002	0.9971	Sulfanilamide
28.12.2015	Sorted cardboard, composite, textiles, wood	0.9918	1.0619	1.0024	1.0105	Sulfanilamide
28.12.2015	Sorted cardboard, composite, textiles, wood	0.9889	1.0629	0.9948	1.0032	Sulfanilamide
22.07.2016	RDF C&I, RDF MSW+C&I	1.0060	1.0421	1.0124	1.0086	Sulfanilamide
23.07.2016	RDF C&I, RDF MSW+C&I	1.0106	1.0363	1.0301	1.2379	Sulfanilamide
25.07.2016	RDF C&I, RDF MSW+C&I	1.0267	1.0571	1.0224	1.3300	Sulfanilamide
26.07.2016	Ignition residue	0.9919	1.1165	1.0655	0.9307	Sulfanilamide
29.07.2016	RDF C&I, RDF MSW+C&I	1.0017	1.0589	1.0096	1.0276	Sulfanilamide
02.08.2016	Sorted cardboard, composite, textiles, wood	1.0068	1.0450	1.0132	1.0147	Sulfanilamide
02.08.2016	Sorted cardboard, composite, textiles, wood	1.0017	1.0806	1.0160	0.9989	Sulfanilamide
18.08.2016	ignition residue	0.9855	1.3804	1.0102	0.9151	Sulfanilamide
19.08.2016	ignition residue	0.9840	1.3701	1.0106	0.9131	Sulfanilamide
19.08.2016	ignition residue	0.9873	1.4498	1.0161	0.8739	Sulfanilamide
24.08.2016	Sorted plastics	0.9952	1.0940	-	-	Polyethylene
25.08.2016	Sorted cardboard, composite, textiles, wood	0.9936	1.1267	1.0023	1.0252	Sulfanilamide
05.01.2017	Sorted cardboard, composite, textiles, wood	0.9837	1.0496	0.9980	1.0783	Sulfanilamide
11.01.2017	dissolution residue	0.9851	1.0543	-	-	Polyethylene
11.01.2017	dissolution residue	0.9861	1.0565	-	-	Polyethylene
12.01.2017	dissolution residue	0.9864	1.0598	-	-	Polyethylene
12.01.2017	dissolution residue	0.9864	1.0604	-	-	Polyethylene
09.03.2017	dissolution residue	0.9949	1.0652	-	-	Polyethylene

[1] Daily correction factors outside the set control limits can appear due measurements in the lower part of the calibration curve (e.g. when ignition residues or plastics are measured which contain very low amounts of H, N, or S). Thus, in these cases increased uncertainties of the measurement results are considered.

[2] Polyethylene does not contain N or S, thus no correction factor for these elements can be determined when polyethylene is used as standard. A factor of 1.0 is considered together with increased uncertainties of the measurement results.

Table K.2: Calibration correction factors for the oxygen analysis instrument Elementar Vario El; determined for days when measurements of the investigated RDFs are conducted using a standard reference material. Control limits of 0.90 to 1.1 are considered (acc. to manufacturer recommendations)[1].

Measurement date	**Sample**	**Daily correction factor O**	**Used standard material**
11.11.2015	Paper Reject	0.9315	Benzoic acid
16.11.2015	Paper Reject	0.9491	Benzoic acid
18.11.2015	Paper Reject	1.2092	Benzoic acid
02.12.2015	ignition residue	1.1222	Benzoic acid
03.12.2015	ignition residue	1.1291	Benzoic acid
07.12.2015	ignition residue	1.1553	Benzoic acid
02.02.2016	Sorted cardboard, composite, textiles, wood	1.1523	Benzoic acid
08.02.2016	Sorted cardboard, composite, textiles, wood	1.1388	Benzoic acid
16.02.2016	Sorted cardboard, composite, textiles, wood	1.1828	Benzoic acid
18.08.2016	Sorted composite, plastics	0.9899	Benzoic acid
22.08.2016	Sorted composite, plastics, wood	1.0838	Benzoic acid
23.08.2016	RDF C&I, RDF MSW+C&I	1.0471	Benzoic acid
24.08.2016	RDF C&I, RDF MSW+C&I	1.1233	Benzoic acid
18.10.2016	Ignition residue	0.9949	Benzoic acid
29.12.2016	RDF C&I, RDF MSW+C&I	0.9118	Benzoic acid
06.03.2016	Sorted composite, textiles	0.9967	Benzoic acid
09.03.2016	RDF C&I, RDF MSW+C&I	1.0408	Benzoic acid
10.03.2016	Sorted cardboard	1.0346	Benzoic acid
15.03.2016	Sorted textiles, wood	1.0715	Benzoic acid

[1] Daily correction factors outside the set control limits can appear due measurements in the lower part of the calibration curve (e.g. when ignition residues or plastics are measured which contain very low amounts O). Thus, in these cases increased uncertainties of the measurement results are considered.

Paper VI

Klimarelevanz von Ersatzbrennstoffen – Anwendung und Vergleich verschiedener Bestimmungsmethoden

[Climate relevance of refuse-derived fuels – Application and comparison of different determination methods]

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Österreichische Wasser- und Abfallwirtschaft, 2018, 70, 3-4, 179-193

DOI: 10.1007/s00506-018-0466-8

Österr Wasser- und Abfallw 2018 · 70:179–193
https://doi.org/10.1007/s00506-018-0466-8

Klimarelevanz von Ersatzbrennstoffen – Anwendung und Vergleich verschiedener Bestimmungsmethoden

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Zusammenfassung Der Einsatz von alternativen Brennstoffen – wie aus Abfall hergestellte Ersatzbrennstoffe (EBS) – kann in industriellen thermischen Verwertungsanlagen (beispielsweise in Zementwerken) neben der Einsparung von Primärrohstoffen auch zu einer Reduzierung der klimarelevanten CO_2-Emissionen führen. Um diese CO_2-Einsparungen nachzuweisen, bedarf es einer Methode, die der Heterogenität der Abfallgemische gerecht wird und den fossilen Kohlenstoffanteil bzw. den fossilen CO_2-Emissionsfaktor der EBS zuverlässig bestimmen lässt. Die Studie befasst sich mit der Erprobung einer alternativen Bestimmungsmethode, der sogenannten adaptierten Bilanzenmethode (aBM), die auf der Bestimmung der Elementarzusammensetzung des EBS beruht. Insgesamt wurden sechs verschiedene EBS auf ihre Klimarelevanz mittels aBM untersucht und mit Ergebnissen standardisierter Verfahren verglichen. Dabei zeigte sich eine sehr gute Übereinstimmung der aBM-Werte mit denen der Radiokarbonmethode (^{14}C-Methode), die als Vergleichsmethode herangezogen werden kann. Die mittlere Abweichung von der ^{14}C-Methode lag bei 0,6 ± 1,4 %absolut bezogen auf den mittleren fossilen Kohlenstoffanteil. Für die zwei weiteren standardisierten Methoden (Selektive Lösemethode und Manuelle Sortierung) zeigten sich beim Vergleich der Ergebnisse deutliche methodische Einschränkungen in Abhängigkeit von der Zusammensetzung der EBS. Die aBM ist damit neben der analytisch aufwendigen ^{14}C-Methode das einzige Bestimmungsverfahren, das unabhängig vom EBS-Typ zuverlässige Werte zur Klimarelevanz generiert. Zudem weist die Praktikabilität (Zeit- und Kostenaufwand) der aBM, insbesondere bei Routineanwendungen, Vorteile gegenüber standardisierten Verfahren auf. Einzig bei erstmaliger Anwendung ist eine Ermittlung von EBS-spezifischen Eingangswerten zur Elementarzusammensetzung der enthaltenen biogenen und fossilen Materialien notwendig, welche mit erhöhtem Aufwand verbunden sein kann.

Climate-relevance of refuse-derived fuels – Application and comparison of different determination methods

Abstract Refuse-derived fuels (RDF) are utilized in industrial processes (e. g. cement plants) to reduce costs for primary energy carriers, to lessen natural resource consumption, but also to lower the amount of climate-relevant CO_2 emissions associated with the production process. In order to account for the CO_2 savings, a practical method is required which accounts for the heterogeneity of RDF and allows the share of fossil carbon and fossil CO_2 emissions to be reliably determined. The study examines an alternative method, the so-called adapted Balance Method (aBM), which relies on the determination of the elementary composition of the RDF. Six different RDFs were investigated by means of aBM and the results were compared to three standardized methods. The results of aBM are in excellent agreement with the ones of ^{14}C-Method which is regarded as reference method (mean deviation of 0.6 ± 1.4%absolute based on the share of fossil carbon). Both other standardized methods, the Selective Dissolution Method and the method of Manual Sorting show methodological limitations leading to allegedly false estimates for single RDFs. Thus, the aBM is—besides the ^{14}C-Method, which requires highly specialist equipment and personnel—the only determination method which delivers reliable data on the climate-relevant CO2 emissions independently of the type of RDF. Further benefits of the aBM in comparison to the standardized methods include its practicability for routine application (expenditure of time and money). Only during initial application of the aBM the determination of RDF-specific input parameters (elemental composition of biogenic and fossil materials in the RDF) may lead to increased efforts.

1 Einleitung

Der Einsatz von Ersatzbrennstoffen in energieintensiven Industriebranchen, wie beispielsweise in Zementwerken oder in der Stahlproduktion, hat in den letzten Jahren stark an Bedeutung gewonnen. Vor dem Hintergrund der Einsparung von Primärrohstoffen und der Reduktion von klimarelevanten CO_2-Emissionen, liegt beispielsweise die thermische Substitutionsrate in der Zementindustrie in der Europäischen Union bei mittlerweile mehr als 34 % (VÖZ 2015). In einzelnen Ländern werden bereits mehr als 50 % des thermischen Energiebedarfs in Zementwerken durch Ersatzbrennstoffe gedeckt – z. B. Österreich 76 %, Deutschland 65 %, Belgien 60 %, Schweiz 54 % (cemsuisse 2016; Rahman et al. 2015; VDZ 2017; VÖZ 2015).

Die Untersuchung und Deklaration von technischen und ökologischen Eigenschaften alternativer Brennstoffe ist sowohl für Produzenten als auch für deren Abnehmer von Relevanz. Beispielsweise ist laut europäischem Standard EN 15359:2011 neben der

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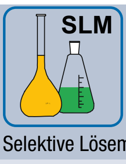
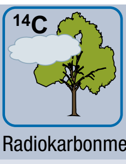
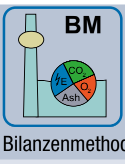
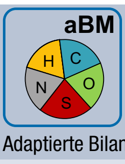
Tab. 1 Gegenüberstellung der Methoden zur Bestimmung des fossilen/biogenen Anteils in Abfallgemischen und Ersatzbrennstoffen

	 MS Manuelle Sortierung	 SLM Selektive Lösemethode	 ^{14}C Radiokarbonmethode	 BM Bilanzenmethode	 aBM Adaptierte Bilanzenmethode
Standardisiert	✔ EN 15440:2011	✔ EN 15440:2011	✔ EN 15440:2011	✔ ISO 18466:2016	–
Grundprinzip	Manuelle Sortierung in biogen und fossil	Chemische Lösung von biogenen Massenanteilen	Unterschiedlicher Gehalt des ^{14}C-Isotops in biogenen und fossilen Anteilen	Abgleich von Massen-, Stoff- und Energiebilanzgleichungen in MVA	Abgleich von Stoffbilanzgleichungen (C, H, N, S, O)
Analyse von	Feststoffprobe	Feststoffprobe	Feststoffprobe oder Rauchgas	Anlagenbetriebsdaten	Feststoffprobe
Bestimmung von fossil/biogen:					
Massenanteil	✔	✔	–	✔	✔
Kohlenstoffanteil (CO_2-Emissionen)	(✔)	(✔)	✔	✔	✔
Energieanteil	(✔)	(✔)	(✔)	✔	✔

✔ Direkt ableitbar bei Anwendung der Methode
(✔) Ableitbar nur mittels zusätzlichen Informationen/Analysen: z. B. Informationen zu Kohlenstoff- oder Energiegehalt der biogenen und fossilen Materialien der sortierten Fraktionen (MS), zu Kohlenstoff- oder Energiegehalt des Löserückstands (SLM), zu Energiegehalt der biogenen und fossilen Materialien (^{14}C).

verpflichtenden Deklaration des Heizwertes, des Chlor- und Quecksilbergehalts auch der Biomassegehalt optional auszuweisen. Als Biomasse in Ersatzbrennstoffen ist derjenige Anteil zu verstehen, der biogenen Ursprungs ist (Papier, Holz, Gartenabfälle, etc.) und daher als erneuerbare Energiequelle gilt. Demnach sind die bei der thermischen Verwertung entstehenden CO_2-Emissionen als nicht klimarelevant einzustufen. Dadurch ergibt sich durch den Einsatz von biomassehaltigen Ersatzbrennstoffen eine Einsparung klimarelevanter CO_2-Emissionen im Vergleich zum Einsatz von fossilen Brennstoffen (wie Kohle, Erdöl, Erdgas). Um die tatsächliche Einsparung zu bestimmen und entsprechend nachzuweisen (z. B. im Zuge des Erwerbs von Emissionszertifikaten), ist es erforderlich, den fossilen Kohlenstoffanteil bzw. den fossilen CO_2-Emissionsfaktor der eingesetzten Ersatzbrennstoffe zu bestimmen. Durch die typischerweise stark variierende Zusammensetzung der Ausgangsmaterialien für die Produktion von Ersatzbrennstoffen (wie Siedlungsabfälle, Gewerbeabfälle), ist eine zuverlässige Aussage jedoch nur bei periodisch wiederkehrender Bestimmung des fossilen Anteils gegeben. Generell bedarf es einer Bestimmungsmethode, die der Heterogenität der Abfallgemische gerecht wird, verlässliche Werte liefert und mit vertretbarem finanziellem und zeitlichem Aufwand verbunden ist.

2 Verfügbare Methoden zur Bestimmung der Klimarelevanz von Ersatzbrennstoffen

Bisher werden drei Methoden zur Bestimmung des fossilen Anteils in Ersatzbrennstoffen in der Norm EN 15440:2011 angeführt: Manuelle Sortierung (MS), Selektive Lösemethode (SLM) und Radiokarbonmethode (^{14}C-Methode). Alle drei Methoden sind auf feste Ersatzbrennstoffproben (sprich vor der thermischen Verwertung) anwendbar, jedoch teils limitiert in ihrer Anwendbarkeit und Parameterbereitstellung (Tab. 1). Eine kostengünstige Alternative stellt die sogenannte Bilanzenmethode (BM) dar, die kürzlich im Standard ISO 18466:2016 beschrieben wurde und in ihrer ursprünglichen Version eine Auswertung von Betriebsdaten von Müllverbrennungsanlagen (MVA) vorsieht (sprich nach der thermischen Verwertung durch Messungen im Rauchgas bzw. anderer Anlagenbetriebsdaten). Basierend auf dieser Methode wurde die adaptierte Bilanzenmethode (aBM) entwickelt, welche nach dem gleichen Grundprinzip wie die Ursprungsversion arbeitet (Abgleich von Bilanzgleichungen), jedoch eine Charakterisierung von Feststoffproben im Labor erlaubt. Damit können diese neue Methode sowie die bereits standardisierten Methoden MS, SLM, und ^{14}C-Methode auf Ersatzbrennstoffe vor deren thermischer Verwertung angewandt werden. Bisherige Untersuchungen zeigen, dass die aBM einige methodische Vorteile bietet und bei Anwendung auf vordefinierte Abfallgemische präzise und richtige Ergebnisse liefert (Aschenbrenner et al. 2009; Fellner et al. 2011; Schwarzböck et al. 2016). Beispielsweise können diverse Parameter (wie der fossile/biogene Massen- Kohlenstoff- und Energieanteil, Emissionsfaktoren, Kunststoffgehalt) direkt abgeleitet werden ohne Zusatzinformationen oder -analysen zu benötigen, wie dies bei den standardisierten Methoden der Fall ist (Tab. 1). Zudem konnten im Vergleich zu alternativen Bestimmungsmethoden verringerte Unsicherheiten beobachtet werden (Schwarzböck et al. 2016).

3 Zielsetzung der Studie

Übergeordnetes Ziel der vorliegenden Studie ist es, die adaptierte Bilanzenmethode (aBM) an verschiedenen Ersatzbrennstoffproben zu testen und mit standardisierten Verfahren zu vergleichen. Letzteres ist als Validierung der aBM zu verstehen.

Im Konkreten werden im vorliegenden Beitrag Untersuchungen mit realen Ersatzbrennstoffen vorgestellt und Fragen zur Zuverlässigkeit, Robustheit sowie praktischen Anwendbarkeit der neuen Methode behandelt. Dazu wurden

- Sortierungen durchgeführt um EBS-spezifische Eingangsparameter der

Tab. 2 Untersuchte Ersatzbrennstoffe und angewandte Methoden

	Herkunft	Anzahl an Proben (Tagesstichproben)	MS	SLM	^{14}C	aBM
Papier Rejekt	Ausgeschleustes Material aus der Altpapieraufbereitung	15 (je rund 10 kg trocken)	✔	✔	✔	✔
EBS 1	EBS produziert aus voraufbereiteten Siedlungsabfällen sowie Gewerbe- und Industrieabfällen	8 (je rund 5 kg trocken)	✔	✔	✔	✔
EBS 2	EBS produziert aus vorwiegend Gewerbe- und Industrieabfällen	8 (je rund 5 kg trocken)	✔	✔	✔	✔
EBS 3	EBS produziert aus vorwiegend Gewerbe- und Industrieabfällen	3	✔	–	–	✔
EBS 4	EBS produziert aus vorwiegend Gewerbe- und Industrieabfällen	2	✔	–	–	✔
EBS 5	EBS produziert aus vorwiegend Gewerbe- und Industrieabfällen	3	✔	–	–	✔

MS Manuelle Sortierung, *SLM* Selektive Lösemethode, *^{14}C* Radiokarbonmethode, *aBM* adaptierte Bilanzenmethode

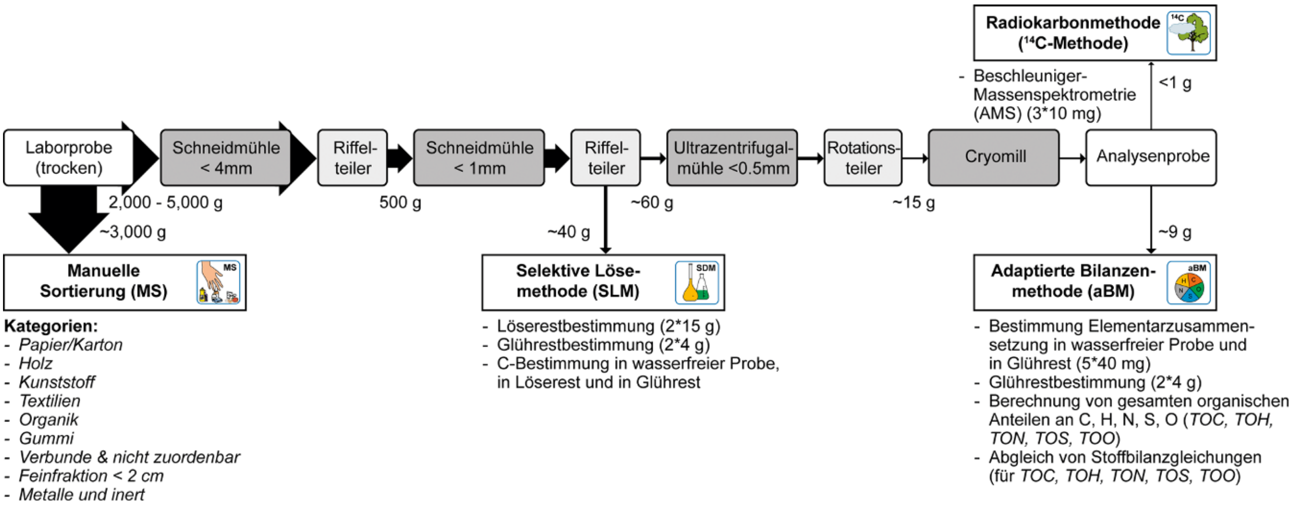


Abb. 1 Schema der Probenaufbereitung und der angewandten Bestimmungsmethoden

aBM zu generieren und mit Literaturdaten zu vergleichen,

- Ergebnisse aus der Anwendung der aBM mit Ergebnissen der drei bereits standardisierten Methoden verglichen und
- die Praktikabilität (Arbeitsaufwand, Verfügbarkeit, Kosten) der verfügbaren Bestimmungsmethoden gegenübergestellt.

4 Methodik

4.1 Untersuchte Ersatzbrennstoffe und Probenaufbereitung

Im Zuge der Studie wurden Proben sechs verschiedener Ersatzbrennstoffe mithilfe der aBM auf ihre Klimarelevanz untersucht (Tab. 2), wobei für alle Ersatzbrennstoffe auch eine Manuelle Sortierung (MS) durchgeführt wurde. Zusätzlich wurden für drei der EBS die Selektive Lösemethode (SLM) sowie die Radiokarbonmethode (^{14}C-Methode) (Tab. 2) angewandt. Die Methoden werden in Abschn. 4.2–4.5 näher erläutert.

In Abhängigkeit von der jeweiligen Analysemethode sind verschiedene Aufbereitungsschritte für die EBS-Proben notwendig (Abb. 1). Die aBM erfordert beispielsweise eine sehr feine Partikelgröße (0,5 mm oder kleiner), da die Elementaranalyse mittels katalytischer Verbrennung nur eine geringe Probeneinwaage (rund 40 mg pro Analyse) zulässt. Dies ist ähnlich bei der ^{14}C-Methode. Die SLM hingegen sieht die chemische Behandlung der Proben bei einer Partikelgröße von <1 mm vor.

4.2 Adaptierte Bilanzenmethode (aBM)

4.2.1 Methodenbeschreibung und notwendige Eingangswerte

Die adaptierte Bilanzenmethode beruht auf der unterschiedlichen Elementarzusammensetzung von biogenen und fossilen Materialien. Während (wasser- und aschefreie) biogene Materialien einen Kohlenstoff- und Sauerstoffgehalt im Bereich von 40–50 % aufweisen, sind fossile Materialien (Kunststoffe) zumeist durch geringe Sauerstoffgehalte (<15 %) und höhere Kohlenstoffgehalte (>70 %) gekennzeichnet. Dieser Unterschied wird gemeinsam mit der über Laboranalysen bestimmten Elementarzusammensetzung des Ersatzbrennstoffs verwendet, um den Anteil an biogenen bzw. fossilen Materialien zu berechnen.

Eine schematische Darstellung des Konzeptes findet sich in Abb. 2. Im Konkreten verwendet die aBM pro Element (Kohlenstoff, Wasserstoff, Stickstoff, Schwefel und Sauerstoff) eine Bilanzgleichung, wobei jede der insgesamt fünf Bilanzgleichungen die gesuchten Massenanteile an biogenen und fossilen Materialien (unbekannte Variablen m_B und m_F) enthält. Die Koeffizienten und Variablen der Gleichungen werden auf wasser- und aschefreier Basis berücksichtigt. So können valide Elementarzusammensetzungen für biogene und fossile Materialien, unabhängig von ihrem Wasser- und Aschegehalt, abgeleitet und verwendet werden (Koeffizienten der linken Seite der Bilanzgleichungen). Werte der rechten Seite der Bilanzgleichungen repräsen-

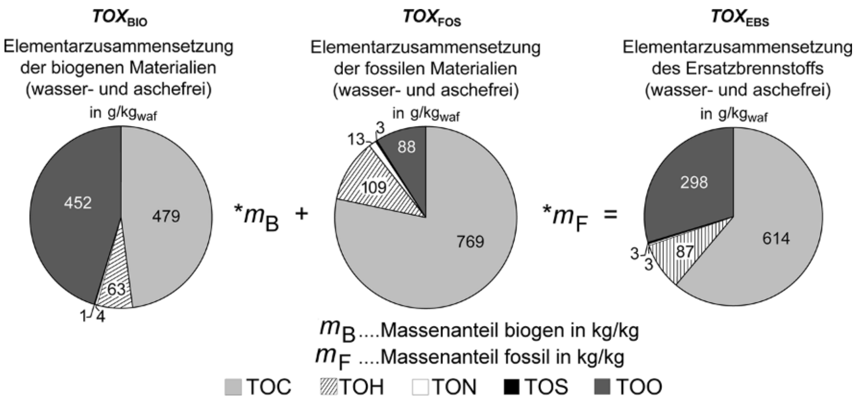


Abb. 2 Schematische Darstellung der adaptierten Bilanzenmethode anhand derer Bilanzgleichungen für *TOC*, *TOH*, *TON*, *TOS* und *TOO* aufgestellt werden. (Nach Schwarzböck et al. 2016)

tieren die Elementarzusammensetzung des zu untersuchenden Ersatzbrennstoffs, die durch Analysen im Labor bestimmbar ist. Zusätzlich zu den fünf Bilanzgleichungen für den organischen Kohlenstoff *(TOC)*, organischen Wasserstoff *(TOH)*, organischen Stickstoff *(TON)*, organischen Schwefel *(TOS)*, organischen Sauerstoff *(TOO)* gilt die Randbedingung, dass die Summe aus Massenanteil biogen und fossil per Definition gleich 1 ist. Das Gleichungssystem der aBM besteht in Summe somit aus 6 Bilanzgleichungen (*TOC*, *TOH*, *TON*, *TOS*, *TOO*, Summe aus m_B und m_F) mit 2 unbekannten Massenanteilen (m_B und m_F). Für jeden Eingabewert des Gleichungssystems wird eine entsprechende Unsicherheit definiert. Es handelt sich somit um ein überbestimmtes System, das mithilfe nichtlinearer Ausgleichsrechnung zu lösen ist. Konkret wird dazu die Methode der schrittweisen linearen Ausgleichsrechnung angewandt. Als Ergebnis erhält man die berechneten Massenanteile biogener und fossiler Materialien m_B, m_F, sowie die zugehörigen Unsicherheitsbereiche (Detailinformationen in Fellner et al. 2011).

Neben dem biogenen und fossilen Massenanteil lässt sich durch die aBM auch der fossile Kohlenstoffanteil ($m_{F,TC}$) (gleichzusetzen mit dem fossilen CO_2-Anteil) ableiten. Dazu wird das Ergebnis von m_F in die Bilanzgleichung für Kohlenstoff eingesetzt:

$$m_{F,TC} = ((m_F * \mathrm{TOC_{FOS}}) * (1 - A) + A * \mathrm{TIC_{EBS}}) / \mathrm{TC_{EBS}} \tag{1}$$

mit

$m_{F,TC}$ = fossiler Kohlenstoffanteil in kg/kg
m_F = fossiler Massenanteil in kg/kg
TOC_{FOS} = gesamter organischer Kohlenstoff in der fossilen Fraktion in g/kg
A = Aschegehalt in kg/kg
TIC_{EBS} = gesamter Kohlenstoff im Glührest des EBS in g/kg
TC_{EBS} = Gesamtkohlenstoff im EBS in g/kg

Der mittels Elementaranalysen bestimmte Kohlenstoffgehalt im EBS (TC_{EBS}) und in der Asche des EBS (TIC_{EBS}) kann hierfür verwendet werden.

Zusätzlich ermöglicht es die Methode, den biogenen und fossilen Energieanteil abzuschätzen. Dazu werden empirische Formeln zur Bestimmung des Heizwertes herangezogen, welche sich der Elementarzusammensetzung bedienen (z. B. Verbandsformel nach Dulong, Boie, Steurer oder Scheurer-Kestner, zitiert u. a. in Kost 2001; Liu et al. 1996; Rotter et al. 2011). In vorliegender Studie wurde die Formel von Boie nach Kost (2001) verwendet.

Schließlich können auch EBS-spezifische fossile CO_2-Emissionsfaktoren berechnet werden, die die Menge an emittiertem fossilem CO_2 auf die EBS-Masse oder den Energieinhalt (Heizwert) beziehen:

$$\text{Emissionsfaktor in } \mathrm{kg_{CO2,fos}}/t_{\mathrm{EBS}} = \mathrm{TC_{EBS}} * m_{F,TC} * M_{C02}/M_C \tag{2}$$

$$\text{Emissionsfaktor in } \mathrm{kg_{CO2,fos}}/\mathrm{GJ} = \left(\mathrm{TC_{EBS}} * m_{F,TC} * \frac{M_{C02}}{M_C}\right) / q_{\mathrm{EBS}} \tag{3}$$

mit

M_{CO2} und M_C = molare Masse von CO_2 bzw. von Kohlenstoff in g/mol
q_{EBS} = unterer Heizwert des EBS in GJ/t

Notwendige Eingangswerte der aBM sind dementsprechend:

1. Daten zur Elementarzusammensetzung des wasser- und aschefreien Ersatzbrennstoffs (TOX_{EBS})[1]. Diese sind ableitbar aus Elementaranalysen (C-, H-, N-, S-, O-Analysen) zusammen mit der Bestimmung des Aschegehalts des Ersatzbrennstoffs.
2. Daten zur Elementarzusammensetzung der wasser- und aschefreien biogenen und fossilen Materialien im Ersatzbrennstoff (TOX_{BIO}, TOX_{FOS}). Diese Informationen können der Literatur entnommen oder durch Sortierungen und anschließende Laboranalysen für den jeweiligen Ersatzbrennstoff spezifisch bestimmt werden. Eine einmalige Bestimmung der Werte für den jeweiligen Ersatzbrennstoff ist dabei in der Regel ausreichend. In vorliegender Studie wurden TOX_{BIO} und TOX_{FOS} für 6 verschiedene Ersatzbrennstoffe einzeln bestimmt, um sie mit Literaturwerten zu vergleichen und mögliche Variationen abzuschätzen (siehe Abschn. 4.2.2.).

4.2.2 Bestimmung der EBS-spezifischen Elementarzusammensetzung von biogenen und fossilen Materialien

Um die Gültigkeit von Literaturwerten zur Elementarzusammensetzung biogener und fossiler Materialien (TOX_{BIO} und TOX_{FOS} aus Abb. 2) zu überprüfen sowie weitere Daten für zukünftige Anwendungen zu generieren, wurden detaillierte Werte zur Elementarzusammensetzung der wasser- und aschefreien biogenen und fossilen Materialien für sechs verschiedene Ersatzbrennstoffe erhoben. Diese Erhebung kann bei routinemäßiger Anwendung der aBM auf bereits bekannte Ersatzbrennstoffe entfallen. In der gegenständlichen Studie zur Validierung der aBM wurden die Ersatzbrennstoffproben manuell jeweils in 9 Fraktionen sortiert: *Papier/Karton, Holz, Kunststoffe, Textilien, Organik, Gummi, Verbunde & nicht*

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[1] X = C, H, N, S oder O

zuordenbar, Feinfraktion <~2 cm, Metalle & inert. Für jede sortierte Fraktion wurde zuerst ein biogener bzw. fossiler Massenanteil abgeschätzt.

In einem weiteren Schritt wurden den sortierten biogenen bzw. fossilen Fraktionen die entsprechende Elementarzusammensetzung (*TOC, TOH, TON, TOS, TOO*) zugeordnet. Für die Fraktionen *Papier/Karton, Holz, Organik* und *Kunststoffe* konnten dazu Analysewerte verwendet werden, da diese fast gänzlich als biogen bzw. *Kunststoffe* fast ausschließlich als fossil eingestuft werden können. Diese Zuordnung biogen oder fossil ist bei den Fraktionen *Textilien, Gummi, Verbunde & nicht zuordenbar* sowie *Feinfraktion* nicht unmittelbar möglich. Folgende Annahmen und Zusatzuntersuchungen wurden daher für diese „gemischten" Fraktionen berücksichtigt:

a) Vernachlässigung der Fraktion *Gummi*, wenn der Massenanteil weniger als 1 % ausmacht (mit Ausnahme von EBS 5, wo ein Anteil an Gummi von 1,2 % gefunden wurde, konnte diese Vereinfachung angewandt werden).
b) Durchführung von Auswertungen mittels aBM unter Verwendung der Analyseergebnisse der eindeutig in biogen und fossil sortierbaren Fraktionen (Elementarzusammensetzung) für TOX_{BIO} und TOX_{FOS}, um grobe Massenanteile für die gemischten Fraktionen abzuschätzen.
c) Anwendung der SLM auf einzelne Fraktionen, um biogene und fossile Massenanteile abzuschätzen.
d) Anwendung der ^{14}C-Methode auf einzelne Fraktionen, um biogene und fossile Kohlenstoffanteile abzuschätzen.
e) Annahme, dass der biogene Anteil in der Fraktion *Verbunde & nicht zuordenbar* Papier / Karton entspricht und der fossile Anteil aus Kunststoffen besteht, wobei angenommen wird, dass die Elementarzusammensetzung biogener und fossiler Materialien in dieser Fraktion den mittleren Werten gemäß Kost (2001) entspricht.
f) Annahme, dass die in den EBS enthaltenen Naturfasern aus 90 % Zellulose und 10 % Wolle bestehen und Kunstfasern aus Polyamid (30 %), Polyester (49 %), Polyacrylnitril (15 %), Polypropylen (6 %) zusammengesetzt sind (basierend auf Auswertungen in Kost 2001). Die entsprechende Elementarzusammensetzung der einzelnen Materialien folgt jeweils aus theoretischen Daten.
g) Vernachlässigung der Fraktion *Metalle & inert*, da diese für die Auswertung des Kohlenstoffanteils nicht relevant ist.

Dadurch konnte sowohl die Sortierpräzision der „reinen" biogenen bzw. fossilen Fraktionen abgeschätzt werden, als auch eine Annahme zur Zusammensetzung der gemischten Fraktionen getroffen werden.

Detailergebnisse zur Sortierung sowie zur Elementarzusammensetzung der einzelnen sortierten Fraktionen der untersuchten Ersatzbrennstoffe sind in Schwarzböck et al. (2017) zu finden. In selbiger Publikation konnte auch die generelle Eignung der Vorgehensweise zur Bestimmung der notwendigen Eingangsparameter TOX_{BIO} und TOX_{FOS} für die aBM bestätigt werden.

4.3 Manuelle Sortierung (MS)

Für die Anwendung der Manuellen Sortierung gemäß EN 15440:2011 wurden die Sortierergebnisse wie in Abschn. 4.2.2. beschrieben verwendet (Sortierung in 9 verschiedene Fraktionen). Wie für die Generierung der Eingangswerte für die aBM ist es auch für die MS erforderlich, einen biogenen bzw. fossilen Massenanteil pro sortierter Fraktion zuzuordnen. Für die MS wurde dafür auf Angaben in der Norm zurückgegriffen, wobei für die Fraktion Verbund keine Zuordnung vorgegeben wird und ein fossiler Massenanteil von 50 % angenommen wurde. Mithilfe der sortierten Fraktionen und der jeweiligen Massenanteile in den Fraktionen kann schlussendlich ein fossiler Massenanteil pro EBS berechnet werden. Die Berechnungen dazu wurden nach EN 15440:2011 durchgeführt, wobei die Sortierpräzision gemäß Norm nicht abschätzbar war und vereinfacht mit 100 % angenommen wurde. Diese Annahme scheint durch die äußerst penible Sortierung der Fraktionen gerechtfertigt. Eine Unsicherheit wurde berücksichtigt, indem auf Auswertungen einzelner sortierter Fraktionen gemäß aBM, SLM und ^{14}C-Methode zurückgegriffen wurde (Ergebnisse aus Abschn. 4.2.2.).

Um von den Sortierergebnissen auch auf einen fossilen Kohlenstoffanteil zu schließen, muss ein fossiler bzw. biogener Kohlenstoffgehalt in den sortierten Fraktionen angenommen oder bestimmt werden. Hierfür wurde auf Angaben in Kost (2001) zurückgegriffen, insbesondere auf die Kohlenstoffgehalte in Papier, Holz, Wolle, gemischter Organik und gemischten Kunststoffen. Kohlenstoffgehalte in Naturfasern und Kunstfasern konnten mittels chemischer Strukturformel von Zellulose, Polyamid, Polyester, Polyacrylnitril und Polypropylen und deren jeweiliger Anteile (gemäß Kost 2001) abgeschätzt werden.

4.4 Selektive Lösemethode (SLM)

Die Selektive Lösemethode beruht auf der selektiven Auflösung der Probenmatrix und Oxidation der biogenen Anteile bei Behandlung mit konzentrierter Schwefelsäure und anschließender Zugabe von Wasserstoffperoxid. Die fossilen und inerten Bestandteile verbleiben – so die Erwartung – als Rückstand (EN 15440:2011).

Nicht alle Materialien folgen dieser Annahme, beispielsweise lösen sich einige biogene Substanzen nicht (z. B. Leder, Lignin, Wolle, Gummi aus Naturkautschuk) und werden somit als fossil quantifiziert, während sich insbesondere Kunststoffe mit Aminogruppen ungewollt lösen und damit fälschlicherweise als biogen eingestuft werden (z. B. Nylon, Polyurethan) (Cuperus et al. 2005; EN 15440:2011; Staber et al. 2008). Bei Vorhandensein signifikanter Anteile an den genannten Materialien führt die Methodik der SLM zu Fehleinschätzungen, wobei die Unsicherheit bzw. der mögliche Fehler zumeist schwer abzuschätzen ist.

Die SLM wurde im Zuge der Studie gemäß EN 15440:2011 angewandt. Um der Heterogenität der Proben gerecht zu werden, wurde eine Prüfmenge von 15 g gewählt (bei einer Partikelgröße von <1 mm laut Norm). Zusätzlich wurden Doppelbestimmungen pro Probe durchgeführt. Der Kohlenstoffgehalt der Proben <1 mm, des Löserestes und des Glührestes wurde mittels katalytischer Verbrennung in einem Elementaranalysator (Elementar Vario Macro, Elementar Analysensysteme GmbH) bestimmt. Über die Differenz der Kohlenstoffanalyse in der Ausgangs- und der gelösten Probe lässt sich der fossile Kohlenstoffanteil berechnen.

Gesamt wurden 25 Proben mittels SLM untersucht: 15 Papier-Rejekt-Proben, 5 EBS 1-Proben und 5 EBS 2-Proben (Begrenzungen des Probenum-

Tab. 3 ^{14}C-Gehalt in der biogenen Fraktion der EBS, verwendet als Referenzwert zur Bestimmung des fossilen Kohlenstoffanteils mittels ^{14}C-Methode

	Papier-Rejekt	EBS 1	EBS 2
^{14}C-Gehalt F^{14}C$_{\mathrm{bio}}$ in pMC	1,080 ± 0,024	1,088 ± 0,038	1,101 ± 0,038
Angaben als Mittelwert mit Standardabweichung			

fangs aufgrund von Zeit- und Budgetlimitierung).

Die Unsicherheit der Ergebnisse wurde anhand der Doppelbestimmung (als Wiederholpräzision) und mit Verwendung von Angaben zur Vergleichspräzision in der Norm (Tabelle F. 1.4 in EN 15440:2011) berechnet.

4.5 Radiokarbonmethode (^{14}C-Methode)

Die Radiokarbonmethode (^{14}C-Methode) stammt aus der Altersdatierung und macht sich das unterschiedliche Verhältnis von ^{14}C und ^{12}C in biogenen und fossilen Materialien zu Nutze. Der F^{14}C ist definiert als das ^{14}C/^{12}C Verhältnis einer Probe im Vergleich zu dem Isotopenverhältnis des Referenzjahres 1950 (Reimer et al. 2004). Biogene Materialien haben dementsprechend einen F^{14}C Wert von rund 1, während ^{14}C in fossilen Materialien zerfallen ist und dementsprechend der F^{14}C Wert bei 0 liegt. Neben dem Isotopenverhältnis in der untersuchten Probe wird für die Berechnung des biogenen Kohlenstoffanteils der mittlere F^{14}C-Gehalt in der reinen biogenen Fraktion des EBS als Referenzwert benötigt. Der F^{14}C-Referenzwert ist abhängig vom Alter bzw. den Wachstumsjahren der Biomasse und bestimmt im Wesentlichen die Unsicherheit der Methode. Grund dafür sind Atomwaffentests im letzten Jahrhundert, die den ^{14}C-Gehalt der Atmosphäre maßgebend verändert haben. Dennoch gilt die ^{14}C-Methode unter den verfügbaren Verfahren zur Bestimmung des fossilen Anteils in Ersatzbrennstoffen als die zuverlässigste mit der geringsten analytischen Unsicherheit; z. B. Beschleuniger-Massenspektrometrie AMS <3–7 % relative Unsicherheit (Mohn et al. 2008, 2012; Palstra und Meijer 2010). Daher wird sie in dieser Studie als primäre Vergleichsmethode herangezogen.

Für die untersuchten EBS-Proben wurden Radiokarbonanalysen gemäß EN 15440:2011 mittels AMS durchgeführt. Fein zermahlene Proben wurden einer Dreifachbestimmung von je 10 mg unterzogen. Insgesamt wurden 16 Proben analysiert: 8 Papier-Rejekt-Proben, 4 EBS 1-Proben, 4 EBS 2-Proben. Eine Bestimmung mittels ^{14}C-Methode für alle Proben konnte aufgrund budgetärer Beschränkungen nicht durchgeführt werden.

Die F^{14}C-Referenzwerte der verschiedenen biogenen Materialien in den EBS wurden gemäß Mohn et al. (2008) bestimmt und mithilfe der ungefähren Anteile an *Papier/Karton*, *Holz*, *Textilien* und *Organik*, die aus den Ergebnissen der manuellen Sortierung der EBS bekannt waren, kombiniert. Für *Papier/Karton* in Papier-Rejekt wurden zusätzliche ^{14}C-Analysen durchgeführt um die Unsicherheit des Referenzwertes zu reduzieren (der Anteil von *Papier/Karton* in der gesamten biogenen Fraktion des Papier-Rejekts beträgt rund 92 %). F^{14}C-Referenzwerte für die biogene Fraktion in den einzelnen EBS konnten damit abgeleitet werden (Tab. 3).

Die Gesamtunsicherheit (Standardabweichung) der Ergebnisse der Radiokarbonanalysen ergibt sich vorwiegend aus der Unsicherheit des F^{14}C-Referenzwertes der enthaltenen Biomasse (wurde mit 3 % relativ abgeschätzt). Hinzu kommt die Messunsicherheit aus den Messwiederholungen (2–3 %relativ).

4.6 Chemische Analysen

4.6.1 Wasser- und Aschegehalt

Der Wassergehalt der Laborproben wurde durch Trocknung bei 105 °C für mindestens 24 h bestimmt (Beginn der Trocknung direkt nach der Anlieferung im Labor). Der Aschegehalt (*A*) wurde gemäß Norm EN 15403:2011 ermittelt, indem rund 4 g des aufbereiteten Probenmaterials nach einer Trocknung bei 105 °C einem Muffelofen zugeführt und bei 350 °C für eine Stunde und anschließend unter Lufteinblasung bei 550 °C für vier Stunden verascht wurden.

4.6.2 Elementaranalysen

Alle Elementaranalysen (inklusive der Kohlenstoffgehalte) wurden mittels katalytischer Verbrennung in einem Elementaranalysator (Elementar Vario Macro und Elementar Vario EL, Elementar Analysensysteme GmbH) durchgeführt (gemäß DIN 51732:2014). Bei einer Verbrennungstemperatur von 1150 °C wurden der Gesamtkohlenstoff (*TC*), Gesamtwasserstoff (*TH*), Gesamtstickstoff (*TN*), Gesamtschwefel (*TS*) und Gesamtsauerstoff (*TO*) ermittelt, wobei die Sauerstoffbestimmung unter Sauerstoffabschluss erfolgt. Pro Probe wurden fünf Messungen mit je 40 mg (*TC, TH, TN, TS*) bzw. sieben Messungen mit je 4 mg (*TO*) durchgeführt. Die geringere Einwaage für die *TO*-Bestimmungen ist durch eine gerätespezifische Limitierung der maximalen Sauerstoffmenge von 2 mg absolut bedingt.

Für die aBM wurden aus den Gesamtgehalten (*TC, TH, TN, TS, TO*) zusammen mit dem Aschegehalt sowie Gesamtgehalten in der Asche (*TIC, TIH, TIN, TIS, TIO*), Elementargehalte auf wasser- und aschefreier Basis berechnet (*TOC, TOH, TON, TOS, TOO*) (Berechnung gemäß Schwarzböck et al. 2016, Formel (1)).

5 Ergebnisse und Diskussion

5.1 Elementarzusammensetzung der biogenen und fossilen Materialien

Für die Anwendung der aBM sind Informationen zur Elementarzusammensetzung der wasser- und aschefreien biogenen und fossilen Materialien im Ersatzbrennstoff (TOX_{BIO}, TOX_{FOS}) erforderlich. In vorliegender Studie wurden diese für sechs verschiedene EBS ermittelt (siehe Abschn. 4.2.2.). Aus Abb. 3 ist ersichtlich, dass der Wertebereich für die ermittelten Daten für fast alle Parameter gut einzugrenzen ist. Insbesondere die Kennwerte für *TOC* und *TOH* liegen sowohl bei biogen als auch bei fossil für alle EBS sehr nahe beisammen und stimmen gut mit den aus der Literatur abgeleiteten Werten in Fellner et al. (2011) überein. Unter Berücksichtigung aller neu generierten Werte zeigt sich eine Variabilität für *TOC* und *TOH* von weniger als 2 %relativ (in biogenen Materialien) und weniger als 6 %relativ (in fossilen Materialien). Am deutlichsten variieren die einzelnen Werte für TOO_{FOS} mit knapp 40 %relativ. Diese Streuung zeugt von einer signifikanten Abhängigkeit von TOO_{FOS} von der Kunststoffzusam-

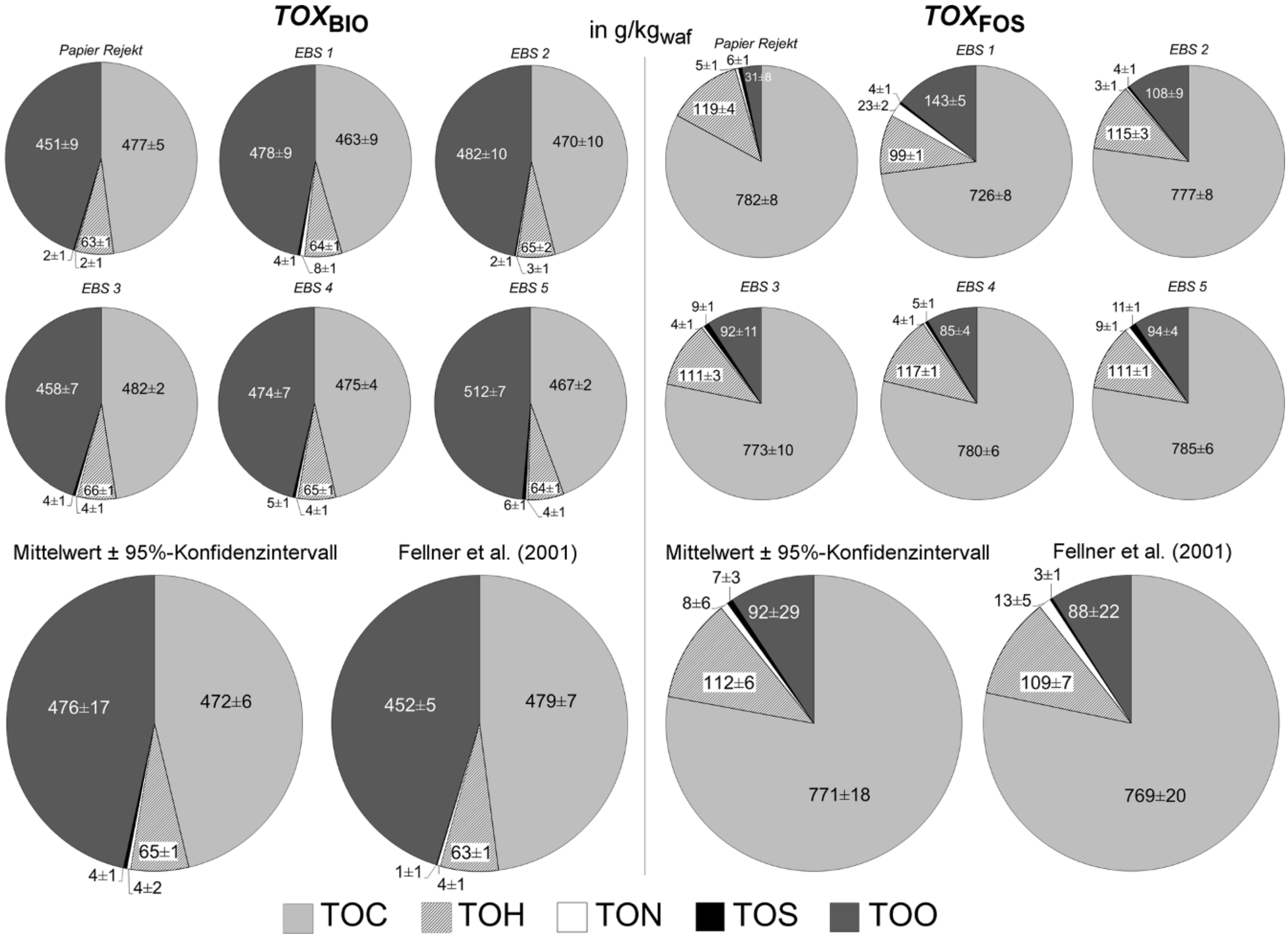


Abb. 3 Elementare Zusammensetzung der biogenen und fossilen Materialien auf wasser- und aschefreier Basis (waf), bestimmt für sechs verschiedene Ersatzbrennstoffe. Mittelwerte pro EBS mit Standardabweichung und Gesamtmittelwerte über alle EBS mit 95-%-Konfidenzintervall

mensetzung in den EBS. Ein höherer *TOO*-Gehalt in den fossilen Materialien von EBS 1 (bei gleichzeitig niedrigerem *TOC*- und *TOH*-Gehalt) im Vergleich zu den anderen EBS deutet auf Anteile an Polyamid, Polyurethan oder Polyethylenterephthalat in diesem EBS hin. Diese Polymere, die einen höheren Gehalt an Sauerstoff aufweisen, dürften in den übrigen fünf EBS unwesentlich vertreten sein. In Papier-Rejekt dagegen ist anzunehmen, dass Polyethylene und Polypropylen die wesentlichen Bestandteile der Kunststofffraktion sind (*TOO*-Gehalt sehr gering).

Die sehr geringe Variabilität der Elementarzusammensetzung für biogene Materialien (TOX_{BIO}) weist darauf hin, dass verschiedene Anteile an Materialien in der biogenen Fraktion der EBS (z. B. Karton, Papier, Holz, Textilien) die Kennwerte nur unwesentlich beeinflussen. Trotz signifikant höherer Anteile an Papier in Papier-Rejekt (37 %, andere EBS <7 %) oder Textilien in EBS 1 (23 %, andere EBS <8 %) liegen die generierten Kennwerte für diese EBS im Wertebereich der anderen EBS. Daher ist davon auszugehen, dass Daten zu TOX_{BIO} auch ohne aufwendige Sortierungen und Analysen abgeleitet werden können und allgemein für die aBM einsetzbar sind.

Die generierten Kennwerte legen zudem nahe, dass typische Werte für TOX_{BIO} und TOX_{FOS} für EBS desselben Typs abgeleitet werden können. Werte aller vier untersuchten EBS, die vorwiegend aus Gewerbe- und Industrieabfällen hergestellt werden (EBS 2, EBS 3, EBS 4, EBS 5) liegen im Konfidenzintervall von 95 % und zeigen unter sich sehr geringe Schwankungen bis maximal 10 %relativ (für TOO_{FOS}; exklusive *TON* und *TOS*). Es ist daher davon auszugehen, dass die generierten Kennwerte auch für andere EBS desselben Typs für die Anwendung der aBM Gültigkeit besitzen.

5.2 Fossiler Anteil der CO_2-Emissionen aus Ersatzbrennstoffen, bestimmt mittels verschiedener Methoden

Der fossile Kohlenstoffanteil von sechs verschiedenen EBS wurde mithilfe der in Abschn. 4.2–4.5 beschriebenen Methoden bestimmt. Unter der Annahme, dass der gesamte Kohlenstoff während der Verbrennung zu CO_2 oxidiert, ist der fossile Kohlenstoffanteil gleichzusetzen mit dem Anteil an fossilen CO_2-Emissionen nach der thermischen Verwertung der EBS.

Der Anteil der fossilen und damit klimarelevanten CO_2-Emissionen für die untersuchten Ersatzbrennstoffproben wurde mit 51,8–91,1 % bestimmt (Abb. 4). Für Papier-Rejekt ist im Vergleich zu den anderen EBS ein deutlich geringerer CO_2-Anteil als klimarele-

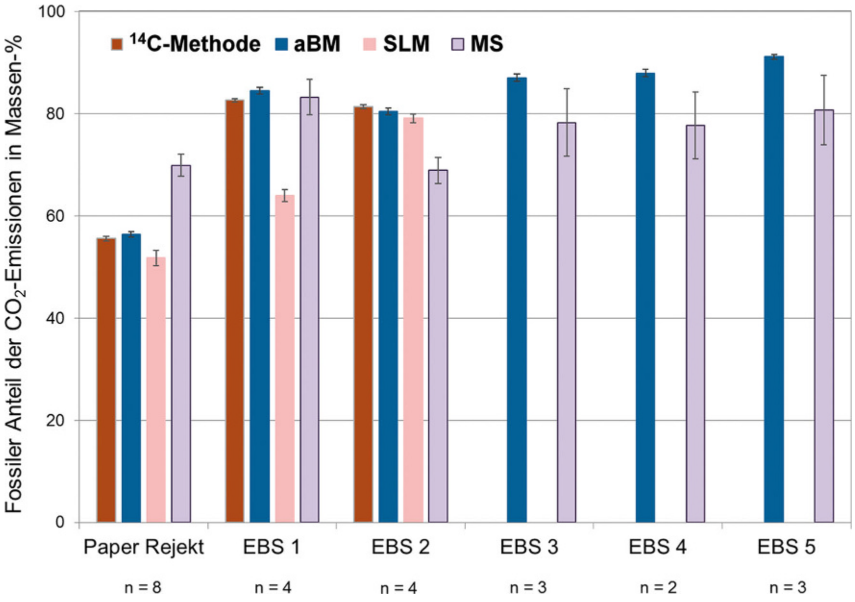


Abb. 4 Fossiler Anteil der CO_2-Emissionen bestimmt für sechs verschiedene Ersatzbrennstoffe unter Anwendung unterschiedlicher Bestimmungsmethoden (^{14}C-Methode, aBM, SLM, MS), Mittelwerte mit Standardabweichung (*n* Anzahl untersuchter Proben)

vant einzustufen (unter 60 %). Dies ist durch einen höheren Anteil an Papier und Karton bzw. geringeren Anteil an Kunststoffen in diesem EBS zu erklären. Laut Sortierungen ergaben sich rund 41 % Kunststoffe im Papier-Rejekt, während für alle anderen EBS ein Massenanteil an Kunststoffen von über 50 % gefunden wurde.

Abb. 4 zeigt eine sehr gute Übereinstimmung der mittels aBM gefundenen Werte zu den Werten der ^{14}C-Methode (Vergleichsmessungen für 3 verschiedene EBS verfügbar). Bezogen auf den mittleren fossilen Kohlenstoffanteil dreier verschiedener EBS (Paper-Rejekt, EBS 1, EBS 2) liegt die mittlere Abweichung bei 0,6 ± 1,4 %absolut. Diese geringe Differenz zwischen den zwei Methoden deutet auf die Richtigkeit der aBM hin, da die ^{14}C-Methode als Verfahren mit der geringsten analytischen Untersicherheit gilt. Betrachtet man die Ergebnisse der SLM im Vergleich zu den Werten der ^{14}C-Methode, ist erkennbar, dass tendenziell mit einer Unterschätzung des fossilen CO_2-Anteils durch die SLM zu rechnen ist. Im Konkreten weichen die Ergebnisse der SLM im Mittel –8,2 ± 9,1 %absolut von der ^{14}C-Methode ab. Der deutlichste Unterschied zwischen dem SLM-Ergebnis und den Werten der anderen Methoden ist für EBS 1 erkennbar, wo sich eine Unterschätzung von knapp 19 %absolut im Vergleich zur ^{14}C-Methode ergibt. Es ist anzunehmen, dass dieser höchst signifikante Unterschied auf einen vergleichsweise hohen Anteil an chemisch lösbaren Materialien fossilen Ursprungs zurückzuführen ist. In EBS 1 konnten beispielsweise relevante Massenanteile an geschäumten Kunststoffen (rund 16–26 %) und Textilien (fast 23 %) beobachtet werden; beides Materialgruppen, die potenziell Polymere mit Aminogruppen enthalten. Bei Behandlung mit konzentrierter Schwefelsäure werden diese Polymere fast gänzlich aufgelöst und deren Massenanteile daher fälschlicherweise dem biogenen Anteil zugeordnet. Diese Fehleinschätzung einzelner Materialgruppen durch die SLM ist auch in Abb. 5 erkennbar, in der fossile Kohlenstoffanteile für sortierte Fraktionen dargestellt werden. Speziell bei den Fraktionen *Kunststoffe, Textilien* und *Verbunde* zeigen sich durch die SLM Minderbefunde an fossilem Kohlenstoff.

Bei Vergleich der Ergebnisse der Manuellen Sortierung zur ^{14}C-Methode sind ebenfalls signifikante Unterschiede erkennbar (Abb. 4). Auffallend ist diese Differenz vorwiegend bei Proben des Papier-Rejekts, wo im Mittel durch die MS eine Überschätzung des fossilen CO_2-Anteils von 14,3 %absolut bestimmt wurde. Bei Proben des EBS 2 hingegen ist von einer Unterschätzung durch MS auszugehen (rund –5,4 %absolut). Gesamt gesehen ergibt sich eine mittlere Abweichung der MS-Ergebnisse von ^{14}C-Resultaten ohne klare Tendenz nach oben oder unten von 3,4 ± 10 %absolut. Diese Abweichungen sind auf verschiedene methodische Faktoren der MS begründet, u. a.:

a) Ein hoher Anteil der Feinfraktion (bei Papier-Rejekt mehr als 65 %) oder Textilien kann das Ergebnis verzerren, da hier gemäß EN 15440:2011 pauschal ein Massenanteil von 50 % fossil angenommen wird. In den Papier-Rejekt-Proben wurde beispielsweise durch Zusatzanalysen ein fossiler Massenanteil in der Feinfraktion von nur 40 % abgeschätzt, was zusammen mit dem hohen Feinfraktionanteil von 65 % im Papier-Rejekt zu einer Verzerrung des gesamten fossilen Anteils von 5–6 %absolut führt. Der Textilanteil der betrachteten EBS liegt zwischen 1 und 23 % (höchster Anteil in EBS 1), wobei analytisch (mittels aBM und ^{14}C-Methode) ein fossiler Anteil zwischen 35 und 97 % abgeschätzt wurde.
b) Eine Vorgabe für den fossilen Anteil in Verbundstoffen und nicht zuordenbaren Materialien wird in der Norm nicht gegeben. Diese Fraktion kann jedoch auch einen signifikanten Massenanteil ausmachen (z. B. in EBS 2 mehr als 40 %) und beeinflusst demnach gegebenenfalls das Ergebnis ebenfalls wesentlich.
c) Für die Abschätzung des fossilen Kohlenstoffanteils mittels MS sind Informationen zum Kohlenstoffgehalt in den sortierten Fraktionen notwendig. Durch Verwendung von Literaturwerten werden damit weitere Unsicherheiten in das Ergebnis eingebracht. Beispielsweise liegt der in dieser Studie aus der Literatur abgeleitete Kohlenstoffgehalt für biogene Materialien TOC_{BIO} rund 9 %absolut unter dem analytisch bestimmten Wert (im Fall von Papier-Rejekt).
d) Dazu kommt klarerweise noch die Unschärfe der Massenanteile, die durch das Sortieren an sich verursacht wird und die schwer quantifizierbar ist (gemäß Norm sollte dazu SLM durchgeführt werden). Auswertungen mittels aBM, SLM, und ^{14}C-Methode in der vorliegenden Studie weisen auf „Verunreinigungen“ der *Papier/Karton* Fraktionen und sortierten *Kunststoffe* von jeweils bis zu 8 Masseprozent hin. Diese Ergebnisse wurden nicht als Sortierpräzision, sondern als Unsicherheit der

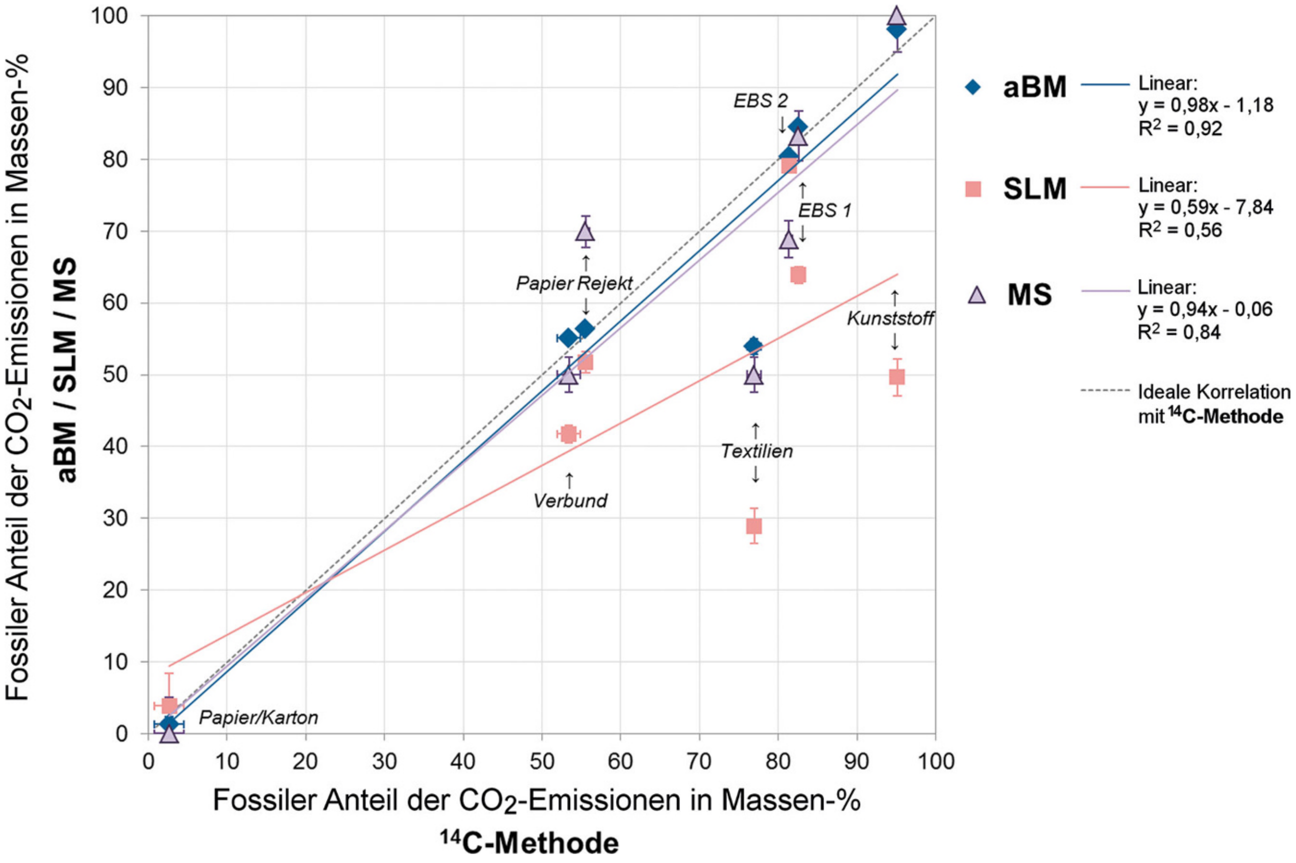


Abb. 5 Fossiler Kohlenstoffanteil bestimmt für drei Ersatzbrennstoffe und für sortierte Fraktionen der Ersatzbrennstoffe. Korrelation der Ergebnisse aus ^{14}C-Methode mit den Ergebnissen aus adaptierter Bilanzenemethode (aBM), Selektiver Lösemethode (SLM) und Manueller Sortierung (MS). Mittelwerte mit Standardabweichungen

MS-Ergebnisse berücksichtigt, da solche umfangreichen zusätzlichen Untersuchungen im Normalfall nicht machbar sind oder durch reine SLM-Auswertungen nicht zuverlässig sind (aufgrund vorher genannter Fehleinschätzung einzelner Materialgruppen durch die SLM). Im Falle von Papier-Rejekt spielen bei der Sortierpräzision beispielsweise signifikante Anteile kleiner Partikel (<10 mm) oder halbaufgelöste Kartonteile und Zellulosefasern, die an Kunststoffen haften, eine Rolle.

5.3 Fossile CO_2-Emissionsfaktoren, bestimmt mittels adaptierter Bilanzenmethode

Aus den Ergebnissen der aBM können neben den fossilen/biogenen Massenanteilen, Kohlenstoff- bzw. CO_2-Anteilen und Energieanteilen auch spezifische fossile CO_2-Emissionen (fossile CO_2-Emissionsfaktoren) bestimmt werden, wie sie üblicherweise für herkömmliche Energieträger angegeben werden. Damit kann ein direkter Vergleich der Brennstoffe in Bezug auf die Klimarelevanz angestellt und die gesamten fossilen CO_2-Emissionen aus der thermischen Verwertung von EBS einfach bestimmt werden (z. B. für CO_2-Emissionszertifikate oder die Ausweisung für die nationale Klimabilanz). Tab. 4 präsentiert die in der vorliegenden Studie bestimmten spezifischen fossilen CO_2-Emissionen bezogen auf verschieden Bezugsgrößen (Feuchtsubstanz, Trockensubstanz und unterer Heizwert) für die sechs untersuchten EBS. Es ergeben sich zwischen 650 und 2190 kg fossiles CO_2 pro Tonne EBS Feuchtsubstanz. Bei Bezug auf Trockensubstanz zeigt sich erwartungsgemäß eine etwas geringere Streuung der Werte (zwischen 1130 und 2300 kg fossiles CO_2 pro Tonne trockener EBS). Die fossilen CO_2-Emissionsfaktoren bezogen auf den Heizwert liegen zwischen 48 und 73 $kgCO_{2,fos}/GJ$ und damit etwas unter dem Bereich von Heizöl leicht und durchwegs unter dem Wert für Steinkohle (jedoch meist über dem Wert für Erdgas).

Der Variationskoeffizient (relative Streuung zwischen den einzelnen untersuchten EBS-Proben) der heizwertbezogenen Emissionsfaktoren ist im Vergleich zu den massebezogenen Emissionsfaktoren geringer. Zur Beurteilung der Klimarelevanz und der Einsparungen an CO_2 durch den Einsatz von EBS ist es förderlich, die CO_2-Emissionen auf den Heizwert zu beziehen, um der tatsächlichen energetischen Substitution von fossilen Energieträgern Rechnung zu tragen. Dabei gilt es insbesondere den Wassergehalt bei der Bestimmung des Heizwertes entsprechend zu berücksichtigen. Welche Bedeutung der Wassergehalt auf den Emissionsfaktor hat, zeigt sich anschaulich für Papier-Rejekt mit einem Wassergehalt von rund 42 %. Der fossile CO_2-Emissionsfaktor des Papier-Rejekts bezogen auf Feuchtsubstanz ist erwartungsgemäß deutlich geringer als bezogen auf Trockensubstanz. Ferner ist zu beobachten, dass sich pro Tonne feuch-

Tab. 4 Mittels aBM bestimmte fossile CO_2-Emissionsfaktoren verglichen mit Literaturangaben

	n /Quelle	WG	Fossiler CO_2-Emissionsfaktor bezogen auf Feuchtsubstanz	VK	Fossiler CO_2-Emissionsfaktor bezogen auf Trockensubstanz	Fossiler CO_2-Emissionsfaktor bezogen auf unteren Heizwert[a]	VK
		%rel	$kgCO_{2,fos}/t$	%rel	$kgCO_{2,fos}/t$ wasserfrei	$kgCO_{2,fos}/GJ$	%rel
Papier-Rejekt	15	42	650 ± 9	18	1130 ± 9	48 ± 3	9
EBS 1	8	10	1710 ± 16	3	1900 ± 17	71 ± 3	6
EBS 2	8	5	1800 ± 16	12	1900 ± 17	66 ± 3	6
EBS 3	3	11	1880 ± 30	3	2120 ± 30	70 ± 3	2
EBS 4	2	9	1840 ± 30	9	2030 ± 30	70 ± 3	5
EBS 5	3	5	2190 ± 20	3	2300 ± 20	73 ± 3	2
Siedlungsabfälle	IPCC (2000)		557	–	–	–	–
Siedlungsabfälle	Anderl et al. (2015)		–	–	–	49	–
Industrieabfälle	Anderl et al. (2015)		–	–	–	104	–
Alternativer Brennstoffmix in Zementwerken	VÖZ (2015)		–	–	–	59	–
EBS (mittel- bis hochkalorisch)	Bilitewski (2006)		–	–	–	40–54	–
EBS aus Gewerbe- und Industrieabfällen	Glorius (2006, 2014)		–	–	–	50–60	–
EBS aus Siedlungsabfällen	Glorius (2014)		–	–	–	20–40	–
EBS aus MBA	Hoffmann et al. (2010)		470	–	–	–	–
Sortierreste Leichtverpackungen	Hoffmann et al. (2010)		892	–	–	50	–
Erdgas	Wieser und Kurzweil (2004)		–	–	–	55	–
Steinkohle	Wieser und Kurzweil (2004)		–	–	–	95	–
Heizöl leicht	Wieser und Kurzweil (2004)		–	–	–	78	–

n Anzahl untersuchter Proben
VK Variationskoeffizient: Standardabweichung über Probenergebnisse bezogen auf den Mittelwert in %relativ
WG Wassergehalt bestimmt gemäß Abschn. 4.6.1, bezogen auf Feuchtsubstanz in relativen Massenprozent
MBA Mechanisch-biologische Anlage
[a] unterer Heizwert bestimmt mit empirischer Formel nach Boie in Kost (2001)

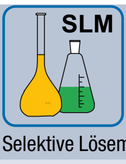
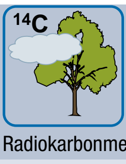
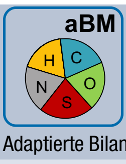
tes Papier-Rejekt fossile CO_2-Emissionen ergeben, die um mindestens einen Faktor 2,6 geringer einzustufen sind als die der anderen EBS. Dieser Faktor verringert sich jedoch bei Betrachtung der fossilen CO_2-Emissionen bezogen auf den Energieinhalt (Faktor von maximal 1,5). Dieses unterschiedliche Verhältnis zwischen den beiden Emissionsfaktoren ist bedingt durch einen vergleichsweise geringeren Heizwert des Papier-Rejekts, der durch den hohen Wassergehalt deutlich niedriger anzusetzen ist und somit die spezifischen CO_2-Emissionen ansteigen lässt. Bei Berücksichtigung von 0 % Wassergehalt für die Berechnung des Heizwertes läge der Emissionsfaktor für Papier-Rejekt bei nur rund 26 $kgCO_{2,fos}/GJ$ und damit im selben Verhältnis zu den anderen EBS bei Betrachtung des massebezogenen Emissionsfaktors. Ein ähnliches Bild zeigt sich beim Vergleich von EBS 1 mit EBS 2. Der leicht höhere Kohlenstoffgehalt in EBS 2 zusammen mit einem niedrigen Wassergehalt bewirken einen höheren Heizwert und damit liegen die heizwertspezifischen fossilen CO_2-Emissionen unter denen von EBS 1 (der auf die Feuchtsubstanz bezogene Emissionsfaktor von EBS 2 hingegen liegt leicht über dem von EBS 1).

Vergleicht man die generierten fossilen CO_2-Emissionsfaktoren mit Angaben aus der Literatur für EBS, fällt auf, dass bisher meist geringere Werte als in vorliegender Studie berichtet werden. Dies ist natürlich in erster Linie auf andere Zusammensetzungen der jeweiligen EBS begründet, jedoch ist eine methodische Unschärfe aufgrund der in Abschn. 5.2. gefunden Differenzen der Bestimmungsmethoden nicht auszuschließen. Da die SLM in den meisten Fällen zur Anwendung kommt (relativ einfache und kostengünstige Methode), kann angenommen werden, dass es teils zu Fehleinschätzungen der fossilen CO_2-Emissionsfaktoren kommt (siehe Abschn. 4.4 und 5.2).

5.4 Praktikabilität der Bestimmungsmethoden

Da die Wahl einer Bestimmungsmethode neben den Ansprüchen an Zuverlässigkeit auch von der Verfügbarkeit sowie dem Zeit- und Kostenaufwand abhängt, wurden die angewandten Methoden zur Bestimmung der Klimarelevanz von EBS auch auf ihre Praktikabilität hin verglichen (Tab. 5). Alle Angaben in Tab. 5 gehen von einer Bestimmung des fossilen Anteils der CO_2-Emissionen für eine EBS-Probe aus. Der abgeschätzte Arbeitsaufwand für Probenaufbereitung sowie Analyse und Berechnung pro Probe reicht von rund 4–6 h (SLM, aBM, ^{14}C-Methode) bis zu über 60 h für die MS. Bei SLM, aBM und ^{14}C-Methode muss jeweils mindestens die Hälfte dieser Zeit (bei aBM sogar zwei Drittel) für die Probenaufbereitung aufgewendet werden. Dies ist durch die kleine Probengröße für die Analysen bedingt, was eine Mahlung der Proben auf sehr kleine Partikel-

Tab. 5 Vergleich der vier Methoden bezüglich Arbeits- und Zeitaufwand, Verfügbarkeit und Kosten (bezogen auf die Bestimmung des fossilen Anteils der CO_2-Emissionen einer Probe)

	 Manuelle Sortierung	 Selektive Lösemethode	 Radiokarbonmethode	 Adaptierte Bilanzenmethode
Probenaufbereitung				
Notwendige Arbeiten	Trocknung	Trocknung, Mahlung, Teilung, bis <1 mm	Trocknung, Mahlung, Teilung, bis <0,2 mm oder feiner	Trocknung, Mahlung, Teilung, bis <0,5 mm oder feiner
Geschätzter Aufwand	~0,5 h	~2 h	~3,5 h	~3,5 h
Optional (bei erstmaliger Anwendung)	+~18 h (Mahlung für C-Bestimmung der sortierten Fraktionen)	–	+~3,5 h (Mahlung der sortierten biogenen Fraktion)	+~18 h (Mahlung für Bestimmung CHNSO-Gehalt der sortierten Fraktionen)
Analyse & Berechnung				
Notwendige Arbeiten	Sortierung	Bestimmung Löserückstand, Glührückstand, C-Gehalt	Graphitisierung, AMS-Analyse	Bestimmung CHNSO-Gehalt, Glührückstand
Geschätzter Analyseaufwand	>60 h[a]	~1,7 h	~2,5 h	~2 h
Optional (z. B. bei erstmaliger Anwendung)[b]	+~3–6 h (Bestimmung C-Gehalt und Sortierpräzision der sortierten Fraktionen)	–	+~20 h (Sortierung und Nachmessung des pMC Referenzwertes)	+~25 h (Sortierung und Bestimmung CHNSO-Gehalt der sortierten Fraktionen)
Dauer bis Analyseergebnis vorliegt				
Geschätzte Dauer	~8 Tage	4–5 Tage	>20 Tage	~3 Tage
Optional (z. B. bei erstmaliger Anwendung)[b]	+~2,5 Tage (Bestimmung C-Gehalt der sortierten Fraktionen)	–	–	+~10 Tage (Bestimmung CHNSO-Gehalt der sortierten Fraktionen)
Verfügbarkeit				
	✔✔	✔	(✔)	✔
Notwendige Laborausstattung	Keine spezielle Ausstattung notwendig Optional: Bestimmung C-Gehalt in den meisten analytischen Laboren verfügbar	Bestimmung C-Gehalt in den meisten analytischen Laboren verfügbar; für Massenanteil nasschemisches Labor ohne spezielle Ausstattung notwendig	Spezialisierte Geräte erforderlich ~64 Labore in Europa (~134 weltweit) verfügbar[c]	Bestimmung CHNS-Gehalt in den meisten analytischen Laboren verfügbar; O-Gehalt seltener
Analysekosten				
Geschätzt pro Probe (exkl. Probenaufbereitung)	>700 €	80–150 €	360–650 €	80–150 €

[a] Geschätzt für eine Sortierung von 30 kg EBS und einem Arbeitsaufwand von mindestens 2 h für die Sortierung von 1 kg EBS

[b] MS: für die Ermittlung des fossilen Kohlenstoffanteils sind neben der Sortierung Informationen zum Kohlenstoffgehalt der einzelnen Fraktionen nötig, diese können spezifisch bestimmt oder gegebenenfalls aus der Literatur entnommen werden; aBM: bei erstmaliger Anwendung ist es gegebenenfalls nötig Sortierungen durchzuführen um EBS-spezifische Kennwerte zu generieren (Elementarzusammensetzung wasser- und aschefreier biogener und fossiler Materialien). Entsprechende Datenbanken könnten hierfür diesen (in der Regel einmaligen) Zusatzaufwand deutlich reduzieren.

[c] http://www.radiocarbon.org/Info/lablist.html (aktualisiert im Oktober 2017)

größen notwendig macht (bei aBM mindestens <0,5 mm). Bei der MS fließt erwartungsgemäß der überwiegende Anteil der Arbeit in die Sortierung, die jedoch stark von der ausführenden Person, der Zusammensetzung und der Struktur des EBS abhängig ist. Neben dem Arbeitsaufwand wird die Dauer, bis ein Analysenergebnis vorliegt, zu einem wesentlichen Anteil durch Warte- und Reaktionszeiten bestimmt (bei SLM, ^{14}C-Methode und aBM). Diese Dauer wird bei Anwendung der aBM mit rund 3 Tagen abgeschätzt, bei SLM mit 4–5 Tagen, bei MS mit rund 8 Tagen und mit mehr als 20 Tagen bei Anwendung der ^{14}C-Methode. Die bestimmenden Faktoren sind dabei die Dauer der Sortierung (MS), Dauer der CHNSO- und Aschegehaltsbestimmungen (aBM, SLM), die Löse- und Oxidationsreaktionen (SLM) und die Überführung zu Graphit (^{14}C-Methode). Bei erstmaliger Anwendung oder bei sehr hohen Ansprüchen an die Genauigkeit der Methoden können zudem Zusatzanalysen notwendig sein. Um die Richtigkeit zu erhöhen, macht es möglicherweise Sinn, die sortierten Fraktionen der MS auf ihren Kohlenstoffgehalt zu untersuchen, statt auf Literaturwerte zurückzugreifen. Für die ^{14}C-Methode kann die Nachmessung des pMC-Referenzwertes des reinen biogenen Materials im EBS die Unsicherheit der Methode reduzieren, was ebenfalls zusätzliche Analytik erfordert. Wenn notwendige Informationen für die aBM zur Elementarzusammensetzung der wasser- und aschefreien biogenen und fossilen Materialien nicht aus der Literatur ableitbar oder aus einer Datenbank entnommen werden können, dann sind einmalig Sortierungen und Elementaranalysen der sortierten Fraktionen erforderlich (beispielsweise wie in Abschn. 4.2.2 beschrieben).

Weitere wesentliche Faktoren für die Praktikabilität einer Methode sind zudem die Verfügbarkeit und die Analysekosten. Beispielsweise kann die ^{14}C-Methode nur von Labors mit hoch spezialisierter Ausstattung durchgeführt werden, während die notwendigen Analysegeräte für die Bestimmung mittels aBM und SLM in den meisten analytischen Labors zur Verfügung stehen. Sollte ausschließlich der fossile bzw. biogene Massenanteil gefragt sein, kann die SLM in jedem nasschemischen Labor angewandt werden. Ebenso ist für die MS außer zum Trocknen und Wiegen der Proben keine spezielle Laborausstattung notwendig.

Die Komplexität und Verfügbarkeit der Analysen spiegelt sich in den Analysekosten, insbesondere bei denen der ^{14}C-Methode wider. Die ungefähren Kosten liegen mit 360–650 € pro Messung im Vergleich zu aBM und SLM um den Faktor 2–8 höher. Die Kosten für eine Bestimmung des fossilen Kohlenstoffanteils mittels aBM und SLM liegen für beide Methoden im Bereich zwischen 80 und 150 € pro Probe.

6 Schlussfolgerungen

Die vorliegende Studie zeigt, dass die Methodik der adaptierten Bilanzenmethode (aBM) als Alternative zu standardisierten Verfahren zur Bestimmung des fossilen Kohlenstoffanteils in EBS angewandt werden kann. Es ist eine sehr gute Übereinstimmung zwischen generierten Werten der aBM und Ergebnissen der Vergleichsmethode (^{14}C-Methode) zu verzeichnen. Eine mittlere Abweichung von der ^{14}C-Methode von 0,6 ± 1,4 %absolut bezogen auf den mittleren Anteil an fossilen CO_2-Emissionen drei verschiedener EBS deutet auf die Richtigkeit der aBM-Ergebnisse hin. Für die zwei weiteren angewandten und bereits standardisierten Methoden – die Selektive Lösemethode (SLM) und die Manuelle Sortierung (MS) – zeigen sich deutliche methodische Einschränkungen in Abhängigkeit von der Zusammensetzung der EBS. Die aBM ist damit neben der ^{14}C-Methode die einzige Methode mit der, unabhängig vom EBS-Typ, zuverlässige Werte zur Klimarelevanz generiert werden konnten.

Die Anwendung der SLM führte tendenziell zu einer Unterschätzung des fossilen Kohlenstoffanteils, wobei diese Fehleinschätzung besonders deutlich bei Anwendung auf EBS 1 auftritt (knapp 19 % absolute Abweichung von der ^{14}C-Methode). Dieser EBS wird unter anderem aus aufbereiteten Siedlungsabfällen hergestellt und enthält signifikante Anteile an fossilen Bestandteilen, die sich bei chemischer Behandlung auflösen und damit mittels SLM fälschlicherweise als biogen eingestuft werden.

Die Zuverlässigkeit der MS-Ergebnisse wird neben den unbekannten Unsicherheiten aus der manuellen Sortierung, auch durch signifikante Anteile an nicht sortierbaren Fraktionen mit unbekannten Anteilen an biogenen oder fossilen Materialien beeinflusst (Feinfraktion, Textilien, Verbunde, Gummi).

Kritischster Faktor bei der Anwendung der aBM ist die Wahl der Eingangswerte zur Elementarzusammensetzung der wasser- und aschefreien biogenen und fossilen Materialien im Ersatzbrennstoff (TOX_{BIO}, TOX_{FOS}). Diese Werte werden idealerweise für jeden EBS spezifisch erhoben (durch einmalige Sortierungen und Analysen). Die Ergebnisse der vorliegenden Studie zeigen jedoch, dass die Werte, generiert für 6 verschiedene EBS, in einem sehr engen Bereich liegen. Es kann also angenommen werden, dass zukünftig Arbeitsaufwand für die Erstellung dieser Kennwerte eingespart werden kann, indem auf vorhandene Literaturwerte zurückgegriffen wird. Da jedoch Variationen in der Zusammensetzung der Kunststoffe in den verschiedenen EBS nicht ausgeschlossen werden können (erkennbar hauptsächlich an den unterschiedlichen TOO_{FOS}-Gehalten), scheint es sinnvoll, eine Datenbasis mit typischen Kennwerten zur Elementarzusammensetzung biogener und fossiler Materialien pro EBS-Typ zu erstellen. Beispielsweise enthalten EBS aus Siedlungsabfällen typischerweise höherer Anteile an Kunststoffen mit hohem *TOO*-Gehalt (z. B. Polyamid, Polyethylenterephthalat, Polyurethane) als EBS produziert aus Gewerbe- und Industrieabfällen (vorwiegend Polyethylen und Polypropylen).

Die aBM kann neben ihrer Zuverlässigkeit auch mit ihrer Praktikabilität gegenüber standardisierten Bestimmungsmethoden punkten. Einzig bei erstmaliger Anwendung auf einen EBS kann eine Ermittlung von EBS-spezifischen Eingangswerten den Kosten- und Zeitaufwand etwas erhöhen. In einer Routineanwendung übertrifft sie jedenfalls die momentan vorwiegend angewandte SLM in ihrer Zweckmäßigkeit, da Analysewerte verlässlicher und meist schneller generiert werden können. Im Vergleich zur ^{14}C-Methode, die sehr zuverlässige Werte liefert, ist die aBM deutlich kostengünstiger und kann von einer wesentlich größeren Anzahl an Labors durchgeführt werden. Die Methode der MS kann für eine Routinebestimmung des fossilen CO_2-Anteils als nur bedingt zweckmäßig eingestuft werden, da sie neben den unbekannten Unsicherheiten auch einen sehr hohen Arbeitsaufwand erfordert.

Zusammenfassend lässt sich festhalten, dass die aBM methodische und monetäre Einschränkungen standardisierter Methoden überwindet und gleichzeitig eine praktikable und zuverlässige Anwendung erlaubt.

Danksagung Vielen Dank an die Betreiber der Ersatzbrennstoff- und Altpapieraufbereitungsanlagen für die Unterstützung und Mitwirkung bei den Probenahmen. Zusätzlicher Dank gilt Edith Vogel für die Unterstützung bei ^{14}C-Analysen, dem Team des Labors der TU Wien und Inge Hengl für die Unterstützung bei der grafischen Gestaltung.

Förderung Die Autoren danken dem Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Projektnummer TRP 285-N28, für die Finanzierung der Studie sowie dem Bundesministerium für Wissenschaft, Forschung und Wirtschaft für die finanzielle Unterstützung.

Funding Open access funding provided by TU Wien (TUW).

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Paper VII

Determination of the climate relevance of refuse derived fuels – validity of literature-derived values in comparison to analysis-derived values

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Detritus, 2018, 2, 120-132

DOI: 10.31025/2611-4135/2018.13649

detritus Multidisciplinary Journal for Waste Resources & Residues

CISA

DETERMINING THE CLIMATE RELEVANCE OF REFUSE-DERIVED FUELS - VALIDITY OF LITERATURE-DERIVED VALUES IN COMPARISON TO ANALYSIS-DERIVED VALUES

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Article Info:
Received:
23 January 2018
Revised:
15 May 2018
Accepted:
25 June 2018
Available online:
30 June 2018

Keywords:
Refuse derived fuels
Balance method
Biomass content
Fossil carbon
Elemental composition
Manual sorting

ABSTRACT

The adapted Balance Method (aBM) represents a cost efficient method for determining the fossil share in solid refuse-derived fuels (RDF). The method requires data on the elemental composition of the RDF on water-and-ash-free basis (TOX_{RDF}) and on the elemental composition of biogenic and fossil organic matter on water-and-ash-free basis present in the RDF (TOX_{Bio} and TOX_{Fos}). TOX_{Bio} and TOX_{Fos} generally need to be defined only once (e.g., before a routine application). After these data are known, only TOX_{RDF} needs to be determined analytically for any RDF sample in order to apply the aBM. As TOX_{Bio} and TOX_{Fos} are crucial input parameter for the aBM, the presented paper aims to assess the most suitable and practical way for their reliable determination. Within this study, 6 different solid RDFs are investigated and the aBM is applied, whereby the suitability of literature values is compared to own analysis data for TOX_{Bio} and TOX_{Fos}. The potential utilization of literature data could save the initial workload when applying the aBM and could make the method even more economical and practical compared to other methods. Altogether, seven aBM results are compared utilizing seven different methods for generating input values of TOX_{Bio} and TOX_{Fos}: using generic values, literature values only, analyses results only, or combinations of literature and analyses data. The study results suggest that the usage of analysis data together with information from literature is the best option to derive reliable input data (TOX_{Bio} and TOX_{Fos}) for the aBM (mean deviation from standardized methods of below 2%). The findings further suggest that there is a typical composition of the biogenic and fossil organic matter present in RDFs produced out of commercial and industrial waste. Thus, the initial workload for conducting RDF-specific analyses could be significantly reduced when some more data about different types of RDFs are collected (e.g in a database).

1. INTRODUCTION

Within the European Union, in 2012 already 34% of primary energy carriers in cement kilns are substituted by mixed wastes and refuse-derived fuels (RDF). In Austria an average substitution rate of 75% is reported (VÖZ, 2015). The utilization of alternative fuels in energy-intensive industry branches is a means to reduce the exploitation of natural resources, reduce costs and to lower fossil carbon dioxide emissions (Aranda Usón et al., 2013; Pomberger and Sarc, 2014). For the appraisal on the fossil CO_2-savings (and therewith connected economic savings for emission certificates), it is required to know on the one hand the carbon content originating from materials of fossil origin in the RDF and on the other hand the overall calorific value of the RDF. Both depend, among others (e.g., water content), on the shares of fossil and of biogenic materials. In solid RDFs fossil materials comprise mainly plastics and synthetic textiles; biogenic materials could be paper, natural fibers, wood, etc. The shares of the compounds in solid RDFs are usually not known and may vary significantly depending on the material used for RDF production. The material used is usually pre-treated municipal solid waste (MSW), commercial waste (CW) and industrial waste (IW). The composition thus, strongly depends on the input material and hence, on the collection and sorting schemes, and also on local industries. Further, the shares of fossil and biogenic materials present in the RDF are decided by

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Detritus / Volume 02 - 2018 / pages 120-132
https://doi.org/10.31025/2611-4135/2018.13649

the production process (processing units used) which is designed based on the target application (e.g., cement kiln, waste-to-energy plant) (Lorber et al., 2012; Nasrullah et al., 2014a,b; Nasrullah et al., 2015; Sarc et al., 2014).

To distinguish between CO_2-emissions originating from fossil (climate relevant) and biogenic (carbon neutral) sources in solid RDFs, different methods are available: The Selective Dissolution Method (SDM), the Radiocarbon Method (^{14}C-method), the Manual Sorting (MS), and the Balance Method (BM). The former three are described in the standard for solid recovered fuels EN 15440:2011; the Balance Method has recently been published in the standard ISO 18466:2016. The methods all have critical limitations, such as high and hardly quantifiable uncertainties (SDM, MS), high workload (MS), high chemical demand (SDM), high analytical costs (^{14}C-method) and solely post-combustion application (BM) (Jones et al., 2013; Schwarzböck et al., 2018; Schwarzböck et al., 2016b; Staber et al., 2008).

A practical, and cost-efficient approach to determine the climate-relevant (fossil) CO_2-emissions from the utilization of solid RDF is provided by the so-called "adapted Balance Method" (aBM) (Fellner et al., 2011). This method combines data about the elemental composition of the RDF – TOX_{RDF} (C, H, N, S, O-content on water-and-ash free basis) – with the RDF-specific elemental composition of pure biogenic and pure fossil organic matter – TOX_{Bio} and TOX_{Fos} (C, H, N, S, O-content on water-and-ash free basis). By setting up mass balances for each element, the fossil carbon content in the RDF can be derived. The aBM has recently been demonstrated to produce robust results which are in good agreement with the radiocarbon method (usually regarded as reference method) (Schwarzböck et al., 2016a; Schwarzböck et al., 2016b).

The necessary data for the application of the aBM are TOX_{RDF}, TOX_{Bio} and TOX_{Fos}. The determination of TOX_{RDF} always requires elemental analysis in the laboratory. To validate the method, in previous works TOX_{Bio} and TOX_{Fos} have also been analytically appraised for each investigated RDF (initially). This initial investigation requires sorting of the RDF into its different compounds (paper, wood, plastics, etc.) and elemental analyses of each compound. In order to reduce the initial workload and costs, available data on the elemental composition of different materials present in the RDF could be used. Potential sources for these data are literature values, information from industries or theoretical considerations (e.g., theoretical chemical structure of cellulose, polyethylene, etc.).

For example in Fellner et al. (2011) data for TOX_{Bio} and TOX_{Fos} in RDF are provided, which were collected from various literature sources and production statistics in Austria. Monte Carlo simulations were applied to derive TOX_{Bio} and TOX_{Fos} which should be valid for RDF. However, it is not clear if these values are generally valid for RDF or maybe only for a certain type of RDF (e.g., for RDF produced out of MSW).

In Schwarzböck et al. (2017) it is shown, that the probable range of TOX_{Bio} only varies to a minor extend as the different compounds (paper, wood, garden waste, natural fibers) have a very similar chemical composition on water-and ash-free basis. Values for TOX_{Fos} depend on the shares of the different polymers. Schwarzböck et al. (2017) assume that polyethylene and polypropylene represent the major part (around 80wt%) in mixed wastes which are fed into waste-to-energy plants in Austria. Kost (2001) conducted an extensive study on the characterization of waste compounds and collected literature data and own analysis data on the fractional and elemental composition of MSW.

Due to varying origins of the RDF production material (MSW, CW, IW), the composition of RDF may vary, depending on the characteristics of the waste catchment area (urban, rural, types of industry and businesses, etc.) and waste collection and treatment schemes.

The objective of the present paper is to evaluate the suitability of literature values for the application of the aBM in comparison to RDF-specific values (derived via extensive analyses) to determine the fossil carbon content in RDF. Therefore, the following parameter necessary to derive TOX_{Bio} and TOX_{Fos} in the RDF are varied, either based on literature or own analyses:

- Fossil and biogenic mass share in each compound k of the RDF (e.g., fossil share in composite materials); $x_{mF,k}$, $x_{mB,k}$
- Chemical composition of fossil and biogenic matter in each sorted compound k; TOX_k^{Fos} and TOX_k^{Bio}

Additionally the so generated results are compared to TOX_{Bio} and TOX_{Fos} given in Fellner et al. (2011) to estimate the validity of the previously collected literature data.

2. MATERIAL AND METHODS

2.1 Adapted Balance Method (aBM)

The aBM combines data about the elemental composition of the RDF (carbon, hydrogen, oxygen, nitrogen, and sulphur-content on water-and-ash free basis) with the theoretical composition of pure biogenic and fossil organic matter present in the RDF (C, H, O, N, S-content on water-and-ash free basis) – see Figure 1. For each element (C, H, O, N, S) a mass balance equation is set up which contains the unknown mass fractions of fossil (m_F) and biogenic matter (m_B). As illustrated in Figure 1, the elemental composition of the biogenic and fossil matter is significantly different. This allows the 5 balance equations to be solved by data reconciliation and the mass fractions of fossil and biogenic matter to be derived. By inserting the results (m_B, m_F) into the carbon balance, the fraction of fossil carbon as percentage of the total carbon can be determined.

The aBM requires the following input data:

1. Elemental composition of the water-and-ash-free RDF (TOX_{RDF}): Determination by CHNSO-analyses and ash content determination
2. Information on the elemental composition of the water-and-ash-free biogenic and fossil organic matter present in the RDF (TOX_{Bio}, TOX_{Fos}). The following options are available:
   - Collection of necessary information from literature
   - Determination by manual sorting together with CHNSO-analyses and ash content determination of the sorted compounds

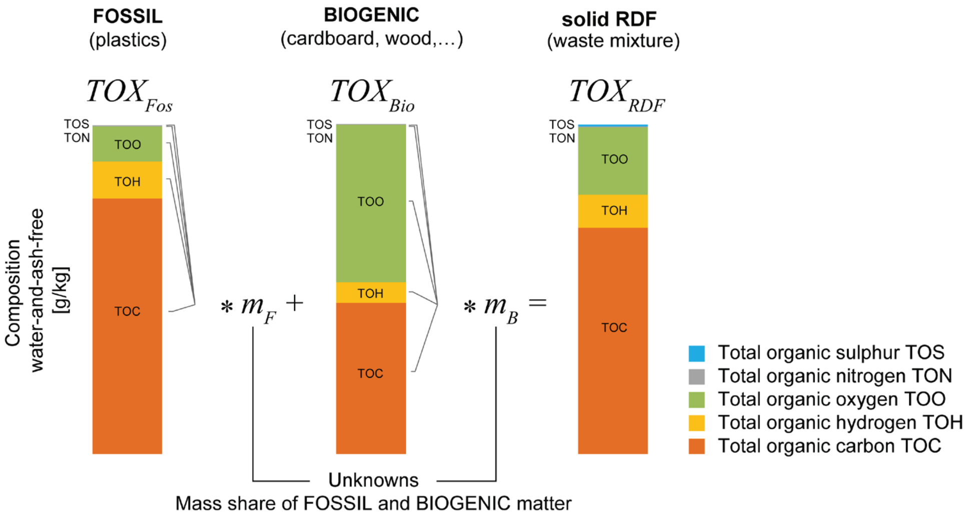


FIGURE 1: Schematic illustration of the adapted Balance Method, showing the relation between the elemental composition of the water-and-ash-free biogenic and fossil organic matter present in the RDF (TOX_{Bio}, TOX_{Fos}), the elemental composition of the water-and-ash-free RDF (TOX_{RDF}) and the respective mass shares of fossil and biogenic matter (mF and mB), which are unknown and determined by the aBM.

- Combination of information from literature and analyses

Within this study, the different options to gather the necessary information for the aBM are compared. The different variants used are described in Table 2.

2.2 Samples and sample preparation

Six different solid refuse-derived fuels (RDF) are subject of the study. Table 1 lists the different samples and their origin and indicates which methods to determine the fossil share, besides the aBM, are applied to the samples.

As only a few hundred milligrams of sample are necessary for the CHNSO-elemental analysis, the samples are comminuted down to a grain size of below 0.2 mm. The sample preparation is carried out in agreement with EN 15413:2011 and based on findings of Schwarzböck et al., 2016a. Two cutting mills (Essa CM 1000 and Retsch SM 2000), an ultracentrifugal mill (Retsch ZM 200), and a cryogenic mixer mill (Cryomill, Retsch) are used to produce representative analysis samples. Additionally riffle divider and rotary divider are used to reduce the sample mass between the grinding steps.

2.3 Analyses

2.3.1 CHNSO-elemental analysis

CHNSO elemental analysis is used to derive the elemental composition in the water-and-ash-free RDF samples, which is necessary in order to apply the aBM.

The water free (dried at 105°C for 24 hours) analysis samples undergo a CHNSO-elemental analysis using an Elementar Vario Macro instrument (for CHNS-analysis) and an Elementar Vario El instrument (for O-analysis, based on pyrolysis) (Elementar Analysensysteme GmbH, Hanau, Germany). At a combustion temperature of 1,150°C, the total carbon (TC), total hydrogen (TH), total nitrogen (TN), total sulphur (TS), and total oxygen (TO) content is determined according to EN 15407:2011. Additionally the ash content of each test sample is determined according to EN 15403:2011 and analyzed for its elemental composition to appraise the total inorganic content of C, H, N, S, and O.

TABLE 1: Investigated refuse-derived fuels and number of samples analyzed

Name	Origin / type of RDF	No of samples N	Sorting analysis	^{14}C-method[1]
Paper Reject	Residues of paper & board industry	15	✓	✓
RDF MSW+C&I	RDF prepared from pre-processed municipal solid waste and commercial & industrial waste (RDF production plant A)	8	✓	✓
RDF C&I (1)	RDF prepared from mainly commercial & industrial waste (RDF production plant A)	8	✓	✓
RDF C&I (2)	RDF prepared from mainly commercial & industrial waste (RDF production plant B)	3	✓	-
RDF C&I (3)	RDF prepared from mainly commercial & industrial waste (RDF production plant B)	2	✓	-
RDF C&I (4)	RDF prepared from mainly commercial & industrial waste (RDF production plant B)	3	✓	-

[1] *... tick indicates that Radiocarbon analyses (^{14}C-method) are additionally conducted according to EN 15440:2011 for selected samples to support the findings by aBM and sorting.*

Five measurements per sample, each of them comprising 40 mg of sample material, are carried out for C, H, N, and S. For the analysis of O, sample specimens of only 4 to 6 mg are used and 7 measurements per sample are conducted.

The measured values are converted according to Formula (1) in order to determine the elemental composition on a water-and-ash-free reference base.

$$TOX = \frac{TX - TIX * A}{(1 - A)} \tag{1}$$

TOX: total organic fraction of C, H, O, N and S in the water-and-ash-free sample [g/kg$_{waf]}$

TX: total fraction of C, H, O, N and S in the water free sample [g/kg$_{wf]}$

TIX: total fraction of C, H, O, N, and S in the water free ash (inorganic) [g/kg$_{wf}$]

A: ash content [kg/kg$_{wf}$]

The thereby obtained values for total organic carbon (TOC), total organic hydrogen (TOH), total organic nitrogen (TON), total organic sulphur (TOS), and total organic oxygen represent the input data required for the adapted Balance Method.

2.3.2 Radiocarbon method (^{14}C-method) to determine the share of fossil carbon present in RDF

The Radiocarbon method (^{14}C-method) is based on the distinctly different concentration of ^{14}C isotope in fossil carbon sources (where ^{14}C is completely decayed) and in modern (biogenic) carbon sources, which exhibit in a first approximation the current ^{14}C atmospheric levels. Thus, the ^{14}C-concentration in the emitted CO_2 when a waste mixture is combusted is directly proportional to the fraction of biogenic carbon in the combusted sample (Mohn et al., 2008). However, owing to anthropogenic activities the background level of ^{14}C levels in the atmosphere was altered, which complicates the calculation as it requires reference basis to be recalculated for each grow year of biomass (Fellner and Rechberger, 2009). Yet, the method is regarded as very reliable method for the determination of the biomass content in secondary fuels as it has the lowest analytical uncertainty (accelerator mass spectrometry <1% relative; Mohn et al., 2008).

Within the presented study, the ^{14}C-method is applied according to EN 15440:2011 utilizing accelerator mass spectrometry (AMS). Around 10 mg of 16 RDF samples at a grain size of < 0.2 mm are combusted at 900°C and the carbon isotope ^{14}C is separated from the stable carbon isotopes ^{12}C and ^{13}C before the mass analysis (for details see Szidat et al., 2014). The biogenic content in the sample is given as percent of modern carbon, allowing the fossil carbon to be calculated. A fossil mass share cannot be provided by this method.

2.3.3 Manual sorting

In order to determine the elemental composition of biogenic and fossil organic matter in the RDFs (see section 2.4), manual sorting analyses are conducted. Samples of each RDF are sorted into the following compounds:

- Paper
- Wood
- Plastics
- Composites & unrecognizable materials
- Textiles
- Rubber – only further considered for RDF C&I (B3); for other RDFs share is below 0.8wt%
- Fine fraction (around < 1-2 cm)
- Metals and inert materials – not further considered as this fraction is neither considered biogenic nor fossil

300 to 500 g (for Paper Reject up to 3.000 g) per sample are sorted. For Paper Reject and RDF from producer A – RDF MSW+C&I and RDF C&I (1) – a part of the fine fraction is further sorted into the above listed compounds. The so determined mass shares of the fine fraction are accounted for in order to estimate the total share of each compound in the RDF.

The results of the sorting analysis are on the one hand used to determine the respective input parameter of the aBM, and on the other hand the outcomes are utilized to estimate the overall share of the fossil mass present in the RDF. The latter are finally compared to the results generated by the aBM. However, some deviations from the procedure given in EN 15440:2011 for the manual sorting method are considered in order to generate more reliable results: the fine fraction is partly further sorted and the fossil and biogenic share in each compound are estimated analytically instead of relying on the information given in the standard. Yet, the manual sorting method is connected with high uncertainties, especially when high shares of mixed compounds (fine fraction, composites, textiles) are present in the RDF.

2.4 Determination of the elemental composition of biogenic and fossil organic matter present in RDF (TOX_{Bio}, TOX_{Fos})

Besides the elemental composition of the water-and-ash-free RDF (TOX_{RDF}), the application of the aBM requires information on the elemental composition of the water-and-ash-free biogenic and fossil organic matter (TOX_{Bio}, TOX_{Fos}). Seven different alternatives (Variants) are chosen in order to derive these data sets (description see Table 2).

The following assumptions are applied for all variants:

1. No analyses are available for the composition of fossil (synthetic) and biogenic textiles (cotton, wool) – $TOX_{textile}^{Fos}$ and TOX_{texile}^{Bio} Thus, for all applied variants, the chemical composition of textiles is based on data published by Kost (2001) and on theoretical considerations.
2. The biogenic share in the composite & unrecognizable materials represents paper and the fossil share represents plastics (all on water-and-ash-free basis).

The first variant (Variant L) only relies on the data given in Fellner et al. (2011), thus no analyses are considered for this option. For the other variants, at least information on the mass share of the different compounds ($x_{m,k}$) is necessary, which can be derived from manual sorting. Besides $x_{m,k}$, three further parameter are necessary to arrive at TOX_{Bio} and TOX_{Fos}: The share of fossil or biogenic matter in in each sorted compound ($x_{mF,k}$ or $x_{mB,k}$), and the chemical composition of fossil and biogenic matter of each sorted compound (TOX_k^{Fos} and TOX_k^{Bio}). In the second variant, these parameters are all derived from literature (Variant LL); where xmB,k is used as given in EN 15440:2011 and values for TOX_k^{Fos} and TOX_k^{Bio} are used as published by Kost (2001). In Variant AL and Variant LA either $x_{mB,k}$ or TOX_k^{Fos} and TOX_k^{Bio} are used as revealed by own analyses (see section 2.4.1. for details on how xmB,k is derived from analyses). Another option is to use all parameters, $x_{mB,k}$ and TOX_k^{Fos} and TOX_k^{Bio} as derived by own analyses (Variant AA).

However, assumption 2) implies that the composition of the sorted paper and plastics are representative for the composition of the paper and plastics contained in composite & unrecognizable materials. This is expected to be false, especially for plastics, as different polymers have a different chemical composition. Plastics in composite materials are presumably dominated by plastics foils (e.g., made out of polyethylene), but the sorted plastics also contain significant shares of other polymers (e.g., PET, foamed plastics, polyamide).

Thus, the sixth Variant AAL to determine TOX_{Bio}, TOX_{Fos} uses analyses results for $x_{mB,k}$, and considers both sources (analyses and literature) for TOX_k^{Fos} and TOX_k^{Bio}. For example, analysis results are used for the sorted plastics but the composition of the plastics within the fine fraction and the composite & unrecognizable materials fraction is assumed to correspond to a literature value for mixed plastics.

A sevenths variant (Variant Mean) is introduced which considers the mean value calculated of all values generated with "Variant AAL" of all RDF. This is to estimate the versatility and transferability of the generated data within this study.

Deviations for each variant from results of radiocarbon analyses or from manual sorting results are calculated as relative value (referred to the result of the standardized method). Negative deviations indicate that a lower value is found by aBM compared to the standardized method. Mean deviations between the aBM results and results of the radiocarbon/manual sorting are calculated by the mean aBM result of all RDFs compared to the mean radiocarbon/manual sorting result of all RDFs. Thus, no weighting according to the number of samples analyzed for the different RDFs is considered for the mean value.

Once one variant from Table 2 is chosen, the elemental composition of the water-and-ash-free biogenic and fossil organic matter ($TOX_{Bio,}$ TOX_{Fos}) is calculated. The equations (2) and (3) are given exemplary for the determination of the water-and-ash-free carbon content in fossil matter (TOC_{Fos}). First the relative share of each compound in the water-and-ash-free fossil matter is calculated by:

$$x_k^{Fos} = \frac{x_{m,k} * x_{mF,k}}{\sum_{k=1}^{k=n} x_{m,k} * x_{mF,k}} \tag{2}$$

- x_k^{Fos}: relative mass share of water-and-ash-free fossil compound k referred to total water-and-ash-free fossil matter in the RDF [kg_{waf}/kg_{waf}] (e.g., fossil matter is composed out of plastics, foamed plastics, synthetic fibers, plastics in compounds)
- $x_{m,k}$: relative mass share of water-and-ash-free compound k referred to total water-and-ash-free matter in the RDF [kg_{waf}/kg_{waf}] (e.g., share of plastics in the RDF)
- $x_{mF,k}$: relative mass share of water-and-ash-free fossil matter in compound k referred to total water-and-ash-free matter in compound k [kg_{waf}/kg_{waf}] (e.g., in pure plastics there is 100wt% of fossil matter if the sorting is precise; in composite materials there might be only 50wt% fossil and the rest biogenic).

Then the carbon content in the water-and-ash-free fossil matter is calculated by:

$$TOC_{Fos} = \frac{\sum_{k=1}^{k=n} TOC_k^{Fos} * x_k^{Fos}}{\sum_{k=1}^{k=n} x_k^{Fos}} \tag{3}$$

TOC_{Fos}: carbon content in the water-and-ash-free fossil matter [g/kg_{waf}]
TOC_k^{Fos}: carbon content in the water-and-ash-free fossil matter of compound k [g/kg_{waf}]

Formula (3) is likewise used for the determination of the hydrogen, oxygen, nitrogen, and sulphur content in the water-and-ash-free fossil matter (TOH_{Fos}, TOO_{Fos}, TON_{Fos}, TOS_{Fos}). Replacing the fossil share and fossil compounds by the biogenic share and biogenic compounds in formula (2)

TABLE 2: Variants within the study to derive information on the elemental composition of the water-and-ash-free biogenic and fossil organic matter present in the RDF (TOX_{Bio}, TOX_{Fos}; necessary input for aBM).

	Parameter	**Mass share of compounds in RDF $x_{m,k}$**	**Fossil and biogenic mass share in each sorted compound $x_{mF,k}$ and $x_{mB,k}$ [1]**		**Chemical composition of fossil and biogenic matter in each sorted compound TOX_k^{Fos} and TOX_k^{Bio}**	
				Source/analysis method		Source/analysis method
1	**Variant L**	not necessary	Literature	-	Literature	TOX_{Bio} and TOX_{Fos} given in Fellner et al. (2011)
2	**Variant LL**	Manual Sorting	Literature	EN 15440:2011	Literature	Kost (2001)
3	**Variant AL**	Manual Sorting	Analyses	aBM, SDM, ^{14}C	Literature	Kost (2001)
4	**Variant LA**	Manual Sorting	Literature	EN 15440:2011	Analyses	CHNSO-analyses + ash content
5	**Variant AA**	Manual Sorting	Analyses	aBM, SDM, ^{14}C	Analyses	CHNSO-analyses + ash content
6	**Variant AAL**	Manual Sorting	Analyses	aBM, SDM, ^{14}C	Analyses & Literature values	CHNSO-analyses + ash content; Kost (2001)
7	**Variant Mean**	mean of TOX_{Bio} and TOX_{Fos} of all 6 RDFs determined by **Variant AAL**				

[1] ... *Only $x_{mB,k}$ or $x_{mF,k}$ needs to be appraised as the other can be derived by $x_{mB,k} = 1 - x_{mF,k}$*

gives the relative share of each biogenic compound within the water-and-ash-free biogenic matter. Subsequently formula (3) can be applied to determine TOX_{Bio} in the same manner as TOX_{Fos}. Results are then the carbon, hydrogen, oxygen, nitrogen, and sulphur content in the water-and-ash-free biogenic matter (TOC_{Bio}, TOH_{Bio}, TOO_{Bio}, TON_{Bio}, TOS_{Bio}).

According to Table 2, different data sets for TOXBio, TOX_{Fos} are generated; using different sources of data (literature values and/or analysis results). Evaluations by means of the aBM are conducted for each RDF sample by combining the analysis results on the elemental composition of the water-and-ash-free RDF (TOX_{RDF}) with each generated data set of TOX_{Bio} and TOX_{Fos}. Thus, for each RDF seven different results on the fossil share are obtained.

In order to appraise if the results are in the range of the true value, they are compared to radiocarbon analyses (regarded as method with highest accuracy). For RDF from producer B – RDF C&I (2), (3), and (4) – no radiocarbon analyses are available. Thus, the results are compared to the sorting results only.

2.5 Estimation of mass share of fossil and biogenic matter in each sorted compound k ($x_{mF,k}$ and $x_{mB,k}$)

For each sorted compound, a fossil and biogenic share needs to be allocated. To do this, the standard EN 15440:2011 provides some guiding values. However, these generic values are assumed to not be valid for every RDF. For example, the fossil content of composite materials and of textiles can vary, depending on the type of RDF. Textiles from industry usually contain a much higher share of synthetic fibers than natural fibers. Similarly, the plastic content in the fine fraction can easily vary between RDFs. In addition, the sorted compounds of alleged “pure” materials (like plastics or paper) may be contaminated by other compounds as the sorting cannot be conducted precisely and is also prone to subjective assessments.

Thus, within this study, the fossil and biogenic mass shares for each sorted compound are appraised. This is done by utilizing the analysis results of the elemental composition of each compound and conducting a preliminary evaluation using the aBM. TOX_{Bio} and TOX_{Fos} for these preliminary aBM evaluations stem from literature (Kost, 2011, Fellner et al., 2011) and theoretical considerations (e.g., composition of cotton and wool to derive TOX_{Bio} in the textiles).

In addition, the radiocarbon method (according to EN 15440:2011) is conducted for selected compounds to support and confirm the aBM results.

3. RESULTS AND DISCUSSION

3.1 Composition of RDFs (sorting results) and assignment of fossil share for each compound

Table 3 presents the result of the sorting analyses of each investigated RDF. A share of plastics of at least 50wt% is found for all RDFs except Paper Reject (41wt%). The fine fraction has a considerable share with 24wt% to 65wt%; with the highest being found in Paper Reject. Table 4 shows that the fossil share (plastics content) in the fine fraction can vary significantly between the RDFs (between 40 and 78wt%). Thus, additional sorting of the this fraction are carried out for 3 RDFs to obtain more accurate results on the fractional composition of the RDFs.

The fine fraction, the composition of the composite & unrecognizable materials is uncertain, which represents between 3 and 22wt%. Fossil shares within this compound in the range of 32 and 66wt% are found (Table 4).

3.2 Elemental composition of sorted RDF compounds

Table 5 presents the average elemental composition on water-and-ash-free basis of the different compounds found by analyses within this study. Comparing the results to values published in Kost (2001) shows that they are generally in a similar range. The small differences in TOC, TOH, and TOO in plastics indicate the dependency on the

TABLE 3: Sorting results for the investigated RDFs – mass shares of compounds in each RDF.

	Mass share $x_{m,k}$ [wt% dry]								
	Paper Reject		**RDF MSW+C&I**		**RDF C&I (1)**		**RDF C&I (2)**	**RDF C&I (3)**	**RDF C&I (4)**
		incl. sorting of fine fraction		incl. sorting of fine fraction		incl. sorting of fine fraction			
Paper	5.9%	37.4%	4.1%	5.1%	2.8%	6.9%	5.0%	5.1%	8.5%
Wood	1.6%	2.5%	2.2%	1.9%	0.1%	0.2%	0.4%	0.3%%	0.2%
Plastics	20.4%	41.0%	47.1%	56.5%	32.5%	49.6%	54.0%	53.3%	50.1%
Composite & unrecognizable materials	3.0%	15.0%	8.4%	11.7%	21.8%	40.7%	9.4%	4.4%	4.7%
Textiles	1.1%	1.1%	12.1%	22.6%	0.7%	1.4%	1.3%	0.9%	7.3%
Rubber	0.7%	0.7%	0.8%	0.9%	0.1%	0.4%	0.4%	0.3%	1.2%
Fine fraction (around <1-2 cm)	65.1%	-	24.1%	-	41.3%	-	28.4%	32.9%	27.1%
Metals & inert materials [1]	2.2%	2.3%	1.2%	1.3%	0.7%	0.8%	1.1%	2.8%	0.9%

[1] *Metals & inert materials are not further considered in the study (these compounds are neither of fossil nor of biogenic origin).*

TABLE 4: Allocated fossil share in each sorted compound in the RDF.

	Allocated fossil share $x_{mF,k}$ [wt%, dry]						
	Paper Reject	**RDF MSW+C&I**	**RDF C&I (1)**	**RDF C&I (2)**	**RDF C&I (3)**	**RDF C&I (4)**	**EN 15440:2011 [1]**
Paper	7%	8%	7%	7%	6%	4%	0%
Wood	1%	1%	1%	5%	2%	4%	0%
Plastics	95%	92%	96%	96%	98%	98%	100%
Composite & unrecognizable materials	66%	54%	42%	40%	32%	56%	NA [2]
Textiles	35%	55%	55%	40%	45%	98%	50%
Rubber	NA	NA	NA	84%	84%	75%	80%
Fine fraction (around <1-2 cm)	40%	62%	55%	72%	78%	77%	50%

[1] Used for Variant LL and Variant LA

[2] 50% were used as there is no guiding value in the EN 15440:2011

TABLE 5: Elemental composition of different waste compounds analyzed in this study, compared to data published in Kost (2001).

	Elemental composition (water-and-ash-free)					
	N	**TOC $[g/kg_{waf}]$**	**TOH $[g/kg_{waf}]$**	**TOO $[g/kg_{waf}]$**	**TON $[g/kg_{waf}]$**	**TOS $[g/kg_{waf}]$**
Paper						
this study	21	476 ± 3	65 ± 1	497 ± 4	3.6 ± 0.5	5.1 ± 1.0
Kost (2001) [1]	43-62	467 ± 6	65 ± 1	443 ± 9	2 ± 1	1 ± 0
Wood						
this study	10	498 ± 2	62 ± 1	453 ± 2	6.3 ± 0.5	7.6 ± 1.2
Kost (2001) [1]	21-30	494 ± 2	60 ± 1	443 ± 4	1 ± 0	0 ± 0
Plastics (mixed)						
this study	24	771 ± 6	109 ± 1	103 ± 2	7.0 ± 0.5	8.4 ± 0.5
Kost (2001)1	11-15	790 ± 29	130 ± 9	30 ± 32	2 ± 2	1 ± 2
Composite & unrecognizable materials						
this study	16	620 ± 13	88 ± 2	286 ± 5	2.9 ± 0.5	9.5 ± 1.0
Kost (2001) [2]	1-8	560 ± 16	80 ± 3	320 ± 4	11 ±	4 ±
Textiles						
this study	15	564 ± 4	65 ± 1	355 ± 5	13.5 ± 0.6	11.2 ± 1.5
Kost (2001)	4-11	510 ± 16	70 ± 3	360 ± 7	27 ± 11	4 ± 2
Rubber						
this study	6-9	733 ± 4	90 ± 1	78 ± 4	14.6 ± 1.2	24.9 ± 2.7
Kost (2001)	4-5	860 ± 13	80 ± 9	60 ± 21	4 ± 1	17 ± 4

N Number of analyzed samples / number of literature values collected (by Kost, 2001).

[1] *Used for Variant LL and Variant AL.*

[2] *Composite packaging.*

plastics composition (shares of polyethylene, polyethylene terephthalate, polyurethane, etc.).

Further, differences of the analyzed values compared to the literature values are noticeable for rubber and textiles. For textiles this could be explained by high shares of synthetic fibers (with higher TOC, TOH and lower TOO content) which were observed for some RDF samples within this study.

Some differences in the oxygen content (TOO) are noticeable for almost all compounds. One factor explaining this phenomenon is assumed to be the chosen determination method. In literature, the O-content is often derived by subtracting all other elements from 1000 g/kg. Within this study, O-analyses are conducted by means of pyrolysis. It is assumed that the subtracting method holds higher uncertainties than actual analyses and can easily lead to different or wrong estimations of the O-content because the analytical uncertainty of the other elements is not considered.

3.3 Share of fossil carbon present in RDFs - aBM results based on literature values and based on analysis values

Figure 2 shows the outcomes of the aBM, namely the share of fossil carbon for each investigated RDF. In particular, the different results depending on the variant utilized to derive the input data (elemental composition of biogenic and fossil organic matter TOX_{Bio} and TOX_{Fos}) are presented.

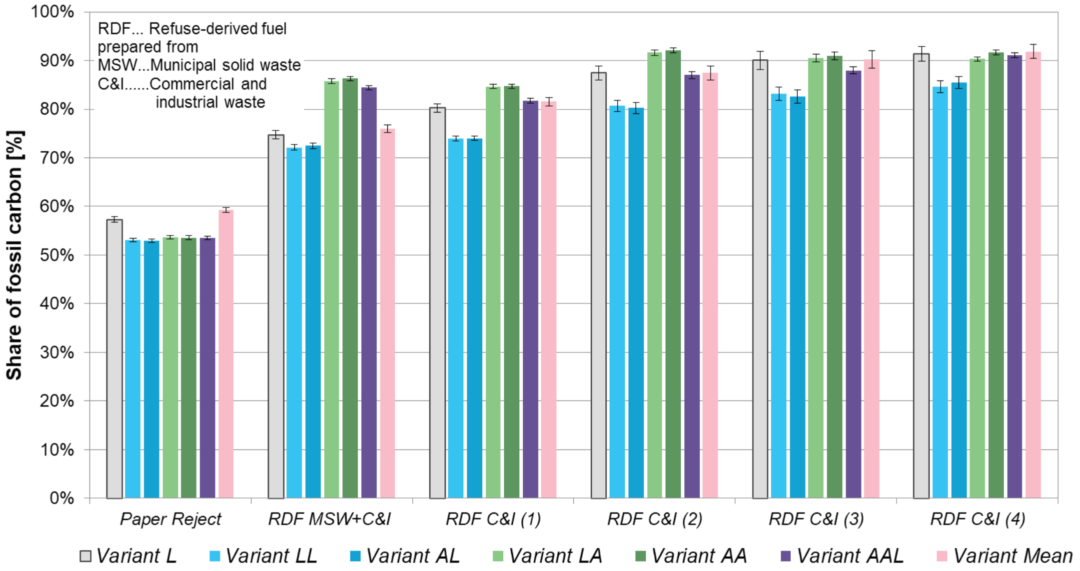
The results for the fossil carbon share (which represents also the share of fossil CO_2-emissions when the RDF are thermally utilized) vary only in a small range for Paper Reject (52-59% fossil carbon); no significant difference can be detected when comparing results generated with literature values, analysis values or a combination of both (Variant LL, AL, LA, AA, AAL). This is different for the other RDFs: The determined fossil carbon shares range from 72 to 92%. A significant difference can be observed for values where the elemental composition of biogenic and fossil organic matter in the compounds (TOX_k^{Fos} and TOX_k^{Bio}) is derived from literature values only (blue bars in Figure 2) and where these values are determined by own analyses (green bars in Figure 2). The differences between the variants where the fossil mass share per compound ($x_{mF,k}$) was varied (according to EN 15440:2011 or own appraisal) appear to be minor (differences between Variant LL and AL and difference between Variant LA and AA). This suggests that the choice of the chemical composition of the different compounds (TOX_k^{Fos} and TOX_k^{Bio}) has a much higher influence on the aBM result than the estimated fossil and biogenic mass share in each sorted compound ($x_{mF,k}$ and $x_{mB,k}$). The small differences between Variant LL and AL and between Variant LA and AA are mainly caused by the allegedly false estimation of the fossil mass share in the fine fraction and textiles (as given in EN 15440:2011) and of composite & unrecognizable materials (50% were estimated) (see Table 4). If the shares of these "non-pure" compounds are high, then the result according to the standard are expected to be more prone to errors.

From Figure 2 it can be seen, that the estimated fossil shares are lowest when literature values are used for TOX_k^{Fos} and TOX_k^{Bio} (blue bars, Variant LL and AL). This implies that the generated TOX_{Bio} is closer to the measured values in the RDFs (TOX_{RDF}) than TOX_{Fos} for Variant LL and AL. This, in turn indicates that the actual carbon and hydrogen content in the TOX_{Fos} is lower than expected from literature values; and the oxygen content is higher. As the TOX_{Fos} depends on the different shares of polymers and their respective chemical composition, it can be expected that the polyethylene and polypropylene shares in the investigated RDF is lower than typically found in MSW. They may contain slightly higher shares of plastics with lower carbon and hydrogen and higher oxygen contents (e.g., polyamide, polyethylene terephthalate, or polyurethane). For example, in RDF MSW+C&I significant shares of foamed polymers could be observed, which are expected to account for around 16 to 26wt%. In RDF C&I (2), (3), and (4) shares of foamed plastics between 2 to 3wt% could be assessed by sorting, which corresponds to 4 to 5wt% in the plastic compound sorted out.

The fact that there are much smaller differences for Paper Reject (than for the other RDFs) when comparing results obtained using different TOX_k^{Fos} and TOX_k^{Bio} (green bars versus blue bars in Figure 2), suggests that the polymer composition in the Paper Reject is similar to the one typically found in MSW.

For all RDFs prepared from mainly C&I (4 of the 6 RDFs investigated), the results generated using values for TOX_{Bio} and TOX_{Fos} from Fellner et al. (2011) (Variant L, grey bar in Figure 2) are close to the results generated when using TOX_k^{Fos} and TOX_k^{Bio} from own analyses or combining own analyses with literature values (Variant LA, AA, and AAL).

The Variant AAL delivers aBM results on the fossil car-



Grey: *Variant L: Elemental composition of biogenic and fossil organic matter (TOX_{Bio} and TOX_{Fos}) are used from Fellner et al. (2011)*

Blue: *Variant LL and AL: Elemental composition of fossil and biogenic organic matter in sorted compounds (TOX_k^{Fos} and TOX_k^{Bio}) is taken from literature*

Green: *Variant LA and AA: Elemental composition of fossil and biogenic organic matter in sorted compounds (TOX_k^{Fos} and TOX_k^{Bio}) is taken from own analyses*

Purple: *Variant AAL: Elemental composition of fossil and biogenic organic matter in sorted compounds (TOX_k^{Fos} and TOX_k^{Bio}) is taken from own analyses AND literature*

FIGURE 2: Share of fossil carbon for the different RDFs, determined by utilizing the aBM with different input values of TOX_{Fos} and TOX_{Bio} (estimated by using 7 different variants as listed in Table 2).

bon share which are slightly below the ones when using TOX$_k^{Fos}$ and TOX$_k^{Bio}$ from own analyses (Variant LA and AA, green bars), but are in most cases considerably above the ones when using literature values (Variant LL and AL). The Variant Mean, which uses the mean values of all investigated RDFs for TOX$_{Bio}$ and TOX$_{Fos}$ from Variant AAL, leads to results in a similar range as Variant AAL except for Paper Reject and RDF MSW+C&I.

In general, by trend a slightly higher fossil share can be detected for RDFs prepared from C&I (RDF C&I), compared to the RDF containing also compounds of MSW (RDF MSW+C&I).

3.4 Comparison of aBM results to alternative methods

In order to decide on the most probable result determined by aBM (to identify which variant delivers the lowest deviation from a comparable value), the outcomes are compared to values generated with alternative analysis methods.

Figure 3 shows the deviation of the aBM results from values generated by using the Radiocarbon method (^{14}C-method) for 3 of the investigated RDFs. Figure 4 presents the deviation of the aBM results from the manual sorting results for the other 3 RDFs (no Radiocarbon analyses are available for these RDFs). However, it must be kept in mind that the manual sorting results are connected with a significantly higher uncertainty than the results of Radiocarbon analyses. Even though the sorting is conducted very painstakingly, some errors (such as subjectiveness when sorting, wrong estimation of the composition of fine fraction or composite & unrecognizable materials) are hardly quantifiable.

For Paper Reject and RDF MSW+C&I using generic values or mean values for TOX$_{Fos}$ and TOX$_{Bio}$ (Variant L and Variant M) seems not to be suitable (+8 to +12% deviation for Paper Reject and –8 to –10% deviation for RDF MSW+C&I compared to Radiocarbon analyses).

For the other RDFs, which are the ones mainly produced out of C&I, a relatively good agreement of the aBM results to the results of alternative methods is observed when using Variant L or Variant M. Low deviations between -2.9% and +3.2% from results of alternative methods are found. This indicates that the usage of generic values is suitable and RDF produced out of C&I have typical compositions regarding the shares of the different synthetic polymers (within the fossil fraction) and regarding the composition within the biogenic materials (shares of paper, wood, natural fibers, etc.).

The results for all other variants than Variant L and Variants M, are in a close range when regarding Paper Reject. As Variant LL, AL, LA, AA, and AAL also show a low deviation from the alleged true value (0.5 to1.6%), it can be assumed that the most decisive factor when generating TOX$_{Fos}$ and TOX$_{Bio}$ is the usage of the actual shares of compounds present in Paper Reject. This means that an initial sorting campaign before applying the aBM to Paper Reject might results in a considerably higher reliability of the results.

A somehow different observation is made for the other RDFs: Significant underestimations of the fossil share can be observed when Variant LL and LA are used, where the information of the chemical composition of biogenic and fossil organic matter in the compounds stem from literature (mean deviation –9 to –13%). But the usage of the analyzed chemical composition of the compounds (Variant LA) or only analysis results (Variant AA) seems to rather overestimate the fossil carbon share for all RDFs. For example, for RDF C&I (2) the relative deviation when using Variant AA is considerably higher than when using Variant L where the input values for TOX$_{Fos}$ and TOX$_{Bio}$ are used without any analysis (values from Fellner et al., 2011). A possible explanation for this phenomenon is that the fossil and biogenic matter in the fine fraction, which represents

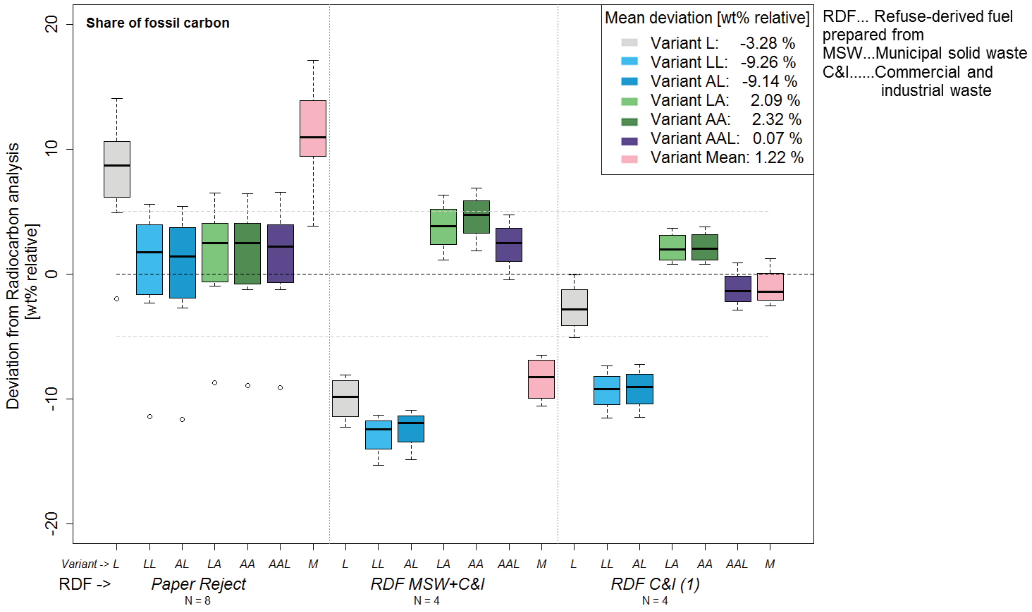


FIGURE 3: Deviations of the fossil carbon share as determined by the aBM from results determined by the Radiocarbon method; aBM results are generated by utilizing different input values of TOX$_{Fos}$ and TOX$_{Bio}$ (7 different variants as listed in Table 2 are used); negative deviations mean a lower value is found by aBM compared to the Radiocarbon method. One outlier is identified for Paper Reject.

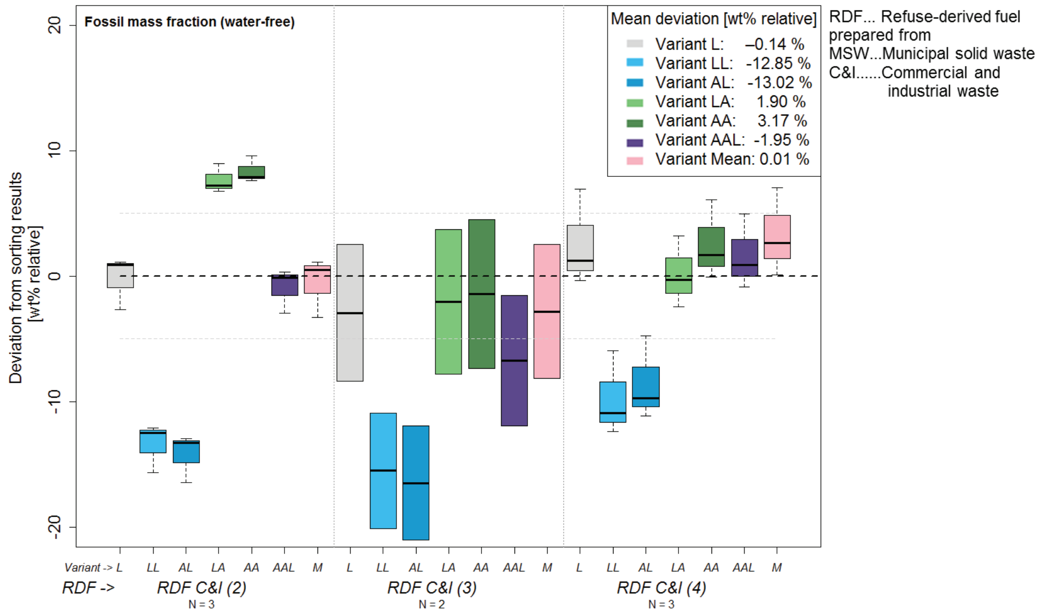


FIGURE 4: Deviations of the fossil mass fraction (water-free) as determined by the aBM from results determined by manual sorting; aBM results are generated by utilizing different input values of TOX_{Fos} and TOX_{Bio} (7 different variants as listed in Table 2 are used); negative deviations mean a lower value is found by aBM compared to manual sorting.

almost 1/3 of the mass of the RDF, has a significantly different chemical composition than the fossil and biogenic matter in the rest of the RDF. This would make the assignment of analysis results of, for example, plastics, and paper to the fine fraction incorrect (which is done for Variant LA and Variant AA). For Variant AAL, it is assumed that the fine fraction has a chemical composition similar to the one reported in the literature. This assumption appears to lead to more accurate results compared to the other variants. The boxplots per RDF in Figure 3 and Figure 4 show that the results of Variant AAL deviate from the result of the alternative method less than 2.5% (except for RDF C&I (3) where only 2 values are available and thus, one value can easily distort the average deviation).

A mean deviation for the Variant AAL of 0.07% is found when comparing the aBM results to the Radiocarbon results (see Figure 5a). When considering the sorting results as alleged target value (although the uncertainty of these values are relatively high) a mean deviation of -1.95% is found (Figure 5b). Although this mean deviation might be higher than found for other variants, a lower variation of results is visible from Figure 5b for this variant than for the

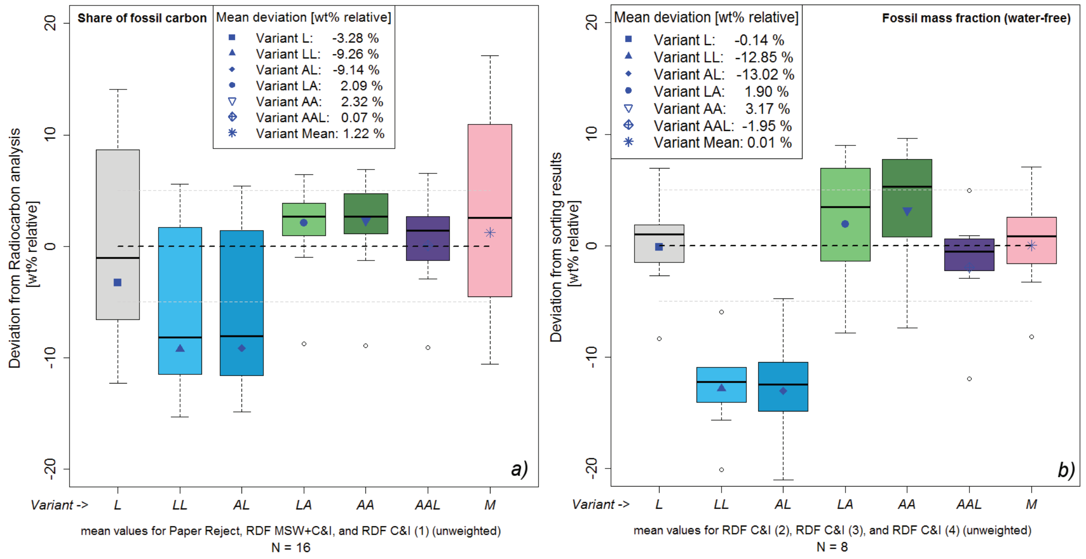


FIGURE 5: a) Deviations of the fossil carbon share as determined by the aBM from results determined by the Radiocarbon method.
b) Deviations of the fossil mass fraction (water-free) as determined by the aBM from results determined by manual sorting. Negative deviations mean a lower value is found by aBM compared to the alternative method; Outliers in a) stem from one Paper Reject sample and in b) from one sample of RDF C&I (3) and from one sample of RDF C&I (4).

other options. Treating one of the values for RDF C&I (3) as outlier (only 2 values available, so no clear judgement can be made), results in a mean deviation of only -0.2% for Variant AAL when compared to manual sorting. The results which are obtained by applying Variant AAL are considered to result in a good agreement with the alternative methods.

3.5 Elemental composition of biogenic and fossil organic matter present in RDFs

Based on the results found in the previous sections, the Variant AAL is identified as the most suitable option to generate the input parameter (TOX_{Fos} and TOX_{Bio}) required for the aBM. In Figure 6 and Figure 7 the results for these parameters are presented and compared to values given in Fellner et al. (2011). Additionally the mean for each element is indicated together with the 95-% confidence interval determined for all the RDFs investigated in this study.

It can be seen that the values for all RDFs are in a relatively close range and also similarly to values found in Fellner et al. (2011) for most elements. The most varying value seems to be the total organic oxygen content (TOO). The TOO values generated within this study vary ± 21 g/kg on average in the fossil organic matter and ± 36 g/kg on average in the biogenic organic matter. This variation is partly due to the fact that conducting oxygen analyses is more difficult than for the other elements. Higher uncertainties need to be considered. Further, values reported in literature often only estimate the O-content based on the subtraction of the all other elements from 1000 g/kg.

The higher TOO content found in the fossil organic matter of RDF MSW+C&I indicates higher shares of polyamide, polyethylene terephthalate, or polyurethane. Whereas, the

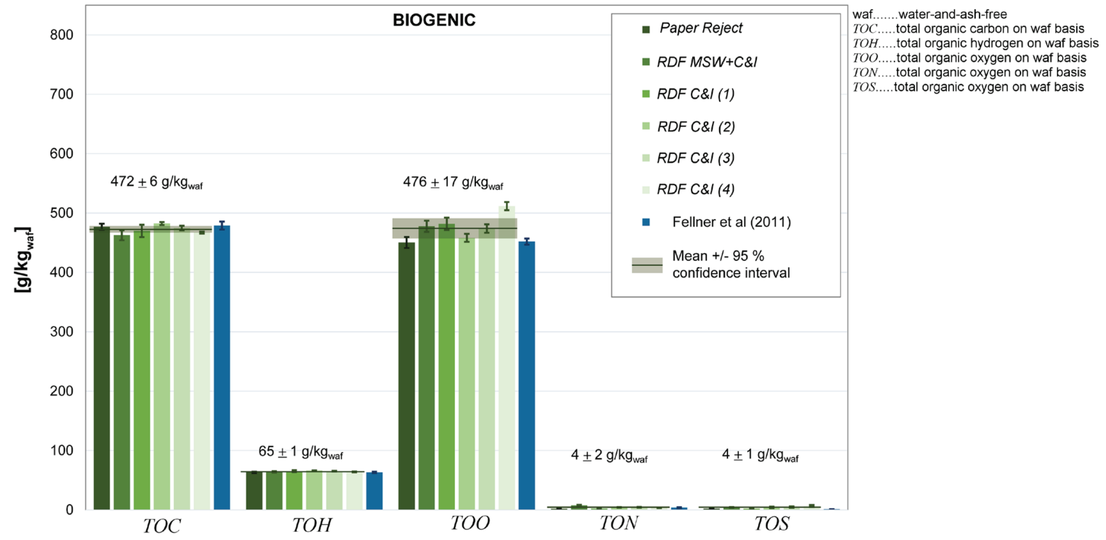


FIGURE 6: Elemental composition of biogenic organic matter (TOX_{Bio}) present in the RDFs (determined according to Variant AAL described in Table 2).

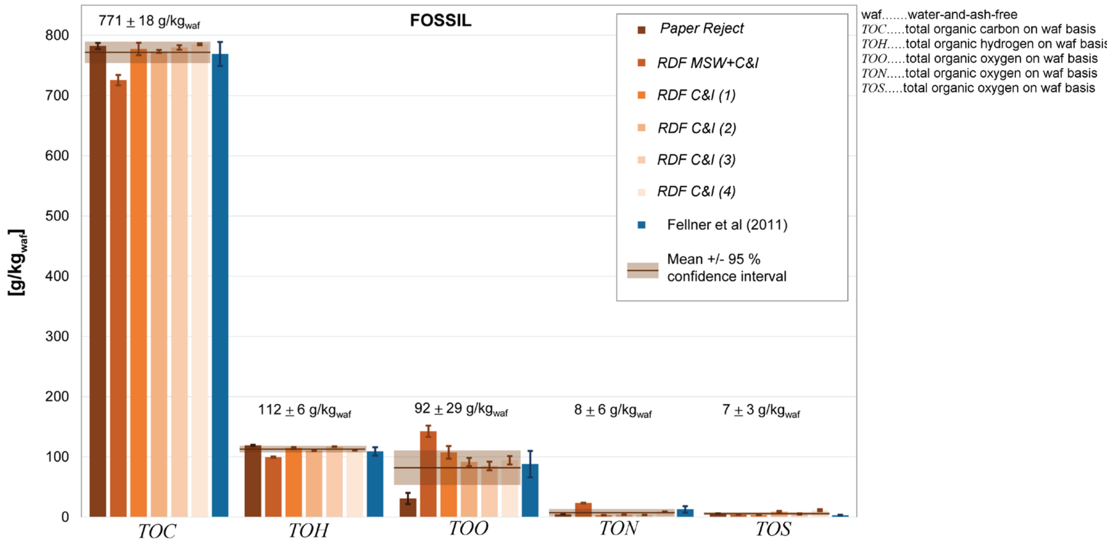


FIGURE 7: Elemental composition of fossil organic matter (TOX_{Fos}) present in the RDFs (determined according to Variant AAL described in Table 2).

Paper Reject can be estimated to contain high shares of polyethylene and polypropylene, which are characterized by a low or even zero oxygen content.

It can be seen that the values found for the RDFs C&I (1), (2), (3), (4) are in an even closer range than when all RDFs are regarded. Except for the TOC_{Bio} of RDF C&I (2) and TOO_{Bio} of RDF C&I (4) all values are within the 95-% confidence interval given in Figure 6 and 7.

4. CONCLUSION

The presented study shows that the shares of different compounds in RDFs (such as paper, plastics, textiles, etc.) can vary significantly, even when the RDFs are produced from allegedly similar waste material (such as C&I). Also the fossil shares in mixed compounds (mix of biogenic and fossil materials, such as in composite materials, textiles, fine fraction) can be considerably different between RDFs and compared to the suggested values in EN 15440:2011. However, for most RDFs these inaccuracies hardly influence the results of the adapted Balance method (aBM) and thus the determination of the fossil carbon share when applying this method.

The usage of generic values from literature or of an overall mean from this study leads to deviations from the allegedly true value of <3.5% when 4 different RDFs C&I are regarded. This finding suggests that there is a typical elemental composition of biogenic and fossil organic matter present in RDFs which are produced out of C&I (RDF C&I). It is expected that the values derived for this type of RDF on TOX_{Fos} and TOX_{Bio} can also be used for other RDFs of the same type. Yet, as the investigated samples stem from Austrian RDF producers, the question on the country-specific dependency remains unclear.

For RDFs where the input is more prone to strong variations (which might be expected from MSW), the initial generation of RDF-specific values on the chemical composition of biogenic and fossil organic matter (TOX_{Fos} and TOX_{Bio}) is recommended to increase the reliability of the aBM results. This also applies when special types of RDF are to be analyzed for their climate relevance (like Paper Reject).

The usage of previously collected literature values for MSW compounds seem not to be suitable for most of the investigated RDFs. Thus, if sorting analyses are conducted it makes sense to generate some data on the elemental composition of the different compounds. These could not only be used to increase the accuracy of the results but could also be collected in a database for different RDF types to be accessed for future investigations.

However, in the case of Paper Reject, the usage of the actual shares of the different compounds in the RDF appears to be the most decisive factor. Thus, if this type of RDF is to be analyzed for its fossil carbon content by means of the aBM, manual sorting campaigns for determining the share of the different compounds are sufficient; the chemical composition of the sorted compounds can be taken from previously analyzed Paper Reject (e.g., from this study).

Some workload can be saved for the determination of the fossil and biogenic share in each compound of the RDF ($x_{mF,k}$ and $x_{mB,k}$); this parameter seems to have a minor influence on the aBM result. Only when the share of textiles, composite & unrecognizable materials or of the fine fraction is significant (and compounds are expected to contain a significantly higher amount of plastics than 50wt%), then $x_{mF,k}$ and $x_{mB,k}$ should also be investigated specifically for these "mixed" compounds (mix of fossil and biogenic constituents).

In general, the results obtained by combining own analysis data with information from the literature are in a good agreement with the outcomes of alternative methods (relative mean deviation <2%). Moreover, the results are also less scattered when choosing this option. Thus, it is assumed Variant AAL represents the best option to generate the necessary input data for the aBM (TOX_{Fos} and TOX_{Bio}).

It can be concluded that if more data on TOX_{Fos} and TOX_{Bio} are collected in a database, generic values can be derived for different RDF types and the initial workload and costs for conducting sorting analyses of RDF before applying the aBM can be saved.

The aBM delivers information on the fossil and biogenic mass share, the fossil and biogenic carbon (CO_2) share and also the share of biogenic and fossil energy recovered from the RDF can be estimated. The heating value for the biogenic and fossil matter in the RDF can, for example, be estimated using an empirical equation based on the elemental composition (e.g., Garcés et al., 2016; Kost, 2001; Meraz et al., 2003). Thus, the aBM can be regarded as cost-efficient method which has been demonstrated to deliver reliable results.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the funding of the present study, which was provided by the Austrian Science Fund (FWF), project number TRP 285-N28. Further, the work was partly supported by a large-scale research initiative on anthropogenic resources (Christian Doppler Laboratory for Anthropogenic Resources). The financial support of this research initiative by the Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development is gratefully acknowledged. We thank the RDF-plant operators and paper & board plant operators for their support and assistance for drawing samples. Thanks to the laboratory team of TU Wien for their contribution as well as Inge Hengl for graphical support. In addition, we are grateful for the assistance of Edith Vogel during ^{14}C analysis.

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Conference contribution 1

Cost efficient Quantification of Microplastics

Stefan Spacek, Ole Mallow, Therese Schwarzböck, Helmut Rechberger and Johann Fellner

European Conference on Plastics in Freshwater Environments,
21.-22.06.2016, Berlin, Germany

Microplastic content in freshwater – an easy and cost-efficient analysis approach

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In contrast to macroplastic analysis, there is no accepted standard for the characterization and quantification of microplastics. The most commonly used techniques include density-gradient-separation and microscope sorting followed by IR-analysis or Pyrolysis-GC. These techniques are error-prone, time consuming, expensive and are somewhat restricted when taking microplastic particles of a grain size below 100 µm into account.

In the last years, a method (the so called Balance Method) for the determination of fossil matter in mixed waste has been developed at the TU Wien (Fellner et al. 2007/2011). The Balance Method is based on the distinctly different chemical composition of moisture- and ash-free biogenic and fossil organic matter. At laboratory scale, an elemental analysis is used to determine the content of the elements C, H, N, S and O in the dried sample as well as the ignition residue.

$$X_b \cdot m_b + X_f \cdot m_f = TX_{sample} - TX_i \cdot m_i$$

Based on different mathematical balances, a system of equations can be created, which is defined by the individual contributions of the elements (X = C, H, N, S, O), their corresponding material data and the measurable values TX_{sample} and TX_i (b = biogenic, f = fossil and i = inert). A data reconciliation algorithm is applied to reveal the quantity of the unknown mass fractions (biogenic m_b, fossil m_f and inert matter m_i) including their uncertainties.

Currently, this method is modified in order to be applied to water and wastewater samples. In a first test series the microplastic content in different samples taken from a wastewater stream has been successfully quantified. The method demonstrated good results by either making use of an oxidation before the elemental analysis (utilizing hydrogen peroxide to reduce the organic part to a hardly oxidisable lignin matrix) or by analysing the unaltered sample for its C, H, N, S, and O content. Either way used, a sample volume of 2 – 3 g was enough to precisely quantify the contained fossil matter (microplastic) by means of the adapted Balance Method.

In contrast to the above-mentioned methods, which are limited to certain grain sizes, the described technique offers the possibility to characterize solid samples independent from the size of the microplastic particles. However a routine application of the adapted Balance Method ultimately requires detailed knowledge about the elemental composition of both, the organic (biogenic) and the fossil part (plastics).

Cost efficient Quantification of Microplastics

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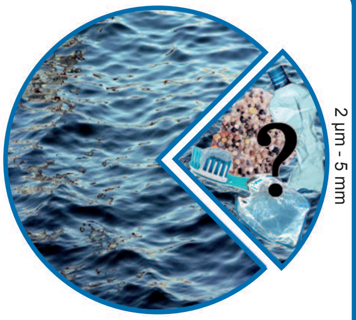
Introduction

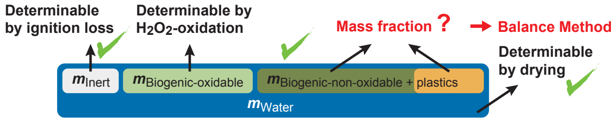
Recent studies show that significant amounts of plastic particles are found in fresh as well as marine waters. Particularly microplastics (~2 µm – 5 mm) are critical, since they possess an immense potential for harming ecosystems. The most common methods for the quantification of microplastics are either time-consuming (sorting) or expensive (FT-IR-Microscopy).

In the present project a method (the **Balance Method**) which has successfully been applied for determining the composition of waste and refuse derived fuels with respect to their contents of biomass and fossil organic matter, has been adapted to provide reliable information about the microplastic content in aquatic samples. The applied method is based on easily available elemental analysis (content of C, H and O) and on the distinct difference in **elemental composition** of microplastics and biogenic matter present in aquatic samples.



Method

Composition of aquatic microplastic samples



Determinable by ignition loss ✓

Determinable by H_2O_2-oxidation ✓

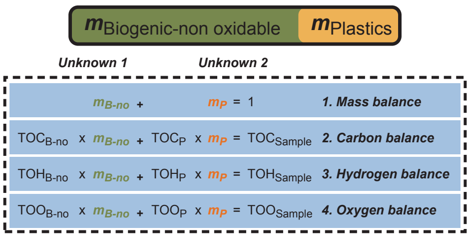
Mass fraction ? → **Balance Method**

Determinable by drying ✓

m_{Inert} | $m_{Biogenic\text{-}oxidable}$ | $m_{Biogenic\text{-}non\text{-}oxidable}$ + plastics | m_{Water}

$$m_{Sample} - m_{Residual\ water} - m_{Inert} - m_{Biogenic\text{-}oxidable} = m_{Biogenic\text{-}non\text{-}oxidable\ +\ plastics}$$

Balance Method



Mass fraction ?

$m_{Biogenic\text{-}non\ oxidable}$ | $m_{Plastics}$

Unknown 1 *Unknown 2*

$m_{B\text{-}no} + m_P = 1$ *1. Mass balance*

$TOC_{B\text{-}no} \times m_{B\text{-}no} + TOC_P \times m_P = TOC_{Sample}$ *2. Carbon balance*

$TOH_{B\text{-}no} \times m_{B\text{-}no} + TOH_P \times m_P = TOH_{Sample}$ *3. Hydrogen balance*

$TOO_{B\text{-}no} \times m_{B\text{-}no} + TOO_P \times m_P = TOO_{Sample}$ *4. Oxygen balance*

The analysis is conducted in several steps: First the content of inert matter m_{Inert} is determined via the ignition loss. Subsequently the easily degradable biogenic matter $m_{Biogenic\text{-}oxidable}$ is oxidized via H_2O_2. And in a last step the elemental composition (C,H,O) of the remaining mixture (microplastics $m_{Plastics}$ and hardly degradable biogenic matter $m_{Biogenic\text{-}non\ oxidable}$) is determined. Finally the data of these analyses are used together with information about the elemental composition of microplastics and hardly degradable biogenic matter to determine the mass fraction of microplastics $m_{Plastics}$.

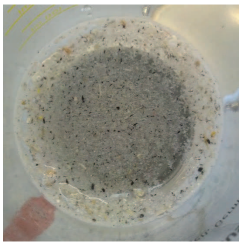
H_2O_2-Oxidation

H_2O_2-treatment allows oxidizing a large share of the biogenic matter present in the sample. Thereby the elemental composition of the remaining biomass can be assessed with higher accuracy, which results in lower overall uncertainties of the Balance Method.

Before H_2O_2

Sediment sample (m_{Sample}) with high biogenic content. The microplastic particles are partially embedded in dried biogenic components.

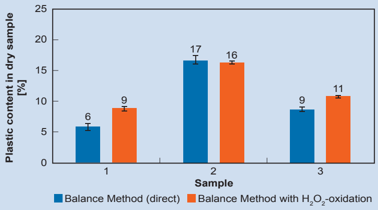
After H_2O_2



Sediment sample after H_2O_2-treatment ($m_{B\text{-}no+p}$). Besides inert material, the sample contains only wood and microplastics.

Results

Microplastic content in sediments of industrial wastewater:



- ▶ The Balance Method has been successfully applied for determining the microplastic content in aquatic samples.
- ▶ It was shown that sample preparation including H_2O_2-treatment may significantly lower the uncertainty of the final results.

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Conference contribution 2

The added-value of the Balance Method for Waste-to-Energy operators and national authorities

Therese Schwarzböck, Helmut Rechberger and Johann Fellner

IRRC Waste-to-Energy, 05.-06.09.2016, Vienna, Austria

The Added Value of the Balance Method for Waste-to-Energy Operators and National Authorities

Therese Schwarzböck, Helmut Rechberger and Johann Fellner

Different directives of the European Union may require operators of Waste to Energy WTE plants to monitor the composition of their waste feed with respect to the content of biomass and fossil organic matter. The mass fractions of both materials are not only of relevance for the amount of fossil and thus climate relevant CO_2 emissions of the plant, but also for the ratio of renewable energy generated, as biomass in wastes is considered as renewable energy source [3, 4].

In recent years different methods, including manual sorting [15, 20], selective dissolution [2, 20], the radiocarbon method [12] and the Balance Method [6] have been developed to determine the biomass content of waste, and thus the fraction of renewable energy and fossil CO_2 emissions produced by WTE plants. Until now all of these methods have been applied to different WTE plants [7, 10, 12, 14] and different wastes [5, 11, 16] aiming at, on the one hand, the determination of characteristic values for the biomass content and fossil CO_2 emissions and on the other hand, at a comparison of the different analysis methods. With respect to the latter, results of the different studies indicate that methods requiring waste feed sampling – e.g. sorting analysis or selective dissolution method – are much more vulnerable to waste heterogeneity and temporal changes in waste composition as quantities of manageable waste samples (at maximum a few tons) are very small in comparison to the total amount thermally utilized.

The Balance Method as well as the radiocarbon method largely avoid problems associated with waste heterogeneity as the measurements or sampling take place in the highly homogeneous flue gas. Compared to the other methods, these two methods have additionally been proven to be practical for a continuous monitoring of the biomass content in the feed of WTE plants which provides the possibility to investigate temporal differences with a high resolution [14, 7, 13]. A further advantage of the Balance Method is the fact that it is based on routinely recorded operating data of WTE plants which usually avoids the need for additional sampling and measurement efforts. During the last years the concept of the Balance Method has been implemented in the software BIOMA (http://iwr.tuwien.ac.at/ressourcen/downloads/bioma.html), which enables a user-friendly application of the Balance Method.

In a recent research study [17] the BIOMA software has successfully been applied to 10 Austrian WTE plants to determine their fossil CO_2 emissions and also the ratio of energy from renewable sources. Despite the fact that the overall budget of the project was below 100 kEUR (and thus smaller than 10 kEUR per plant), it was possible to assess the waste composition of 10 plants with high accuracy – uncertainty below 5 percent relative – and to evaluate the overall climate impact of Austria´s waste incineration plants. The results of the study are given in detail in Schwarzböck et al. [17, 18].

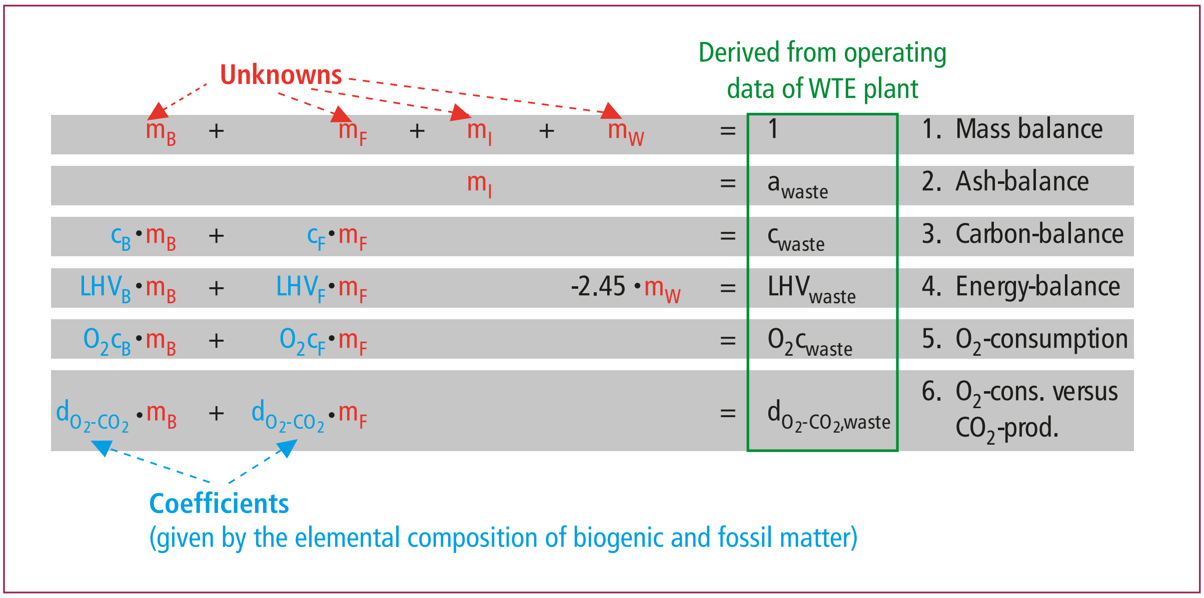
Besides the evaluation of the waste feed composition and the therewith associated CO_2 emissions and energy production of the plants, the application of the software provided further benefits for the operators of the WTE plants and also for authorities. The aim of the present paper is to summarize the major outcomes of the study including the added values of the Balance Method. Therefore results and experiences gained throughout the application to the 10 Austrian WTE plants are described and evaluated.

1. Materials and methods

1.1. Balance Method

The Balance Method, applied in the present study, combines data on the elemental composition of moisture- and ash-free (maaf) biogenic and fossil organic matter with routinely measured operating data of the WTE plant in order to determine the composition of the waste feed. In principle the method utilizes one energy balance and five mass balances, whereby each balance describes a certain waste characteristic – e.g. content of organic carbon, lower calorific value, ash content. Each balance equation contains a theoretically derived term (left side of equations) that has to be attuned to measured data of the incineration plant (right side of equations). A simplified structure of the set of equations is illustrated in Figure 1. A detailed mathematical description of each equation is provided by Fellner et al. [6].

For setting up the 6 balance equations (Figure 1), the waste mass is virtually divided into four *material groups*: inert (m_I), biogenic and fossil organic materials (m_B, m_F) and water (m_W). Inert materials include all incombustible solid residues like glass, stones, ashes or other inorganic matter from biowaste and plastics – e.g. kaolin in paper or inorganic additives in plastics. Biogenic and fossil organic material groups refer only to the maaf organic matter (Figure 2). As the qualitative composition of organic materials in mixed wastes is usually well known – e.g. biogenic matter encompasses paper, wood, kitchen waste, etc. and fossil organic matter includes polymers, such as PP, PE, PET, PVC, etc. – the content of C, H, O, N, S and Cl of the maaf biogenic and fossil organic materials (m_B and m_F) can be derived.



$$m_B + m_F + m_I + m_W = 1 \quad \text{1. Mass balance}$$

$$m_I = a_{waste} \quad \text{2. Ash-balance}$$

$$c_B \cdot m_B + c_F \cdot m_F = c_{waste} \quad \text{3. Carbon-balance}$$

$$LHV_B \cdot m_B + LHV_F \cdot m_F - 2.45 \cdot m_W = LHV_{waste} \quad \text{4. Energy-balance}$$

$$O_2c_B \cdot m_B + O_2c_F \cdot m_F = O_2c_{waste} \quad \text{5. } O_2\text{-consumption}$$

$$d_{O_2\text{-}CO_2} \cdot m_B + d_{O_2\text{-}CO_2} \cdot m_F = d_{O_2\text{-}CO_2,waste} \quad \text{6. } O_2\text{-cons. versus } CO_2\text{-prod.}$$

Figure 1: Set of equations (simplified) used by the Balance Method; the left side of the equations represent the theoretical balance (utilizing information on the elemental composition of maaf biogenic and fossil organic matter) that has to be attuned to the different waste characteristics derived from operation data of the WTE plant (right side of the equations)

based on Schwarzböck, T.; Van Eygen, E.; Rechberger, H.; Fellner, J.: Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities. Waste Management & Research (accepted for publication). 2016

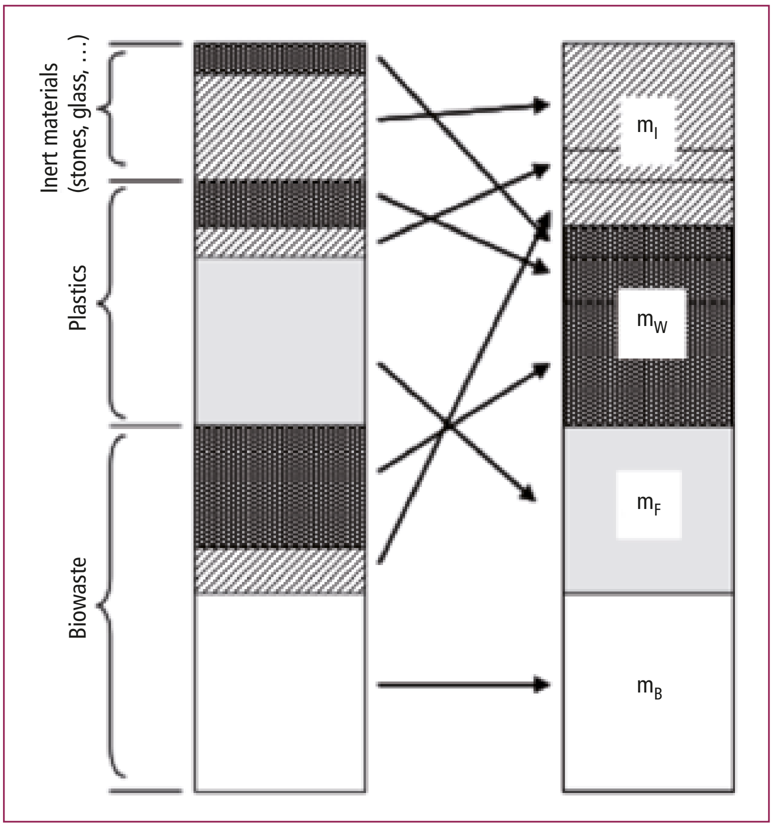


Figure 2:

Split-up of waste fractions into the four *material groups* (m_B, m_F, m_W, and m_I), which represent the unknowns in the set of 6 equations

based on Fellner, J.; Cencic, O.; Rechberger, H.: A new method to determine the ratio of electricity production from fossil and biogenic sources in waste-to-energy plants. Environ Sci Technol 41, 2007, pp. 2579-2586

The input data required for the Balance Method comprise information on the elemental composition of maaf biogenic and fossil organic matter present in the waste feed, information on the quantity of fuels incinerated (waste mass and auxiliary fuels), the amount of solid residues and steam produced, as well as data on the volume and composition (O_2 and CO_2 content) of the dry flue gas. A graphical overview of the required input data is provided in Figure 3.

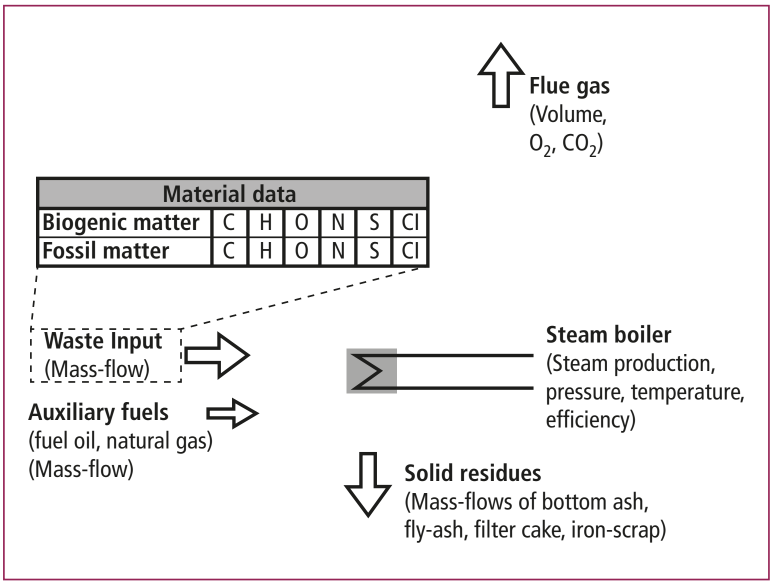


Figure 3:

Required input data for the Balance Method

based on Schwarzböck, T.; Van Eygen, E.; Rechberger, H.; Fellner, J.: Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities. Waste Management & Research (accepted for publication). 2016

Because the system of equations (set of constraints) used is over-determined (6 equations for 4 unknowns), data reconciliation has to be performed to eliminate data contradiction and to improve the accuracy of the results. The reconciled values are subsequently used to compute the unknown quantities (m_B, m_F, m_W, and m_I) including their uncertainties.

Prior to solving the set of equations for calculating the unknown mass fractions (m_F, m_B, m_W, and m_I) the input data (operating data of the WTE plant) are checked regarding their plausibility. Thereto, correlations between the flue gas and its composition and the steam production are used – e.g., during the combustion of organic matter the consumption of 1 mole O_2 corresponds to an energy generation of 360 to 400 kJ; and the combustion of 1 g organic carbon produces a heat amount of 34 up to a maximum of 44 kJ. The calculations according to the Balance Method (solving the set of 6 equations) are only performed with plausible data, whereby the temporal resolution of the data used is preferably in the range of hourly averages for most input data.

1.2. Austrian Waste-to-Energy plants investigated

The feed of 10 Austrian WTE plants, which represents 91 percent of the waste incinerated in Austria in 2014, has been investigated with respect to the composition of the waste feed, the climate relevant CO_2 emissions and the ratio of energy generated by renewable sources. Three facilities could not be included in the study as they did not provide all operating data required for the Balance Method or were under reconstruction in the respective time period.

In Table 1 and Figure 4 an overview of the 10 Austrian waste incineration plants investigated is given. The annual capacity of these plants amounts to about 2.3 million tons of waste [1], whereby different types of combustion technologies (grate incineration GI or fluidized bed combustion FBC) are utilized. The plants mainly combust municipal solid waste, commercial and industrial waste, sewage sludge and refuse derived fuels (Table 1), whereby the share of the different wastes may vary significantly during the investigated time period of one year.

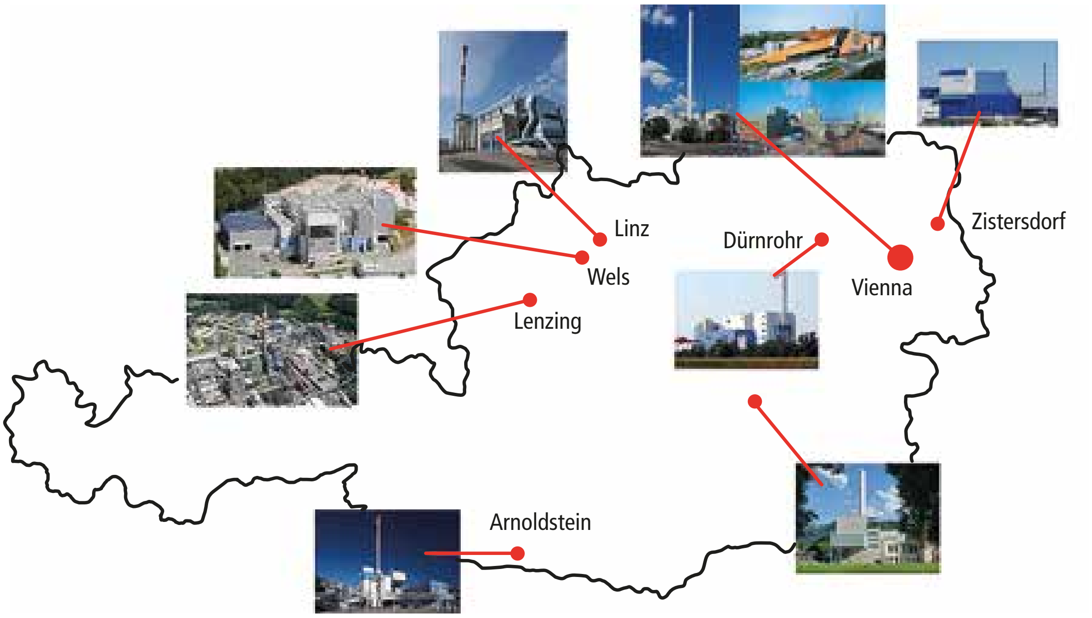


Figure 4: Location of Austrian Waste-to-Energy plants investigated

Table 1: Summary of the WTE plants including information about the combustion technology utilized and the type of waste incinerated

WTE plant	Combustion technology	Waste combusted
A	Grate incinerator (GI)	MSW
B	Grate incinerator (GI)	MSW and CW and IW
C	Fluidized bed combustion (FBC)	RDF and SS
D	Fluidized bed combustion (FBC)	RDF and SS
E	Fluidized bed combustion (FBC)	RDF and SS
F	Grate incinerator (GI)	CW and IW and minor amounts of MSW
G	Stationary fluidized bed combustion (FBC)	RDF and minor amounts of SS
H	Grate incinerator (GI)	MSW, CW and IW & minor amounts of SS
I	Grate incinerator (GI)	MSW
J	Grate incinerator (GI)	MSW, CW and IW & minor amounts of SS

MSW = Municipal solid waste, CW and IW = commercial and industrial waste, SS = sewage sludge, RDF = refuse derived fuels

based on Schwarzböck, T.; Van Eygen, E.; Rechberger, H.; Fellner, J.: Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities. Waste Management & Research (accepted for publication). 2016

2. Results

In the subsequent chapters various results obtained by the application of the Balance Method to different Austrian WTE plants are summarized and highlighted.

2.1. Detection of errors in the plant operating data recorded

Prior utilizing the operating data of the WTE plants for determining the waste feed composition plausibility checks are conducted. Thereto hourly values of the operating data are aggregated to 6-hour averages (in order to account for the fact that there is obviously a temporal difference between certain input and output flows of the facility – Figure 3), which are subsequently tested for their correlation between oxygen consumption, carbon content and lower calorific value of the waste.

Results of the plausibility tests are exemplary given for the operating data of plant F (Figure 5). From the relations in Figure 5 it can be seen that a large share of the data points displayed are outside the theoretically plausible band. Based on the fact that for both figures (O_2 vs. calorific value and C-content vs. calorific value) a similar pattern for the data points outlying the theoretical band is observable, it can be concluded that the flue gas volume measurements at plant F are implausibly high and very likely defective. Furthermore the results of the plausibility check even allow valuing that the measured flue gas volume is about 20 percent above the plausible level.

By conducting control measurements at the respective plant, the error in flue gas volume detected via the Balance Method could be proven and could subsequently be corrected. The observed implausible data sets could be attributed to a significant amount of leak air entering the plant between the measuring points for the flue gas volume and for the O_2 and CO_2 content of the flue gas.

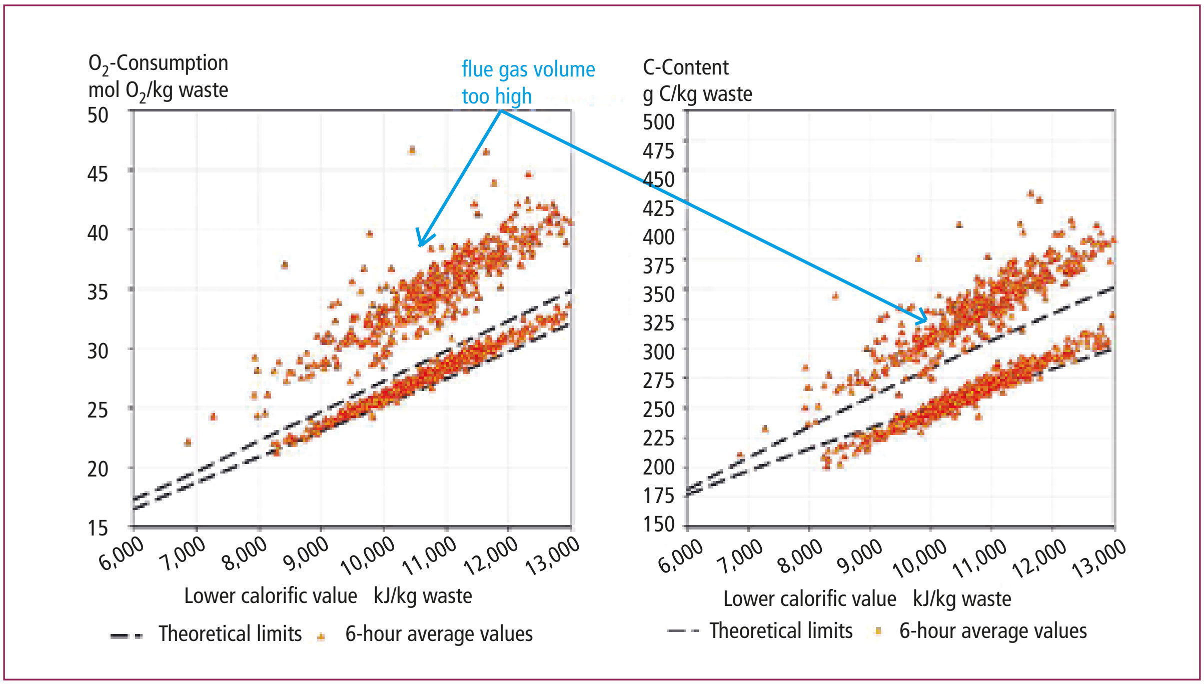


Figure 5: Results of plausibility checks (correlation between lower calorific value and O_2 consumption and carbon content of the waste, respectively) for the operating data of WTE plant F (data points represent 6-hourly averages)

Besides *wrong* flue gas volume measurements, also data transfer errors and conversion errors – e.g., related to 11 percent O_2 or dry vs. wet flue gas – have been identified at different plants and could subsequently be corrected.

After obtaining different additional information from the plant operators on e.g. the calibration practices, the combustion process or experiences with measurement devices, the plausibility tests finally showed that all plant operators (with the exception of two) were able to provide operating data with a plausibility of more than 95 percent, meaning that more than 95 percent of the 6-hourly averages were assessed as plausible and thus utilized for the analyses according to the Balance Method.

2.2. Climate relevant (fossil) CO_2 emissions from Austrian WTE plants

All plausible operating data of the WTE plants were used for the analysis according to the Balance Method. By inserting the calculated composition of the waste feed (content of m_B, m_F, m_I and m_W) into the carbon balance, it was possible to determine the content of fossil carbon and thereon based the amount of fossil CO_2 emissions for any time period of interest.

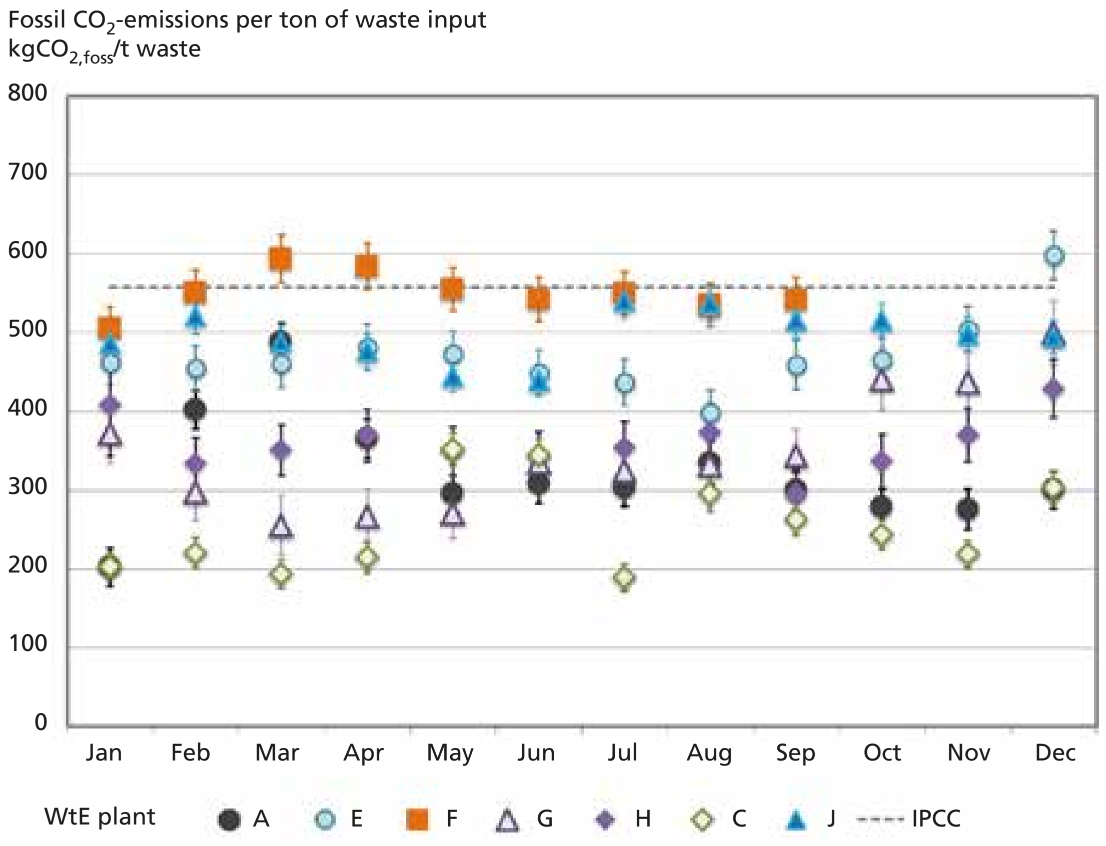


Figure 6: Monthly averages (incl. standard deviation) of specific fossil CO_2 emissions (given in kg CO_2 per ton of waste) for 7 Austrian WTE plants in comparison to the default value recommended

by IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories - Chapter 5 -Waste http://www.ipcc-nggip.iges.or.jp/public/gp/english/, p. 32

In Figure 6 the specific fossil CO_2 emissions (given as monthly averages in kg CO_2 per ton waste) of different plants are summarized. The results clearly indicate large temporal variations in the waste composition and thus also in CO_2 emissions. Furthermore, significant differences in the waste feed of the plants are observable, resulting in specific CO_2 emissions ranging from 200 (plant C) to almost 600 kg $CO_{2,\,foss}$/t waste (plant F). These significant differences further indicate that the usage of generic emission factors – e.g., 557 kg$CO_{2,foss}$/t waste as default given by the IPCC [8] – may result in considerable overestimations (or in some cases also underestimations) of fossil CO_2 emissions. Thus, a plant-specific and continuous evaluation of the waste composition is considered mandatory as it constitutes the only reliable means for quantifying fossil CO_2 emissions. These emissions are of particular interest for WTE plants already participating in greenhouse gas emissions trading schemes but also for authorities reporting overall national greenhouse gas emissions.

2.3. Ratio of energy from biogenic (renewable) sources

Besides the fossil CO_2 emission also the ratio of energy from biogenic sources have been determined by the software BIOMA. Thereto the energy balance has been utilized in conjunction with the outcomes of the waste composition (m_B, m_F, m_W, and m_I). The results of these calculations are summarized in Figure 7, which displays the annual averages for the ratio of energy produced out of biogenic sources in different plants. This information is of particular interested for incineration plants producing electricity, as they are on the one hand obligated to label the electricity put on the market (quantifying the energy carriers used for electricity generation) and on the other hand they may acquire a higher feed-in tariff – e.g. green electricity certificate – for electricity produced out of biogenic and thus renewable sources.

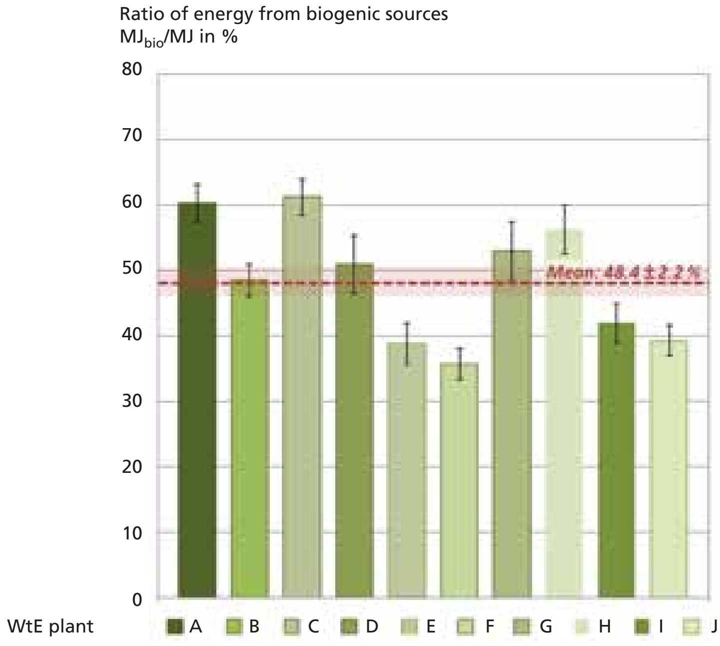


Figure 7:

Annual averages (incl. standard deviation) and weighted means for the ratio of energy produced out of biogenic sources (given in MJ of energy produced out of biogenic sources referred to MJ of total energy generated) for the 10 Austrian WTE plants investigated

In analogy to the specific CO_2 emissions also for the ratio of energy produced out of biogenic sources large difference between the plants can be observed. Plant C shows the highest ratio of renewable energy (61 percent), whereas plant F is characterized by the lowest share of renewables (36 percent). This might be explained by the fact that plant F almost exclusively utilizes commercial and industrial waste.

2.4. Content of plastics in the feed of Austrian WTE plants

In addition to the determination of fossil CO_2 emissions and the energy carriers utilized, which are both of interest for the plant operators, the Balance Method also allows assessing the amount/content of plastics in the waste feed. Thereto results about the mass fraction of fossil matter m_F in the feed have to be combined with data about the average content of inorganic plastics additives.

Information about the plastics content in the feed of waste incineration plants might be of interest for waste authorities for different reasons: First of all, these data allow evaluating the performance of different waste plastics collection schemes in place by simply comparing the amount of plastics separately and not separately collected. Secondly, continuous information about the plastics amount in the feed of WTE plants enables to analyse the trend of waste plastics generation. And thirdly, the overall potential for plastics recycling becomes evident.

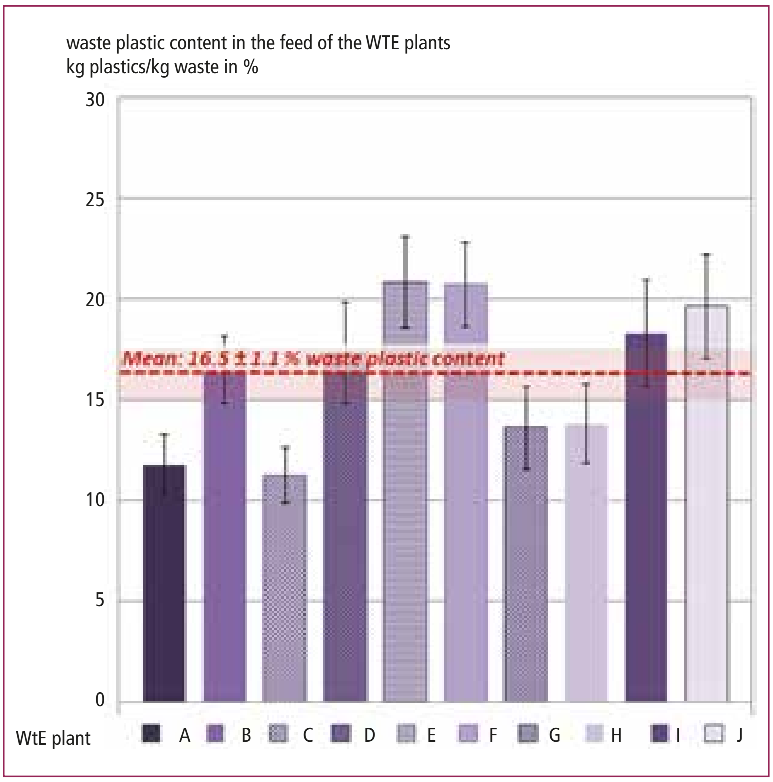


Figure 8:

Annual averages (incl. standard deviation) and overall annual mean of the plastics content in the feed of 10 Austrian WTE plants investigated (figures given in kg plastics per kg waste)

based on Schwarzböck, T.; Van Eygen, E.; Rechberger, H.; Fellner, J.: Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities. Waste Management & Research (accepted for publication). 2016

From the results presented in Figure 8 it can be concluded that also the content of plastics in the waste feed of the different plants varies significantly. The average plastics content of the waste thermally utilized in Austria in 2014 was determined to 16.5 percent (per weight) and is thus significantly higher than results obtained via waste sorting campaigns – e.g. 12.3 percent found by IUT&SDAG [9] or 9.7 percent given in [1]. This discrepancy can be explained by the fact that sorting analyses always generate sorting fractions – e.g. composite materials, hygienic products, textiles – that contain both plastics and biogenic matter, whereby the plastics content of these fractions is difficult to assess and hence usually not considered in the final results about the plastics content in waste. Thus, the herein applied Balance Method represents the only practical approach that allows assessing the *total* content of plastics in wastes.

2.5. Mixing of the waste feed and its impact on steam production and auxiliary fuel consumption

In addition to information about the plausibility of the plant operating data, the amount of fossil CO_2 emission generated, the ratio of energy from renewable sources, or the plastics content in the waste feed, the Balance Method also allows assessing the performance of the waste crane operator with respect to the mixing of the waste (in the receiving bunker) prior its feeding into the shut of the incinerator.

In Figure 9 the results of such analysis are summarized. In particular the steam production (tons/hour), the consumption of auxiliary fuel oil (tons/hour) as well as the water content of the waste feed (%-mass) and the ratio between fossil matter and biogenic matter m_F/m_B are displayed for an exemplary period of 12 days for plant B. The data are given as hourly averages. The first two parameters are obtained from the operating data of the plant, whereas the latter two have been determined via the software BIOMA. The temporal trend of the 4 parameters clearly indicates that within the time period 30/05/2014 until 01/06/2014 the plant yields the most constant and thus also the highest rate of steam production. During these 2 days the water content and also the ratio of fossil and biogenic matter in the waste feed show comparatively small variations, indicating a well mixing of the waste prior its combustion. In contrary, the time periods before 30/05 and also after 01/06 are characterized by significant changes in waste composition. This variation in waste composition is most probably a consequence of insufficient mixing of the waste received, which would per se not be a problem. However, as it can be seen in Figure 9, insufficient mixing of the waste goes along with strongly varying and thus reduced steam (energy) production of the plant. Furthermore, the consumption of auxiliary fuels is increased during these times of variable waste composition.

In Table 2 the average values for the period of well and insufficient waste mixing are summarized. Thereby it becomes obvious that despite the fact that the average water content of the waste feed was higher in times of well waste mixing (35.5 vs. 32.7 percent), the steam production was significantly higher during this time (52.0 vs. 49.6 t/h). Besides an increased steam production also a lower consumption rate of fuel oil is observable (1.8 vs. 40 kg/h). The average ratio of fossil matter and biogenic matter in the waste feed appears to be the same for both presented periods in Table 2. This indicates that the evaluation based on hourly mean values provides much more valuable information on the actual process conditions than for example daily values.

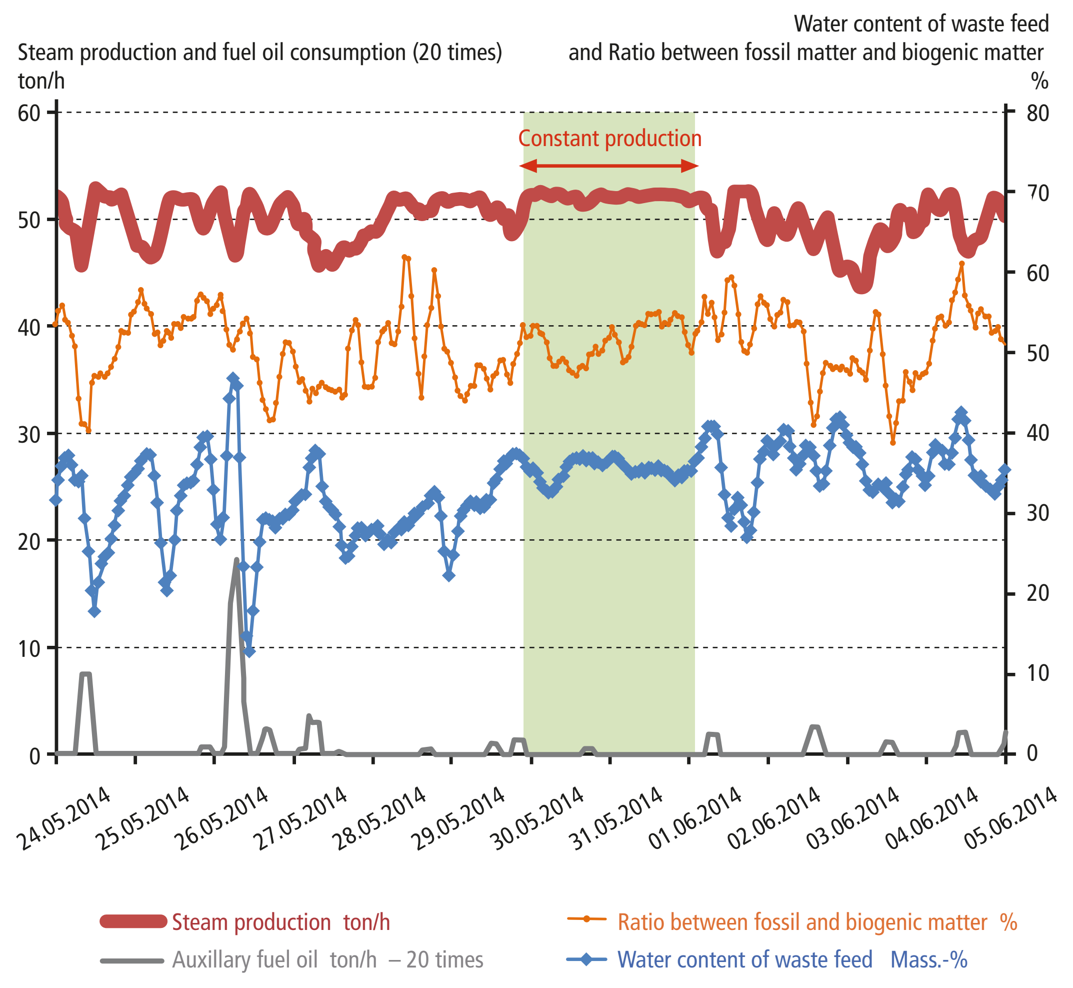


Figure 9: Hourly averages for steam production, fuel oil consumption, water content and ratio between fossil and biogenic matter m_F/m_B in the waste feed of plant B for a period of 12 days

The higher steam production and the lower fuel oil consumption can also be expressed in economic terms. Considering the enthalpy difference of feed water and the steam and assuming an electrical efficiency of 30 percent for converting steam into electricity, the electricity generation rate amounts to 0.21 MWh_{elec}/t steam. The average market price for electricity is about 35 EUR/MWh in 2014. So the financial losses due to insufficient waste mixing for plant B amounts to almost 18 EUR/h or more than 4,000 EUR for the considered period of 10 days. In addition also costs for increased fuel oil (market price of approximately 500 EUR/t heavy fuel oil in 2014) consumption of 38 kg/h and the thereby induced reduction of waste throughput – the combustion of 1 ton fuel oil reduces the waste throughput by almost 4 tons – need to be accounted for, whereby a gate fee for the waste of 90 EUR/tons is assumed. Based on these figures the increased fuel oil consumption during times of insufficient waste mixing causes energy costs of about 20 EUR/h and reduces the waste throughput by 0.15 t/h, which lowers the income via gate fees by almost 14 EUR/h. For the time period of almost 10 day the overall income losses and additional costs induced by increased fuel oil consumption can be expected to amount to more than 7,600 EUR.

Hence, all in all the economic losses caused by insufficient waste mixing (over the considered period of 10 days) can be estimated to almost 12,000 EUR.

The utilization of the software BIOMA at the WTE plant could provide a possibility to control the mixing of the waste in the receiving bunker. Insufficient mixing could immediately be detected and avoided/corrected by monitoring parameters like the ratio between fossil and biogenic matter or the water content. Furthermore, the performance of the personal operating the waste crane could be evaluated and benchmarked.

The overall annual economic benefits of a controlled and improved waste mixing prior combustion are estimated to a few hundred thousand Euros per plant.

Table 2: Averages for steam production, fuel oil consumption, water content and ratio between fossil and biogenic matter in the waste feed of plant B during times of well and insufficient waste mixing

Averages for	**Steam production**	**Auxiliary fuel oil consumption**	**Water content of waste feed**	**Content of fossil matter vs. content of biogenic matter**
	t/h	kg/h	kg H_2O/kg waste	m_F/m_B
Period of insufficient waste mixing (9.7 days)	49.6	40	0.327	0.51
Period of well waste mixing (2.3 days)	52.0	1.8	0.355	0.51

3. Conclusions

The results presented demonstrate the various potentials and benefits of the Balance Method in general and the BIOMA software in particular. Information of direct interest for the operators of WTE plants can be derived: plausibility checks of operating data, ratio of energy from biogenic sources, or control of waste mixing in the receiving bunker. Additionally, general information which is relevant for waste authorities can be generated at comparatively low costs: e.g., the amount of plastics in the waste feed or fossil CO_2 emissions. Finally it was demonstrated that the economic benefits generated by the application of the Balance Method outpaces by far the costs of its application, which are in the range of about EUR 10,000 per plant and year.

Acknowledgements

The authors would like to acknowledge the funding of the present study which was provided by the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management. In addition we thank the operators of the Waste-to-Energy plants for their cooperation.

4. Literature

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