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SFA of POP Polybrominated Diphenyl Ethers – Sources, pathways and sinks

A Master's Thesis submitted for the degree of
"Master of Science"

supervised by

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Vienna, 11.06. 2012

Affidavit

I, **DANA VYZINKAROVA**, hereby declare

1. that I am the sole author of the present Master's Thesis, "SFA OF POP POLYBROMINATED DIPHENYL ETHERS – SOURCES, PATHWAYS AND SINKS ", 41 pages, bound, and that I have not used any source or tool other than those referenced or any other illicit aid or tool, and
2. that I have not prior to this date submitted this Master's Thesis as an examination paper in any form in Austria or abroad.

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Abstract

Polybrominated Diphenyl Ethers (PBDEs) have been widely used as flame retardants in polymers for construction, automotive and electronic industries, and other less known applications. Because some of the PBDEs are classified as persistent organic pollutants (POPs) posing a risk for men and the environment, certain PBDEs such as c-PentaBDE and c-OctaBDE have been regulated by the Stockholm Convention. The presence of POP-PBDEs was reported in Austrian soils, sludge and sediments, too. In particular, the concentrations in Danube sediments downstream of Vienna were about a factor 30 higher than upstream of Vienna. The goal of this thesis was (1) to identify sources, pathways and sinks of POP-PBDEs in Vienna, and (2) to give recommendations to reduce the impact of POP-PBDEs on the environment of Vienna. For this purpose, data about flows and stocks was collected and modeled by the software STAN for the city of Vienna. The main difficulty in performing this task was the lack of data, and the large uncertainty of some material flows and stocks as well as PBDE-concentrations.

For both, c-PentaBDE and c-OctaBDE, it was found that consumer emissions to the environment no longer play a significant role. Instead, waste management and recycling are the key processes for the control of PBDEs.
In case of *c-PentaBDE*, the most significant flow was found to be in construction polymers: 2.69 t/a $\pm$ 0.37 t/a. Therefore, it is important to ensure that all plastic materials used for construction are separated from the rest of the construction material and are properly treated. Incineration in a state of the art MSW incinerator is an appropriate sink for POP-PBDEs, and any disposal in landfills must be avoided. In case of *c-OctaBDE*, the main flows are waste electrical and electronic equipment (WEEE): 1.59 t/a $\pm$ 3.96 t/a, and possibly vehicles: 1.85 t/a $\pm$ 0.96 t/a. Because most end-of-life-vehicles leave Vienna, the focus is on recycling practices. Recycling of plastics is a preferred option from a waste hierarchy and life cycle assessment perspective. Reported presence of c-OctaBDE in European WEEE streams requires taking a cautious approach. For 2010, the SFA model of c-OctaBDE yields an estimated recycling to incineration ratio of 1:7, meaning that about 0.18 t/a $\pm$ 7.34 t/a was returned to consumption via recycled plastics. Rules for POP-PBDEs management are well anchored in the Austrian law, including the ban on recycling of POP-PBDE-containing plastics, but there is little information about to what extent the recycling law is enforced and about periodical controls. The SFA analysis shows that quality management and strict monitoring is necessary, probably not only in the case of Vienna.

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Abbreviations

ABS Acrylonitrilebutadiene-styrene
BAT/BEP Best Available Technology/Best Environmental Practice
BFR Brominated Flame Retardant
c-PentaBDE Commercial mixture of Pentabromodiphenylether
c-OctaBDE Commercial mixture of Octabromodiphenyl ether
CRT Catode Ray Tube
DM Dry Mass
EEE Electrical and Electronic Equipment
EF Emission Factor
ELV End-of-life Vehicle
FR Flame retardant
HIPS High Impact Polystyrene
LC_{50} Lethal concentration for 50 % of tested individuals
LOD Limit of detection
LOQ Limit of quantification
MSW Municipal solid waste
PA Polyamide
PBT Polybutylene Terephthalate
PBDD and PBDF Polybrominated dioxins and furans
PBDE Polybrominated diphenyl ether
PC/ABS Polycarbonate Acrylonitrilebutadiene-styrene
PE Polyethylene
POPs Persistent Organic Pollutants
PUR Polyurethane
PVC Polyvinyle chloride
RoHS Restriction of the use of certain hazardous substances in electrical and electronic equipment
t.c. Transfer coefficient
TES Temperature/Emissivity Separation
WEEE Waste Electrical and Electronic Equipment
WWTP Waste Water Treatment Plant
XRF X-ray Fluorescence

Chapter 1

Introduction

Commercial mixtures of flame retardants pentabromodiphenyl ether (c-PentaBDE) and octabromodiphenyl ether (c-OctaBDE) were listed as new Persistent Organic Pollutants (POPs) under the Stockholm Convention in 2009, after being a controversial topic for many years (UNEP, 2011b, p. 10).

The group of polybrominated diphenyl ethers (PBDEs) consists of 209 congeners differing by the configuration of bromine atoms on the two benzene rings. Each of the two commercial products is a mixture composed of several congeners. Chemical properties vary somewhat from congener to congener but generally, higher brominated PBDEs are less acutely toxic (Umweltbundesamt, 2008a). The main characteristics of congeners classified as POPs (POP-PBDEs) are that they are persistent, lipophilic and bioaccumulative. Although their toxicological data are still incomplete, more is known today about the threat they present to human health and environment. Some congeners are found to be very toxic to aquatic organisms, for instance some inhibit detoxification enzymes in fish.[1] Mechanisms of their toxic effects are still intensively researched (e.g., Blanco, 2012; Mensching, 2012).

Both commercial mixtures were used as flame retardants in various products, mainly in construction, automotive and electronics industry. C-PentaBDE and c-OctaBDE were phased out about a decade ago[2], but different consumer products containing POP-PBDEs are still in use for several years to come, resulting in emissions released to the environment because of the volatilization property of the PBDEs.

[1] Congeners BDE-27, 47 (99, 100) have LC_{50} value for aquatic organisms $< 1\ mg.l^{-1}$, additionally congeners 47 and 99 inhibit detoxification enzymes in Rainbow trout (Umweltbundesamt, 2008a, p. 2).

[2] (UNEP, 2011a, p. 16)

When dealing with POP-PBDEs, there are many unknowns. The information about their presence in various products in use is incomplete, their presence in different environmental compartments was measured but not to such extent that would give full understanding of their sources and pathways. An important challenge related to management of POP-PBDEs is to ensure their transfer from products in use to waste management with lowest possible losses to the environment, and also ensure that they do not return to the consumption stock via recycling. The ultimate objective is that POP-PBDEs, in the end of their life cycle, reach an appropriate sink. PBDEs get effectively destroyed by controlled incineration.[3]

The Master thesis is structured in the following way. In the first chapter, goals are stated (1.1). Information on the composition of c-PentaBDE and c-OctaBDE mixtures (1.2) and their former use (1.3) is provided, followed by an overview of necessary legal background (1.4). Second chapter describes the methodology, followed by third chapter and the main part, the SFA. The results are given in chapter four, chapter five draws conclusions and recommendations.

1.1 Goals

The objective of the present Master thesis is to help reducing the negative effect of POP-PBDEs on Vienna's environment by
(1) identifying their sources, pathways and sinks and by
(2) preparing recommendations on waste management, that would most effectively deal with the above mentioned challenges. Research questions to help accomplish these goals were identified as follows:

How does the Substance Flow Analysis (SFA) system look like?
Which flows and stocks are significant and what are the corresponding quantities?
How big are the emissions to the environment?
What is the most important sink for POP-PBDEs?
Are there large uncertainties affecting the SFA system and if so, how large are they?
What can be improved in the current waste management system in Vienna?

[3]Incineration of PBDEs may lead to formation of brominated dioxins and furans, if not properly managed. The state of the art incineration will be further discussed in section 3.3.3.

1.2 Characteristics of POP-PBDEs

Commercial pentabromodiphenyl ether (c-PentaBDE) refers to complex mixtures of congeners, in which the main components are BDE-47 and BDE-99 and they have the highest concentration by weight with respect to the other components of the mixture.[4] The commercial mixtures contain congeners with three to seven bromines in the molecule, but molecules with four and five bromines predominate (UNEP, 2006, p. 4).

Commercial octabromodiphenyl ether (c-OctaBDE) refers to mixtures, in which the main components were BDE-183 and BDE-197, the latter not listed as POP-PBDE.[5] As a matter of fact, BDE-183 is an indicator of c-OctaBDE mixtures.

Categories of PBDE	Tribromodiphenyl Ethers		Tetrabromodiphenyl Ethers	Pentabromodiphenyl Ethers		Hexabromodiphenyl Ethers		Heptabromodiphenyl Ethers
Congener	BDE-17	BDE-28	BDE-47	BDE-99	BDE-100/85	BDE-153	BDE-154	BDE-183
	Traces	Traces	Major	Major	Minor	Minor	Traces	Traces
Used for calculations			32%	56%		9%		0.5%

Figure 1.1: Composition of c-PentaBDE (UNEP, 2011b, p. 16).

Categories of PBDE	Hexabromodiphenyl Ethers		Heptabromodiphenyl Ethers			Octabromodiphenyl Ethers			Nonabromodiphenyl Ethers		Decabromodiphenyl Ethers
Congener	BDE-154	BDE-153	BDE-183	BDE-180	BDE-171	BDE-197	BDE-203	196	BDE-206	BDE-207	BDE-209
	Traces	Minor	Major	Traces	Traces	Major	Minor	Minor	Minor	Minor	Traces
Used for calculation	11%		43%			35%*			10%*		1%*

Figure 1.2: Composition of c-OctaBDE (UNEP, 2011b, p. 17).
*The Octa-, Nona- and DecaBDE are not listed as POPs and therefore need not to be inventoried.

1.3 Former use of POP-PBDEs

c-PentaBDE was historically used as flame retardant in Polyurethane (PUR) foams in building and automotive industry. This use accounts for the largest use up to 90-95 %, and the rest minor uses, including textiles, printed circuit boards, cable sheets, conveyor belts, account for only less than 5 % of usage (UNEP, 2011b, p. 19). Furthermore, it is assumed that very low amount of textiles containing c-PentaBDE is still in use, since the application stopped about a decade ago (UNEP, 2011a, p. 15). It is acknowledged among the scientific community that EEE plastics do not contain c-PentaBDE

[4] BDE-47: 2,2', 4,4'- tetrabromodiphenyl. BDE-99: 2,2',4,4',5-pentabromodiphenyl ether.

[5] BDE-183: 2,2',3,4,4',5',6-heptabromodiphenyl ether. BDE-197: 2,2',3,3',4,4',6,6'-octabromodiphenyl ether

in concentrations above RoHS threshold value of 1 g/kg. This consensus is supported by various studies, most recently Wäger measured that PentaBDE no longer occurs in mixed polymers from European WEEE in relevant concentrations (Wäger, 2012). For this reason, only construction and automotive industries will be considered in the analysis of c-PentaBDE.

There is not such a clear consensus on the use of **c-OctaBDE**, although there is an agreement that it was mostly used in polymer fraction[6] of casings of EE-appliances, especially in computer and TV monitors of Cathode Ray Tube (CRT), produced before 2005. Some sources estimate that EE-appliances accounted up to approximately 95 % of the use in the European Union (UNEP, 2011b, p. 20-21), while other European studies found significant presence of c-OctaBDE in construction materials and vehicles[7], in addition to EEE (Morf, 2003). As a consequence, all three areas will be considered in the analysis of c-OctaBDE.

1.4 Legislation

POP-PBDEs are administered on a global and more stringent, European level.
Selected brominated flame retardants (BFR) have been listed as new POPs in the Annex A of the Stockholm Convention since 2009 (UNEP, 2011b, p. 10). On the global level, reuse and recycling of articles containing POP-PBDEs is allowed under special circumstances[8], which resulted in need to define Best Available Technology (BAT) and Best Environmental Practices (BEP) for the environmentally sound management of POP-PBDEs.

The European legislation consists of two key directives, published in 2003 and related to electric and electronic equipment: the WEEE Directive and the RoHS Directive. *Directive 2002/96/EC* of the European Parliament and the Council on waste electrical and electronic equipment (WEEE) established Members' reporting obligations, producer responsibilities for collection, transport, recycling and disposal of WEEE from the private households, and removal of pollutants as a basic treatment rule. Furthermore, it established ten WEEE categories for treatment and collection. The Austrian collection and treatment categories differ slightly, because they were established before the WEEE Directive and were not changed due to efficiency reasons (Koordinierungsstelle, 2010, p. 10).

[6] Mostly in Acrylonitrilebutadiene styrene (ABS).

[7] Minor uses include High Impact Polystyrene (HIPS), polybutylene terephthalate (PBT) and Polyamide (PA) polymers (UNEP, 2011b, p. 21).

[8] In accordance with provisions described in (UNEP, 2011a, p. 7)

Directive 2002/95/EC of the European Parliament and the Council on the restriction of the use of certain hazardous substances in EEE (RoHS) was adopted at the same time as WEEE-Directive and introduced a strict prohibition of POP-PBDE-containing EEE.[9] The limit value for PBDE-content in plastics was set to 0.1 wt%.

The WEEE and RoHS Directives were implemented into Austrian law by amendment of the Waste Management Act[10], the WEEE Ordinance[11] and the Waste Treatment Obligations Ordinance[12]. The Waste Treatment Obligations Ordinance (2004) bans recycling of plastics containing POP-PBDEs, as stated in its provisions § 6 and 13. In the novelization of the Waste Management Act in 2002, *Koordinierungsstelle* was created, a body that has a crucial role when it comes to EE-appliances monitoring. In its annual reports, statistics about collection and treatment data, market statistics and the amount of "historical devices" are published (See example in Appendix).

[9] With an exception of medical, surveillance and control equipment, on consumer market as of July 2006. These are not matter of concern of the present master thesis.

[10] Abfallwirtschaftsgesetz (AWG)

[11] Elektroaltgeräteverordnung (EAG-VO), 2005

[12] Abfallbehandlungspflichtenverordnung, 2004

Chapter 2

Methodology

As a basis, Substance Flow Analysis was adopted and is carried out using software STAN.[1] The methodology also comprises uncertainty treatment and scenario analysis.

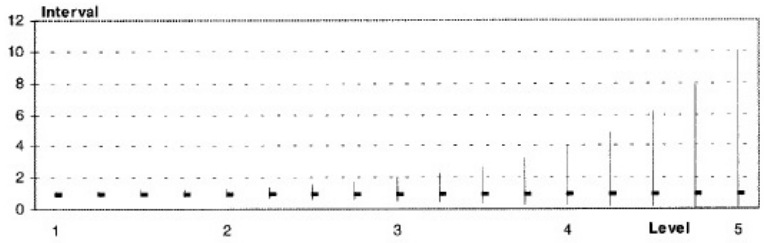
The SFA involves various steps. First, POP-PBDEs (c-PentaBDE and c-OctaBDE) were chosen to be the analysed substances. DecaBDE, which is not acutely toxic and not included in the Annex A of the Stockholm Convention, is not part of this analysis. At the same time, the analysis was limited in space and time, the boundaries were set as federal state of Vienna and year 2010. After setting up the initial conditions, next point was to establish a structure of the system, which includes understanding of where POP-PBDEs are present and a consequent choice of processes and flows. Then, an inventory was done according to the Draft Guidance for the Inventory of PBDEs listed under the Stockholm Convention on POPs, which suggests strategies to find necessary information, gives methods of data collection as well as formulas for POP-PBDEs quantification. Data for the inventory were collected preferably on a federal state level and where not possible, the data were downscaled from national level by using a population factor. In few cases data on national level are not available and in these specific cases, generic figures estimated for Europe are used. The collected data are continuously compared with other studies done in the field. An important example of such study is a SFA of PBDEs and TBBPA in Switzerland (Morf, 2003).

Once the quantities are determined, software STAN is used for modelling of system and the data reconciliation. STAN allows to model system Vienna, 2010 on three different layers: Goods, substances (PentaBDE and OctaBDE). STAN also allows the consideration of data uncertainties and requires data input in form value $\pm$ value. It is

[1] Brunner, P.H. and Rechberger, H. (2003) Practical Handbook of Material Flow Analysis, CRC Lewis Publ., Baton Rouge.
Software STAN can be downloaded on the website of the Institute for Water Quality, Resource and Waste Management, Technical University of Vienna.

assumed that uncertain data are normally distributed, given by their mean value and standard deviation. This approximation offers the possibility to use methods like error propagation and data reconciliation (Cencic, 2008).

In many cases, uncertainties can be a key factor and for this reason, they will be paid a special attention to. Especially in cases of data with high uncertainties, the error interval becomes less symmetric. For description purposes, Hedbrant's method is used to classify them into uncertainty levels 1-5 (Hedbrant and Sörme, 2000).



Level	Factor	Interval
1	1.10	*/ 1.10
2	1.33	*/ 1.33
3	2	*/ 2
4	4	*/ 4
5	10	*/10

Figure 2.1: Levels, factors and interval sizes of uncertain data. The graph on the left shows value 1 with uncertainty levels between 1 to 5. Small uncertainties have symmetrical intervals. Large uncertainties have asymmetrical intervals (Hedbrant and Sörme, 2000, p. 46).

Where there are high uncertainties, or missing information, I work with possible scenarios. The impact of each scenario on the system as a whole will be evaluated. This can only be done by setting all other variables constant i.e. from the possible scenarios, a "most realistic one" has to be chosen. Only this way conclusions can be drawn.

The results, especially those related to the subsystem environment, are cross-checked by comparing the computed values with measured concentrations in soil and waste water in Austria.

Chapter 3

Substance Flow Analysis (Vienna, 2010)

The STAN system for POP-PBDEs is composed of 3 processes, consumption (section 3.1), environment (section 3.2) and waste management (section 3.3), all of which are further organized as subordinate systems. The system has 3 layers: goods and substances, c-PentaBDE and c-OctaBDE.

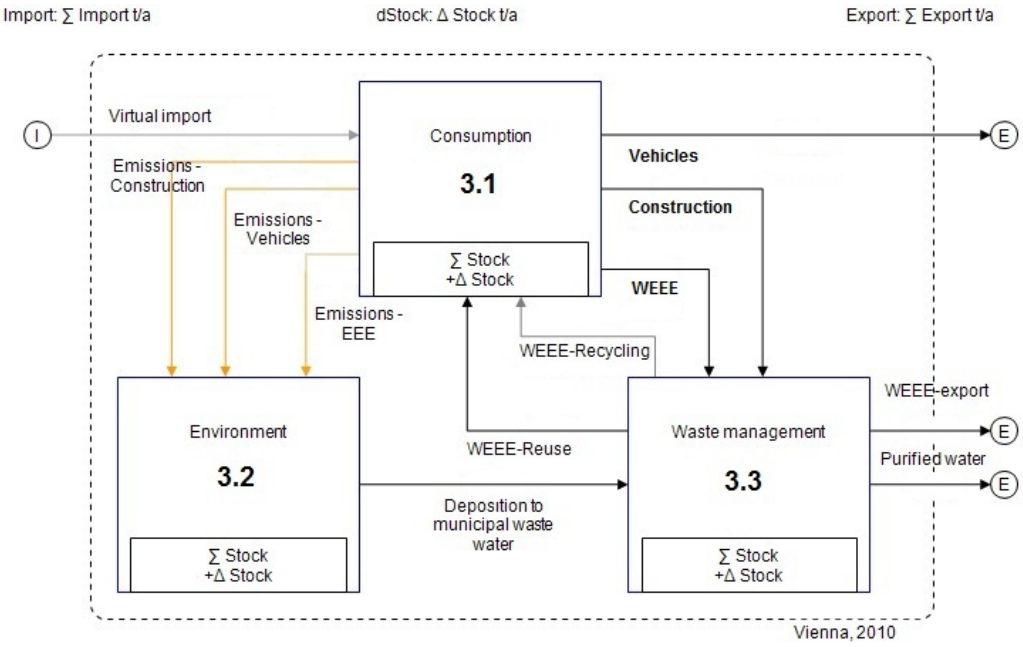


Figure 3.1: STAN system.
Note: The flow virtual import is included because software STAN requires at least one import to the system - its value is zero. The production of POP-PBDEs has been stopped, the only way how they may enter into the consumption is via reuse and recycling.

3.1 CONSUMPTION

Imports (3): (Virtual import), WEEE-Reuse, WEEE-Recycling
Exports (6): Construction waste, Vehicles, WEEE, Emissions from construction, vehicles and EEE
Stock: In buildings, vehicles and EEE that are currently in use

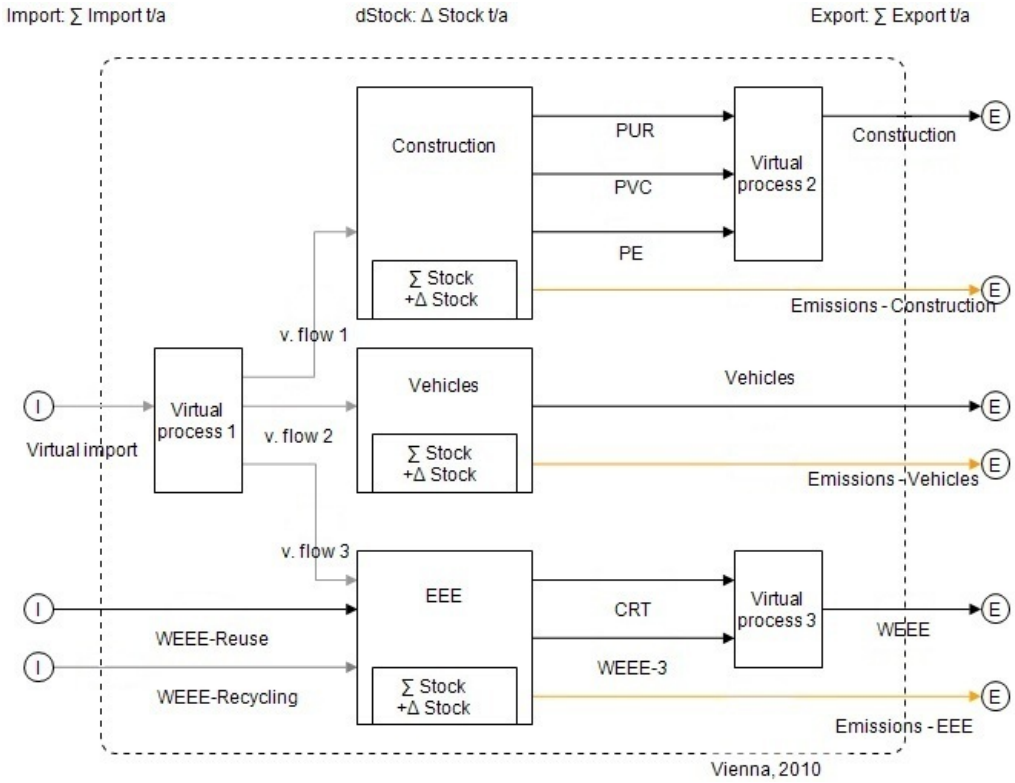


Figure 3.2: STAN subsystem *Consumption*.
Note: Virtual processes 2 and 3 are used to sum up the overall flows of substances in construction and WEEE.

3.1.1 Construction industry

No information is available about the use of FR in construction in Austria. But fortunately, decent approximations can be made from the knowledge of stocks on level of goods in Germany and concentrations of substances and usage factors available in the Swiss study. In Germany, 15.4 kg/capita was an estimated existing stock of PUR insulating foam in 1998, the stock of PE and PVC was 9.54 kg/capita and 4.65 kg/capita, respectively (Leisewitz and Schwarz, 2000; Morf, 2003). C-PentaBDE was implemented in PUR foams and in polyvinyl chloride (PVC) duroplastics sheeting, c-OctaBDE in polyethylene (PE) thermoplastic sheeting (Morf, 2003, p. 80-81, 184). Morf et al. estimated that about 60 % of the stock in Switzerland consists of material, where POP-PBDEs were used (Morf, 2003, p.191, Tab. 9-33).

PUR, PVC and PE	Stock in Germany[1] [kg/capita]	FR content in product[2] [g/kg]	FR treated product[3] [%]
PUR foam *	15,40	6,49	60
PVC film	4,65	1,45	60
PE film	9,54	1,70	60

Figure 3.3: PUR, PVC and PE stocks in Germany, 1998. Estimated flame retardant treated fraction and concentrations of PBDEs.
* including foam filler
[1] Morf et al., p. 180, Tab. 9-26
[2] Morf et al., p. 180, Tab. 9-29
[3] Morf et al., p. 191, Tab. 9-33

Under assumption that the use of POP-PBDEs in building sector in Vienna was similar to that in Germany and Switzerland, calculation based on using population factor can be done. It must be considered, that the stock estimates in Germany and Switzerland are from year 1998. After 1998, POP-PBDEs were no longer used as flame retardants in construction and the stock is decreasing (Morf, 2003, p. 88, Table 5-19). To estimate the current stock, an average service life of construction material, which is given in average as 40 years, is used (Morf, 2003, p. 176).

3.1.2 Vehicles

In case of vehicles, on the other hand, Statistik Austria has good data, including on the level of federal states. The stock of vehicles at the end of years 2009 and 2010 is known, as well as the age distribution of the vehicles at those times. Therefore, the amount of vehicles registered before 2005 in the stock can be easily determined. Vehicles produced after 2005 do not contain POP-PBDEs and therefore are not included in calculation (Appendix).

For the calculation of flows, statistics on new and used vehicles registrations is available. Usually, about twice as many used vehicles are registered as compared to new vehicles registrations. From the knowledge of dStock, we can easily establish the number of deregistrations in 2010. Deregistered cars might have followed three different pathways:

- Again re-registered in Vienna (change of owner)
- Re-registered in another federal state or exported abroad
- Become End-of-life vehicle (ELV), defined as ”an individual vehicle that is no longer suitable for use, and which is intended for dismantling and recovery of spare parts or destined for material recovery and recycling (UNEP, 2011a,b).”

What happens with the vehicles after they have left the stock i.e. were de-registered for the last time? In a European Parliament study, an inconsistency gap of about 60 % between de-registered (and not re-registered) vehicles and ELV arisings was identified

in years 2007-2008 in Austria (Parliament, 2010, p. 22-23). This gap was estimated to be about 70 % in 2010 (Kletzmayr and Neubacher, 2012). Generally, it is about one third of Austrian ELVs that are brought to the Authorized Treatment Facilities, where dismantling and further processing in shredders takes place. Some metal as well as plastic fraction is recovered and recycled. According to EUROSTAT dismantling and de-pollution statistics, recovered/recycled large plastic parts made up for 27,41 tons in Austria in 2009, of which only 0.65 tons were disposed (EUROSTAT, 2009). The remaining two thirds of vehicles are sold via questionable routes abroad to the Eastern Europe, Balkans, Asia and Western Africa (Kletzmayr and Neubacher, 2012, p. 15).[1]

Regarding the use of POP-PBDEs in the transport sector, literature focuses primarily on c-PentaBDE formerly used in PUR foam in upholstery of seats, headrest and ceiling, and application in textile back-coating. The calculation of the c-PentaBDE is straightforward, it is based on the amount of vehicles and and literature values of the concentration of c-PentaBDE per one vehicle. When it comes to c-OctaBDE mixture, the extent to which it was used in vehicles is not completely clear. C-OctaBDE was *not* used in PUR polymers as it is not compatible with flexible polyurethane foam (FPF) products.[2] However, c-OctaBDE was used in other polymer parts such as HIPS, PBT and PA in dashboard and steering wheel (UNEP, 2011a, p. 13, 58). Concentrations of c-OctaBDE per vehicle, as in the case of c-PentaBDE, are not available in the literature.

Because of this missing information, it might be the best to consider two scenarios. First scenario is from rather positive side, which suppose that no c-OctaBDE was used in cars in Europe. This is in line with the inventory guidance. Second scenario follows Morf et al. who determined that approximately 20 percent (143 t) of the total c-OctaBDE stock in Switzerland in 1998, was in vehicles. This estimate is based on Danish study (Lassen and Løkke, 1999, p. 83-84), which determines content of PBDEs in plastic fraction in vehicles without distinction between PentaBDE and OctaBDE and consequently distributes c-PentaBDE and c-OctaBDE according to the world production data (Morf, 2003, p. 178, Tables 9-21 and 9-22). The Swiss approach is acknowledged by the POPs Review Committee (POPRC, 2008, p. 15). When working with the second scenario, c-OctaBDE stock can be calculated from the Swiss estimate by using a population factor.

[1] Note that vehicles will not be discussed in the subsystem waste management because either way, they leave Vienna 2010 system boundaries.

[2] Reported detection of OctaBDE in FPF products could result from FPF absorption properties possibly related to contact and transfer from plastic scrap having PBDE content, or from misidentification (Luedeka, 2011, p. 4).

3.1.3 Electrical and Electronic Equipment

In electrical and electronic equipment (EEE), CRT monitors are target products to be addressed by the inventory and are expected to contain more than 50 % of the total POP-PBDEs present in this group. Since no data are available[3] on the amount of CRT monitors in Austria, an estimate is made by using a figure 7.05 kg CRT weight per capita (Swiss Federal Office of Statistics, 2011), which should serve in these cases for c-OctaBDE estimations in Europe. The mean concentration of c-OctaBDE in CRT monitors is 2.5 g/kg, with minimum 0.14 g/kg and maximum 10.6 g/kg (UNEP, 2011b).

For an in-depth inventory, a possible presence of c-OctaBDE in WEEE categories 1 to 4 is examined.[4] The content of PBDEs in WEEE can be calculated from

$$M_{PBDE(i)} = M_{WEEE(j)} \times f_{polymer} \times C_{PBDE(i);Polymer} \tag{3.1}$$

where

$M_{PBDE(i)}$ is the amount of POP-PBDEs (i) in [g] (in Polymer (k) of WEEE (j))

$M_{WEEE(j)}$ is the amount of WEEE (j) in [kg] (stockpiled or entering the waste stream)

$f_{polymer}$ is the total polymer fraction in [weight percentage]

$C_{PBDE(i);Polymer}$ is the content of the POP-PBDEs (i) in the total polymer fraction in [g/kg] or [kg/t]

In WEEE categories 1 and 2, i.e. large and small household appliances, c-OctaBDE is not expected to be present, or at average concentrations clearly bellow 1 g/kg (UNEP, 2011b; Wäger, 2012). C-OctaBDE may be present in WEEE categories 3 and 4, i.e. IT & T and consumer equipment, but in significantly lower concentrations than in CRT monitors. Average concentrations in categories 3 and 4, CRT monitors excluding, are below or around 1 g/kg (UNEP, 2011b, p. 42). These values were adopted from mixed polymers in WEEE in Europe in 2010:

WEEE-cat. 3 (ICT equipment w/o monitors):

$f_{polymer}$ = 42 %, $C_{PBDE(i);Polymer}$ = **0.225 g/kg** (mean), min. 0.05 g/kg, max. 0.4 g/kg

WEEE-cat. 4 (Consumer equipment w/o monitors):

$f_{polymer}$ = 24 %, $C_{PBDE(i);Polymer}$ = **0.15 g/kg** (mean), min. and max. - n.a. (UNEP, 2011b, p. 51)

Recently, Wäger obtained the same mean concentration of PBDEs in the WEEE cate-

[3] Confirmed with Lebensministerium on 7 May 2012.

[4] 97 % of WEEE products fall under these 4 categories of the WEEE Directive (UNEP, 2011b, p. 42).

gory 4 (0.15 g/kg), which is clearly fulfilling the RoHS limit value (1 g/kg) and therefore does not need to be included in the substance flow analysis (Wäger, 2012). However, Wäger measured higher concentrations than given in the inventory guidance (mean 1 g/kg and max. 1.6 g/kg) in the WEEE category 3. When further examining the WEEE category 3 in Vienna, an additional complication is that an important piece of information is missing, namely the amount of old appliances stockpiled in households is unknown. In this situation, it is desirable to consider 2 scenarios.

First scenario, on the ideal side, sees the c-OctaBDE concentration in WEEE category 3 fulfilling the RoHS limit values, as described in the inventory guidance. This scenario may also consider that the service lives of the products in this category are relatively short.

> EDP equipment (excluding printers) - 5.9 years
>
> Communications technology - 7.5 years
>
> Office equipment 7.4 years (Morf, 2003, p. 174)

With an average service time about 7 years, the stock should have been almost entirely exchanged with POP-PBDE-free products by 2010. First scenario thus considers the content of c-OctaBDE in WEEE category 3 negligible.

The second scenario is a worst case scenario, based on the fact that the highest share of c-OctaBDE treated EEE is expected to be found in private households, as they tend to keep appliances longer and are also the largest buyers of second-hand EEE (UNEP, 2011b, p. 45). It extremely difficult to estimate the amount of old appliances stockpiled in households without making significant errors, since their stocks in cellars and attics are not part of any statistics. The second scenario assumes that each Viennese household has about 25 kg of old appliance of category 3 stored, and it counts with Wäger's (higher) concentration.

3.1.4 Emissions from consumption

Emissions are released to the environment from products in use because of volatilization property of PBDEs and can be quantified by using emission factors. Emission factors (EFs) are defined as the mass fraction of the consumption stock that is annually released to the atmosphere. The annual EFs for PentaBDE are given as 2.3 x 10^{-5} for construction emissions and 5.8 x 10^{-5} for emissions from vehicles, with uncertainty range EF/10 – 10·EF (Morf and Smutny, 2007, p. 54, 65). For OctaBDE, the annual EF is given as 5.4 x 10^{-4} and the same uncertainty range is assumed (Morf, 2003; POPRC, 2008).

3.2 ENVIRONMENT

The subsystem environment is composed of two processes, atmosphere and soil. Process hydrosphere is considered in this section, but it is not included in the STAN system, because as it will be shown, it plays no significant role. Therefore, no sedimentation is included in the system, and either is erosion or resuspension. As a consequence, the process soil is a reservoir, i.e. there is a flow in but no flow out.

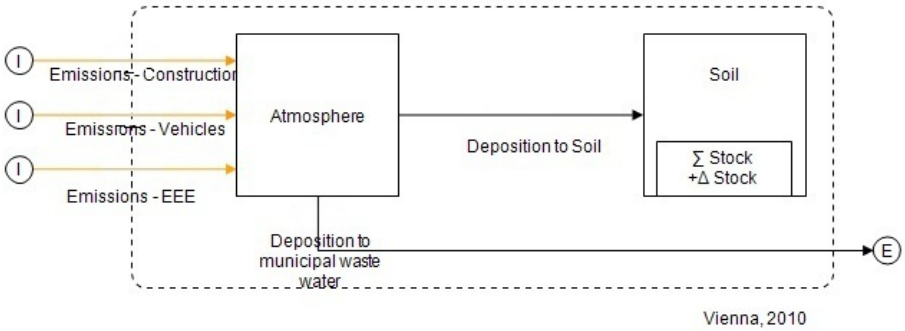


Figure 3.4: STAN subsystem *Environment*.

3.2.1 Process Atmosphere

Imports (3): Emissions from construction, from vehicles and EEE in use
Exports (2): Deposition to soil and municipal waste water

In the atmosphere, PBDEs are transported and then deposited, either through wet or dry deposition[5] into soil, municipal waste water and hydrosphere. Morf et al. estimated that approximately 90 % of the emissions are deposited into soil, 10 % into municipal waste water and the deposition into hydrosphere was negligible in Switzerland (Morf, 2003, p. 118). These output transfer coefficients for process atmosphere will be used for Vienna. The fate of emissions deposited into the municipal waste water will be discussed in section 4.3.3 (Process WWTP).

[5]For BDE-209, 2.3 % is degraded in air, 97.5 % is deposited and 0.2 % is residing in air (Buser, 2007). This distribution is likely similar to other congeners.

3.2.2 Process Soil

Imports (1): Deposition to the soil
Exports: None
Stock: Unknown

Soils receive inputs of POP-PBDEs via atmospheric deposition and since consumer stock and the atmospheric emissions are lower each year, soils are expected to receive less and less POP-PBDEs the following years. Concentrations in soils were measures in the last few years at many sites, including Austria. Concentrations in soils close to the emission sources, e.g. road soils in the cities, are much higher than at remote sites.[6] Still, little is known about behaviour of PBDEs in soils (Hassanin, 2004), but assumptions about their life times were made recently.

In Austria, concentrations of 25 congeners were measured in grassland soils in depth levels of 0-5 cm (surface soils) and 5-10 cm (subsurface soil) in federal provinces of Burgenland, Carinthia, Upper Austria and Styria (Umweltbundesamt, 2008b, p. 52). From the table we see that the measured concentrations of PentaBDE congeners in surface soils were higher than in subsurface soils. This suggests that input rates were higher in recent past with respect to the year of sampling (2004) than previously. For OctaBDE, the opposite is valid.

It was found that concentrations of POP-PBDEs in soils in 2008, at the same sites in Norway and the UK, were in most cases lower than in 1998. 48 samples were compared individually and it was shown that by 2008, concentrations were significantly lower at 79 % of all test sites[7] at around 23 % of the 1998 concentrations. The half-life for sum of 5 PBDE congeners at these sites is 4.6 ± 3.7 years. An average half-life at all sites has a higher error range at lies at 0.7 ± 21 years (Schuster, 2011). This experiment shows that the overall concentration in the soil is not among the most important issues when determining the POP-PBDE flows.

[6] In China, the factor was about 100, the average concentrations of 21 measured congeners - BDE-2, 17, 28, 47, 49, 66, 75, 99, 100, 138, 153, 154, 155, 183, 190, 196, 197, 203, 206, 207, 208 (excluding BDE-209) - were 1150 $ng.g^{-1}$ for road soils and 9.5 $ng.g^{-1}$ for farmland soils (Luo, 2009). Gevao 2011 supported this hypothesis by measuring concentrations in the urban area of Kuwait City and outside of the city. The concentrations in the city soils were significantly higher than those outside (Gevao, 2011).

[7] Not different at 6 % and higher at 15 % of test sites (Schuster, 2011).

Substance	cm	Min.	25. Perc.	Median	75. Perc.	Max.	Average	Std. deviation	Interquartile range	n > BG	NG > n > BG	n < NG
BDE-17/25	0–5	< NG	< NG	0,06	0,21	1,80	0,22	0,47	0,21	8	0	6
	5–10	0,72	1,18	1,45	2,20	3,00	1,62	0,65	1,03	14	0	0
BDE-47	0–5	2,6	6,9	13,5	112,5	590,0	79,5	155,1	105,7	14	0	0
	5–10	9,0	24,0	39,0	91,5	190,0	59,1	51,9	67,5	14	0	0
BDE-49	0–5	< NG	< NG	0,36	1,33	4,60	0,93	1,40	1,33	9	0	5
	5–10	2,10	2,88	3,05	5,60	8,20	4,08	1,94	2,73	14	0	0
BDE-99	0–5	1,7	4,4	6,6	57,0	560,0	65,9	148,4	52,7	14	0	0
	5–10	< NG	8,0	17,5	34,8	400,0	46,6	102,9	26,8	13	0	1
BDE-100	0–5	0,6	1,4	2,6	15,3	120,0	15,1	31,7	13,9	14	0	0
	5–10	0,9	3,7	6,4	15,0	78,0	12,6	19,6	11,4	14	0	0
BDE-153	0–5	< NG	0,3	2,7	6,6	33,0	5,3	8,5	6,2	12	0	2
	5–10	5,7	7,4	10,0	25,8	170,0	27,9	44,7	18,4	14	0	0
BDE-183	0–5	< NG	< NG	2,0	18,0	38,0	8,9	13,2	18,0	7	0	7
	5–10	7,0	14,8	16,0	53,0	81,0	30,1	22,5	38,3	14	0	0
BDE-196	0–5	< NG	< NG	7,15	15,00	23,00	8,14	7,35	15,00	10	0	4
	5–10	< NG	4,00	11,50	18,50	43,00	13,50	11,49	14,50	13	0	1
BDE-197	0–5	< NG	< NG	7,50	20,50	27,00	10,26	9,74	20,50	10	0	4
	5–10	10,00	17,00	26,50	33,50	69,00	28,29	15,72	16,50	14	0	0
BDE-203	0–5	< NG	< NG	7,45	12,25	19,00	7,04	6,10	12,25	10	0	4
	5–10	3,80	9,00	13,00	19,00	37,00	15,06	9,48	10,00	14	0	0
BDE-209	0–5	< NG	75,0	185,0	895,0	3.900,0	673,6	1.078,6	820,0	13	0	1
	5–10	< NG	< NG	< NG	1.150,0	2.800,0	607,7	1.044,4	1.150,0	5	0	9
Σ PBDE	0–5	14,3	102,5	359,2	1.051,9	5.283,9	880,6	1.411,0	949,4			
(Σ 25)	5–10	109,7	122,7	207,6	1.508,7	3.207,4	836,1	1.102,5	1.386,0			

Figure 3.5: Average and mean PBDE concentrations in Austrian soils [ng/kg]. NG (Nachweisgrenze) = LOD, BG (Bestimmungsgrenze) = LOQ. 14 samples per depth level, taken in 2004 (Umweltbundesamt, 2008b, p. 48).

3.2.3 Process Hydrosphere

Hydrosphere accounts for only about 5 % of the surface area in Vienna[8], taking into account low quantities of consumer emissions, depositions to the hydrosphere within the system boundaries appear to be negligible and will not be considered. Since I do not consider hydrosphere as a whole, sedimentation will not be considered either. Although, at this place it must be stated that PBDE concentrations in Danube sediments were measured in Austria (Umweltbundesamt, 2004). POP-PBDEs accumulate in sediment because of their chemical properties and persistence.

13 samples were taken from the River Danube sediments for analysis in 2002-2003, including samples JDS-12, originating from Danube km 1942 (Klosterneuburg - upstream from Vienna) and JDS-13, from km 1913 (Schwechat - downstream from Vienna). All samples were analysed for 18 congeners.[9]

[8] About 1 930 ha of the total surface area 41 487 ha (MA5, 2011, p. 2).

[9] BDE-11, 17/25, 28, 47, 49, 77, 99, 100, 116, 138, 140, 153, 154, 155, 166, 181 and 183.

In the sample JDS-12, the sum of 18 congeners was 0.33 μg/kg DM, whereas in the sample JDS-13 it was 10.43 μg/kg DM. The average sum from all 13 samples was 1.30 μg/kg DM (Umweltbundesamt, 2004, p. 30). It is interesting to notice that the concentrations downstream from Vienna were higher with factor 30 compared to upstream concentrations. The concentrations in sample JDS-13 were probably higher because the sampling point was located at confluence of rivers Schwechat and Danube, next to neighbouring industrial area. It is however likely, that the concentrations in sediments originate, to big extent, from before the production and use of the commercial mixtures was stopped. It is assumed that process the hydrosphere plays little role, if any, in 2010.

JDS-12 Klosterneuburg	ng/kg DM	LOD ng/kg DM	JDS-13 Schwechat	ng/kg DM	LOD ng/kg DM
PBDE			**PBDE**		
# 11	0,1	0,070	# 11	n.n.	0,138
# 17 / 25	0,99	0,128	# 17 / 25	45	0,258
# 28	4,7	0,187	# 28	110	0,480
# 47	130	0,352	# 47	3500	0,636
# 49	6	0,443	# 49	320	0,869
# 77	0,18	0,095	# 77	2,4	0,499
# 99	80	0,530	# 99	4000	1,100
# 100	19	0,381	# 100	810	0,862
# 116	n.n.	1,824	# 116	n.n.	4,002
# 138	2,1	1,001	# 138	93	3,116
# 140	1,5	0,734	# 140	30	1,968
# 153	11	0,604	# 153	520	2,281
# 154	5,6	0,428	# 154	360	0,925
# 155	0,76	0,541	# 155	17	1,483
# 166	n.n.	2,974	# 166	n.n.	8,588
# 181	38	31,885	# 181	190	49,322
# 183	32	1,832	# 183	430	3,610

Figure 3.6: Concentrations of PBDEs in Danube sediments [ng/kg DM], in samples JDS-12 and JDS-13 (Umweltbundesamt, 2004, p. 60-61).

3.3 WASTE MANAGEMENT

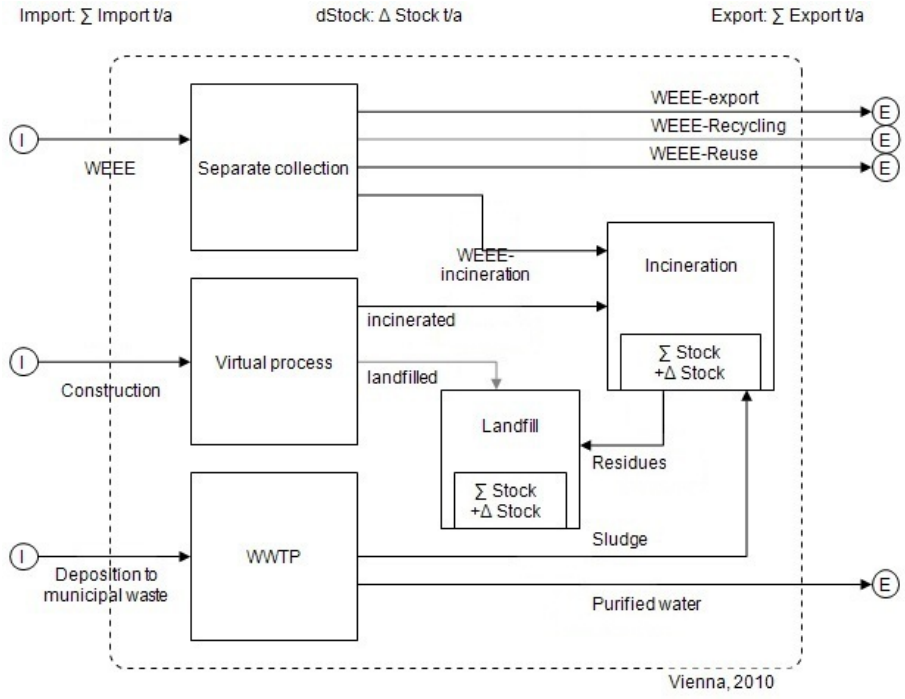


Figure 3.7: STAN subsystem *Waste Management*.

Since the use of POP-PBDE have largely stopped a decade ago, a large share of POP-PBDE-containing materials have already entered the waste management and recycling flow and the rest will come to this stage in several years, the considerations of waste management options play a crucial role in the overall assessment (UNEP, 2011a). In waste management of POP-PBDEs, the most important issue is the management of construction waste and WEEE, and finding their appropriate sink.

3.3.1 Construction waste

It is not clear what happens with construction waste after it is brought to collection and sorting plant. It is likely that most of it end up in the incinerator. PUR insulation foam is difficult to recycle and because of its high calorific content is ideally incinerated. But, it may as well be that some polymer fraction goes instead to the construction waste landfill, together with other construction materials. In Switzerland, approximately 80 % of construction waste combustible fraction was incinerated and 20 % was deposited in landfills in 1998 (Morf, 2003, p. 94). Due to lack of this information in Vienna, I will consider three scenarios: 1) All polymers from construction are incinerated, incineration to landfilling ratio is 2) 80:20 and 3) 50:50.

3.3.2 Separate Collection of WEEE

On the level of products, Austrian EAK conducts statistics about the amount of appliances collected in each WEEE category. Furthermore, the fraction of products, which was separated for reuse (sale as second hand products) and this way returned to the consumption stock, is known. The fraction not suitable for reuse is treated by manual disassembling in dismantling facilities. Polymers from screen devices are mostly collected during the treatment as a separate fraction. We can downscale the Austrian statistics for the federal state Vienna, because the ratio with which Vienna contributes to the national WEEE statistics is documented. However, there is no separate statistic about the amount of CRT monitors collected in Austria. For the substance analysis, concentrations as previously established in subsystem consumption, will be used.

In 2006, the majority (1 288 of 1 313 tons plastic fraction in Austria) was compressed and exported to Asia for purpose of recycling.[10] (Umweltbundesamt, 2008c, p. 21, 25, 42) This should no longer occur, since the European Union fully implemented the Basel Ban in its Waste Shipment Regulation.[11]

Recycling

Since 2006, the mixed plastic fraction from mechanical treatment of WEEE is processed in the MBA Polymers GmbH recycling plant. It is located beyond STAN system spatial boundaries and its operation capacity is 40 000 t/a.[12] From a waste hierarchy and life cycle assessment perspective is mechanical recycling of plastics strongly favoured (UNEP, 2011a, p. 14). However, it is crucial to recognize the limitations of waste recycling in cases where recyclable waste materials contain contaminants such as POP-PBDEs which are unwanted in a recycling context. Alternative to recycling is treatment of polymers for energy recovery, which will be addressed in the following section (process incineration).

It is necessary to look closely at the recycling technologies of this plant, which plays a major role in the POP-PBDEs management. The MBA Polymers plant sorts plastics according to different quality classes mechanically, i.e. no chemical technology is used. Polymers containing RoHS substances, including POP-PBDEs, are removed

[10] According to the information gathered from plant operators by UBA, only 20 % of the components containing hazardous substances removed in the course of WEEE treatment remained in Austria for further treatment, and approximately 80 % were exported in 2006.

[11] Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste is legally binding in all EU Member states and applicable since 12 July 2007. The Basel Ban Amendment prohibits exports of hazardous wastes that are destined for reuse, recycling or recovery operations (Convention, 2011).

[12] From what they receive is plastic 90 % from WEEE and 10 % from car shredders (Umweltbundesamt, 2008c, p. 21, 164).

from the production process and subjected to thermal treatment, while polymers of required quality are used as secondary plastics (Umweltbundesamt, 2008c, p. 165). The concrete set of complex technology, which the MBA Polymers recycling plant uses for the removal of plastics containing bromine, can be assumed from their "Multistep separation of plastics" patent description (Appendix 7.3.2).[13]

Density separation, elutriation, X-ray Fluorescence and Temperature/emissivity separation may be implemented at various steps as automatic separation techniques. Two stage density separation works on a principle, that density of plastics is much higher if a significant amount of bromine is present in the plastic. The mass of each bromine atom is almost 80 $g.mol^{-1}$ and bromine is typically present at levels above 5 %. Therefore, the density of brominated plastics is by 0.05 $g.ml^{-1}$ higher than non-brominated plastics ($\rho < 1.20\ g.ml^{-1}$). It is relatively easy to separate materials with such a significant density difference by automatic processes, using sink-float tanks or hydrocyclones. Because separation by density is not perfect, the process follows in two steps.
Next, elutriation[14] can be used to remove bromine-containing plastics. The material including BFR plastics is fed to gravity concentration system with upward water velocity set to 0.13 m/s.
After techniques such as density separation have been used, X-ray Fluorescence works well for streams yet containing small amounts of bromine. It may be used to control ejection of particles containing bromine.

In cases where there is a significant presence of BFR in plastics, electrical properties of these plastics are expected to be altered. The differences in electrical properties of plastics should result in one type charging to the other, when their surfaces are contacted with each other. Temperature/emissivity separation can be used to separate plastics containing BFR from those not containing BFR. Mixture of plastics is passed through a triboelectrostatic separator and positive and negative products are collected at the electrodes. This works especially well for ABS, but also well enough for HIPS polymers (EPO, 2010, p. 24).

Despite the claim that most of the produced granules at MBA Polymers already met the threshold values as stated in the RoHS Directive in 2008 (Umweltbundesamt, 2008c, p. 165), there is no information about whether or not any recent controls were conducted.

[13] Published in Bulletin 2010/08 of the European Patent Office on 24.02.2010 (EPO, 2010, p. 24).

[14] Elutraition is separating lighter particles from heavier ones using a vertically-directed stream of gas or liquid (Wiki). In this case, water is used.

3.3.3 Process Incineration

Imports (3): WEEE-incineration, construction waste, sludge
Exports (1): Residues to landfill
Stock: Increasing stock designates that POP-PBDEs are destroyed here.

For polymers with POP-PBDE content, thermal recovery is a preferred treatment option, because the PBDE content is almost entirely transformed during incineration into harmless substances. For environmentally sound incineration, attention has to be paid to the possibility of brominated dioxins and furans[15] formation during incineration. However, with carefully controlled incineration fulfilling Western European standards, significant emissions of brominated dioxins and furans do not occur (Morf, 2003, p. 52). Indeed, the three MSW incineration plants and fluidized bed furnace 4 in Vienna are equipped with a dioxin destruction technology. In the fluidized bed 1 to 3 used for incineration of sewage sludge and the rotary kilns 1 and 2 for incineration of hazardous wastes, the dioxins and furans are deposited using fixed-bed adsorbers (MA48, 2007a, p. 26). This is also a recommended way to deal with PBDE waste in environmentally sound manner according to BAT/BEP guidance. This said, controlled incineration is the ideal sink of POP-PBDEs. It has to be made sure, that POP-PBDEs end up in a proper incinerator and not in e.g. home furnaces as a part of artificial wood.[16]

Only trace quantities remain in solid residues of incineration and flue gas and can be determined by using transfer coefficients derived from measurements in Japan, and later applied in the Swiss study.[17] The coefficients are for slag 3.10^{-4}, ash 3.10^{-4} i.e. solid residue 0.6 kg/t, flue gas 3.10^{-10} (Sakai and Inoue, 2001). The value of flue gas transfer coefficient is negligible for these purposes. Slag and bottom ash from all incineration plants in Vienna, including a small amount of fly ash from fluidized bed furnaces 1-3, is mixed with concrete in the treatment plant for incineration residues and then deposited on a landfill since 2004. Fly ash and filter cake from all incineration plants are exported to Heilbronn, Germany.

[15] PBDD+PBDF

[16] This is a theoretical case if recycling is not properly controlled.

[17] Results of the measurement were given at the Stockholm conference in 2001. In an investigation of 2900 g PBDE/t of waste, 1.7 g/t of waste (0.058 %) was found in the solid residue (slag plus ash) (Morf, 2003, p. 103).

3.3.4 Process Landfill

Imports (2): Residues from incineration, (construction waste)
Exports: None
Stock: Unknown

The process landfill is included as a part of scenario, in which not all polymers from construction waste are separated to be incinerated, but instead end up in a landfill.[18] Additionally, some small quantities derived from Sakai's transfer coefficients reach landfill as a part of slag and ash.

The stock of POP-PBDEs, that has accumulated in Viennese landfills during years, is unknown. It must be considered that waste management practices have changed significantly during past years in Vienna, and we do not know how much has accumulated before the collection system for hazardous waste was of today's standards. The main landfill site, Rautenweg, is in operation since 1966. In 2006, about 70 % recycled combustion residues from Viennese incineration plants and the rest about 30 % bulky waste and residual waste from Viennese households were deposited. Since 2008 only recycled residues from Viennese refuse incineration plants are being deposited. All other kinds of refuse only constitute a very small amount (MA48, 2007b, p. 3).

There is a growing evidence that semivolatile compounds like POP-PBDEs are leaching from inappropriate landfills and contaminating the environment.[19] The total PBDE concentrations in leachate in North America ranged from 30 - 250 $ng.l^{-1}$ (UNEP, 2011a, p. 96). In Austria, the measured concentrations of PBDEs in the two landfill leachate samples were about 1000 $ng.l^{-1}$, based on the sum of the most abundant congeners.[20] Because of their limited degradability, POP-PBDEs persist in landfills for many decades (Weber, 2011).

[18] Flow construction waste. The landfill in Vienna for construction waste is Deponie Langes Feld.

[19] Acknowledged by several autors. POP-PBDEs have been also detected in soils close to landfills in Canada (UNEP, 2011a, p. 96).

[20] BDE-47, 99, 100, 153, 154, 181 and 183. These congeners' concentrations in samples DSW1 was 1127.3 ng/L and in DSW2 502.2 ng/L (Umweltbundesamt, 2004, p. 27, 54).

3.3.5 Process Waste water treatment plant

Imports (1): Deposition
Exports (2): Sludge, purified water

After the POP-PBDE emissions have reached the water treatment, the majority accumulates in the sewage sludge due to their chemical properties.[21] A transfer coefficient 9:1 for flows sludge to purified water is used, as previously done in the Swiss SFA (Morf, 2003).

Measurements of PBDE concentrations were done in waste waters at the entrance of Austrian communal and industrial waste water treatment plants.[22] 37 samples were collected in years 2002-2003, two of which were taken at the *inflow* of the same communal WWTP (Umweltbundesamt, 2004, p. 14). The sum of 8 congeners, relevant for c-PentaBDE analysis,[23] was 1.67 ng.L^{-1} (sample 1) and 19.00 ng.L^{-1} (sample 2). Taking these concentrations as min and max values and the annual flow of waste water in Vienna for preliminary assessment, an annual flow of about 0.4 - 4.2 kg of c-PentaBDE in Viennese waste water can be expected. Following the same logic for c-OctaBDE, an annual flow of about 1 kg is expected. The SFA may yield even lower values, because the PBDE flows in 2010 are thought to be lower than in 2002-2003, which makes it clear that the flows reaching and leaving WWTP are close to negligible.

3.4 Considered scenarios

In this chapter, some missing or incomplete information has been identified, where scenario analysis is implemented. In each case three scenarios are considered and the one thought to be most approaching reality is designated in bold. Note that only point 3 may affect the flows of c-PentaBDE.

1. The stock of c-OctaBDE in vehicles
   (1) none, (2) Swiss/worst-case scenario and **(3) average between (1) and (2)**

2. The stock and flows of c-OctaBDE in WEEE category 3
   (1) none, (2) worst-case scenario and **(3) average between (1) and (2)**

3. Waste flows of construction waste Ratio incineration to landfilling (1) 100:0, **(2) 80:20** and (3) 50:50

[21] PBDEs have have low solubility: PentaBDE 2.4 μg/L and OctaBDE <0.5 μg/L (Morf, 2003, p. 116).
[22] No measurements of PBDE concentrations have been done for the sewage sludge, untreated nor purified waste water in Vienna. Confirmed with EbsWien on 27 February 2012.
[23] BDE-17/25, 28, 47, 99, 100, 153, 154 congeners in the inflow (n=2 samples).

Chapter 4

Results

In the following chapter, results of the SFA are given in form of STAN diagrams and the impacts of considered scenarios is assessed.

4.1 c-PentaBDE

In case of c-PentaBDE (fig. 4.1), the most significant flow was found to be in construction polymers, especially PUR insulation foam: 2.69 t/a $\pm$ 0.37 t/a. The ratio incineration to landfilling of construction polymers is not known in Vienna, but if 80 % of the polymers were incinerated, which was assumed to be the most realistic scenario, then the rest 0.54 t/a $\pm$ 0.07 t/a of c-PentaBDE was landfilled. If only 50 % were incinerated, then 1.34 t/a $\pm$ 0.18 t/a c-PentaBDE was landfilled in 2010.

The emissions to environment are not of a special interest in case of c-PentaBDE, because the sum of all emissions from consumption is estimated less than 2 kg/a (Hedbrant's level of uncertainty 5) and will be lower as the consumption stock decreases with time. The soils received $<$ 2 kg of c-PentaBDE in 2010.

4.2 c-OctaBDE

The c-OctaBDE system is more complex. The main flows are, in contrast to c-PentaBDE, vehicles (1.85 t/a $\pm$ 0.96 t/a) and WEEE (1.59 t/a $\pm$ 3.96 t/a). Based on input values, the software STAN estimated recycling to incineration ratio of WEEE to be 1:7, which means that about 0.18 t/a $\pm$ 7.34 t/a returned to the consumption via recycled plastics. The total emissions from consumption to the environment were estimated as $<$ 20 kg, by using literature emission factors (Hedbrant's level of uncertainty 5).

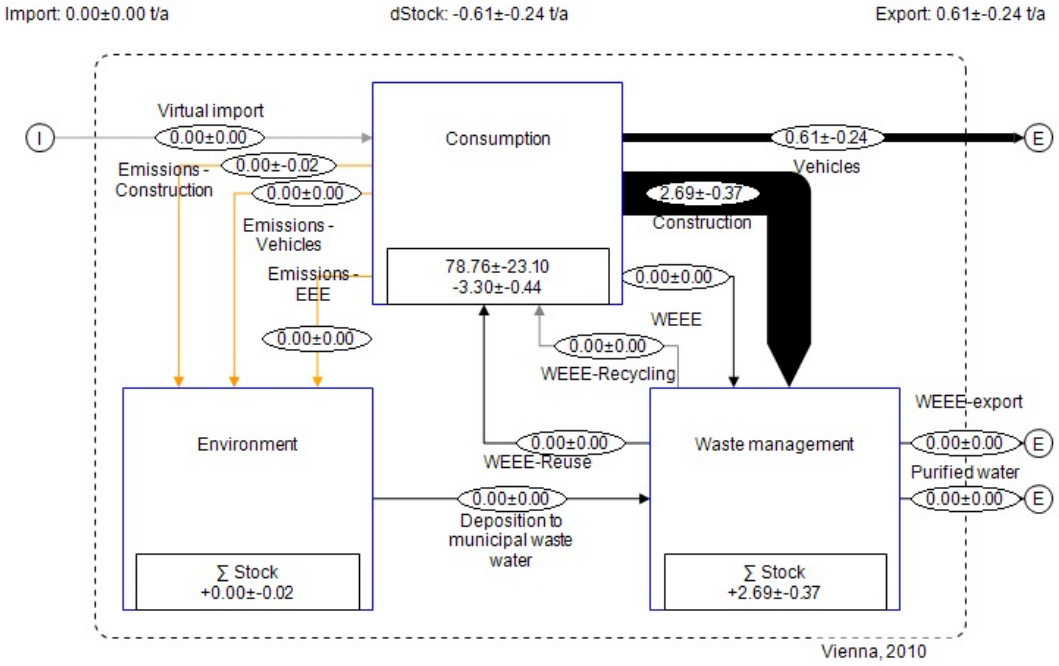


Figure 4.1: STAN system, layer c-PentaBDE.

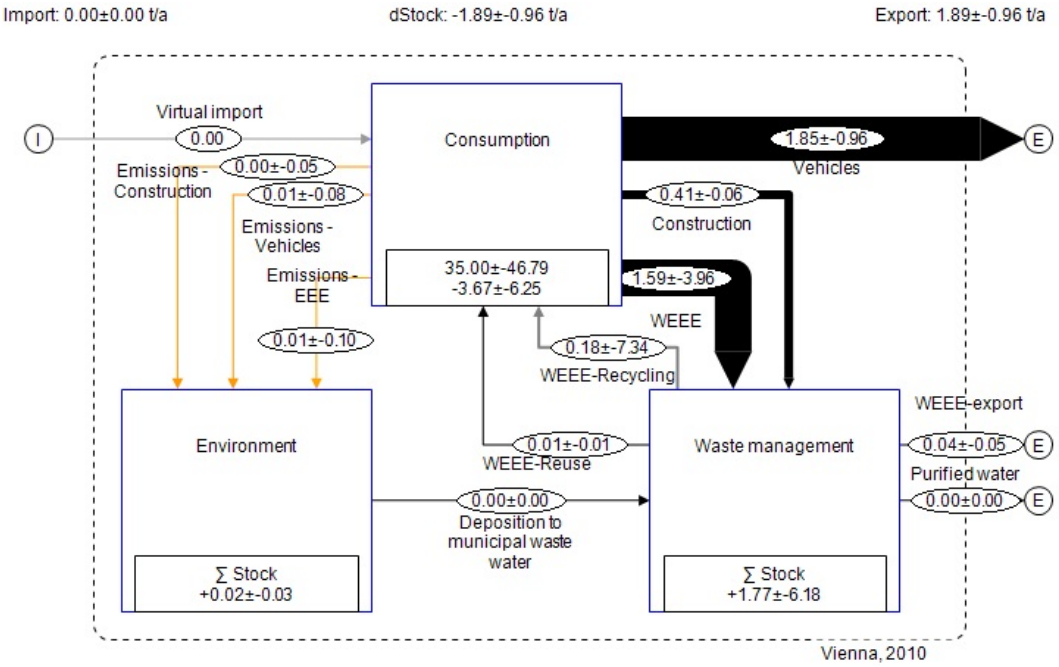


Figure 4.2: STAN system, layer c-OctaBDE.

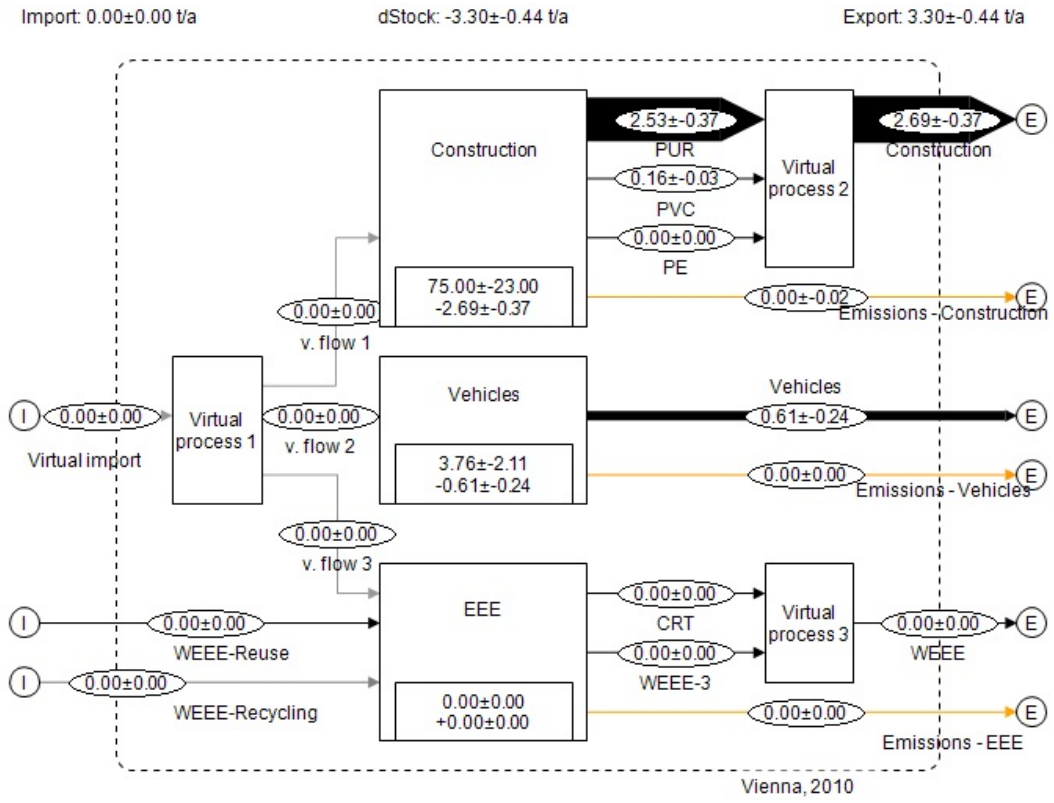


Figure 4.3: STAN subsystem *Consumption*, layer c-PentaBDE.

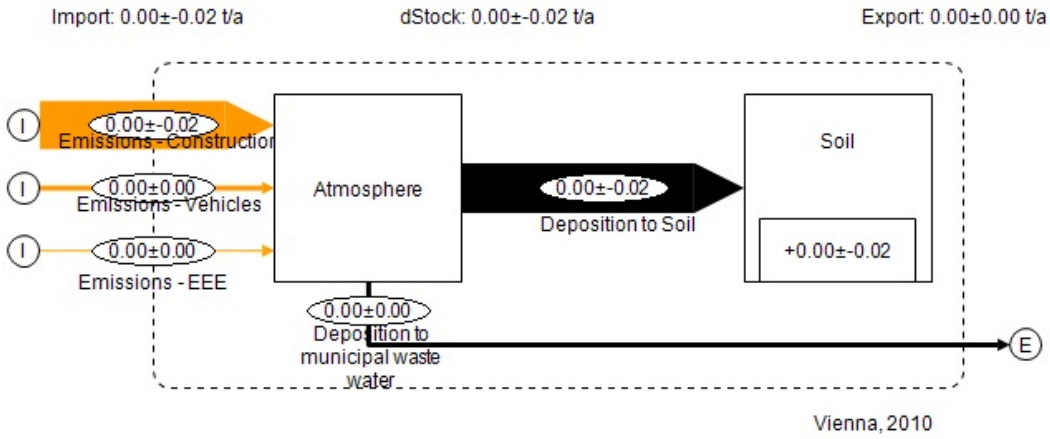


Figure 4.4: STAN subsystem *Environment*, layer c-PentaBDE.

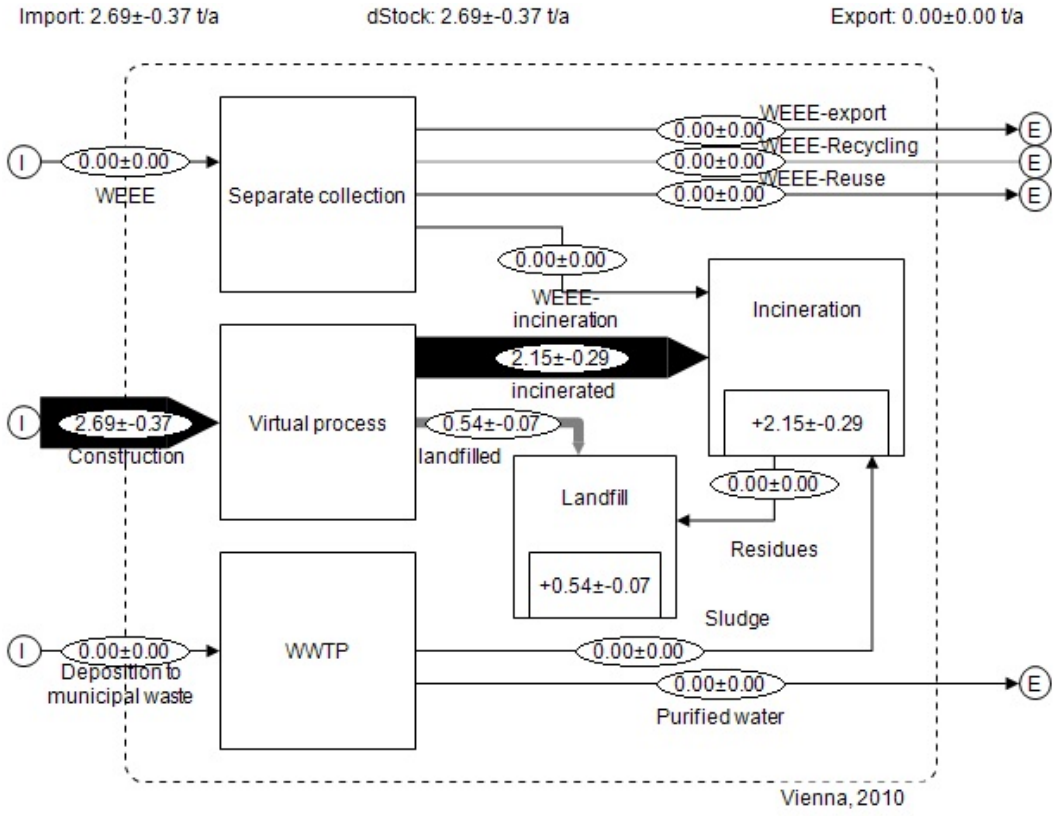


Figure 4.5: STAN subsystem *Waste Management*, layer c-PentaBDE.

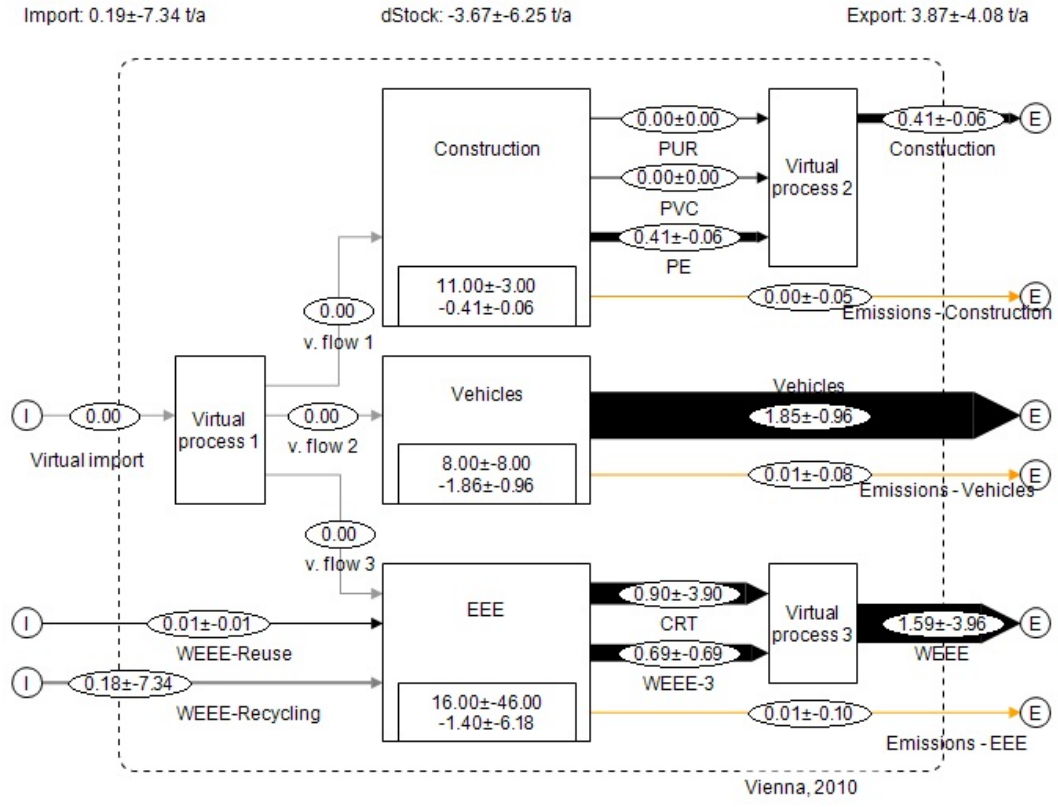


Figure 4.6: STAN subsystem *Consumption*, layer c-OctaBDE.

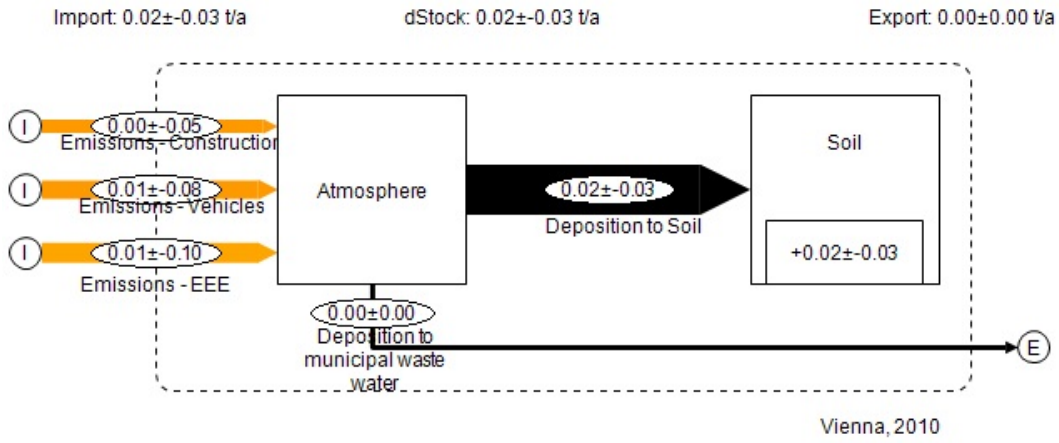


Figure 4.7: STAN subsystem *Environment*, layer c-OctaBDE.

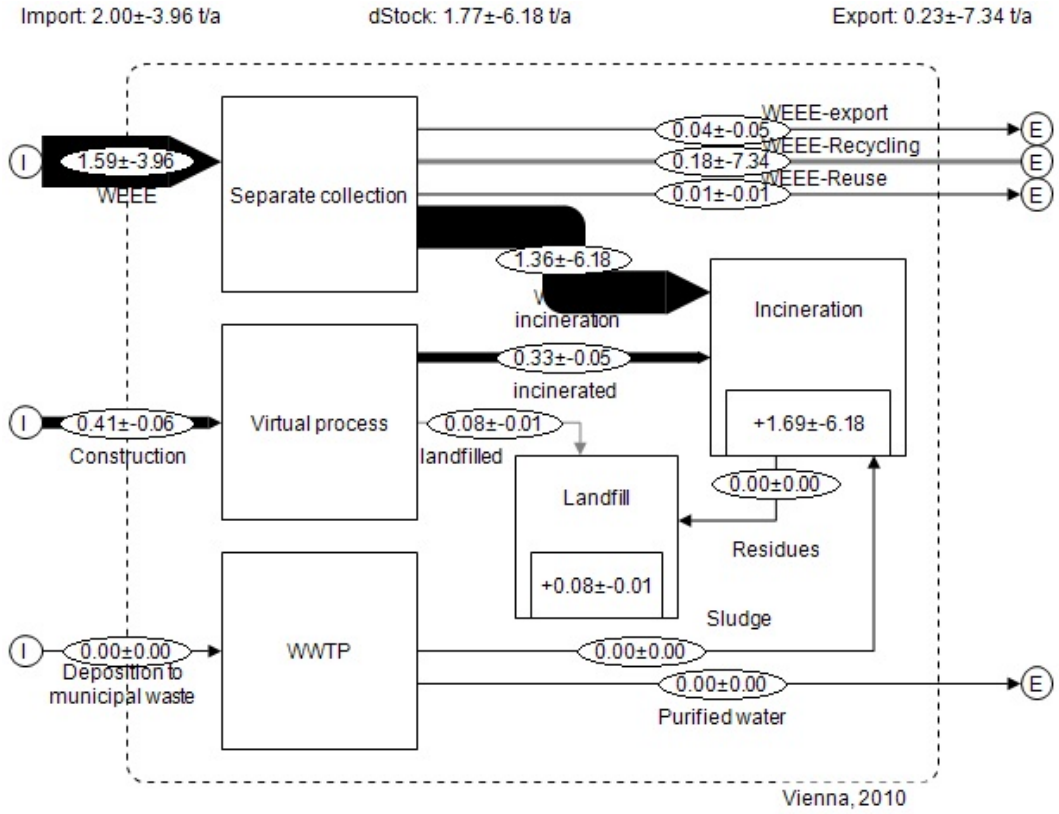


Figure 4.8: STAN subsystem *Waste Management*, layer c-OctaBDE.

Scenario analysis - results

After the initial, most realistic STAN system had been set up, the impact of three possible scenarios was investigated and it was found that:

1. Varying c-OctaBDE concentration in vehicles between the best and worst case scenarios, as well as c-OctaBDE stock in vehicles between 0 - 16 tons, does *not* have any significant impact on the system.

2. Next, the impact of c-OctaBDE presence in WEEE category 3 was analysed by varying the input values between the best and worst case scenarios. Best case scenario assumed no presence of c-OctaBDE in this category (Figure 4.10). When the stock and flows were replaced to zero in the system, the flow recycling was newly estimated in STAN to have a negative value, which shows that this scenario is unlikely. Worst case scenario, which counts with Wäger's maximum coefficient, increased the estimated flow of c-OctaBDE returning to the consumption stock via recycling to 0.86 t/a $\pm$ 7.44 t/a (Figure 4.11).

3. Because the flow of c-OctaBDE in the construction sector is smaller than in case of c-PentaBDE, changing ratio incineration to landfilling has the same effect as in case of c-PentaBDE, only on a smaller scale.

Scenario		c-PentaBDE		c-OctaBDE	
		Key flows in system	Impact on the system	Key flows in system	Impact on the system
1. The stock of c-OctaBDE in vehicles	**average /realistic**	Construction waste	No impact	Vehicles, WEEE	*No significant impact:* the eventually increased flows in the worst-case scenario leave Vienna system boundaries
	none				
	Swiss/ worst-case				
2. The stock and flow of c-OctaBDE in WEEE category 3	**average /realistic**	Construction waste	No impact	Vehicles, WEEE	Recycling flow estimated as 0.18 t/a ± 7.34 t/a
	none			Vehicles, WEEE	*Unlikely scenario:* recyclng flow decreased, in this case to a negative value
	worst-case			WEEE, vehicles	*Recycling flow increased* to 0.86 t/a ± 7.44 t/a
3. Waste flows of construction waste: ratio incineration to landfilling	**80:20**	Construction waste	The flow of c-PentaBDE to landfills was 0.54 t/a ± 0.07 t/a	Vehicles, WEEE	The flow of c-OctaBDE to landfills was 0.08 t/a ± 0.01 t/a
	100:0		*All construction waste would reach its appropriate sink:* the state of the art incinerator		*All construction waste would reach its appropriate sink* : the state of the art incinerator
	50:50		*The flow of c-PentaBDE to landfills increased* to 1.34 t/a ± 0.18 t/a		Less significant impact than in the case of c-PentaBDE

Figure 4.9: Scenario analysis. Key flows and their impact on the system.

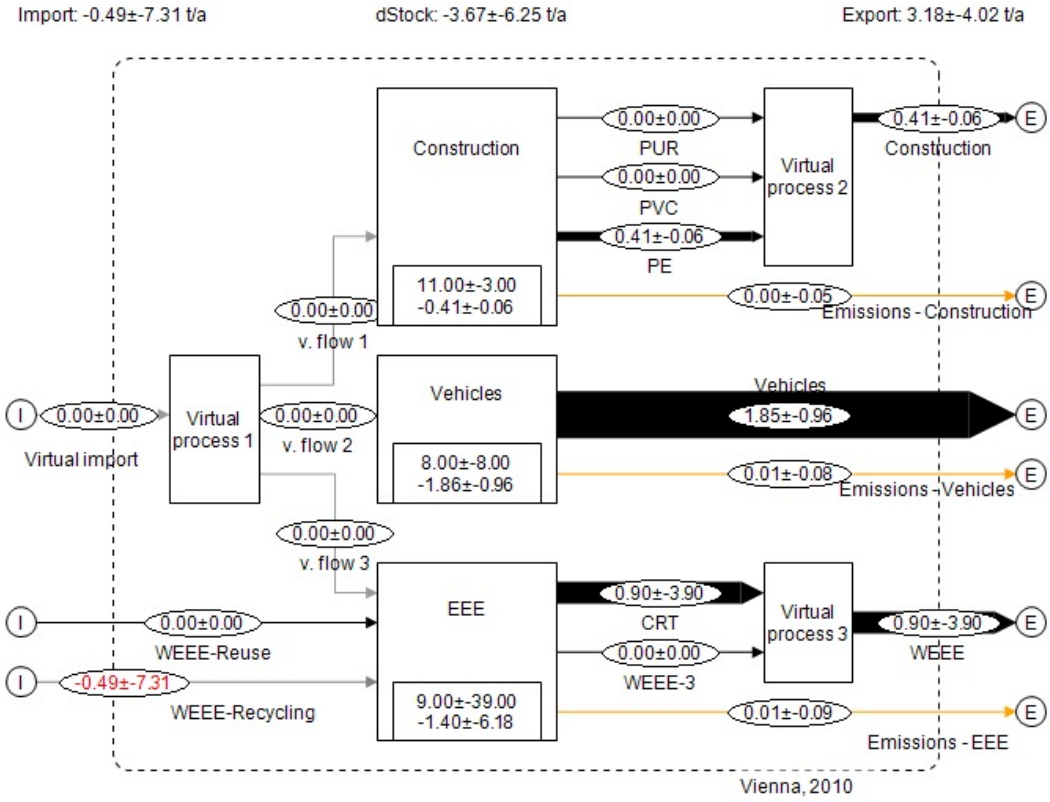


Figure 4.10: Scenario 1 (best case). C-OctaBDE is assumed not to be present in the WEEE category 3. The WEEE-Recycling flow was calculated to be negative. STAN subsystem *Consumption*, layer c-OctaBDE.

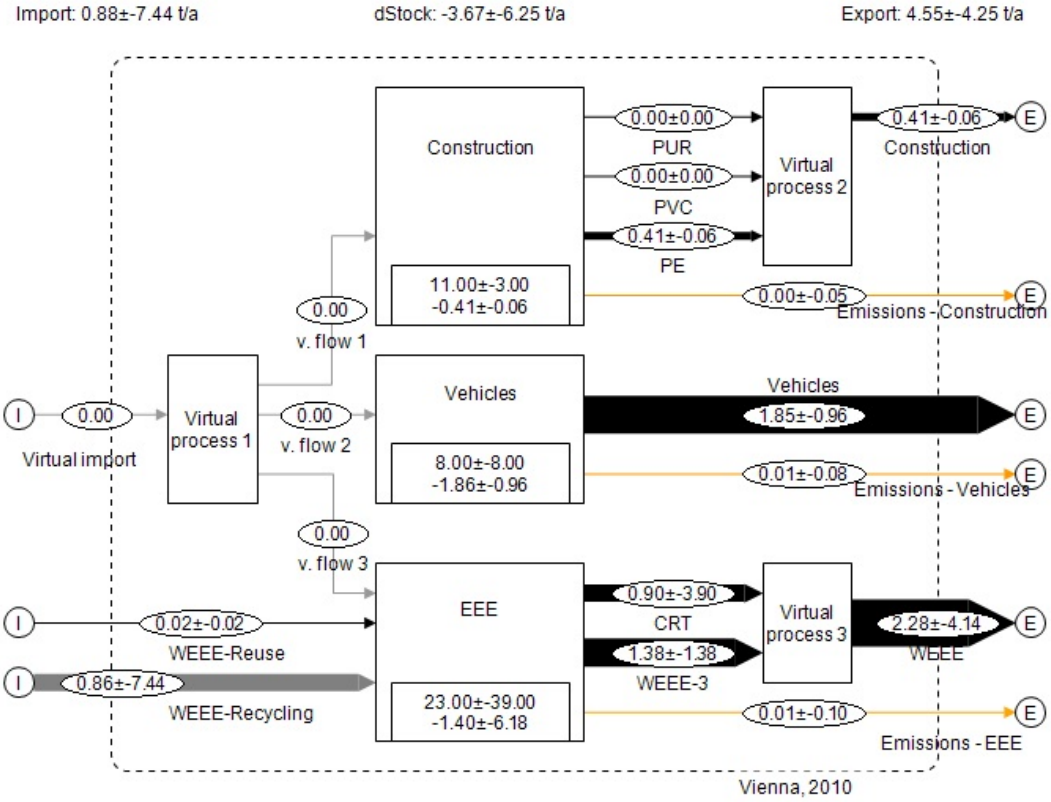


Figure 4.11: Scenario 2 (worst case). C-OctaBDE flow is at highest levels in the WEEE category 3, because Wäger's maximum coefficient is used. The WEEE-Recycling flow was calculated to be 0.86 t/a $\pm$ 7.44 t/a. STAN subsystem *Consumption*, layer c-OctaBDE.

Chapter 5

Conclusions & recommendations

Information about the presence of POP-PBDEs in various products in use is incomplete. Despite this challenge, SFA systems for c-PentaBDE and c-OctaBDE have been modelled and allowed drawing the following conclusions.

Construction sector most likely accounts for a major flow of c-PentaBDE in Vienna: 2.69 ± 0.37 t/a. Therefore, it is important to ensure that all plastic parts used in construction, in this case especially PUR foam insulation and PVC duroplastics sheeting, are separated from the rest construction material and are incinerated. Controlled incineration in a state of the art incinerator is an appropriate sink for POP-PBDEs, and any potential flow to landfills should be avoided.

The c-OctaBDE system is more complex. The most significant flows are EEE and possibly vehicles, too. The c-OctaBDE content in vehicles is unknown, because most literature focuses on c-PentaBDE in relation to vehicles. But, since about 70% of Austrian vehicles are exported abroad, the size of this flow does not have any significant effect on Vienna. However, this certainly is a problem on a global scale.

The crucial issue in case of c-OctaBDE in Vienna is recycling. Recycling of plastics is a preferred option from waste hierarchy and life cycle assessment perspective, but reported presence of c-OctaBDE in European WEEE streams must be taken into account. The SFA model has allowed estimating recycling to incineration ratio of c-OctaBDE of about 1:7, meaning that about 0.18 ± 7.34 t/a was returned to the consumption via recycled plastics in Vienna, in 2010. Rules for the POP-PBDEs management are well anchored in the Austrian law, including the ban on recycling of POP-PBDE-containing plastics. However, it is not clear to what extent this law is enforced by periodical controls. There is very little information available about the compliance of Austrian recycling plants with the RoHS limit values. One of the few information that can be

found on this topic is that most of the produced granules at MBA Polymers, a major plastic recycling plant in Austria, already met the threshold values, as stated in the RoHS Directive, in 2008 (Umweltbundesamt, 2008c, p. 165). If monitoring is in place, it is desirable that this information is available to the public and is up to date.

Wäger (2012), in his recent analysis of RoHS regulated substances in mixed plastics, focused on the implications for the environmentally sound recovery of plastics from WEEE and recommended, that mixed plastics from WEEE are subject to a strict quality management in order to avoid a dissipation of brominated flame retardants into plastics and the environment. The SFA analysis shows that a quality management indeed is very desirable in Vienna.

"Plastics should be traced throughout the entire recycling chain, from the moment they are generated up to the point where they are either reintegrated into new products or properly disposed of (Wäger, 2012)."

Consideration and interpretation of uncertainties is a key issue when performing SFA. The uncertainties in case of c-PentaBDE do not have a significant impact on the system as a whole. The contrary is true for c-OctaBDE, where high uncertainties are affecting the system. They were mainly caused by a very broad interval of concentrations given for CRT monitors, ranging from 0.14 kg/t to 10.6 kg/t (mean 2.5 kg/t), despite the fact that CRT monitors are target products to be addressed by inventory, that parties to the Stockholm Convention are required to conduct as part of their National Implementation Plans. Coupled with other uncertainties, the recycling flow could only be estimated as a wide interval of values: 0.18 ± 7.34 t/a.

In summary, the focus, when it comes to POP-PBDEs management in cities like Vienna, should be on (1) ensuring that the POP-PBDE-containing polymers from construction are incinerated, not landfilled and (2) transparent monitoring of plastics through the entire recycling chain to the final sinks.

Chapter 6

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Chapter 7

Appendices

7.1 Koordinierungsstelle

WEEE category	On market released	Collected (private households)	Collected (other)	Collected (sum)	Treated in Austria	Treated in other EU Member State	Treated outside of the EU
	Total weight [t]	Total weight [t]	Total weight [t]	Total weight [t]	Total weight [t]	Total weight [t]	Total weight [t]
Large appliances	76.944	32.041,0	184,3	32.225,2	32.208,4	16,9	-
Small appliances	17.721	6.168,8	0,7	6.169,5	6.162,7	6,8	-
IT &T	28.656	15.341,2	990,4	16.331,6	15.547,1	784,1	0,5
Consumer equip.	24.822	15.302,9	-	15.302,9	14.005,8	1.297,1	-
Lighting equip.	1.484	1.004,2	-	1.004,2	1.003,1	1,1	-
Gas discharge lamps	1.408	861,0	9,1	870,0	870,0	0,0	-
Tools	6.008	1.839,5	1,9	1.841,3	1.839,4	1,9	-
Toys, leisure and sport equip.	2.723	64,6	-	64,6	64,5	0,1	-
Medical devices	2.111	158,4	54,5	212,9	209,7	3,1	0,0
Monitoring and control devices	2.818	165,0	-	165,0	162,2	2,8	-
Automatic dispensers	1.115	-	68,2	68,2	66,9	1,3	0,0
SUM	165.811	72.946,4	1.309,0	74.255,5	72.139,7	2.115,2	0,5

Figure 7.1: Annual collection of WEEE in Austria (Koordinierungsstelle, 2010, p. 34).

Collection and treatment categories (Annex 3, EAG-VO)	Large appliances	Refrigerators	Screen devices	Small appliances	Gas discharge lamps
"New devices" (M%)	4,59 %	0,02 %	3,30 %	–	–
"Historical devices" (M%)	95,41 %	99,98 %	96,70 %	–	–

Figure 7.2: Distribution of ”new” and ”historical” devices in year 2010 (Koordinierungsstelle, 2010, p. 36).

7.2 STAN input data and calculations related to the subsystem consumption

7.2.1 Construction

Input values of flows of PUR, PVC and PE on level of goods and concentration of substances. Input values of stock values in processes construction, vehicles and WEEE on level of substances, as there are different c-PentaBDE concentrations for different polymers (PUR, PVC).

PUR, PVC and PE flows

Input data:
PUR 390 t ± 78 t
PVC 110 t ± 22 t
PE 241 t ± 48 t

Concentrations:
c-PentaBDE in PUR 6.49 kg/t ± unknown
c-PentaBDE in PVC 1.45 kg/t ± unknown
c-OctaBDE in PE 1.7 kg/t ± unknown

c-PentaBDE and c-OctaBDE stock

Calculation of c-PentaBDE stock in construction. Vienna, 1998
PUR foam incl. foam filter in Germany 1 260 000 t or 15.4 kg/c.
PUR in Vienna 0.0154 t x 1 698 822 = 26 162 t
PentaBDE content 6.49 x 26 162 t x 10^{-3} x 0.6 = 101 t
PVC film in Germany: 380 000 t or 4.65 kg/c.
PVC in Vienna: 0.00465 t x 1 698 822 = 7 900 t
PentaBDE content 1.45 x 7 900 t x 10^{-3} x 0.6 = 6 t
Total c-PentaBDE 107 t

Calculation of c-OctaBDE stock in construction. Vienna, 1998
PE film in Germany: 780 000 t or 9.54 kg/c.
PE in Vienna 0.00954 t x 1 698 822 = 16 207 t
OctaBDE content 1.7 x 16 207 t x 10^{-3} x 0.6 = 16 t
Total c-OctaBDE 16 t

107 t of c-PentaBDE and 16 t c-OctaBDE should be gone out of the consumption stock in 40 years. The approximate flow out is 2.7 t/a for c-PentaBDE and 0.4 t/a for c-OctaBDE. This said, the stock in 2010 is estimated as **75 t c-PentaBDE** and **11 t c-OctaBDE**.

Error propagation:
Flow of building materials ± 20 %, service life ± 30 % (Morf, 2003, p. 84)
Minimum stock of c-PentaBDE (service life 28 years, flow out + 20 %):
107/28 t/a = 3.82 t/a + 20 % = 4.59 t/a, 107 t - 4.59 x 12 t = 52 t
Maximum stock of c-PentaBDE (service life 52 years, flow out -20 %):
107/52 t/a = 2.06 t/a - 20 % = 1.65 t/a, 107 t - 1.65 x 12 t = 87 t
Minimum stock of c-OctaBDE: 8 t
Maximum stock of c-OctaBDE: 13 t

Input values to the STAN system:
c-PentaBDE 75 t ± 23 t
c-OctaBDE 11 t ± 3 t

7.2.2 Vehicles

In case of c-PentaBDE, input to the STAN system is on the level of goods, i.e. number of vehicles and then concentration of c-PentaBDE per one vehicle. This is not possible for c-OctaBDE because no concentrations are available in the literature. In this case, input will be done on the layer of c-OctaBDE.

c-Penta- and c-OctaBDE stock

The stock of all vehicles in Vienna on 31 December 2010 was 821 999 vehicles, which is an increase of 7 375 vehicles as compared to the stock on 31 December 2009. From the statistics on first registration of personal vehicles currently in stock, we know that 382 515 of 669 279 passenger vehicles (57 %) were first registered until the end of 2004.[1] Those produced after 2005 do not contain POP-PBDEs therefore shall not be included in the c-PentaBDE calculation. I assume it is the same percentage for other types of vehicles.

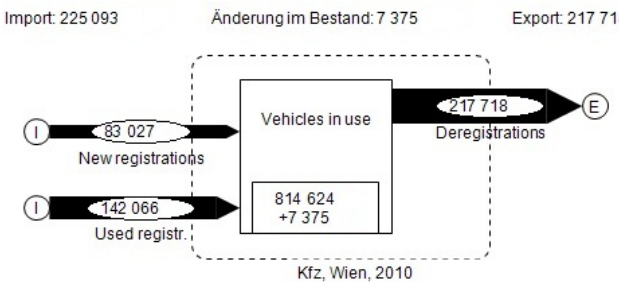

Figure 7.3: MFA-system of vehicles (Vienna, 2010).

Figure 7.4: Age distribution of passenger vehicles stock by the year of first registration. STATISTIK AUSTRIA.

382 515 / 669 279 = 0.57
0.57 x 821 999 = 469 800 vehicles (app. amount of vehicles produced before 2005)
Additionally, f = 0.05 is a factor for European vehicles, where c-Penta was used:
469 800 x 0.05 = 23 490 vehicles.
A mean concentration of c-PentaBDE is 160 g per road vehicle produced before 2005 (UNEP, 2011b, p.58).

Calculation of c-PentaBDE stock in vehicles. Vienna, 2010
23 490 vehicles x 160 g/vehicle = 3.76 t
Error propagation

[1] Source: STATISTIK AUSTRIA, "Pkw nach dem Jahr der Erstzulassung vom Bundesland Wien" received from Ms. Gerda Fischer on 3 May 2012.

The data on vehicles in Vienna are of high quality. The uncertainties here depend mostly on how good is the estimate that one old vehicle contains 160 g c-PentaBDE. It is meant to be "rather upper conservative estimate" and it is in agreement with other from other studies for c-PentaBDE that estimated 250 g/car (ESWI 2011) and 125 g/car (UNEP, 2011b, p. 58). For error propagation we can take 125 g and 250 g as minimum and maximum values and consider 160 g a realistic mean value.
Min: 23 490 x 125 g = 2.94 t c-PentaBDE
Max: 23 490 x 250 g = 5.87 t c-PentaBDE

Calculation of c-OctaBDE stock in vehicles. Vienna, 2010
Scenario 1: 0 t
Scenario 2 (Swiss):
c-PentaBDE/c-OctaBDE in vehicle stock in Switzerland, 1999: 34 t / 143 t = 0.24
c-OctaBDE in vehicle stock in Vienna, 2010, based on this ratio: 3.8 t / 0.24 = 16 t
Scenario 3: an average between the two scenarios, which gives **total c-OctaBDE 8 t**.

Input values to the STAN system:
23 490 vehicles, c(PentaBDE) = 160 g $\pm$ 90 g/vehicle.
c-OctaBDE: 8 t $\pm$ 8 t
Note that STAN will calculate the concentration interval for c-OctaBDE/vehicle.

c-Penta- and c-OctaBDE flows

In 2010 in Vienna, 83 027 new vehicles were registered, of which 68 902 were passenger and combination vehicles and 280 buses. There were 142 066 registrations of used vehicles.[2] From the fact that the stock grew with +7 375 vehicles in 2010, we can easily establish that 225 093 vehicles must have been de-registered, at least temporarily.

Now it is necessary to calculate the amount of vehicles, which left the stock in 2010. This can be done simply by assuming, that the age of the stock does not change significantly i.e. we can take it for being constantly "old", then we can only consider the new registrations (83 027 vehicles), stock increase (7 375 vehicles) and assume an input-output balance: output excluding re-registrations in Vienna was 75 652 vehicles. As previously established, there are currently 469 800 vehicles in Viennese stock, with first registration date before the end of 2004. This means that it will take approximately 6 years until they leave the stock.

c-PentaBDE flow (Vienna, 2010)
c-PentaBDE 75 652 vehicles x 0.05 = 3 783 vehicles
c(PentaBDE)= 160 g $\pm$ 90 g/vehicle
STAN will calculate that the flow is app. 0.6 t/a c-PentaBDE. From there we know the approximate time until stock = 0: 3.8 t / 0.6 t = 6 years (year 2016).

c-OctaBDE flow (Vienna, 2010)
Since the c-PentaBDE and c-OctaBDE must leave the stock with the same velocity because they are contained in the same product, the mean flow can be estimated as **1.3 t/a c-OctaBDE.**
Considering the scenarios 1 and 2 as previously, the input flow to the STAN system is 1.3 $\pm$ 1.3 t/a.

7.2.3 EEE

c-OctaBDE stock

Only c-OctaBDE is present in WEEE, in CRT monitors and possibly in EEE category 3. The input of stock data to STAN will be done on layer c-OctaBDE and calculated in the following section. It is done that way because the stock is composed of different concentrations (in CRT and EEE-3).

Calculation of c-OctaBDE stock in CRT monitors. Vienna, 2010
7.05 kg CRT weight per capita (Swiss Federal Office of Statistics, 2011)
$M_{PBDE(i)}$ = 7.05 x 10^{-3} t x 1 698 822 = 11 977 t CRT
Polymer fraction is 0.3, an average c-OctaBDE content for these polymers in CRT monitors is 2.5 kg/t.
$M_{PBDE(i)}$ = 11 977 t x 0.3 x 0.0025 = **9 t c-OctaBDE**

[2]Source: STATISTIK AUSTRIA, received from Ms. Gerda Fischer on 25 April 2012

Error propagation
$f_{polymer}$ is in range 13 - 38 % (mean 30%) $C_{PBDE(i);Polymer}$ 0.14 kg/t to 10.6 kg/t (mean 2.5 kg/t) (Wäger, 2012) (UNEP, 2011b, p. 50-51, Tables 4-9 and 4-10), which gives the following values: Min 0.2 t, realistic 9 t and max 48 t c-OctaBDE.

c-OctaBDE stock in EEE cat.3 w/o CRT monitors in Vienna, 2010.
Scenario 1: 0 t
Scenario 2 (worst case scenario):
c(OctaBDE)= 1 g/kg (mean, Wäger) and 1.6 g/kg (max, Wäger). Since it is a worst case scenario, I am using the max. concentration.
Cat. 3 (Max): 840 300 x 25 kg x 0.42 x 1.6 kg/t x $10-6$ t = 14 t
(For 840 300 households in Vienna)
Scenario 3: Average between scenarios 1 and 2. c-OctaBDE stock = **7 t**.
Min (Sc. 1): 0 t. Max (Sc. 2): 14 t.

Input values to the STAN system:
Sum of CRT and EEE-3: Realistic 16 t, Min 0 t, Max 62 t i.e. **16 t $\pm$ 46 t.**

c-OctaBDE flow from Consumption to Waste management

In Austria, there were 16 332 t of waste collected in WEEE-category 3 in 2010, of which 15 547 t were also treated in Austria[3] and 270 t of working equipment was separated and sold to be reused. This way, it returned to the consumption stock. It is also known that 96.7 % of *screen devices* were classified as historic devices, meaning they were produced before 2005. Vienna accounts in average for 13.4 % of the total Austrian WEEE collection, which makes about 2 083 t of equipment in this category treated in first step in Vienna and about 36 t returned for reuse (Koordinierungsstelle, 2010, p. 34, 36 and 61).

Flow Export
105 t exported.
Min 0 t
Max 105 t x 0.42 x 1.6 kg/t = 70.7 kg (Wäger)
Realistic 35 kg $\pm$ 35 kg c-OctaBDE exported
Input to the STAN system: goods - 105 x 0.42 t = 44 t. c = 0.8 kg/t $\pm$ 0.8 kg/t.

Flow To reuse
36 tons of appliances in WEEE-3 were returned to reuse, which is a rather small flow. Here we can safely assume that those were not CRT monitors, but rather appliances for which there is demand nowadays. Therefore, concentration for appliances in this category w/o monitors is used.
Min 0 t
Max 36 t x 0.42 x 1.6 kg/t = 24 kg (Wäger)
Realistic 12 kg $\pm$ 12 kg c-OctaBDE to reuse
Input to the STAN system: goods - 36 x 0.42 t = 15.12 t. c = 0.8 kg/t $\pm$ 0.8 kg/t.

Calculation of c-OctaBDE flow in WEEE-3 (Vienna, 2010)
Min 0 t/a
Max 2 047 t x 0.42 x 1.6 kg/t = 1.4 t/a (Wäger)
Realistic 0.7 t/a
Note that this corresponds to 10 years of service life as compared to the stock (7 t / 0.7 t/a = 10 years), which seems very plausible.
Input to the STAN system: goods - 2 047 x 0.42 t = 860 t, c(OctaBDE) = 0.8 kg/t $\pm$ 0.8 kg/t.

Estimation of c-OctaBDE flow in CRT monitors based on the stock and 10 years service time
Min 0 t/a, Mean 0.9 t/a, Max. 4.8 t/a
Input to the STAN system: 0.9 t/a $\pm$ 3.9 t/a.

[3] This means the first step of the treatment.

7.2.4 Consumer emissions

c-PentaBDE emissions - values remain same after STAN reconciliation.
c-OctaBDE emissions - are corrected by STAN to
construction: input 6.194 ± 61.846 kg/a, **corrected 4.81 ± 53.7 kg/a**
vehicles: input 4.32 ± 82.08 kg/a, **corrected 6.41 ± 79.61 kg/a**
EEE: input 8.64 ± 326.16 kg/a, **corrected 6.8 ± 98.37 kg/a**
Note that uncertainties are smaller after reconciliation.

	Stock [t]			**Annual emission factor**			**Emissions [kg/a]**		
PentaBDE	Min	Realistic	Max	Min	Realistic	Max	Min	Realistic	Max
Construction	52	75	87	2E-06	2E-05	0,0002	0,1196	1,725	20,01
Vehicles	2,94	3,76	5,87	6E-06	6E-05	0,0006	0,017052	0,21808	3,4046
EEE	0	0	0	0	0	0	0	0	0
Total	54,94	78,76	92,87				**0,136652**	**1,94308**	**23,4146**
OctaBDE	Min	Realistic	Max	Min	Realistic	Max	Min	Realistic	Max
Construction	9,36	11	12,6	5E-05	0,0005	0,0054	0,50544	5,94	68,04
Vehicles	0	8	16	5E-05	0,0005	0,0054	0	4,32	86,4
EEE	0	16	62	5E-05	0,0005	0,0054	0	8,64	334,8
Total	9,36	35	90,6				**0,50544**	**18,9**	**489,24**

Figure 7.5: C-PentaBDE and c-OctaBDE consumer emissions, with uncertainty range.

7.3 Waste management

7.3.1 WEEE Collection and treatment category 3

IT and telecommunications equipment according to the Annex IB of the Directive 2002/96/EC

Centralised data processing: Mainframes, Minicomputers, Printer units
Personal computing:
Personal computers (CPU, mouse, screen and keyboard included),
Laptop computers (CPU, mouse, screen and keyboard included),
Notebook computers,
Notepad computers
Printers
Copying equipment
Electrical and electronic typewriters
Pocket and desk calculators
and other products and equipment for the collection, storage, processing, presentation or communication of information by electronic means
User terminals and systems
Facsimile
Telex
Telephones, Pay telephones, Cordless telephones, Cellular telephones, Answering systems
and other products or equipment of transmitting sound, images or other information by telecommunications

7.3.2 MBA Polymers patent

Extract from the Multistep separation of plastics patent (EPO, 2010, p. 24).

"A number of automatic separation techniques exist which are capable of separating plastics containing Br from Br-free plastics. ... The density of plastics is much higher if a significant amount of Br is present in the plastic. Since Br is typically present at levels of 5 % or higher, the density of brominated plastics is typically greater than that of the non-flame retarded plastic by 0.05 $g.cm^{-3}$ or greater. It is relatively easy to separate materials with such wide density differences using separators such as sink-float tanks or hydrocyclones.

Separation by density is not perfect, however, and a small but measurable amount of higher density Br-containing plastics can report to lower density product streams. A two stage density cut which is capable of removing almost all of the higher density brominated plastic for broad ranges of feed composition can be used. Example 33 describes the benefits of two stage density separation (DPDS) with carefully controlled separation densities can be used to remove plastics containing bromine. Example 34 demonstrates the removal of most bromine-containing plastics using rising current separators such as elutriation devices.

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Example 34: Elutriation to remove Br-containing plastics.

A Size II feed material derived from Japanese white goods contained a significant amount of metal including large chunks, thin strips of metal, and wires. The material was fed to gravity concentration system with the upward water velocity set to 0.13 m/s. The types of material were categorized as target plastics, heavy plastics and metal. Target plastics consisted of plastics with a density less than 1.20 $g.cm^{-3}$. Heavy plastics included all plastics more dense than 1.20 $g.cm^{-3}$. Metal included chunks of metal, thin strips of metal, and wires. ... These results show that a gravity concentration system can effectively remove all metal and the majority of heavy plastics in a single stage.

...

Devices exist which can eject particles containing Br. The detection of the strong X-ray fluorescence Kα signal of Br can be used to control the ejection of brominated plastics. This technique works best for streams containing small amounts of Br, so it may be best used after other techniques such as separation by density, which can be used with effectiveness for broader ranges of composition.

The presence of significant amounts of BFRs in a plastic should significantly alter the electrical properties of the plastic relative to the Br-free plastic. The electrical property differences of the plastics should therefore result in one type charging positive relative to the other when the plastic surfaces are contacted with each other. Charging differences exist between different plastic types or plastics with different additives, so it should be possible to separate the plastics containing bromine using Temperature/emissivity separation (TES). Examples 27 and 28 demonstrate the feasibility of TES for separating plastics containing Br from those without Br.

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Example 27: Separation of PC/ABS from Flame Retarded ABS using TES.

A 50:50 mixture of PC/ABS and flame retarded ABS (ABS-FR) passed through a triboelectrostatic separator and both positive and negative products were collected. The product compositions are given in Table.

Example 28: Separation of HIPS from Flame Retarded HIPS using TES.

A 50:50 mixture of HIPS and flame retarded HIPS (HIPS-FR) passed through a triboelectrostatic separator and both positive and negative products were collected. The yields and product compositions are given in Table. The negative electrode product is clearly enriched in HIPS and the middle and positive electrode products are enriched in HIPS-FR."

stream	% PC/ABS	% ABS-FR
feed	50	50
negative electrode	96	4
positive electrode	12	88
middle	30	70

stream	Yield %	% HIPS	% HIPS-FR
feed	100	50	50
negative electrode	24	79	21
positive electrode	24	42	58
middle	52	42	58

Figure 7.6: Compositions of products from TES of ABS-FR and PC/ABS, HIPS and HIPS-FR.