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Diplomarbeit

Determination of Oxidative Properties of ambient Particulate Matter based on Ascorbic Acid

ausgeführt am Institut für
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der Technischen Universität Wien

unter der Anleitung von Ao.Univ.Prof. Dipl.-Ing. Dr.techn. Anneliese Kasper-Giebl

durch

Laura Felgitsch

Hasnerstraße 46
1160 Wien

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Contents

1. Introduction and Aim

The awareness about the health risks of ambient particulate matter has been growing over the last decades and a lot of effort was taken to reduce ambient air concentrations by cutting the emissions. Nevertheless, this is still a problem that we have to face. If we regard the IGL (Immissionsschutzgesetz – Luft / immision control act – air BGBl. I Nr. 115/1997) - annual report for Vienna from the year 2011(Augustyn et al. 2012), we see that even if days with exceedances caused by the winter services are excluded, in Vienna still 34 to 60 days with exceedance of the limit value for PM10 (particulate matter with an aerodynamic diameter of 10 µm or smaller) remain. The limit value is a daily mean of 50 µg/m³. This is more than the allowed maximum of exceedance of 25 days per year for a single site. Until now most epidemiological studies investigating health effects of particulate matter are based on measurements of PM10 or PM2.5 – the parameters monitored widely (e.g. Bruckmann et al. 2011).

Since the sources of particulate matter are diverse, its chemical composition is quite variable.

In the recent past it has been suggested that the majority of health effects of ambient particulate matter are due to induced oxidative stress (Gilliland et al. 1999; Li et al. 2003; Nel et al. 2005) and efforts already have been taken to investigate the oxidative properties of particulate matter (Künzli et al. 2006; Nawrot et al. 2009; Orru et al. 2010; Zielinski et al. 1999; Godri et al. 2011). Therefore a limit value system based on mass might not be the best and new ways to classify ambient particulate matter by its effect concerning health issues have to be investigated.

As mentioned above, it has been suggested that the main reason for the negative health effects of ambient particulate matter is induced oxidative stress. The goal my work is the classification of the oxidative properties of ambient particulate matter samples, by incubating them in a buffer solution containing 35ppm ascorbic acid. The depletion of ascorbic acid is monitored in the course of 4 hours. Results of samples collected at different monitoring sites were compared. Furthermore possible links between the oxidative properties and the composition of PM were investigated. Blank filters of several filter types were measured, to determine if they show oxidative properties in regards of ascorbic acid. Since sampling of ambient particulate matter is carried out with different filter materials, it is important to know which filters can be used for the method described here. Especially the investigation of quartz fibre filters was of big importance, since quartz fibre filters are frequently used for ambient air monitoring.

2. State of the art

2.1. Ambient particulate matter

This chapter is mostly based on information out of textbooks e.g. Seinfeld et al. (1998) and Bruckmann et al. (2011) and references therein.

The term ambient particulate matter describes airborne particles that neither belong to clouds nor to fog.

A former factor to rate the air quality was the TSP (Total Suspended Particles) which describes the mass of all airborne particles; however since the 90s the usage of the concentration of particulate matter with a special size cut is preferred.

Ambient particulate matter varies in size, origin and composition. PM10 (particulate matter with an aerodynamic diameter of 10 µm or smaller) is the size fraction that is defined as inhalable particles, meaning that they are the first particles small enough to being able to penetrate the thoracic airways (Pope 2000). The smaller size fractions are named analogically. Next to PM10, also the size fraction PM2.5 is collected frequently (both are needed for controlling the limit values in the European Union). Other important fractions of particulate matter with a smaller aerodynamic diameter are PM1 or PM0.1 (UFP – Ultrafine Particles). (Bruckmann et al. 2011)

The size as well as the chemical composition depend on the source of the ambient particulate matter, the processes involved in its formation, the time of the year and meteorological conditions. While naturally occurring particles, like pollens, windblown dust, sea salt and plant fragments usually show a diameter that is >1µm a.d., combustion generated particles, which are often formed in anthropogenic sources, such as those from power generation and automobiles, can range from a few nanometres up to approx. 1 µm a.d.. Particles that are produced in the atmosphere over photochemical processes are normally found in the size fraction <1µm a.d. as well. (Seinfeld et al. 1998[a])

Ambient particulate matter can be classified into different groups, for example:

-Natural versus anthropogenic:

Anthropogenic sources can be affected by actions. Natural sources like the sea salt emission cannot be influenced.

-Primary versus secondary particles:

Primary particles are directly emitted by the source. An example is the resuspension of mineral dust from the ground. Secondary particles are formed in the air. Hereby the processes can take place in the liquid phase as well as the gas phase. An example is the formation of ammonium nitrate from gaseous NH_3 and HNO_3.

-Biological versus non-biological particles

Airborne particles contain ions like sulphates, nitrates, ammonium as well as carbonaceous material, crustal species, such as silicon, magnesium, aluminium, and iron, sea salt, hydrogen ions, and water. Carbonaceous particles can be divided into organic carbon, elemental carbon or black carbon and carbonates. While the crustal materials as well as biogenic particles as pollen or plant fragments usually belong to the coarse aerosol fraction, sulphate, ammonium, organic and elemental carbon, and certain transition metals mostly belong to the fine particle fraction. Nitrate is found in both fractions. (Seinfeld et al. 1998[c])

Particles, which are smaller than 0.1µm tend to coagulate to bigger particles, and particles bigger than 10µm are deposited rapidly from the atmosphere due to their weight. Unlike those particles, the life span of particles between 0.1µm and 2.5µm in the atmosphere lasts several days (Seinfeld et al. 1998[b]) giving them the possibility to be transported over thousands of kilometres.

Highest pollution can be found in direct proximity of the sources, like industrial plants or traffic hotspots. Also problematic are narrow urban canyons that hinder air exchange. Urban dwelling zones in general show higher concentrations of particulate matter than the country side, though even in rural areas far away from any bigger source of pollution a background level of particulate matter can be measured.

Rural sites in general show a higher content in mineral dust and particulate matter of natural origin (Seinfeld et al. 1998[b,d]). Also it can be seen that wood smoke might show higher contributions than in urban sites (Caseiro et al. 2009).

2.1.1. Health risks

The health risks of ambient particulate matter are known. Epidemiological studies already showed a link between particulate matter and cardiopulmonary (Pope et al. 1999) as well as cardiovascular (Brunekreef et al. 2002) morbidity and mortality, and a high correlation in regard of lung cancer mortality (Abbey et al. 1999). Also, particulate matter can influence allergic inflammation (Nel et al. 1998) and induce an acute exacerbation of asthma (Gilliland et al. 1999).

2.2. Oxidative stress

Aerobic life depends on oxygen. In human organisms O_2 is involved in many enzymatic and non-enzymatic reactions were it serves as an electron acceptor. At the same time oxygen can be toxic, even in atmospheric concentrations. This occurs through the addition of electrons which can lead to reactive oxygen species (ROS). (Bowler et al. 2002)

The main role of oxygen is oxidative phosphorylation which is responsible for the production of ATP. In this process oxygen is needed as an electron acceptor. This process normally requires the addition of four electrons to form H_2O. When it comes to the addition of a single electron, the superoxide radical ($O_2\bullet^-$) is generated. The addition of two electrons leads to hydrogen peroxide (H_2O_2), the addition of three electrons to the hydroxyl radical ($OH\bullet$). Also included in the reactive oxygen species is singlet oxygen ($O\bullet$) and ozone (O_3) as well as reactive anions (e.g. $OCOO^-$) and molecules that contain oxygen and are able to produce free radicals (e.g. $HOCl$). (Li et al. 2003)

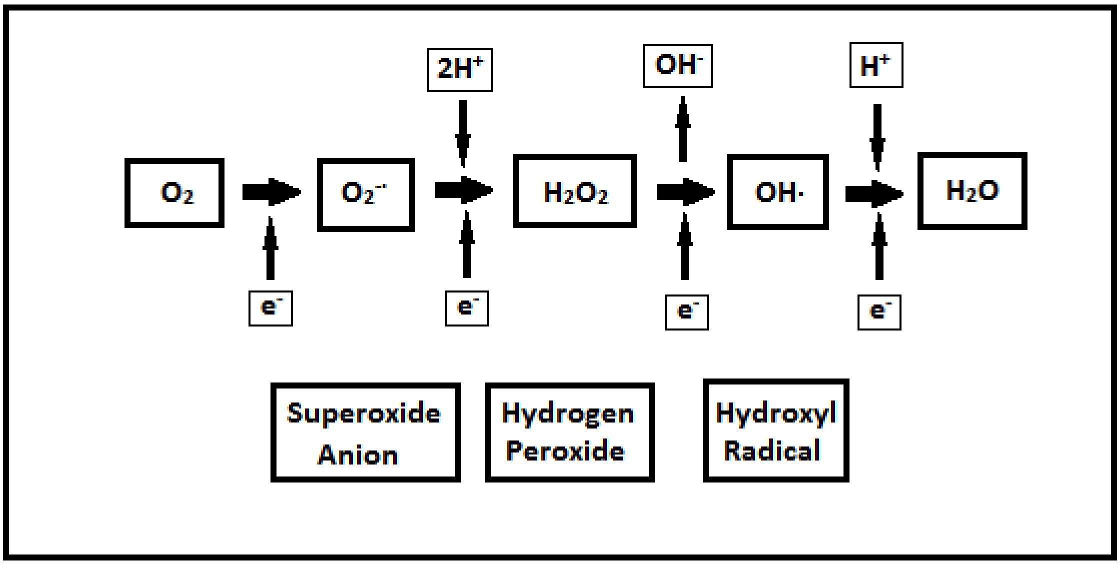


Figure 2.1.: Schematic demonstration of the formation of ROS based on Li et al. 2003.

Oxidative stress can be divided into three steps. Step 1 is antioxidant defence happening at low oxidative stress levels. When reaching a medium oxidative stress level, step 2 takes place: inflammation. Step 3, the highest oxidative stress level finally is cytotoxicity. (Li et al. 2003)

An important role for the lung's defence is played by components of the respiratory extracellular lining fluid (RELF), such as small antioxidant molecules, proteins and unsaturated lipids. The concentration of antioxidants like vitamin C and enzymatic antioxidants like Glutathione S-transferases (GST) is very high, rendering the RELF an important factor when it comes to the defence against oxidants and radicals. (Gilliland et al. 1999)

2.2.1. Through ambient particulate matter induced oxidative stress

Particulate matter not only varies in composition, size and origin but also in its health effects. One task regarding the health effects of particulate air pollution is finding ways to measure these properties. For this purpose we can use the oxidative properties, which can be seen as the capacity to induce oxidative stress and therefore serves as an indicator for the human health issues of particulate matter. (Yanosky et al. 2012)

Ambient particulate matter has proinflammatory effects on the lung. Like in vivo and in vitro studies already proved, generating oxidative stress is one of the major mechanisms leading to its health issues (Li et al. 2008). It is proposed that chronically increased oxidative stress is one of the reasons for long term effects of particulate matter and air pollutions (Gilliland et al. 1999). The lung is a target for a lot of oxidative stressors, which produce irritation, as it has the body's largest surface area that is directly exposed to the environment and therefore to environmental pollutions (Gomez-Mejiba et al. 2009).

Particulate matter shows complex interactions with the lung-tissue leading to oxidative, enzymatic, and radical attacks. Induced oxidative stress is thereby accompanied by an alteration of the immune regulation as well as repeated inflammatory responses which can overcome the lung's defence mechanisms. (Gilliland et al. 1999)

2.3. Ascorbic Acid

The biologically active forms of ascorbic acid are known as vitamin C. The highest bioactivity among these substances is found for the L-ascorbic acid and the dehydro-L-ascorbic acid. (Elmadfa et al. 1996)

Regarding the molecular structure, L-ascorbic acid is a 2,3-enediol-L-gulonic acid-γ-lactone (Nyyssönen et al. 2000) with two enolic hydrogen atoms. Those hydrogen atoms are easily ionizable and due to this are responsible for the acidic character (Elmadfa et al. 1996) (pKa_1=4,25; pKa_2=11,79) (Davis et al. 1991).

Vitamin C is essential and produced by a variety of plants and animals. Throughout mammals humans and some other primates as well as guinea pigs are the only species which are not capable of producing it and therefore depend on the intake of an adequate amount of Vitamin C trough their diet. A lack of vitamin C in the diet causes scurvy. (Nishikimi et al. 1996)

Ascorbic acid can serve as a reductant by donating electrons leading to dehydro-ascorbic acid. Thereby it shows a very high reducting power when compared to other biological molecules, whereas there are a number of biological molecules with the ability to regenerate ascorbic acid (Jacob et al 1996). The opening of the lactonering from the dehydro-ascorbic acid is irreversible and leads to a loss of its biological activity (Berlitz et al. 2001).

In general the transition from ascorbic acid to dehydro-ascorbic acid differs due to the conditions. Several influencing variables can play a role like temperature, pH-value, or oxygen partial pressure. Also the presence of metals can show an influence, since an oxidation catalyzed by metals takes places much faster than a spontaneous one. Notably this effect takes place for Cu^{2+} and Fe^{3+} (Berlitz et al. 2001).

Ascorbic Acid can be detected via UV-absorption. The absorption depends on the pH-value and shows a maximum at 244 nm when the pH-value is 2, at 266 nm when the pH-value is 6-10 and at 294nm when the pH-value is above 10 (Berlitz et al. 2001).

2.3.1. Redox properties

This redox system of ascorbic acid is complex. L-ascorbic acid and dehydro-L-ascorbic acid have acid-base properties, meaning that every redox process involving this species is also affected by proton transfers (Davis et al. 1991). At a pH-value of 7.4, 99.95% of the ascorbic acid exists as $AscH^-$ ion (Van Limburg Stirum 2008).

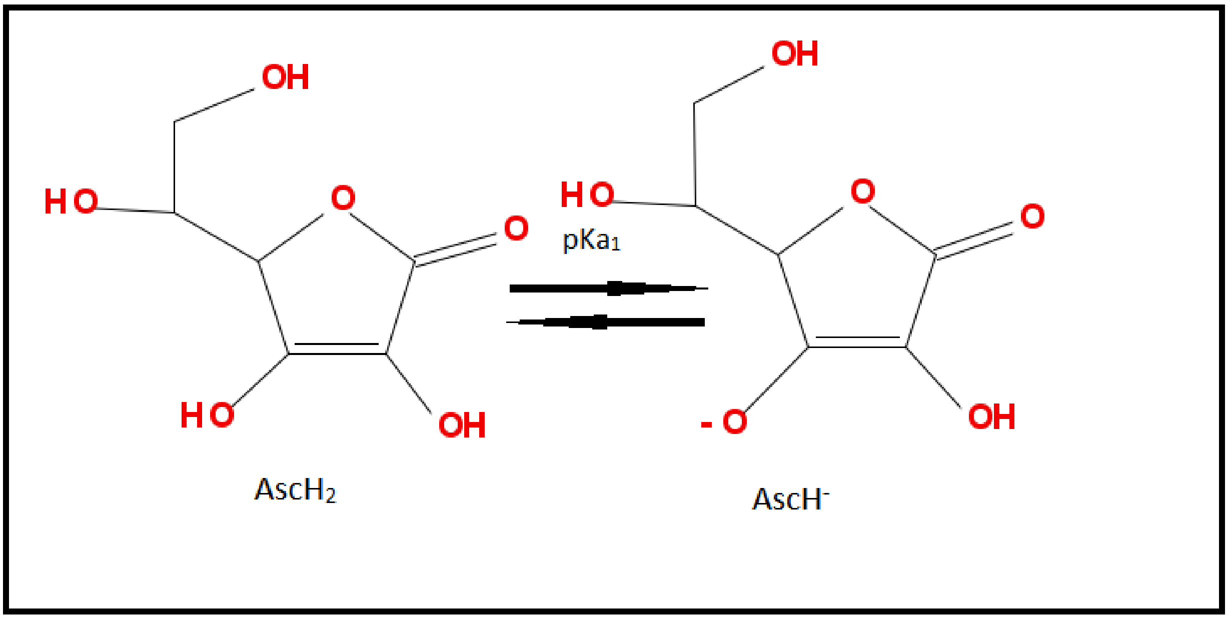


Figure 2.2.: Equilibrium of ascorbic acid based on van Limburg Stirum 2008.

All ascorbic acid species show their own oxidation behavior. In aqueous solution the redox-potential E_0 ranges from -0.05V to +0.70V. The reduction from $AscH_2$ to $AscH^-$ e.g. shows a redox-potential of 0.40V, the further reduction to Asc^{2-} shows one of 0.28V. (Davis et al. 1991)

In aqueous solutions exposed to air, oxygen oxidates ascorbic acid not just to dehydro-ascorbic acid, but also further, over the in chapter 3.3. described irreversible step, into its biological inactive form. It is therefore important to always prepare aqueous ascorbic acid solutions freshly if needed. (Davis et al. 1991)

For simplicity in this work the term ascorbic acid (AA) will be used to cover both species the undissoziated ascorbic acid as well as ascorbate present in the buffer used for the depletion experiment.

3. Materials and methods

3.1. Samples and Sampling

The measurements were done with different ambient and indoor air samples collected within a variety of projects or within the ambient air sampling networks of provincial governments. Details about those projects are listed below.

Furthermore emission samples containing particulate matter that was formed during combustion processes was analyzed. The fuels for those combustion experiments were brown coal, stone coal, beech, cardboard packages of fruit juice, alder, and wood briquettes. Details about the emission sampling are given by Luisser et al. (2008) and Schmidl et al (2008).

Also, two biological samples were measured: dried and grained linden leaves and wood splints. Those samples were prepared within the work presented here.

For the sampling of ambient air samples Digitel High Volume Sampler equipped with quartz fibre filters with a diameter of 150mm were used.

Most of the samples investigated were taken from the Sparkling Science project 'Does particulate matter concern me?'(SPA03-033) (Jankowski et al. 2013). The samples were collected between January and April in two schools in Vienna, the HBLVA Rosensteingasse and the BRG Fichtnergasse, indoors and outdoors.

To get an idea how wide or narrow the oxidation range occurring in our cities and the countryside is, also samples from the projects PMinter (unpublished data) and Aquella (Jankowski et al. 2009; Bauer et al. 2006) as well as samples collected within the ambient air sampling network in Graz were analysed (Gurgul 2013). The samples from Graz were PM2.5 samples, all other ambient and indoor samples were PM10.

Table 3.1.: Summary of different projects, sampling sites and the periods of time of the sampling:

Project	Sampling site	Sampling time
Sparkling Science (SPA03-033)	**Vienna** – Fichtnergasse (urban) and Rosensteingasse (urban)	January – April 2011
Aquella – Vienna	**Vienna** – Kendlerstraße (urban) and Schafberg (urban background)	January and October 2004
PMinter	**Styria** – Arnfels (rural) and Leibnitz (urban) **Carinthia** – Klagenfurt-Völkermarktstraße (urban), Klagenfurt-east (urban background), and Ebenthal-Zell (rural) **Slovenia** – Maribor (urban) and Vrbanski-Plato (rural)	February 2011
Aquella – Upper Austria	**Upper Austria** – Linz Römerberg (urban) and Enzenkirchen (rural)	October 2005 and January 2006
-	**Graz** – Graz north (urban) and Graz south (urban)	January 2013

The samples from previous projects had been stored in a deep freezer set to approx. -20°C at the Institute for Chemical Technologies and Analytics at the University of Technology in Vienna.

3.1.1. Sampling sites

From the Aquella campaign samples from Vienna (Kendlerstraße and Schafberg) and from Upper Austria (Linz-Römerberg and Enzenkirchen) were used. Kendlerstraße and Linz-Römerberg are both urban sites, which show elevated concentrations of ambient particulate matter. Schafberg and Enzenkirchen were used as a background station.

As an example the sampling stations Graz north and Graz south are shown in the figure below.

Figure 3.1.: The sampling stations Graz north (left) and Graz south (right) taken from the homepage of the environmental agency from Austria[1].

The samples from Vienna also gave the opportunity to compare outdoor samples taken from the Sparkling Science project to some different ambient air samples collected in Vienna.

The samples from the Sparkling Science project were collected at two schools, the BRG Fichtnergasse and the HBLVA Rosensteingasse. The HBLVA Rosensteingasse is technical secondary school with educational focus on chemistry with approx. 1000 pupils located at a densely populated residential area showing some traffic influence; the BRG Fichtnergasse is a standard secondary school with approx. 500 pupils located in a residential area with many single-family houses and private gardens.

Further on these sites will be called Fichtnergasse and Rosensteingasse and together will be defined as Vienna school samples.

Figure 3.2.: Sampling sites in Vienna of the Vienna school samples (HBLVA Rosensteingasse and BRG Fichtnergasse) and the Aquella Samples (Kendlerstraße and Schafberg).

From the PMinter-project samples collected in Styria (Leibnitz and Arnfels), Slovenia (Maribor and Vrbanski Plato) and Carinthia (Klagenfurt and Ebenthal-Zell) were used. From Klagenfurt two sets of samples were available: Klagenfurt-east and Klagenfurt-Völkermarkstraße.

Leibnitz, Klagenfurt-Völkermarktstraße, and Maribor are urban sampling sites; Klagenfurt-east is an urban background sampling site; Arnfels, Vrbanski-Plato, and Ebenthal-Zell are rural background stations.

Figure 3.3.: Sampling sites of the PMinter Samples in Carinthia (Klagenfurt and Ebenthal Zell), Styria (Leibnitz and Arnfels) and Slovenia (Maribor and Vrbanski Plato).

Figure 3.4.: Sampling sites of the Aquella Samples in Upper Austria (Linz-Römerberg and Enzenkirchen).

The environmental agency in Styria has several sampling sites in Graz. Samples from the sampling sites Graz- north and Graz-south were used. Graz generally shows above average concentrations of ambient particulate matter due to its position in a basin.

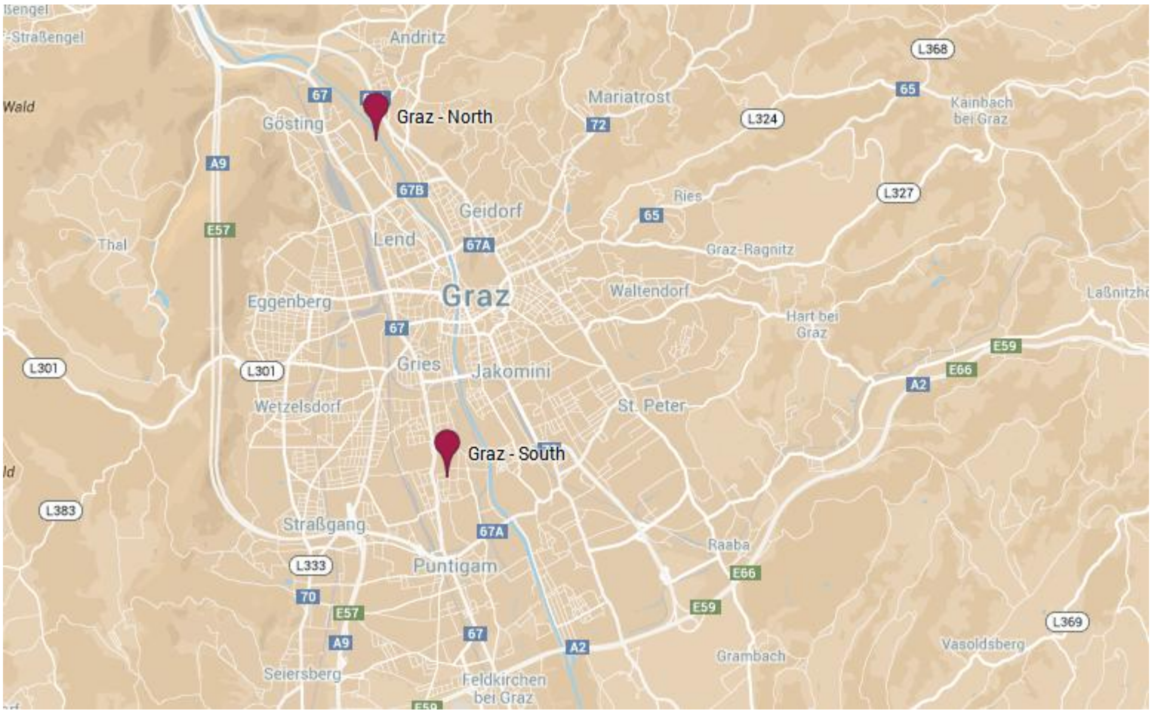


Figure 3.5.: Sampling sites in Graz (north and south).

Figure 3.6.: Overview over the sampling sites.

3.2. Analysis of the aerosol composition

The chemical composition of all aerosol samples had already been analyzed separately from this project. Within the work presented here this data is compared to the depletion of AA determined for the single samples. The analysis of chemical composition had been done at the Institute for Chemical Technologies and Analytics at the University of Technology in Vienna. Results are already published in a number of reports (Jankowski et al. 2013; Jankowski et al. 2009; Bauer et al. 2006; Gurgul 2013; Kistler et al. 2013[a,b,c]). Details about the analytical methods are given in these reports and just briefly mentioned here.

The carbon parameters had been analysed with a thermo-optical method (based on a method by Birch et al. 1996). Inorganic anions and cations were analysed with ion chromatography (IC) using standard techniques. Metals/mineral dust elements were measured with either X-ray fluorescence analysis (XRF) or with inductive-coupled-plasma mass-spectrometry (ICP-MS).

Saccharides were used for the determination of the contribution of wood smoke and were analysed with a high performance liquid chromatography (HPLC) based on a method by Iinuma et al. (2009).

For most samples the content of the mineral dust elements iron, silicium, and aluminium, as well as magnesium and calcium was determined. Since the data of most trace metals was only available for a limited amount of samples, the focus of the comparisons between chemical composition and depletion of AA was put on the mineral dust elements. Other trace metals which have been found to influence the oxidative properties (e.g. Li et al. 2003; Halliwell et al. 1984) are discussed when available.

3.3. Method and Measurement

The method for the determination of the depletion of AA is based on the work of Zielinski et al. 1999 and Mudway et al. 2001 also seen at Künzli et al. 2006 and Godri et al. 2011. To cut the filters, a 5 mm diameter punching tool was used. For the measurement 5 50 ml PE-flasks per filter were prepared (one for each determination of ascorbic acid at the time steps given below). 1-2 filter punches (see chapter 3.4.1.) were put into every flask and 15 ml of the buffer solution containing 35ppm ascorbic acid were added. This buffer solution should imitate the RELF (respiratory extracellular lining fluid, see chapter 3.2.). The flasks were put into a shaker with a heating device holding the temperature at 37°C. This shaker was darkened since light increases the oxidation of ascorbic acid. The concentration of ascorbic acid was determined at the beginning and then again after 60, 120, 180 and 240 minutes. In every series of measurements also two blanks (5 flasks per blank containing a blank filter punch and 15 ml of the buffer solution with 35ppm L-ascorbic acid) were measured, to account for the auto-oxidation of L-ascorbic acid and influences from the filter itself. This blanks showed a depletion of AA of approx. 5ppm after 180 min with some day to day variations.

The actual depletion of ascorbic acid was calculated as the difference between the measured depletion of the sample to the depletion of the blank, at any time step. As result the depletion after 180 minutes was used, since at that time the values were high enough to be distinguishable, but still within the linear range. The loss of AA was first calculated as an absolute mass [µg AA] and then related to the PM mass in µg collected on the filter punch, or the filter punches. Therefore the result was the depletion of AA after 180 minutes in µg AA/µg PM mass.

3.3.1. Analytical Determination, equipment, and chemicals

The analytical detection of ascorbic acid was based on a method described by Stefan (1999). It was detected with a high performance liquid chromatography system from Dionex with a Merck 50983 Li-Chrospher RP-18 column (250x4mm; mean grain size 5µm). The eluent was a H_3PO_4/NaH_2PO_4 buffer, set to a flow rate of 1 ml/min. The system back pressure was 1500-1600 PSI. For detection a Dionex AD25 UV-detector, set to 243nm, was used. The data evaluation was done with the software chromeleon.

For the quantification of AA a multipoint calibration was done before every series of measurements. Therefore standards were prepared daily out of an aqueous stock solution containing 1000ppm AA (VWR Normapur prolabo patch 0403186), prepared daily as well. The final concentrations of the standards were 10, 20, 30, 35, and 40 ppm AA in aqueous solution.

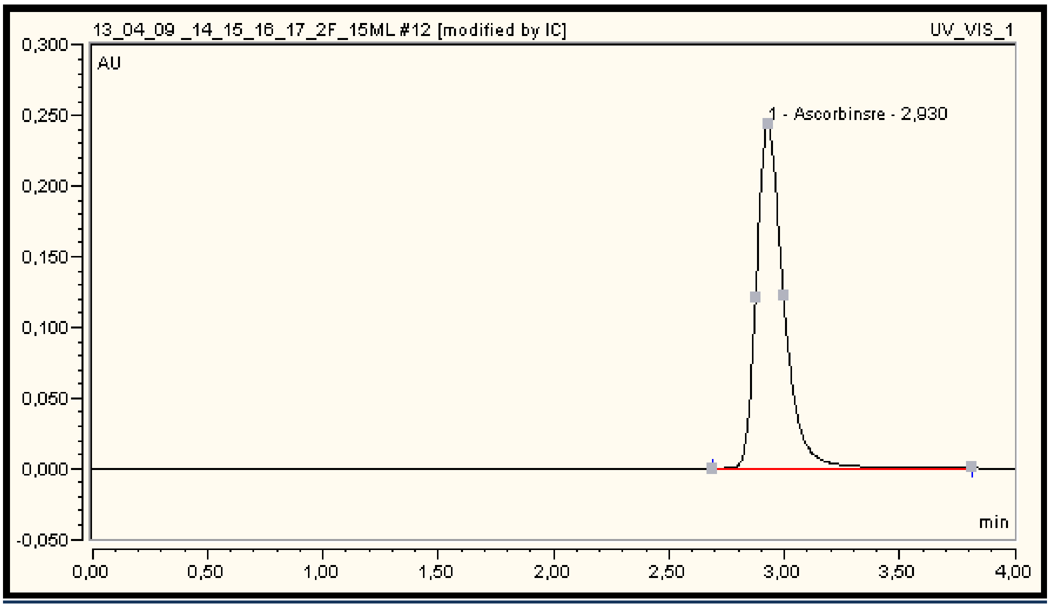


Figure 3.7.: A typical AA peak obtained through the described method.

Details about the preparation of the eluent and the buffer solution imitating the RELF are given below.

Table 3.2..: Preparation of eluent and buffer solution:

Eluent	
Mass/Volume	
2.76g	$NaH_2PO_4 \cdot H_2O$
4ml	Ortho-H_3PO_4
1.9l	H_2O
Buffer	
Mass/Volume	
16.0g	NaCl
0.4g	KCl
7.27g	$Na_2HPO_4\cdot$
0.48g	KH_2PO_4
~10ml	HCl 0,1 mol/l
1.9l	H_2O

The pH-value of the eluent was 2, the pH-value of the buffer solution was adjusted to 7.4 with HCl.

All used chemicals were from Merck with p.a. quality. Every preparation was done with ultrapure water (Milli Q Reference).

3.4. Optimization of the Method

The measurements were done with various punch sizes and volumes of buffer solution in different vessels. The goal was to find a method showing a linear relationship between time and depletion of ascorbic acid since it is important for the comparability of the results.

· **Variations of the Sample Mass**

For the experiments punches with a diameter of 5, 4, 3 and 2mm were used. Results obtained with the smaller punches showed a higher deviation and were hard to evaluate. Also, all filter punches had very frayed edges leading to a higher mass variation for smaller punches. Due to this, the work was continued with 5mm punches and a focus was laid on changing the amount of buffer added.

· **Variations of the Buffer Volume**

The measurements were done with volumes of 3, 8 and 15ml of buffer solution in different vessels. For the 3 and 8ml measurements polyethylene-tubes of different sizes were used; for the 15ml measurements 50 ml polyethylene-flasks were used

The results obtained with 8ml tubes did not turn out as well as expected, therefore a closer look on the shaker was taken. Elderberry-syrup was applied at the bottom of the tubes which then were carefully filled with water, so that syrup and water did not mix. The tubes were placed in the shaker and controlled several times. The results showed that the mixing effect was very poor and also varied depending on where on the shaker the sample was placed. This strong dependence on the position in the shaker explains the weak reproducibility which had been found at the beginning of the investigations.

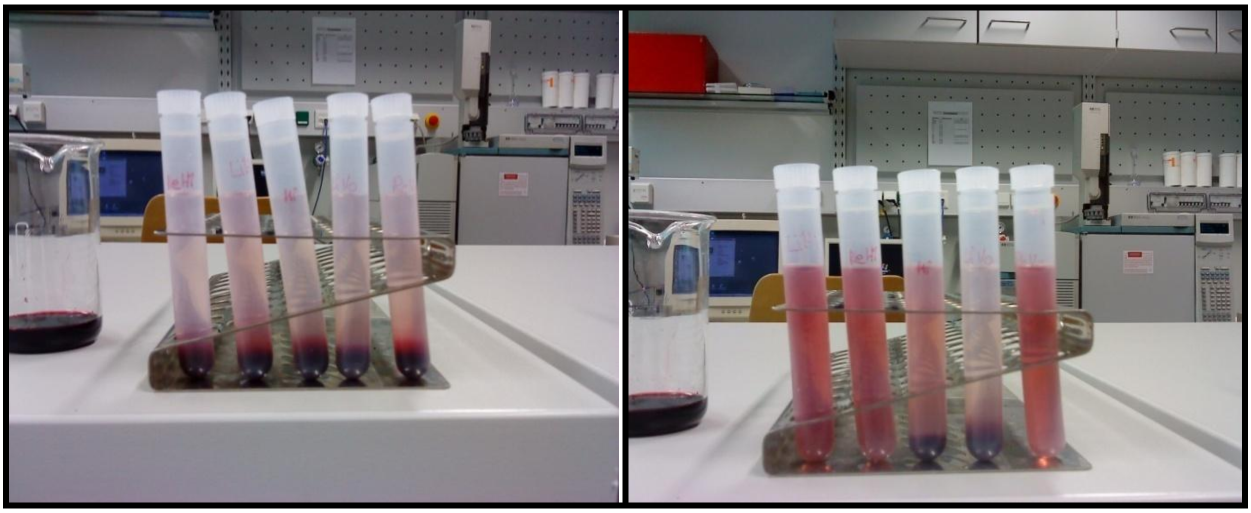


Figure 3.8.: the syrup samples after one hour (left picture) and three hours (right picture) placed in the shaker f.l.t.r. left in the back, right in the back, in the middle, left in the front, right in the front.

Since the poor mixing performance was incompatible with conducting a reliable experiment, small bottles were used instead of tubes. These bottles, with a volume of 50ml had a bigger base area. Therefore the level of the liquid was low and the mixing effect was much higher. Using the flasks made it possible to use a larger volume of buffer solution and consequently more or larger punches containing higher mass of particulate matter.

3.4.1. Deviation of the Method

For the determination of the uncertainty of the used measurement, four different samples collected in Vienna were measured three times with different methods to determine standard deviation and mean depletion of AA, except for sample 101 measured with the 3ml method, which was only repeated twice. The results of these measurements are given below.

Table 3.3.: The relative standard deviations of the measurements with different volumes; all used punches had a 5mm diameter:

	3ml	8ml		15ml		
	1 punch	1 punch	2 punch	1 punch	2 punch	
Sample number	Relative standard deviation [%]					PM mass collected on a 5mm punch [µg]
106				37	14	17,22
117		18	13	10	6	32,93
116		25	4	15	10	34,27
101	12	18	12	8	11	88,02

Table 3.4.: The mean of the AA depletions in µg AA / µg determined within experiments with different buffer volumes; all used punches had a diameter of 5mm:

	3ml	8ml		15ml		
	1 punch	1 punch	2 punch	1 punch	2 punch	
Sample number	Mean of results [µgAA/µgPM]					Mass of a 5mm punch [µg]
106				1.22	1.01	17,22
117		1.46	1.46	1.49	1.52	32,93
116		1.00	0.81	0.85	0.82	34,27
101	0.46	0.87	1.04	0.98	0.8	88,02

The samples used for the 8ml and 15ml measurement got measured three times with each method.

In the measurements there was a visible trend for a higher mass leading to a smaller deviation therefore the samples are ranked by mass.

Regarding table 3.3. it is obvious that 3ml measurements did not work. The mass of AA provided was too little leading to a flattening of the relationship between time and depletion, consequently the depletion determined was too low. Also the 3ml measurements showed relative standard deviations around 20-40% for medium loaded filters and still >10% for heavy loaded filters.

Due to the results the 15ml measurements were chosen using one punch for heavy loaded filters and two punches for little loaded filters. The measurements were started with the Vienna school samples for which 2 punches were used. Since most of the other used samples showed higher oxidative properties in regards of AA in the mean, the measurements were continued with one punch afterwards. As standard deviation related to the measurement an uncertainty of approx. 10% was used, based on this data.

4. Results

4.1. Comparison of different filter materials

Sampling of ambient particulate matter in sampling networks is done on different kind of filters. Thus the most common filter-types were tested for their ability to be used as sampling substrates when the oxidative properties in regards of AA of the aerosol samples should be tested. Following filter-types were used for the experiment:

-quartz fibre filter (47mm) Pall Life Sciences; membrane filters; Tissuquartz 2500QAT-UP; Lot No 56077

-glass fibre filter (150mm) Munktell; „Glass Microfibre Discs“; Grade 277/1/60; Art No 3.01124.150

-glass fibre filter (70mm) Whatman Schleicher & Schuell; Typ GF/A; Cat.No. 1820070

-glass fibre filter (50mm) Ederol; containing organic binders; qual. 277/1/60

-glass fibre filter (47mm) Pall; Typ A/E; P/N 61631

-teflon filter (47mm) Pall; „Zefliuor“; supported PTFE; 1,0µm, P/N P5PL047

-cellulose nitrate filter (50mm) Whatman Schleicher & Schnell; 0,45µm; Membranfilter; REF 10401114; LOT FN 0366-1

-cellulose filter paper(70mm) Schleicher & Schnell; 5891; black ribbon ashless; Ref. No. 300 008

From the quartz fibre filter, the glass fibre filters, and the teflon filters 5mm punches were used for the measurements. Since the cellulose nitrate filters and the cellulose filter papers could not be punched with the used punching tool, they were cut in triangles of an altitude of approx. 25mm for the cellulose nitrate filters and 35mm for the cellulose filter papers, and a base of approx. 5mm.

A punch or a triangle was put into a test tube and 3 ml of the buffer solution containing 35 ppm ascorbic acid was added. In the following the samples were treated as described before in the method section. In case of quartz fiber filters six replicates were analyzed. As quartz fiber filters were used in the present study, these filters were investigated in more detail. All the other filter types were measured only once. To obtain the results shown in figure 4.1. and 4.2., the depletion of ascorbic acid determined for the blank filters was corrected with the depletion determined for a standard solution. This subtraction resulted in negative values, when the blank filters showed less depletion than the standard solution and positive values for depletions higher than those of the standard solution.

The average depletion of the AA concentration in a 3ml standard solution accounted to approx. 30 % after 240 min. The overall uncertainty of the method (as calculated in chapter 3.4.1.) has a standard deviation of 10%, leading to a result of 30% ±3%. Thus depletions of AA of ±3% can already be due to fluctuations of the standard concentrations and need not show an influence of the filter material. Therefore this range is given as a shaded area in Figures 4.1. and 4.2..

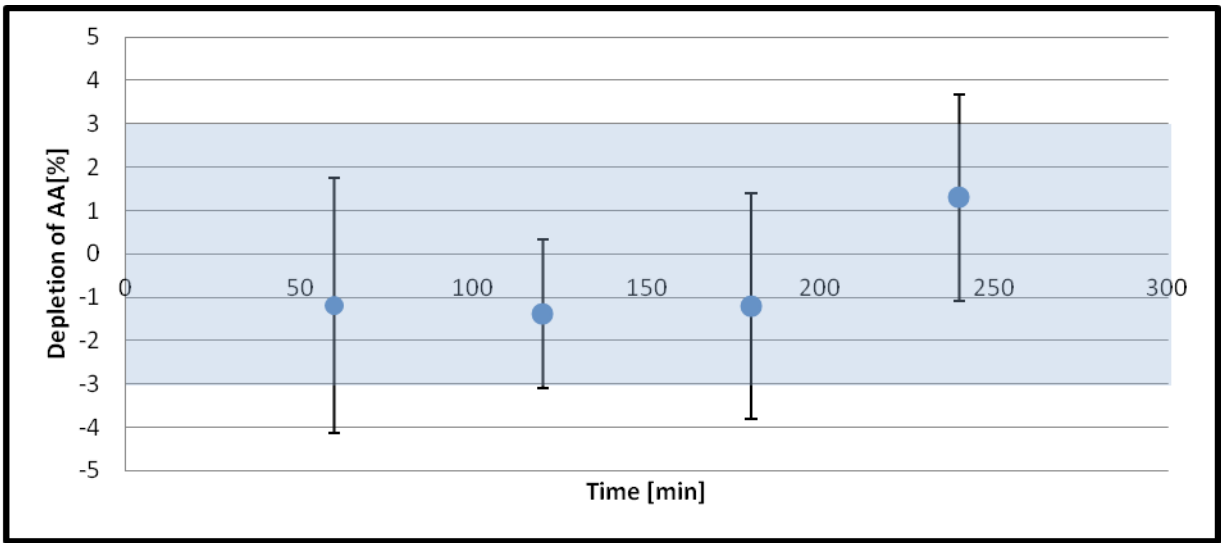


Figure 4.1.: The depletion of AA for quartz fibre filters from six different measurements.

Regarding figure 4.1., the fluctuation of the depletion of AA can be seen very well, but most of the results are within the range determined already due to the variations of the standard concentrations. The figure shows the mean depletion of six different measurements with their standard deviations. The depletion varied from approx. -5 to approx. +5 %. No temporal trend was visible. The results led to the conclusion, that quartz fibre filters show no major influence on the analytical method itself and can be used for the measurements. Nevertheless, since the standard deviation shows higher variations than the 3% determined for the 3ml standard solution, blank filters should be analysed parallel to every set of measurements.

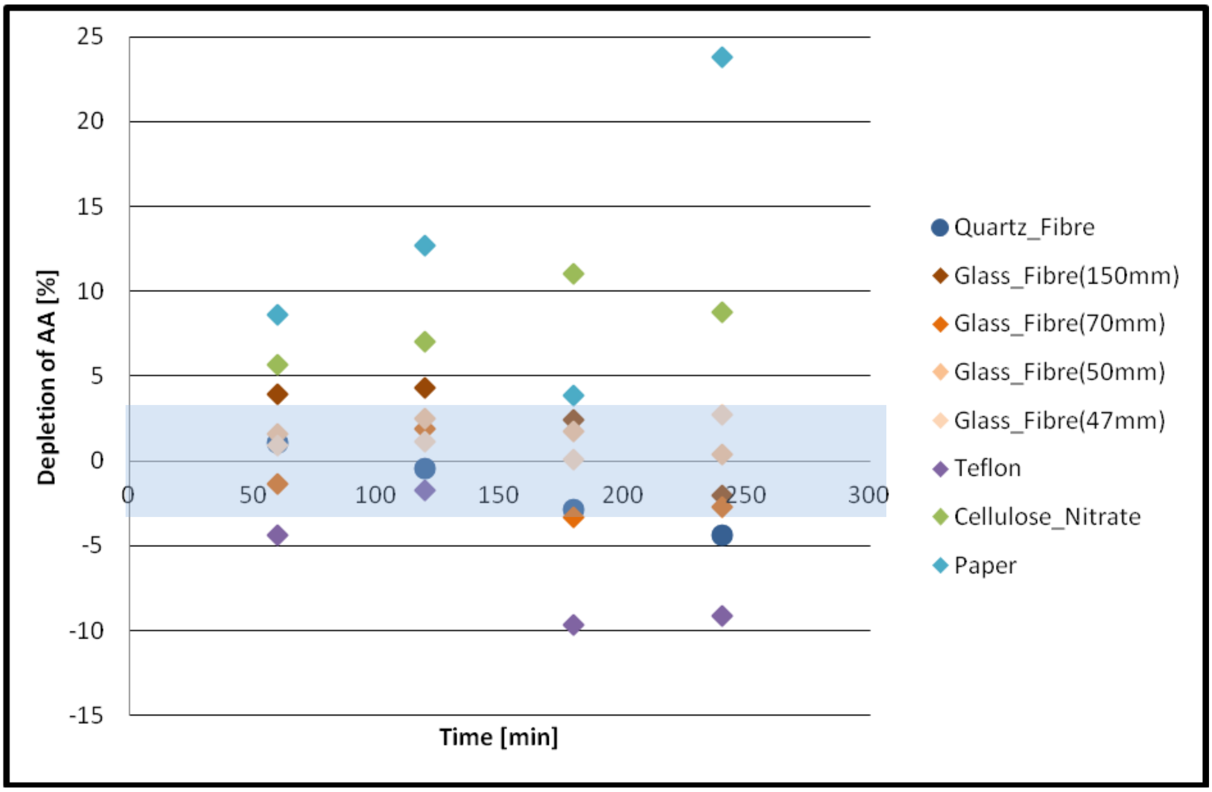


Figure 4.2.: The depletion of AA for the different filter types.

As mentioned above, the quartz fibre filters showed a range of approx. -5 to +5%. If this range was used as the range of fluctuation, the glass fibre filters as well as the quartz fibre filters lay in it, while the cellulose nitrate filters and the cellulose filter papers lay clearly above. For these filters special care should be taken before using them for measurements based on the depletion of AA. The teflon filters showed a high fluctuation and data that went down to nearly -10 percent leading to values below -5% for 180 and 240 min. Here the depletion of AA was even lower, than within the pure standard solutions. Thus this result should be investigated in more detail before using this material for analysis, since only one set of data was analysed here.

4.2. Samples collected in Vienna

4.2.1. Samples collected in and close to two schools in Vienna

The depletion of ascorbic acid obtained for most of the samples collected at Rosensteingasse und Fichtnergasse ranged from 0.4 to 2.4 µgAA/µgPM. Three samples showed much higher values reaching up to 5.3 µgAA/µgPM. On the whole 68 samples have been analysed. In the figures 4.3. and 4.4. the depletion of ascorbic acid is related to the mass of particulate matter collected on a filter punch of 5 mm diameter. As all filters have the same size and the sampled air volumes are nearly constant for all measurements, this value is also proportional to the average ambient air concentration of particulate matter. On a first glance the results suggested a trend of higher depletion at lower mass loadings of the filter. This could point to a systematic error due to an inappropriate analytical set-up, with e.g. inappropriate ratios of ascorbic acid and particulate matter concentrations provided for the experiment. However the experiments with varying volumes of ascorbic acid/buffer mixtures and different punch sizes (Table 3.4.) showed that this was not the case. Further analysis of the data for Fichtnergasse showed a clustering of the results according to indoor and ambient air measurements, as well as, in terms of indoor air samples, to measurements carried out during working days and the weekend.

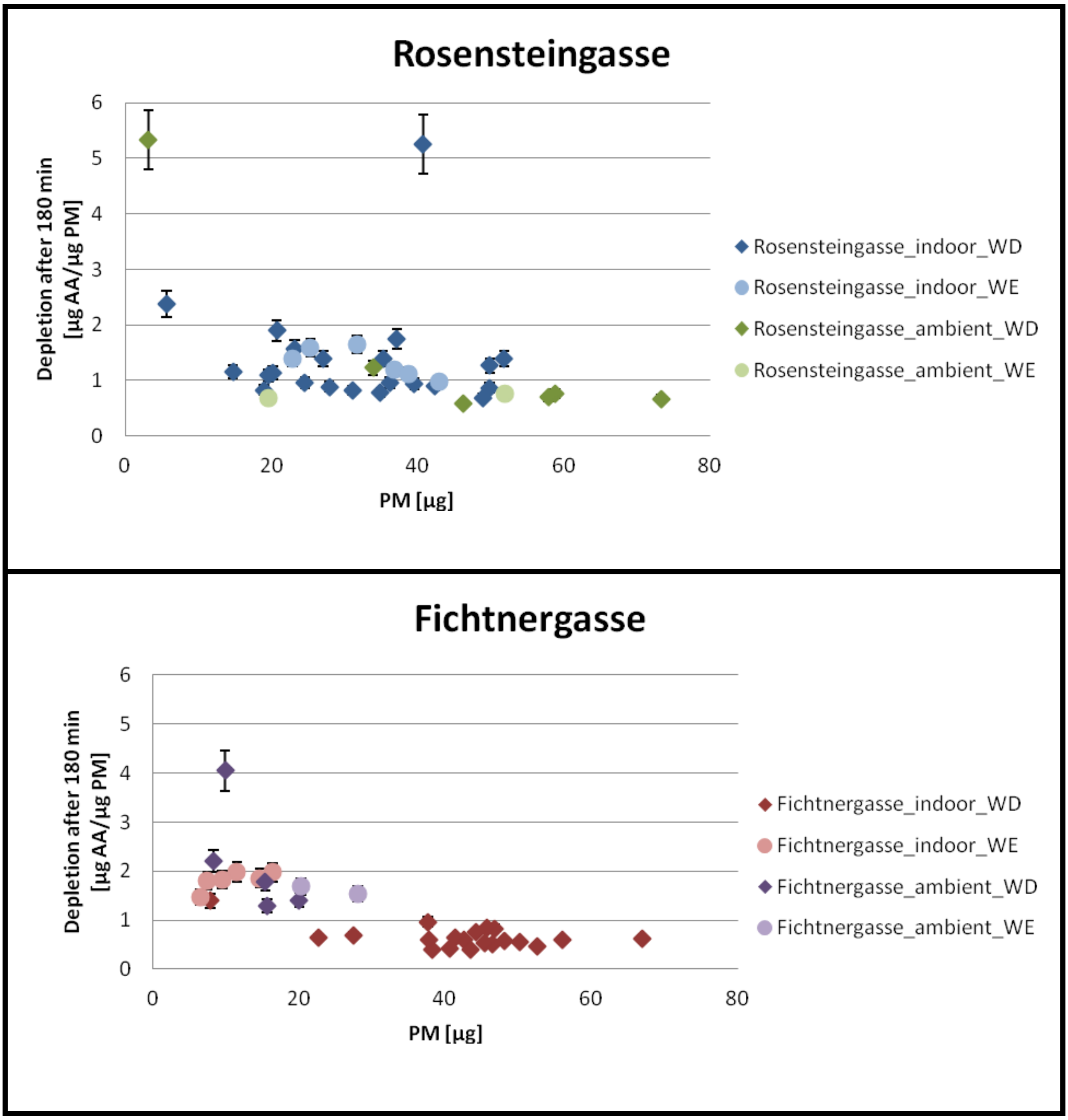


Figure 4.3.: The depletion of AA for samples collected at two schools in Vienna (indoor air and ambient air) related to aerosol mass collected on a filter punch of 5mm diameter. WD refers to samples collected during a working day; WE refers to samples collected on a weekend. Error bars point to a standard deviation of 10% determined during multiple analysis.

As can be seen in figure 4.3., the samples collected at Rosensteingasse showed no apparent difference regarding on whether they were sampled indoors or outdoors, on working days or during the weekend. The distribution was very homogenous with only two samples showing a surprisingly high depletion of AA. One of those two samples was from the indoor area, sampled on a working day. During that day a heating pipe was cleaned right next to the sampling device, which is a logical explanation for this high loss of AA. Since influences occurring outdoors are more difficult to identify, no explanation for the ambient sample with the far above average depletion can be given here.

Different to the samples from Rosensteingasse, the indoor samples from Fichtnergasse showed a clear separation between working days and weekends, and between indoor and ambient samples. While the oxidative properties of the working day samples stayed nearly constant, the samples collected on the weekends showed depletions of AA being much more similar to the ambient samples, showing higher depletions at smaller masses. This is in agreement with the chemical analysis of the filters. Chemical compositions of the filters collected on working days and during the weekend were quite different, if indoor samples were regarded. Due to the lack of resuspension of typical ambient particulate matter that is produced indoors, such as cellulose (Kasper-Giebl et al. 2013), the composition and mass of indoor aerosols collected on weekends is more similar to ambient samples.

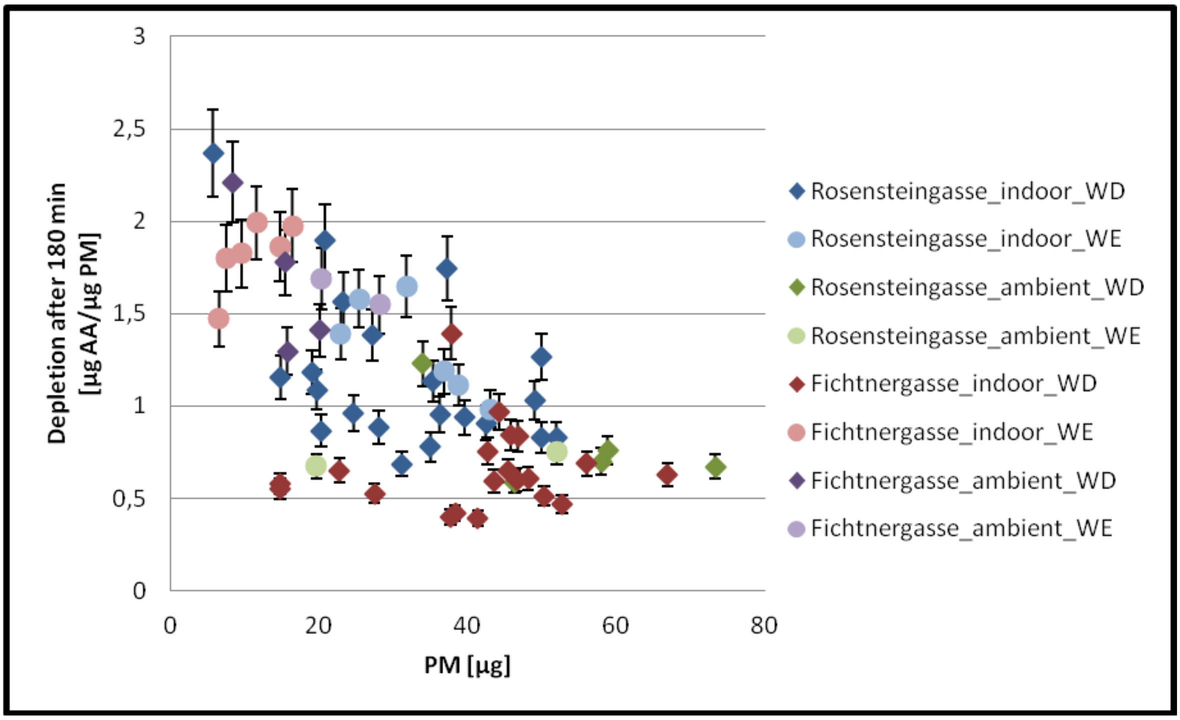


Figure 4.4.: The results of Rosensteingasse and Fichtnergasse in one plot. WD refers to samples collected during a working day; WE refers to samples collected on a weekend. Error bars point to a standard deviation of 10%, determined during multiple analysis. The three values above a depletion of 3 µgAA/µgPM were excluded.

Figure 4.4. summarizes data from both sites. Comparing indoor samples collected during working days, particulate matter mass is well comparable between the two schools, although values tend to be higher in Fichtnergasse. The average loss of AA, on the other hand, is higher in Rosensteingasse compared to Fichtnergasse, but again the data is overlapping. Generally the indoor samples from Rosensteingasse showed higher variations in depletion of AA than the samples from Fichtnergasse, which may had been due to higher ambient particulate matter concentrations. Weekend and working day samples collected indoors differ markedly in Fichtnergasse, but do not show any difference in Rosensteingasse. What also can be seen is that the mass of the ambient and the indoor weekend samples from Fichtnergasse lay together much closer than the ones from Rosensteingasse.

Table 4.1.: The average depletion of AA and its standard deviation of the samples collected in two schools in Vienna. WD refers to samples collected during a working day; WE refers to samples collected on a weekend. Three data points showing maximum values are excluded:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
Rosensteingasse_ indoor_WD	21	1.16	0.42	27	1.20	0.39
Rosensteingasse_ indoor_WE	6	1.32	0.27			
Rosensteingasse_ ambient_WD	5	0.79	0.25	7	0.77	0.21
Rosensteingasse_ ambient_WE	2	0.71	0.06			
Fichtnergasse_ indoor_WD	20	0.65	0.23	26	0.92	0.55
Fichtnergasse_ indoor_WE	6	1.81	0.19			
Fichtnergasse_ ambient_WD	4	1.67	0.41	6	1.66	0.32
Fichtnergasse_ ambient_WE	2	1.62	0.10			

Regarding the deviations in table 4.1. it can be seen that values obtained in Fichtnergasse collected indoors showed less variation than those from Rosensteingasse (though the sample showing a depletion above 3 µgAA/µgPM was excluded), as long as working day and weekend samples were regarded separately. The Rosensteingasse values showed smaller deviations for the ambient samples and when indoor WD and WE samples are combined. While the values separated by working day and weekend showed now big difference for the Rosensteingasse (they do not show any difference when the standard deviation of the data is considered), the Fichtnergasse showed a clear separation between samples collected indoors on a working day and during a weekend. The deviation range of the samples collected during the weekend overlapped with the ambient values from both, working days and weekends.

In general it can be said that Rosensteingasse showed higher depletions for indoor samples and lower depletions for ambient samples compared to Fichtnergasse.

4.2.1.1. Comparison with Chemical Composition

In this section the chemical composition of aerosol samples is compared with the observed depletion of ascorbic acid. Thus it was possible, to check whether the depletion of ascorbic acid was enhanced by special compounds. The concentrations of aerosol constituents were related to the overall aerosol mass concentration, to base the comparison on relative contributions. The maximum value of the x-axis on the plots, showing the depletion of AA, was fixed to 3µgAA/µgPM. This gives a better overview of the majority of data, but excludes the three days with special condition. Therefore they will be discussed separately.

The composition analysis as well as the calculation of source contributions was not done within this thesis, but was taken from the final report of the project ‘Does particulate matter concern me?’(Jankowski et al. 2013)

4.2.1.1.1. Carbon parameters and source contributions

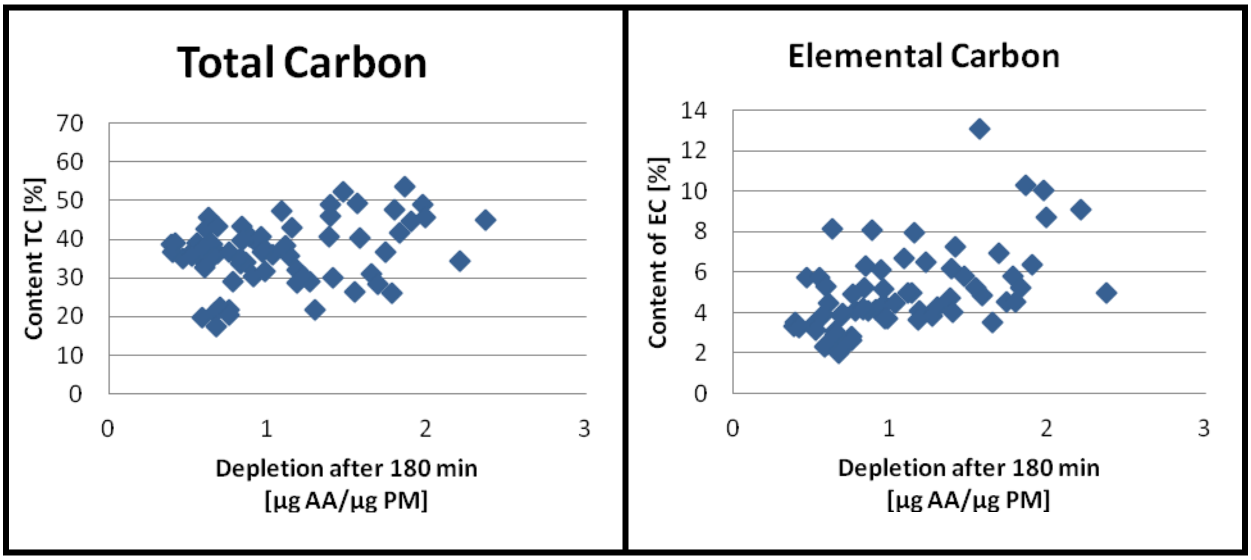
The following chapter is concerned with the influence of different carbon parameters total Carbon (TC), Organic Carbon (OC), Elemental Carbon (EC) and Carbonate Carbon (CC), on the depletion of AA of the Vienna school samples.

Total Carbon can be split into OC, EC and CC. However, CC was not determined for all samples. In that case TC was built by the sum of OC and EC, leading to no remarkable deviation since the CC values were very low compared to EC and OC.

All of this carbon species can be present in different forms with different surfaces and different chemical composition, thus they can vary in their influence on the oxidative properties of the PM.

Additionally the concentration data of carbon parameters together with the concentration of levoglucosan was used to calculate source contributions of traffic exhaust and wood burning, leaving a part of OC (OC-unidentified), which could not be assigned to either wood burning or traffic. These calculations were performed using the Macro-tracer approach (Bauer et al. 2006). Possible influences of the contributions of those aerosol sources were investigated as well.

The TC content found within the samples from Rosensteingasse and Fichtnergasse ranged between 18 and 59 % (a day with special conditions).



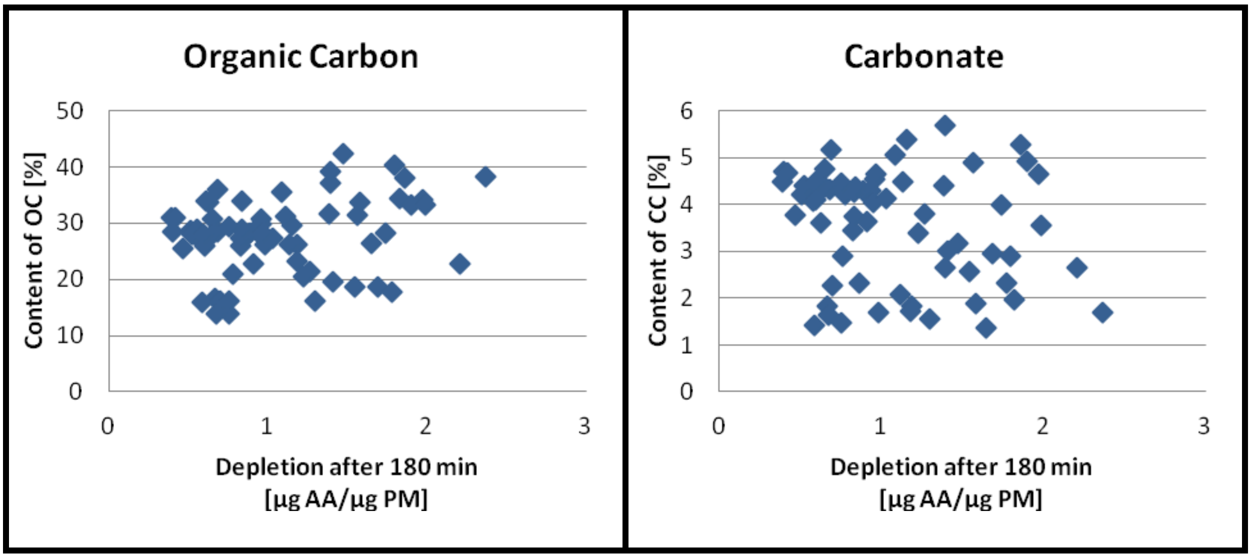


Figure 4.5.: The relation between the content of TC/ different carbon species and the depletion of AA.

The comparison of CC content and depletion of AA showed a broad scattering of data points and no trend. The comparison of OC content and depletion of AA and the comparison of TC content and depletion of AA showed less scatter as that for CC but they still did not show a clear trend when the whole dataset was considered. Further analysis showed that trends emerged when sampling sites and sampling times were considered (see following figures). Since OC showed the highest contribution to TC, the two figures comparing their content and the AA depletion looked very similar.

In terms of EC it seems that higher content leads to higher depletion of AA in the samples collected at Fichtnergasse and Rostensteingasse. This weak trend might point to the very complex mixture of the aerosol samples. Elemental carbon seems to have an influence, but it is not the only compound responsible.

If the two schools as well as the indoor and ambient values are regarded separately, the trends become more visible.

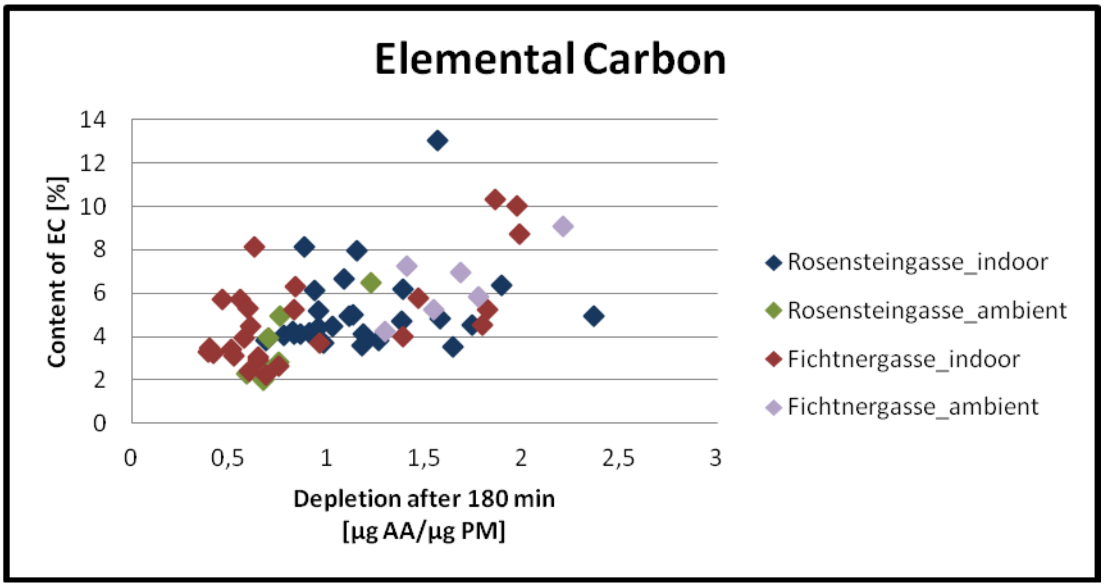


Figure 4.6.: The relation between the content of EC and the depletion of AA.

Figure 4.6. shows that the trend for indoor samples is much less pronounced, than the trend for ambient samples. It also shows that the relative content of EC of indoor and ambient samples lay in the same range.

While the EC content in the four sampling sites was homogenous, the OC and therefore also the TC content varied and showed higher values for the samples collected indoors. The same trend was shown by CC but less clear. This is due to indoor aerosol sources such as cellulose or dust originating from construction material. During the working hours these dust particles get resuspended and form a constant background of particulate matter concentrations.

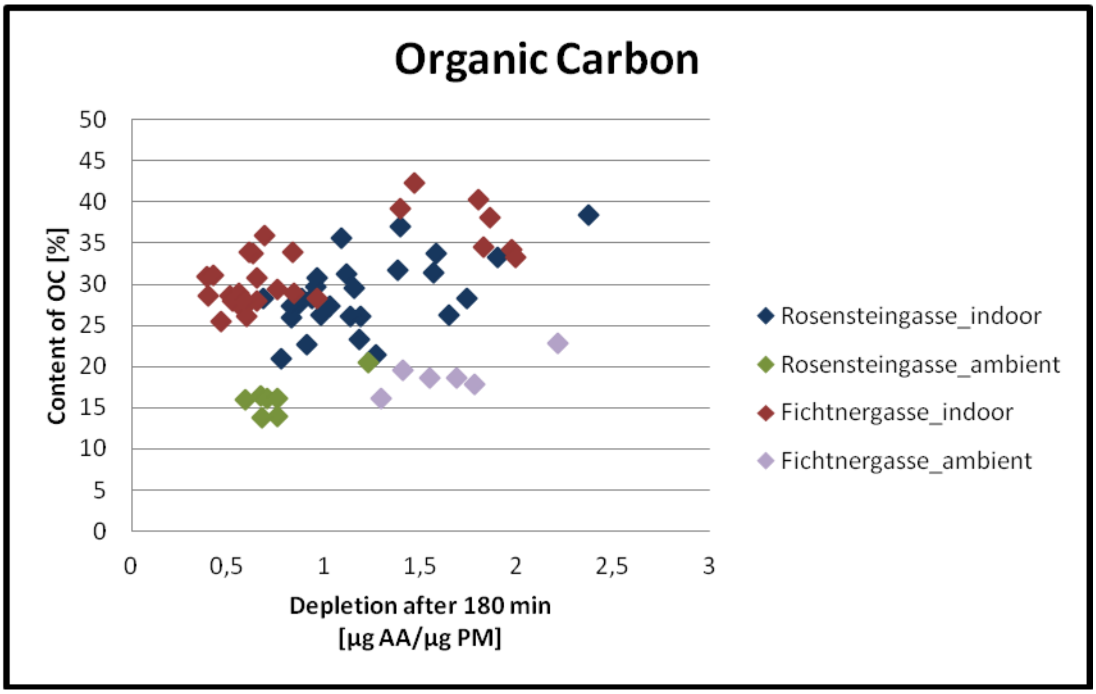


Figure 4.7.: The relation between the content of OC and the depletion of AA.

OC showed a positive trend for all four categories, but marked differences exist between indoor and ambient air. The data points showed again less scattering for the ambient samples while other than for EC, the relative contribution of OC to aerosol mass was much higher for indoor samples than for samples collected in the ambient.

The ambient samples and the indoor samples from the two different schools matched very well.

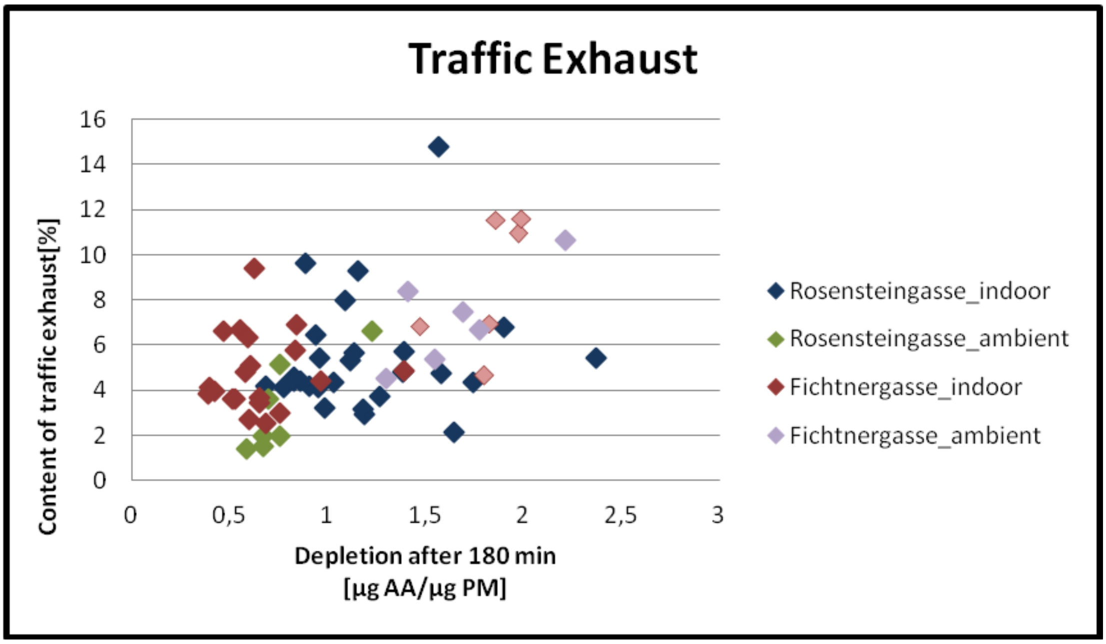


Figure 4.8.: The relation between the content of traffic exhaust and the depletion of AA. Fichtnergasse weekend samples are marked in light red.

Similar to EC, particulate matter related to emissions from traffic exhaust exhibited a general positive trend being especially pronounced for ambient samples. In general ambient samples collected at Fichtnergasse showed a higher contribution of traffic exhaust to particulate matter mass than those collected at Rosensteingasse. This would not be the case when absolute concentrations would be considered, since ambient samples from Fichtnergasse showed smaller PM masses.

Rosensteingasse indoor samples, on the contrary, if considered alone, hardly any trend would be visible.

The indoor samples collected on a weekend at Fichtnergasse (marked in light red) matched the ambient samples very well. This behaviour was not seen for OC (figure 4.7.), but was already identified, when the general loss of AA related to particulate matter mass was discussed (Figure 4.4).

Traffic exhaust is mostly influenced by EC but also contains some OC.

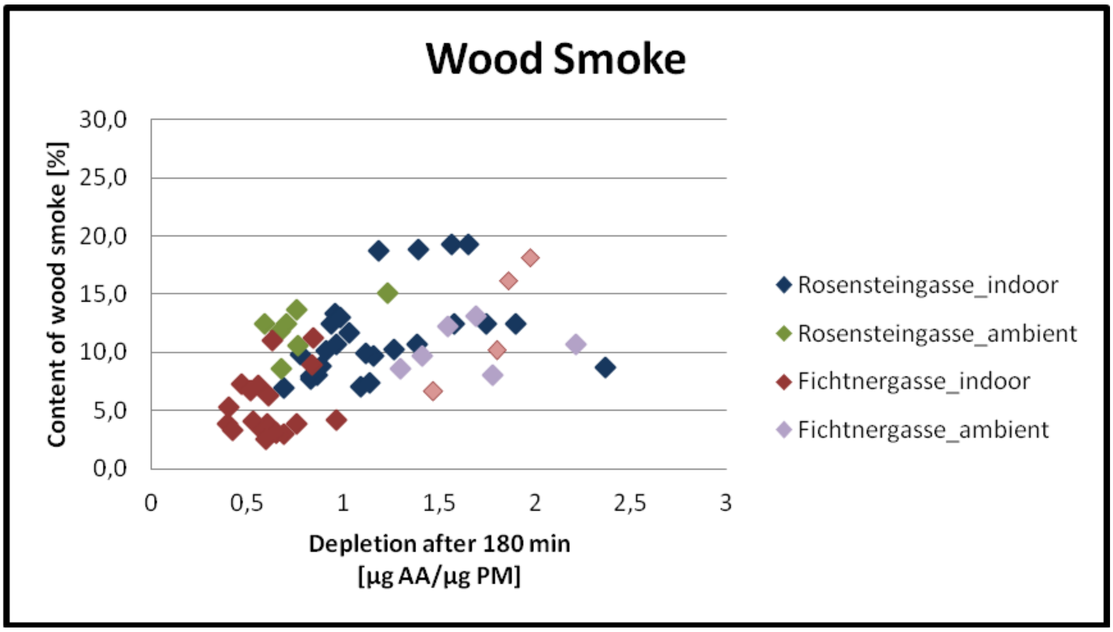


Figure 4.9.: The relation between the content of wood smoke and the depletion of AA. Fichtnergasse weekend samples are marked in light red.

Wood smoke showed a positive trend for the indoor samples while the ambient samples showed a mostly constant content and therefore no trend. The weekend samples from Fichtnergasse were similar to the ambient samples (only four were determined).

In general ambient samples and Rosensteingasse samples collected indoors matched, regarding their contribution of wood smoke, while the Fichtnergasse samples collected indoors showed mostly below average concentrations, especially if the weekend samples are excluded.

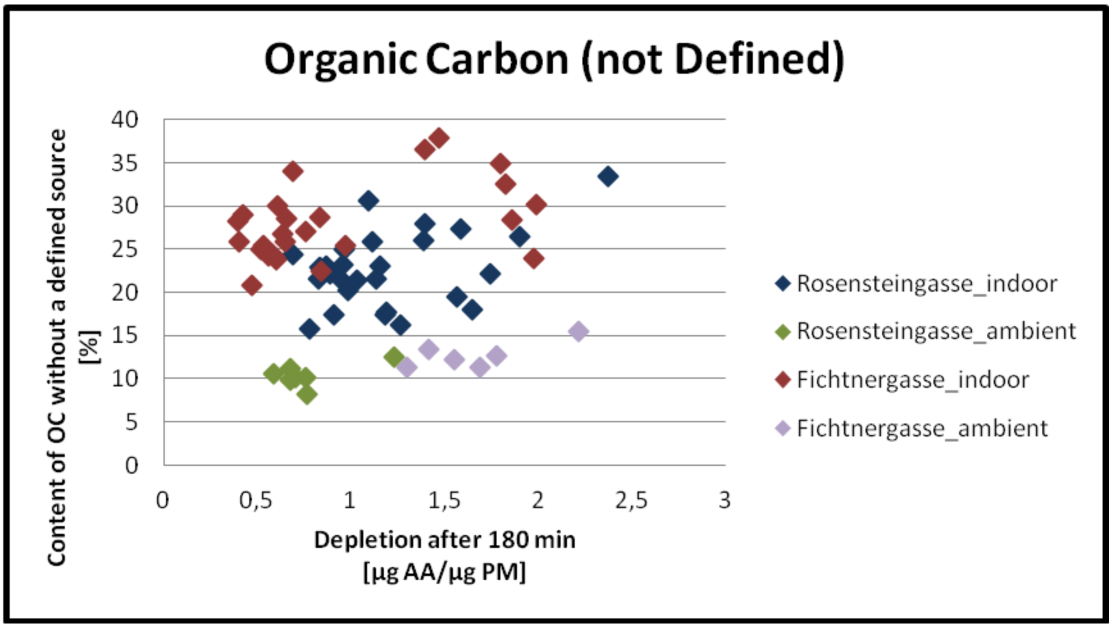


Figure 4.10.: The relation between the content of OC without a defined source and the depletion of AA.

OC without a defined source showed some positive trend for the outdoor samples. A trend for the indoor samples was hard to define. The weekend samples collected indoors at Fichtnergasse did not match the ambient samples.

The broad scattering of data points that was shown by the indoor samples matched the expectations since their OC without a defined source showed high contents in materials like cellulose that are not expected to influence oxidative properties and are not found in ambient PM in such high concentrations (Kasper-Giebl et al. 2013).

As discussed above, depletions above 3 µgAA/µgPM were not regarded in the former figures to show the data below 3 µAA/µgPM in more detail; therefore those three days with special conditions will be discussed in the following.

Three samples with depletions above 3 µgAA/µgPM were found as already mentioned: one Rosensteingasse sample collected indoors and one collected outdoors as well as one ambient Fichtnergasse sample.

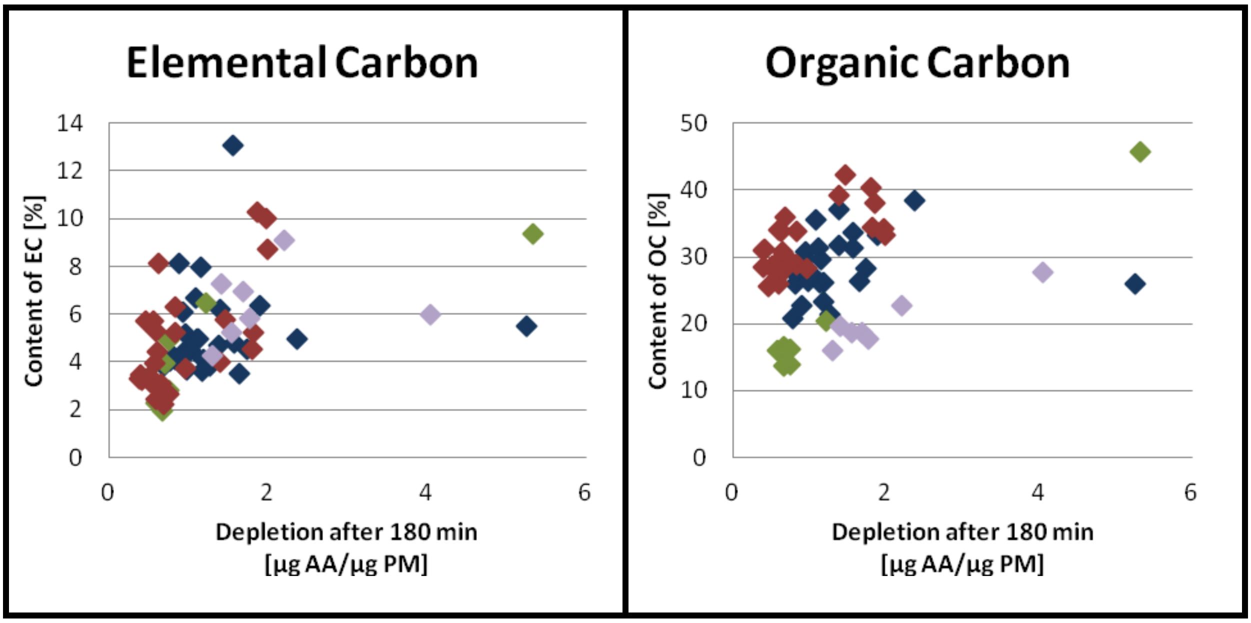


Figure 4.11.: The relation between the organic and elemental carbon content and the depletion of ascorbic acid. The colours used to mark the different categories are chosen similar to the other Vienna school sample plots.

The three samples with a depletion of AA above 3 µgAA/µgPM showed high EC contents, however not as high as to confirm the trends indicated by the rest of the data set. They were above average but they did not show the highest concentrations (except for the ambient Rosensteingasse sample). A different picture is obtained in regards of OC. Both ambient samples matched the trend suggested by the ambient air samples with depletions of AA below 3 µgAA/µgPM. The Rosensteingasse sample collected indoors showed below average content, but as mentioned a heating pipe next to the sampling device was cleaned. Substances might be collected during this process are not expected to show an above average contribution of OC.

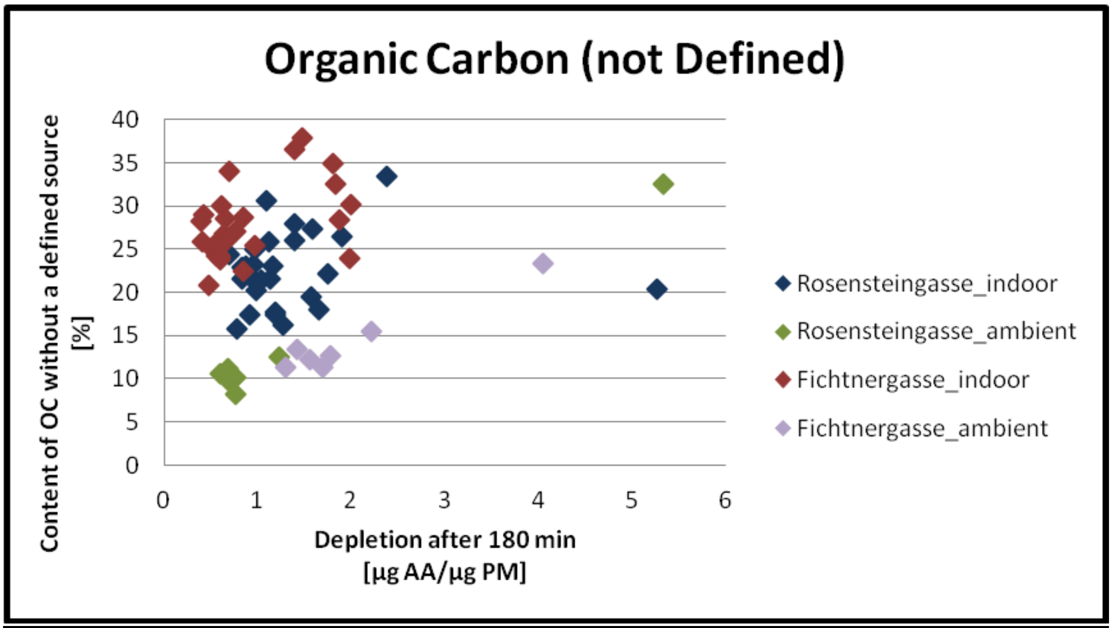


Figure 4.12.: The relation between OC without a defined source and the depletion of AA.

The trend that has been seen for OC relied on undefined OC. A linear trend has not been seen for OC from wood smoke or traffic exhaust.

4.2.1.1.2. Inorganic ions

This chapter discusses the possible influence of inorganic ions on the depletion of AA. The ions were categorized in major and minor ions depending on their ratio of the PM mass. As major ions ammonium, nitrate, and sulfate were defined. Their sum represented 5-60% of the PM mass, while the sum of the minor ions only represented 1-10% of the PM mass. The minor ions determined within the samples from Fichtnergasse and Rosensteingasse were chloride, sodium, potassium, magnesium, and calcium.

In general ambient samples showed a higher ion content than samples collected indoors.

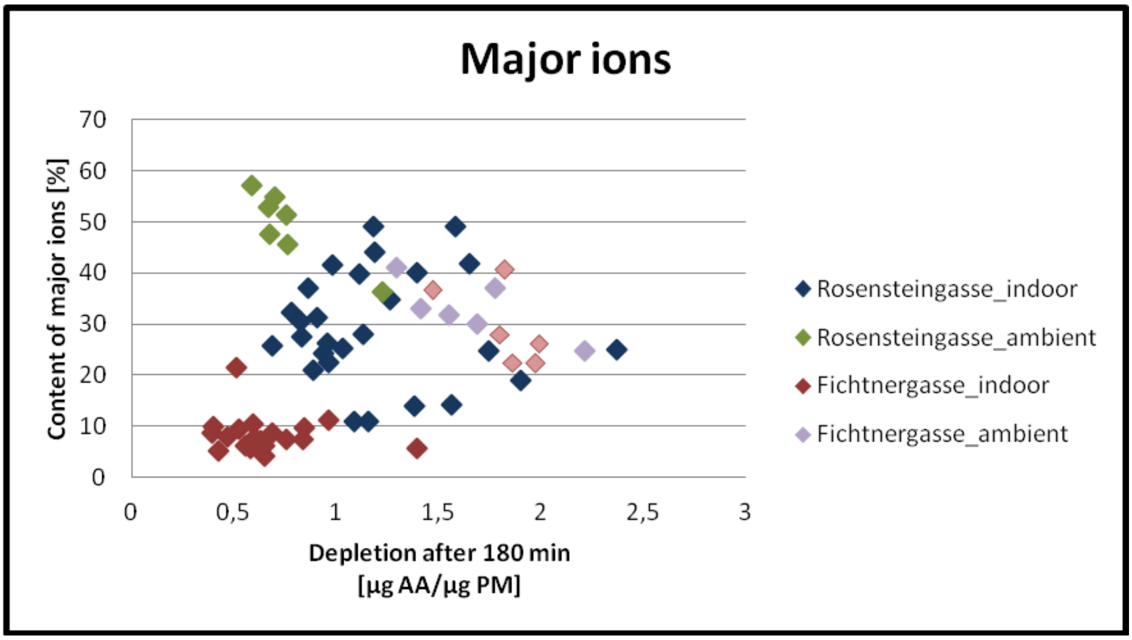
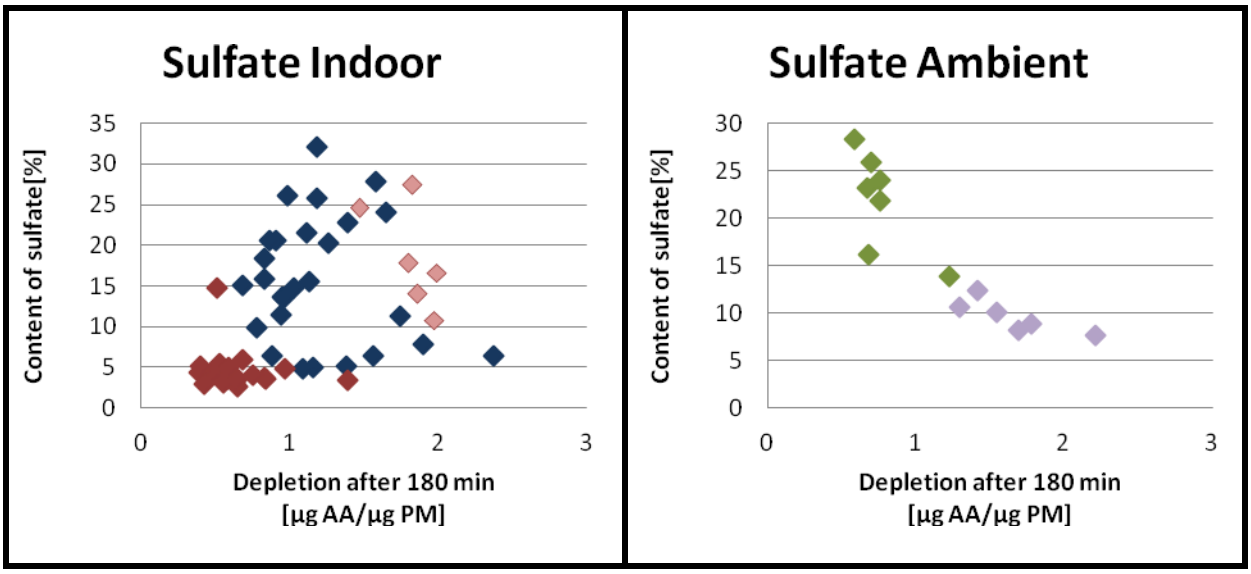


Figure 4.13.: The relation between the sum of major ions (nitrate, sulfate and ammonium) and the depletion of AA. Fichtnergasse weekend samples are marked in light red.

Generally ions are not expected to show a high influence on the oxidative properties.
The depletions of AA in figure 4.13., related to the content of the major ions nitrate, sulfate, and ammonium, showed very different trends for indoor and ambient samples. While the ambient samples showed a clear negative trend, the samples collected indoors, on the first glance, showed a positive one. Remarkable is that the majority of Fichtnergasse indoor samples had a rather low contribution of major ions to aerosol mass. Obviously other sources of indoor aerosol mass exist in Fichtnergasse, reducing the relative contribution of ions and determining the oxidative properties with different intensity. The samples with a higher contribution of ions to PM mass (over 20%) were, with one exception, those with elevated ascorbic acid depletions. All of those were weekend samples and matched the conditions visible for ambient air samples from Fichtnergasse. If only work days are considered for Fichtnergasse, no positive trend between the mass content of major ions and depletion of AA is visible any longer. The positive trend noted before was simply driven by the fact that during weekends the indoor sources (resuspension of dust due to the movement of pupils and teachers) are less pronounced and the chemical composition of the samples resembles ambient air. If just the ambient samples are considered, higher contributions of ions are associated with lower values of depletion of AA. This again points to the fact that other compounds than ions are responsible for the depletion of AA.



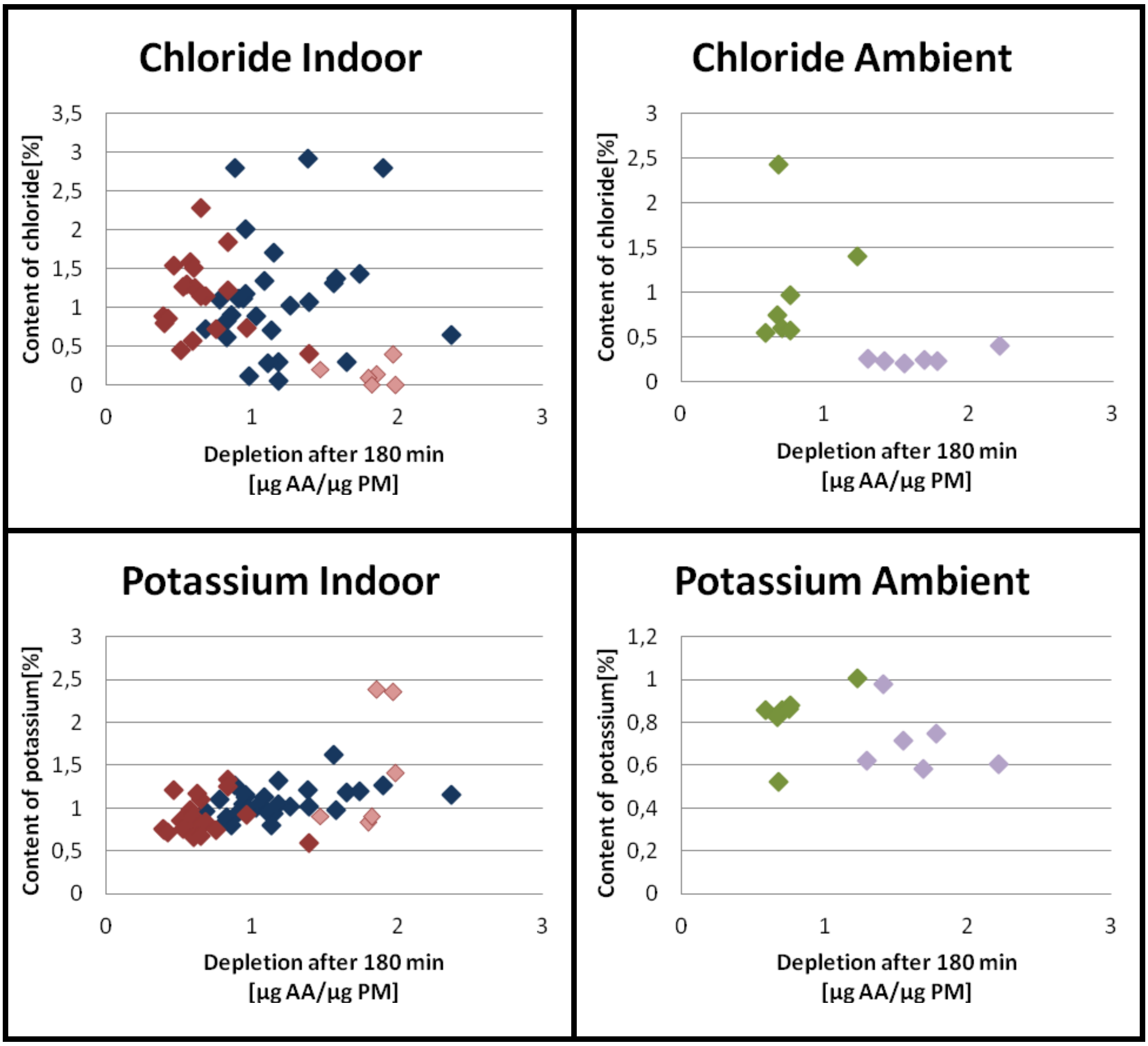


Figure 4.14.: The relation between the content of different ions and the depletion of AA sorted by indoor and ambient samples. The colours used to mark the different sample categories are used analogically to the figures above; Fichtnergasse weekend samples are marked in light red.

Regarding figure 4.14. it is obvious that indoor and ambient samples behaved very different when single ions were considered as well. For indoor samples, depending on the compound, marked differences are observed between Fichtnergasse and Rosensteingasse leading to a lot of scatter. In case of Fichtnergasse the weekend samples for some species again can be compared with ambient air samples. From ambient samples most ions showed a clear negative trend. This statement remains valid when both, Fichtnergasse and Rosensteingasse, are considered. Chloride showed a broad scattering of data points and no trend for indoor samples, while it showed a trend for ambient samples. Potassium showed a slight positive trend for indoor samples and no trend for ambient samples.

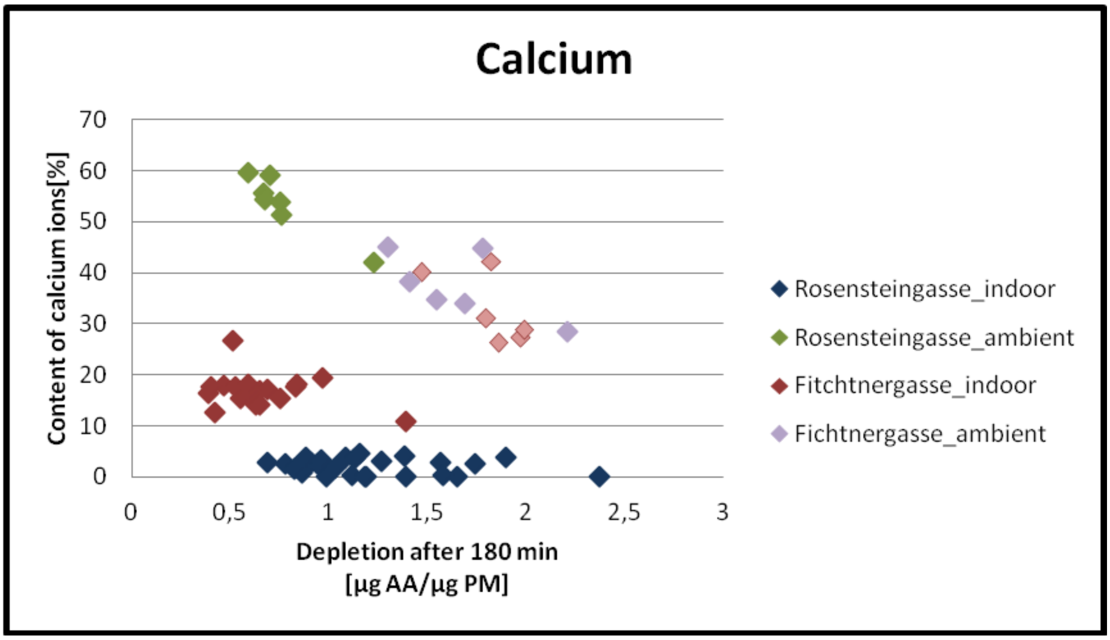


Figure 4.15.: The relation between the content of soluble calcium and the depletion of AA sorted in indoor and ambient samples. Fichtnergasse weekend samples are marked in light red.

As a last example the trend for calcium is given. Its content showed the biggest differences between the different categories of samples. While it showed a negative trend for ambient samples, it showed that in Fichtnergasse indoor calcium concentrations are much higher than in Rosensteingasse. Both sites showed rather constant ratios of calcium with no influence on the depletion of AA.

The data presented in this chapter leads to the suggestion that the relative contributions of ions to aerosol mass varies strongly if indoor and ambient samples from schools are compared. This is due to the different compositions and sources particulate matter derives from.

Compared to indoor samples from Fichtnergasse, indoor samples from Rosensteingasse showed higher concentrations of ions and they also showed a broader scatter, while Fichtnergasse indoor samples mostly showed constant. This leads to the conclusion that Rosensteingasse indoor ions derive from different sources.

A direct influence on the depletion of AA cannot be shown. Considering ambient measurements, high contributions of ions to aerosol mass give a tendency to lower depletion of AA per unit aerosol mass.

4.2.1.1.3. Metals

This chapter is concerned with the influence of the metal content of aerosol samples on the deletion of AA. A number of metals was determined in the samples collected at Rosesteingasse and Fichtnergasse. These were iron, aluminium, silicion, magnesium, titan, chrome, manganese, nickel, cobalt, copper, zinc, molybdenum, palladium, cadmium, tin, barium, and platinum. Also analyzed were strontium and vanadium, but both were not detectable in a concentration above the limit of quantification. As mentioned before analysis was not performed within the present study, but are given in Jankowski et al. (2013).

Analysis was done from cellulose acetate filters sampled in parallel to the quartz fibre filters used for the present study.

Highest concentrations were found for iron, silicon, and aluminium, three elements typically found in mineral dust. Their sum represented up to 20% of the PM mass depending on the sample. This contribution goes up to nearly 40% for the red marked data point explained below.

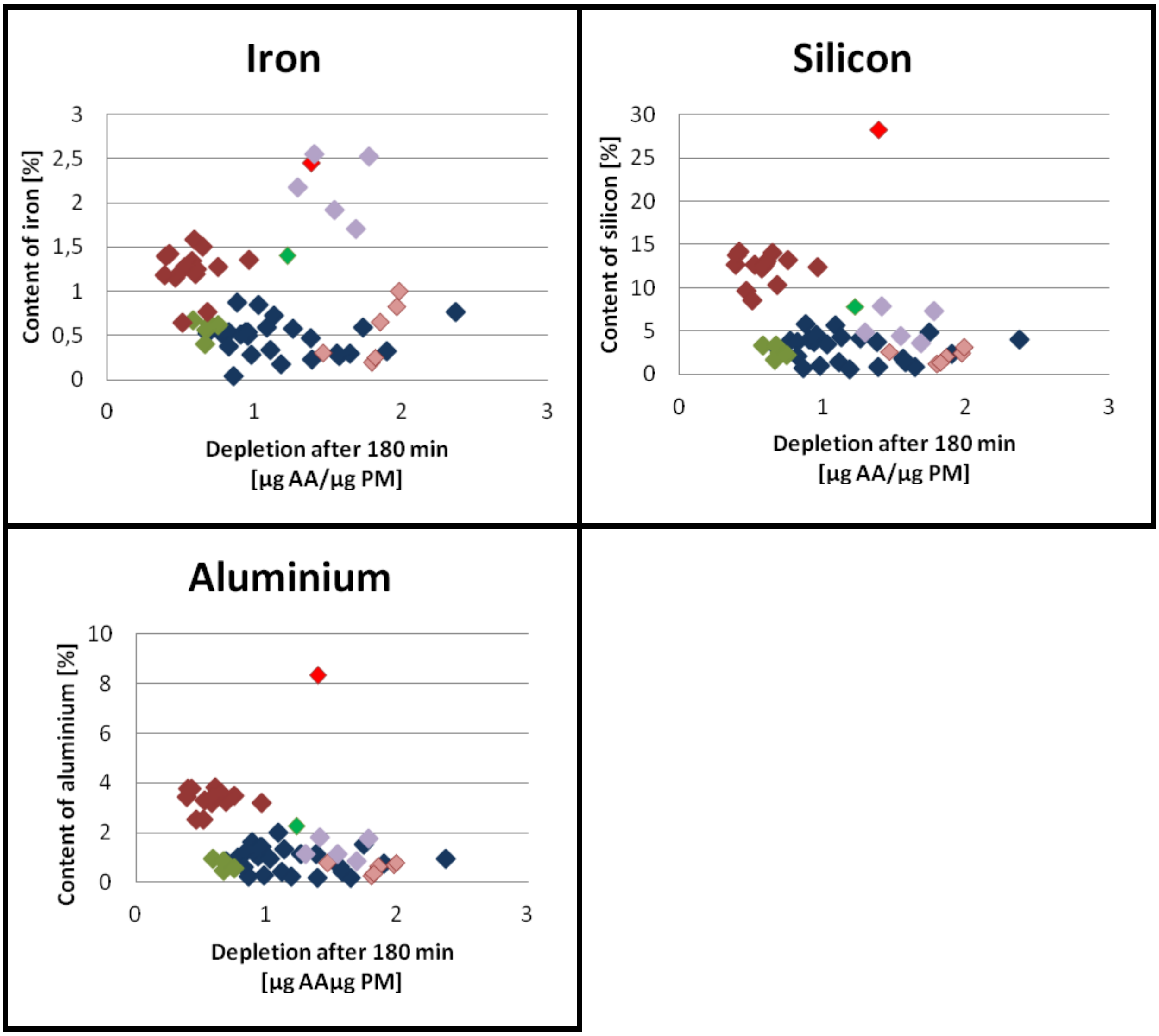


Figure 4.16.: The relation between the iron, silicon, and aluminium content of PM and the depletion of AA. The colours used to mark the different sample categories are used analogically to the figures above; Fichtnergasse weekend samples are marked in light red.

Silicon and aluminium both showed a slight negative trend, while no general trend could be observed when the iron content of PM and the depletion of AA were compared. Interesting is the data point marked in red in figure 4.16.. It was an indoor sample collected at Fichtnergasse on April 1th 2011 (a work day). On that day the PM sampler was moved and therefore it covers up only the PM mass of less than half a day (260m³ air compared to normally around 700m³ per day). This sample showed a very high content of all three metals while it has medium oxidative properties in regards of AA, if all Fichtnergasse indoor samples are regarded. If only the samples collected on a working day are regarded, it showed the highest depletion of AA for this sample category.

A separation of the sampling sites led to another interesting data point. The point marked in green belonged to an ambient sample collected at Rosensteingasse on March 2nd 2011 (a work day). This sample showed an above average content (compared to the other ambient samples collected at Rosensteingasse) in all three discussed metals and it also showed the highest oxidative properties in regards of AA of the ambient samples collected at Rosensteingasse. This led to a positive trend for iron, aluminium, and silicon for these samples. If this data point was not regarded, iron showed no trend, and aluminium and silicon showed a negative trend for the ambient Rosensteingasse samples.

Also remarkable is the big difference that was observable for the content of the Fichtnergasse samples collected indoors. While samples collected on a work day showed high contents in all three metals; samples collected on a weekend showed low content. This phenomenon is due to the resuspension of dust during working days, as already discussed before, and led to a clear separation visible in figure 4.16.. Aluminium and silicon still showed a negative trend for those samples, however, iron showed a positive trend if only the weekend samples were regarded and no clear trend for the work day samples, if the discussed data point marked in red is excluded.

If only ambient samples are regarded, a clear positive trend is visible for iron as well as a slight one for aluminium and silicon. The indoor samples in general showed negative trends for all three metals, except of the positive iron trend of the Fichtnergasse samples collected on a weekend.

Silicon contents above 10% and aluminium content above 3% were only found in Fichtnergasse samples collected indoors, iron contents above 2% only in ambient Fichtnergasse samples and in the red marked sample from Fichtnergasse collected indoors.

What was further observed were high contents in various metals for the three days with AA depletions above 3 µgAA/µgPM. Since transition metals are believed to enhance ROS generation (Li et al. 2003; Halliwell et al. 1984), this was expected.

For example, the sample showing the lowest depletion of the three samples with surprisingly high depletions of AA, which was collected at Fichtnergasse outdoors, showed above average contents in the major metals iron, silicon, and aluminium while the other two samples showed an average content in these metals. The Fichtnergasse sample also showed high concentrations of barium, cobalt, chrome, manganese, tin, molybdenum, titan, nickel, and copper.

The Rosensteingasse indoor sample with a depletion above 3 µgAA/µgPM showed high contents of tin and nickel and a very high copper concentration.

The Rosensteingasse ambient sample with a depletion above 3 µgAA/µgPM showed high concentrations of palladium, chrome, and titan and very high concentrations of zinc.

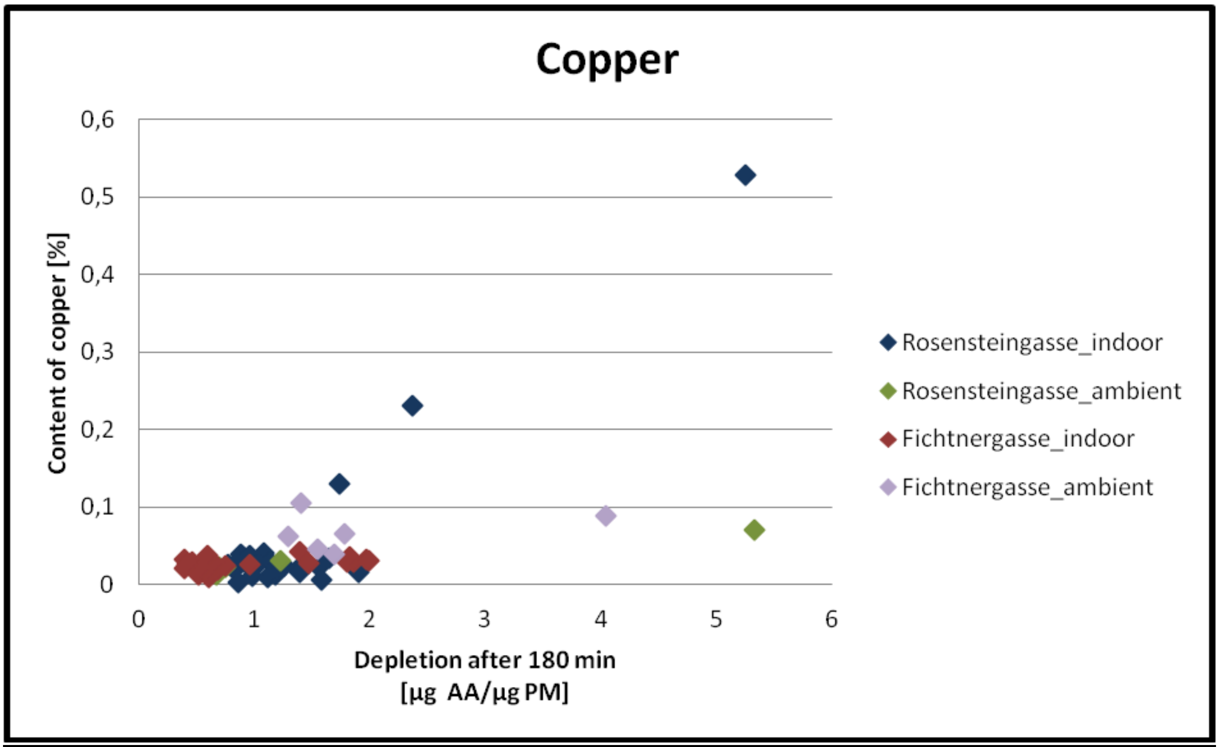


Figure 4.17.: Relation between the copper content and the depletion of AA.

Copper was found to an above average content in all three samples that showed a depletion of AA above 3 µgAA/µgPM, but only the sample collected at Rosensteingasse indoors showed a remarkable high concentration. It is hard to confirm the responsibility of copper on the depletion of AA since the samples showed above average concentrations in various metals.

In general trace metals showed broad scattering and no clear trends.

4.2.2. Aquella Samples from Vienna

To compare the data determined for Fichtnergasse und Rosensteingasse with other ambient data from Vienna, six samples from the Aquella project collected in 2004 were measured. 5 samples were collected at Kendlerstraße, and urban sampling site that shows some traffic exposure. The last sample was collected at Schafberg, a background station in Vienna. Three of the Kendlerstraße samples as well as the Schafberg sample were collected in January, while the remaining two Kendlerstraße samples were collected in October. The general depletion of AA matched with those from the ambient Fichtnergasse and Rosensteingasse samples.

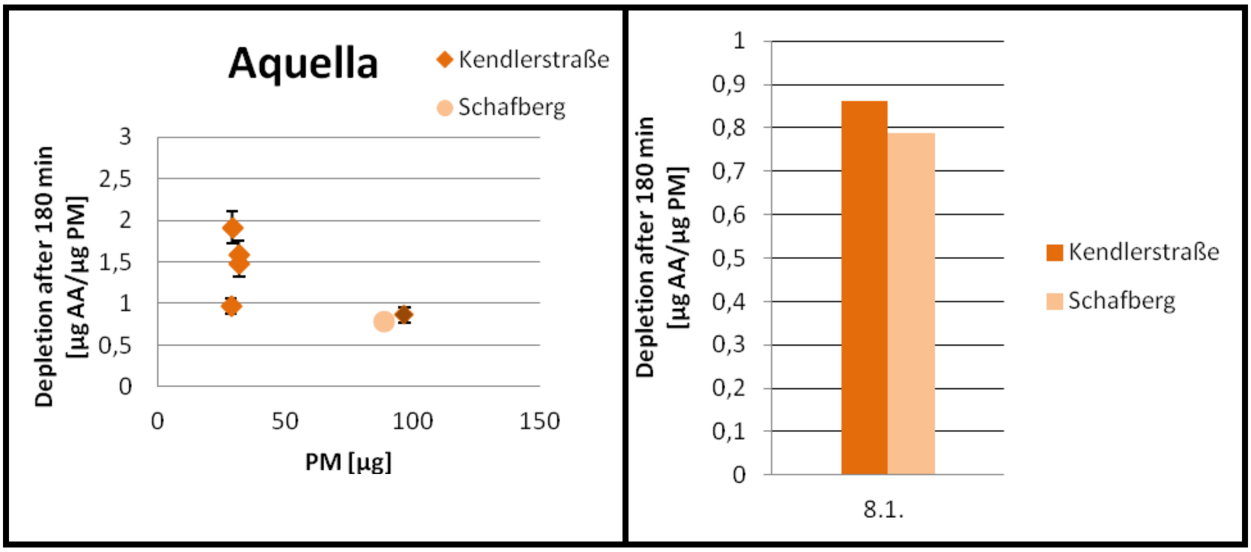


Figure 4.18.: The depletion of AA for the Kendlerstraße and Schafberg measurements. Error bars point to a standard deviation of 10%, determined during multiple analysis. The mass on the x-axis of the left plot is the mass of ambient particulate matter collected on a punch with a 5mm diameter.

Figure 4.18. shows the depletion of AA for all samples on the left plot. The point marked in dark orange refers to the sample from Kendlerstraße collected on the same day as the sample from Schafberg. The right plot of figure 4.18. shows the difference between Kendlerstraße and Schafberg from January 8th 2004 in detail. They both matched well and as visible they also lay in a very close mass range. Both, mass and oxidative properties in regards of AA are slightly higher for the Kendlerstraße sample.

What also can be seen is that four of the samples from Kendlerstraße (two from the beginning of January and two from the end of October 2004) showed a low mass compared to the samples from January 8th. By whatever reason this big mass difference was caused, it obviously did not lead towards an increase of the depletion of AA.

The two samples with the highest oxidation both were obtained in October 2004.

Table 4.2.: The average depletion of AA as well as its standard deviation from the ambient samples collected in Vienna during the Aquella campaign including both, samples from Kendlerstraße and the sample from Schafberg:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
Ambient Vienna samples from the Aquelle campaign	6	1.27	0.46

4.2.2.1. Comparison with Chemical Composition

Again composition analysis and source contribution calculations were not done within this thesis, but were already available in literature (Bauer et al. 2006).

4.2.2.1.1. Carbon parameters and source contributions

The chemical composition of the aerosol samples was compared to the oxidative properties expressed by the depletion of AA, starting with the carbon parameters and different aerosol sources determined on the base of carbonaceous aerosols. CC was not determined within these samples and is therefore not discussed in this chapter. Especially for EC a clear trend can be seen.
The TC content of PM mass ranged between 25 and 34%.

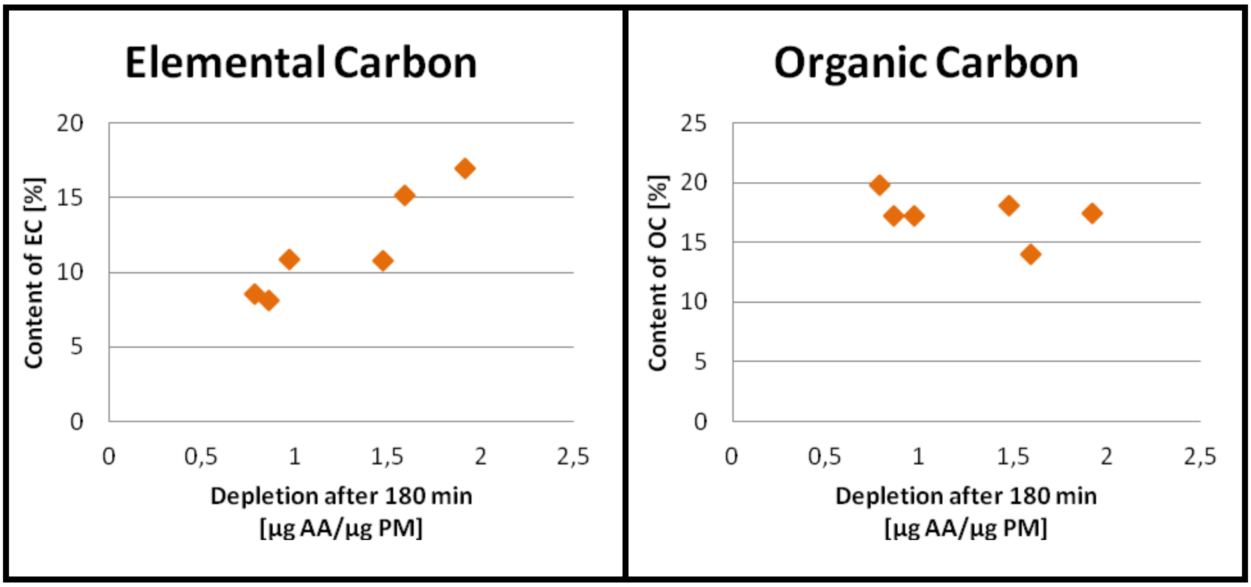


Figure 4.19.: The relation between the EC and OC content and the depletion of AA.

EC again showed a trend of higher EC content leading to higher depletions of AA. This trend was clear and showed only little scatter of data points, which might be due to the high concentrations of EC and the homogeneity of the conditions at the sampling sites. OC did not show any trend.

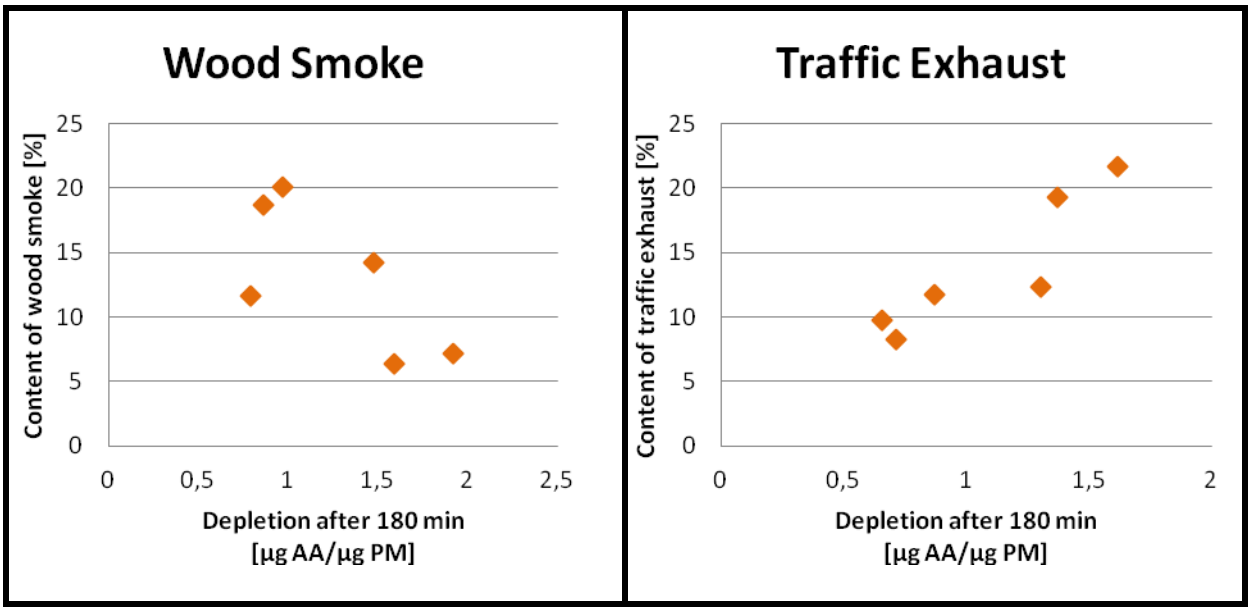


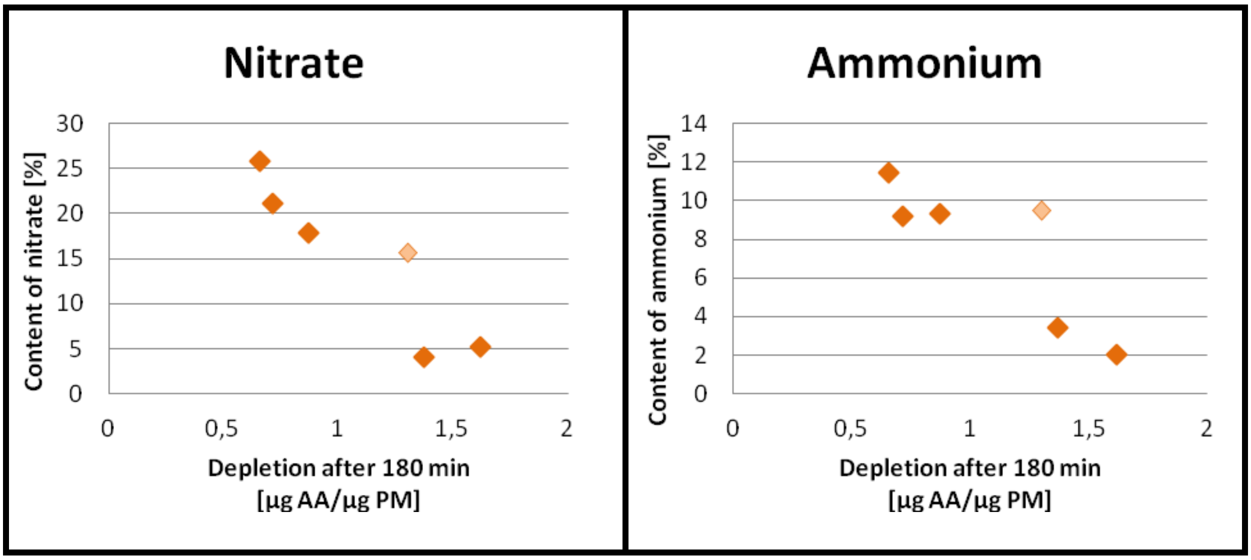
Figure 4.20.: The relation between the content of wood smoke and traffic exhaust and the depletion of AA.

PM related to wood smoke seemed to show a negative trend but with broader scattering if compared to the EC trend. Traffic exhaust showed the same patterns as EC, because it is strongly based on that parameter. OC without a defined source did not show any trends and is not shown here.

4.2.2.1.2. Inorganic Ions

Again ions were separated into major (ammonium, nitrate and sulfate) and minor ions. The minor ions determined within the samples were chloride, sodium, potassium, magnesium, and calcium.

The major ions represented 15-50% of the PM mass depending on the sample (the 50% refer to the Schafberg sample). The minor ions represented 2-5% of the PM mass.



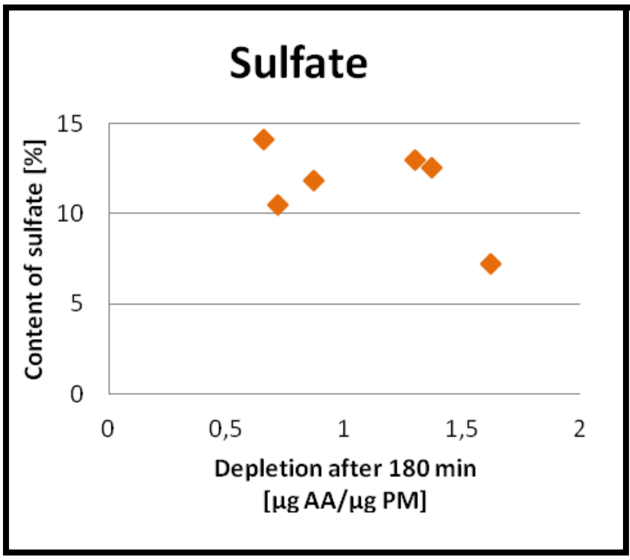
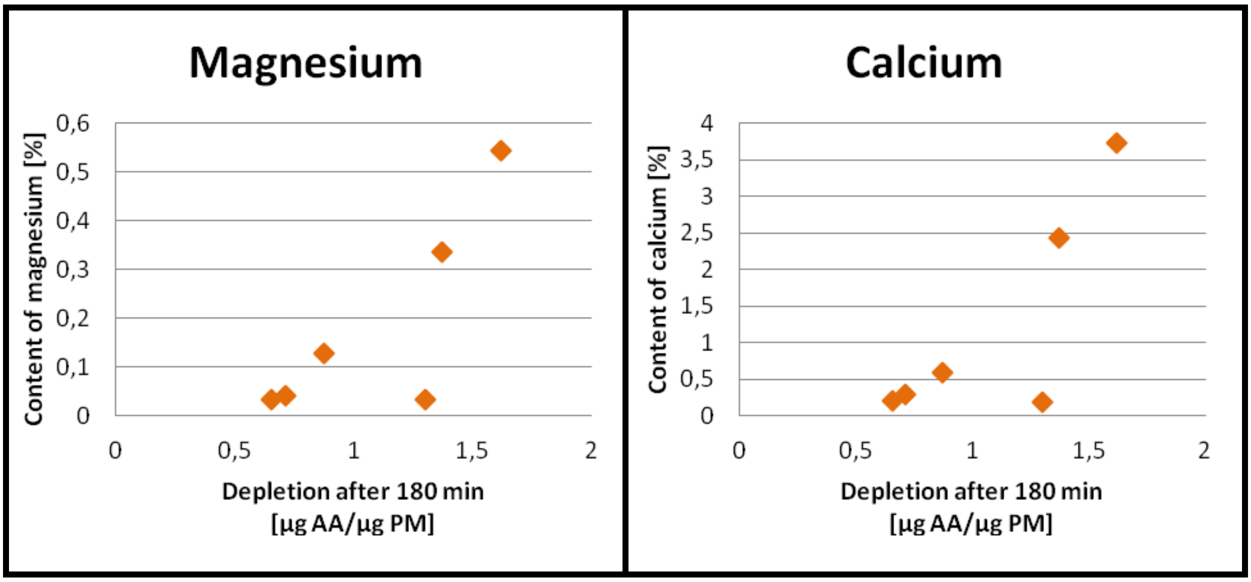


Figure 4.21.: The relation between the content of the major ions (nitrate, sulfate and ammonium) and the depletion of AA.

All major ions showed a negative trend. This trend was best visible for ammonium and nitrate and got less pronounced for sulfate. The patterns for ammonium and nitrate visible in figure 4.21. matched well. This got especially obvious when regarding the data point at a depletion of 1.3 µgAA/µgPM (sample from Kendlerstraße collected on January 6th2004, marked in light colour) that showed an above the trend content for both, ammonium and nitrate.

The result matched well with the major ion result for the ambient samples from Rosensteingasse and Fichtnergasse.



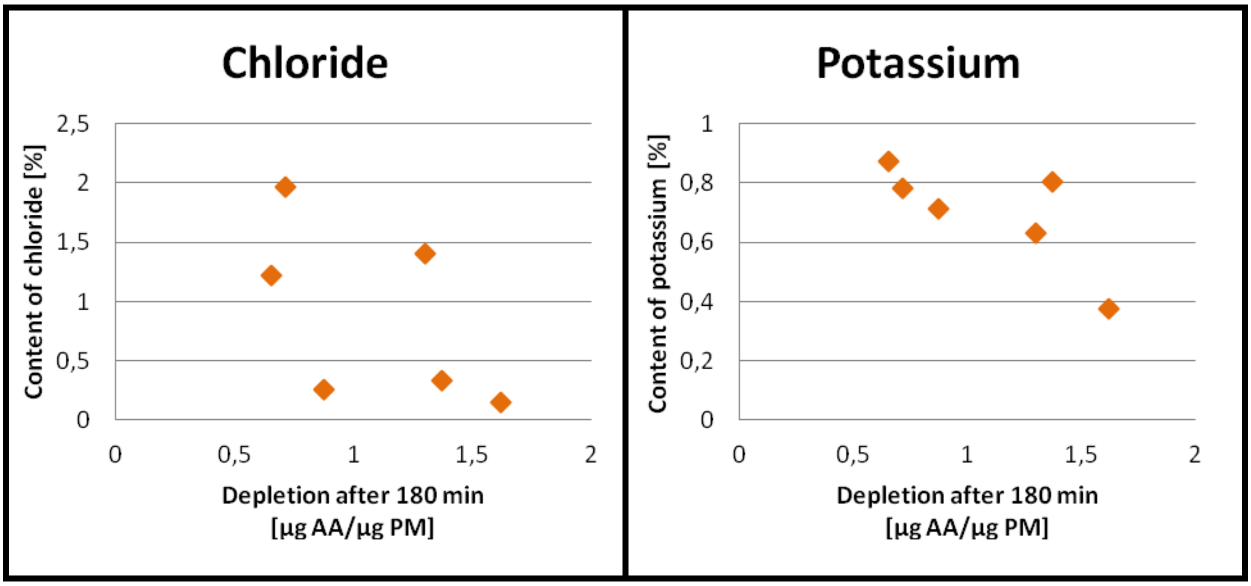


Figure 4.22.: The relation between the content of some minor ions and the depletion of AA.

Magnesium and calcium showed a positive trend, while potassium showed a clear negative trend and chloride a negative trend with broad scattered data points. If magnesium and calcium are compared, it is visible that the patterns matched well. Actually no positive trend of elevated calcium or magnesium content of aerosol samples and depletion of AA was expected. As these patterns can also be observed for EC, this leads to the suggestion that they were emitted by the same source, meaning that calcium and magnesium might not increase the oxidative properties, but rather were emitted together with EC and probably other unknown substances linked to it. This could happen when traffic leads to the resuspension of mineral dust from the streets.

Other than calcium and magnesium, potassium did not match EC but it matched the major ions patterns. Chloride seemed to follow the same trend albeit with a stronger variation. Also this group showed slight similarities to the OC patterns, best visible for potassium. This renders it difficult to determine which of those components actually showed this trend and which of them just were emitted alongside with other substances that did.

What can be said is that the major ions in general showed a negative trend. The minor ions are split into two groups showing opposed trends. Potassium can also be used as a tracer of wood burning. This would explain at least part of the similarity with the OC and wood smoke patterns.

4.2.2.1.3. Metals

Highest concentrations and consequently more pronounced contributions to PM mass were represented by silicon, aluminium, iron, and calcium, all of them are elements typically found in mineral dust. Their content ranged from 2-16% (2% refers to the Schafberg sample). Other metals determined were magnesium, vanadium, chrome, manganese, copper, zinc, strontium, cadmium, barium, titan, tin, nickel, cobalt, and lead.

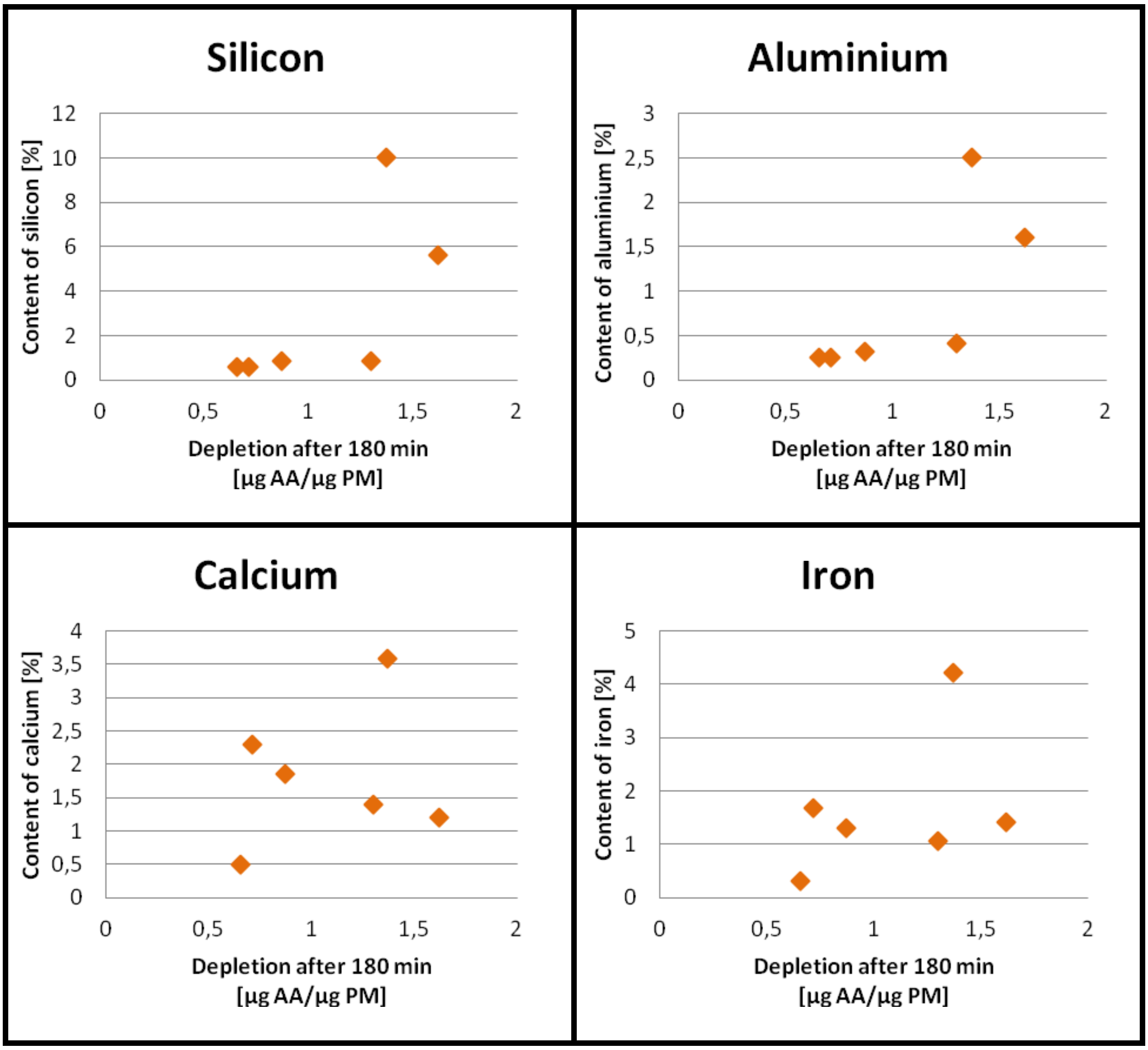


Figure 4.23.: The relation between the content of the major metals (silicon, aluminium, calcium, and iron) and the depletion of AA.

Following the data shown in figure 4.23., silicon and aluminium showed the same patterns as well as calcium and iron, leading to the conclusion that they were emitted alongside each other. Both groups showed a positive trend with broad scattering of the data points.
Interesting is the opposed behaviour of soluble (see figure 4.22.) and total calcium.

Several trace elements showed similar patterns (e.g. titan and barium resembled aluminium and silicon), but clear trends cannot be determined.

4.2.3. Comparison of the depletion of AA for the samples from Vienna

Figure 4.24. shows that the depletion of AA from the ambient samples from the Aquella campaign fitted very well to those from Rosensteingasse and Fichtnergasse.
Thus results obtained in 2011 were well comparable to those in 2004. Obviously the back-up samples from former projects did not change during storage.

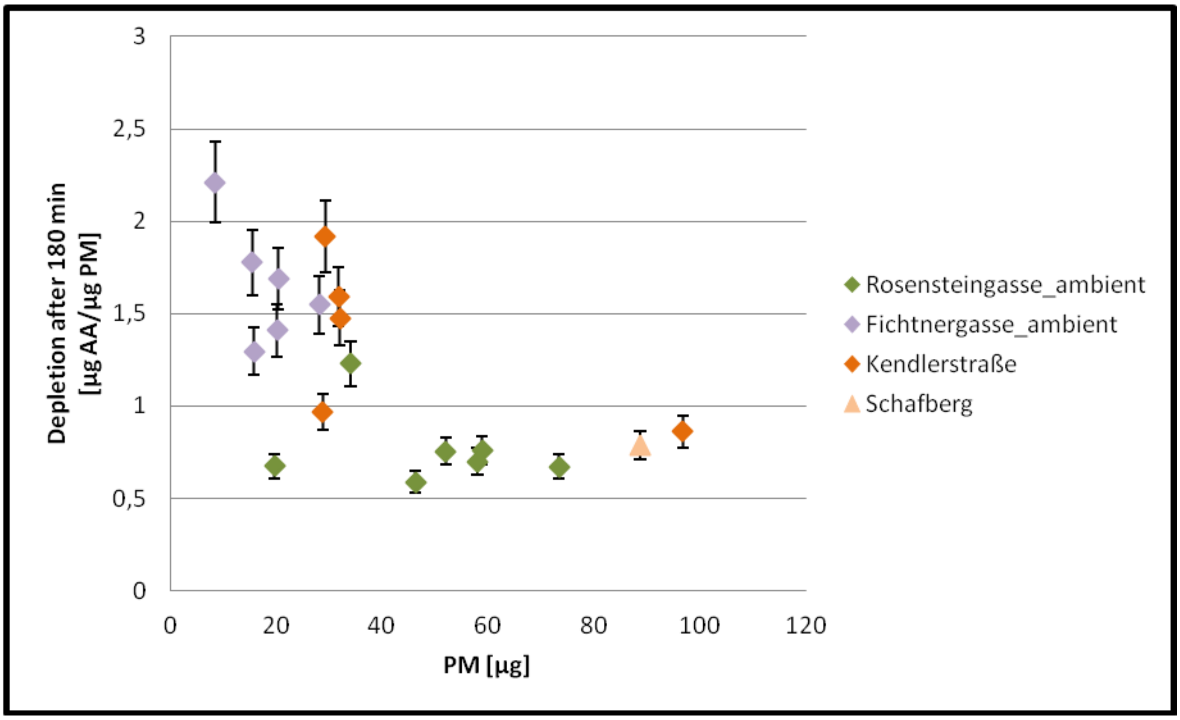
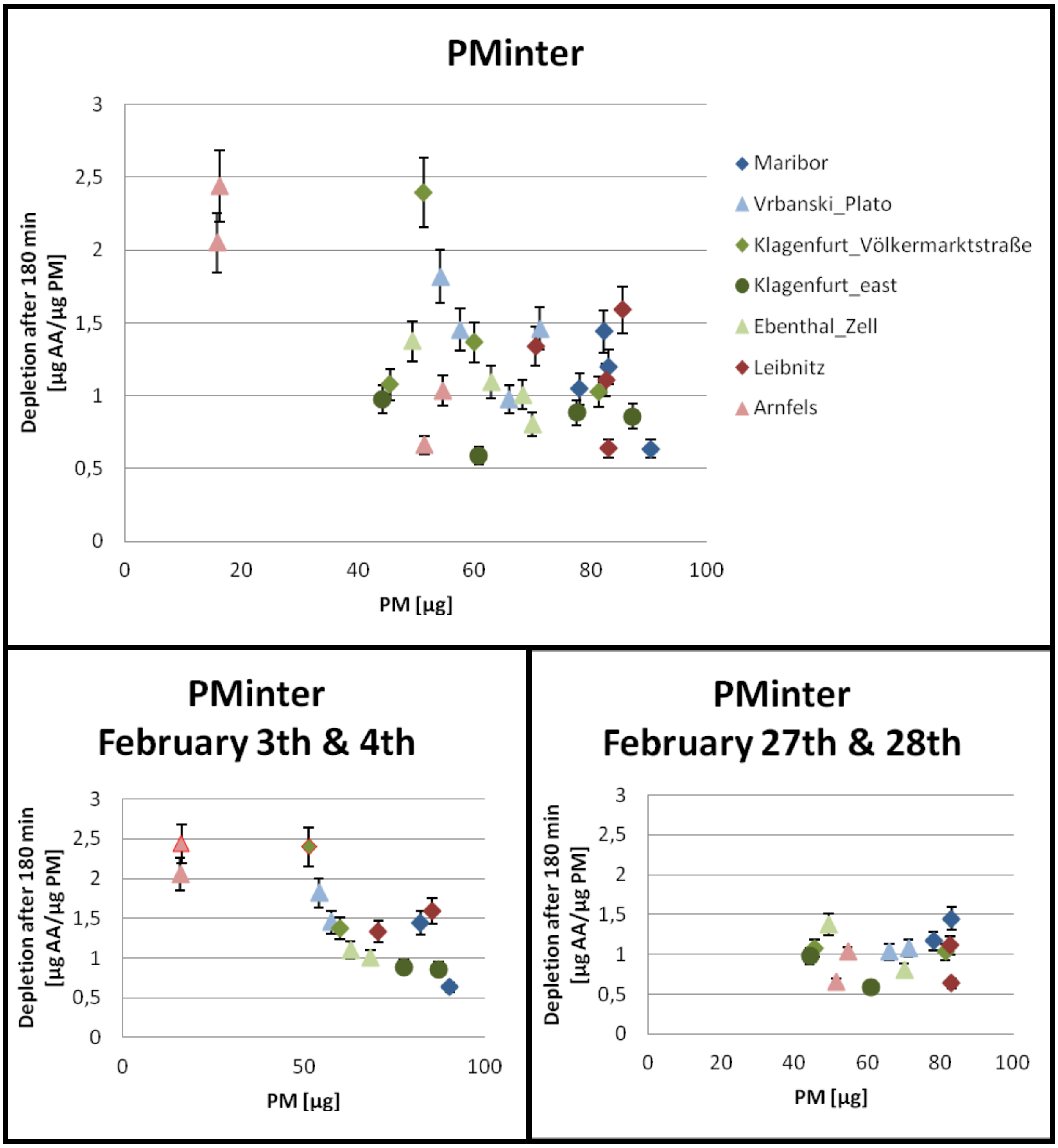


Figure 4.24.: Comparison of the results for the ambient samples collected at in Vienna. Error bars point to a standard deviation of 10% determined during multiple analysis. The mass on the x-axis is the mass of ambient particulate matter collected on a punch with a 5mm diameter. Again samples showing a depletion above 3µgAA/µgPM were not regarded.

4.3. PMinter Samples

In February 2011 a sampling campaign was performed at a number of sites in Carinthia, Styria and Slovenia within the PMinter project (Kistler et al 2013[a,b,c]). The samples were collected on seven different sampling sites and can be split into urban and background sampling stations. The urban sampling sites were Maribor (Slovenia), Leibnitz (Styria), and Klagenfurt Völkermarktstraße (Carinthia). The background stations were Vrbanski Plato (Slovenia), Arnfels (Styria), Klagenfurt east and Ebenthal Zell (both Carinthia). Analysis of chemical composition was performed within the PMinter project. Here four samples from each station were selected to determine the depletion of AA. Two samples were chosen from the beginning from February 2011, the other two from the end of February 2011. While the samples from the end of February matched very well, the samples from the beginning of February showed broader variations in the depletion of AA, suggesting different conditions prevailing at some of the sampling stations (e.g. Arnfels and Klagenfurt Völkermarktstraße). This was also seen in the chemical analysis of those samples (Kistler et al. 2013[a,b,c]).



PMinter

PMinter February 3th & 4th

PMinter February 27th & 28th

Figure 4.25.: The depletion of AA for the samples from the PMinter project. Error bars point to a standard deviation of 10%, determined during multiple analysis. The mass on the x-axis is the mass of ambient particulate matter collected on a punch with a 5mm diameter.

In figure 4.25. the depletions of AA for the measurements of all measured samples from the PMinter project are shown. The values for the background stations are marked with a triangle and a circle for Klagenfurt east. The lower two plots split the results into two groups, the results from the samples collected on 3th and 4th of February and from those collected on 27th and 28th of February. In general it can be said that even though the data from the end of February matched better than that of the beginning, the depletion lay in the expected range that had already been shown as normal through the samples from Vienna.

Table 4.3.: The average depletion of the AA and its standard deviation for all PMinter samples as well as separated by beginning and end of February and for each sampling station:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
All data	28	1.23	0.49
3rd and 4th of Feb	14	1.46	0.56
27th and 28th of Feb	14	1.00	0.26
Maribor	4	1.08	0.34
Vrbanski Plato	4	1.43	0.34
Klagenfurt Völkermarktstraße	4	1.47	0.64
Klagenfurt east	4	0.83	0.17
Ebenthal Zell	4	1.07	0.24
Leibnitz	4	1.17	0.41
Arnfels	4	1.55	0.83

Table 4.3. points out even clearer what has already been discussed above. The samples from end of February were quite similar with an average depletion of AA of 1.00 µgAA/µgPM and a standard deviation of 0.26 µgAA/µgPM. Other than that, the samples from beginning of February 2011 showed an average depletion of 1.46 µgAA/µgPM and a standard deviation of 0.56 µgAA/µgPM. Regarding the standard deviations from the single sampling sites it can be seen that Arnfels and Klagenfurt Völkermarktstraße showed the highest variation.

4.3.1. Comparison with Chemical Composition

Again chemical composition and aerosol source analysis was not done within this thesis, but were already available in the reports (Kistler et al. 2013[a,b,c]).

4.3.1.1. Carbon parameters and source contributions

The impact of the different carbon species on the depletion of AA was regarded. If the sampling sites were compared, differences got visible. Here especially the difference between urban sampling sites and background stations needed to be investigated since traffic exhaust has a bigger impact on urban sites while wood smoke has a bigger ratio in rural sites.

In general TC represented 18-43% of the PM mass. No big differences were observed between urban and rural sampling sites. The highest values had been determined in Leibnitz while the samples from Slovenia showed the lowest contents. EC made up 3-11% of the PM mass, OC 8-35%. For both no big differences were found between urban and rural sampling sites. The highest EC contents have been found in Leibnitz, the highest OC contents in Arnfels.

The results of the comparisons given below are in general agreement with the samples from Vienna.

Since the trend determined for TC is very much the same as for OC, TC again is not discussed here.

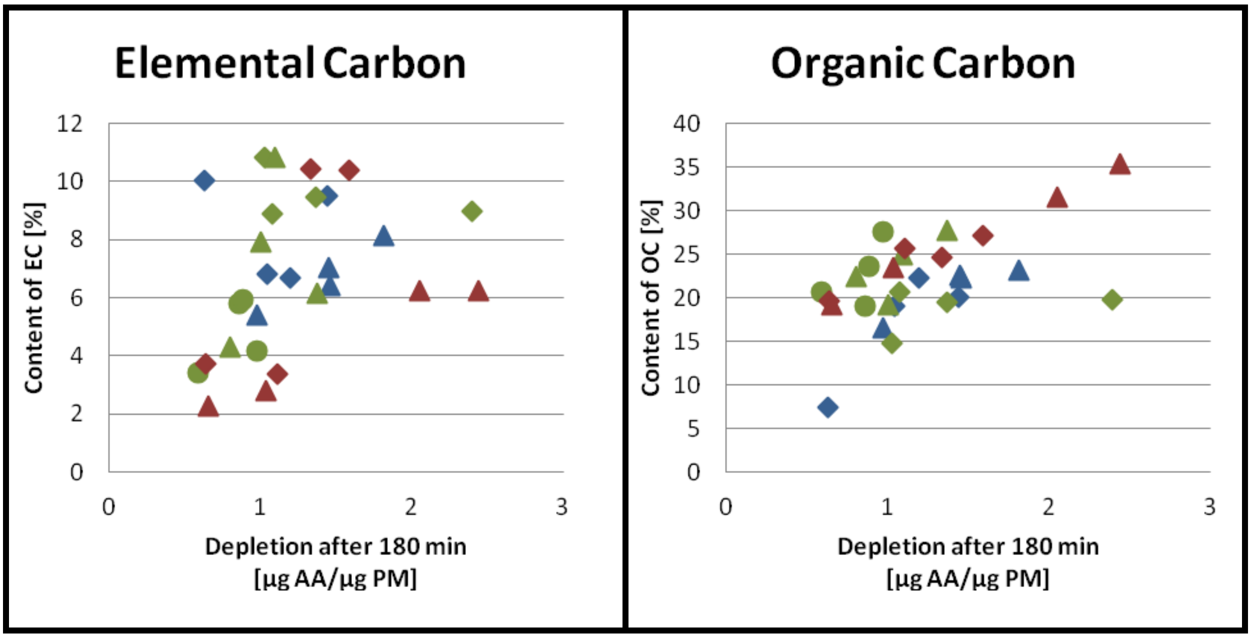


Figure 4.26.: The relation between the content of OC and EC and the depletion of AA. The colours and forms used to mark the different categories are chosen similar to the other PMinter plots.

The comparisons between the depletion of AA and the content of different carbon species showed a positive trend for both, OC and EC. OC however showed a clearer trend, especially in regard of the background stations, while EC showed a higher scattering of data points.

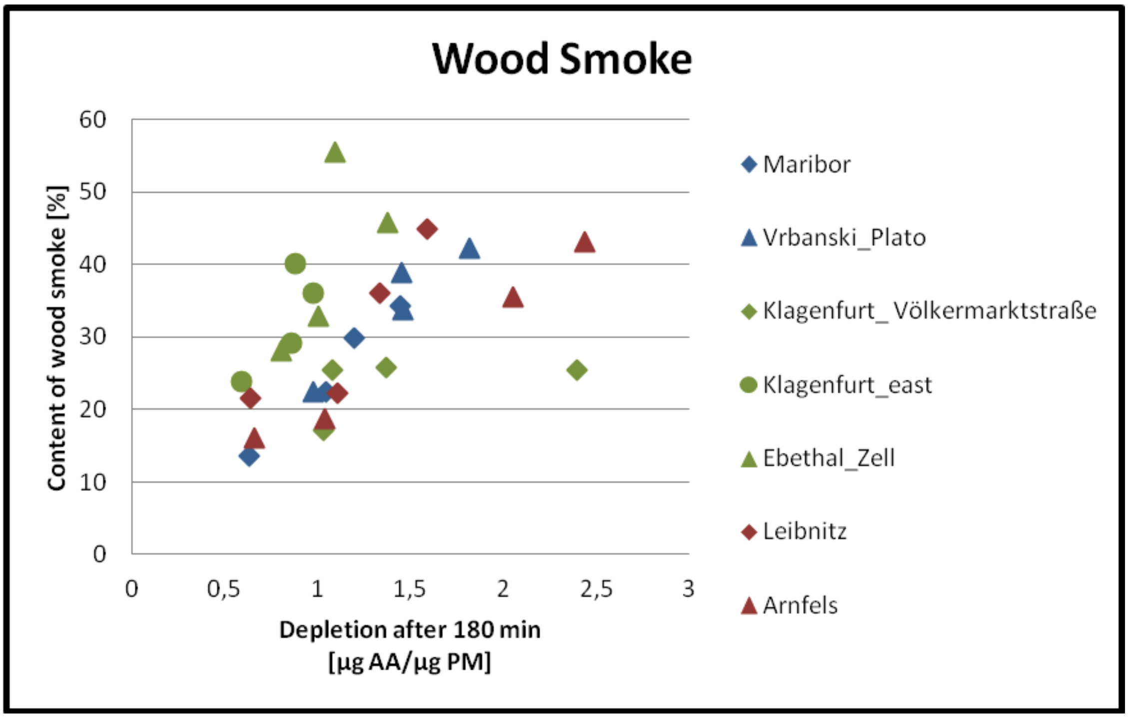


Figure 4.27.: The relation between the content of wood smoke and the depletion of AA.

PM related to wood smok showed a positive trend for the background stations Vrbanski Plato, Ebenthal Zell, and Arnfels with the highest gradient for Ebenthal Zell. What also can be seen is a positive trend for Leibnitz and Maribor and a positive trend though with scattered data points for Klagenfurt east matching the one of Ebenthal Zell, but showing a smaller ratio on the PM mass. Klagenfurt Völkermarktstraße showed constant ratios of wood smoke with only one sample not following this distribution and therefore no trend.

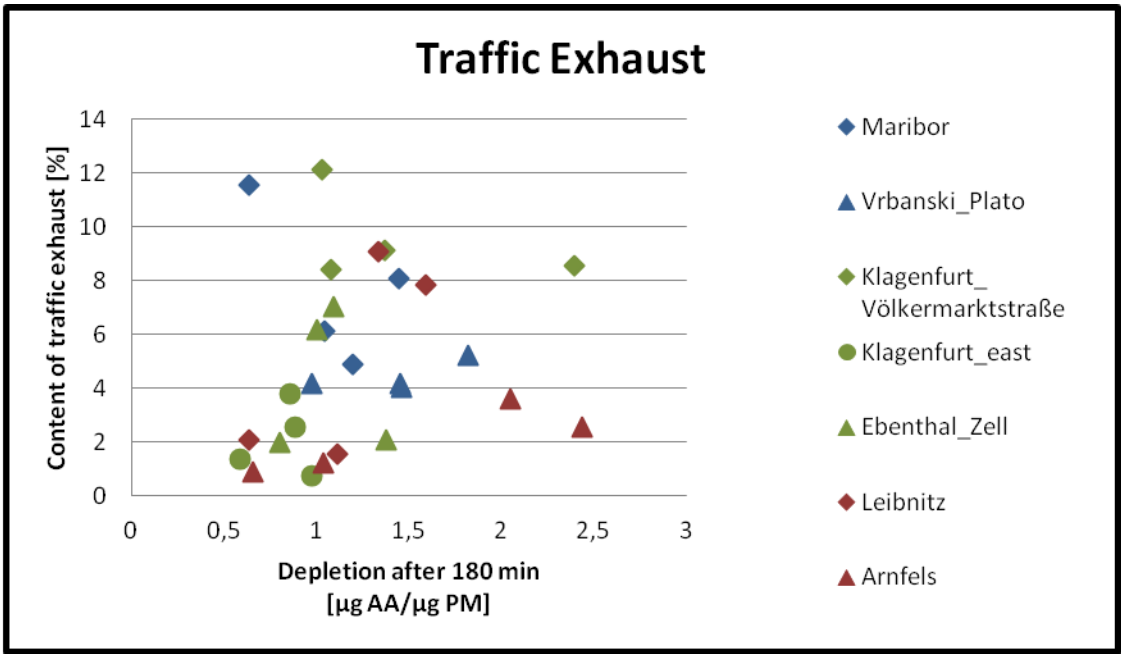


Figure 4.28.: The relation between the content of traffic exhaust and the depletion of AA.

As opposed to wood smoke, the background stations did not show any trend for traffic exhaust. Leibnitz showed a slight positive trend with scattered data points that was hard to define for only four samples. Klagenfurt Völkermarktstraße did not show a clear trend, however it is remarkable that the data point with the highest value showed its lowermost depletion of AA. The highest content ratios can be seen for the urban stations Leibnitz, Klagenfurt Völkermarktstraße, and Maribor while the background stations showed a smaller ratio of traffic exhaust.

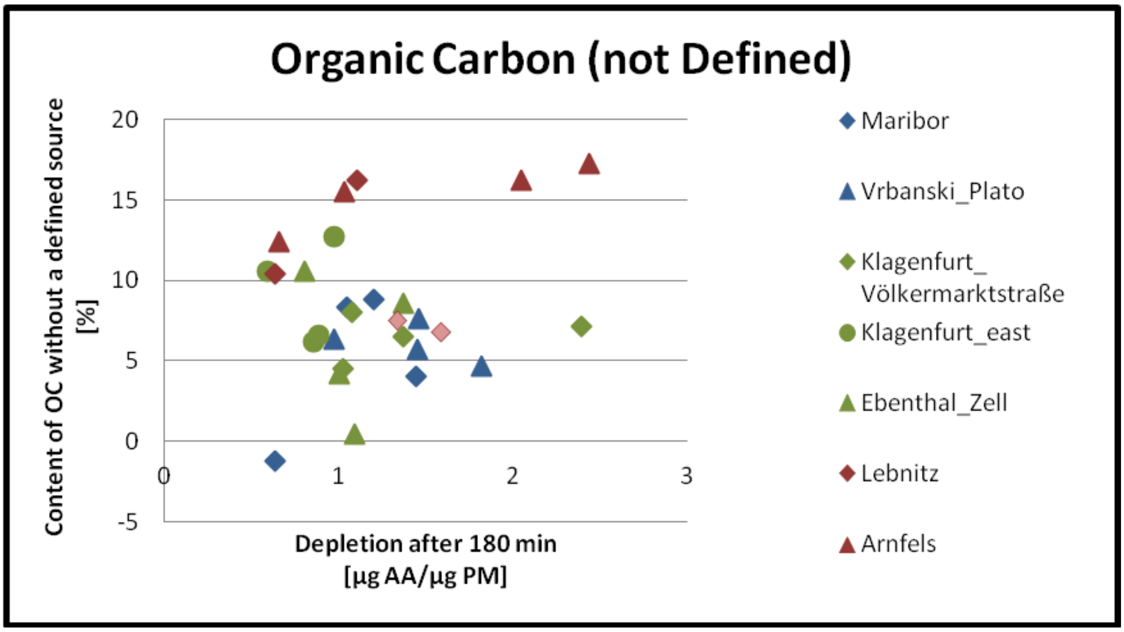


Figure 4.29.: The relation between the OC without a defined source and the depletion of AA.

In general OC without a defined source showed a negative trend that got clearer when the values for Arnfels from the beginning of February were not regarded. Those values were remarkable since they matched those from the end from February but compared to those from Leibnitz at the beginning of February (marked in light colour) they exhibited a more than doubled content. Since those two stations lie in a close proximity to each other, this showed a very local emission and could probably explain the high oxidative properties from Arnfels at the beginning of February.

Since the data for the organic carbon without a defined source is calculated with help of the makro tracer approach, it is obtained through a mathematical process. Hereby OC related to wood smoke and traffic exhaust matter are calculated and the difference between the sum of those two and OC leads to the result. If only little to no undefined OC is present, the uncertainty of this method can lead to negative values as seen for one sample from Maribor in figure 4.29..

4.3.1.2. Inorganic Ions

The major ions nitrate, sulfate, and ammonium represented 9-65% of the PM mass depending on the sample, showing its highest values for background stations (27-65%) and smaller ratios for urban sampling sites (9-46%). For these ions opposed but clear trends were visible.

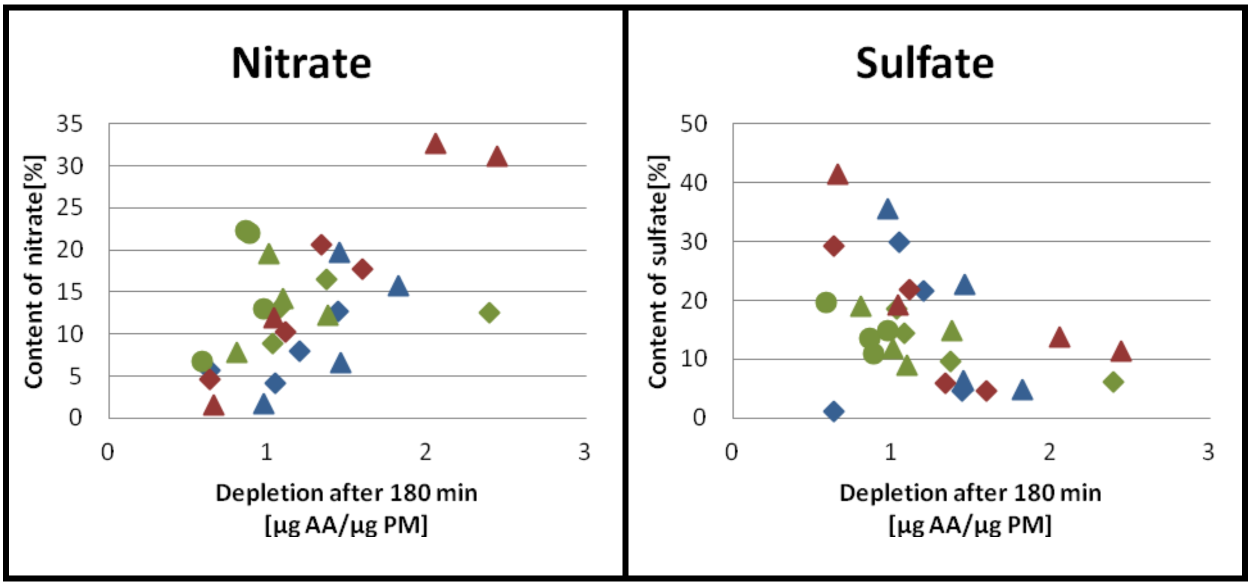


Figure 4.30.: The relation between the content of sulfate and nitrate and the depletion of AA. The colours and forms used to mark the different categories are chosen similar to the other PMinter plots.

Nitrate and sulfate were the two ions that showed a general trend in all stations. While nitrate showed a positive trend (opposed to the ambient samples from Vienna) sulfate showed a negative one.

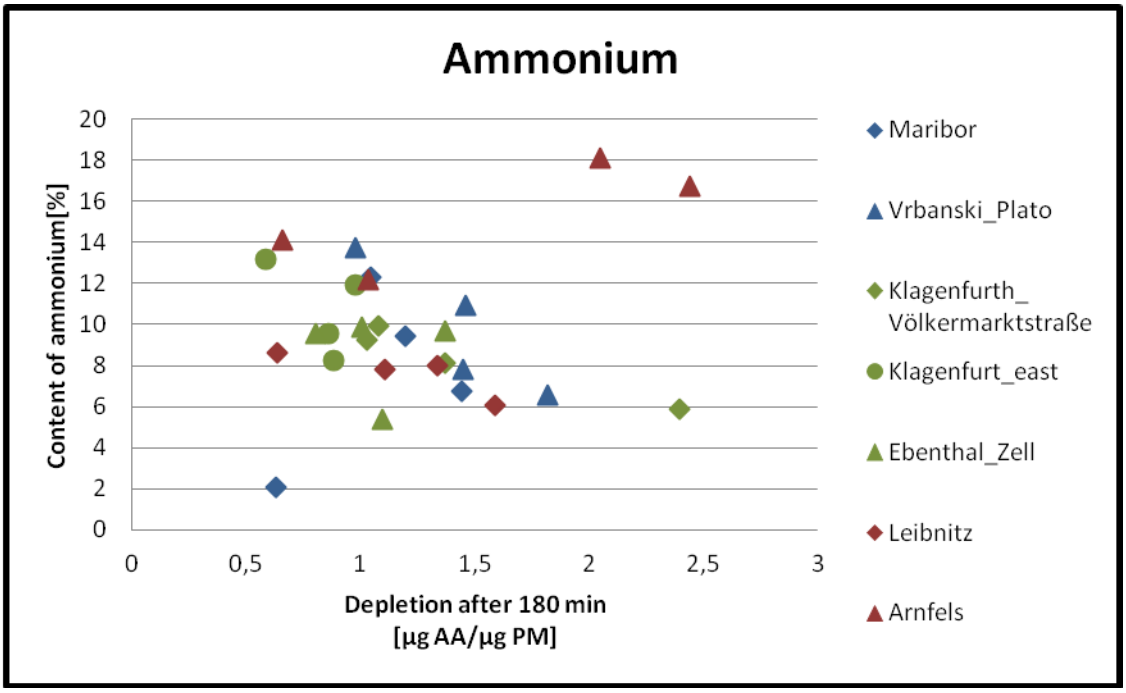


Figure 4.31.: The relation between the content of ammonium and the depletion of AA.

Interesting was the behaviour of ammonium. In general it showed a negative trend. Surprising results were obtained in Arnfels at the beginning of February. Ammonium accounted for an above average content to PM and seemed to give a slight positive trend that had only been seen for the samples from Arnfels. This emitted ammonium was probably linked to the high concentrations in OC without a defined source or other unknown substances that led to the high oxidations of AA for these two samples.

4.3.1.3. Metals

Within all PMinter samples the metals iron, aluminium and calcium were determined which made up 1-5% of the PM mass depending on the sample. The highest contents had been shown within the samples from Leibnitz and Klagenfurt Völkermarktstraße.

For silicon only data from Leibnitz and Arnfels (both Styria) was available. If it is included, the determined metals made up 2-13% of the PM mass of the Styrian samples.

All of the metals determined were typical mineral dust elements.

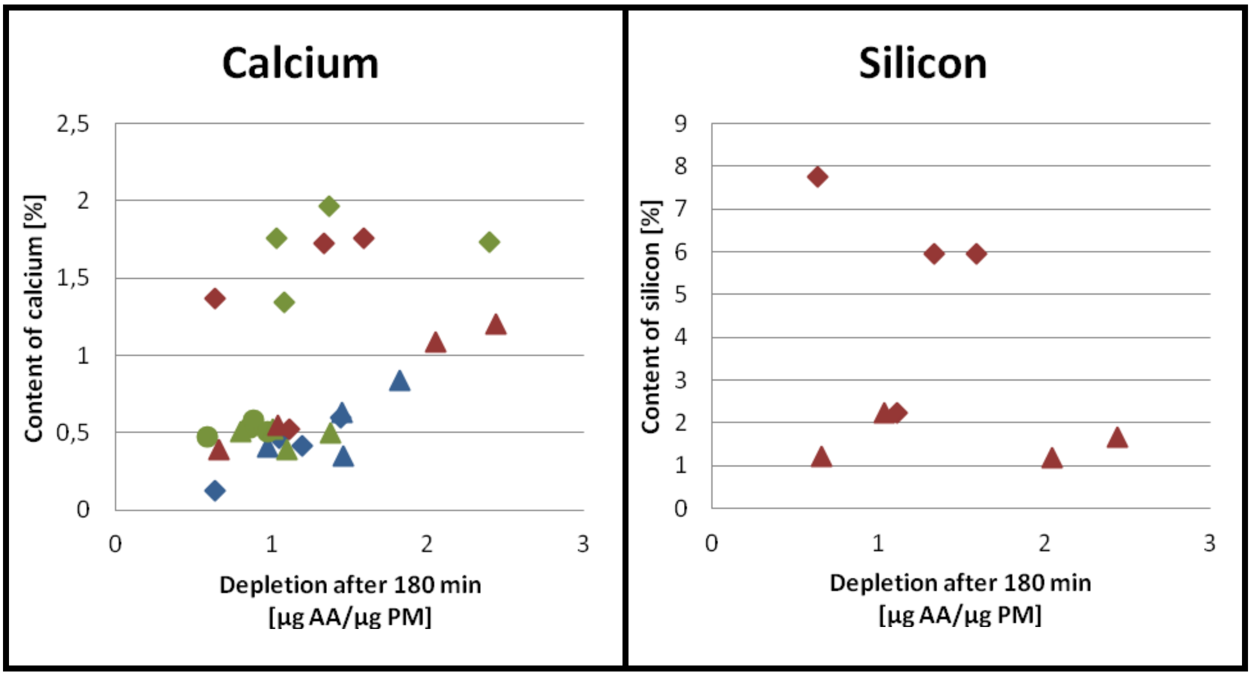


Figure 4.32.: The relation between the content of calcium and silicon and the depletion of AA. The colours and forms used to mark the different categories are chosen similar to the other PMinter plots.

In Figure 4.32. the broad scattering of the data points from Leibnitz and Klagenfurt Völkermarktstraße for calcium can be seen. If only the background stations and Maribor were regarded, they showed a clear positive trend. Silicon did not show any trend.

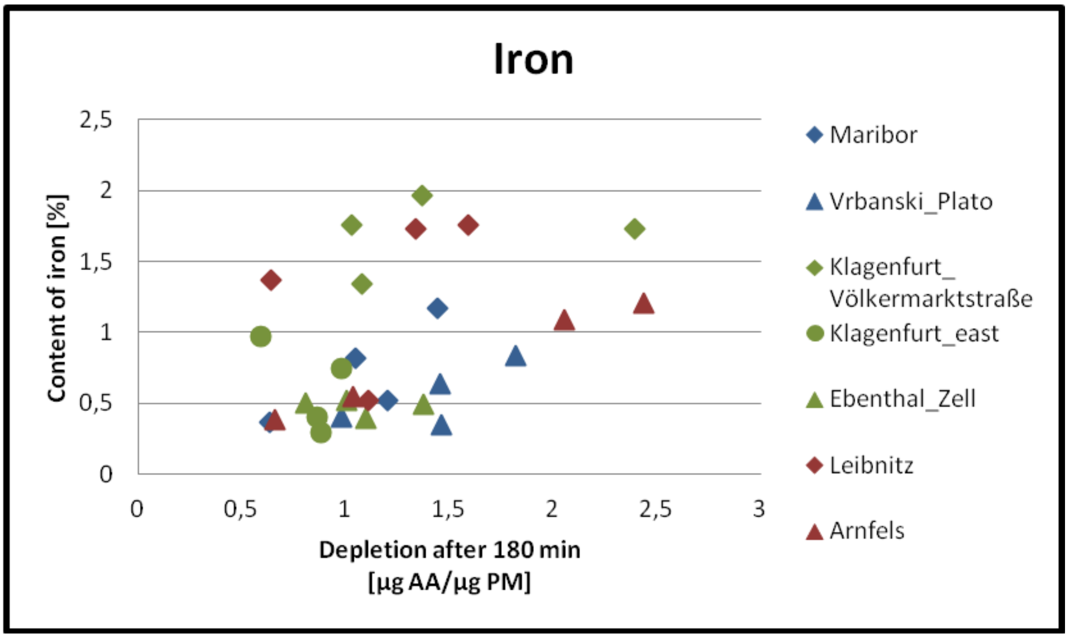


Figure 4.33.: The relation between the content of iron and the depletion of AA.

Iron showed a positive linear trend for the samples from Arnfels and Vrbanski Plato that matched well. There was no clear trend visible for Ebenthal Zell since the gradient was small and the data lay close together, but the data points lay on the line formed by Arnfels and Vrbanski Plato. Therefore this line contains three background stations. The urban samples and those from Klagenfurt east did not show any trends.

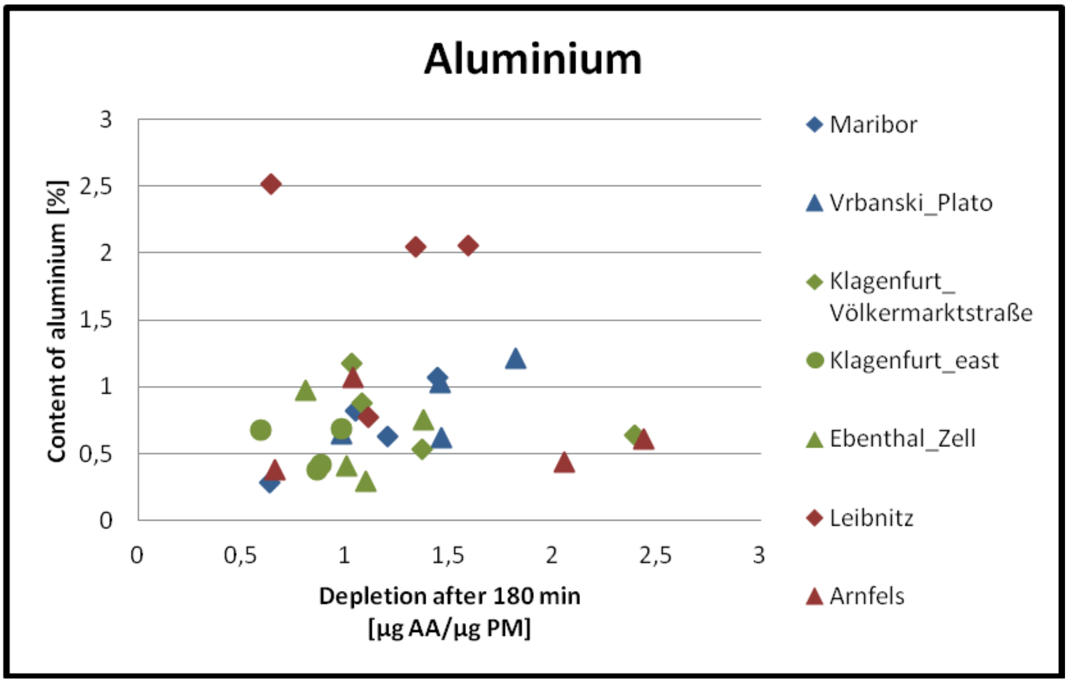


Figure 4.34.: The relation between the content of aluminium and the depletion of AA.

Aluminium did not show any trend for the samples from Klagenfurt as well as for the samples from Arnfels. For Leibnitz it showed a slight negative trend but with broad scattering of the data points. The samples from Slovenia (Maribor and Vrbanski Plato) showed a clear positive trend, both sampling sites matched well.

4.4. Samples from Upper Austria

From Upper Austria six samples were analysed, all collected during the Aquella project in October 2005 and January 2006. The samples were collected at two stations. Three samples were from Enzenkirchen, a rural background station and three further samples were from Linz-Römerberg, an urban sampling site.

The samples from Upper Austria showed very interesting results that did not match the other obtained results presented in this thesis well. This is probably due to the very complex conditions at the sampling sites in Upper Austria, which show a dense industry in their surroundings.

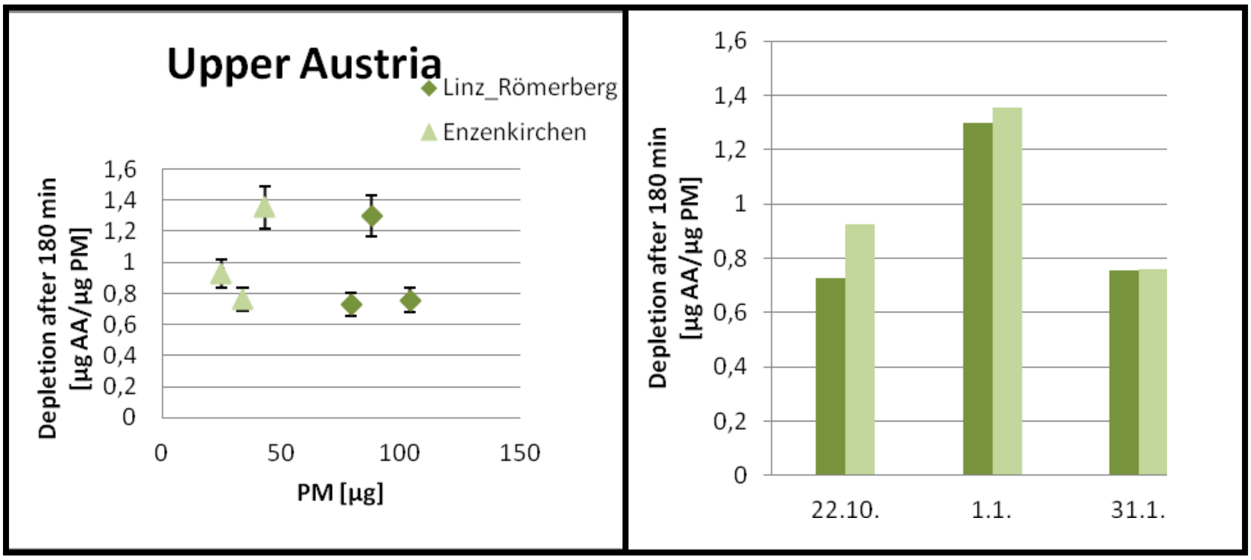


Figure 4.35.: The depletion of AA for the upper Austria samples. Error bars point to a standard deviation of 10%, determined during multiple analysis. The mass on the x-axis of the left plot is the mass of ambient particulate matter collected on a punch with a 5mm diameter. The right plot compares the urban station Linz-Römerberg (marked in dark green) with the background station Enzenkirchen (marked in light green).

In Figure 4.35. the left plot shows the depletion of AA for the samples collected in Upper Austria, the right one the relation between the samples from Linz-Römerberg and Enzenirchen (the x-axis is the sampling date).

Though the samples collected at Enzenkirchen showed less than 50% of the PM mass collected at Linz-Römerberg, the results only showed little variations between both sampling sites that lay in the 10% deviation range determined for the method. This leads to the conclusion that lower mass loadings on the filter do not lead to a higher depletion.

Table 4.4.: The average depletion of AA as well as its standard deviation for the Upper Austria samples in general and the two sampling sites in detail:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
Linz-Römerberg	3	0.80	0.20
Enzenkirchen	3	1.1	0.22
Upper Austria in general	6	0.93	0.24

Table 4.4. shows again how well the data from the two sampling sites matched by the standard deviation that was only slightly higher if both sampling sites are regarded together than for each individual sampling site.

4.4.1. Comparison with Chemical Composition

Composition analysis and source contribution calculations were not done within this thesis, but were already available in literature (Jankowski et al. 2009).

4.4.1.1. Carbon parameters and source contributions

The different behaviour of the Upper Austria samples, compared to other samples analysed, was especially visible in the relations between the different carbon species and the depletion of AA. Therefore especially OC and EC were regarded further as well as traffic exhaust and EC from wood smoke.

The TC content ranged between 19 and 26% depending on the sample regarded, representing a slight below average content range, if compared to the other analyzed samples.

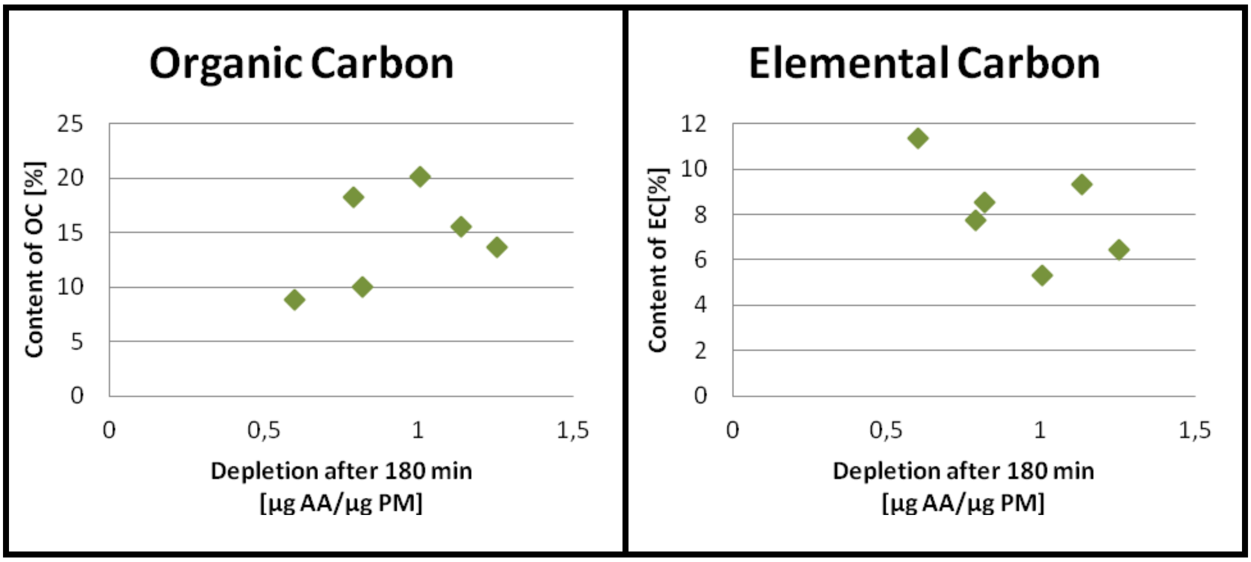


Figure 4.36.: The relation between the content of EC and OC and the depletion of AA.

The samples from Upper Austria were the only samples showing a negative trend for EC, however, the differences in relative contribution of EC to aerosol mass were rather low. On the other hand they showed a positive trend for OC. The two plots seemed related to each other. OC mostly showed high values for low EC values and the other way round. This behaviour was not seen for the other samples which showed constant or increasing ratios of OC for increasing ratios of EC. This behaviour of these two carbon species is a possible explanation for the contrary behaviour compared to other measured samples.

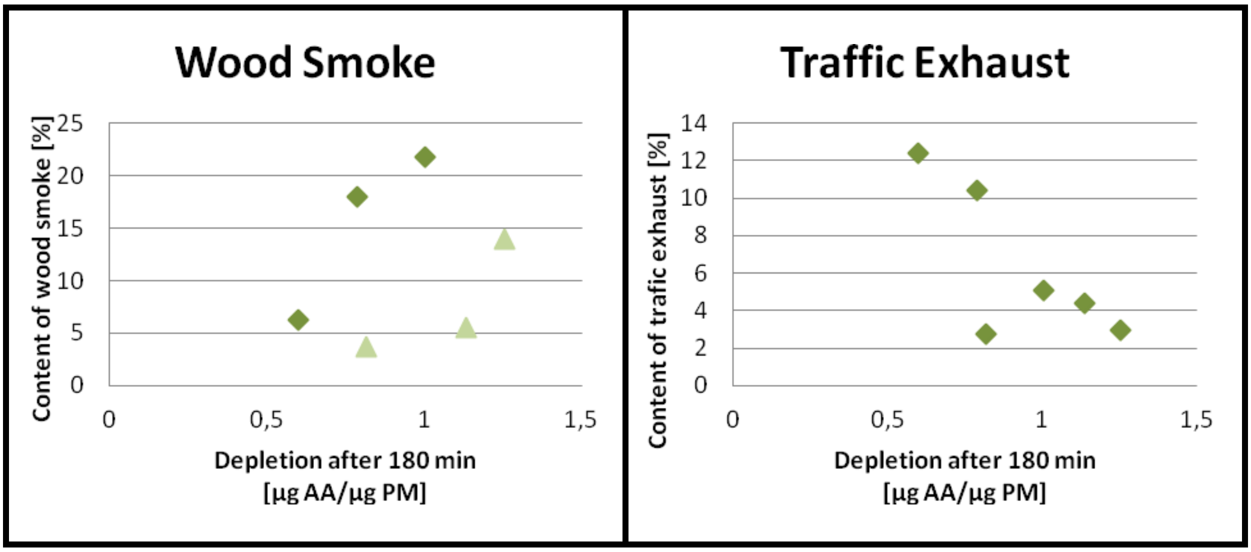


Figure 4.37.: The relation between the content wood smoke and traffic exhaust and the depletion of AA. On the left plot dark green refers to Linz-Römerberg and Enzenkirchen, on the right plot dark green is used for all six samples measured.

The samples from Upper Austria showed a clear negative trend for traffic exhaust, which could also be related to the problems discussed above for EC. Wood smoke showed no general trend, however if separated by the sampling sites, both sites (Linz Römerberg marked in dark green and Enzenkirchen marked in light green) showed a positive trend, though those trends showed a different offset. It is remarkable that wood smoke showed clearly higher contents in the urban sampling site Linz than in the rural sampling site Enzenkirchen.

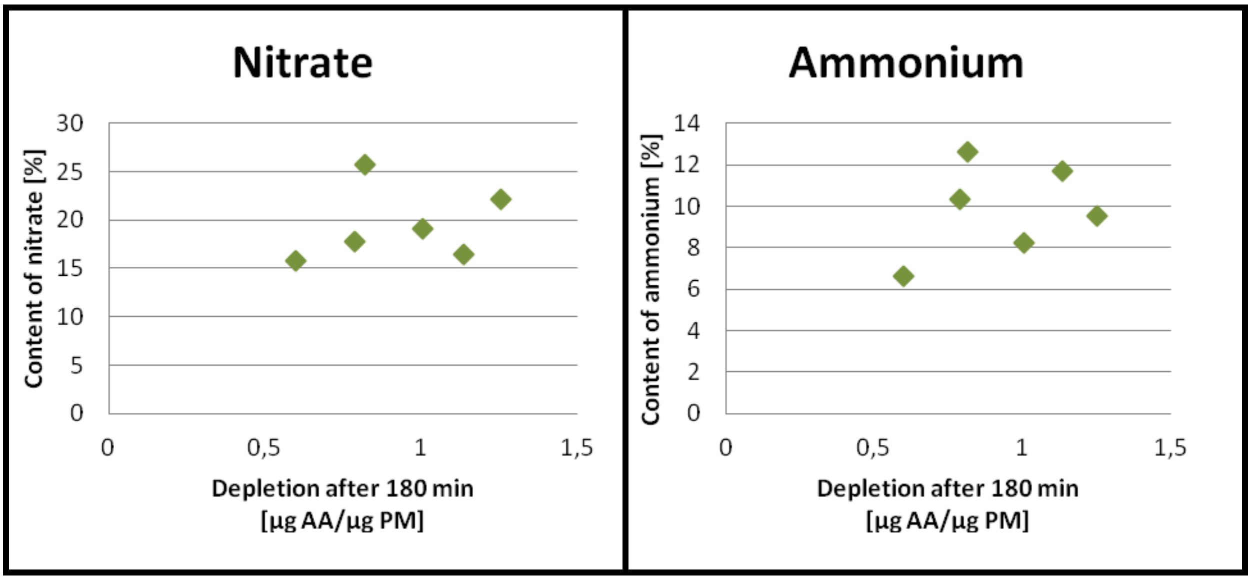
OC without a defined source did not show any trends.

4.4.1.2. Inorganic Ions

The major ions nitrate, sulfate, and ammonium showed a content of 31 to 54% depending on the sample. The rural sampling site Enzenkirchen showed in general higher concentrations ranging from 42 to 54%, while the values for Linz-Römerberg ranged from 31-44%.

The minor ions determined within the samples were chloride sodium, potassium, magnesium, and calcium, representing 2-7% of the PM mass with slightly higher concentrations for the urban sampling site.

Other than for the ambient samples from Vienna and other sampling sites, results for the comparison of ion content and depletion of AA for the Upper Austria samples showed a broad scatter of data points. Only calcium showed a clear trend.



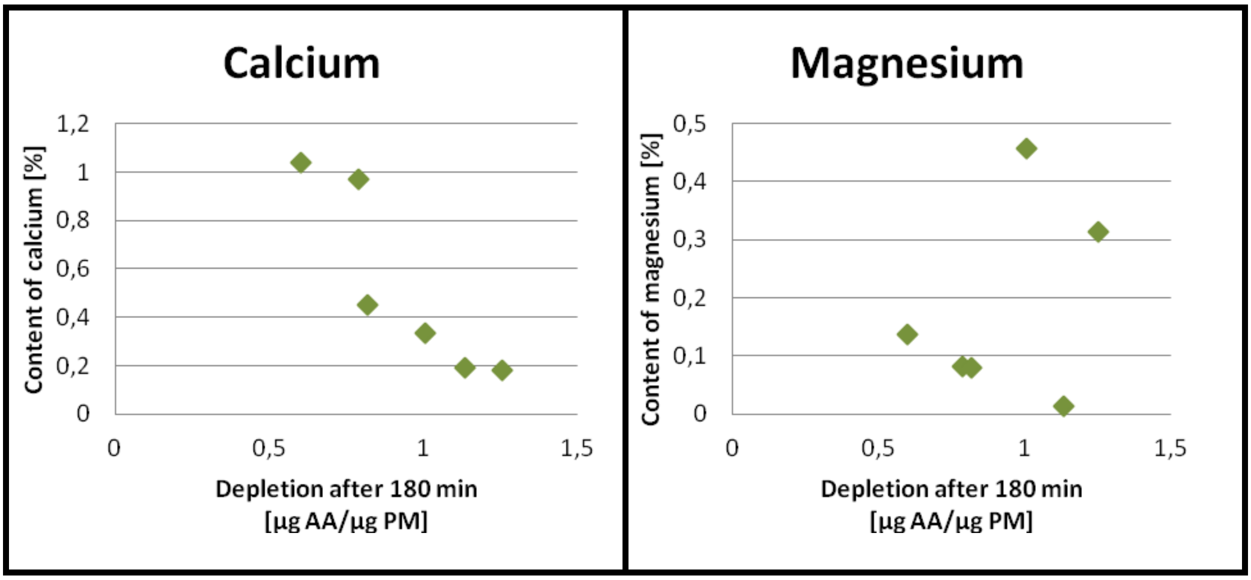


Figure 4.38.: The relation between the content of different ions and the depletion of AA.

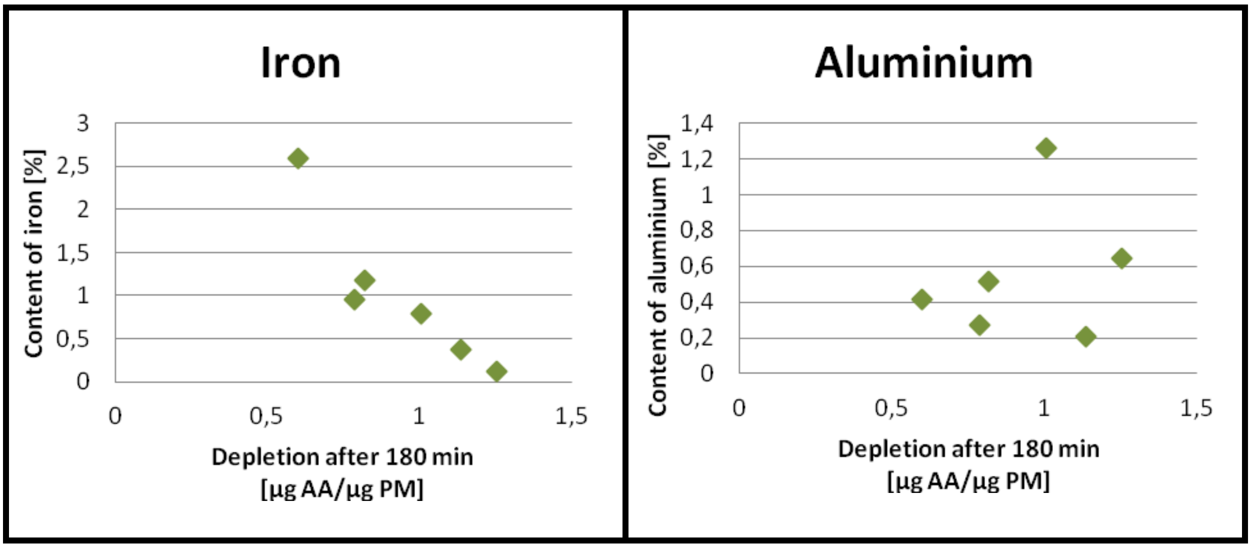
The inorganic ions clearly formed groups. All major ions, ammonium, nitrate, and sulfate, matched well.

Magnesium, chloride, and potassium formed a group too.

Calcium was the only ion with a clear, negative trend. It did not match any other ion but resembled the traffic exhaust patterns.

4.4.1.3. Metals

The major contributors of the metals were iron, aluminium, calcium, and silicon, typical mineral dust elements, which represented 1 to 5% of the PM mass, what is low compared to most other measured samples presented in this thesis. Other determined metals were magnesium, vanadium, chrome, manganese, copper, zinc, strontium, barium, titan, tin, nickel, and lead. Also analyzed were cadmium and cobalt but both were not traceable over the limit of quantification within these samples. The comparisons between metal content and depletion of AA showed mostly broad scattered patterns, though some showed a clear trend.



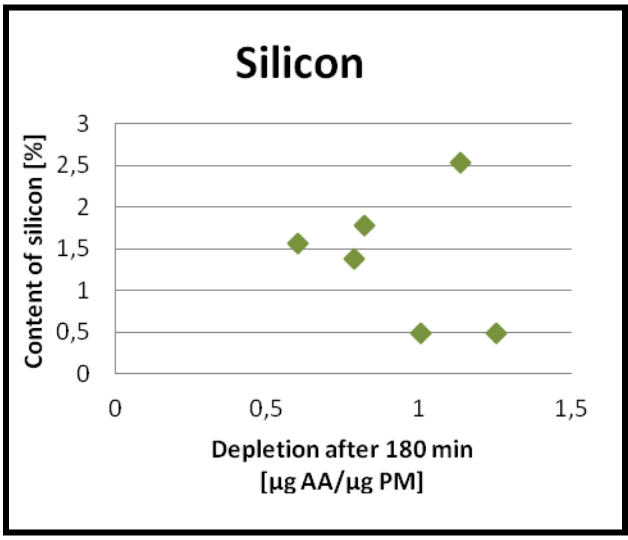


Figure 4.39.: The relation between the content of different metals and the depletion of AA.

Iron showed similarities to calcium. These similarities were also seen for manganese, zinc and chrome which all matched the traffic exhaust patterns.

Silicon matched the major ions just as lead.

Another group was formed by aluminium, barium and strontium which matched magnesium, chloride and potassium. This group only showed high concentrations for higher depletions of AA, but the data points showed broad scattering.

The other determined metals showed no trend and no affiliation to one of the groups.

4.5. Samples from Graz

From Graz eight samples from two sampling sites were measured. The samples were collected on eight sequent days. The samples of the first four days were collected at the sampling-station Graz south, the other four were collected at sampling-station Graz north. All samples were from January 2013 and were provided from the ambient air sampling network of Styria (agency of the Styrian federal state government, division 15, department of air pollution control)).

The samples collected in Graz showed mostly an above average depletion of ascorbic acid. Since only samples of eight days were measured it is hard to define if particulate matter collected in Graz shows high depletions in general or if it only showed those high properties during that short period of time.

It has to be remarked that the samples collected in Graz were the only PM2.5 samples used for the measurements presented in this thesis. This might explains the high depletions of AA, since PM2.5 shows higher relative surface and higher ratios of combustion emissions like carbon species and trace metals.

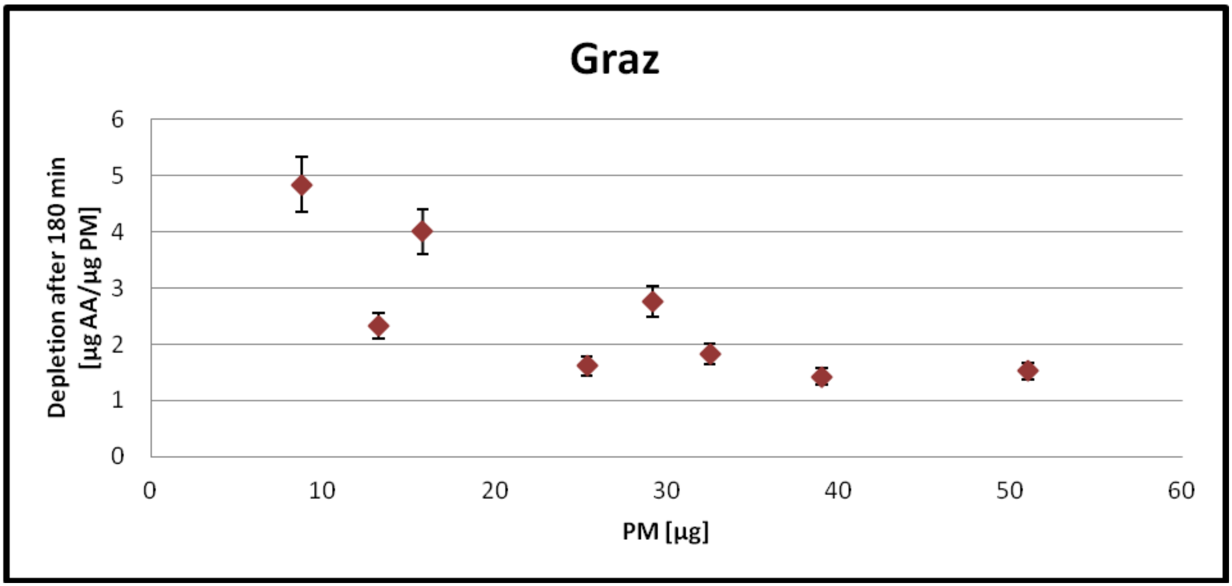


Figure 4.40.: The depletion of AA related to the mass of ambient particulate matter collected on a 5mm punch. Error bars point to a standard deviation of 10%, determined during multiple analysis.

The depletions of AA were rather high, starting at a depletion of 1.4µg and reaching a depletion of nearly 5µg ascorbic acid per µg particulate matter as a maximum, but as mentioned, the samples used were PM2.5 and are therefore not directly comparable to the other measured samples.

Table 4.5.: The average depletion of AA and its deviation for the sampling sites Graz south and Graz north as well as for all Graz samples regarded together:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
Graz south	4	3.3	1.5
Graz north	4	1.8	0.4
Graz in general	8	2.5	1.3

The deviation in Graz south was much higher than in Graz north due to the two samples that showed depletions above 4 µgAA/µgPM. Those two samples also increased the mean and the deviation of the summed up regard of the samples from Graz.

4.5.1. Comparison with Chemical Composition

The elemental composition and carbon parameters were not analysed during this thesis but was already available in literature (Gurgul 2013).

4.5.1.1. Carbon parameters

Graz showed a general high TC content of 35 to 68%. The four samples from Graz south showed a content of 47 to 68% and were mainly responsible for the high TC values. Especially the EC contents were high compared to the other measured samples, ranging from 14 to 27%.

Carbon parameters generally showed positive trends for the samples from Graz. Further investigated were OC, EC, wood smoke mass and traffic exhaust.

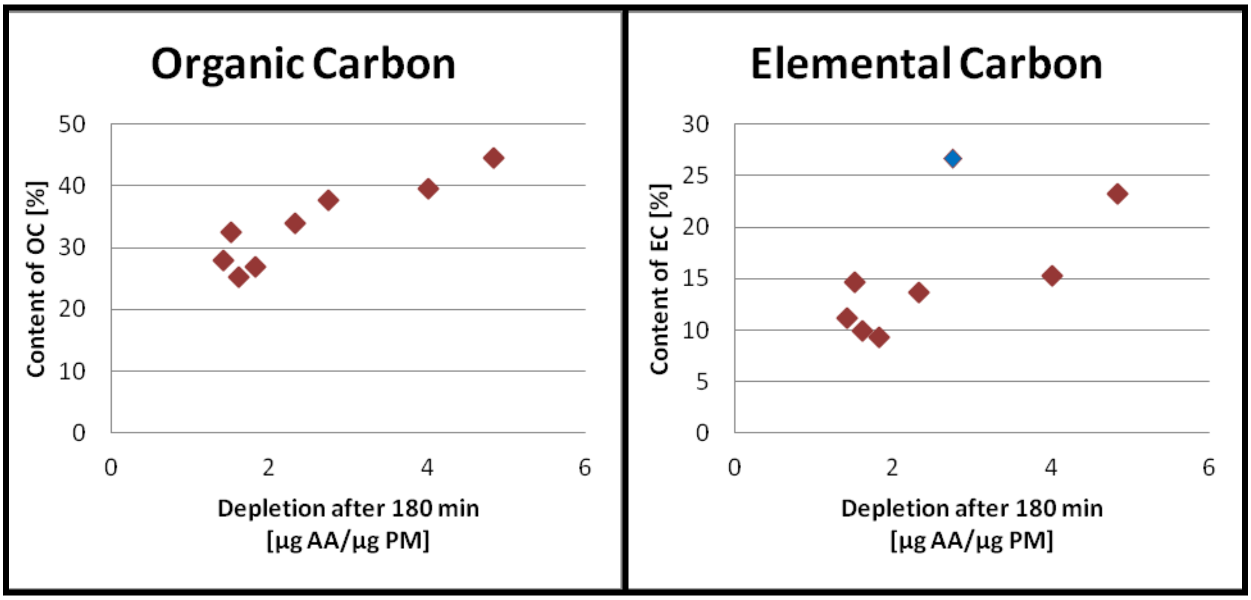
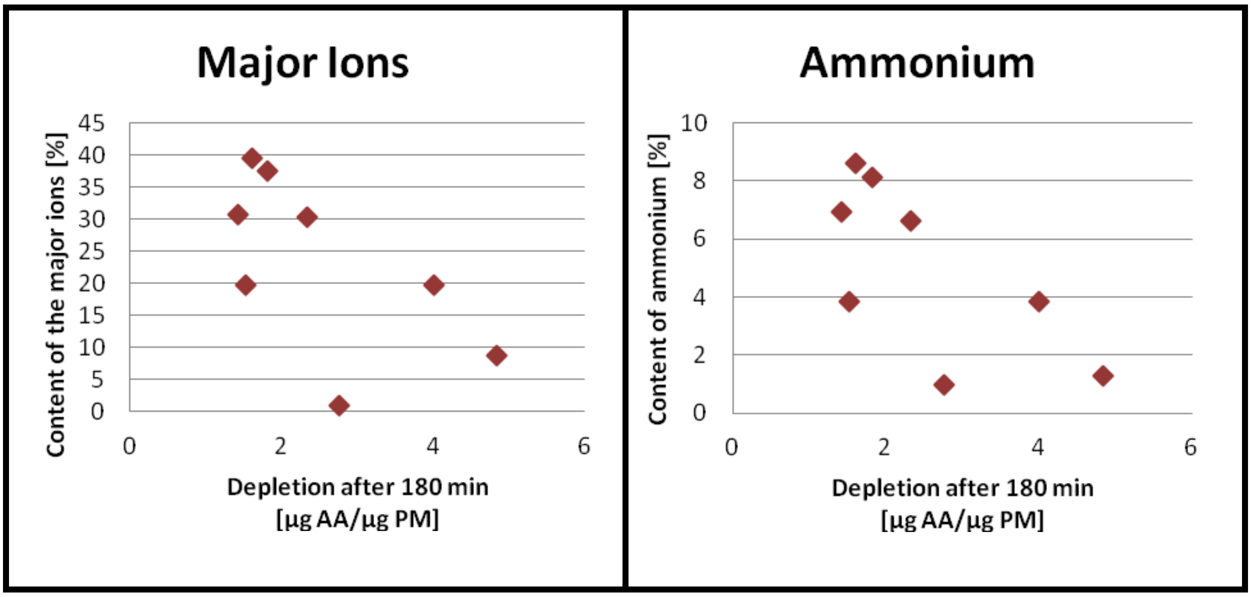


Figure 4.41.: Relation between the content of EC and OC and the depletion of AA.

EC and OC both showed positive trends. EC showed nearly the same patterns as OC except for the point visible in figure 4.41. marked in blue, which showed a much higher content in EC related to the other data points than the data point for OC. This led to the suggestion that EC and OC from the Graz samples mostly showed the same sources, except for one day were EC got released in a higher ratio or through another source.

4.5.1.2. Inorganic Ions

The content of the major ions nitrate, sulfate, and ammonium ranged from 9 to 40% of the PM mass depending on the sample. Next to the major ions chloride, sodium, potassium, magnesium, and calcium were determined. Their ratio lay in the range of 4-10% of the PM mass. From the sample of January 4th (Graz south) no data was available for sulfate, nitrate, and chloride.



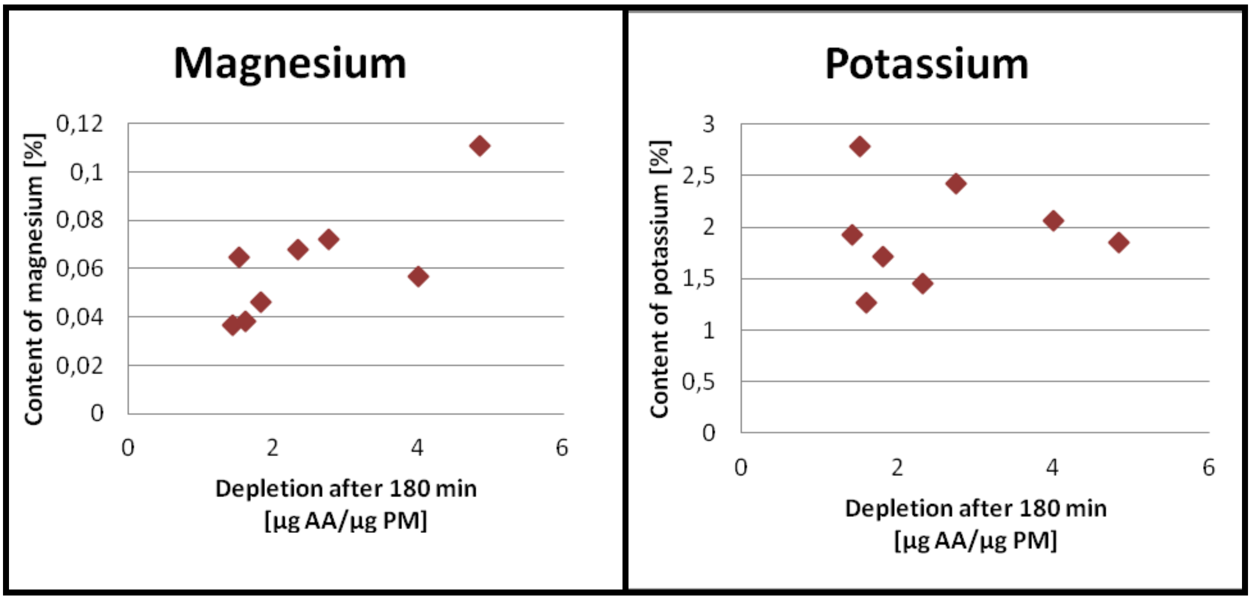


Figure 4.42.: The relation between the content of different ions as well as the sum of the major ions and the depletion of the AA.

All major ions, sulfate, nitrate, and ammonium showed a negative trend and matched each other well. As example the relation between the sum of major ions as well as the content of ammonium and the depletion of AA are shown in Figure 4.42.. Potassium acted likewise but with slightly different patterns.

All other determined minor ions showed the same positive trend as magnesium and matched its patterns. These patterns showed similarities to the OC patterns. As already mentioned the OC and the EC patterns looked very much alike but in this case all ions showed the same aberration to the EC patterns as OC did, leading to the suggestion that the minor ions, except for potassium, mostly get co-emitted with organic carbon.

4.5.1.3. Metals

Aluminium and iron were the two major metals determined for the samples collected in Graz. Together they only showed 0.5-2% of the PM mass, which are low values compared to most other measured samples, that lay in the range of those seen for the samples from Upper Austria.

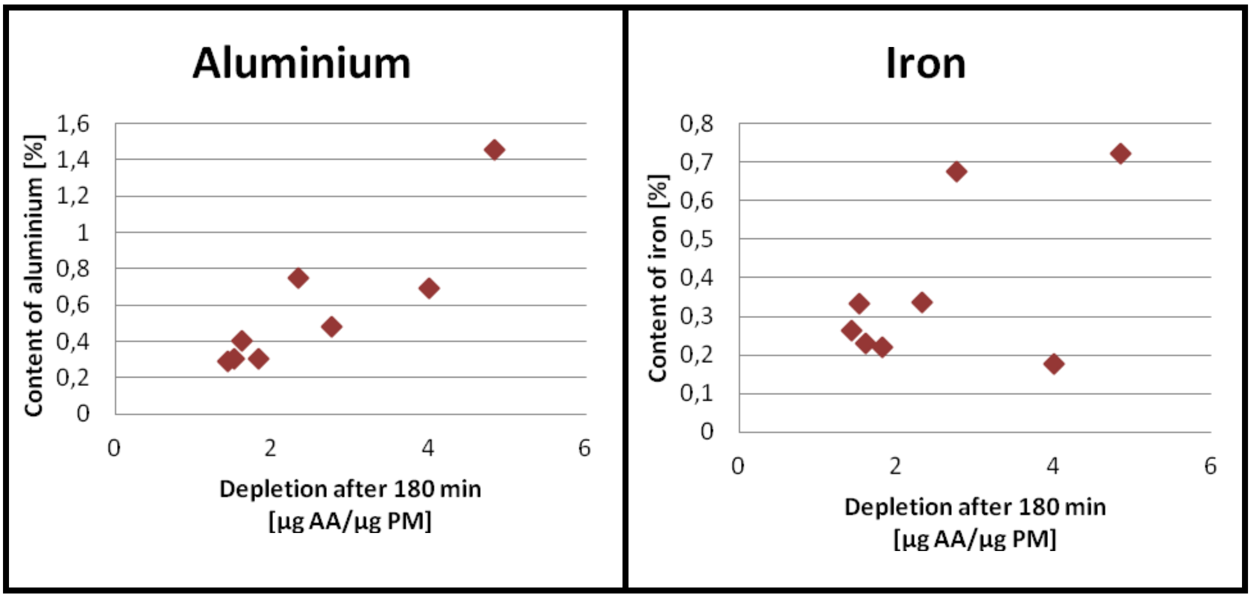


Figure 4.43.: The relation between the content of different content elements and the depletion of AA.

Aluminium and iron showed a positive trend and seemed to be linked to the magnesium/OC group. Especially iron showed a broader scattering of the data points.

4.6. Smoke and Biological Samples

In addition to the samples collected in the ambient and indoors, the oxidative properties in regards of AA of artificially prepared samples were measured. Those samples were emission samples of different wood species (alder and beech) and wood briquettes, different coal species (brown coal and stone coal), and cardboard packages of fruit juice. Also two biological samples were measured. Those were grinded linden leaves and splints. The size of those biological samples was >10µm a.d..

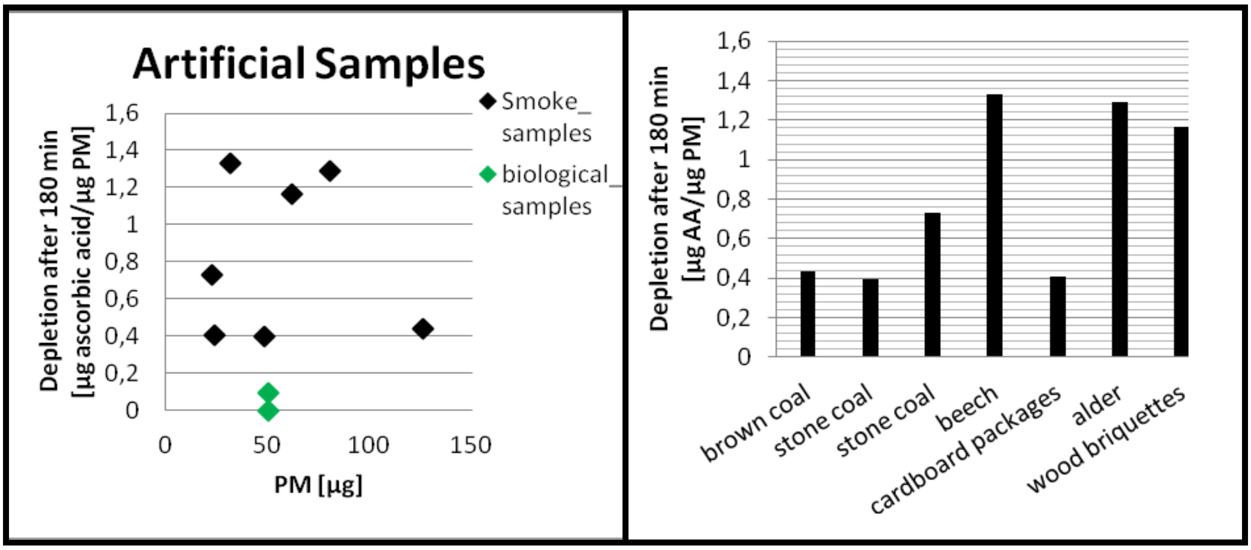


Figure 4.44.: The plot on the left shows the depletion of AA related to the mass of particulate matter (smoke samples) collected on a 5mm punch, the masses of the biological samples were chosen randomly since the used masses were too high to plot them with the smoke samples on one graph. Error bars point to a standard deviation of 10%, determined during multiple analysis. The plot on the right shows the depletion of AA for the smoke samples related to the fuel.

In figure 4.44. the depletion of AA related to the mass of PM and the biological samples is shown. It can be seen that the oxidative properties of smoke samples lay in the medium to low range compared to those of the measured ambient and indoor samples shown in this theses. However as just a limited number of emission samples was investigated, the method was not adopted for these samples especially. They show a high content of carbonaceous species like tar and are therefore probably not perfectly suitable for a measurement in aqueous solutions. If the different emission sources are compared, it can be seen that the wood samples, represented by alder, beech, and briquettes, showed the highest degrees of oxidation in regards of AA, while coal and the drink carton emissions showed little depletions of AA.

The biological samples did not show mentionable depletions. The data point showing no depletion in figure 4.44. belonged to the linden leaves. It was set to 0 µgAA/µgPM and originally showed a depletion of -0.02 µgAA/µgPM. Since the depletion of the ascorbic acid from the blank and that of the samples were subtracted, this means that the ascorbic acid in the linden leave bottles showed less depletion than that in the blank bottles (in this case without a blank filter since the biological samples were used directly and not deposited on a filter). If this is not due to fluctuations, this can ether mean that the linden leaves delivered substances that eluted at the same time as ascorbic acid did and therefore increased the peak, or that they delivered substances that hindered oxidation.

The splints showed very little oxidative properties in regards of AA.

Table 4.6.: The average depletion of the artificial samples and their standard deviations, separated by smoke and biological samples as well as by the burned matter. Coal samples are related to the emissions of the brown coal and the two stone coal samples, wood samples are related to alder, beech, and wood briquettes emissions:

	Number of samples	Average depletion of AA [µgAA/µgPM]	Standard deviation [µgAA/µgPM]
Smoke samples	7	0.82	0.43
Biological samples	2	0.04	0.07
Coal samples	3	0.52	0.18
Wood samples	3	1.26	0.09

4.6.1. Comparison with Chemical Composition

Since the measured samples were artificially prepared, the comparisons were not influenced by substances not generated directly through the burning process giving the opportunity to observe the influence of directly emitted components on the oxidative properties in regards of AA. Further data about the sampling and the chemical composition of emission samples can be found in the reports by Luisser et al. (2008) and Schmidl et al. (2008).

4.6.1.1. Carbon parameters

Carbon represented the highest contents in the emission samples compared to the other samples presented in this thesis. It ranged from 47 to 79% TC (CC was not determined). The OC content ranged from 10 to 69%, the EC content ranged from 10 to 48%. Hereby the generation of EC and OC are competing reactions and not increased alongside each other. The highest OC contents have been seen for the coal samples and cardboard packages ranging from 46 to 69% while those samples only show EC in a content of 10 to 24%. High OC contents also have been seen for beech (40%) which only showed an EC content of 15%. The other wood samples, alder and wood briquettes, showed an OC content of only 10-11 %, while they showed an EC content of 37 to 48%.

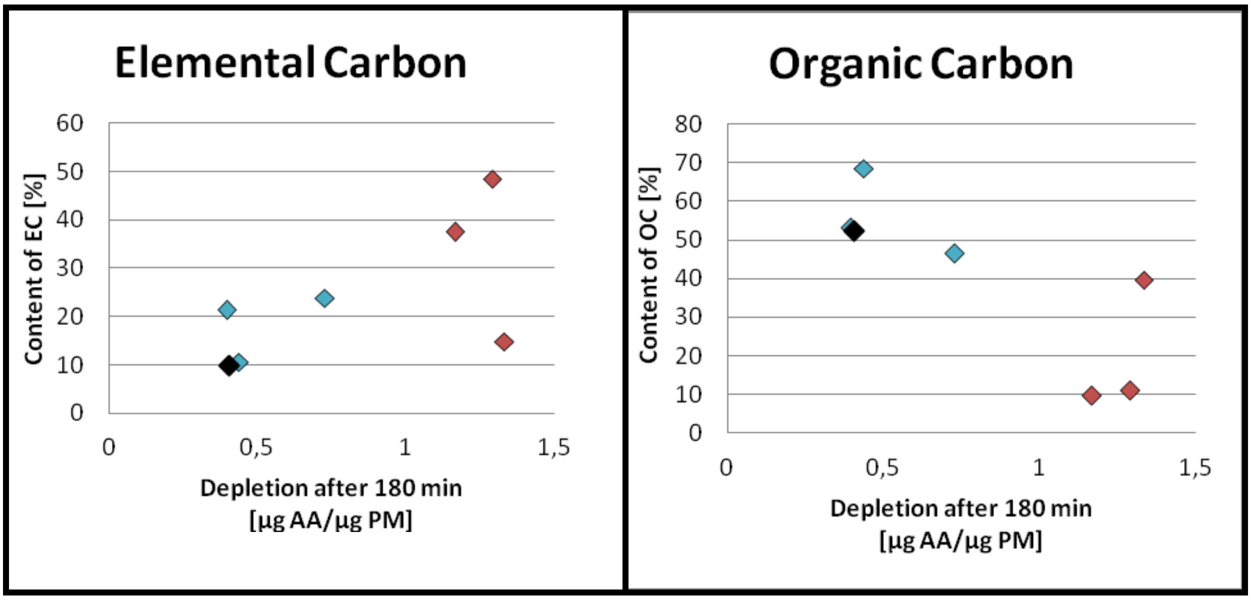


Figure 4.45.: The relation between the content of EC and OC and depletion of AA. Coal samples are marked in blue and wood samples are marked in red. The remaining black data point refers to cardboard packages.

The competing character of the formation of EC and OC mentioned above is well visible in figure 4.45.. The two plots shown there form complementary patterns.

In general a positive trend was visible for EC and a negative one for OC. Interesting is the beech which did not follow the positive trend, showing low EC contents with a high depletion. If the data was separated by wood and coal samples, a different picture was obtained. However, since only three samples were measured of both groups, no trends can be determined.

4.6.1.2. Inorganic Ions

The major ion content of the smoke samples ranged from 0.5 to 3%, which is low compared to ambient samples showing again the special character of this emission samples. The minor ions determined were sodium, magnesium, potassium, and chloride. Their content ranged from 0.5 to 9%. This high content was mostly due to the high calcium content in the cardboard package emission. If this sample is excluded, the content ranged from 0.5 to 4%.

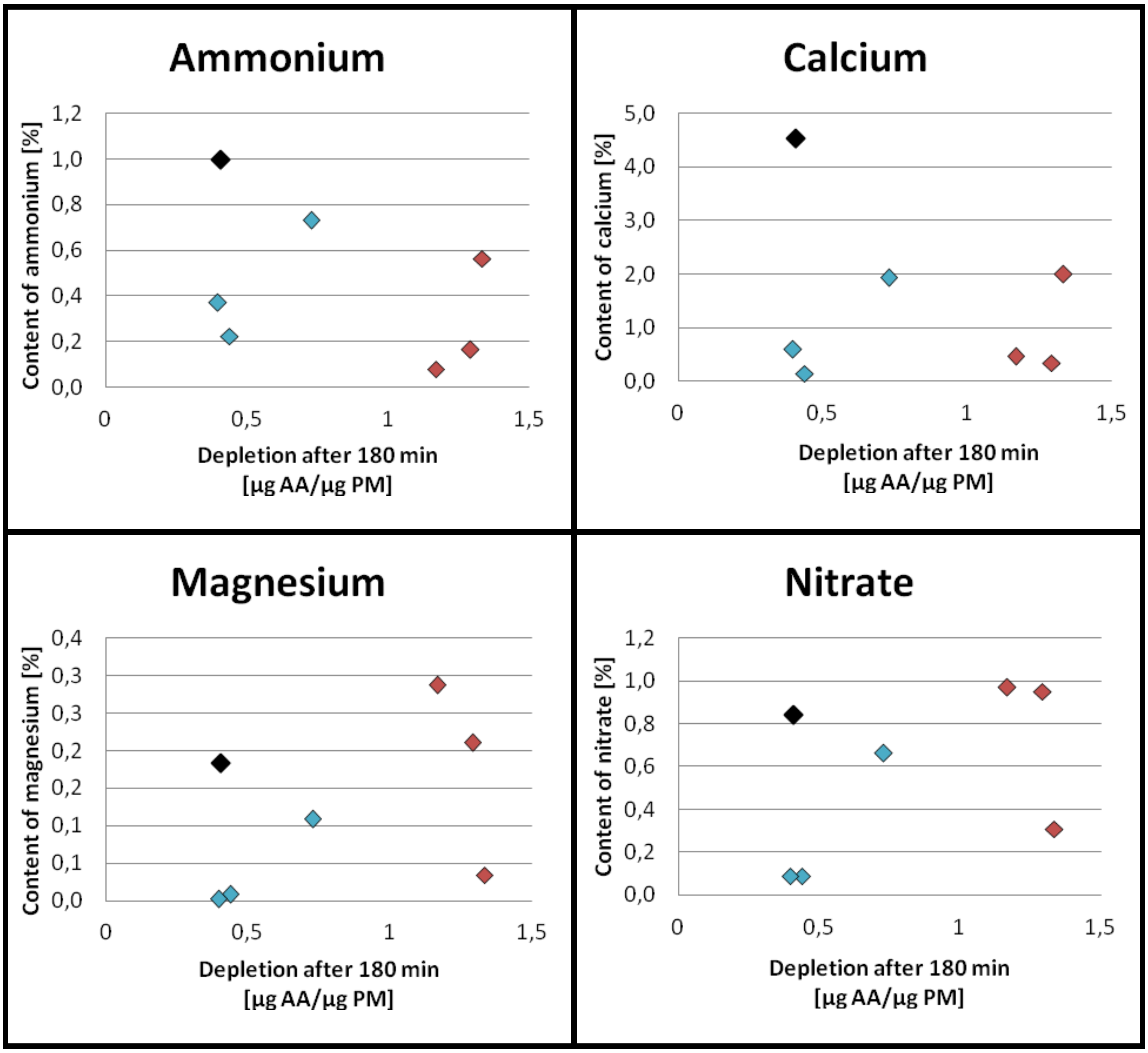


Figure 4.46.: The relation between the content of different ions and the depletion of AA. Coal samples are marked in blue and wood samples are marked in red. The remaining black data point refers to cardboard packages.

There was a strong group formation, which is interesting, since those samples were from the emissions of different substances. It is remarkable that the ratios of ammonium and calcium as well as the ratios of magnesium and nitrate resembled each other meaning those substances were emitted in the same ratios in all different emission samples.

4.7. Summary

Figure 4.47 summarizes all analysis performed for the depletion of ascorbic acid. Figure 4.48 gives the results for ambient air samples only. On the whole a similar trend is visible as was already discussed in chapter 4.2.1., when just samples from Vienna were considered. For most of the data points the depletion of AA ranges between 0.5 and 2 µgAA/µgPM. Higher values are only determined for samples showing comparable low mass loadings. The PM mass of 20 µg given on the x-axis refers to an ambient PM mass concentration of 22µg/m^3, when sampling on High Volume filters and a sample volume of 700m^3 is assumed. This tendency has already been discussed before. The replicate analysis done for the characterization of the analytical method pointed out, that no systematical error occurred. Samples collected in Vienna comprise the biggest data set and consequently also the widest range of aerosol mass. Although the other data sets would not show statistically different signals when overall averages are considered, they formed cluster with different average masses and different average oxidative properties in regards of AA. In that context it has to be mentioned again, that samples from Graz were PM2.5 samples while all other samples were PM10. This could be a reason for the slightly higher depletion of ascorbic acid and the lower PM mass loadings determined in Graz.

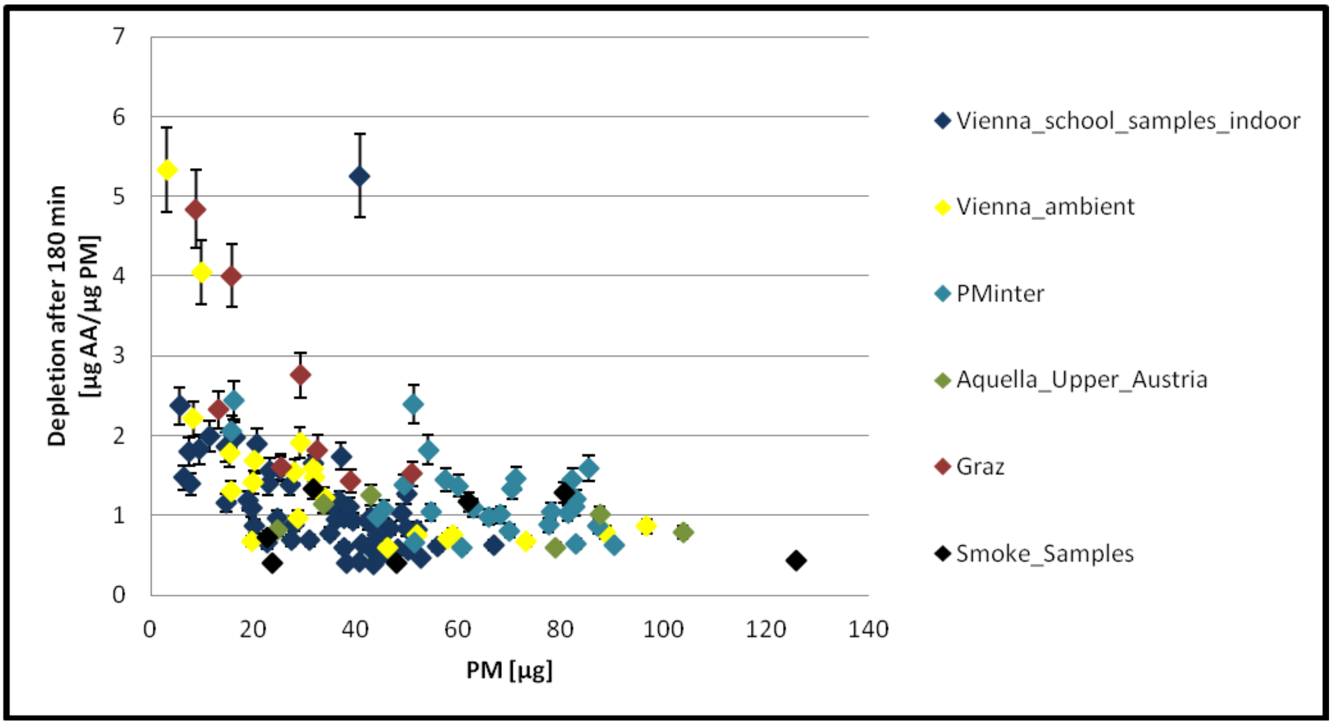


Figure 4.47.: The oxidative properties of ambient and indoor samples as well as smoke samples in regards of AA. Error bars point to a standard deviation of 10% determined during multiple analysis. The mass on the x-axis is the mass of ambient particulate matter collected on a punch with a 5mm diameter.

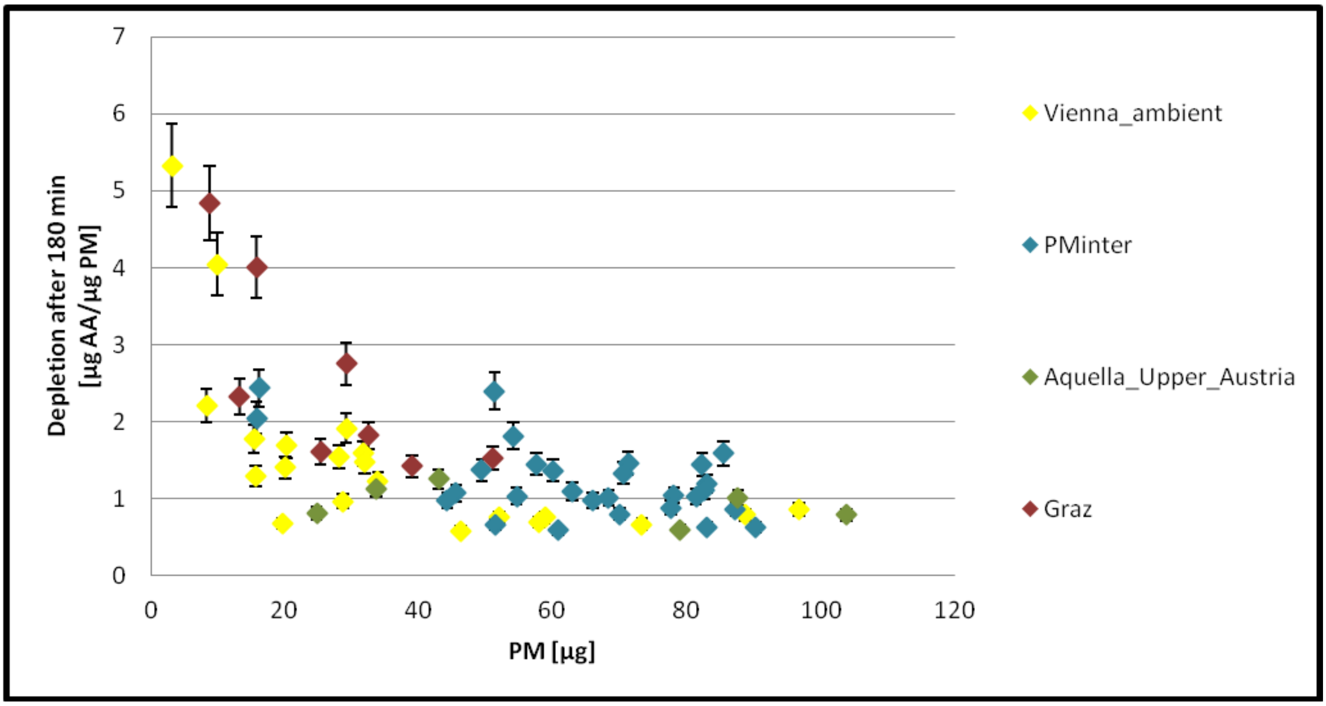


Figure 4.48.: The oxidative properties of ambient air samples in regards of AA. Error bars point to a standard deviation of 10% determined during multiple analysis. The mass on the x-axis is the mass of ambient particulate matter collected on a punch with a 5mm diameter.

Possible reasons for the trends seen in figures 4.47. and 4.48. can be based in the chemical composition of the samples. Although a number of similarities could be found in the comparisons of chemical composition and oxidative properties, no overall trend valid for all data sets could be deduced. One general trend was that filters with lower amounts of PM mass tended to show a higher mass contribution of carbonaceous aerosols and metals and a lower ratio in major ions, as will be shown in the following.

In the following chapters the comparisons between chemical composition and depletion of AA from ambient samples will be discussed. 'Vienna_ambient' refers to the sum of ambient samples from Fichtnergasse and Rosensteingasse and samples collected during the Aquella campaign in Vienna. As already mentioned before, the concentration data of the chemical analysis of carbon parameters and source contributions as well as the elemental composition and ions can be found in the literature (Jankowski et al. 2013; Bauer et al. 2006; Jankowski et al. 2009; Kistler et al. 2013[a,b,c]; Gurgul 2013).

4.7.1. Carbon parameters and source contributions

In this chapter TC, EC, OC, wood smoke, traffic exhausts, and OC without a defined source are discussed.

The TC content of the samples varied strongly from 15 to nearly 70% of aerosol mass, showing its highest contribution to PM in Graz. The majority of the samples ranged between 20 and 50% TC in aerosol mass.

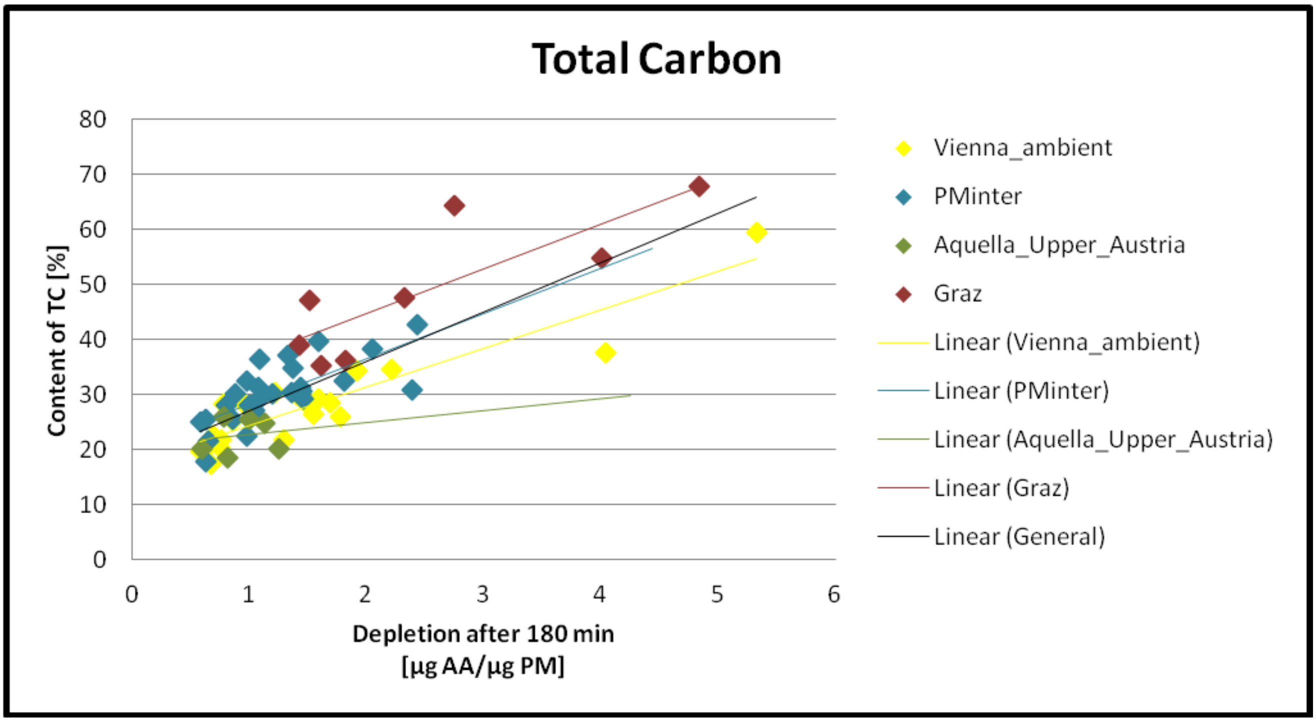


Figure 4.49.: The relation between the content of TC and the depletion of AA with trendlines for the different sampling sites and a general trendline.

TC showed a general positive trend. In addition to the trendlines given for all subsets of samples, a general trendline is given in figure 4.49., which sums up all samples. Hereby the samples from Vienna and PMinter matched well. The samples from Upper Austria showed a smaller slope and also an extremely low correlation coefficient, which is most likely due to the limited variation of data points. The trendline for the samples from Graz showed nearly the same slope, but a higher offset. This could be due to the fact, that PM2.5 samples are considered here.

The smallest scattering of data points was visible for the ambient samples from Vienna.

Table 4.7.: Trendline parameters for the comparison between the TC contribution to aerosol mass and the depletion of AA for the different sampling sites as well as for the general trend line:

	Slope (k)	Offset (d)	correlation coefficient (R^2)
Vienna_ambient	7.0	17.4	0.841
PMinter	8.2	20.1	0.517
Upper_Austria	2.2	28.5	0.027
Graz	8.1	20.4	0.675
General	9.0	18.0	0.685

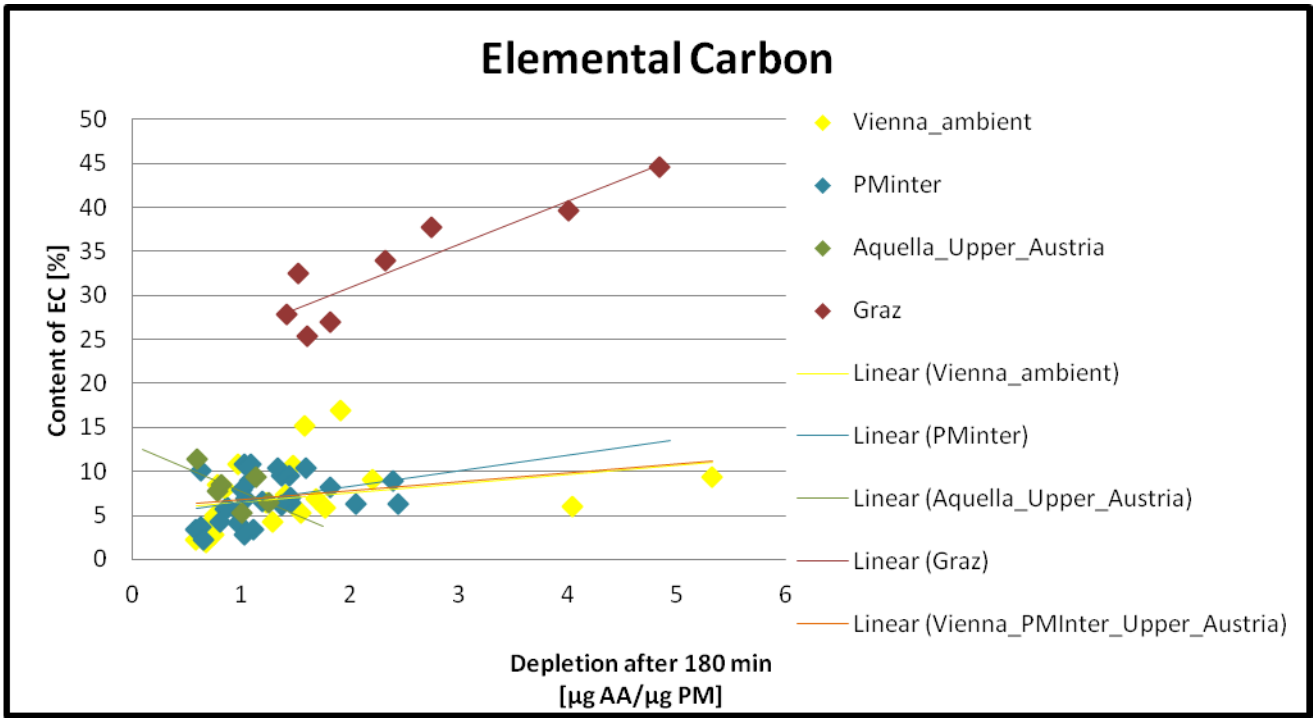


Figure 4.50.: The relation between the content of EC and the depletion of AA with trendlines for the different sampling sites and a general trendline (samples from Graz are excluded).

Regarding EC, the picture is not as consistent as for TC. The sampling sites in Upper Austria gave a negative trend, which could again be influenced by the comparable small variation of data (for both the EC contribution and the depletion of AA) at those two sites in addition with one sampling showing rather low depletion values of AA at a comparable high contribution of EC to aerosol mass. For all other data sets clear positive trends were visible. Graz showed a trendline quite different, probably again due to the other size cut of the samples.

Since the difference between Graz and the other samples was so pronounced, the general trendline (marked in orange), is summing up the results from PMinter, Upper Austria and Vienna, only. This trendline matched the ambient Vienna samples and PMinter samples in regards of slope reasonably well, but like in Vienna the correlation coefficient was really low. Further analysis should consider the possibility of two subsets of samples. EC defiantly is not the only species defining the depletion of AA.

The smallest scattering of data points can be seen for the PMinter samples. The samples from Upper Austria matched the PMinter samples and the samples from Vienna again well, if only the data points are regarded.

Table 4.8.: Trendline parameters for the comparison between the EC contribution to aerosol mass and the depletion of AA for the different sampling sites as well as for the general trend line (samples from Graz are excluded):

	Slope (k)	Offset (d)	correlation coefficient (R^2)
Vienna_ambient	1.0	5.5	0.092
PMinter	2.0	3.3	0.109
Upper_Austria	-5.3	13.1	0.362
Graz	4.9	21.1	0.837
General	1.1	5.1	0.074

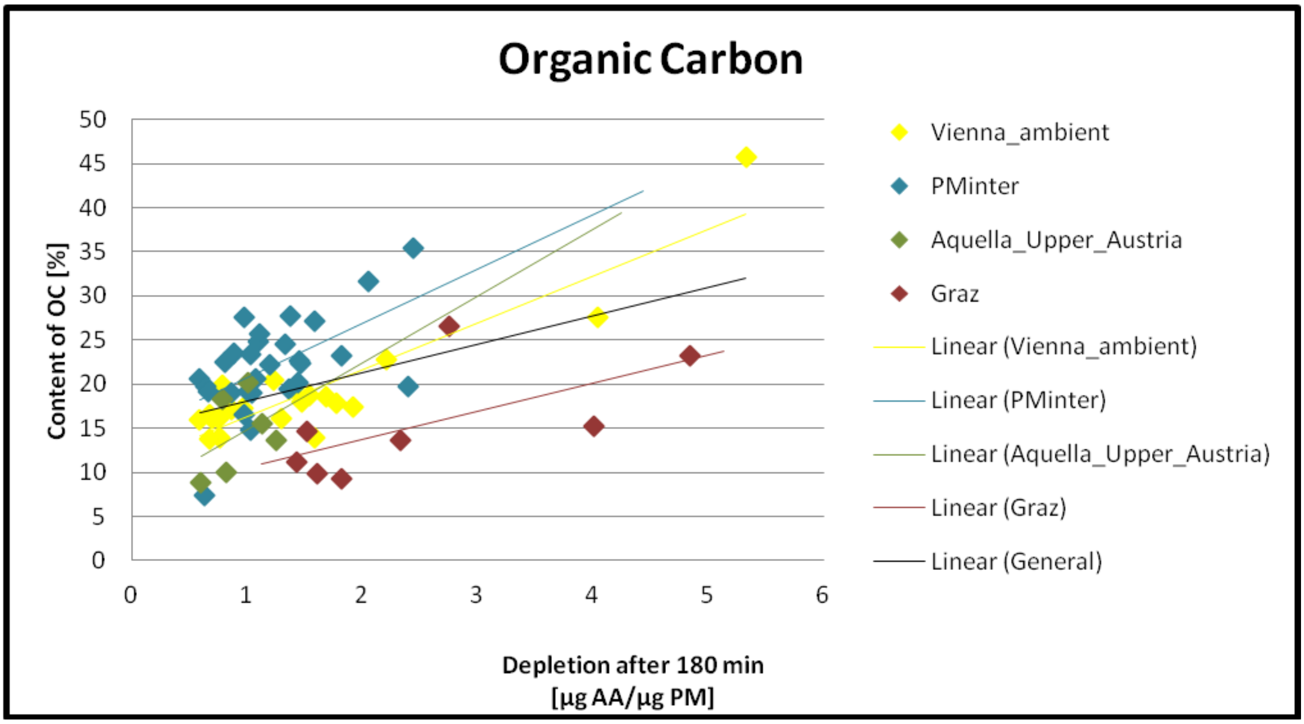


Figure 4.51.: The relation between the content of OC and the depletion of AA with trendlines for the different sampling sites and a general trendline.

OC showed again a positive relationship to the depletion of AA for each subgroup of samples, and consequently also for the overall trendline. Nevertheless marked differences could be observed for the single trendlines, when slope and offset were regarded. If only the data points were regarded, the samples from Vienna and Upper Austria matched well.

Table 4.9.: Trendline parameters for the comparison between the OC contribution to aerosol mass and the depletion of AA for the different sampling sites as well as for the general trendline:

	Slope (k)	Offset (d)	correlation coefficient (R^2)
Vienna_ambient	5.3	11.1	0.818
PMinter	6.1	14.6	0.322
Upper_Austria	7.5	7.4	0.165
Graz	3.1	7.4	0.409
General	3.2	15.0	0.232

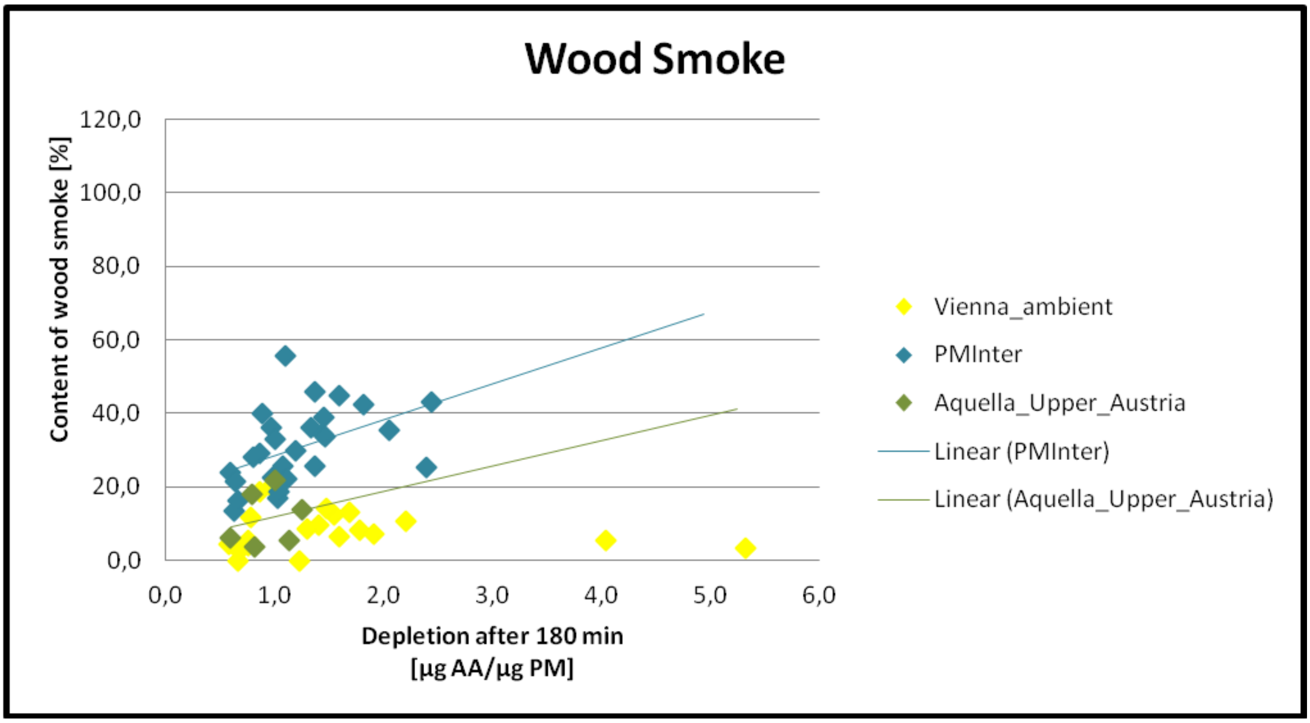


Figure 4.52.: The relation between the content of wood smoke and the depletion of AA with trendlines for the different sampling sites and a general trendline.

While the relative contribution of wood smoke to PM mass showed a positive trend on the depletion of AA for samples from Upper Austria and the PMinter project, which both included at least a number of rural sampling sites, it showed no trend for the samples from Vienna. This was expected since wood smoke has a higher influence on rural areas than on urban areas (Caseiro et al. 2009). The correlation coefficient for Upper Austria was very poor.

In Vienna the variation of the depletion of AA was obviously induced by other factors than wood smoke. Due to the different picture observed for the subgroups no general trendline was calculated.

Table 4.10.: Trendline parameters for the comparison between the wood smoke contribution to aerosol mass and the depletion of AA for the different sampling sites as well as for the general trendline:

	Slope (k)	Offset (d)	correlation coefficient (R^2)
PMinter	9.7	18.8	0.211
Upper_Austria	6.9	5.1	0.050

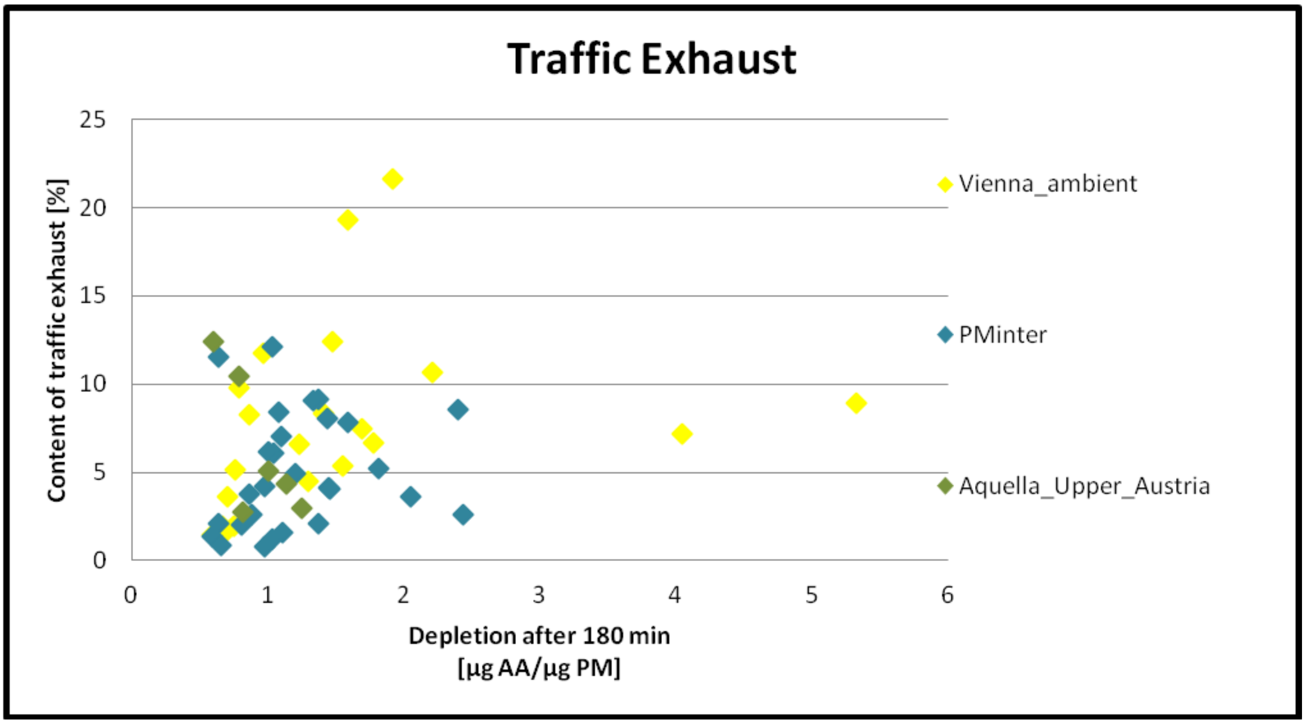


Figure 4.53.: The relation between the content of traffic exhaust and the depletion of AA.

The contribution of traffic exhaust to PM mass showed a positive trend for most of the data points. However, because of the marked scatter of data no trendlines were calculated here.

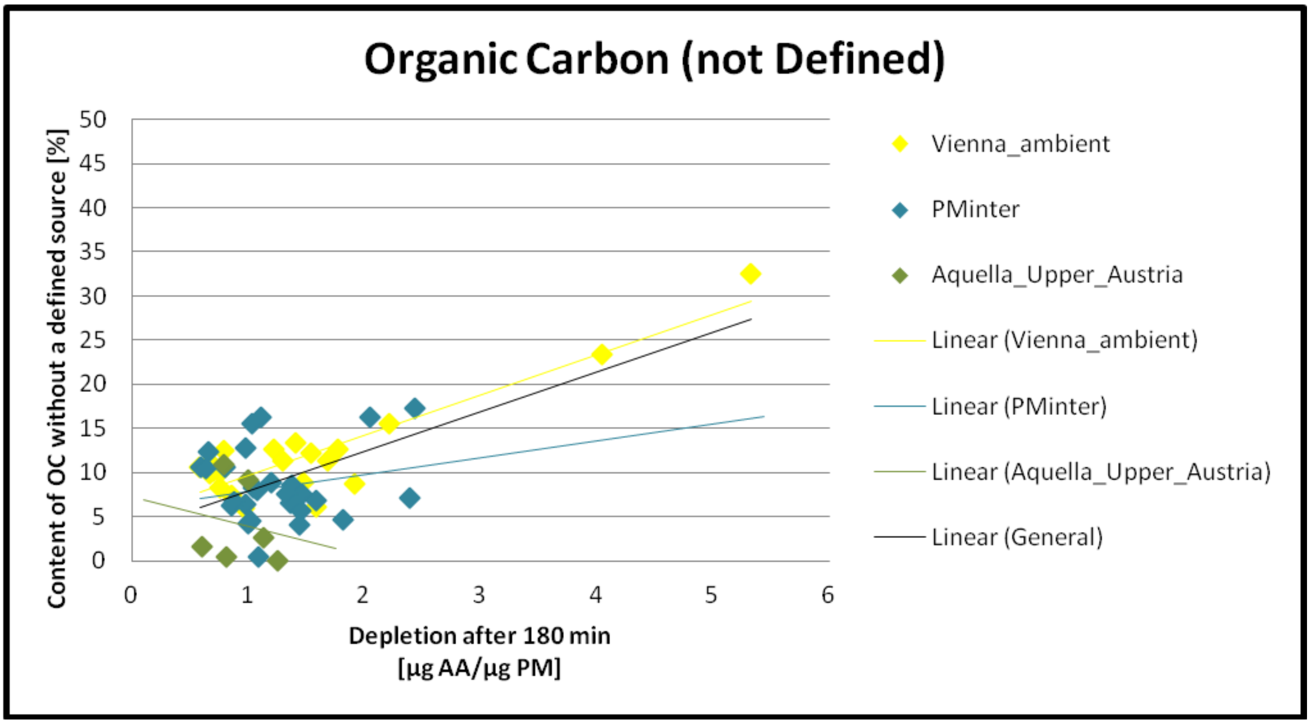


Figure 4.54.: The relation between the content of OC without a defined source and the depletion of AA with trendlines for the different sampling sites and a general trendline.

OC without a defined source showed a general positive trend for Vienna and PMinter, but not for Upper Austria.

Remarkable was the high linearity of the samples from Vienna, especially in regards of elevated depletions of AA, which either points to the high influence OC without a defined source had on those high depletions, or to a covariation of OC and other species inducing an increased depletion.

The offsets of all sample groups lay close together.

Table 4.11.: Trend line parameters for the comparison between the OC (undefined) contribution to aerosol mass and the depletion of AA for the different sampling sites as well as for the general trend line:

	Slope (k)	Offset (d)	correlation coefficient (R^2)
Vienna_ambient	4.5	5.1	0.790
PMinter	1.9	6.0	0.042
Upper_Austria	-3,3	7.2	0.030
General	4.5	3.4	0.424

4.7.2. Inorganic Ions

The major ions nitrate, sulfate, and ammonium were from special interest since their ratio on the filter is high. In the regarded samples their contribution to PM mass ranged from 1 to 65%. On the other hand it is not likely, that those compounds influence the oxidative properties a lot. Some minor ions were investigated as well.

In general most ions showed different trends leading to the suggestion, that oxidative properties in regards of AA are mostly influenced by other substances and elevated contributions of major ions lower the oxidative properties of the samples calculated per µg of PM.

Within most of the samples the minor ions chloride, potassium, sodium, calcium, and magnesium were determined.

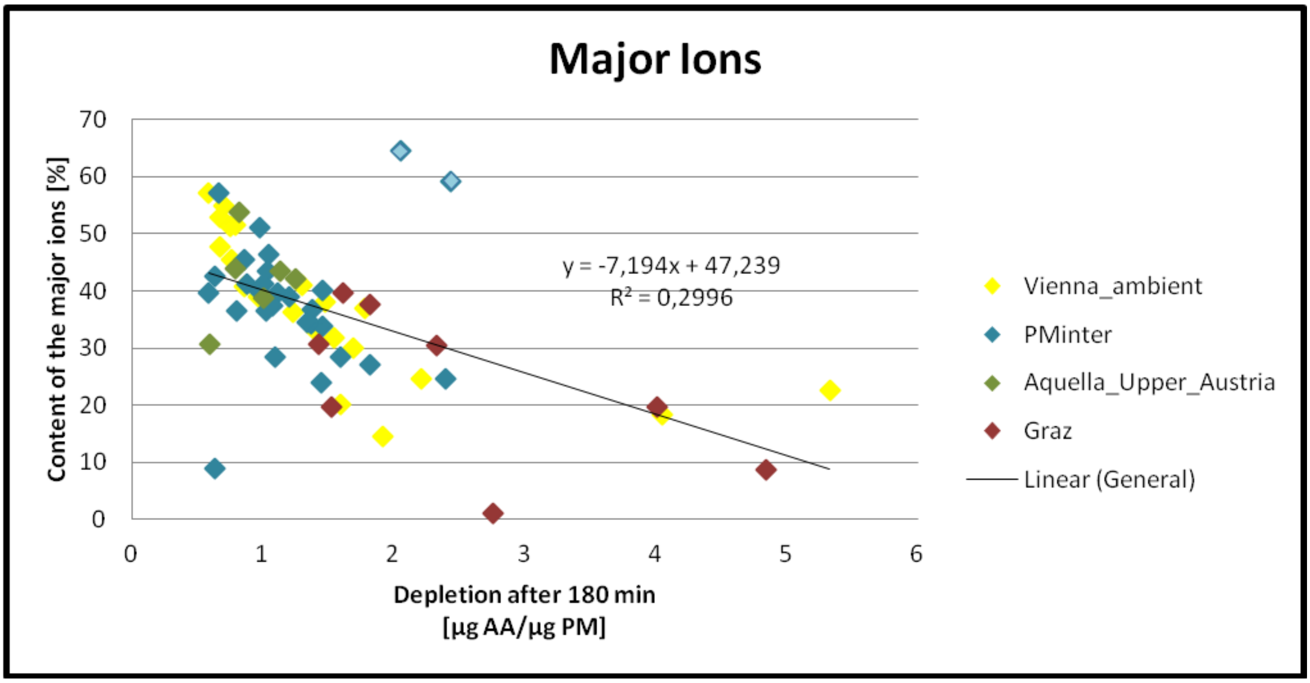


Figure 4.55.: The relation between the content of the major ions (ammonium, sulfate, and nitrate) and the depletion of AA as well as the general trendline with its parameters.

If figure 4.55. is regarded, it is obvious that the data points match well. The major ions showed a general negative trend. This trend was clear for the ambient samples from Graz and Vienna. Samples from the PMinter project and Upper Austria showed much larger scatter. Thus no trendlines were calculated.

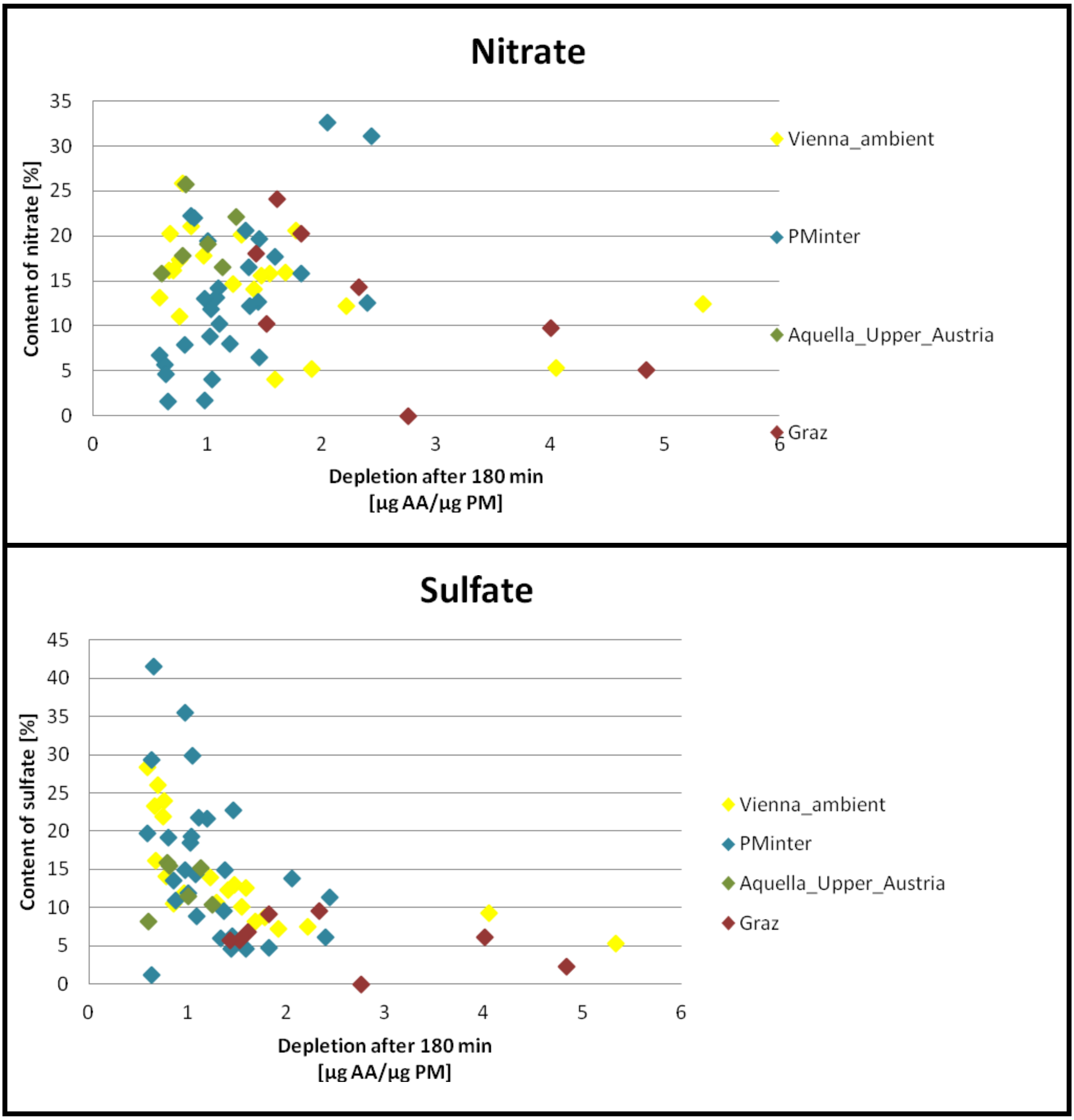


Figure 4.56.: The relation between the content of sulfate and nitrate and the depletion of AA as well as the general trendlines with their parameters.

While ammonium matched the sum of major ions well, sulfate and nitrate showed differences. Nitrate showed a clear positive trend for the PMinter samples and the samples from Graz and Vienna showed a bigger scattering of data points, leading to a less clear negative trend than for the major ions. Therefore no trendlines were calculated.

Sulfate was the major ion that showed the clearest negative trend, when all samples were considered. This got especially obvious if depletions above 4 µgAA/µgPM were not regarded. All data points matched well, though trendlines for the different subsets of samples would differ a lot.

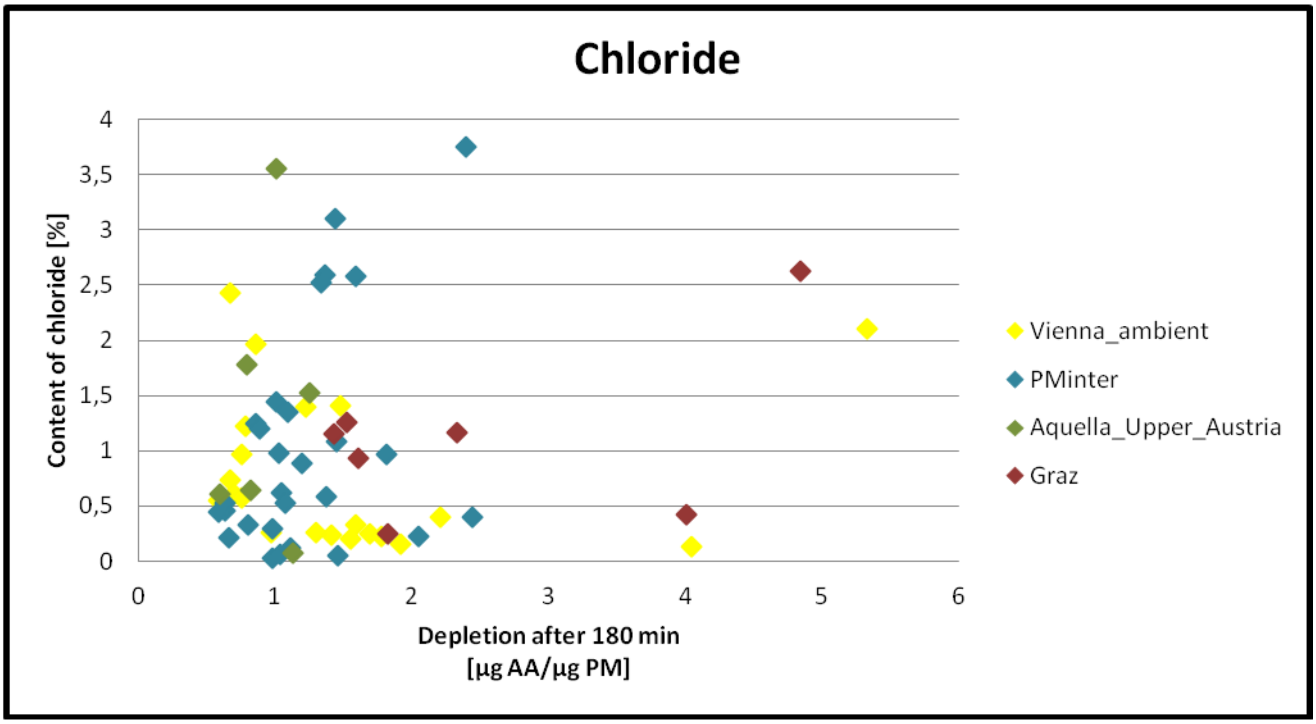


Figure 4.57.: The relation between the content of chloride and the depletion of AA.

As an example for a minor ion chloride is given. It showed a broad scattering of data points. Thus no trendlines were calculated.

4.7.3. Metals

Four metals showed in general a contribution of aerosol mass above one percent. Those are the typical mineral dust elements iron, silicon, aluminium, and calcium. Regarding only iron silicon, and aluminium, all three of them were analyzed for the Rosensteingasse and Fichtnergasse samples as well as for the other ambient samples from Vienna, Upper Austria, PMinter, and Graz. In general they represented <20% of the PM mass.

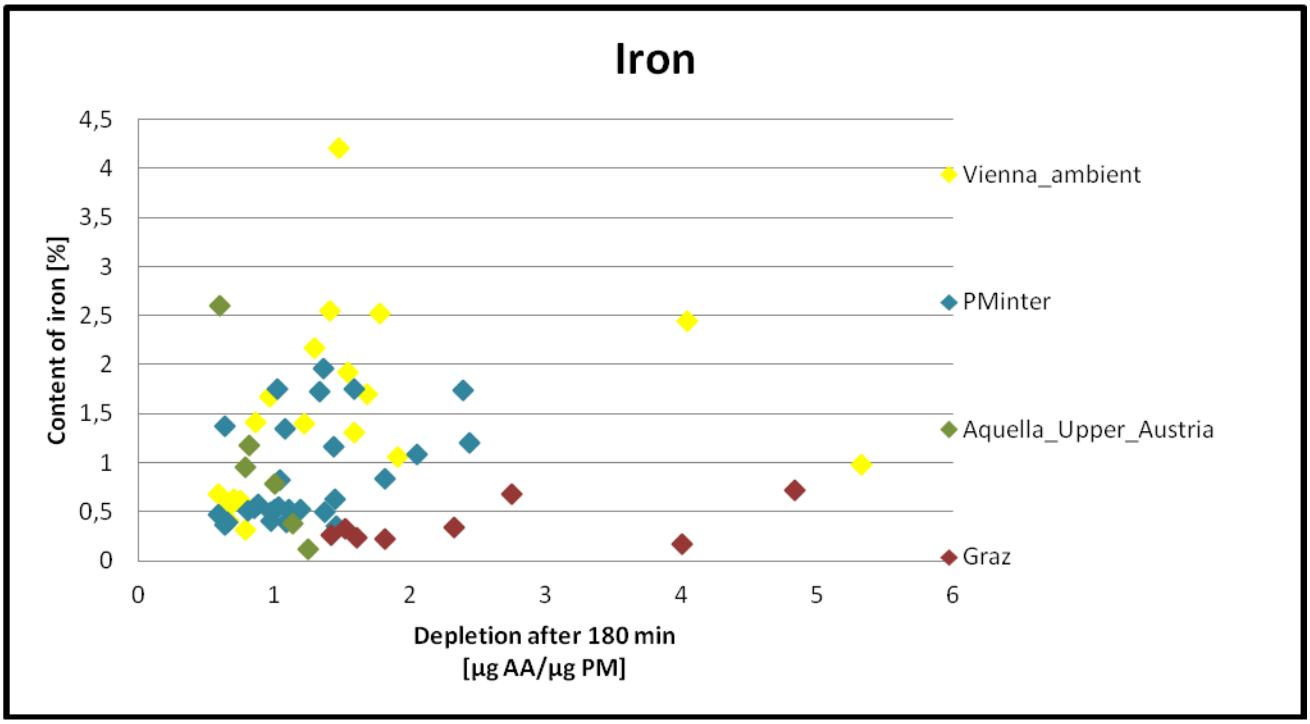


Figure 4.58.: The relation between the content of iron and the depletion of AA.

Iron showed a slight positive trend for most of the samples, but for Vienna and PMinter the correlation coefficients were quite small. Thus no trendlines were calculated. Some correlation was found for Graz. The best correlation was observed for Upper Austria, but here the linear trendline shows, surprisingly, a negative slope.

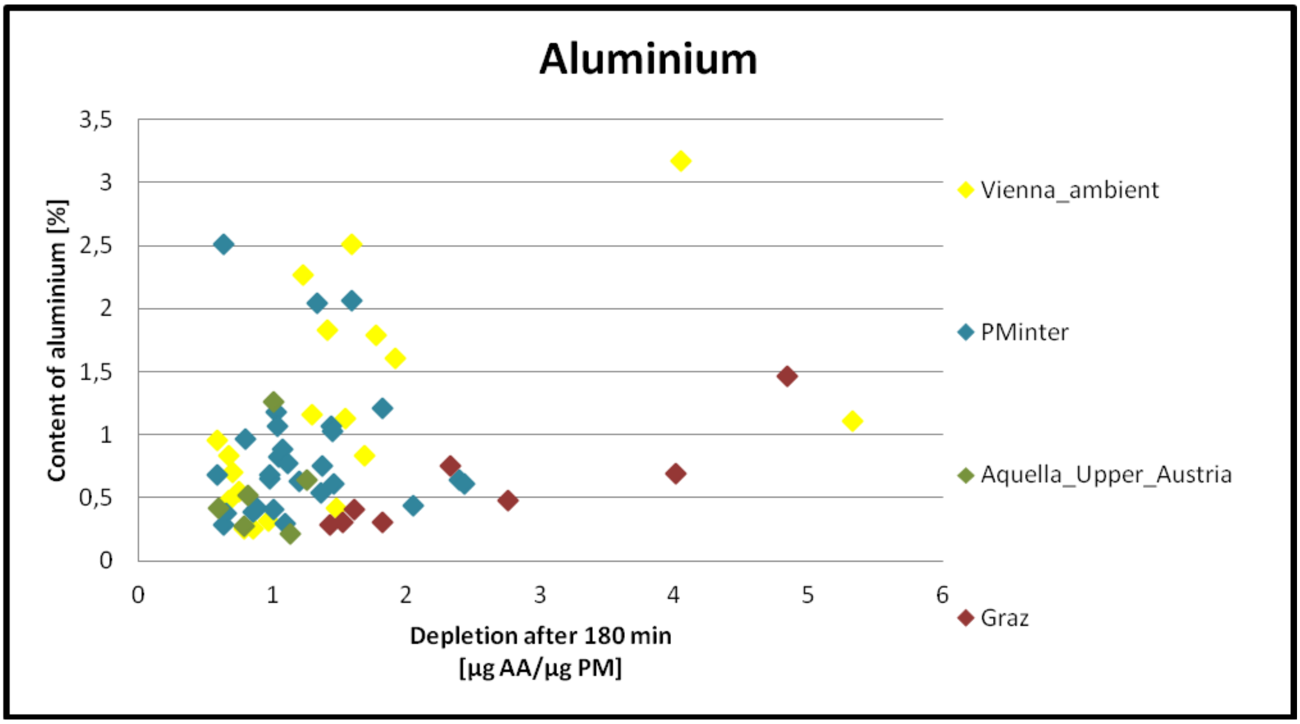


Figure 4.59.: The relation between the content of aluminium and the depletion of AA.

In general aluminium showed a positive trend, but again the correlation coefficients were quite low for all subsets of samples despite Graz. This could again be due to the fact, that PM2.5 samples were collected in Graz.

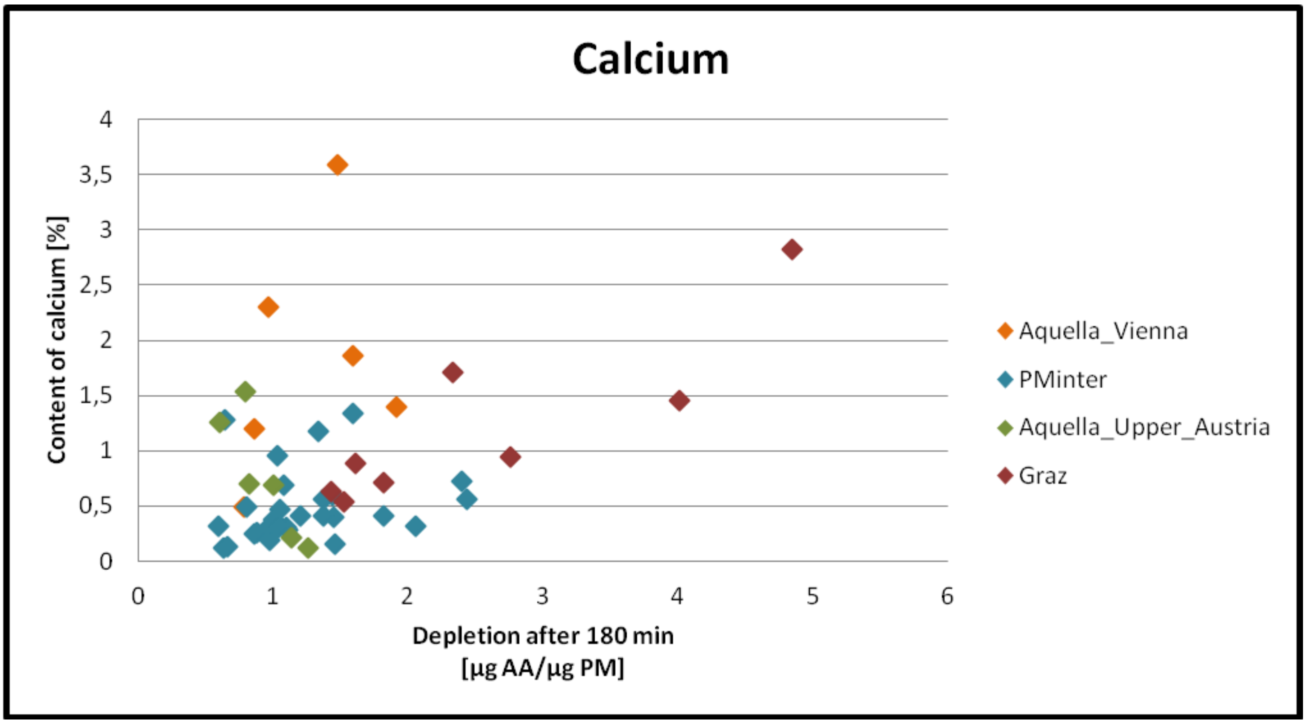


Figure 4.60.: The relation between the content of calcium and the depletion of AA.

In figure 4.60 the relation between the total calcium content of PM mass and the depletion of AA is shown. The Vienna samples refer to the samples collected during the Aquella campaign, since total calcium was not determined for the samples from Fichtnergasse and Rosensteingasse.

Again a general positive trend is visible for all subsets of samples, except for Upper Austria, which showed a negative trend. The scattering of data was smaller than seen for iron and aluminium.

Summing this up, it can be said that the data, presented in this thesis, suggests that carbonaceous species, except for carbonate which was not investigated, enhance the depletion of AA. Similar conditions could also be observed for iron, aluminium, and silicon, although the scatter of the data was much more pronounced. Other than that, ions showed no general oxidative properties in regards of AA, best visible for the sum of major ions (sulfate, nitrate, and ammonium).

5. Conclusion

5.1. Oxidative Properties of the Measured Samples

Particulate matter is a complex mixture of different substances showing not only differences in the composition, but also differences in size and in surface distributions, which all could affect the oxidative properties.

The results obtained in this work led to the suggestion that the depletion of ascorbic acid in a range of 0.5-2.5 µgAA/µgPM can be seen as an average range for the oxidative properties of PM10, when using the explained method. Vienna school samples collected indoors showed in general a smaller depletion of the ascorbic acid related to the mass of the particulate matter than the ambient samples collected in close vicinity to the schools. This is most likely due to the different indoor aerosol sources, leading to a different chemical composition. Thus indoor aerosols show a special composition with a high content in cellulose and sometimes mineral dust (Kasper-Giebl et al. 2013), but this need not be related to indoor samples in general.

Generally the oxidative properties of ambient samples seemed to tend to show higher depletions of AA for smaller filter loads. This trend was not seen for the indoor samples, which showed a slight positive trend, or the wood smoke samples, which behaved linear. Also the samples from Upper Austria showed that two samples collected on the same day exhibited nearly the same oxidative properties in regards of AA, although different amounts of mass were accumulated on the filters.

5.2. Comparison with Chemical Composition

Carbon parameters showed general positive trends. The different gradients and offsets of the comparison between content and depletion of AA lead to assumptions of the influence the different carbon species had on the different sampling sites. This was especially visible for OC and EC, while TC showed gradients that matched well.

Though the samples from Upper Austria showed a negative trend for most carbon parameters, their data points matched those from the other samples, leading to the suggestion, that measurements of a bigger set of samples from that area could probably change that trend.

While wood smoke did not seem to influence the samples from Vienna, it showed an influence on the depletion of AA, for samples from the PMinter project and Upper Austria. Other than that, Traffic Exhaust showed positive trends for the samples from Vienna and PMinter as well.

Organic carbon without a defined source seemed to be important for the higher oxidative properties in regards of AA, since it showed linear trends for several samples with surprisingly high depletions. This parameter ‘un-identified organic carbon’ covers all organic matter that cannot be linked to any specific source. The possible substances and oxidative properties in regards of AA are therefore widely spread.

Inorganic ions sulphate, nitrate and ammonium generally show a high contribution to aerosol mass. On the other hand it is not likely that they influence the oxidative properties of particulate matter. Generally a weak trend of lower depletion of AA at higher contributions of major ions was noticed. The minor ions showed mostly broadly scattered data points. This leads to the conclusion that the investigated inorganic ions do not increase oxidative properties in regards of AA but if present in big enough quantities, they have the potential, to decrease the depletion of AA, simply by forming a bigger non-active PM load.

Elevated contributions of the investigated mineral dust elements iron, aluminium, silicon, and calcium generally increased the depletion of ascorbic aicd, but data scattered markedly. Nawrot et al (2009) investigated the oxidative properties of PM through the generation of OH• radicals, instead the depletion of AA. With their method they also found a positive trend for iron, but for aluminium a negative trend was visible and silicon barely showed a trend at all.
Künzli et al. (2006), who investigated oxidative properties of PM over the depletion of AA, showed a strong correlation between the depletion of AA and the concentration of iron. Correlations for the concentrations of aluminium and silicon were found as well, however not as strong as seen for iron.

The investigations of several trace metals did not show clear trends. Most of them could be linked to the influences of other sources, when patterns were compared. However samples with above average depletions of AA often showed high contributions of trace metals, leading to the conclusion that they play an important role for those high depletions. In the literature e.g. copper can be found, where Künzli et al. (2006) and Nawrot et al. (2009) found a trend that can also be seen for the Rosensteingasse indoor samples, while Godri at al. (2011) found no clear link for the depletion of AA.

6. Literature

[1] http://luft.umweltbundesamt.at/pub/gmap/start.html (November 6th 2013)

Abbey D.E., Nishino N., McDonnell W.F., Burchette R.J., Knutsen S.F., Beeson W.L., Yang J.X.; Long-Term Inhalable Particles and Other Air Pollutants Related to Mortality in Nonsmokers; American Journal of Respiratory and Critical Care Medicine Vol 159; 1999; pp 373-382

Augustyn R., Bachl R., Plank R., Riess P.; Jahresbericht 2011, Luftgütemessung der Umweltschutzabteilung der Stadt Wien; gemäß Immisionsschutzgesätz – Luft; MA 22 – 50/2010; 2012

Bauer H., Marr I., Kasper-Giebl A., Limbeck A., Caseiro A., Handler M., Jankowski N., Klatzer B., Katianove P., Pouresmaeil P., Schmidl Ch., Sageder M. Puxbaum H., Aquella Team; „AQUELLA" Wien, Bestimmung von Immissionsbeiträgen in Feinstaubproben; MA 22 . 3869/03; UA/AQWien 2006r-174S; December 2006

Berlitz H.D., Grosch W., Schieberle P.; Lehrbuch der Lebensmittelchemie; 5. edition; Springer 2001; pp 410ff

Birch M.E., Cary R.A.; Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust; Aerosol Science and Technology 25; 1996; pp 221-241

Bowler R.P., Crapo J.D.; Oxidative Stress in Allergic Respiratory Diseases; journal of allergy and clinical immunology Vol. 110 Nr. 3; September 2002; pp 349-356

Bruckmann P., Kuhlbusch T.A.J., John A., Quass U., Kasper M.; Staub ist überall – Auch in der Luft, Chemie über den Wolken … und darunter; published by Zellner R. and the society of German chemists; Wiley-VCG; 1. edition 2011; pp 105-127

Brunekreef B., Holgate S.T.; Air pollution and health; The Lancet; Vol 360; October 2002; pp 1233-1242

Caseiro A., Bauer H., Schmidl C., Pio C.A., Puxbaum H., Wood burning impact on PM_{10} in three Austrian regions; Atmospheric Environment 43; 2009; pp 2186-2195

Davis M.B., Austin J., Partridge D.A.; Vitamin C: Its Chemistry and Biochemistry; the royal society of chemistry, 1991; pp 127ff

Elmadfa I., König J.; Ascorbic Acid Transport and Availability; Subcellular Biochemistry Volume 25; Ascorbic Acid: Biochemistry and Biomedical Cell Biology; Plenum Press, 1996; edited by Harris J.R.; pp 137-156

Gilliland F.D., McConnell R., Peters J., Gong H., Jr.; A Theoretical Basis for Investigating Ambient Air Pollution and Children's Respiratory Health; Environmental Heallth Perspectives Vol. 107 Supplement 3; June 1999; pp 403-407

Godri K.J., Harrison R.M., Evans T., Baker T., Dunster C., Mudway I.S., Kelly F.J.; Increased Oxidative Burden Associated witht Traffic Component of Ambient Particulate Matter at Roadside and Urban Background Schools Sites in London; Plos One; Vol 6; Issue 7; July 2011; e21961

Gomez-Mejiba S.E., Zhai Z., Akram H., Pye Q. N., Hensley K., Kurien B.T., Scofield R.H., Ramirez D.C.; Inhalation of Environmental Stressors & Chronic Inflammation: Autoimmunity and Neurodegeneration; Mutation Research 674; 2009; pp 62-72

Gurgul A.; „Charakterystyka chemiczna aerozoli atmosferycznych z poludniowej Austrii w zaleznosci od zrodla pochodzenia"; Diploma Thesis; AGH Krakow; 2013

Halliwell B., Gutteridge J.M.C.; Oxygen toxicity, oxygen radicals, transition metals and disease; Biochemical Journal 219; 1984; pp 1-14

Iinuma Y., Engling G., Puxbaum H., Hermann H.; A highly resolved anion-exchange chromatographig method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol; Atmospheric Environment 43; 2009; pp 1367-1371

Jacob R.A.; Introduction, Three Eras of Vitamin C Discovery; Subcellular Biochemistry Volume 25; Ascorbic Acid: Biochemistry and Biomedical Cell Biology; Plenum Press, 1996; edited by Harris J.R.; pp 1-16

Jankowski N., Moragues J.A., Béguin A., Cetintas E.C., Firmkranz J., Gerhardus M., Kassin K., Kirchbacher J., Krzysztoch M., Meixner B., Ramirez-Santa Cruz C. Cordeiro-Wagner L. S., Striok L., Szramowiat K., Wolf N., Bauer H., Grothe H., Kasper-Giebl A.; Was geht mich der Feinstaub an?, Abschlussbericht; October 2013

Jankowski N., Sageder M., Bauer H., Marr I., Kasper-Giebl A., Limbeck A., Caseiro A., Handler M., Klatzer B., Kotianova P., Pouresmaeil P., Schmidl Ch., Ramirez-Santa Cruz C., DAttler A., Andrade-Sanchez L., Puxbaum H., Aquella Team; "AQUELLA Linz-Oberösterreich", Aerosolquellen für Linz-Oberösterreich; UA/Endbericht AQ OÖ 2009; April 2009

Kasper-Giebl A., Jankowski N., Kassin K., Centitas E.C., H. Bauer, H. Grothe; Particulate Matter in Indoor Air in two Schools in Vienna, Austria; presented at the European aerosol conference; September 2013

[a]**Kistler** M. Kasper-Giebl A., Cetintas E.C., Ramirez Santa-Cruz C., Schreiner E., Sampaio Cordeiro Wagner L., Bauer H.; Analysis of Filters for Chemical Parameters and Identification of Gaseous Nitric Acid and Nitrates in particles from Filter Sets for the purpose of PMinterProject; report No CTA-EAC-10/13-5; 2013

[b]**Kistler** M. Kasper-Giebl A., Cetintas E.C., Ramirez Santa-Cruz C., Schreiner E., Sampaio Cordeiro Wagner L., Bauer H., Szidat S., Zhang Y.; Projekt PMinter, Durchführung von Staubanalysen in Leibnitz und Arnfels; report No CTA-EAC-11/13-6; 2013

[c]**Kistler** M. Kasper-Giebl A., Cetintas E.C., Ramirez Santa-Cruz C., Schreiner E., Sampaio Cordeiro Wagner L., Bauer H., Szidat S., Zhang Y; Projekt PMinter, Filteranalysen und C14-Messungen in Feinstaubproben; report No CTA-EAC-11/13-7; 2013

Künzli N., Mudway I.S., Götschi T., Shi T., Kelly F.J., Cook S., Burney P., Forsberg B., Gauderman J.W., Hazenkamp M.E., Heinrich J., Jarvis D., Norbäck D., Payo-Losa F., Poli A., Sunyer J. Borm P.J.A.; Comparison of Oxidative Properties, Light Absorbance, and Total and Elemental Mass Concentration of Ambient $PM_{2.5}$ Collected at 20 European Sites; Environmental Health Perspectives, Vol. 114, No. 5; May 2006; pp 684-690

Li N., Hao M., Phalen R.F., Hinds W.C., Nel A.E.; Particulate Air Pollutants and Asthma; A Paradigm for the Role of Oxidative Stress in PM-induced Adverse Health Effects; Clinical Immunology 109; 2003; pp 250-265

Li N., Xia T., Nel A.E.; The Role of Oxidative Stress in Ambient Particulate Matter-Induces Lung Diseases And its Implications in the Toxicity of Engineered Nanoparticles; Free Radical Biology & Medicine 44; 2008; pp 1689-1699

Luisser M., Schmidl C., Padouvas E., Lasselsberger L., Haslinger W., Friedl G.; BIOCOMB - Biomass Combustion and its Impact on PM10 and PM2.5 Emissions in Lower Austria and West Hungary - Implications for Biomass Combustion Technologies; report No 259TR nK-I-121; 2008

Mudway I.S., Stenfors N., Blomberg A., Helleday R., Dunster C., Marklund S.L., Frew A.J., Sandström T., Kelly F.J., Differnces in Basal Airway Antioxidant Concentrations are not Predictive of Individual Responsiveness to Ozone: A Comparison of Healthy and Mild Asthmathic Subjects, Free Radical Biology & Medicine; Vol 31; No8; 2001; pp 962-974

Nawrot T.S., Kuenzli N., Sunyer J., Shi T., Moreno T., Viana M., Heinrich J., Forsberg B., Kelly F.J., Sughis M., Nemery B., Borm P.; Oxidative properties of ambient PM2.5 and elemental composition: Heterogeneous associations in 19 European cities; Atmospheric Environment 43; 2009; pp 4595-4602

Nel A.; Air Pollution-Related Illness: Effects of Particles; Science 308; 2005; pp 804-806

Nishikimi M., Yagi K.; Biochemistry and Molecular Biology of Ascorbic Acid Biosynthesis; Subcellular Biochemistry Volume 25; Ascorbic Acid: Biochemistry and Bioedical Cell Biology; Plenum Press, 1996; edited by Harris J.R.; pp 17-40

Nyyssönen K., Salonen J.T., Parviainen M.T.; Ascorbic Acid; Modern Chromatographic Analysis of Vitamins; Third Edition, Revised and Explained; edited by De Leenheer A.P., Lambert W.E., Van Bocxlaer J.F.; 2000, pp 252-280

Orru H., Kimmel V., Kikas Ü.,Soon A., Künzli N., Schins R.P.F., Borm P.J.A., Forsberg B.; Elemental composition and oxidative properties of PM2.5 in Estonia in relation to origin of air masses — results from the ECRHS II in Tartu; Science of the Total Environment; 408; 2010; pp 1515-1522

Pope III C.A., Dockery D.W., Kanner R.E., Villegas G.M., Schwartz J.; Oxygen Saturation, Pulse Rate, and Particulate Air Pollution; A Daily Time-Series Panel Study; American Journal of Respiratory and Critical Care Medicine Vol. 159; 1999; pp 365-372

Pope III C.A.; Epidemiology of Fine Particulate Air Pollution and Human Health; Environmental Health Perspectives Vol. 108 Supplement 4; August 2000; pp 713-723

Schmidl C., Peng G., Bauer H., Puxbaum H., and the AQUELLA Team; „Aquellis – FB" Aerosolquellen – Verbrennung fester Brennstoffe; final report from the Institute of Chemical Technologies and Analytics of the University of Technology Vienna; 2008

[a]**Seinfeld** J.H., Spyros N.P.; Atmospheric Chemistry and Physics; From Air Pollution to Climate Change; John Wiley & Sons 1998; p 408

[b]**Seinfeld** J.H., Spyros N.P.; Atmospheric Chemistry and Physics; From Air Pollution to Climate Change; John Wiley & Sons 1998; pp 442f

[c] **Seinfeld** J.H., Spyros N.P.; Atmospheric Chemistry and Physics; From Air Pollution to Climate Change; John Wiley & Sons 1998; pp 440f

[d] **Seinfeld** J.H., Spyros N.P.; Atmospheric Chemistry and Physics; From Air Pollution to Climate Change; John Wiley & Sons 1998; p 435

Stefan J.; Bestimmung von L-Ascorbinsäure und Dehydro-L- ascorbinsäure in Humanplasma und Leukozyten mit HPLC/UV und HPLC/EC: Methodenentwicklung, Validierung und Anwendung; PhD University of Paderborn; 1999

Van Limburg Stirum J.; Moderne Säure-Basen-Medizin; Physiologie-Diagnostik-Therapie; first edition; Hippokrates Verlag; 2008; p 114

Yanosky J.D., Tonne C.C., Beevers S.D., Wilkinson P., Kelly F.J.; Modeling Exposures to the Oxidative Potential of PM10; Environmental Science & Technology 46; ACS Publications; 2012; pp 7612-7620

Zielinski H., Mudway I.S., Bérubé K.A., Murphy S., Richards R., Kelly F.J.; Modeling the interactions of particulates with epithelial lining fluid antioxidants; the American Physiological Society; 1040-0605/99; 1999; pp L719-L726

7. Annex

Table 7.1.: General data from the Vienna school samples as well as carbon parameters and source distributions in percent related to PM mass. Sample 1-38 were collected at Rosensteingasse; sample 39-68 were collected at Fichtnergasse; I marks indoor samples, A marks ambient samples, WD samples collected on a work day und WE samples collected during a weekend:

Sample name	Depletion of AA after 180 min [µgAA/µg PM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m³]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]	Elemental Carbon from Wood Smoke [%]	PM from Diesel Exhaust [%]	Organic Carbon without a defined source [%]	PM from Wood Smoke [%]
1_I_WD	1.15	14.7	11560	348.9	42.9	29.5	8.0	5.4	1.0	9.3	23.1	9.7
2_I_WD	1.57	23.2	18190	729.4	49.3	31.4	13.1	4.9	1.9	14.8	19.5	19.3
3_I_WD	1.09	19.6	15380	731.9	47.3	35.6	6.7	5.0	0.7	8.0	30.6	7.0
4_I_WD	0.94	39.6	31020	727.0	38.7	28.3	6.1	4.3	1.3	6.5	21.5	12.5
5_I_WD	5.26	40.8	31970	724.2	35.3	26.0	5.5	3.7	1.0	6.1	20.5	9.7
6_I_WE	1.65	31.7	24880	724.8	31.2	26.3	3.5	1.4	1.9	2.1	17.9	19.2
7_I_WE	1.19	36.8	28850	726.7	32.0	26.1	4.1	1.8	1.9	3.0	17.7	18.7
8_I_WD	0.91	42.4	33260	725.6	30.5	22.7	4.2	3.6	1.0	4.2	17.5	10.2
9_I_WD	1.27	49.9	39110	724.1	29.0	21.4	3.8	3.8	1.0	3.7	16.3	10.2
10_I_WD	0.78	34.9	27400	723.1	29.2	20.9	4.1	4.2	1.0	4.1	15.8	9.8
11_I_WD	0.89	27.9	21910	723.7	40.7	28.3	8.1	4.3	0.9	9.6	22.2	8.8
12_I_WD	2.37	5.7	4430	244.4	45.0	38.4	4.9	1.7	0.9	5.4	33.4	8.7
14_I_WD	1.90	20.8	16270	444.4	44.6	33.3	6.4	4.9	1.3	6.8	26.4	12.5
15_I_WD	1.38	27.1	21520	730.6	40.7	31.6	4.7	4.4	1.1	4.8	26.0	10.6
16_I_WD	1.74	37.2	29130	731.0	36.8	28.3	4.5	4.0	1.2	4.3	22.1	12.4
17_I_WD	0.96	36.2	28390	731.6	38.2	29.8	4.4	4.1	1.3	4.1	23.2	13.4
18_I_WD	0.96	24.6	19290	729.2	40.5	30.8	5.2	4.5	1.1	5.4	25.0	10.7
19_I_WE	1.39	22.9	17940	729.2	45.9	37.1	6.2	2.7	1.9	5.7	27.9	18.8
20_I_WE	1.58	25.3	19850	727.6	40.4	33.7	4.8	1.9	1.2	4.8	27.4	12.5
21_I_WD	1.13	35.3	27660	728.1	35.6	26.1	5.0	4.5	0.7	5.6	21.6	7.4

Table 7.1. continued:

22_I_WD	0.83	51.9	40670	727.1	33.6	25.9	4.2	3.5	0.8	4.6	21.5	7.7
23_I_WD	0.86	20.2	15840	323.1	33.9	27.5	4.1	2.3	0.8	4.4	23.0	8.0
24_I_WD	0.69	31.1	24360	385.2	36.5	28.4	3.8	4.3	0.7	4.2	24.4	6.9
25_I_WD	0.83	49.9	39100	723.0	35.2	27.3	4.1	3.7	0.8	4.4	22.9	7.9
26_I_WD	1.03	49.0	38390	722.1	36.0	27.4	4.5	4.1	1.2	4.4	21.5	11.7
27_I_WE	1.11	38.8	30380	723.3	38.3	31.3	5.0	2.1	1.0	5.3	25.8	10.0
28_I_WE	0.98	43.0	33720	725.2	31.7	26.3	3.7	1.7	1.3	3.2	20.2	13.0
29_I_WD	1.18	19.0	14890	233.7	28.6	23.3	3.6	1.7	1.2	3.2	17.4	12.5
31_A_WD	0.76	58.8	46120	438.4	21.8	13.9	4.9	2.9	1.1	5.2	8.2	10.6
32_A_WD	0.67	73.3	57470	705.3	21.0	16.5	2.7	1.8	1.2	2.0	11.2	11.8
33_A_WD	1.23	33.9	26580	704.9	30.4	20.5	6.5	3.4	1.5	6.6	12.6	15.1
34_A_WD	0.59	46.2	36250	699.5	19.7	16.0	2.3	1.4	1.2	1.4	10.6	12.4
35_A_WD	0.70	58.0	45440	704.2	22.4	16.1	4.0	2.3	1.2	3.6	10.1	12.5
36_A_WE	0.76	52.0	40750	711.7	20.4	16.1	2.8	1.5	1.4	1.9	10.1	13.6
37_A_WE	0.67	19.6	15370	711.5	17.4	13.8	2.0	1.7	0.9	1.5	9.9	8.6
38_A_WD	5.33	3.2	2500	256.1	59.4	45.8	9.4	4.2	2.7	9.0	32.6	26.6
41_I_WD	0.65	22.7	17800	370.6	38.6	30.8	3.1	4.7	0.3	3.7	28.6	3.1
42_I_WD	0.83	46.7	36640	720.0	43.4	33.9	5.2	4.3	0.9	5.8	28.7	9.0
43_I_WD	0.84	45.8	35880	722.6	39.6	28.9	6.3	4.4	1.1	6.9	22.5	11.2
44_I_WD	0.63	66.9	52430	724.9	45.6	33.8	8.2	3.6	1.1	9.4	26.8	11.0
45_I_WD	0.47	52.6	41260	724.5	35.0	25.5	5.7	3.8	0.7	6.6	20.8	7.3
46_I_WE	1.97	16.4	12840	725.9	48.9	34.3	10.0	4.7	1.8	10.9	23.9	18.2
47_I_WE	1.86	14.7	11500	727.7	53.7	38.1	10.3	5.3	1.6	11.6	28.4	16.2
48_I_WD	0.58	48.1	37720	727.6	35.0	27.0	3.9	4.1	0.3	4.8	24.4	3.2
49_I_WD	0.55	50.2	39370	726.0	38.9	28.9	5.7	4.3	0.7	6.7	24.2	7.1
50_I_WD	0.61	56.0	43890	727.9	42.8	34.0	4.5	4.4	0.6	5.1	30.1	6.2
51_I_WD	0.51	46.5	36480	730.8	36.2	28.6	3.4	4.2	0.7	3.6	24.9	6.7
52_I_WD	0.69	27.4	21500	727.1	43.3	36.0	2.2	5.2	0.3	2.5	34.1	3.0
53_I_WE	1.47	6.5	5090	723.9	52.2	42.3	5.8	3.2	0.7	6.8	37.8	6.6
54_I_WE	1.80	7.5	5850	721.4	47.8	40.3	4.5	2.9	1.0	4.7	35.0	10.2
55_I_WD	0.60	42.6	33430	721.2	32.6	26.0	2.4	4.1	0.4	2.7	23.7	3.9
56_I_WD	0.53	45.4	35610	721.0	35.5	28.0	3.1	4.4	0.4	3.6	25.4	4.1
57_I_WD	0.76	44.2	34670	721.4	36.6	29.4	2.7	4.5	0.4	3.0	27.0	3.9
58_I_WD	0.65	41.3	32390	722.1	35.3	28.0	2.9	4.4	0.3	3.5	25.8	3.0

Table 7.1. continued:

59_I_WD	0.96	37.7	29520	727.7	36.7	28.3	3.7	4.7	0.4	4.4	25.4	4.1
60_I_WE	1.99	11.5	9030	730.3	45.5	33.2	8.7	3.5	0.0	11.6	30.1	0.0
61_I_WE	1.82	9.5	7450	727.4	41.7	34.5	5.2	2.0	0.0	7.0	32.6	0.0
62_I_WE	0.39	43.5	34120	727.9	38.8	31.0	3.3	4.5	0.4	3.8	28.2	4.4
63_I_WD	0.40	38.3	30000	727.6	36.7	28.5	3.5	4.7	0.4	4.1	25.8	3.9
64_I_WD	0.59	37.7	29590	727.7	37.7	27.9	5.3	4.5	0.5	6.3	24.1	5.3
65_I_WD	0.42	40.7	31900	727.9	39.0	31.1	3.2	4.7	0.3	4.0	28.9	2.6
66_I_WD	1.39	7.9	6160	259.4	48.9	39.2	4.0	5.7	0.3	4.9	36.6	3.3
69_A_WD	2.21	8.3	6530	410.2	34.5	22.8	9.1	2.7	1.1	10.7	15.6	10.7
70_A_WE	1.69	20.3	15900	719.3	28.5	18.6	6.9	3.0	1.3	7.5	11.3	13.2
71_A_WE	1.55	28.1	22020	719.3	26.5	18.7	5.3	2.6	1.2	5.4	12.3	12.3
72_A_WD	1.41	20.1	15720	717.9	29.9	19.6	7.3	3.0	1.0	8.4	13.4	9.7
73_A_WD	1.30	15.7	12280	714.7	21.9	16.1	4.2	1.6	0.9	4.5	11.4	8.6
74_A_WD	1.78	15.4	12070	717.0	25.9	17.8	5.8	2.3	0.8	6.7	12.7	8.1

Table 7.2.: Ion and mineral dust data from the Vienna school samples in percent related to PM mass. Sample 1-38 were collected at Rosensteingasse; sample 39-68 were collected at Fichtnergasse, I marks indoor samples, A marks ambient samples, WD samples collected on a work day und WE samples collected during a weekend:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	Aluminim [%]	Iron [%]
1_I_WD	1.7	4.8	4.9	1.5	1.3	0.9	0.5	4.5	1.8	0.6	0.3
2_I_WD	1.3	6.2	6.3	1.4	1.7	1.6	0.3	2.9	5.6	2.0	0.6
3_I_WD	1.3	4.7	4.9	1.4	1.3	1.1	0.4	3.9	3.7	1.1	0.5
4_I_WD	1.1	7.0	11.5	0.7	5.7	1.0	0.4	2.7	3.8	1.0	0.5
5_I_WD	2.2	4.8	18.8	1.0	8.6	1.0	0.4	2.7	0.9	0.2	0.3
6_I_WE	0.3	6.2	24.1	0.3	11.6	1.2	0.0	0.1	0.7	0.2	0.2
7_I_WE	0.3	6.1	25.7	0.3	12.2	1.3	0.0	0.2	4.1	1.2	0.5
8_I_WD	1.1	3.0	20.5	0.8	7.8	1.0	0.4	2.9	4.1	1.2	0.6
9_I_WD	1.0	6.6	20.3	1.0	7.8	1.0	0.4	3.1	3.8	1.0	0.5
10_I_WD	1.1	14.9	9.9	0.9	7.4	1.1	0.4	2.6	5.8	1.6	0.9
11_I_WD	2.8	10.5	6.3	1.4	4.1	1.3	0.5	3.9	4.0	0.9	0.8
12_I_WD	0.7	12.1	6.3	0.3	6.6	1.2	0.0	0.0	2.4	0.8	0.3
14_I_WD	2.8	7.0	7.7	1.1	4.2	1.3	0.4	3.7	3.8	1.1	0.5

Table 7.2. continued:

15_I_WD	2.9	5.9	5.2	1.3	2.9	1.2	0.5	4.0	4.8	1.5	0.6
16_I_WD	1.4	7.4	11.3	0.8	6.0	1.2	0.3	2.7	4.4	1.4	0.5
17_I_WD	1.2	5.7	13.6	0.6	6.9	1.1	0.3	2.3	4.6	1.4	0.5
18_I_WD	2.0	3.2	13.5	0.9	5.9	1.2	0.3	3.4	0.9	0.2	0.2
19_I_WE	1.1	5.0	22.9	0.3	12.2	1.0	0.0	0.1	1.5	0.4	0.3
20_I_WE	1.4	6.9	27.9	0.4	14.5	1.0	0.0	0.4	4.2	1.4	0.7
21_I_WD	0.7	5.8	15.5	0.8	6.8	0.8	0.3	3.6	3.8	1.2	0.5
22_I_WD	0.8	5.0	18.3	1.0	7.2	0.9	0.2	1.7	0.7	0.2	0.0
23_I_WD	0.9	5.2	20.7	0.5	11.1	0.8	0.1	0.8	3.0	0.8	0.5
24_I_WD	0.7	3.6	15.1	0.7	7.0	1.0	0.3	2.8	2.0	0.6	0.4
25_I_WD	0.6	4.7	15.9	0.6	7.0	0.9	0.2	1.8	3.5	0.9	0.8
26_I_WD	0.9	4.6	14.8	0.7	5.9	1.0	0.2	1.8	1.4	0.4	0.3
27_I_WE	0.3	6.9	21.6	0.5	11.3	0.9	0.0	0.2	1.0	0.3	0.3
28_I_WE	0.1	4.5	26.1	0.3	11.1	1.0	0.0	0.1	0.0	0.0	0.0
29_I_WD	0.1	2.7	32.1	0.1	14.3	1.1	0.0	0.1	0.0	0.0	0.0
31_A_WD	1.0	11.0	24.0	0.7	10.5	0.9	0.2	3.2	1.7	0.5	0.4
32_A_WD	0.7	16.2	23.2	0.4	13.5	0.8	0.1	0.6	7.8	2.3	1.4
33_A_WD	1.4	14.6	13.9	1.0	7.7	1.0	0.3	2.0	3.3	1.0	0.7
34_A_WD	0.5	13.1	28.4	0.3	15.7	0.9	0.1	0.7	2.5	0.7	0.6
35_A_WD	0.6	16.2	26.0	0.4	12.7	0.9	0.1	2.4	2.2	0.6	0.6
36_A_WE	0.6	17.3	21.9	0.4	12.2	0.9	0.1	0.6	3.4	0.8	0.6
37_A_WE	2.4	20.2	16.1	2.5	11.3	0.5	0.4	0.8	4.3	1.1	1.0
38_A_WD	2.1	12.5	5.2	2.7	4.8	0.9	0.3	0.3	0.0	0.0	0.0
41_I_WD	2.3	1.2	2.5	1.8	0.6	1.1	0.7	6.8	0.0	0.0	0.0
42_I_WD	1.8	2.9	3.8	1.4	0.8	1.3	0.7	5.1	0.0	0.0	0.0
43_I_WD	1.2	5.1	3.6	1.1	0.9	1.2	0.5	4.4	0.0	0.0	0.0
44_I_WD	1.2	3.3	3.1	1.0	0.7	1.2	0.4	3.1	9.7	2.5	1.2
45_I_WD	1.5	2.6	4.2	1.3	1.0	1.2	0.6	5.4	2.4	0.7	0.8
46_I_WE	0.4	7.0	10.7	0.8	4.5	2.4	0.2	1.3	2.1	0.6	0.7
47_I_WE	0.1	3.2	14.0	0.6	5.2	2.4	0.1	0.6	12.2	3.2	1.3
48_I_WD	1.6	1.2	3.6	1.3	0.9	1.0	0.7	6.7	0.0	0.0	0.0
49_I_WD	1.3	2.4	3.1	1.1	0.7	0.9	0.7	5.3	13.1	3.8	1.2
50_I_WD	1.2	2.2	4.2	1.0	1.0	0.8	0.6	5.3	8.5	2.5	0.7
51_I_WD	0.5	2.2	14.7	0.6	4.5	0.9	0.3	3.1	10.4	3.3	0.8

Table 7.2. continued:

52_I_WD	1.1	0.6	6.0	0.9	2.0	0.8	0.5	5.2	2.6	0.8	0.3
53_I_WE	0.2	2.1	24.6	0.6	10.0	0.9	0.2	1.6	1.2	0.3	0.2
54_I_WE	0.1	2.7	17.8	1.1	7.5	0.8	0.2	0.8	12.8	3.3	1.2
55_I_WD	1.5	2.0	4.4	1.3	1.4	0.7	0.6	5.2	12.6	3.3	1.3
56_I_WD	1.3	2.3	5.4	1.1	1.7	0.8	0.6	4.5	13.3	3.5	1.3
57_I_WD	0.7	2.1	4.0	0.9	1.3	0.7	0.6	4.9	14.0	3.6	1.5
58_I_WD	1.2	1.7	3.5	0.9	1.0	0.7	0.6	4.4	12.4	3.2	1.4
59_I_WD	0.7	4.8	4.9	0.9	1.4	0.9	0.6	5.1	3.1	0.8	1.0
60_I_WE	0.0	3.1	16.6	0.3	6.5	1.4	0.1	0.7	1.4	0.4	0.3
61_I_WE	0.0	1.9	27.4	0.2	11.4	0.9	0.1	0.3	12.6	3.4	1.2
62_I_WE	0.9	2.9	4.4	0.8	1.5	0.8	0.6	4.7	13.7	3.8	1.4
63_I_WD	0.8	3.2	5.2	0.8	1.6	0.7	0.5	4.9	12.5	3.5	1.6
64_I_WD	0.6	3.9	5.0	0.7	1.6	0.9	0.5	4.9	14.1	3.8	1.4
65_I_WD	0.9	1.3	2.9	0.6	0.9	0.7	0.6	4.8	28.2	8.3	2.4
66_I_WD	0.4	1.1	3.4	0.4	1.1	0.6	0.3	3.5	0.0	0.0	0.0
69_A_WD	0.4	12.2	7.6	0.5	4.9	0.6	0.3	1.9	3.6	0.8	1.7
70_A_WE	0.3	15.9	8.1	1.0	5.9	0.6	0.4	1.7	4.5	1.1	1.9
71_A_WE	0.2	15.8	10.1	0.8	6.0	0.7	0.2	1.0	7.8	1.8	2.6
72_A_WD	0.2	14.1	12.3	0.9	6.5	1.0	0.5	2.6	4.9	1.2	2.2
73_A_WD	0.3	20.1	10.6	1.0	10.3	0.6	0.4	1.6	7.4	1.8	2.5
74_A_WD	0.2	20.6	8.8	0.9	7.6	0.7	0.5	5.4	13.3	3.2	2.4

Table 7.3.: General data from the ambient Vienna samples collected during the Aquella campaign as well as carbon parameters and source distributions in percent related to PM mass. KS refers to Kendlerstraße; SB refers to Schafberg:

Sample name	Depletion of AA after 180 min [µgAA/µg PM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m³]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]	Elemental Carbon from Wood Smoke [%]	PM from Diesel Exhaust [%]	Organic Carbon without a defined source [%]	PM from Wood Smoke [%]
KS_2810	1.59	31.7	24850	763.9	29.1	14.0	15.1	0.0	0.6	19.3	6.2	6.4
KS_2910	1.92	29.2	22870	762.3	34.4	17.4	17.0	0.0	0.7	21.7	8.7	7.1
KS_0501	0.97	28.7	22500	708.7	28.1	17.3	10.9	0.0	2.0	11.8	5.9	20.1
KS_0601	1.48	31.9	25010	706.1	28.8	18.0	10.7	0.0	1.4	12.4	8.9	14.2
KS_0801	0.86	96.7	75830	714.8	25.3	17.2	8.1	0.0	1.9	8.3	7.4	18.7
SB_0801	0.79	88.7	69540	735.3	28.4	19.8	8.5	0.0	1.2	9.8	12.5	11.6

Table 7.4.: Ion and mineral dust data from the ambient Vienna samples collected during the Aquella campaign in percent related to PM mass. KS refers to Kendlerstraße; SB refers to Schafberg:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	Aluminium [%]	Iron [%]
KS_2810	0.3	4.1	12.6	0.9	3.4	0.8	0.3	2.4	10.0	2.5	1.3
KS_2910	0.2	5.2	7.3	0.7	2.0	0.4	0.5	3.7	5.6	1.6	1.1
KS_0501	0.3	17.9	11.8	0.3	9.3	0.7	0.1	0.6	0.9	0.3	1.7
KS_0601	1.4	15.6	13.0	0.7	9.5	0.6	0.0	0.2	0.9	0.4	4.2
KS_0801	2.0	21.1	10.5	1.0	9.2	0.8	0.0	0.3	0.6	0.3	1.4
SB_0801	1.2	25.9	14.1	0.4	11.4	0.9	0.0	0.2	0.6	0.3	0.3

Table 7.5.: General data from samples collected during the PMinter project as well as carbon parameters and source distributions in percent related to PM mass. M refers to Maribor, VP to Vrbanski Plato, KV to Klagenfurt Völkermarktstraße, KE to Klagenfurt east, EZ to Ebental Zell, LB to Leibnitz and A to Arnfels:

Sample name	Depletion of AA after 180 min [µgAA/µg PM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m^3]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]	Elemental Carbon from Wood Smoke [%]	PM from Diesel Exhaust [%]	Organic Carbon without a defined source [%]	PM from Wood Smoke [%]
M_0302	1.44	82.3	65254	675.5	31.4	20.1	6.4	1.7	3.4	6.1	8.1	34.3
M_0402	0.63	90.3	58114	679.7	17.8	7.4	3.7	0.3	1.4	8.7	11.6	13.6
M_2702	1.20	83.0	65109	683.9	30.1	22.2	2.7	1.2	3.0	3.7	4.9	29.8
M_2802	1.05	78.1	61222	684.8	27.2	19.0	3.1	1.3	2.2	4.6	6.1	22.4
VP_0302	1.45	57.5	47016	697.6	30.6	22.6	3.9	1.0	3.9	3.1	4.2	38.9
VP_0402	1.82	54.1	40493	704.2	32.3	23.2	5.0	1.0	4.2	3.9	5.2	42.3
VP_2702	1.46	71.3	55861	699.1	29.1	22.3	2.3	0.4	3.4	3.0	4.0	33.7
VP_2802	0.98	66.0	51727	699.0	22.5	16.6	1.6	0.5	2.3	3.1	4.2	22.5
KV_0302	1.37	60.0	66640	698.0	30.4	19.5	9.5	1.5	2.6	9.1	6.5	25.8
KV_0402	2.40	51.3	72856	699.3	30.8	19.8	9.0	2.1	2.5	8.6	7.2	25.4
KV_2702	1.08	45.5	35703	709.8	31.2	20.6	8.9	1.7	2.6	8.4	8.0	25.5
KV_2802	1.03	81.4	63788	710.0	27.9	14.7	10.8	2.4	1.7	12.1	4.5	17.1
KE_0302	0.86	87.3	45801	708.2	25.6	19.1	5.8	0.7	2.9	3.8	6.2	29.2
KE_0402	0.88	77.6	42896	711.7	30.2	23.5	5.9	0.7	4.0	2.6	6.6	40.1
KE_2702	0.98	44.2	34656	720.5	32.5	27.6	4.2	0.8	3.6	0.8	12.8	36.1
KE_2802	0.59	60.8	47669	719.4	25.0	20.6	3.4	0.9	2.4	1.3	10.6	23.9
EZ_0302	1.01	68.3	53545	700.5	28.1	19.2	7.9	0.9	3.3	6.2	4.2	32.9
EZ_0402	1.10	62.9	49292	702.1	36.3	24.9	10.8	0.6	5.6	7.0	0.5	55.6
EZ_2702	1.37	49.4	38714	712.4	34.8	27.7	6.1	1.0	4.6	2.1	8.6	45.8
EZ_2702	0.80	70.0	54879	715.4	28.0	22.5	4.3	1.2	2.8	2.0	10.6	28.1
LB_0302	1.34	70.5	55299	750.0	37.1	24.6	10.4	2.1	3.6	9.1	7.5	36.1
LB_0402	1.59	85.5	66998	742.8	39.7	27.1	10.4	2.2	4.5	7.9	6.8	44.9
LB_2702	1.11	82.7	64799	745.2	29.7	25.7	3.4	0.6	2.2	1.6	16.3	22.2
LB_2802	0.64	83.0	65102	745.4	25.6	19.7	3.7	2.1	2.1	2.1	10.4	21.5

Table 7.5. continued:

A_0302	2.05	15.8	12399	705.7	38.3	31.6	6.3	0.4	3.6	3.6	16.2	35.6
A_0402	2.44	16.2	12702	701.8	42.8	35.4	6.3	1.1	4.3	2.6	17.3	43.1
A_2702	1.04	54.6	42797	697.5	26.7	23.4	2.8	0.5	1.9	1.2	15.5	18.8
A_2802	0.66	51.4	40301	702.7	21.6	19.1	2.3	0.2	1.6	0.9	12.4	16.1

Table 7.6.: Ion and mineral dust data from the samples collected during the PMinter project in percent related to PM mass. M refers to Maribor, VP to Vrbanski Plato, KV to Klagenfurt Völkermarktstraße, KE to Klagenfurt east, EZ to Ebental Zell, LB to Leibnitz and A to Arnfels:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	Aluminium [%]	Iron [%]
M_0302	3.1	12.6	4.6	-	6.8	-	-	1.2	-	1.1	1.2
M_0402	0.5	5.6	1.2	-	2.1	-	-	0.2	-	0.3	0.4
M_2702	0.9	8.0	21.6	-	9.4	-	-	0.8	-	0.6	0.5
M_2802	0.6	4.1	29.9	-	12.3	-	-	0.9	-	0.8	0.8
VP_0302	1.1	19.7	6.3	-	7.8	-	-	0.6	-	1.0	0.6
VP_0402	1.0	15.8	4.8	-	6.6	-	-	0.7	-	1.2	0.8
VP_2702	0.0	6.5	22.7	-	11.0	-	-	0.2	-	0.6	0.3
VP_2802	0.0	1.8	35.5	-	13.8	-	-	0.4	-	0.6	0.4
KV_0302	2.6	16.5	9.6	-	8.1	-	-	1.0	-	0.5	2.0
KV_0402	3.7	12.5	6.2	-	5.9	-	-	1.4	-	0.6	1.7
KV_2702	0.5	13.1	14.4	-	9.9	-	-	1.1	-	0.9	1.3
KV_2802	1.0	8.8	18.5	-	9.3	-	-	1.6	-	1.2	1.8
KE_0302	1.3	22.3	13.6	-	9.6	-	-	0.5	-	0.4	0.5
KE_0402	1.2	22.1	10.9	-	8.2	-	-	0.5	-	0.4	0.6
KE_2702	0.3	13.0	15.0	-	12.0	-	-	0.5	-	0.7	0.5
KE_2802	0.4	6.7	19.7	-	13.2	-	-	0.6	-	0.7	0.5
EZ_0302	1.4	19.5	11.9	-	9.9	-	-	0.6	-	0.4	0.5
EZ_0402	1.3	14.2	8.9	-	5.4	-	-	0.4	-	0.3	0.4
EZ_2702	0.6	12.2	14.9	-	9.7	-	-	0.6	-	0.7	0.5
EZ_2702	0.3	7.9	19.1	-	9.6	-	-	0.8	-	1.0	0.5
LB_0302	2.5	20.6	6.0	-	8.0	-	-	1.4	6.0	2.0	1.7
LB_0402	2.6	17.7	4.7	-	6.1	-	-	1.5	6.0	2.1	1.8
LB_2702	0.1	10.2	21.7	-	7.8	-	-	0.4	2.2	0.8	0.5

Table 7.6. continued:

LB_2802	0.5	4.6	29.3	-	8.6	-	-	1.4	7.8	2.5	1.4
A_0302	0.2	32.6	13.8	-	18.1	-	-	0.3	1.2	0.4	1.1
A_0402	0.4	31.1	11.3	-	16.7	-	-	0.7	1.7	0.6	1.2
A_2702	0.1	11.9	19.3	-	12.2	-	-	0.4	2.2	1.1	0.5
A_2802	0.2	1.5	41.5	-	14.1	-	-	0.1	1.2	0.4	0.4

Table 7.7.: General data from the samples collected in Upper Austria during the Aquella campaign as well as carbon parameters and source distributions in percent related to PM mass. R refers to Römerberg and E to Enzenkirchen:

Sample name	Depletion of AA after 180 min [µgAA/µgPM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m³]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]	Elemental Carbon from Wood Smoke [%]	PM from Diesel Exhaust [%]	Organic Carbon without a defined source [%]	PM from Wood Smoke [%]
R_2210	0.60	79.0	61960	724.0	20.1	8.8	11.3	-	0.6	12.4	1.6	6.3
R_0101	1.01	87.6	68690	718.0	25.5	20.2	5.3	-	2.2	5.0	9.1	21.8
R_3101	0.79	103.8	81390	707.0	26.0	18.2	7.7	-	1.8	10.4	10.9	17.9
E_2210	0.82	24.8	19420	730.4	18.5	10.0	8.5	-	0.4	2.7	0.4	3.7
E_0101	1.25	42.9	33650	705.1	20.1	13.6	6.4	-	1.4	3.0	0.0	13.9
E_3101	1.13	33.7	26390	681.1	24.9	15.5	9.3	-	0.6	4.4	2.6	5.5

Table 7.8.: Ion and mineral dust data from the samples collected in Upper Austria during the Aquella campaign in percent related to PM mass. R refers to Römerberg and E to Enzenkirchen:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	ALuminium [%]	Iron [%]
R_2210	0.6	15.8	8.3	0.1	6.6	0.7	0.1	1.0	1.6	0.4	2.6
R_0101	3.6	19.1	11.5	0.7	8.3	5.5	0.5	0.3	0.5	1.3	0.8
R_3101	1.8	17.7	15.8	1.2	10.4	1.3	0.1	1.0	1.4	0.3	1.0
E_2210	0.6	25.8	15.4	0.3	12.6	1.3	0.1	0.5	1.8	0.5	1.2
E_0101	1.5	22.2	10.4	0.2	9.5	4.5	0.3	0.2	0.5	0.6	0.1
E_3101	0.1	16.5	15.2	0.2	11.7	1.6	0.0	0.2	2.5	0.2	0.4

Table 7.9.: General data from the samples collected in Graz as well as carbon parameters and source distributions in percent related to PM mass. G refers to Graz, S to south and N to north:

Sample name	Depletion of AA after 180 min [µgAA/µgPM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m³]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]	Elemental Carbon from Wood Smoke [%]	PM from Diesel Exhaust [%]	Organic Carbon without a defined source [%]	PM from Wood Smoke [%]
G_0301_S	1.52	51.0	40000	701.9	47.2	14.6	32.6	-	-	-	-	-
G_0401_S	2.76	29.2	22900	697.0	64.4	26.6	37.8	-	-	-	-	-
G_0501_S	4.84	8.8	6900	693.8	67.8	23.2	44.6	-	-	-	-	-
G_0601_S	4.01	15.8	12400	696.9	54.9	15.2	39.6	-	-	-	-	-
G_0701_N	2.33	13.3	10400	705.9	47.6	13.7	33.9	-	-	-	-	-
G_0801_N	1.61	25.4	19900	706.7	35.2	9.9	25.3	-	-	-	-	-
G_0901_N	1.43	39.0	30600	702.5	39.0	11.2	27.9	-	-	-	-	-
G_1001_N	1.82	32.5	25500	697.9	36.2	9.3	26.9	-	-	-	-	-

Table 7.10.: Ion and mineral dust data from the samples collected in Graz in percent related to PM mass. G refers to Graz, S to south and N to north:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	ALuminium [%]	Iron [%]
G_0301_S	1.3	10.2	5.8	1.4	3.9	2.8	0.1	0.3	-	0.3	0.3
G_0401_S	0.0	0.0	0.0	2.3	1.0	2.4	0.1	0.5	-	0.5	0.7
G_0501_S	2.6	5.1	2.4	4.5	1.3	1.8	0.1	0.9	-	1.5	0.7
G_0601_S	0.4	9.7	6.1	2.7	3.9	2.1	0.1	0.4	-	0.7	0.2
G_0701_N	1.2	14.3	9.5	4.0	6.6	1.5	0.1	0.4	-	0.8	0.3
G_0801_N	0.9	24.1	6.8	2.0	8.6	1.3	0.0	0.2	-	0.4	0.2
G_0901_N	1.1	18.0	5.7	1.4	6.9	1.9	0.0	0.3	-	0.3	0.3
G_1001_N	0.3	20.2	9.2	1.8	8.1	1.7	0.0	0.2	-	0.3	0.2

Table 7.11.: General data from the smoke samples as well as carbon parameters and source distributions in percent related to PM mass. The samples are from top to bottom emissions from the combustion of brown coal, stone coal, stone coal, beech, cardboard packages from fruit juice, alder, and wood briquettes. Linden and splints refer to the biological samples:

Sample name	Depletion of AA after 180 min [µgAA/µgPM]	Mass collected on a 5mm punch [µg]	Total Mass [µg]	Air volume [m³]	Total Carbon [%]	Organic Carbon [%]	Elemental Carbon [%]	Carbonate [%]
F1e	0.44	126.0	3150	-	79.1	68.6	10.5	-
F2e	0.40	48.0	1200	-	74.4	53.1	21.3	-
F3e	0.73	22.8	570	-	70.2	46.5	23.8	-
F4e	1.33	31.6	790	-	54.5	39.6	14.9	-
F5e	0.41	23.8	595	-	62.2	52.4	9.8	-
F44	1.29	80.6	2015	-	59.3	10.9	48.4	-
F50	1.17	62.0	1550	-	47.1	9.6	37.5	-
Linden	-0.02	-	-	-	-	-	-	-
Splints	0.09	-	-	-	-	-	-	-

Table 7.12.: Ion and mineral dust data from the smoke samples in percent related to PM mass. The samples are from top to bottom emissions from the combustion of brown coal, stone coal, stone coal, beech, cardboard packages from fruit juice, alder, and wood briquettes:

Sample name	Chloride [%]	Nitrate [%]	Sulfate [%]	Sodium [%]	Ammonium [%]	Potassium [%]	Magnesium (soluble) [%]	Calcium (soluble) [%]	Silicium [%]	ALuminium [%]	Iron [%]
F1e	0.1	0.1	0.8	0.0	0.2	0.2	0.0	0.1	0.0	-	-
F2e	0.7	0.1	0.2	0.1	0.4	0.0	0.0	0.6	0.1	-	-
F3e	1.4	0.7	0.4	0.2	0.7	0.5	0.1	1.9	0.1	-	-
F4e	0.8	0.3	0.4	0.2	0.6	0.6	0.0	2.0	0.2	-	-
F5e	0.9	0.8	0.5	1.7	1.0	0.9	0.2	4.5	0.2	-	-
F44	0.6	0.9	1.6	0.1	0.2	1.9	0.2	0.3	0.3	-	-
F50	0.1	1.0	0.9	0.1	0.1	0.5	0.3	0.5	0.1	-	-