Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland

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Abstract

Daily PM2.5 and PM10 samples were taken from April 1998 to March 1999 at urban kerbside, urban background, near-city, and rural sites in Switzerland. The samples were analysed for mass, water soluble ions, trace elements, as well as elemental and organic carbon. The present paper focuses on the variation of element concentration between different site types and on the chemical mass closure of atmospheric particulate matter.

Information on emission sources of trace elements is obtained by evaluation of the element abundances at sites that represent different pollution levels. The abundances of Ba, Ca, Ce, Cu, Fe, La, Mo, Mn, Pb, Sb, and Rh are gradually decreasing from urban kerbside to urban background, near-city and rural sites, indicating that road traffic is a main source of these elements. On the other hand, the abundances of Al, As, Cd, K, and V are similar for the different site types, which implies that emission sources are either spatially uniformly distributed (e.g. mineral dust), or there are no important regional emission sources and the ambient concentration of these elements might be dominated by long-range transport.

When performing a mass closure, the annual average of the sum of aerosol chemical components was 22–27% for PM10 and 8–15% for PM2.5 lower than the PM mass. A drying procedure applied to a subset of PM10 samples and model calculations for PM2.5 samples according to their inorganic composition were used to estimate the contribution of retained water to the unaccounted mass at 50% RH. The obtained average water content was 10.6% for PM10 and 13–23% for PM2.5, clearly indicating that water is a major contributor to the unaccounted mass. Furthermore, a pronounced seasonal variation was observed with relatively lower water content in the colder season, indicating that the inorganic salts were mainly crystalline in winter, whereas they were probably dissolved during the rest of the year.
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1. Introduction

The current interest in atmospheric particulate matter (PM) is mainly due to its effect on human health

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(Dockery and Pope, 1994; Schwartz, 1994; Ackermann-Liebrich et al., 1997; Braun-Fahrländer et al., 1997; Pope et al., 2002) and its role in climate change (IPCC, 2001). Atmospheric PM is a complex mixture of elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements, and water. Detailed investigations of the chemical characteristics of atmospheric PM are important for both, elucidating the particle toxicity and its role in climate change.

In this paper the chemical composition of atmospheric PM from rural, near-city, urban background, and urban kerbside sites in Switzerland is investigated. Part of the presented data is also included in a recent synthesis of aerosol data (Putaud et al., 2004; Van Dingenen et al., 2004), where chemical and physical properties of atmospheric PM from background, rural, urban and kerbside sites in Europe are extensively discussed. This paper therefore focuses on aspects that are not covered by Putaud et al. (2004) and Van Dingenen et al. (2004), i.e. the concentration and variation of trace elements in different size fractions (PM2.5, PM10 and the coarse fraction PM10–PM2.5) for different site types and seasons, as well as the day-of-week variation of trace elements. Moreover, the data is discussed in the context of available trace element measurements in atmospheric PM from other Swiss sites (Gälli et al., 1990; Röösli et al., 2001). The study of Gälli et al. (1990) contains concentrations of selected metals in weekly samples of seven different size fractions collected at rural sites during the time period from October 1985 to September 1986. The total element concentration in all different size fractions can be considered as PM8, and are compared here with our measurements in order to investigate how element concentrations changed from the mid-1980s to the end of the 1990s.

Finally, the water content of atmospheric PM as collected by use of a high volume sampler is assessed. Depending on the chemical composition, water can be an important constituent of atmospheric PM (Pilinis et al., 1989). Especially inorganic salts like ammonium sulphate and ammonium nitrate can absorb water. Inorganic salts are solid until the ambient relative humidity (RH) reaches the deliquescence point. At the deliquescence points of the individual inorganic salts water is absorbed until a saturated aqueous solution of that salt is formed. As the ambient relative humidity decreases, evaporation of absorbed water occurs. However, the salts do not crystallise at their deliquescence points but remain supersaturated until a much lower relative humidity (crystallisation point). The deliquescence points of relevant inorganic salts can be found in Tang and Munkelwitz (1993), e.g. the given deliquescence points of ammonium sulphate and ammonium nitrate at 298 K are 80% RH and 62% RH, respectively. On the other hand, the crystallisation points for ammonium sulphate is around 42% RH, while it was found that ammonium nitrate could not be dried at a relative humidity as low as 8% (Dougle et al., 1998). Furthermore, the deliquescence relative humidity of multicomponent particles is lower than that of its components (Wexler and Seinfeld, 1991) and decreases significantly, if inorganic salts are mixed with organic salts such as dicarboxylic acids (Marcolli et al., 2004). As a consequence, PM samples that contain aqueous solutions of inorganic and organic components are not necessarily dried by a treatment according to the reference method for gravimetric determination of the PM mass concentration (re-conditioning of the collected PM samples at 50% RH in an air conditioned room according to CEN, 1998). In order to estimate the water content of atmospheric filter samples, two different approaches were used here for PM10 and PM2.5 (Section 2.3). The water content of PM10 samples is obtained from the mass difference of the filter sample between 50% RH and dry conditions (RH < 5%) including a correction for the evaporation of volatile material. The potential water content of PM2.5 samples is calculated from their chemical composition using a thermodynamical model for inorganic salts.

2. Methodology

2.1. Measuring sites and sample collection

Sampling of PM10 and PM2.5 was performed at various sites of the Swiss National Air Pollution Monitoring Network (NABEL), and one site of the Department of Health and Environment of the City of Zurich. The mass concentration of the coarse fraction was calculated from the difference of simultaneously collected PM10 and PM2.5 samples (PM10–PM2.5). The sites are located in the northern and north-western part of the country (Fig. 1), and were selected to represent typical and important ambient air quality situations in Switzerland (Table 1). Samples were taken
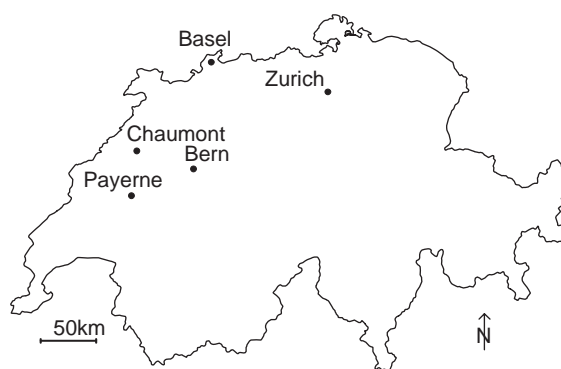

Fig. 1. Map of Switzerland with the sampling locations.

Table 1
Overview of the sampling sites and determined parameters

Site	Site characteristics	Parameter	Number of samples
Bern	City centre, kerbside	PM10/PM2.5/coarse	103/79/76
Zurich-Wiedikon	City centre, kerbside	PM10	59
Zurich-Kaserne	City centre, in courtyard	PM10/PM2.5/coarse	104/79/71
Basel	Suburban	PM10/PM2.5/coarse	103/77/68
Payerne	Rural, below 1000 m a.s.l.	PM10	17
Chaumont	Rural, above 1000 m a.s.l.	PM10/PM2.5/coarse	104/78/64

during 24 h (from midnight to midnight of the following day) on pre-fired ($\geqslant 2$ h at 600 °C) pre-conditioned (48 h in air conditioned room at 22 ± 0.5 °C and $50 \pm 2\%$ RH) and pre-weighted quartz fibre filters (Schleicher und Schuell QF20, $\varnothing = 150$ mm) using high-volume samplers Digitel DA80 ($30 \, \text{m}^3 \, \text{h}^{-1}$ flow rate). The set-up of the instrument is described in a VDI guideline (VDI, 1996). After particle collection, the filters are re-conditioned for another 48 h in the air conditioned room and subsequently analysed for total mass. After re-weighing, the exposed filters were stored in a freezer at -18 °C to limit losses of volatile components. The described PM2.5 and PM10 measurements are in accordance with the European reference method for PM10 (CEN, 1998), which is used in Switzerland to control the standards. It should be noted that the use of quartz fibre filters for gravimetric determination of PM mass is delicate. They are mechanically not very stable and there is a certain risk of losing filter material during the different work steps that are necessary for PM sampling. In order to avoid or at least minimise losses of filter material, the filters were handled with as much care as possible. Losses of filter material would lead to too low PM masses, but has no effect for the determination of concentrations of PM constituents, unless the concentrations are expressed relative to PM mass.

During the period from 01.04.1998 to 31.03.1999 the chemical composition of PM10 and PM2.5 samples from the sites at Basel, Bern, Chaumont and Zurich-Kaserne were extensively characterised on a regular basis: Samples from every 4th day were analysed, except for the period from 01.04.1998 to 31.07.1998, where PM2.5 samples from every 12th day were analysed. The lower sampling frequency for PM2.5 during the first months was due to limited resources for performing chemical analyses. This could introduce a bias when seasonal or annual values are calculated. The bias is expected to be within 15% as estimated from comparing the annual mean PM2.5 concentrations derived from the analysed filter samples (77–79 samples) and the annual mean PM2.5 concentrations as calculated from all available daily values within the considered one year period (approximately 365 samples). During two measuring campaigns in July/August 1998 and January/

February 1999, additional PM10 samples from an extremely traffic influenced site in Zurich-Wiedikon were collected and analysed. Moreover, a total of 17 PM10 samples were collected at the rural site at Payerne during two campaigns in May/June and September/October 1999. The chemical composition data from Basel, Bern, Chaumont and the two sites in Zurich were obtained to serve as input data for a source apportionment study (Hueglin, 2000; Gehrig et al., 2001), while the additional samples at Payerne were collected to obtain information about the chemical composition of PM10 from a rural site at a typical altitude for the Swiss plateau. In order to determine a variety of chemical compounds by applying different analytical methods, the PM-samples had to be cut into portions of known area. Circular filter portions with diameters of 30 mm (4.6% of total filter area) were used. For this approach, it is essential that the particulate matter is homogeneously distributed over the entire filter. In order to account for the measurement uncertainty introduced by inhomogeneous deposition of the material on the filter, repeated analyses of the chemical compounds in different portions of the same filter were regularly performed during the sampling period. The measurement uncertainty of the chemical compounds was derived from repeated analysis and therefore includes the error caused by inhomogeneity of the PM deposition on the filter (Table 2). For quality assurance and for estimating the detection limit of the analytical methods, a total of 82 field blank filters were analysed. Every filter batch that was sent to the monitoring sites contained a field blank filter that was treated in the same way as the filters used for collecting the PM samples. The detection limit was calculated as twice the standard deviation of the field blanks (Table 2); data below the detection limit were set to $\frac{2}{3}$ of the detection limit.

2.2. Chemical analyses

Two filter portions were cut from each filter sample for determination of 26 trace elements (Na, Mg, Al, K, Ca, V, Mn, Fe, Ni, Cu, Ga, As, Se, Br, Rb, Y, Mo, Rh, Cd, Sb, Ba, La, Ce, Nd, Tl, Pb) by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer Sciex

Table 2
Detection limits of the analysed chemical compounds determined from 82 field blank filters, the coefficient of variation (cv = S.D. of repeated analyses/mean of repeated analyses) and the recovery rates of the elements as obtained with the applied HNO_3/H_2O_2 extraction method

Compound	Detection limit DL ($ng\,m^{-3}$)	cv (%)	Recovery (%)	Standard deviation (%)
Mass[a]	*1000*	*2.9*		
Na^+	45	11.7	—	—
K^+	1	8.4	—	—
Mg^{2+}	5	9.2	—	—
Ca^{2+}	44	6.6	—	—
NH_4^+	3	2.8	—	—
NO_3^-	18	4.1	—	—
SO_4^{2-}	19	1.9	—	—
Cl^-	32	23.4	—	—
EC	180	3.8	—	—
OC	460	4.9	—	—
Na	41	8.8	88	9
Mg	2.9	4.1	79	7
Al	32	11.0	74	15
K	68	7.2	78	2
Ca	59	8.4	93	11
V	0.38	3.7	86	6
Mn	0.26	6.1	<DL	<DL
Fe	26	7.0	87	7
Ni	1.9	11.5	77	36
Cu	9.0	6.3	108	46
Ga	0.01	5.3	84	31
As	0.05	4.0	112	29
Se	0.15	18.7	100	34
Rb	0.02	4.2	83	18
Y	0.01	7.4	77	8
Mo	0.18	3.9	<DL	<DL
Rh	<0.01	11.0	<DL	<DL
Cd	0.07	6.9	112	13
Sb	0.18	16.9	<DL	<DL
Ba	4.2	6.4	<DL	<DL
La	0.03	29.3	78	4
Ce	0.14	15.8	<DL	<DL
Nd	0.02	17.9	81	4
Tl	<0.01	3.7	104	13
Pb	0.78	4.8	98	7

The given recovery rates are calculated with respect to concentrations obtained by total digestion using a HNO_3/HF solution (number of filter samples = 5).

[a] Detection limit and coefficient of variation for PM mass were determined in an earlier unpublished investigation.

Elan 6000). The filter portions were extracted in teflon tubes by adding 5 ml HNO_3 and 1 ml H_2O_2 and subsequent microwave digestion (5 min at 250 W, 8 min at 600 W, and 7 min at 350 W). Indium was added to the cooled digest as an internal standard and the digest was then filled up to 50 ml. All measurements were calibrated by analysis of standard solutions containing known amounts of the trace elements. The relatively mild extraction method was selected because a HNO_3/HF digestion of the filter samples lead to clearly higher detection limits for some of the elements due to contamination from the filter material. The recovery rates of the selected extraction method was compared to a HNO_3/HF digestion using a series of five PM10 samples collected on teflon filters (Schleicher und Schuell TE37, pore size 1 μm) as well as by using a certified standard material (National Bureau of Standards—NIST, Reference Material 1648, Urban Particulate Matter). Application of the HNO_3/H_2O_2 extraction method lead to total recovery for most of the elements, while for Na, Mg, Al, K, Y, La and Nb the determined recovery rates ranged between 74% (Al) and

88% (Na) (Table 2). Another filter portion with a diameter of 30 mm was extracted in 50 ml nanopure water during 24 h shaking the aqueous solution repeatedly during the extraction period. Ion chromatography (Dionex DX-500) was used to determine the concentrations of water soluble inorganic ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}). Two further filter portions were used for elemental carbon (EC) and total carbon (TC) determination according to the VDI method (VDI, 1996): The TC concentration was measured by burning one of the two filter portions in an oxidising atmosphere (pure oxygen) at 650 °C, and the emerging CO_2 was detected by coulometry. EC was determined in the same way after removal of the extractable organic carbon fraction from the second filter portion. The extractable organic fraction was removed by solvent extraction in a 50:50 vol%-mixture of toluene and 2-propanol for 24 h at room temperature and subsequent removal of the solvent using a pipette and drying of the filter for another 24 h at 40 °C. The non-extractable organic carbon was removed from the dried filter by thermal desorption in a nitrogen flow for 1 min at 200 °C and 7 min at 500 °C. The carbon fraction that remained on the filter was assigned to be elemental carbon. The concentration of organic carbon (OC) was then calculated as the difference of TC and EC.

2.3. Assessing the water content of PM10 and PM2.5

A series of 17 PM10 samples collected in May, October and November 1999 at some of the sampling sites listed in Table 1 were additionally examined for their water content. After determination of the PM10 mass concentration, filter portions were immediately taken from the samples and analysed for compounds that can at least partially get lost during storage of the samples at ambient temperature (i.e. ammonium, nitrate and OC). The remainder of the PM10 samples were subsequently put in an open glove-box that was placed in an air conditioned room equipped with a microbalance (Mettler Toledo AE200) and a hygroscopicity sensor. The remainder of the PM10 samples were weighted at 22 °C and 50% RH. Next, a vessel filled with a drying agent (Silicagel) was placed into the glovebox, which resulted in a relative humidity of below 5%. The PM10 samples were kept in the glove box for fourteen days and regularly weighed until the weight of the samples was constant (typically after seven days). The observed loss of weight was assumed to be due to desorption of semi-volatile compounds, i.e. ammonium nitrate, organic species and water. Therefore, the mass of ammonium, nitrate and OC was again determined after the PM10 samples reached constant weight. The observed loss of weight was corrected for the difference of the mass of ammonium nitrate and organic matter as measured before and after the drying procedure. The

remaining loss of mass was interpreted as the water content of the PM10 samples. In order to account for the changing weight of the filter material, a set of twenty blank filters was additionally subjected to the drying procedure. The weight loss of the PM10 samples was corrected by the average weight loss of the blank filters.

The potential water content of PM2.5 samples at 50% RH was estimated from their chemical composition. Towards this aim the thermodynamic aerosol inorganics model (AIM) by Clegg et al. (1998) (http://www.hpc1.uea.ac.uk/~e770/aim/aim.htm) for the H^+–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O system was used to calculate the water content associated with the inorganic salts. Excess anions were compensated by H^+ to adjust the charge balance, and the formation of solids was suppressed, i.e. the inorganic salts were assumed to be dissolved. Since inorganic salts may partially crystallise at 50% RH, this approach provides an upper limit of the water associated with inorganic salts. On the other hand, the organic matter is also expected to absorb some water, but this effect was not considered in the model calculations since no information about the amount of water-soluble organic matter was available.

2.4. PM mass balance closure

Summation of the individually analysed chemical components is expected to explain more or less the total PM10 and PM2.5 mass. Therefore, a PM mass balance is performed by application of the following steps: (a) Mineral dust was estimated from the measured concentrations of Al, Mg, K, Ca, Fe, and the estimated concentration of Si. The silicon concentration was estimated from the average ratio of Si and Al in the earth's crust as Si = 3.41Al (Mason, 1966), the concentration of mineral dust was then estimated by scaling the crustal elements with the corresponding recovery rate (Table 2) and by assuming that the elements existed as oxides (Chow et al., 1994) (i.e. mineral dust = 1.89Al + 1.66Mg + 1.21K + 1.40Ca + 1.43Fe + 2.14Si). (b) The trace elements were also assumed to exist as oxides, and the concentrations of the analysed elements were multiplied with corresponding factors to account for the oxygen mass. (c) To account for the mass of unmeasured hydrogen and oxygen in organic material (OM), the OM concentration was expressed as 1.4OC (Grosjean and Friedlander, 1975).

3. Results and discussion

3.1. Summary of the chemical composition of PM

Table 3 summarises the results of the elemental analysis for PM10, PM2.5 and PM10–PM2.5, the

Table 3
Concentrations of water soluble compounds and trace elements in daily PM samples from different site types. At the sites in Bern, Zurich-Kaserne, Basel and Chaumont the calculations are based on PM samples collected on a regular basis during one year (01.04.1998–31.03.1999), while at Zurich-Wiedikon and Payerne, the given mean concentrations are based on PM samples collected during measuring campaigns (see text)

Site characteristics	City centre, kerbside			City centre, kerbside	City centre, in courtyard			Suburban			Rural, below 1000 m a.s.l.	Rural, above 1000 m a.s.l.		
Site	Bern			Zurich-Wiedikon	Zurich-Kaserne			Basel			Payerne	Chaumont		
n	79	103	76	59	79	104	71	77	103	68	17	78	104	64
Parameter	PM2.5	PM10	Coarse	PM10	PM2.5	PM10	Coarse	PM2.5	PM10	Coarse	PM10	PM2.5	PM10	Coarse
	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$	$(ng\,m^{-3})$
Compound														
Na^+	94	612	746	591	76	181	106	111	243	128	118	71	138	65
K^+	180	197	48	233	183	190	28	218	221	28	89	51	63	11
Mg^{2+}	8.5	46	37	50	11	37	21	13	46	26	33	12	36	20
Ca^{2+}	132	1526	1420	463	66	320	209	71	391	279	288	67	233	139
Cl^-	102	769	1012	756	72	97	42	145	212	111	82	48	61	16
Na	84	665	848	690	96	192	140	117	260	147	298	68	151	72
Mg	13	85	76	76	17	49	33	16	52	34	48	10	40	23
Al	26	152	130	107	48	81	37	37	98	51	91	34	91	38
K	186	255	102	312	223	219	43	224	404	41	98	68	91	15
Ca	106	1199	1135	424	54	242	178	64	368	196	100	46	138	82
V	1.6	1.4	1.0	1.6	1.1	1.0	0.3	1.2	2.4	0.3	0.7	0.8	0.8	1.0
Mn	4.4	25	20	17	3.5	7.3	5.1	3.1	7.9	5.3	2.8	0.8	2.4	1.2
Fe	204	2048	1997	1611	124	474	414	66	295	221	89	26	93	50
Ni	1.3	3.0	1.9	3.6	3.1	1.8	0.11	1.7	2.2	0.46	1.2	1.3	1.3	0.04
Cu	8.7	74	68	75	6.1	17	12	6.0	8.5	3.4	6.0	6.0	6.5	0.3
Ga	0.03	0.10	0.07	0.07	0.04	0.05	0.02	0.07	0.11	0.03	0.03	0.02	0.04	0.01
As	0.40	0.80	0.42	0.68	0.47	0.44	0.10	0.40	0.60	0.11	0.53	0.16	0.18	0.02
Se	0.21	0.30	0.09	0.57	0.56	0.43	0.07	0.40	0.44	0.05	0.16	0.22	0.23	0.00
Rb	0.44	0.68	0.34	0.61	0.50	0.50	0.12	0.58	0.69	0.14	0.30	0.15	0.26	0.09
Y	0.01	0.12	0.11	0.05	0.01	0.05	0.03	0.01	0.05	0.03	0.04	0.01	0.04	0.02
Mo	0.72	4.46	4.11	5.00	0.70	1.28	0.93	0.39	0.75	0.42	0.32	0.16	0.19	0.04
Rh	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.21	0.26	0.08	0.26	0.31	0.23	0.03	0.48	0.42	0.04	0.32	0.12	0.11	1.00
Sb	0.95	5.6	4.8	8.8	0.57	1.4	1.1	0.41	0.66	0.29	0.26	0.16	0.19	0.05
La	0.09	0.23	0.14	0.15	0.06	0.10	0.05	0.05	0.11	0.05	0.06	0.20	0.08	1.00
Nd	0.07	0.17	0.10	0.08	0.04	0.07	0.03	0.02	0.08	0.04	0.05	0.02	0.06	0.03
Tl	0.05	0.06	0.01	0.03	0.04	0.03	0.01	0.03	0.03	0.01	0.03	0.01	0.01	0.00
Pb	30	49	22	50	21	20	5.9	19	21	4.4	10	4.7	5.4	0.8

The values for total mass, ammonium, nitrate, sulphate, elemental carbon and organic matter are given in Table 4.

annual mean concentrations of the main components of PM10, PM2.5 and PM10–PM2.5 are given in Table 4. The annual mean concentrations of the main aerosol components in Bern, Zurich, Basel and Chaumont, and seasonal variations of the chemical composition are discussed in detail by Putaud et al. (2004) and Van Dingenen et al. (2004).

Organic matter, sulphate, and nitrate are the main contributors to the annual PM2.5 and PM10 mass concentration at rural, near-city, and urban background sites. These constituents are mainly associated with PM2.5 (Fig. 2). At kerbside sites, organic matter and elemental carbon are the two main contributors to annual PM2.5 and PM10. The elemental carbon concentrations at the kerbside sites in Bern and Zurich-Wiedikon comprise 14–18% of PM2.5 and PM10. At rural, near-city, and urban background sites, EC averages to 5–10% of the PM2.5 and PM10 mass concentration. Nitrate shows a high seasonality, with much lower concentrations during summer than during winter (see also Fig. 6). This seasonality is explained by a greater partitioning of nitrates in the aerosol phase during colder periods. It is interesting to note that while at the sites close to the sources nitrate and sulphate are present in similar concentrations, at the remote site nitrate is much less abundant (Table 4). The same was shown for the high-alpine site Jungfraujoch (Henning et al., 2003), and was explained by the competition between sulphate and nitrate for ammonia, where sulphate is fully neutralised before ammonia is available for nitrate.

At the kerbside sites in Bern and Zurich-Wiedikon, the soil and trace element fraction is higher than at the other site types, indicating the importance of re-suspended road dust at kerbside sites. Fig. 2 shows the relative contributions of the main PM constituents and some selected trace elements to PM2.5 and PM10–PM2.5. Shown is the median for analyses that are above the detection limit for simultaneously sampled PM2.5 and PM10. The median is used because it is robust against outliers, which sometimes occur especially for low concentrations at the rural site in Chaumont. At the rural and the near-city site crustal elements like Al, Mg, Ca, and Fe are predominantly in the PM10–PM2.5 fraction, while typical anthropogenic elements like As, Cd, Tl, and Pb are mainly associated with PM2.5, and elements like Cu, Mn, Mo, Na, and Sb are roughly evenly distributed between PM2.5 and PM10–PM2.5. At the urban background site, the above-mentioned elements Cu, Mn, Mo, Na, and Sb are (similar to the crustal elements Al, Mg, Ca, and Fe) mainly associated with the PM10–PM2.5 fraction. At the kerbside site it seems that the percentage of most constituents in the PM10–PM2.5 fraction is higher than at the urban background site. Moreover, the PM2.5–PM10 ratio is lowest at the kerbside site, which

is believed to be due to the contribution of re-suspended road dust and re-suspension of mechanically generated particles (e.g. tyre wear and brake lining dust) to the PM10–PM2.5 fraction (Gehrig and Buchmann, 2003). Concentrations of Rh (not shown in Fig. 2) are above the detection limit only at the kerbside sites in Bern and Zurich-Wiedikon and are predominantly found in the PM10–PM2.5 fraction, as also shown by Kanitsar et al. (2003). Rhodium concentrations at the kerbside sites indicate particle emissions from abrasion of catalytic converter material as used by gasoline powered vehicles (Cubelic et al., 1997).

3.2. Variation of trace element concentrations in PM

Figs. 3 and 4 shows the day-of-week variation of PM2.5, PM10, PM10–PM2.5, some major components of PM10, as well as of Mn and Cu. The most pronounced day-of-week variation is found at the kerbside site. The average traffic density on the road beside the kerbside site in Bern is about 35,000 vehicles per day from Monday to Friday, about 28,000 vehicles per day on Saturdays, and about 22,000 vehicles per day on Sundays. Average PM concentrations are lowest on Sundays, when heavy duty traffic is banned from Swiss roads. In particular, the average PM10–PM2.5 level is markedly lower on Sundays, indicating the importance of emissions of re-suspended road dust and mechanically generated particles from road traffic. The average concentration of EC, mineral dust, Mn, and Cu is also clearly lower at weekends than from Mondays to Fridays. A similar behaviour is found for Al, Ba, Ca, Ce, Fe, Ga, La, Mg, Mo, Ni, Pb, Rh, and Sb (not shown in Fig. 4). The fact that the described day-of-week variation is *distinct* at the kerbside site and *much less pronounced* at the urban background site, and that on the other hand, the concentrations of these elements at the kerbside site are considerably higher than at the urban background site indicates that these elements are emitted by road traffic. This finding is consistent with the results of a receptor modelling study performed with the presented data (Hueglin, 2000; Gehrig et al., 2001).

For OM, the average concentration on Sundays is lower than on the other days. Nitrate seems to follow the same pattern as OM, with lowest concentrations on Sundays. The effect is not that clear as it might be partially masked by the seasonal dependence of nitrate concentrations in atmospheric PM. For sulphate and ammonium (not shown in Fig. 4), no day-of-week variation is observed, as one would expect for components that are not locally produced.

Fig. 5 shows the relative contributions of Al, As, Cd, Fe, K, Na, Pb, and V to PM10 at the different site types separately for the four seasons. Relative seasonal contributions of other elements will also be discussed, although they are not included in Fig. 5. Based on this

Table 4
Chemical composition of PM2.5, PM10, and the coarse particle fraction (PM10–PM2.5) at different site types in Switzerland. The values are annual means (01.04.1998–31.03.1999), except for Zurich-Wiedikon and Payerne (campaign measurement)

Site characteristics	City centre, kerbside			City centre, kerbside		City centre, in courtyard			Suburban			Rural, below 1000 m a.s.l.	Rural, above 1000 m a.s.l.		
Site	Bern			Zurich-Wiedikon		Zurich-Kaserne			Basel			Payerne	Chaumont		
n	79	103	76	79	59	79	104	71	77	103	68	17	78	104	64
Parameter	PM2.5 (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	Coarse (μg m⁻³) (%)	PM2.5 (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	PM2.5 (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	Coarse (μg m⁻³) (%)	PM2.5 (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	Coarse (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	PM2.5 (μg m⁻³) (%)	PM10 (μg m⁻³) (%)	Coarse (μg m⁻³) (%)
Mass	24.6 (100.0)	40.2 (100.0)	19.6 (100.0)	20.0 (100.0)	43.0 (100.0)	20.0 (100.0)	24.4 (100.0)	6.3 (100.0)	18.9 (100.0)	24.8 (100.0)	6.7 (100.0)	13.7 (100.0)	7.7 (100.0)	10.8 (100.0)	2.6 (100.0)
NH_4^+	1.6 (6.6)	1.4 (3.6)	0.0 (0.0)	2.1 (10.4)	2.6 (6.0)	2.0 (10.8)	2.0 (8.0)	0.2 (2.5)	2.0 (10.8)	1.9 (7.8)	0.1 (1.4)	1.0 (7.3)	0.8 (10.8)	0.8 (7.7)	0.0 (0.8)
NO_3^-	3.0 (12.1)	3.5 (8.7)	1.1 (5.6)	3.5 (17.3)	4.7 (10.8)	3.5 (17.3)	3.4 (13.9)	0.6 (10.3)	4.1 (21.8)	3.2 (12.8)	0.7 (9.9)	1.1 (7.9)	0.6 (7.4)	0.8 (7.2)	0.3 (11.8)
SO_4^{2-}	2.8 (11.3)	3.3 (8.2)	0.7 (3.8)	3.5 (17.3)	4.2 (9.7)	3.5 (17.3)	3.6 (14.9)	0.4 (6.7)	4.1 (21.8)	3.9 (15.5)	0.1 (1.9)	2.2 (15.9)	2.3 (30.0)	2.0 (18.7)	0.0 (0.0)
EC	4.2 (17.3)	5.6 (13.9)	1.8 (9.1)	1.8 (8.8)	7.7 (17.9)	1.8 (8.8)	2.0 (8.3)	0.5 (7.4)	1.6 (8.5)	1.8 (7.4)	0.4 (5.8)	1.3 (9.2)	0.4 (5.2)	0.6 (5.3)	0.2 (6.0)
OM	7.5 (30.4)	8.9 (22.2)	2.6 (13.2)	4.7 (23.7)	9.0 (21.0)	4.7 (23.7)	4.9 (20.2)	0.6 (9.6)	4.5 (23.7)	4.7 (19.0)	0.6 (9.3)	3.4 (24.6)	1.6 (20.8)	1.7 (15.5)	0.1 (1.2)
Mineral dust	1.2 (4.8)	5.8 (14.3)	4.9 (25.2)	1.5 (7.4)	4.7 (11.0)	1.5 (7.4)	2.4 (10.0)	1.3 (19.9)	0.7 (3.6)	2.9 (11.9)	1.2 (17.1)	1.6 (12.1)	0.7 (8.8)	1.6 (15.0)	0.6 (25.0)
Trace elements	0.6 (2.2)	2.1 (5.3)	2.3 (11.8)	0.4 (2.2)	2.4 (5.5)	0.4 (2.2)	0.7 (2.7)	0.3 (5.2)	0.7 (3.6)	1.0 (4.0)	0.5 (7.2)	0.5 (3.8)	0.3 (3.6)	0.4 (3.7)	0.1 (5.3)
Unknown	3.7 (15.2)	9.5 (23.8)	6.1 (31.3)	2.6 (12.9)	7.7 (18.0)	2.6 (12.9)	5.4 (22.0)	2.4 (38.4)	1.6 (8.3)	5.4 (21.6)	3.2 (47.4)	2.6 (19.3)	1.0 (13.4)	2.9 (26.8)	1.3 (49.8)
Calculated water	3.2 (13.0)			3.5 (17.5)					4.1 (21.7)				1.8 (23.4)		

analysis, the elements can be grouped into two different classes: (1) Elements with gradually decreasing percentages (and/or concentrations, not shown in Fig. 5) from polluted (kerbside) to clean (rural) sites. These elements are Ba, Ce, Cu, La, Mo, Mn, Nd, Sb, as well as Ca, Fe and Pb. For these elements, road traffic seems to be a major emission source. EC and OM behave similar to these elements, although OM percentages are almost constant within the different site types (Putaud et al., 2004). (2) Elements with similar percentages and/or concentrations at sites that represent different pollution levels (except the elevated rural site at Chaumont, 1140 m a.s.l, which during wintertime is mostly above the inversion layer and therefore protected from the emissions of the densely populated Swiss plateau). Similar concentrations of elements at sites that are distributed over a large geographical area and representing different pollution levels indicate that these elements are uniformly distributed. Emission sources are therefore also expected to be either spatially uniformly distributed or no major regional sources exist and the corresponding elements in PM10 are mainly transported to Switzerland over longer distances. This is true for As, Se, Ni, V, typically associated with emissions from coal and oil combustion (Huang et al., 1994; Lee et al., 1994), as well as for Al, Ga, Cd, Tl, and K. Al and Ga can be associated with re-suspended crustal material, Cd and Tl are mainly due to emissions from stationary sources (BUWAL, 1995), Potassium is recognised as a marker for combustion of biomass (Huang et al., 1994). The dependence of the percentage and concentration on site type for sulphate, nitrate and ammonium is similar to the elements of this second group (Putaud et al., 2004).

Some elements show a seasonal dependency of the concentration in PM10 that differs from the typical seasonal variation caused by meteorology (higher concentrations during colder seasons with stronger inversions). At the kerbside site and the urban background site, the concentration and percentage of sodium in PM10 is highest in spring and winter, which is very likely due to the influence of re-suspended road salt particles. Aluminium shows the highest percentages in PM10 in summer and fall, which is explained by higher emissions of re-suspended mineral dust particles during the drier periods of the year. A similar seasonal pattern as for Al is observed for Ca, Ga, Nd and Y. Elevated Ca concentrations at the kerbside sites (as well as high kerbside concentrations of Fe) indicate road traffic emissions due to re-suspension of road dust.

Earlier trace element data of atmospheric PM from Swiss sites are available from studies by Gälli et al. (1990) and Röösli et al. (2001). Gälli et al. (1990) reported on metal concentrations (Na, V, Mn, Cu, Zn, As, Cd, and Pb determined by atomic absorption spectroscopy) in weekly samples of seven size fractions, ranging from 0.06 to 8 μm, collected at rural sites from
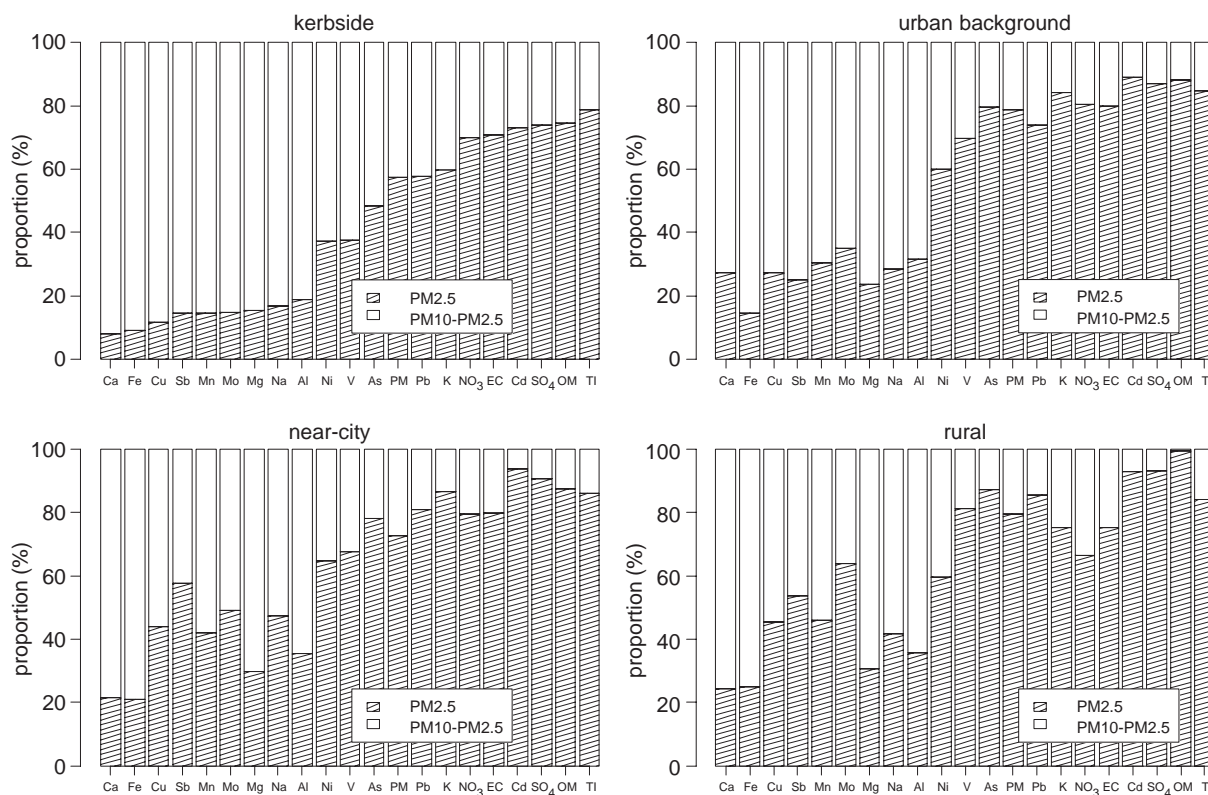
Fig. 2. Proportion of main constituents and trace elements to PM2.5 and the coarse fraction (PM10–PM2.5) at different site types (median values for selected components for analyses above the detection limit).

October 1985 to September 1986. The sampling sites were located south of Bern at different elevations along the slope of a mountain range. One of the sites (Belp, 515 m a.s.l) can be compared to the characteristics of the site in Basel, while the type of a second site (Uecht, 940 m a.s.l) is comparable to the site in Chaumont. Though the comparison of the measurements from the two different sampling periods might be hampered by the fact that the sites, sampling method, analytical methods and meteorology are different, a clear decrease of V, Mn, As, Cd, and Pb in PM10 from 1985/1986 to 1998/1999 can be noticed. Na concentrations in atmospheric PM seem more or less unchanged (Table 5). For Cu and Zn a comparison of the concentrations is not possible, because of the relatively high detection limit for Cu in this study and because Zn was not measured here. Recent measurements of Zn in PM10 are available in Röösli et al. (2001). They reported on concentrations of main constituents of PM10 and the concentrations of Zn, Pb, and Cd collected at two urban and two rural sites in the Basel area during the same time period as the data presented in this study (April 1998 to March 1999). The obtained average element concentrations from Röösli et al. (2001) are in good agreement with the values reported here. Their values for Zn at the two rural

sites indicate that the Zn concentration in PM10 decreased also markedly at rural sites in Switzerland since the mid 1980s. The observed decreases in metal concentrations in PM10 are consistent with implemented emission control measures. Metal emissions from stationary sources were restricted in 1986, Pb was banned from gasoline in 1985. The decreases of Pb and Cd concentrations reported in this study are consistent with the reported emission reductions: Pb and Cd emissions decreased from 1985 to 2000 by a factor four and two, respectively (BUWAL, 1995).

3.3. PM2.5 and PM10 mass closure

Annual mean mass closures for PM2.5 and PM10 at all measurement sites are listed in Table 4 and seasonally resolved values for PM2.5 are shown in Fig. 6. As in other studies (Chow et al., 1994; Heintzenberg et al., 1998; Röösli et al., 2001; Putaud et al., 2004), a total chemical mass closure of atmospheric PM is not achieved here, i.e. there is generally a considerable difference between the gravimetrically measured PM mass concentration and the sum of the concentrations of the analysed components (see "unaccounted mass" in Table 4). The annual mean unaccounted mass constitu-
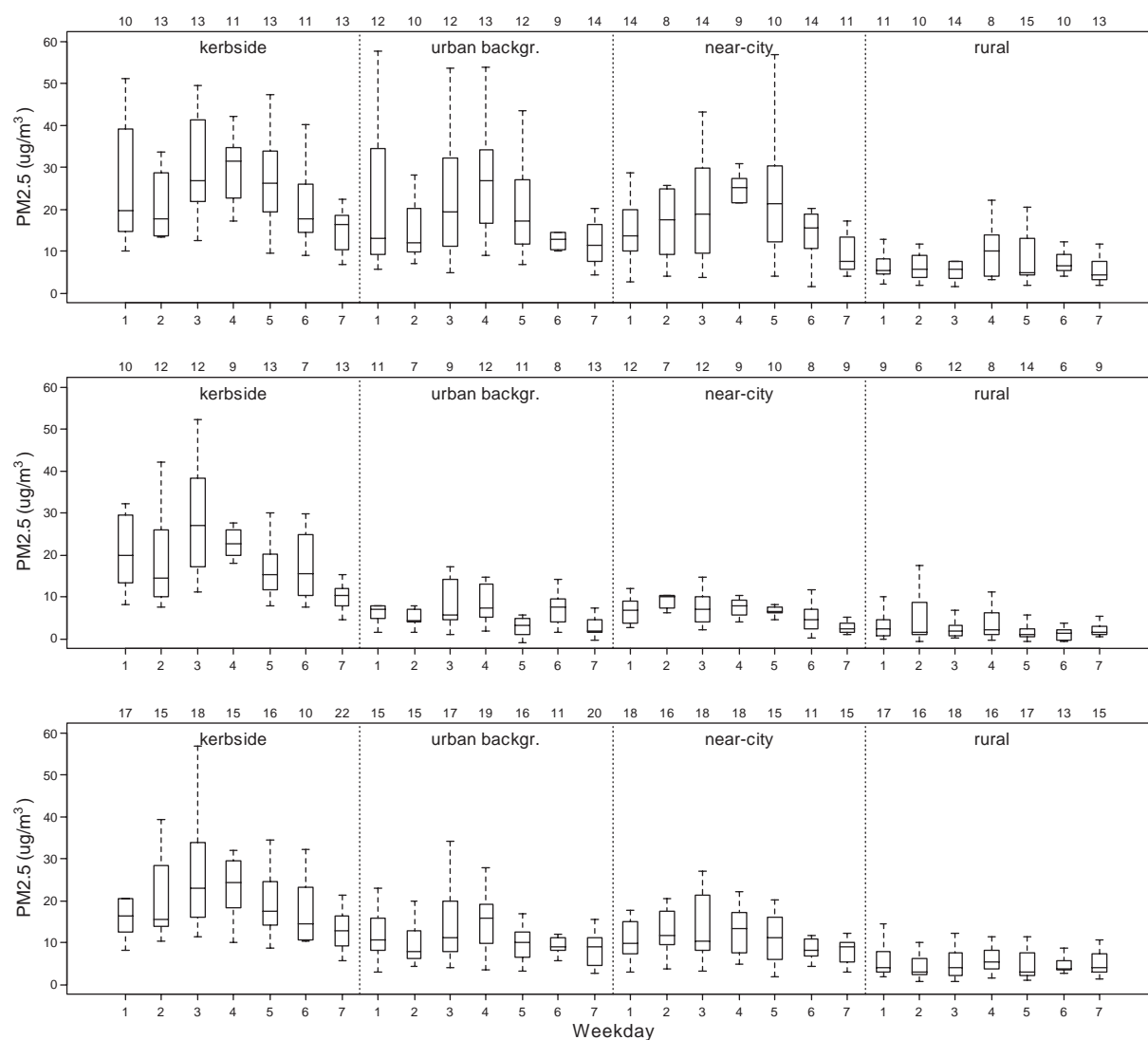
Fig. 3. Boxplots of PM2.5, PM10–PM2.5, and PM10 at a kerbside site (Bern), an urban background site (Zurich-Kaserne), a near-city site (Basel), and a rural site (Chaumont) for different weekdays (1 = Mon,...,7 = Sun). The horizontal line in a box indicates the median, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the furthermost values within the standard range of 1.5 times the inter-quartile range (length of box). The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

tes 22–27% of PM10 and 8–15% of PM2.5, and it shows a seasonal variation, being lower during winter (12–24% of PM10 and 6–14% of PM2.5) than during summer (33–40% of PM10 and 29–36% of PM2.5). The small mean negative discrepancy between PM2.5 mass and the sum of measured chemical components in winter was obtained at the rural and elevated site at Chaumont. At Chaumont, some of the negative discrepancies were obtained at very low PM concentrations and caused by the replacement of below detection limit concentrations by $\frac{2}{3}$ DL. However, negative discrepancies were also

obtained for some PM2.5 (Fig. 6) and PM10 samples from the other sites.

There are presumably four main factors leading to the generally positive discrepancy between PM2.5 mass and the sum of measured chemical components: (1) The mass fraction of organic matter might be underestimated because the applied factor of 1.4 might not adequately account for non-C atoms associated with OM. As an example, Turpin and Lim (2001) suggested conversion factors of 1.6 ± 0.2 and 2.1 ± 0.2 for urban and aged (non-urban) aerosols, respectively. The effect of under-
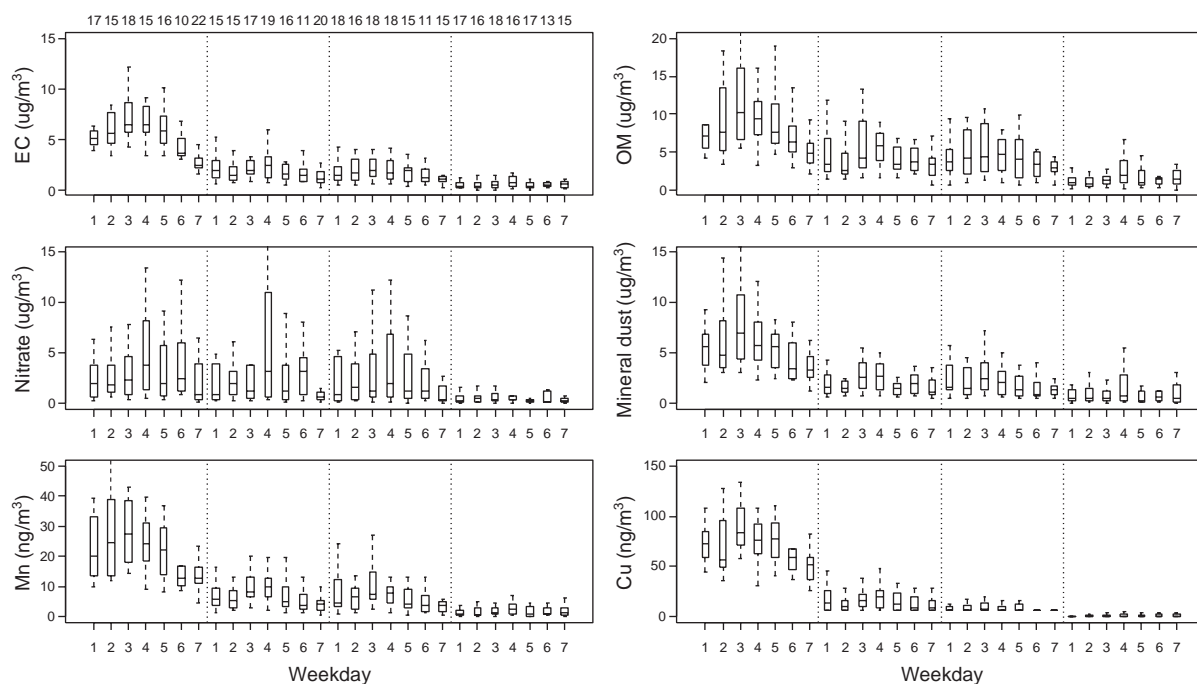
Fig. 4. Boxplots of the day-of-week variation of some of the main constituents of PM10, and of the concentrations of Mn and Cu in PM10 (1 = Mon,...,7 = Sun). The numbers on top of the left upper graph indicate the number of values that were considered for calculating the corresponding box (for boxplot explanation see Fig. 3).

estimation of OM might be especially pronounced during the warmer seasons when the fractions of biological material and of secondary organic material in PM are highest. For biological material the conversion factor was suggested to be around 2.2 (Kunit and Puxbaum, 1996). (2) The applied analytical method for OC and EC may introduce some errors, since it does not correct for charring during pyrolysis of the PM samples. The sum of OC and EC should be correct, however charring causes an overestimation of EC and an underestimation of OC (Schmid et al., 2001). As a consequence, the total carbonaceous PM fraction (OM + EC) is underestimated. In addition, the mass contribution of biological particles is expected to be not correctly taken into account by measuring OM as outlined. (3) The especially high unaccounted mass for the coarse PM fraction (31–50%) indicates that the estimation of the mineral dust concentration and/or the trace element concentration according to Section 2.4 is inadequate. (4) The hysteresis behaviour of aerosol particles can cause water to be retained on PM although the filter samples are post-conditioned to 50% RH. Specific measurements and model calculations were conducted in order to estimate the water content of PM10 and PM2.5, respectively (Section 2.3).

Table 6 gives the weight loss of the considered PM10 samples during the drying procedure. The weight loss of volatile material (ammonium, nitrate and organic

matter) was negligible for the PM10 samples from May, but substantial for the samples from October and November (Table 6). The weight difference of volatile material was smaller than the total measured weight difference in both seasons, and the weight loss after correction for losses of volatile material was hence interpreted as the weight of absorbed water. The obtained average water content of PM10 is 10.6%, with higher values during the warmer season (17.2% for PM10 samples from May), than during the colder season (6.0% for PM10 samples from October and November). The seasonal variation of the water content is in line with the observed seasonal variation of the unaccounted mass in PM10.

The model calculations for PM2.5 revealed that at 50% RH between 13 and 23% of PM2.5 may be water (Table 4). Estimated water fractions are slightly higher in winter compared to summer due to slightly larger inorganic mass fractions in winter (Fig. 6). The mass balance including water estimates explains actual PM2.5 masses generally well in spring and autumn. In summer the mass balance including water is still too low which is possibly caused by artefact number (1) as discussed above. In winter the sum of all determined chemical constituents is generally close to 100%, whereas the addition of calculated water content to the mass balance overestimates the actual PM2.5 mass. This indicates that in winter the inorganic salts are not completely
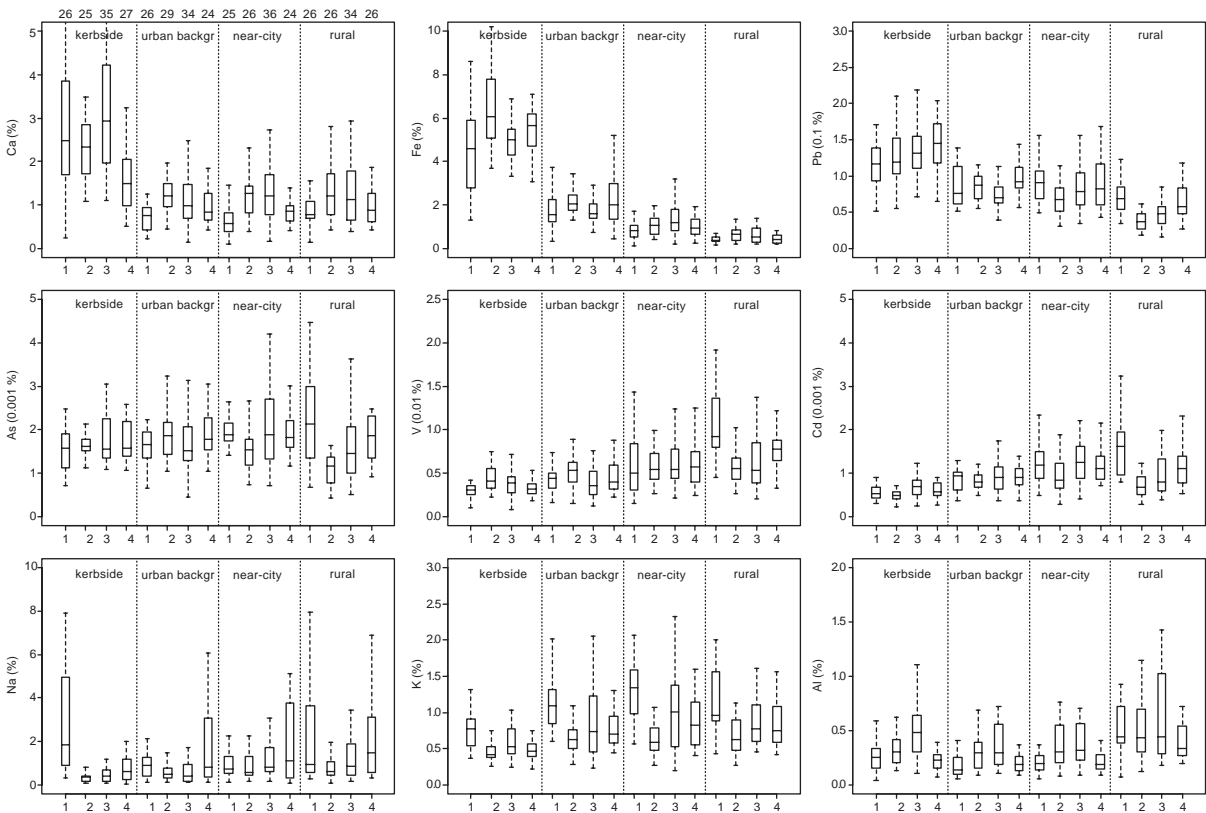
Fig. 5. Boxplots of the seasonal variation of selected trace element percentages in PM10 at different site types (seasons: 1 = MAM, 2 = JJA, 3 = SON, 4 = DJF). The numbers on top of the left upper graph indicate the number of values that were considered for calculating the corresponding box (for boxplot explanation see Fig. 3).

Table 5
Comparison of annual mean element concentrations in PM10 at Basel and Chaumont (collected from April 1998–March 1999) with the corresponding element concentrations in the size fraction 0.06–8 µm at Belp and Uecht (collected from October 1985–September 1986) taken from Gälli et al. (1990)

Mean concentration ($ng\,m^{-3}$)					Ratio	
Element	Belp	Uecht	Basel	Chaumont	Basel/Belp	Chaumont/Uecht
Na	170	138	260.1	150.8	1.53	1.09
V	3.9	3.1	2.4	0.8	0.62	0.26
Mn	31.7	25.4	7.9	2.4	0.25	0.09
Cu	7.9	3.4	8.5	6.5	—	—
Zn	65.0	34.9	—	—	—	—
As	2.2	1.7	0.6	0.18	0.27	0.11
Cd	0.88	0.59	0.42	0.11	0.48	0.19
Pb	134	39.1	21.3	5.4	0.16	0.14
PM	37,100	25,000	24,800	10,800	0.67	0.43

dissolved, as it was assumed for the water content calculations, but that they are mainly present in crystalline form. This is in agreement with small water losses during drying of PM10 samples from the cold season, and similar results were also found in a recent study in Pittsburgh (Rees et al., 2004). Rees et al. (2004) found that the water content of PM2.5 has a strong relationship with the acidity of the aerosol.
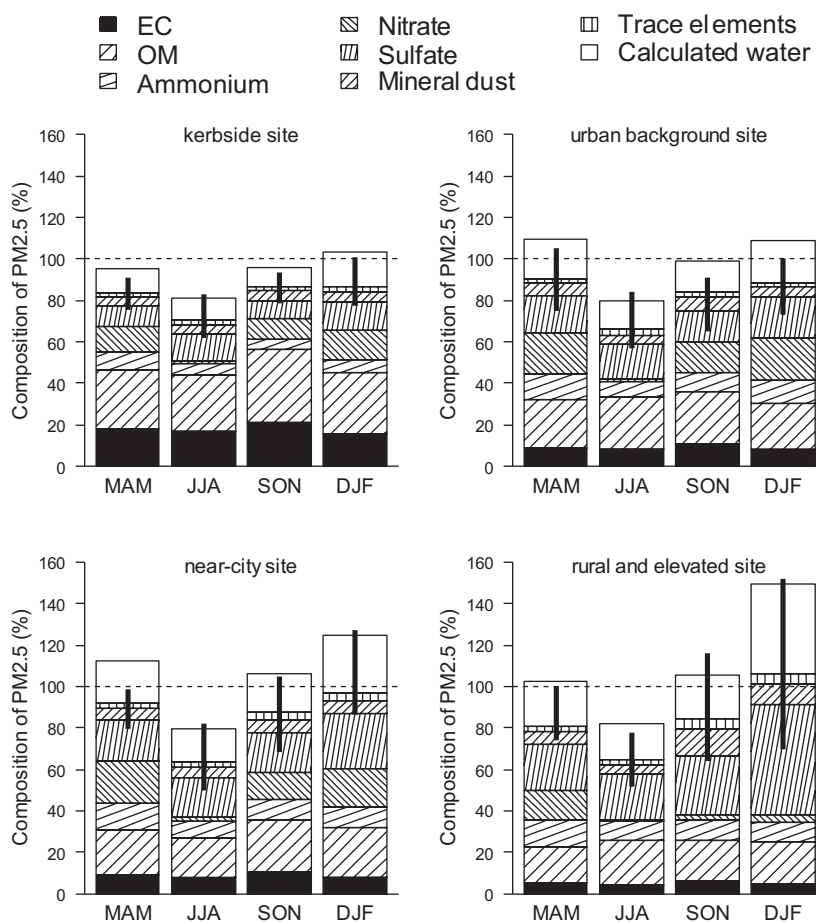
Fig. 6. Seasonal variation of the chemical composition of PM2.5 at a kerbside site (Bern), an urban background site (Zurich-Kaserne), a near-city site (Basel), and a rural and elevated site (Chaumont). Shown is the trimmed mean (10%) of the obtained main PM2.5 constituents. The trimmed mean is used instead of the common arithmetic mean, because it is a more robust measure. The vertical black lines indicate the range between the 10th and 90th percentile of the sum of the measured constituents (sum of all constituents except water). They also indicate that especially during cold seasons some samples with negative discrepancy between PM2.5 mass and the sum of the measured c components were obtained. For three samples (two from Chaumont and one from Basel), the negative discrepancy was larger than the PM2.5 mass concentration. These three samples were considered as outliers and not included here. Losses of filter material as mentioned in Section 2.1 might have caused these outliers. Dotted lines at 100% niveau indicate the measured PM2.5 mass.

It is concluded that a major portion of the positive discrepancy between PM mass concentration and the sum of measured chemical compounds is very likely to be due to the water content of atmospheric aerosols.

4. Conclusions

A comprehensive chemical characterisation of PM2.5, PM10 and the coarse PM fraction (PM10–PM2.5) was performed for samples from different site types in Switzerland. Trace elements known to be mainly emitted by anthropogenic processes were predominantly in the PM2.5 fraction. Crustal elements were found to be mainly in the PM10–PM2.5 fraction, except at the kerbside site where impact of re-suspended mineral dust particles and re-suspension of mechanically generated particles prevailed. Comparison of the element abundances at the different site types gave information about corresponding emission sources. Road traffic was found to be a significant source of a variety of trace elements. Comparison with available data from the mid-1980s shows that in Switzerland the concentration of V, Mn, As, Cd, and Pb in atmospheric PM has clearly been decreasing since then.

Water is a main constituent of atmospheric PM as determined with the European reference method for PM10 (CEN, 1998). Methods for quantitative

Table 6
Estimation of the water content of daily PM10 samples collected at different measuring sites in May, October and November 1999

Date	Site	PM10 ($\mu g \, m^{-3}$)	Δ PM10 ($\mu g \, m^{-3}$)	Δ ($OM + NH_4NO_3$) ($\mu g \, m^{-3}$)	H_2O ($\mu g \, m^{-3}$)	%
18.05.99	Bern	38.2	−7.5	0.2	7.7	20.3
18.05.99	Zurich-Kaserne	22.5	−2.7	−0.2	2.4	10.8
22.05.99	Bern	20.6	−2.7	−0.2	2.5	12.2
22.05.99	Zurich-Kaserne	17.5	−0.6	0.2	0.8	4.5
26.05.99	Basel	19.4	−6.7	−0.1	6.6	34.1
26.05.99	Zurich-Kaserne	20.0	−2.8	0.0	2.8	14.0
30.05.99	Basel	18.2	−4.5	0.1	4.5	24.9
17.10.99	Payerne	30.8	−3.5	−0.9	2.6	8.4
21.10.99	Basel	43.9	−2.8	−1.1	1.7	3.9
21.10.99	Bern	55.7	−3.2	−2.4	0.8	1.4
21.10.99	Payerne	42.9	−5.4	−1.8	3.6	8.4
29.10.99	Basel	32.2	−2.4	−1.4	0.9	2.9
29.10.99	Bern	61.0	−3.6	−0.7	3.0	4.9
29.10.99	Zurich-Kaserne	81.4	−1.2	−0.2	1.0	1.2
29.10.99	Payerne	48.7	−5.9	−1.3	4.6	9.5
02.11.99	Bern	36.7	−5.6	−1.8	3.8	10.3
02.11.99	Zurich-Kaserne	29.9	−3.0	−0.3	2.7	9.0
Mean		49.6	−3.7	−1.2	2.5	10.6
S.D.		16.5	1.5	0.7	1.3	8.7

determination of the water content of atmospheric PM are not available but highly desirable. Although the drying procedure and model calculations applied here for PM10 and PM2.5 samples cannot fill this analytical gap, they are useful approaches for estimating the water content of PM samples. However, the drying procedure should be repeated for a larger number of samples, in order to evaluate opportunities and limitations in more detail.

Acknowledgements

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