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Time study of trace elements and major ions during two cloud events at the Mt. Brocken

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Abstract

Cloud water investigations have been performed at the highest elevation of Central Germany in 1997. Results of extensive trace element measurements are presented. Besides conductivity, pH, liquid water content and major ions the data set includes 49 minor and trace elements. Estimation of crustal enrichment factors (EFs) provides an indication of the anthropogenic contributions to the cloud water concentrations. The variation of cloud composition with time has been illustrated for two selected events with different air mass origins. The chemical composition of the cloud condensation nuclei on which the droplets grow mainly determines the cloud water chemistry. For a cloud event in June 1997 the concentrations of the crustally derived elements Si, Al, Fe, Ti, Ce, La and Nd follow each other closely. The fact that SO_4^{2-} , NO_3^- and NH_4^+ are only moderately correlated with the particular pollutants with high enrichment factors such as Cd, Sb, Pb, Zn, Cu, As, Bi, Sn, Mo, Ni, Tl and V indicates that their source regions are more widespread. During an event in October 1997 the time trends for most minor and trace elements follow rather closely those for the major ions NH_4^+ , SO_4^{2-} and NO_3^- . Back trajectories show that the transport from continental and marine European sources was the likely cause of the sample concentrations. EFs of trace elements in cloud water samples during the June and October event show a strong correlation with those obtained for urban particulate matter. Although both events are influenced by air masses of different origin, there is a good agreement between the EF signatures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Time trends; Multi-element analysis; Cloud water; Back trajectories; Enrichment factors

1. Introduction

Studies on the budget of atmospheric trace elements and major ions include research on sources, transport mechanisms and sinks. The concentrations of organic and inorganic air pollutants are highly variable, depending on the sampling site (e.g. Clarke et al., 1984; Maenhaut et al., 1989; Harrison and Jones, 1995). Low concentrations are found in remote areas, whereas the highest concentrations are observed in industrialized and densely populated areas. Natural and anthropogenic emissions originate from a multitude of different sources.

Released into the atmosphere they undergo various transport processes and chemical reactions. Before aerosol particles are removed by precipitation, they are subjected to repeated wetting and drying cycles during cloud formation and evaporation. Cloud processing affects the chemical and physical properties of the aerosol.

During the last decades many cloud investigations have been made to understand the complex multiphase systems in clouds and fogs (e.g. Saxena and Lin, 1990 with a review of former investigations; Fuzzi et al., 1992; Baltensperger et al., 1998; Collett et al., 1999; Bower et al., 1999). Little information is available on concentrations of trace elements in cloud water (e.g. Munger et al., 1983; Lammel and Metzger, 1991; Noone et al., 1992; Burkhard et al., 1992; Chérif et al., 1998). Trace elements in the atmosphere are generally derived from the combustion of

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fossil fuel, along with industrial high temperature processes and from traffic. They are bound in accumulation mode aerosols and can be regarded as long range pollutants (e.g. Rahn and Lowenthal, 1984). Their use as tracers for transport of air pollutants requires an accurate determination of the atmospheric concentrations. The surface of particles containing trace elements is highly soluble, particularly at the acidity levels common in hydrometeores (Winkler et al., 1991). In terms of the chemistry that can occur within atmospheric liquid phase, transition metals may be important as possible catalysts for redox processes (e.g. Welscher et al., 1986; Sedlak et al., 1997).

We provide basic data of inorganic constituents in clouds at a remote mountain site in Central Germany. The variation of cloud composition with time has been illustrated for trace elements and major ions during two events and shows the chemical evolution of aerosol particles during interaction with the liquid phase. The origin of the air masses is calculated by back trajectories for both events. This information will be useful for model evaluation like receptor models and chemical mass balances and for the further identification of aerosol sources and transport mechanisms by clouds. In a first approach, the element concentrations in cloud water are compared with a mean urban aerosol composition (literature data) by using enrichment factors. Urban particulate matter can be regarded as a mixture from various sources of anthropogenic emissions. Therefore, its composition represents a main source for atmospheric concentrations of trace elements.

2. Experimental

2.1. Site description, sampling and meteorological situation

Cloud investigations have been performed at Mt. Brocken/Harz (51.80°N, 10.67°E, 1142 m a.s.l.), the highest elevation of Central Germany. Mt. Brocken has a high frequency of cloud events (30–50% of time in the period from April to October) due to its exposed location. The wind field at the station is dominated by low tropospheric winds from west/southwest. The German Weather Service runs a meteorological station at Mt. Brocken. Routine measurements of cloud parameters and collection of cloud water have been taken since 1991 by the BTU group. For hourly sampling of cloud water a passive string collector (ARSC-Type, Mohnen and Kadlecik, 1989), installed within an automatic wet-only sampling unit, is used at this site. The liquid water content (LWC) of clouds is measured continuously using a particulate volume monitor (Gerber PVM 100). Detailed description of the sampling site and the measurement program is given by Möller et al. (1996) and Acker

et al. (1998). Sixty hourly averaged cloud water samples were collected from eight nonprecipitating cloud events (duration 2–11 h) in May and June 1997 and from one cloud event (duration 16 h) in October 1997 for the determination of element concentrations.

Two longer lasted events (01/02 June 97 and 20 October 97) were chosen to show variations in element concentrations within one event and between events with different air mass origins. The air mass origin for each event is classified using 72 h back trajectories in 5 h intervals starting at 900 hPa station level (see Fig. 1a and b). The transport analysis is based on an isentropic (3D-) model (Reimer and Scherer, 1992; Naumann, 1997). On 01/02 June a high-pressure system over Island determined the weather. With strong NE–E winds, cold continental air masses were advected. The air mass origin was in Middle-Sweden near the Baltic Sea coast. Cloud water samples were taken for 10 h from 1 June 19:00 Central European time (CET) to 2 June 5:00 CET. The observed cumulus cloud had a mean cloud base height of 1060 m a.s.l. in the middle of the event. On 20 October 1997 cloud water was collected from a 16 h lasting cloud event. A weak cold front passed Germany in southerly directions, the daily mean temperature dropped from 9.9 to 0.4°C. Most of the sampling time the cloud base of the observed stratus clouds laid 200 m below the Mt. Brocken summit. Air masses originated from the northern part of Switzerland and in the further course of the event from the Saarland at the French/German border. Cloud water sampling started at 01:00 CET and ended at 17:00 CET. A slight drizzle occurred from 08:00 to 13:00 CET.

2.2. Analysis of cloud water samples

The samples were divided into two aliquots immediately after collection. One sample aliquot was filtered through 0.2 µm (one-way) filters (FP 30/30 Schleicher and Schüll). The other sample aliquot was stabilized for trace element determination with high-purity nitric acid from sub-boiling distillation (2% v/v HNO₃). All samples were stored in polyethylene bottles at 4°C in a refrigerator and measured within two weeks after preparation. The filtered samples were analyzed by the BTU for major ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺) by ionchromatography (SYKAM), for pH (WTW pH196) and conductivity (WTW LF96). The acidified samples were analyzed by the Göttingen group for trace elements. To dissolve silicon and other non water-soluble cations suprapur hydrofluoric acid was added (0.1% v/v HF). The samples were treated in an ultrasonic bath for 30 min. Hydrofluoric acid is a suitable solvent for many metal ions due to the formation of fluoro complexes. After ultrasonic treatment, four samples from May 97 showed visible residues of soot carbon. Only these samples were filtered through 0.45 µm

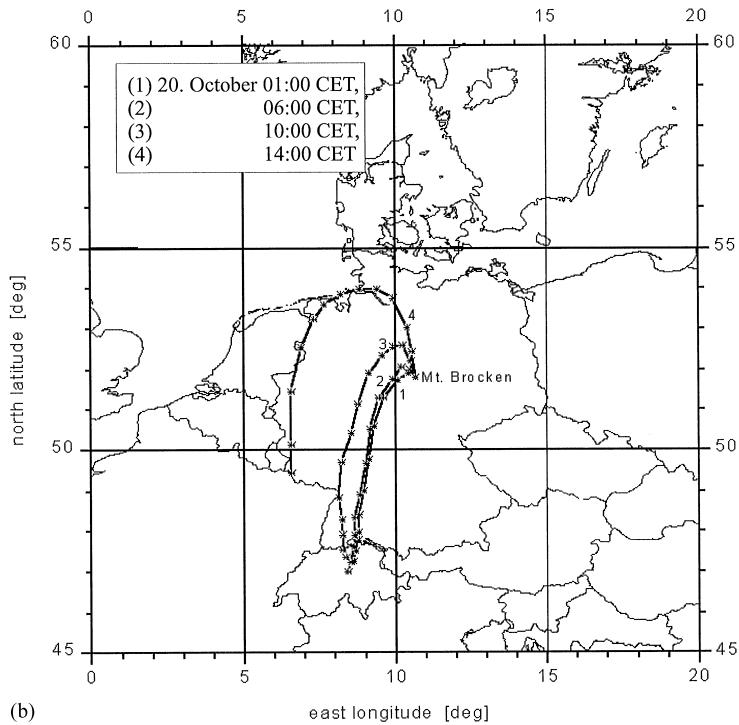
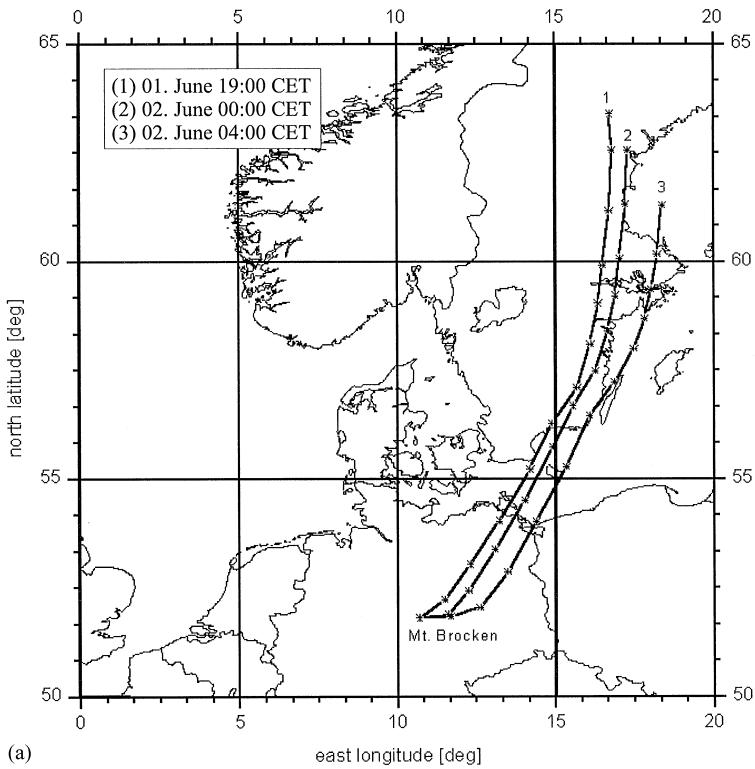


Fig. 1. 72-h back trajectories calculated for the air masses at 900 hPa for the two periods in (a) June 1997 and (b) October 1997.

Table 1
Mean chemical composition of Mt. Brocken cloud water samples and crustal enrichment factors for particular elements

	Min-max	Median	Min-max	Median	EF(Al) median
pH	3.4–6.8	4.3			
Conductivity ($\mu\text{S}/\text{cm}$)	19.3–316	65.0			
LWC (mg/m^3)	63–1011	548			
SMI (meq/l)	0.097–4.042	0.588			
<i>Major species</i>	$[\mu\text{g}/\text{l}]$	$\mu\text{g}/\text{l}$	$[\text{ng}/\text{m}^3]$	$[\text{ng}/\text{m}^3]$	EF (Al) median
C ^a	1390–10,910	2340	590–3860	1780	
NO ₃	1730–99,100	7550	360–35,080	4490	
NH ₄	380–29,500	3580	245–10,440	1655	
Na	70–6220	535	17–1560	255	16
Mg	< 5–740	115	< 3–300	55	5
Al	9–15,500	85	7–5870	45	1
Si	316–35,220	700	125–13,350	360	2
P	< 5–580	30	< 3–220	10	33
SO ₄	1230–28,110	6020	560–13,910	3220	
Cl	40–10,450	640	10–2720	335	
K	< 5–800	80	< 3–340	40	2
Ca	10–7310	385	9–2770	195	11
Ti	< 1–466	2.3	< 0.2–177	1.3	< 1
Mn	1.0–158	7.8	0.8–60.0	4.0	13
Fe	29–10,430	134	21–3950	63	4
<i>Trace elements</i>					
Li	< 0.05–3.6	0.08	< 0.03–1.4	0.04	4
Be	< 0.05–0.18	< 0.05	< 0.03–0.07	< 0.03	
V	0.4–15.0	1.8	0.11–5.3	0.84	34
Cr	< 0.3–9.0	< 0.3	< 0.2–3.4	< 0.2	
Co	< 0.02–2.1	0.08	< 0.01–0.81	0.04	6
Ni	0.2–11.4	1.0	0.10–4.3	0.51	51
Cu	0.5–173	5.7	0.42–60.6	3.18	390
Zn	3.1–910	37.2	2.5–421	20.5	580
Ga	< 0.05–1.3	< 0.05	< 0.03–0.5	< 0.03	
Ge	< 0.1–0.3	< 0.1	< 0.08–0.2	< 0.08	
As	0.1–6.6	0.4	0.04–4.4	0.24	220
Rb	< 1–6	< 1	< 0.7–2.3	< 0.7	
Sr	0.1–68.7	2.3	0.10–26.0	1.09	6
Y	< 0.03–1.8	0.04	< 0.02–0.7	0.02	1
Zr	< 0.05–3.4	0.07	0.03–1.3	0.03	< 1
Nb	< 0.03–1.8	< 0.03	< 0.01–0.6	< 0.01	
Mo	0.05–2.0	0.28	0.03–1.1	0.14	180
Cd	0.02–5.5	0.28	0.01–2.5	< 0.16	2400
Sn	0.07–3.0	0.37	0.04–1.4	0.20	180
Sb	0.09–3.9	0.36	0.04–1.5	0.18	1200
Cs	< 0.05–1.0	0.08	< 0.03–0.2	0.04	12
Ba	0.4–125	3.2	0.3–47.6	1.6	4
La	< 0.03–2.57	0.05	< 0.02–0.98	0.03	1
Ce	< 0.03–6.26	0.08	< 0.02–2.37	0.03	< 1
Pr	< 0.02–0.82	< 0.02	< 0.01–0.31	< 0.01	
Nd	< 0.02–3.26	0.05	< 0.01–1.24	0.02	1
Sm	< 0.03–0.52	< 0.03	< 0.02–0.26	< 0.02	
Eu	< 0.02–0.14	< 0.02	< 0.01–0.05	< 0.01	
Gd	< 0.03–0.69	< 0.03	< 0.02–0.20	< 0.02	
Tb	< 0.02–0.08	< 0.02	< 0.01–0.03	< 0.01	
Dy	< 0.02–0.44	< 0.02	< 0.01–0.16	< 0.01	
Ho	< 0.02–0.08	< 0.02	< 0.01–0.03	< 0.01	

Table 1 (continued)

	Min-max	Median	Min-max	Median	EF(Al) median
Er	< 0.02–0.22	< 0.02	< 0.01–0.08	< 0.01	
Tm	< 0.02–0.03	< 0.02	< 0.01–0.01	< 0.01	
Yb	< 0.02–0.19	< 0.02	< 0.01–0.07	< 0.01	
Lu	< 0.02–0.52	< 0.02	< 0.01–0.01	< 0.01	
Hf	< 0.02–0.19	< 0.02	< 0.01–0.07	< 0.01	
Ti	< 0.02–0.52	0.04	< 0.01–0.13	0.03	49
Pb	1.97–84.0	11.0	0.82–42.8	6.51	770
Bi	< 0.02–0.28	0.03	< 0.01–0.11	0.01	220
Th	< 0.04–0.52	< 0.04	< 0.02–0.20	< 0.02	
U	< 0.02–0.26	< 0.01	< 0.10–0.10	< 0.01	

^aDetermined for $n = 16$ cloud water samples.

one-way filters (Sartorius Minisart-RC 450). All samples were analyzed in duplicate by ICPMS (Fisons VG PQ 2 Plus) for Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Pb, Bi, Th and U and by ICPOES (Perkin-Elmer Optima 3300 DV) for Al, Si, P, Ti, Mn, Fe, Sr and Ba. Detailed instrument operating conditions are described in Rocholl et al. (1997) and Hinnert et al. (1998) for ICPMS and in Boss and Fredeen (1997) for ICPOES. For the determination of carbon aliquots of cloud water (10–15 ml of the sample) were evaporated to dryness at 80°C, oxidized to CO₂ and measured by infrared detection in a carbon analyzer (Eltra Methalyt CS 100/100 RF) against international standard reference materials (EGKS-CECA-ECSC 286-1/484-1). The fraction of carbonate C in cloud water samples is less significant. Volatile organic C was lost by sample preparation due to evaporation to dryness at 80°C. So we assume that a considerable amount of the measured carbon is black carbon.

The quality of the ICPMS and ICPOES data has been judged against the analysis of one standard reference water (NRC-SLRS-3) and three international standard reference materials (GSJ-JB-3, GSJ-JLK-1, NIST-SRM-1648). The acid digestions of the standard reference materials were adjusted to the different concentration ranges by dilution, because of the lack of elements for which the international standard reference water has been certified. On the basis of multiple analyses the accuracy of the determinations is judged better than $\pm 5\%$ for Sr, Ba, Mn, Fe, Sn, Sb, La, Gd, Tb, Yb, Tl and Pb; $\pm 10\%$ for Li, Co, Ni, Zn, Ga, Rb, Zr, Mo, Cs, Ce, Pr, Nd, Sm, Eu, Dy, Ho, Er, Hf and U; $\pm 15\%$ for Al, Si, Ti, Cu, As, Tm and Lu; $\pm 20\%$ for Be, V, Y, Nb, Cd and Bi; $\pm 25\%$ for P, Cr, Ge and Th. But the minimal concentrations of many elements in the cloud water samples such as Li, Be, Mg, P, K, Ti, Cr, Ga, Ge, Rb, Y, Zr, Nb, Cs, La, lanthanoids, Hf, Tl, Bi, Th and U were below the determination limit (Table 1).

3. Results and discussion

3.1. Mt. Brocken: cloud water concentrations

Mass transfer processes into the liquid phase are a function of supersaturation and duration of exposure to high ambient humidity, acidity as well as of chemical composition of the particles. Particularly the size and solubility of a particle determine its effectiveness as cloud condensation nucleus (CCN) (e.g. Svenningsson et al., 1994; Spokes et al., 1994). The data presented here yield concentrations for elements dissolved or suspended in the cloud droplets. The concentrations of the major ions refer to the dissolved fraction. Studies on the soluble and insoluble fractions in aerosols and in cloud waters indicate that the majority of particles forming cloud droplets were soluble (Hallberg et al., 1994; Krämer, 1993). About 90% of the anthropogenic elements' (Cd, Zn, Pb, Cu, Ni, As, Sb, Se) total contents were soluble in cloud water and wet precipitation as determined by Pattenden et al. (1982); Winkler et al. (1991); Dutkiewicz et al. (1996). Aerosols from anthropogenic and marine sources contribute more soluble particles than crustal emissions. It can be deduced from this findings that the species determined here are mainly present in the dissolved form. However, most likely a high amount of the crustally derived elements (Si, Al, Ti, Fe, Ga, Y, Zr, Nb, lanthanoids, Th, U) and elemental carbon is insoluble.

Table 1 lists range and median values for pH, conductivity, sum of major ions (SMI), liquid water content (LWC) and inorganic constituents from 60 hourly averaged cloud water samples. Species concentrations are expressed as $\mu\text{g l}^{-1}$ and as ng m^{-3} air volume. The normalization to air concentrations was done by multiplying the concentrations for major ions and trace elements of the individual sample by the LWC observed during the hour of sampling. SMI is the sum of the equivalent liquid-phase concentrations of Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} as major ions

without hydrogen ions. The cloud water composition is dominated by ammonium, sulfate and nitrate. On average, contributions of these ions to SMI run up to 86% for all samples. This is consistent with prior studies at the Mt. Brocken (Acker et al., 1998). Calculation of the ion balances for the major solutes and comparison of measured and computed conductivity indicate that no major ion is missing in the analysis.

Median concentrations of $C > Si > Fe > Al$ and P as major components are ranging between 2340 and $30 \mu\text{g l}^{-1}$. Zn and Pb are the most prominent trace metals with median concentrations of 37 and $11 \mu\text{g l}^{-1}$, respectively. The median concentrations of $Mn > Cu > Ba > Ti = Sr > V > Ni$ occur in a narrow range from 7.8 to $1 \mu\text{g l}^{-1}$. The elements $Li, Be, Cr, Co, Ga, Ge, As, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Bi, Th$ and U are characterized by being found in relatively low median concentrations of $< 1 \mu\text{g l}^{-1}$. The minimal concentrations of several elements are presented as “less than” values, which also show the weakness of our current knowledge. Maximum concentration variations over the sampling duration are found for $Y > Zr > \text{lanthanoids} > Be > H > Al > Cr > U > Ti > Cs > Sr > Fe$, etc., which are mainly elements of crustal origin. Particles with crustal-like composition have their mass predominantly in the coarse mode and have short residence times. Thus, their atmospheric concentrations range widely in space and time.

The data material for trace element concentrations in cloud water is limited. With the data available, the median values of elements, given in Table 1, are similar to those reported in previous studies. Burkhard et al. (1992) and Noone et al. (1992) analyzed some lower concentrations for Fe, Mn, Zn, Cu, Sb at Whiteface Mountain, US and in the Po Valley, respectively. Higher trace element concentrations are reported of course for urban areas such as Los Angeles, US and Strasbourg, France (Munger et al., 1983; Chérif et al., 1998) or for sampling sites (Black Forest/Germany, Vosges Mtn./France) which were more influenced by industrialized regions during the observed events (Lammel and Metzger, 1991). The Mt. Brocken cloud water chemistry shows a considerable variation which is reflected by larger ranges of species concentrations than in the above-mentioned studies. This could be due to the relative high number of determined events on a hour-to-hour basis.

3.2. Crustal enrichment factors $EF(Al)$

A substantial fraction of the atmospheric aerosol is entrained soil dust, which is expected to have a composition similar to that of average rock dust from the earth's upper continental crust. One way of interpreting concentrations of elements in atmospheric samples is to use enrichment factors as the result of a double

normalization technique (Zoller et al., 1974; Rahn, 1976). The ratio of a given element X to a reference element in the sample is compared to the same ratio for average upper continental crust: $EF = (X/RefEl)_{\text{sample}} / (X/RefEl)_{\text{crust}}$. Hence, the metal concentrations are corrected to the average aluminosilicate fractions in the atmospheric particulates. The composition of the upper continental crust is given by Wedepohl (1995), Al is used as geogenic reference element.

Table 1 (right side) shows the median of crustal enrichment factors for particular elements which are undergoing aerosol scavenging mainly. The results document that $Co, Sr, Mg, Ba, Fe, Li, Si, K, Y, La, Nd, Al, Ti, Zr$ and Ce would be attributed to direct mechanical transfer of crustal materials into the atmosphere with $EF(Al)$ values close to unity ($7 \leq 1$). Ni, Tl, V, P, Na, Mn, Cs and Ca take an intermediate position ranging from 51 to 11. Enrichment factors for many elements are far in excess of unity. $Cd, Sb, Pb, Zn, Cu, As, Bi, Mo$ and Sn are highly enriched ($EF(Al) = 2400\text{--}180$). These volatile elements are generally derived from high-temperature processes such as fossil fuel combustion and motor vehicle exhaust. The enrichment factor for metals is related to the boiling point of the metal species, which are preferentially associated with particle surfaces as a result of condensation from the vapor phase (Natusch et al., 1974). Some elements also play an important role as wear metals. Zn of tire dust contributes significantly to the urban particulate matter. Finest brake-lining dust is definitely accompanied by Cu, Sb and Mo (Polasek and Jervis, 1994; Heinrichs and Brumsack, 1997a). A sizeable fraction of the so-called crustal component may be actually of anthropogenic origin and cannot be attributed to direct mechanical transfer of crustal materials. Fly ashes derived from high-temperature processes often consist of crystalline and amorphous mineral phases with relatively high contents of alkaline earth and alkali oxides (e.g. Heinrichs et al., 1997b; Lee and Pacyna, 1999).

3.3. Time studies of Mt. Brocken cloud chemistry

The initial cloud water composition is determined by the composition of the activated aerosol particles and by soluble gases such as NH_3, SO_2 and HNO_3 dissolving into the droplets. Moreover, the LWC plays an important role in controlling the concentrations of bulk cloud water samples. It can be verified by field measurements (not shown here), that a change of the cloud base height relatively to the sampling position is connected with a change in the droplet size distribution of the clouds. For most cloud types the increase of LWC with altitude above cloud base follows approximately a linear function (adiabatic conditions), only disturbed near cloud base and cloud top (Möller et al., 1996, 1997).

Temporal variability of liquid water content (LWC), conductivity, pH and sum of major ions (SMI) during the

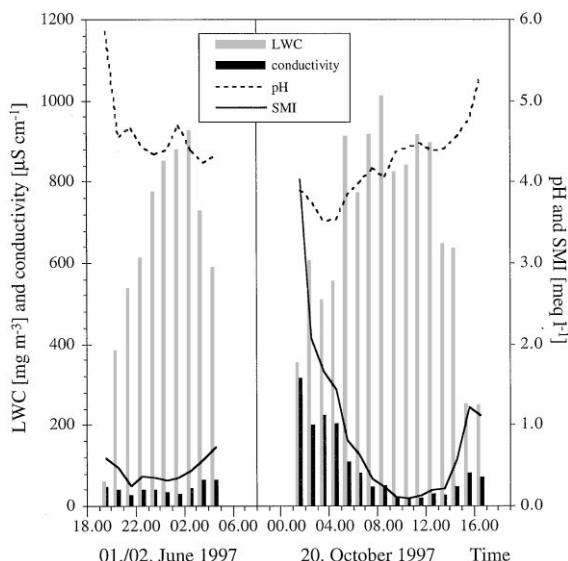


Fig. 2. Liquid water content (LWC), conductivity, pH and sum of major ions (SMI) during specific cloud events.

two investigated cloud events are summarized in Fig. 2. The mean SMI of about 0.6 meq l^{-1} for both events is typical for a medium pollutant loading. The June event was characterized by low fluctuations of the SMI in a 3-fold range while the LWC varied in a 15-fold range (Fig. 2, left side). The steep increase of the LWC from the first to the second hourly sample can be deduced from a decrease of the cloud base level, the station is more inside the cloud. The pH decreased rapidly from high initial 5.9 in the first hourly sample to values between 4.6 and 4.3 during the further course of event. During the October event (Fig. 2, right side) SMI and LWC varied in a wide range and are being inversely correlated with each other. The ionic content decreased from initially 4.0 meq l^{-1} to minimum values around 10:00 CET. In the same time the LWC increased from relatively high initial values (345 mg m^{-3}) to maximum values (around 1000 mg m^{-3}). Subsequently the SMI rose by decreasing LWC. The pH increased from 3.9 at the beginning to 5.3 at the end. For both events the signatures of conductivity reflect the SMI. At lower cloud water pH the hydrogen ions would have the most determining influence on the conductivity. The strong acid species, H_2SO_4 and HNO_3 , have a predominantly anthropogenic origin. During these events the sum of $[\text{NH}_4^+]$ plus $[\text{H}^+]$ counterbalanced the strong acid's anions $[\text{NO}_3^-]$ plus $[\text{SO}_4^{2-}]$ and had an equivalent ratio close to unity.

In order to understand the sample to sample variation within an individual cloud event and for comparisons of samples of different cloud events any variations on LWC were removed by normalizing to air concentration. This was done by multiplying the element concentrations by

the LWC as described above. Fig. 3a–f depicts the temporal variations in cloud water concentrations, given as nmol m^{-3} air volume, of up to 32 selected species during the events of June and October. Trace elements and major ions with similar patterns are grouped to improve the understanding. In Fig. 3a–d time trends of trace elements are compared with the time trend of SO_4 . Studies of cloud scavenging use SO_4 (e.g. Dutkiewicz et al., 1996) which is almost entirely bound in the accumulation mode and has vapour pressure properties which enable it to be the particle-bound substance with the maximum of residence time (Seinfeld and Pandis, 1998).

For the *June event* the main feature was the steep increase of all concentrations from the first to the second hourly sample (Fig. 3a–f, left side). The first sample was collected at cloud base level, where entrainment processes (droplet evaporation by mixing with sub-saturated air, aerosol and gas scavenging) occur. Subsequently, the general trend for NH_4^+ , SO_4^{2-} , Ca, K (Fig. 3a, left side), As, Bi (Fig. 3b, left side), Pb, Tl (Fig. 3c, left side), NO_3^- , Sb, Sn (Fig. 3d, left side) and Mg (Fig. 3e, left side) became less steep and indicated irregularly rising concentrations with time. Apart from the steep increase of the first to the second hourly sample the concentrations of the other analyzed elements did not show a clear upward or downward trend. The fact that SO_4 , NO_3 and NH_4 are only moderately correlated with the particular pollutants of high enrichment factors such as Cd, Sb, Pb, Zn, Cu, As, Bi, Sn, Mo, Ni, Tl and V indicates that their source regions are more wide spread. The time trends for Na and Cl illustrate the variability in the sea-salt component of the cloud water. Mg originates from the same sea-salt component too, but additionally from continental source regions. Si, Al, Fe and Ti are typical marker elements for soil dust. At the beginning, their contribution to the total mass load was about 33% but over the entire event their average sum accounted for only 11%. This is in correspondence to the high initial pH of 5.9 (Fig. 2, left side). Particles of crustal origin partly consist of basic compounds which may increase the pH of the sample. A substantial fraction of entrained soil dust might be advected by local or regional sources. As expected, the time trends of the crustally derived elements Si, Al, Fe, Ti, Ce, La and Nd follow each other closely (Fig. 3f, left side).

During the *October event* the time trends for Ca, K, Mn, Sr and Ba follow rather closely that of NH_4 and SO_4 (Fig. 3a, right side). Cd, Sb, Pb, Zn, Cu, As, Bi, Sn, Mo, Ni, Tl and V are used to indicate the variation in the pollution component. Like SO_4 , NO_3 and NH_4 are these elements clearly of anthropogenic origin (Fig. 3b–d, right side). During the first 7 h content of many suspended trace elements and soluted major ions showed downward trends (Fig. 3a–f). Very high depletions of more than 95% were observed for NH_4 , NO_3 , Ca, Sr (Fig. 3a, right side) and Tl (Fig. 3c, right side) whereas

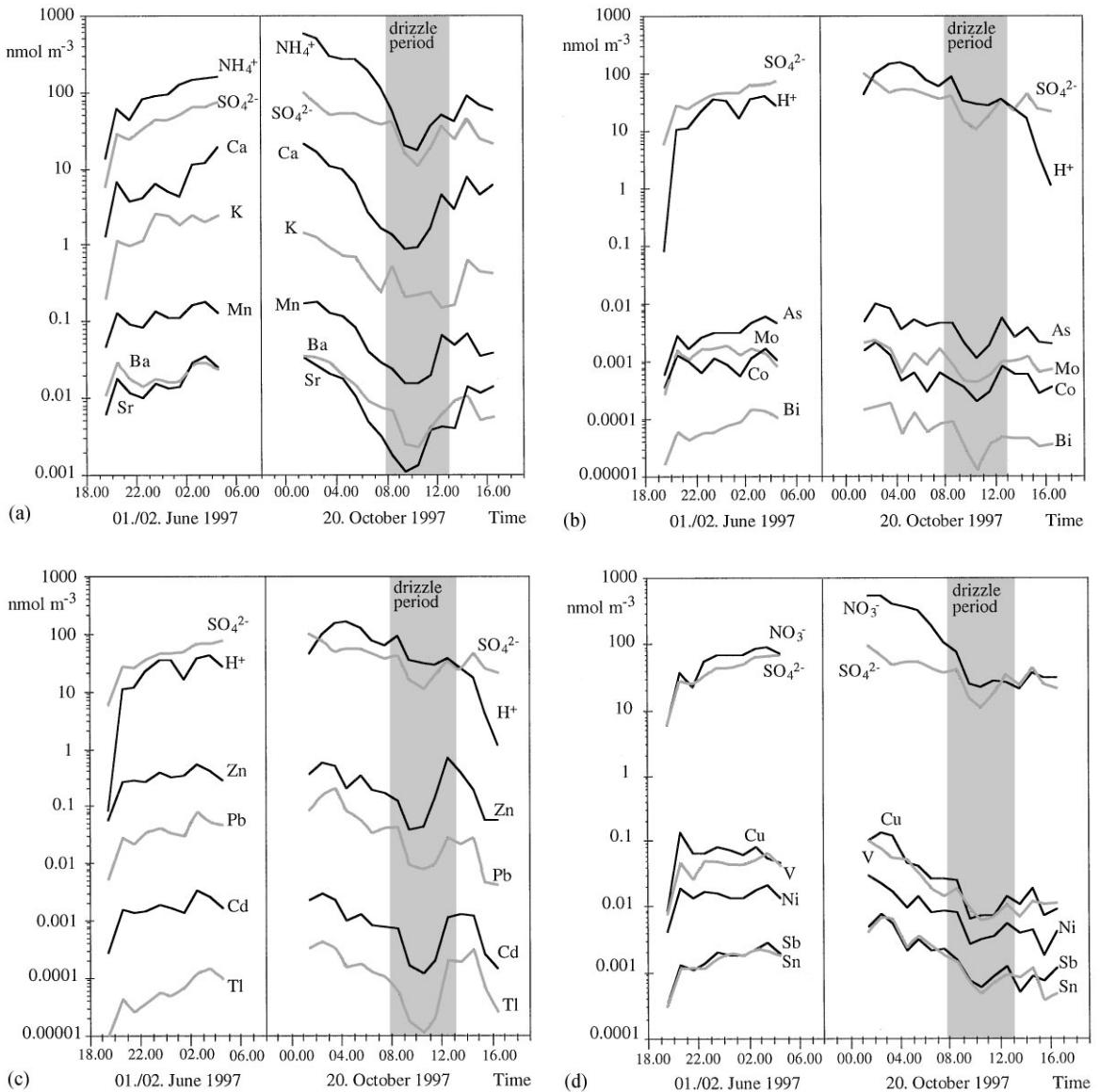


Fig. 3. (a) Time trends for NH_4^+ , SO_4^{2-} , Ca, K, Mn, Ba and Sr during two cloud events; (b) time trends for SO_4^{2-} , H^+ , As, Mo, Co and Bi during two cloud events; (c) time trends for SO_4^{2-} , H^+ , Zn, Pb, Cd and Tl during two cloud events; (d) time trends for NO_3^- , SO_4^{2-} , Cu, V, Ni, Sb and Sn during two cloud events; (e) Time trends for Na, Cl, and Mg during two cloud events; (f) Time trends for C, Si, Fe, Al, Ti, Ce, La and Nd during two cloud events.

concentrations of Si, C and also Cl (Fig. 3e and f, right side) showed a relatively slight decrease of 72–52%. Minimum air concentrations as well as minimum SMI-values (Fig. 2, right side) coincided with a drizzle period observed from 08:00 to 13:00 CET. This leads to the suggestion that droplet sedimentation contributes in part to the depletion of solute mass load. Fog and cloud events at mountain sites are frequently accompanied by light precipitation in the form of drizzle or snow. Such a drizzle

period occurred at Mt. Brocken during the October event. Altogether one mm precipitation was deposited at the site during the whole day.

After this episode a change in the air mass origin is observed (Fig. 1b). The contributions of NH_4^+ , NO_3^- and SO_4^{2-} to the SMI decrease from 94% at the onset to 50% for the last 2 h of the event. Conversely, the contributions of Cl, Na and Mg to the SMI rise up to 50% for the last 2 h. The equimolar increases of Cl, Na and Mg (Fig. 3e,

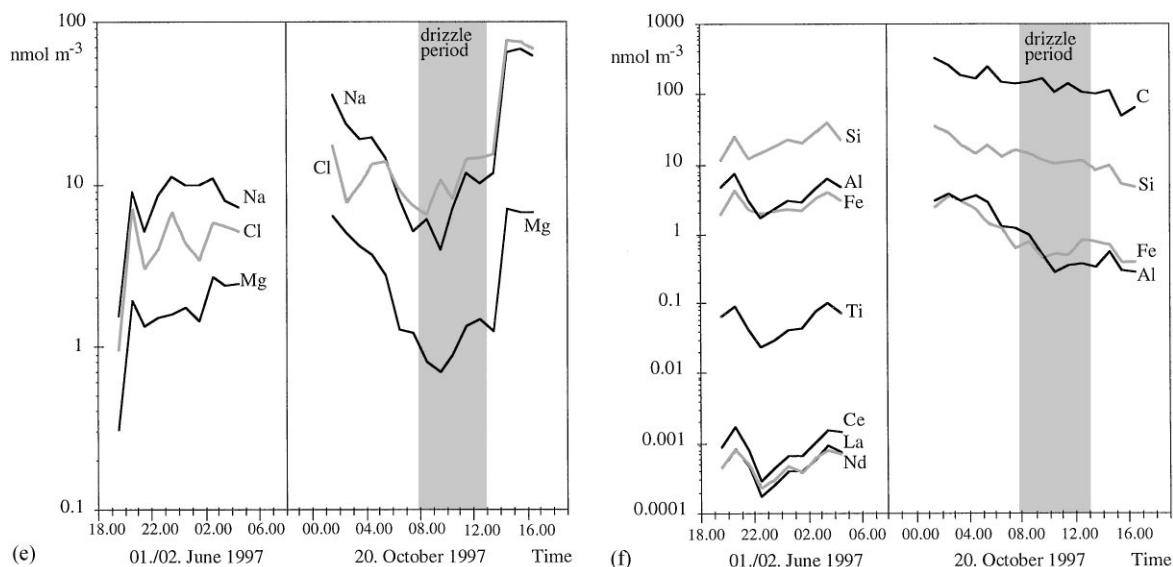


Fig. 3. (continued).

right side) indicate the advection of air of marine origin at the site. As expected, the air masses are transported along the North Sea coastline towards the end of the cloud event (trajectory 4 in Fig. 1b). For most species now little temporal variations in the liquid phase of the cloud are observed. Only Zn, Pb, Cd and Tl (Fig. 3c, right side) exhibit a pronounced decrease of concentration at the end of the cloud event (15:00–17:00 CET). The pH, known to be a main factor controlling the solubility of metals, climbs to values of 5.3 in this time interval. Therefore, this behavior might be due to lower acidity. The cloud water concentrations of carbon and silicon show a systematic downward trend without the distinct depletion observed for other species (Fig. 3f). A possible explanation could be different mechanisms in scavenging and cloud processing between primary (C, Si) and other pollutants as for instance secondary aerosols (NH_4 , SO_4). The pattern of crustal elements such as Fe and Al is similar to that of C and Si (Fig. 3f, right side), deviations only exist during the drizzle period.

3.4. Comparison with urban particulates on the basis of enrichment factors

Urban aerosols are extremely complex mixtures of gaseous and particulate components. The latter comprise motor vehicle emissions, abrasion of tires and brake linings, paved road dust, abrasion of buildings, fly ashes from coal, lignite and oil combustion, refuse incineration, cement and steel production and further dust from crustal weathering, sea spray and plant detritus. The composition of urban aerosols represents a main source for atmospheric concentrations of trace elements. The calculation of a mean composition of urban particulate

Table 2

Mean concentrations in urban particulates (calculation from prior German studies as cited in the text)

Element	mg/kg
Na	9000
Mg	6800
Al	16500
Si	52000
K	9000
Ca	47000
Ti	810
V	150
Mn	800
Fe	20000
Co	17
Ni	90
Cu	800
Zn	4800
As	60
Sr	240
Mo	19
Cd	27
Sn	64
Sb	74
Ba	700
La	10
Tl	3
Pb	1800
Bi	6

matter is a result from several aerosol and dry precipitation sampling campaigns in 25 German cities and conurbations (e.g. Berlin, Frankfurt, Ruhrgebiet, Hamburg among others) during 1986 and 1994. Contributions

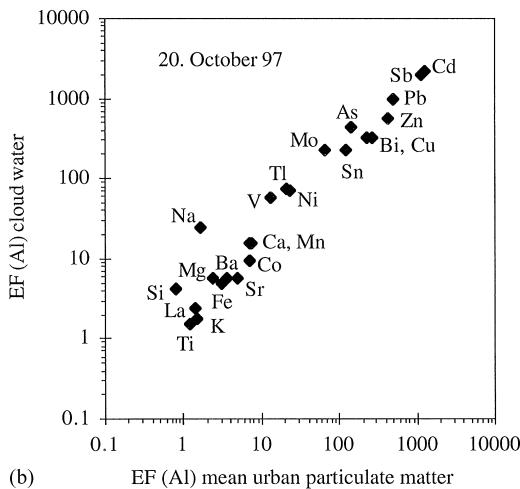
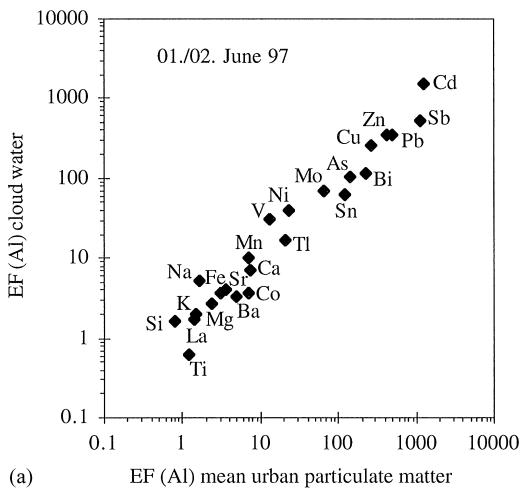


Fig. 4. Crustal enrichment factors of particular elements in cloud water from (a) June and (b) October compared with those for urban particulate matter.

originate from the following German studies: Dannecker et al. (1986), Krivan and Egger (1986), Rachold et al. (1992), Heinrichs (1993), Heinrichs and Brumsack (1997a,b). Table 2 lists the calculated values for the most relevant elements.

Crustal enrichment factors of particular elements in cloud water samples during the two investigated events show a strong correlation with those obtained for urban particulates (Fig. 4a and b). The chemical composition of particulate matter is at any time and location a product of its sources, depending on the different particle size distributions of the volatile and non-volatile elements and the chemical changes due to fractionation and gas-phase reactions. The general increase from non-volatile to volatile elements is evident. Not surprisingly, the

volatile elements (Table 1, right side) are the most enriched elements in cloud water and in urban aerosols. Although both events are influenced by air masses of different origin, there are only little differences between the EF signatures. This fact suggests the existence of a widespread anthropogenic aerosol component with a remarkably similar trace element composition. Elements of high enrichment factors (Cd, Sb, Pb, Zn, Cu, As, Bi, Sn, Mo, Ni, Tl, V) are preferably bound on accumulation mode particles. Due to their long residence time a good partitioning is possible. Before reaching Mt. Brocken, air masses are transported over densely populated and industrialized European areas for several hundred km. On a broad basis the variety of anthropogenic emission sources which are located in any directions tend to lead to similar aerosol compositions in the accumulation range. According to our results Berg et al. (1994) estimated high enrichment factors for the same volatile elements in precipitation samples from Norway, Scandinavia and attributed these enrichments to the long-range transport from European sources.

4. Conclusions

The time trends for many elements illustrate the variability of various components, their divergent behavior and the heterogeneity of concentrations during a cloud water event. Different element patterns in part could be due to differences in sources, transport and incorporation into the cloud droplets. Back trajectories show that the transport from continental and marine European sources was the likely cause of the sample concentrations. Concentrations averaged over longer time-periods may not be representative for short-time periods, which are reflected by wide ranges of concentrations. Maximum concentration variations are found for elements of crustal origin. For single hourly samples the contribution of these elements to the total mass load climbs to about 33%.

The fact, that there is only a little divergence between the enrichment factor signatures in cloud water and urban particulates indicates the existence of a widespread anthropogenic aerosol component with a remarkably similar trace element composition. Furthermore, it shows that the chemical composition of the activated aerosol particles on which the droplets grow mainly determines the cloud water chemistry.

We have to keep in mind that the concentration data of this work are based on bulk sample collection. Mass transport processes in multiphase systems are a function of supersaturation as well as of chemical composition and particle size. Moreover, droplet size distribution may vary with time. The knowledge of all these conditions would allow a better understanding of the aerosol processing and transport by clouds.

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