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Chemical composition of fog and cloud water at the Erzgebirge summit, Germany

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Abstract

The Erzgebirge, part of the former "Black Triangle", was one of the most polluted forested areas in Central Europe. The local climate is characterized by above-average stable air stratification leading to an above-average amount of inversions with advection fog. "Acid fog" was thought to play an important role in the acidic deposition and in the forest decline on both sides of the Erzgebirge ridge (800 – 900 m a.s.l.). The last data on chemical composition and deposition of fog and cloud water were reported from the 1990's. This work delivers the current chemical composition of fog and cloud water from the region. Fog data are reported from two sites: (1) Zinnwald, 877 m a.s.l., eastern Erzgebirge, and (2) Fichtelberg, 1214 m a.s.l. Passive fog collectors were used. Electrical conductivity, pH-value, and the concentration of major ions and trace metals (Ba, Pb, Zn, Al, Mn, Ti, V, Ni, Cu, Sr, Cd, Sb, As, Cr) were determined.

1. Introduction

Several studies dealt with fogwater chemistry on global and local scales (Warneck 1991; Grasserbauer et al. 1994; Acker et al. 1995; Millet al. 1996; Acker et al. 1998; Collett et al. 1998; Collett and Pandis 1999; Bridges et al. 2001, Hoag et al. 2001; Bridgman et al. 2002; Marinoni et al. 2004). The key measurements related to pH, conductivity and ionic composition. Since the knowledge in this field seems to be "saturated", there where only a few studies within the last years. The environmental composition changed due to altered emission conditions in the meantime. Particularly high variations were reported for the Krusne Hory region situated in the former called "Black Triangle" by Ardo et al. (1997) and by Bridgman et al. (2002). Therefore new studies are justified to test if similar changes in fog composition can also be seen in the German part of the "Black Triangle", the Erzgebirge.

Based on newly collected data and in comparison with former studies we analysed the current chemical composition of fog water and discuss the development of the different components in the samples.

2. Sampling and Analysis

2.1 Sampling sites

Field samples were collected at two different sites: Zinnwald-Georgenfeld (ZIW) and Fichtelberg, Oberwiesental (FIB). These experimental sites are situated in the highland region of the Eastern and the Central Erzgebirge, respectively. The Fichtelberg, with 1,214.6 m a.s.l., is the highest elevation in Saxony. Due to its altitude, mountain and station are situated above the cloud base. This results in a high average fog frequency of 287 days (Zimmermann 2002, after Fojt 1970).
The experimental site Zinnwald-Georgenfeld lies at 877 m a.s.l.. The average annual air temperature is 4.3°C with a gradient of 18.1° K between July and January. The average annual precipitation reaches values up to 978 mm with a maximum in summer and a minimum in winter. This pattern reveals a continental-atlantic climate (Zimmermann 2002).

2.2 Cloud water collection and analysis

Passive string collectors were used (Zier, 1992). The samplers consist of two horizontal disks with a diameter of 20 cm, installed vertically and 40 cm apart. Nylon strings (diameter 0.2 mm) were stretched between these disks. Two samplers were used at Zinnwald-Georgenfeld (one for ion analysis and one for trace elements) and one at Fichtelberg (ion analysis). The samplers were only exposed if fog was visible for the operating staff of the weather station. The total yield of the passive collector was 40 samples for 40 different fog events between October and December 2009. The collection periods varied between 4 h 30 min and 48 h.

The samples were stored in precleaned 100 mL LDPE bottles. All samples were filtered in the laboratory prior to analysis (0.47 mm cellulose acetate for major ions and Nuclepore track-etched membrane filter for trace elements). A sample aliquot was used to determine pH and electric conductivity. Major inorganic ions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were quantified by ion chromatography with DIONEX DX 120 for anions and Metrohm Ion Chromatograph 690 for cations. Trace elements were measured by ICP-MS (Perkin Elmer Sciex ELAN 9000).
Quality control of the analytical data was performed by comparing calculated vs. measured conductivity and cation vs. anion balances for each sample.

2.3 Calculation of fog water content

The liquid water content (LWC) is one of the most important parameters determining the chemical composition of fog samples. Given the lack of direct measurements, we used a parameterization developed by Queck (2003) to estimate LWC. Based on the visible range measured with meteorological conditions, the LWC is calculated as follows:

VV>100 m: $LWC=35.91*VV^{-1,15}$ (1)

VV<100 m:

$$LWC=10^{-0,49*(\log(VV))^2+1,25*\log(VV)-1,25)} \quad (2)$$

with VV: measured visible range (in m) and LWC: liquid water content (in g/m³).

3. Results

3.1 Fog frequency

Time series of fog observation from weather stations in the Erzgebirge show a significant dependence of the number of fog events on altitude: the amount of fog increases with altitude (Figure 1). There were more fog hours on Fichtelberg (1,214 m a.s.l.) than on Zinnwald (877 m a.s.l.).

The observed fog frequency is comparable to long-term observations.

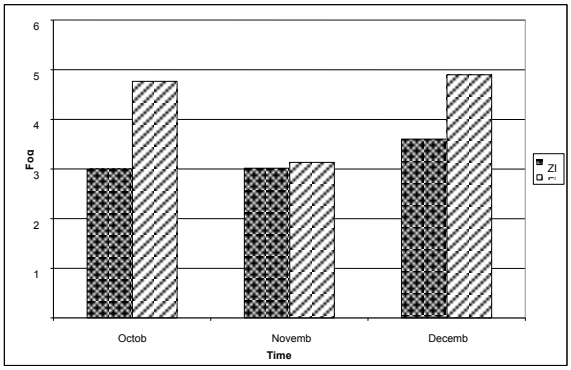

Figure 1: Distribution of fog hours at Zinnwald and Fichtelberg.

3.2 Liquid water content (LWC)

The calculated LWC for Zinnwald and Fichtelberg is presented in Table 1. Calculations are based on formula 1 and 2, respectively.

Table 1: LWC [g/m³] for Zinnwald and Fichtelberg

station	Mean value	Min	max
Fichtelberg	0,202	0,194	0,280
Zinnwald	0,204	0,035	0,323

These values are in good agreement with those mentioned by Pleßow et al. (2001) for Mt. Brocken, (475 – 625 mg/m³), a typical range for German low elevation mountains.

3.3 Composition of fog samples

The mean volume-weighted ionic concentrations of fog water samples are presented in Table 2.

The chemical composition of fog and cloud water differed considerably between the sites. Zinnwald still is polluted, influenced by the "Bohemian Fog" with high concentrations of sulphate, nitrate and ammonium, while Fichtelberg is much less influenced by air pollution. There, sodium and chloride dominated the composition. To discriminate between the marine and the non-marine origin of ions, the sea-salt and the non-sea-salt fraction was calculated for SO_4^{2-} and Ca^{2+} with Na^+ as a reference. The concentration of non-sea-salt sulphate (nss-SO_4^{2-}) was calculated by the formula:

$$[\text{nss-}SO_4^{2-}] = [SO_4^{2-}]_{total} - ([Na^+]*0,12). \quad (3)$$

Similarly the concentration for nss-Ca^{2+} was calculated from the ratio Ca^{2+}/Na^{+} using 0.038 as the multiplication factor (Kang et al. 2010). The large values at both sampling sites indicate a contribution from anthropogenic or crustal sources.

The minimum pH was 3.5 for Zinnwald and 3.7 for Fichtelberg (Table 2), both of phytotoxic relevance. At both sites ionic concentrations were much higher than in wet deposition: the maximum enrichment factors were observed for NO_3^- (42) at Zinnwald and for Cl^- (69) at Fichtelberg.

Table 2: Mean volume-weighted ionic concentrations in fog water at *ZIW* and *FiB* (µeq/L)

	Zinnwald	Fichtelberg
F^-	8	3
Cl	69	338
NO_2^-	1,34	1,68
NO_3^-	768	325
PO_4^{3-}	23	17
SO_4^{2-}	227	235
nss-SO_4^{2-}	218	191
ss-SO_4^{2-}	8	44
H^+	0,05	$9{,}57*10^{-5}$
Na^+	72	367
NH_4^+	347	310
K^+	13	27
Ca^{2+}	111	134
nss-Ca^{2+}	109	120
ss-Ca^{2+}	3	14
Mg^{2+}	19	91

Another aspect of our work relates to trace elements at Zinnwald. Ba, Pb, Zn, Al, Mn, Ti, V, Ni, Cu, Sr, Cd, Sb, As and Cr were detectable. The dominant species was Al (160 µg/L) followed by Zn (136 µg/L), Pb (77 µg/L) and Cu (71 µg/L). Aluminium is a marker for soil dust, while the other three elements rather indicate pollution by anthropogenic activity.

3.4 Composition development

In order to make statements about the evolution of individual components found in fog water we compared our measurements with data from Bridges et al. (2001). The results are presented in Table 3.

A clear trend could only be seen for SO_4^{2-}. The major reduction is related to decreasing sulphur emissions over the last years. The so called "Entschwefelungsanlagen" should be mentioned in this context. A related average decrease for NO_3^- was also expected, only a light decrease emerged at Fichtelberg while an increase was registered at Zinnwald (Table 3). A possible explanation is given by the hypothesis of the "new type of winter smog" (Brimblecombe 1996). Caused by low temperatures, measured during the sampling period, the normally unimportant reaction

$$2NO + O_2 \rightarrow 2NO_2 \qquad (R1)$$

can be a significant source of NO_2. Prerequisites are significant concentrations of NO which have risen considerably in line with increasing urban traffic in this region. Due to the low temperatures the rate constant for R1 increases as the temperatures falls resulting in higher production rates of NO_2. Because of the sensitivity of R1 to reactant concentration even small improvements in emission of NO (under new winter smog conditions) can yield great improvements in the NO_2 level.

Table 3: Comparison of ZIW and FIB data with those from Krusne Hory Plateau [µeq/L]

	Zinnwald	Fichtelberg	Krusne Hory Plateau
anions			
Cl^-	69	338	155
NO_3^-	768	325	726
SO_4^{2-}	227	235	625
cations			
Na^+	72	367	64
NH_4^+	347	310	203
K^+	13	27	19.4
Ca^{2+}	111	134	67.9
Mg^{2+}	19	91	20.2

Explaining the evolution of the other components is difficult because their behaviour differs significantly between the two sampling sites. One reason could be the different sample characteristic: at Zinnwald pure inversion fog was sampled while at Fichtelberg, sampling was interrupted by cloud occurrence and in this context by the composition of cloud water. To clearly explain the individual components and their

development, it is necessary to look at the sampling sites separately (not shown here).

4. Conclusion

The chemical composition of fog samples is reported from two sites: (1) Zinnwald, 877 m a.s.l., eastern Erzgebirge, and (2) Fichtelberg, 1214 m a.s.l. Fog frequency in the investigation period (10.2009 – 12.2009) was comparable to long-term observations. Modelled liquid water contents (LWC) were in the range of typical values for German low elevation mountains. Minimum pH values, 3.5 for Zinnwald and 3.7 for Fichtelberg, were still of phytotoxic relevance. The chemical composition of fog and cloud water differed considerably between the sites. Zinnwald still is a polluted site with high concentrations of sulphate, nitrate, ammonium and organic compounds, while Fichtelberg is much less influenced by air pollution. There, sodium and chloride dominated the composition. At Zinnwald, Al, Zn, Pb, and Cu showed the highest trace metal concentrations, while As, Ni, Cr, and Cd were also detected. Sulphate concentrations were lower than in 2001, while nitrate concentrations were higher than before. This is surprising in the light of decreasing NO_x emissions in Saxony and needs further investigations.

References

[1] Acker K, Möller D, Wieprecht W, Naumann S (1995) Mt. Brocken, a site for a cloud chemistry measurement programme in central Europe. Water, Air and Soil Pollution 85: 1979-1984.

[2] Acker K, Möller D, Wieprecht W, Kalaß D, Auel R (1998) Investigations of ground-based clouds at Mt. Brocken. Fresenius Journal of Analytical Chemistry 361: 59-64.

[3] Brimblecombe P (1996) Air composition and chemistry. Cambridge University Press 2nd Edition

[4] Bridges KS, Jickells TD, Davies TD, Zeman Z, Hunova I (2001) Aerosol, precipitation and cloud water chemistry observations on the Czech Krusne Hory plateau adjacent to a heavily industrialized valley. Atmospheric Environment 36: 353-360.

[5] Bridgman HA, Davies TD, Jickells T, Hunova I, Towey K, Bridges K, Surapipith V (2002) Air pollution in the Krusne Hory region, Czech Republic during the 1990s. Atmospheric Environment 36: 3375-3389.

[6] Collet Jr JL, Hoag KJ, Sherman DE, Bator A, Richards LW (1998) Spatial and temporal variations in San Joaquin Valley fog chemistry. Atmospheric Environment 33: 129-140.

[7] Grasserbauer M, Paleczek S, Rendl J, Kasper A, Puxbaum H (1994) Inorganic constituents in aerosols, cloud water and precipitation collected at the high alpine measurement station Sonnblick: Sampling, analysis and exemplary results. Fresenius Journal of Analytical Chemistry 350: 431-439.

[8] Herckes P, Wendling R, Sauret N, Mirabel P, Wortham H (2001) Cloudwater studies at a high elevation site in the Vosges Mountains (France). Environmental Pollution 117: 169-177.

[9] Hoag KJ, Collet Jr JL, Pandis SN (1999) The influence of drop size-dependent fog chemistry on aerosol processing by San Joaquin Valley fogs. Atmospheric Environment 33: 4817-4832.

[10] Kang J, Byung CC, Lee C-B (2010) Atmospheric Transport of water soluble ions (NO_3^-, NH_4^+, and nss-SO_4^{2-}) to the southern East Sea (Sea of Japan). Science of the Total Environment 408: 2369-2377

[11] Marinoni A, Laj P, Sellegri K, Mailhot G (2004) Cloud chemistry at the Puy de Dome: variability and relationships with environmental factors. Atmospheric Chemistry and Physics 4: 715-728.

[12] Millet M, Sanusi A, Wortham H (1996) Chemical composition of fogwater in an urban area: Strasbourg (France). Environmental Pollution 94: 345-354.

[13] Plessow K, Acker K, Heinrichs H, Möller D (2000) Time study of trace elements and major ions during two cloud events at the Mt. Brocken. Atmospheric Environment 35: 367-378.

[14] Queck R (2003): Fraktionierung und zeitliche Differenzierung von Depositionsraten in Waldbeständen. Unpubl. Diplomarbeit, TU Dresden, Institut für Hydrologie und Meteorologie

[15] Warneck P (1991) Chemical reactions in clouds. Fresenius Journal of Analytical Chemistry 340: 585-590.

[16] Zimmermann L, Zimmermann F (2002) Fog deposition to Norway Spruce stands at high-elevation sites in the Eastern Erzgebirge (Germany). Journal of Hydrology 256: 166-175