Nitrophenols and Haloacetates in Fog and Rain

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Introduction

Nitrophenols and haloacetates are ubiquitous environmental trace substances originating from both anthropogenic and biogenic sources. As they are of potential ecotoxicological relevance, it is important to determine their concentrations in the atmosphere, particularly in fog and rain.

Deposition of fog droplets may play a significant role in the water balance of forest ecosystems in mountainous regions in Central Europe (Grunow 1955). Therefore fog may contribute a significant portion to the total input of trace substances. A novel aspect of this work is the fog collection at two different sites at the same time.

Location and Methods

Sampling sites (Figure 1)

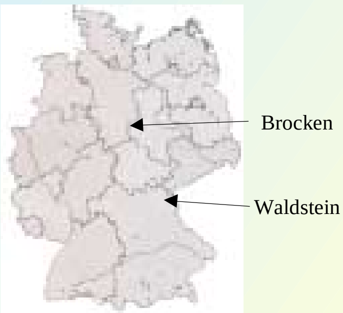

Figure 1:

Location of the two sampling sites in different mountain ranges shown on a map of Germany

Waldstein: Ecosystem research site (810 m a.s.l., 50°08'N, 11°52' E) in the Fichtelgebirge, a mountain range in northeastern Bavaria, Germany

Period: July 1998 to March 1999 and February to July 2000

Sampler: modified Catech Active Strand Cloudwater Collector (Figure 2)
for rain "wet-only" sampler

Brocken: Mt. Brocken (1142 m a.s.l., 51°37'N, 10°40' E), highest elevation in the Harz mountains in northern Germany

Period: April to June 2000

Sampler: passive strand cloudwater collector

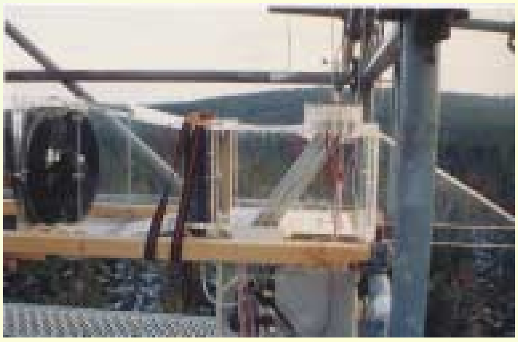

Figure 2: Fog collector on the tower at the Waldstein

Analytical methods

Samples were stored at –20 °C until analysis

- Nitrophenols:2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-ortho-cresol were analysed by SPE-GC-MS with isotope labelled internal standard
- Haloacetates:trifluoroacetate (TFA) and trichloroacetate (TCA) extracted with MTBE, derivatised with 1-(pentafluorophenyl)-diazoethane, and analysed by GC-MS
- Inorganic ions: Na^+, K^+, Mg^{2+}, Ca^{2+} by ICP-AES
NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} by ion chromatography

Results

Correlations of nitrophenols

4-NP, 2,4-DNP, and DNOC have a significant correlation (99 %)

- to nitrate, ammonium and to the electric conductivity
- among each other

Comparison of fog and rain

	concentration [mg/L]		ratio
	rain	fog	fog/rain
H^+	0.003	0.05	7.2
NH_4^+	0.7	11	19
NO_3^-	2.5	29	9.8
SO_4^{2-}	1.5	16	13
conductivity [µS/cm]	12	166	11
	[µg/L]		
4-NP	2.2	31	4.7
2,4-DNP	0.8	3.8	3.8
DNOC	0.3	1.1	3.0
TFA	0.04	0.23	6.6
TCA	0.10	0.28	4.4

Table 1: Concentrations of inorganic ions, nitrophenols and haloacetates in fog and rain and their concentration ratios (fog/rain)

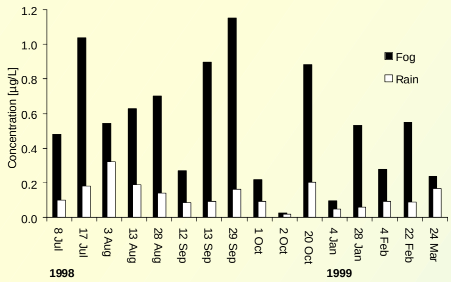

Figure 3: TCA concentrations in fog and rain

Comparison of Waldstein and Brocken

	fog Waldstein (n=32)		fog Brocken (n=22)	
	µg/L	ng/m^3	µg/L	ng/m^3
4-NP	31	3.2	11	3.9
2,4-DNP	3.8	0.7	2.0	1.3
DNOC	1.1	0.2	0.8	0.4
	µeq/L	neq/m^3	µeq/L	neq/m^3
NH_4^+	754	89	212	67
NO_3^-	484	48	147	70
SO_4^{2-}	408	39	142	52
TIC		192		223
LWC [mg/m^3]	110		350	
NO_x [$\mu g/m^3$]	9.5		3.6	
O_3 [$\mu g/m^3$]	54		83	
v [m/s]	2.9		7.6	

Table 2: Average nitrophenol and ion concentrations and the means of dissolved pollutants per m^3 air, n: number of analysed samples TIC: Total Ionic Content, Liquid water content (LWC), gas concentrations and wind speed (v) for both sites

Conclusion

→ Atmospheric formation of nitrophenols may involve different NO_y-species. Similar formation processes of nitrophenols may be suggested.

→ Concentrations of nitrophenols, haloacetates, and inorganic ions are higher in fog than in rain (Table 1, Figure 3). This shows the differences in formation processes of rain and fog.

→ Average concentrations of nitrophenols and inorganic ions in fog are higher at the Waldstein due to higher liquid water content at the Brocken. The average load per m³ air is slightly higher at the Brocken (Table 2).

Literature: Grunow, J. 1955. Der Nebelniederschlag im Bergwald. *Forstw.Cbl.* **74**, 21-36.

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