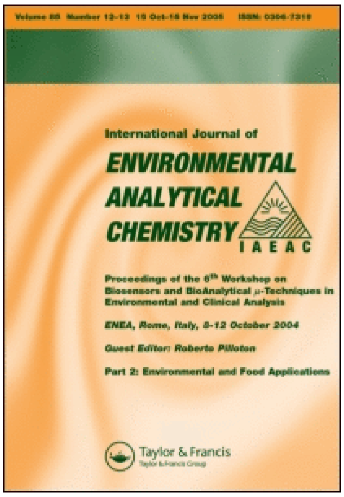

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ORGANIC COMPOUNDS IN CLOUD AND RAIN WATER

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Cloud and rain water samples have been collected in spring 1991 in the Vosges mountains (France) and analyzed for aldehydes, phenols and polycyclic aromatic hydrocarbons (PAHs). Both passive and active cloud collectors have been employed. A mean concentration of formaldehyde of 197 μg/l (6.6 μM) has been found in cloud water while on the average only 100 μg/l (3.3 μM) were observed in rain water. The average phenol concentration was 3.5 μg/l (37 nM), but only 1.6 μg/l (17 nM) in rain water. Finally, the mean concentration of PAHs (only determined in cloud water) amounts to 0.37 μg/l. The PAH profile is similar to that observed for rain water sampled in Hannover (Germany).

KEY WORDS: Aldehydes, phenols, polycyclic aromatic hydrocarbons, rain, cloud water.

INTRODUCTION

While a variety of studies on the contamination of rain water by organic compounds have appeared (see ref. 1) the reports on the pollution of both radiation fog and cloud water by organic compounds are scarce. Leuenberger *et al.*[2], Czuczwa *et al.*[3] and Capel *et al.*[4] report on the determination of aliphatic and aromatic hydrocarbons, polycyclic chlorinated biphenyls, chlorinated dioxins and furans in radiation fog in Switzerland. Grosjean and Wright[5], Steinberg and Kaplan[6], Munger *et al.*[7,8], Igawa *et al.*[9] determined formaldehyde and other aldehydes and ketones in fog and cloud water, collected mainly in California (USA). Carboxylic acids were observed by Munger *et al.*[8] in fog and cloud water in California. Glotfelty *et al.*[10] and Schomburg *et al.*[11] found a large variety of pesticides in fog in California (both coastal and central valley fog). Richartz *et al.*[12] and Capel *et al.*[4] determined phenol and several nitrophenols in radiation fog in Switzerland, radiation fog in Bayreuth and cloud water in the Fichtelgebirge mountains (Germany).

Although usually rain water was not collected and analyzed at these sites comparison with published data revealed that fog and cloud water not only shows up to 10-fold higher concentrations of inorganic compounds[13], but apparently also a much higher pollution by organic compounds as compared to precipitation. Thus, Munger *et al.*[7,8], Igawa *et al.*[9], Grosjean and Wright[5] and Steinberg and Kaplan[6] observed mean formaldehyde concentrations in fog and cloud water in California ranging from 1–2 mg/l (33–67 μM) with peak values of 5.6 mg/l (187 μM) for urban fog in Los Angeles, while the mean concentrations reported for rain water (see references in ref. 1) ranged from 8–262 μg/l (0.3–8.7 μM). Capel *et al.*[4] report PAH, n-alkane and PCB concentrations in radiation fog which are higher than those reported in precipitation which is particularly the case for PCBs the concentration of which is more than three orders of magnitude higher in fog as compared to rain. Moreover, higher phenol and nitrophenol concentrations have been reported by Capel *et al.*[4] and Richartz *et al.*[12], if compared with published rain data although the differences are less pronounced as for the compounds discussed so far. Thus, the maximum concentration of phenol observed in cloud water in the Fichtelgebirge mountains (14 μg/l = 149 nM)[12] is comparable to that observed by us in rain in Hannover (Germany)[1] while the mean concentration of 4-nitrophenol observed by Richartz *et al.*[12] in the Fichtelgebirge mountains (20.1 μg/l = 145 nM) is 3.5 times that observed by us in precipitation in Hannover.[1]

It is obvious that fog droplets both in radiation fog and clouds scavenge organic compounds more efficiently than rain droplets which is apparently a result of the smaller droplet size (few μm) and the much longer residence time of fog droplets. Thus, gas/liquid exchange of organic compounds will be more efficient. Moreover, it is known that particles and thus particle-bound organic compounds are more efficiently scavenged by fog than by rain droplets.[3]

However, as mentioned above, up to now no comparative studies of the concentration of organic compounds in cloud and rain water (collected at the same site) have been published. Here we report on the determination of two aldehydes and three phenols in cloud and rain water collected in spring 1991 in the Vosges mountains (France). In addition, PAHs have been determined in cloud water and the PAH profile of cloud water is compared with that of rain water collected in Hannover (Germany). Finally, the influence of the fog collector on the observed concentrations is discussed.

EXPERIMENTAL

Sampling

Cloud water was mainly collected using passive samplers with PTFE strings manufactured by Icare, Paris (France). In addition, during a few cloud events an active collector of the impactor type constructed according to the design of Winkler[13] was employed. Samples integrated over a full cloud event (5–20 h) were collected leading to a sample volume with the passive collector of 50–1000 ml, while with the active collector of considerably smaller volume of 8–130 ml was collected. The PTFE strings of the passive collector as well as the PTFE cone of the active collector were thoroughly cleaned after each cloud event by first removing the particles with a wet wipe tissue followed by cleaning with acetone.

Many cloud events were accompanied or interrupted by short or in some cases continuous rain events. Although the passive sampler had a shielding against rain fall, penetration of rain drops into the collector cannot be excluded in all instances due to the in part high wind speed as detailed below.

Methods

Samples were extracted or derivatized as soon as possible, where the time between sampling and extraction did not exceed three days. A separate fraction of the sample (or the whole sample in some instances) was used to determine the aldehydes (using a volume of 8–250 ml aqueous sample). Aldehydes were derivatized with 2,4-dinitrophenylhydrazine in acidic medium. The hydrazones were extracted three times with tetrachloromethane as described previously[1] leading to a recovery of 99–100%. The extracts were evaporated to dryness and redissolved in 1 ml acetonitrile and determined by HPLC, using UV detection at 355 nm (quantitation by the external standard method).

To the remaining sample the internal standards (see below) were added and the sample was made basic (pH 12) using potassium hydroxide. The PAHs and other neutral compounds were extracted three times with 50 ml dichloromethane. The combined organic phases were dried over anhydrous sodium sulphate, reduced in volume and subjected to column chromatography on silica gel using cyclohexane as solvent. The cyclohexane extract was reduced in volume using a rotary evaporator and redissolved in acetonitrile. PAHs were determined by HPLC and fluorescence detection with variable wavelength using 2,2'-binaphthyl as internal standard. The recovery of benzo[a]pyrene was determined as 100.5 ± 1.0%.

The aqueous phase (containing the phenols) was made acidic (pH 2–3) with 6 N hydrochloric acid and extracted three times with 10 ml dichloromethane, reduced in volume by a rotary evaporator followed by nitrogen blow off to a volume of > 1 ml. Phenols were derivatized by adding 10 μl of heptafluorobutyric anhydride. The reaction solution was warmed to 30° C for 1 h and kept at room temperature overnight.

The phenols were quantified using phenol-d_6, p-cresol-d_4 and 4-nitrophenol-d_4 as internal standards. Determination was carried out by GC-MS in the selected ion monitoring mode using m/z 290 for phenol, m/z 294 and 295 for deuterated phenol, m/z 304 for m- and p-cresol, m/z 307 and 308 for deuterated p-cresol, m/z 335 for 4-nitrophenol and m/z 338 and 339 for deuterated 4-nitrophenol. Although the extraction method described above leads to poor recoveries for the very water soluble phenols (19.3 ± 4.6% for phenol, 46.0 ± 1.7% for p-cresol, 19 ± 3% for 4-nitrophenol) reliable quantitation is possible by using deuterated isotopomers. If quantitation with these deuterated compounds is carried out, one has to take into account that not only the acidic, but in part also one of the ring deuterium atoms are exchanged against hydrogen (see above).

Instruments

The HPLC instrument was from Waters (Waters pumps 501 and 510, autosampler WISP 712). For the determination of the aldehydes a Waters UV detector 490 and a Lichrospher 60 RP-Select B column (Merck), (5 μm, 250 × 4 mm) was used. The mobile phase consisted of acetonitrile (A) and water (B) where a gradient of 50%–15% B in 25 minutes at a flow of 1.2 ml/min was used.

PAHs were determined with an identical HPLC-system, but equipped with a fluorescence detector from Hewlett Packard, HP 1046A with variable wavelengths. Again the mobile phase consisted of acetonitrile (A) and water (B) with a gradient of 48%–100% A in 24 min at a flow of 1.8 ml/min followed by a flow of 0.8 ml from 24–29 min and a flow 2.2 ml from 29–34 min.

For the determination of the phenols a Finnigan 4500 mass spectrometer was used under electron impact conditions (70 eV) and a source temperature of 150° C. The mass spectrometer was coupled to a gas chromatograph from Hewlett Packard, type 5890 A using a DB5 column and helium as carrier gas (temperature gradient: 5° C/min from 70° C up to 270° C, split/splitless injection).

Chemicals

Deuterated internal standards were from Merck (Germany), Sharp & Dohme (Canada), 2,2′-binaphthyl from Radiant Dyes, all other chemicals from Fluka (Switzerland), Merck (Germany), Riedel-de Haën (Germany) or Aldrich (USA).

RESULTS

Sampling sites

Cloud and rain water was collected during the NUAC campaign in the Vosges mountains from the end of April to the end of June 1991 at two sites at an elevation of ~ 800 m (station 2, Col du Hantz) and ~ 1000 m (station 3, Kreuzberg) where the station 3 is situated approximately 16 km east of the station 2. In general stratospheric clouds approaching the mountain with westerly or north-westerly winds were studied where the cloud basis usually was situated at the station 2. Rain was sampled before, after as well as during cloud events, which however does not implicate, that the collected rain during a cloud event always originate from the same air masses. As a result of the oreography polluted air below the clouds is pressed into the cloud when the cloud reaches the station 2.

Aldehydes

Table 1 summarizes the concentrations of formaldehyde and acetaldehyde in 19 cloud water and 5 rain water samples. Some samples may have been diluted by rain droplets penetrating into the cloud collector at high wind speeds. These samples are indicated by an asterisk. If only passively collected samples are considered, a mean concentration of 197 μg/l (6.6 μM) formaldehyde and 17 μg/l (0.39 μM) acetaldehyde was found in the cloud water samples, but only 100 μg/l (3.3 μM) formaldehyde and 12 μg/l (0.27 μM) acetaldehyde in the rain

Table 1 Aldehydes in cloud and rain water [μg/l].

Date (d-m-y)	*Sample/Site/Collector*	*Formaldehyde*	*Acetaldehyde*	*Sum*^{m}
30-04-91	Cloud 1 /2/passive*	113	13	126
30-04-91	Cloud 1 /3/passive*	121	15	136
14-05-91	Cloud 2 /2/active	231	55	286
14-05-91	Cloud 2 /2/passive	321	35	356
14-05-91	Cloud 2 /3/passive	375	58	433
06-06-91	Cloud 3 /2/active	128	25	153
06-06-91	Cloud 3 /2/passive	216	9	225
06-06-91	Cloud 3a/3/passive*	116	5	121
06-06-91	Cloud 3b/3/passive	115	8	123
07-06-91	Cloud 4 /2/active	162	n. d.	162
07-06-91	Cloud 4 /3/passive	293	15	308
08-06-91	Cloud 5 /2/active	284	53	337
08-06-91	Cloud 5a/2/passive*	89	15	104
08/09-06-91	Cloud 5b/3/passive	346	n. d.	346
18-06-91	Cloud 8 /2/active	120	29	149
18-06-91	Cloud 8 /2/passive	149	12	161
19/20-06-91	Cloud 9 /2/active	192	42	234
19/20-06-91	Cloud 9 /2/passive*	133	13	146
20/21-06-91	Cloud 10/3/passive*	177	9	186
mean**		197	17	213
28-04-91	Rain 1	86	10	96
06-06-91	Rain 4	134	13	147
07/08-06-91	Rain 5	125	13	138
20-06-91	Rain 9b	102	8	110
07-06-91	Rain 10	53	17	70
mean		100	12	112

* may contain some rain
** only passively collected samples are considered
n. d. not detected

water samples. Several cloud events were both monitored by active and passive sampling (cloud 2–5,8–9). In all but one instance the formaldehyde concentration in the actively collected sample is lower (up to a factor of 1.7) while in the case of cloud 9 the formaldehyde concentration is higher in the actively collected sample.

If the same cloud was monitored at both sites 2 and 3 over a very similar time range, almost identical results were obtained (cloud 1 and 2) which demonstrates that the two passive collectors lead at least to reproducible results.

Phenols

Table 2 summarizes the concentrations of phenol, m/p-cresol and 4-nitrophenol in 7 cloud water and 8 rain water samples. Excluding the actively collected samples the following mean

Table 2 Phenols in cloud and rain water [μg/l].

Date (d-m-y)	*Sample/Site/Collector*	*Phenol*	*m/p-Cresol*	*4-Nitrophenol*
08-06-91	Cloud 5a/2/passive*	2.49	1.33	3.04
09-06-91	Cloud 5b/3/passive	5.54	1.98	16.27
18-06-91	Cloud 8 /2/active	4.36	2.23	9.08
20-06-91	Cloud 9 /2/passive*	3.92	0.79	2.57
19/20-06-91	Cloud 9 /2/active	6.18	2.75	6.21
19-06-91	Cloud 9 /3/passive*	3.56	0.92	3.76
20/21-06-91	Cloud 10/3/passive*	1.76	0.47	1.66
mean**		3.45	1.10	5.46
06-06-91	Rain 4 /2	2.21	0.56	1.81
07/08-06-91	Rain 5 /2	2.35	0.76	6.09
14-06-91	Rain 6a/2	0.77	0.11	2.80
14-06-91	Rain 6b/2	2.41	0.47	1.11
15/16-06-91	Rain 7 /2	0.94	1.21	7.57
18-06-91	Rain 8 /2	0.71	0.21	1.45
20-06-91	Rain 9a/2	2.19	0.58	1.57
20-06-91	Rain 9b/2	1.08	0.24	1.16
mean		1.58	0.52	2.95

* may contain some rain
** only passively collected samples are considered

concentrations were observed in the cloud water samples: Phenol = 3.5 μg/l (37 nM), m/p-cresol = 1.1 μg/l (10 nM) and 4-nitrophenol = 5.5 μg/l (40 nM). The mean concentration in the rain water samples are again lower: Phenol = 1.6 μg/l (17 nM), m/p-cresol = 0.52 μg/l (4.8 nM) and 4-nitrophenol = 3.0 μg/l (22 nM).

Unfortunately, there is only one actively collected sample where a higher concentration (by a factor of 1.6 for phenol and 2.4 for 4-nitrophenol) has been observed as compared to the passively collected sample. Cloud 9 was also monitored both at station 2 and 3 (although during a somewhat different time interval). Very similar concentrations are observed for the two stations.

Polycyclic aromatic hydrocarbons (PAHs)

Only cloud water has been analyzed for PAHs as summarized for 1 cloud events and 9 PAHs in Table 3. Nine additional cloud water samples were analyzed, but the HPLC chromatograms could not be evaluated reliably due to the low PAH concentration which was due to the fact that many cloud water samples showed very weak PAH concentrations and in addition several samples had such a small volume that PAHs could not be analyzed reliably. As also observed for rain water collected in Hannover (Levsen *et al.*, 1990) the concentration of the sum of the 9 PAHs determined varies considerably ranging from 60–990 ng/l. Excluding the actively collected sample one arrives at a mean concentration of 371 ng/l. The concentration of PAHs in all clouds is likely even lower as several samples could not be

Table 3 Polycyclic aromatic hydrocarbons in cloud water [ng/l].

Date (d-m) *year 1991*	*30-4*	*30-4*	*6-6*	*8-6*	*8-6*	*14-6*	*14-6*	*19/20-6*	*19/20-6*	*19/20-6*	*20/21-6*	*mean***
Sample	*Cloud 1**	*Cloud 1**	*Cloud 3a**	*Cloud 5a**	*Cloud 5a*	*Cloud 6*	*Cloud 6*	*Cloud 9*	*Cloud 9**	*Cloud 9**	*Cloud 10**	
Site	*2*	*3*	*3*	*2*	*3*	*2*	*3*	*2*	*2*	*3*	*3*	
Collector	*passive*	*passive*	*passive*	*passive*	*passive*	*active*	*passive*	*active*	*passive*	*passive*	*passive*	
Fluoranthene	32	27	37	26	90	259	52	484	180	265	133	94
Pyrene	19	11	15	n. d.	28	61	11	378	95	79	27	36
Benz(a)-anthracene	7	12	4	5	14	29	8	160	47	54	22	19
Chrysene	17	23	12	9	30	51	11	404	104	104	44	40
Benz(e)-pyrene	22	27	8	6	22	31	8	489	142	112	59	45
Benzo(b)-fluoranthene	24	25	12	7	39	46	17	507	165	129	67	55
Benzo(k)-fluoranthene	9	15	3	3	20	17	8	183	54	49	23	21
Benzo(a)-pyrene	13	11	4	1	21	22	9	153	49	55	19	20
Benzo(ghi)-perylene	20	23	10	3	19	30	8	475	149	114	58	48
Sum Σ	163	186	107	61	284	547	135	3233	988	962	451	$\Sigma = 371$

* may contain some rain

** only passively collected samples are considered analyzed due to the low PAH content.

If a cloud event was monitored at both sites almost identical concentrations were determined (cloud 1 and 9), while in the case of cloud 5 a substantial different concentrations were observed for the two sites. The cloud water volume of only two actively collected samples (cloud 6 and 9) was sufficiently large to be analyzed for PAHs. Here the actively collected samples 6a and 9 show higher concentrations (by a factor of 3) than the passively collected samples. Cloud 9 happens to be the cloud where also phenols were determined with both collection methods leading to the observation of higher concentrations in the actively collected sample and the only cloud for which the formaldehyde concentration is higher in the actively collected sample than in the passively collected one.

DISCUSSION

Cloud collectors

The data obtained in particular for formaldehyde demonstrate that the results depend on the collector type. According to Winkler[13] only active samplers based on the impactor principle give reliable results. Unfortunately we have only collected relatively few samples with a prototype of an active collector based on Winkler's design[13]. In addition, the sample volume obtained with this collector even over extended sampling periods is often very small, so that organic compounds, which are present in significant lower concentrations in precipitation than most inorganic compounds can only be analyzed with difficulties if present at traces (such as PAHs). The discussion is thus based on data obtained with the passive collectors, which—as the data presented above demonstrate—operate at least reproducible although the determined concentration may be in error by a factor of about two.

If a cloud event is accompanied by rain, rain droplets may penetrate into the passive collector at high wind speeds which, as a result of its geometry, is less likely in the case of the active collector. Thus, the differences observed between formaldehyde concentrations collected actively and passively cannot be due to a dilution by rain droplets which should lead to lower concentrations in the passively collected samples.

Sampling site

While the clouds hit the mountains at the site 2 (incorporating polluted air below the cloud) the air masses are then forced into the direction of site 3 as a result of the oreography of the mountain which (depending on the wind speed) they reach after 10–30 min. The available data demonstrate that (with one exception) the concentrations of the organic compounds analyzed remain constant during this passage. (There are no significant anthropogenic pollution sources during the two sites except occasional wood firing which may lead to an enhanced PAH concentration). Polluted air is forced into the cloud in front of site 2. Thus, an equilibrium between gas and liquid phase is obviously already reached at site 2.

Comparison of cloud and rain water

Aldehydes. Although the number of samples analyzed is limited it is obvious that the concentration of aldehydes is higher by a factor of about two in cloud water as compared to rain water (this factor is even lower if the actively collected samples are compared). Even if cloud events, where rain droplets may have penetrated into the cloud collector (indicated by an asterisk in Table 1) are excluded no significant increase of this factor is observed. It is of interest to compare these results with published data. Thus, Munger *et al.*[7] report a mean value for formaldehyde (cloud water) for 3 sites in California ranging from 1.5–2.1 mg/l (50–70 μM) and only one site with a significant lower value (0.07 mg/l = 2.3 μM) while Grosjean and Wright[5] report a mean value of 0.45 mg/l = 15 μM. (Fog water concentrations are even higher). If on the other hand these values are compared to other published data on rain water pollution by formaldehyde, the formaldehyde concentration in cloud water exceeds that of rain water by at least a factor of 5–10. Thus, we observe the same trend (higher concentrations in cloud water as compared to rain water), but the effect is by far less pronounced than described by others in the literature.

However, one has to take into account that all four reports on formaldehyde concentrations in cloud water refer to cloud water collected in Southern California where a higher air pollution and photochemical activity may lead to a higher gas phase concentration of formaldehyde and thus to a higher cloud water concentration as compared to this study.

Rain and cloud water reported in this study originate from the same or at least similar air masses and rain formed during a cloud event may, but must not* originate from coagulating cloud droplets of the same cloud where gas/liquid equilibrium is already reached in the cloud droplet.

Thus, there is no apparent reason why the concentration in rain water should differ significantly from that in cloud water.

The mean formaldehyde concentration observed in rain water in the Vosges mountains (100 μg/l) is very similar to that observed in rain in Hannover 1989[1] and is approximately in the middle of the concentration range reported for formaldehyde in rain water by other authors (as reviewed by Levsen *et al.*[1]).

Phenols. The average phenol concentration in rain water collected in the Vosges mountains (1.6 μg/l) is considerably lower than that reported for rain in Hannover (5.6 μg/l) and Dübendorf (Switzerland) (8 μg/l) demonstrating that both the air masses below the clouds and in the clouds hitting the Vosges mountains are less polluted, while the difference between rain water in the Vosges (France) and Hannover (Germany) is less pronounced for 4-nitrophenol (mean value in Hannover in 1989 = 5.7 μg/l).

Again the mean concentrations of phenol, m/p-cresol and 4-nitrophenol are higher in cloud water than in rain water. As several of the analyzed cloud water samples may be slightly diluted by rain droplets the concentration difference between cloud and rain water may be even higher. The average concentration of 4-nitrophenol observed in cloud water in the Fichtelgebirge mountains by Richartz *et al.*[12] exceeds that observed in the Vosges

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*Rain observed during a cloud event must not originate from the same cloud but may be formed from a second cloud layer above the monitored cloud.

mountains by us by almost a factor of 7 demonstrating the significantly higher pollution of the former site.

The higher concentrations of the phenols in cloud water as compared to rain water demonstrate again that these compounds are scavenged more efficiently by cloud droplets compared to rain droplets (the concentration ratio of phenols in cloud water as compared to rain water is similar to that cited by Richartz *et al.*[12]) No extreme differences between cloud and rain water is expected as both originate in most instances from similar air masses as detailed above. Surprisingly, the mean ratio of phenol in cloud water as compared to rain water (2.2) is similar to that of 4-nitrophenol (1.8). If both compounds were in the gas phase Henry's law constant (in m^3 atm/mol) $1.3 \cdot 10^{-8}$ for 4-nitrophenol and $6.4 \cdot 10^{-7}$ for phenol,[14] Tremp *et al.*, in press), would favour the partitioning of 4-nitrophenol into the liquid phase. The low vapour pressure of 4-nitrophenol ($5.3 \cdot 10^{-3}$ Pa at 25° C)[15] as compared to phenol (83 Pa at 25° C),[15] suggests that 4-nitrophenol is at least partially particle-bound.

As particle-bound compounds are more efficiently scavenged by cloud droplets[3] a higher ratio for the concentration in cloud as compared to rain water is expected for 4-nitrophenol which is not born out by the experimental data.

Polycyclic aromatic hydrocarbons

PAHs have only been determined in cloud water. As reported above, an average value of 371 ng/l was found in the passively collected samples which is comparable to the mean concentration of summer rain as reported by Levsen *et al.*[1] for precipitation in Hannover. The mean cloud water concentration falls into the concentration range reported by others for PAHs in rain (see references in Levsen *et al.*, 1990).

In contrast, Capel *et al.*[4] determined mean PAH concentrations in radiation fog in Switzerland for the sum of 21 PAHs and found values (28 μg/l), well above ours, while concentrations determined in rain water ranged from 0.1–0.6 μg/l. Clearly, radiation fog droplets scavenge PAHs much more efficiently than cloud water droplets.

Leuenberger *et al.*[2] observed for PAHs in fog a distribution of the individual PAHs which differs substantially from that observed in rain water and snow, i.e. the fog samples were dominated by the higher PAHs indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

Figure 1 compares the relative distribution of 9 PAHs determined in cloud water samples in the Vosges mountains with the average distribution observed for rain water in Hannover.[1] Surprisingly and in contrast to a report by Leuenberger *et al.*[2] the relative distribution of the PAHs does not differ significantly between cloud and rain water, although not only different hydrometeors, but also sampling sites very apart from each other were compared. (The most pronounced differences are observed for pyrene. However, this may be a measuring artefact, as it is in particular pyrene the fluorescence of which is readily quenched by the presence of traces of oxygen). The relative contribution of benzo[b]fluoranthene and benzo[g,h,i]perylene to the sum of all PAHs is more pronounced in the fog than in the rain water samples. However, the effect is by far less pronounced than that published by Leuenberger *et al.*[2]. A second publication of these authors[3] does not show the extreme preference of PAHs with high molecular weight relative to those with low molecular weight, so that the earlier report on two radiation fog events may represent a singular event.

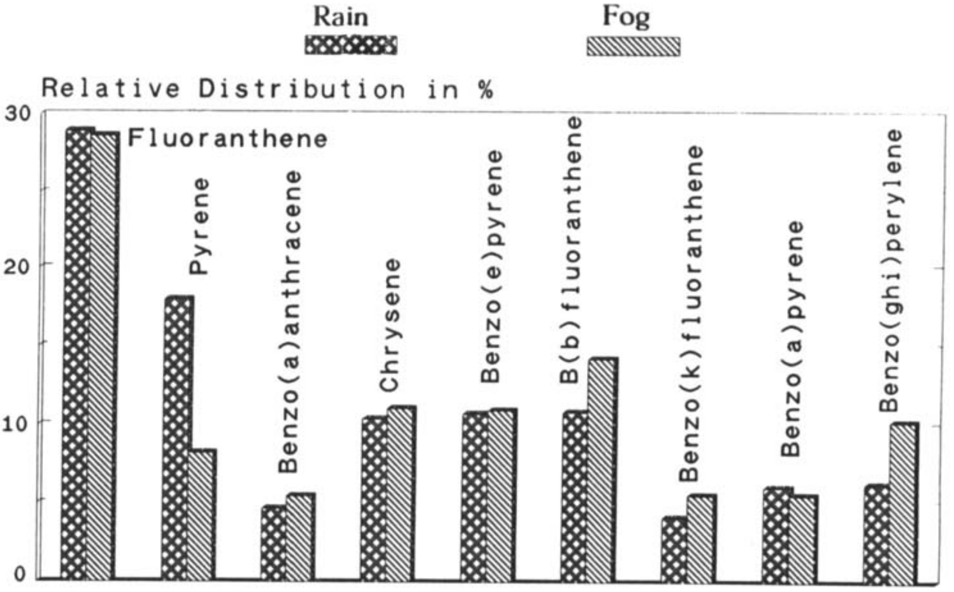

Figure 1 Relative distribution of nine polycyclic aromatic hydrocarbons in cloud and rain water.

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