

Chemical behaviour of hydrophobic micro-pollutants during the melting of snow

NORBERT SIMMLEIT*

*Institut Fresenius, Im Maisel 14, D-6204
Taurusstein 4, Federal Republic of Germany*

REIMER HERRMANN & WOLFGANG THOMAS

*Lehrstuhl für Hydrologie, Universität Bayreuth,
Postfach 10 12 51, D-8580 Bayreuth, Federal
Republic of Germany*

ABSTRACT During two periods of snow melting daily bulk samples of snow were taken on a Dolomite plateau in the rural karst region of northeast Bavaria (Federal Republic of Germany). The snow samples were analysed for PAHs by HPTLC and for BHCs by GC. Conductivity and pH were also measured. Molecular substance ratios, pollutant loadings and enrichment factors in the meltwater were calculated from the concentration data. With the first 40% of meltwater 90% of H⁺-ions, 70-80% of BHCs and 60-70% of PAHs were released from the snow cover. In the first 20% of meltwater the H⁺-ions were enriched by 4-6 times and some PAHs were enriched by 2.5 times. BHCs showed a more continuous release in the first 40% of meltwater causing 1.5-fold increased concentrations. During the melting of snow the ratios of more hydrophobic to less hydrophobic micropollutants increased in the snow cover. After a long period of melting hydrophobic contaminants were accumulated in the snow cover towards the end of one melting event investigated. The dynamics of the release of pollutants from the snow cover is discussed in terms of the micro-distribution of atmospheric pollutants in the snow crystal. It is possible to use a nearby karst spring as a natural lysimeter for tracing the release of snow constituents during the melting. However, only 1-3% of the input of micropollutants were detected in the karst water.

Le comportement chimique des micropolluants hydrophobes pendant la fonte des neiges

RESUME Pendant deux périodes de la fonte des neiges des échantillons journaliers de neige ont été pris sur un plateau des Dolomites dans une région rurale karstique en Bavière du nord-est (Republique Federale d'Allemagne). Les échantillons de neige ont été analysés pour les PAHs par HPTLC et pour les HCHs par GC. En plus, la conductivité et le pH ont été déterminés. Les résultats des mesures de concentration ont été utilisés pour

*The experiments were carried out at the Lehrstuhl f. Hydrologie (University of Bayreuth, FRG).

calculer les rapports et les charges des polluants et les facteurs d'accumulation dans l'eau de fonte. Dans les premiers 40% de l'eau de fonte, 90% des ions H^+ , 70-80% des HCHs et 60-70% des PAHs ont été libérés par la couche de neige. Dans les premiers 20% de l'eau, les ions d'hydrogène ont été enrichis 4-6 fois et quelques PAHs ont été enrichis 2.5 fois. Les HCHs ont été libérés d'une manière plus continue dans les premiers 40% de l'eau fonte, provoquant une accumulation de 1.5 fois. Pendant les fontes des neiges le rapport entre les polluants plus hydrophobes et les polluants moins hydrophobes augmentait dans la couche de neige. Après une fonte des neiges de longue durée, les polluants hydrophobes se sont accumulés dans la couche de neige vers la fin de la fonte. En partant de la distribution microscopique des polluants atmosphériques dans les flocons de neige, la dynamique de la libération des polluants par la couche de neige a été discuté. Il est possible d'utiliser une source karstique avoisinante comme lysimètre naturel pour observer la libération des constituants de la neige au cours de la fonte. Pourtant seulement 1-3% des micro-polluants initiaux ont été détectés dans l'eau karstique.

INTRODUCTION

During the last decades several investigations have dealt with the inorganic chemical composition of snow (Sendtner, 1887; Henriksen, 1972; LaBarre, 1973; Gjessing & Gjessing, 1973; Oliver *et al.*, 1974; Herrmann, 1977). A very wide range of concentrations were found especially between polluted and unpolluted snow. However, only a few publications in which the organic constituents of snow were analysed (Herrmann, 1978; Schrimpff *et al.*, 1979; Meyers & Hites, 1982) are known to the authors.

Herrmann (1978) and Schrimpff *et al.* (1979) first determined the concentration of organic micropollutants in the snow cover. The occurrence of contaminants in snow is due to the deposition of airborne pollutants either by wet deposition (scavenging effect of snow flakes) or by dry deposition of aerosol particles. The authors of these publications showed that there is a regional pattern of contaminants in the snow cover of northeast Bavaria (Federal Republic of Germany), which can be explained by anthropogenic influences and orographic effects.

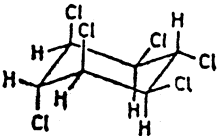
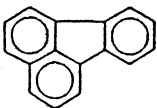
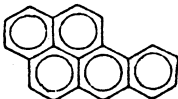
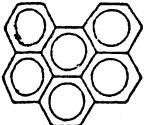
Until the melting of snow the pollutant load of the snow cover is increased by atmospheric deposition processes (Førland & Gjessing, 1975). Since the work of Johanesson & Henrikssen (1978) it is known that with the first 30% of meltwater, 90% of the ions accumulated are released from the snow cover. This can result in a sudden increase of the acidity of natural waters in geologically poorly buffered basins, causing in extreme cases an extinction of fish populations. In the meantime the observation of the sudden release of ionic species from the snow cover in the first fraction of meltwater has been confirmed in other studies and

different regions (Benarie & Munn, 1980; Jeffries & Senkin, 1983; Johannes *et al.*, 1980; Zöttl *et al.*, 1985).

Within the scope of a research project which was aimed at the evaluation of the impact of atmospheric deposition of organic micropollutants on the groundwaters in a karst region (Simmleit & Herrmann, 1986), we also considered the pollutant load of the snow cover during winter. Assuming that due to the very high permeability of the geological structure the accumulated pollutants in the snow cover could reach the groundwater quite rapidly, we were interested in the chemical behaviour of non-ionic, hydrophobic micropollutants in meltwater, soil water and groundwater during the melting of snow. For that purpose we analysed some selected organic contaminants during and after the melting of snow in the snow cover and in the groundwater sampled in a nearby karst spring, in order to detect any possible changes in the groundwater quality due to a potential release of pollutants from the snow cover.

As model substances we chose some carcinogenic species of the polycyclic aromatic hydrocarbons (PAHs) (Schoental, 1964), which are products of combustion processes, and the α - and γ -isomers of hexachlorocyclohexane (BHC) (Table 1). The latter chemical is commonly used as a pesticide (lindane) and is found, like the

TABLE 1 Organic micropollutants investigated

Compound	Structure	Molecular weight	Water solubility (25°C, $\mu\text{mol l}^{-1}$)
BHC		292	α -BHC 24* γ -BHC 10†
Fa		202	1.3‡ 5°C 0.35‡
BaP		252	0.015§
BghiP		276	0.00094§

* *Industrieverband Pflanzenschutz* (1982).

† *Oehme & Manø* (1984).

‡ *May & Wasik* (1978).

§ *McKay & Shiu* (1977).

PAHs, in the bulk precipitation of the sampling area throughout the year (Thomas, 1981).

MATERIAL AND METHODS

Sampling sites and sampling period

During the winter of 1984 snow, bulk precipitation and karst water samples were taken from two sampling sites, situated on a Dolomite plateau (450 m a.m.s.l.) in Upper Franconia, Federal Republic of Germany (Simmleit & Herrmann, 1986). In this rural area the composition of snow is very uniform and the concentrations of contaminants are low, as the regional survey of Herrmann (1978) and Schrimpff et al. (1979) showed.

The sampling station NF was situated in the basin of the karst spring in the Leipoldstal. The hydrological situation of this area is described in detail by Kanz et al. (1978). The snow cover (24 cm thick) was mainly a result of snowfalls during January. At the beginning of February the melting started very rapidly and the water content of the snowpack was reduced by 60% in the first four days. On the fifth day the period of melting was finished by a rainstorm (30 mm). During the melting bulk samples of snow were taken from an area of 10 x 10 m² in daily intervals. Water samples from the nearby karst spring were collected daily throughout February.

The second sampling station VF was situated directly above the cave in Steinamwasser. The snow cover (18 cm thick) was due to snowfalls at the end of February. At the beginning of March the melting of snow started. Because of the large daily temperature variations (day: 1-10°C, night: 0 to -9°C) the melting lasted three weeks. During this time 8 mm precipitation were deposited on the snowpack. Again bulk samples of snow were taken daily from a small, uniform area above the cave. Throughout March and April additional samples of trickling water were collected from two trickling sites in the cave 2 m and 7 m below the snow cover.

Analysis

The bulk samples of snow were taken with a glass plate and transported in 5 l glass beakers to the laboratory for melting. All glassware was cleaned with acetone and heated to 175°C. After thawing, the pH and the specific conductivity (20°C) of the snow were determined by using a pH-glass electrode (Ingold 405-88) and a conductivity electrode (Metrohm EA 1070). The melted snow and the bulk precipitation samples were liquid-liquid extracted with distilled dichloromethane. The concentrated extract was purified on an Al₂O₃-column (Bierl et al., 1984) and analysed for PAHs (benzo(a)pyrene (BaP), fluoranthene (Fa), benzo(ghi)perylene (BghiP)) by high performance thin layer chromatography (HPTLC) according to the method of Herrmann (1978). The BHCs were determined by gas chromatography (GC) using a glass capillary column (OV 101) (Thomas, 1981). The average recovery rates were 95% for PAHs (detection limit 0.45 ng l⁻¹) and 90% for BHCs (detection limit

0.04 ng l⁻¹).

Another, more selective extraction method was chosen for the karst water samples in order to achieve lower detection limits. These water samples from the spring and the cave were taken in 2 l glass bottles and were liquid-liquid extracted with distilled hexane. The concentrated extract could be used without further purification for the analysis of PAHs by HPTLC and BHCs by GC. The mean recovery rates were 90% for BHCs (detection limit 0.03 ng l⁻¹) and 85% for PAHs (detection limit 0.15 ng l⁻¹).

RESULTS

The first melting event

The melting of snow The behaviour of selected parameters of the snow cover during the melting of snow at station NF is shown in Fig.1. The rapid melting during the first days until the rainfall is indicated by the water loss of 60% of the original water content. On account of the snow cover sinking in the course of the melting,

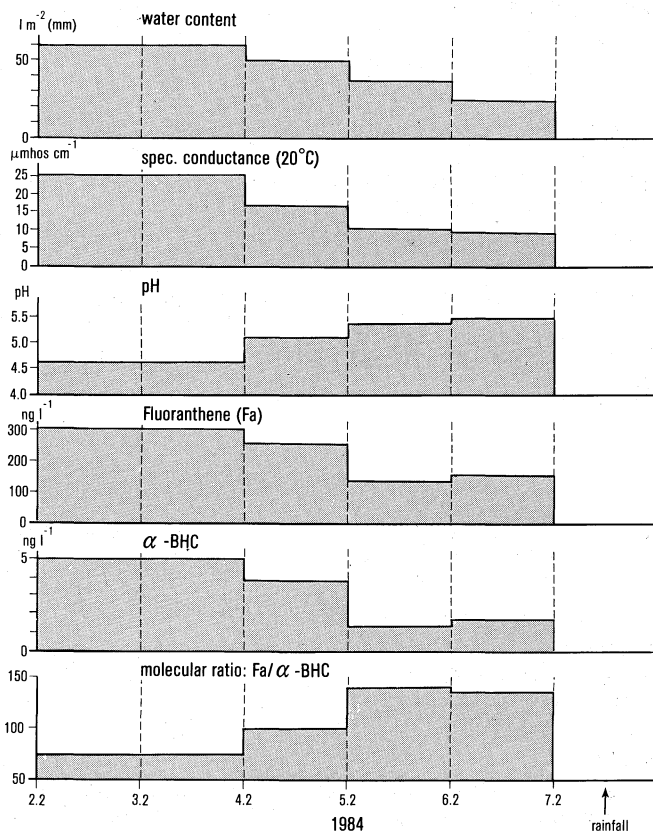


FIG.1 Variation of the chemical composition of the snow cover during melting from 3 to 7 February 1984 at station NF.

the snow density varied between 0.25 and 0.30 g cm⁻³.

With the first 40% of meltwater the conductivity of the snow cover decreased by 60% showing that the ions were released immediately from the snowpack with the first meltwater fractions. As an example the pH-curve is shown in Fig.1. Due to the loss of 90% of the original hydrogen content with the first 40% of meltwater, the pH of the snow cover increased from 4.6 to 5.6. This result is in accordance with the results of other investigations cited above.

In principle, all organic micropollutants investigated show the same behaviour as the ions. They are also released mainly with the first 40% of meltwater. But the molecular ratios between the less soluble and the more water soluble contaminants (water solubility data: Table 1) increase during the melting. As an example the molecular ration Fa/ α -BHC is shown in Fig.1; it increases from 77 to 133 in the course of the melting. This indicates that the more water soluble pollutants are released more easily from the snow cover than the less water soluble; more hydrophobic micropollutants. Therefore with the first 40% of meltwater 60% of BghiP and BaP, 70% of Fa, 65% of γ -BHC and 80% of α -BHC molecules were released from the snowpack.

Knowing the water loss of the snow cover and the changes of the pollutant concentrations, it is possible to calculate the concentrations of pollutants in the meltwater. In Table 2 we relate these concentration values to the original concentration data

TABLE 2 Relative meltwater concentrations of snow constituents related to their concentrations in the snow cover at the beginning of the melting at station NF

Fraction of meltwater (%)	Calculated enrichment factors (underlined if ≥ 1):					
	H ⁺	BghiP	BaP	Fa	α -BHC	γ -BHC
0-20	<u>3.8</u>	<u>2.6</u>	<u>2.5</u>	<u>1.3</u>	<u>1.5</u>	<u>1.0</u>
20-40	<u>0.9</u>	<u>0.2</u>	<u>0.3</u>	<u>2.0</u>	<u>1.7</u>	<u>1.5</u>
40-60	0.3	0.9	0.7	<u>0.3</u>	0.1	0.9

of the snowpack at the beginning of the melt in order to obtain enrichment factors of the concentrations in the first fractions of meltwater. In the first 20% of the meltwater the hydrogen ion activity was 3.8 times higher than in the original snowpack. This is in accordance with the investigations of Johannesson & Henriksen (1978) who measured a 3 to 6 times enrichment of ions in the first meltwater fraction. However, the more hydrophobic PAHs (BghiP, BaP) were enriched only 2.5 times in the first 20% of meltwater. In contrast, the less hydrophobic organic contaminants are concentrated about 1.5 times in the first 40% of meltwater, showing a more continuous release.

The response of the karst spring The response of the karst spring due to the melting of snow and the rainstorm is shown in Fig.2. The meltwater caused a tenfold increase of the discharge of the karst spring. The sudden release of ions from the snowpack can be observed in the spring water by the increase of conductivity. At the same time the pH of the calcareous water decreased by 0.4 pH units, indicating the arrival of the meltwater enriched in hydrogen ions.

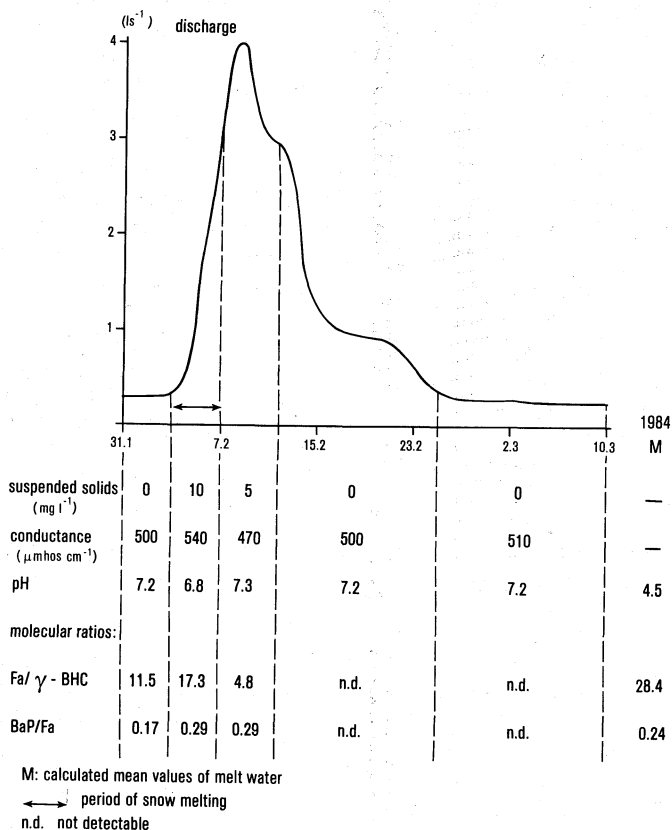


FIG.2 Mean parameter values for different discharge phases of the karst spring at station NF.

The discharge maximum is mainly due to the rainstorm which diluted the spring water from 500 to 470 μmhos cm⁻¹. In general the concentrations of organic micropollutants in this karst water are 125 times lower for PAHs and 25 times lower for BHCs than in the original meltwater. The decreasing molecular ratios of less water soluble to more water soluble substances between meltwater and spring water suggest that adsorption in the karst system happens preferentially to the less water soluble contaminants. With the occurrence of suspended solids in the spring water these ratios increase again, because in this case a large amount of less water soluble pollutants reach the karst spring adsorbed on suspended

particles.

Micropollutant balances Since there was no other precipitation input to this basin during the following weeks, we were able to observe the hydrograph recession to the initial low water level. Knowing the meltwater and precipitation input, it is possible to calculate input and output (spring water) loadings of micropollutants for this karst system by integrating the hydrograph (Simmleit & Herrmann, 1986).

As shown in Fig.3 the adsorption of the hydrophobic micropollutants in the karst system seems to be very high, because

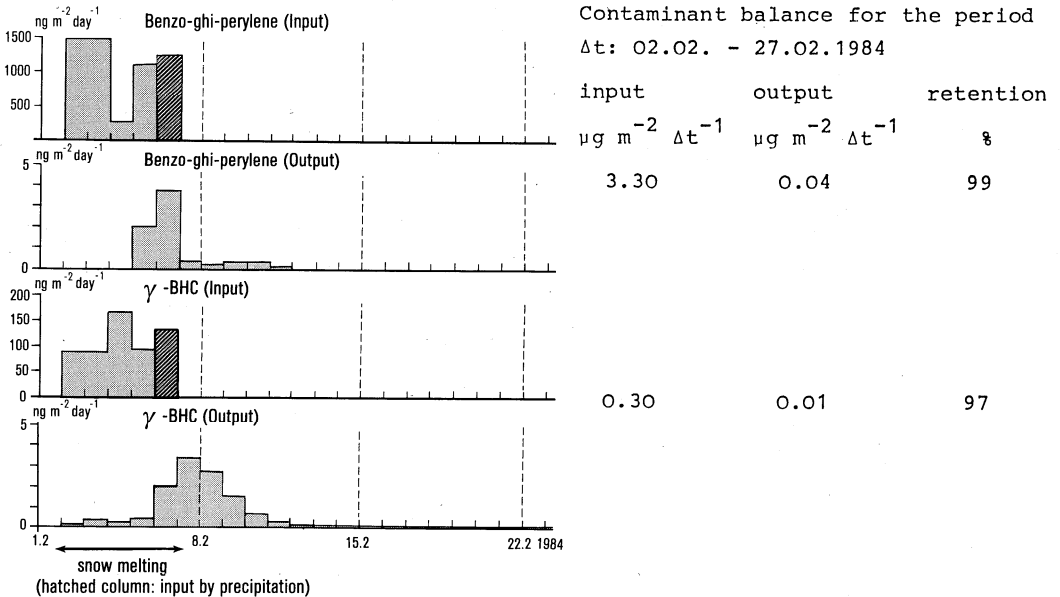


FIG.3 Daily loadings of selected micropollutants in a small karst basin during February 1984:

input: meltwater + precipitation (hatched) at station NF,

output: karst spring in the Leipoldstal.

only 1-3% of the total input reaches the karst spring. Despite the high retention, it is possible to observe the arrival of the PAHs together with the increase of suspended solids in the spring water. The more water soluble BHCs reach the spring independently from the suspended particles at highwater flow and can be detected a long time after the input has ceased, indicating a leaching effect.

The second melting event

The melting of snow The snow cover was due to snowfall at the end of February and the melting started at the beginning of March. The first period of melting lasted until further snowfall increased

the water content of the snow cover again. In this period 25% of the original water content was lost as meltwater (Fig.4). Again with this first meltwater 90% of the H^+ -ions (5.6 times enrichment in the meltwater), and 80% of the BHCs- as well as 50% of the PAHs-molecules were released from the snow cover, confirming the results of the first melting event. The molecular ratios of more hydrophobic to less hydrophobic organic compounds increased during this period (Fig.4).

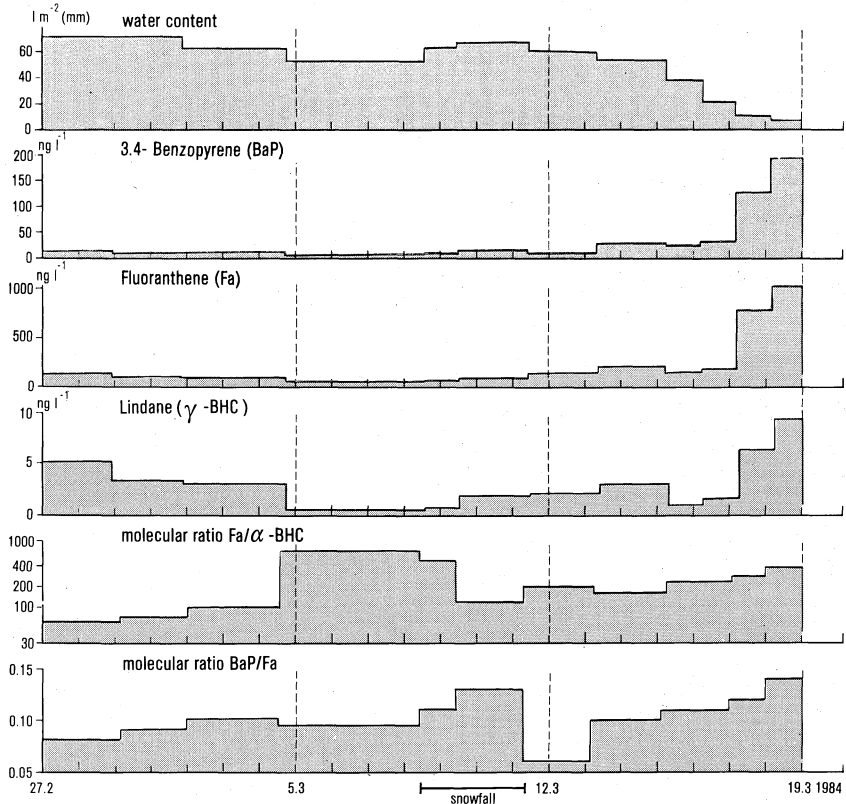


FIG.4 Variation of the chemical composition of the snow cover during melting from 29 February to 19 March 1984 at station VF.

New snowfalls increased the water content of the snowpack again and deposited additional airborne pollutants on the snow cover. Afterwards a rapid, final melting of snow began, which caused a compaction of the snowpack (snow density increased from 0.2 to 0.4 $g\ cm^{-3}$). During this period of melting the ratios between less water soluble and more water soluble organic pollutants increased slightly. However, in contrast to the first period the absolute concentrations of the organic constituents augmented, indicating that they were no longer continuously released with the meltwater. This resulted in a 3-4 fold accumulation of organic micropollutants in the last patch of snow existing which could not be explained only

by dry deposition onto the remnant snowpack. The ionic species were once more suddenly released from the snow cover with the first meltwater.

Response of the percolation water

After each of the two melting periods the dripping rate of the two percolation sites in the cave below the snow cover increased, with a delay of one to two days. However no organic micropollutants could be detected in this karst water. This can only be explained by the high adsorption of the contaminants in the soil layer. For this reason dripping stones cannot be used as natural lysimeters for the investigation of the behaviour of organic micropollutants in the karst system.

DISCUSSION

Johannesson & Henriksen (1978) supposed that snow crystals are formed in a relatively clean atmosphere. As they fall the crystals can scavenge aerosol particles and gases can be adsorbed on their surface. At the beginning of the snow melting process, water films are formed between the snow crystals in which the ions from the crystal surface can dissolve. For this reason a sudden release of ionic species can be observed in the first fraction of meltwater.

Atmospheric, hydrophobic contaminants are mainly adsorbed on aerosol particles smaller than 10 μm (Müller, 1984). First of all these particles can act as condensation nuclei during the formation of snow crystals. Secondly these particles are scavenged by falling snow flakes and thirdly they can be deposited directly on the snow cover by dry deposition processes (Ibrahim et al., 1983). Nothing is known about the micro-distribution of pollutants in snow crystals. But we can presume that the hydrophobic, airborne pollutants are concentrated in the centre of a snow flake due to adsorption on the condensation nuclei and on the surface of a snow flake due to the scavenging effect. Therefore at the same time as the sudden release of ions, hydrophobic compounds which are adsorbed on suspended aerosol particles in the water film between the snow crystals can be released. These particles can penetrate the snowpack because at the beginning of snowmelt macropores are formed (Marsh & Woo, 1984). However, as snowmelt continues the snow cover will consolidate and its density increase. With increasing snow density the permeability of the snowpack decreases (Colbeck & Anderson, 1982). Therefore it might be possible that no further transport of particles through the snowpack can occur, despite the loss of bulk snow during melting. This would result in an accumulation of micropollutants at the end of a lengthy melting period. It is probable that we could not observe this effect in our first melting event because this event was terminated prematurely by a rainstorm.

As far as the water solubility of the investigated micropollutants is concerned, slight differences in their behaviour can be detected between different compounds. PAHs show a sudden release with the first flush of meltwater containing the scavenged

aerosol particles and most of the H^+ -ions. In contrast, the less hydrophobic BHCs which are dissolved in meltwater to a larger extent show a more continuous leaching with the first 40% of meltwater.

In any case less than 3% of the organic micropollutant input reaches the groundwaters in carbonate terrains despite the high permeability of the karst systems. The organic contaminants are adsorbed on the top layer of the soils, as the analysis of soil material from the sampling sites showed (Simmleit & Herrmann, 1986). However, further research is needed to trace organic contaminants during the snowmelt and to detect their sinks in different environmental systems.

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