

## **Transport and Chemodynamics of Organic Micropollutants and Ions during Snowmelt**

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By means of laboratory experiments and field measurements we investigated the chemodynamics and transport behaviour of organic micropollutants and inorganic ions in melting snowpacks. Dissolved substances (e.g. ions) were released from the snowpack by convection and diffusion within the melt water. Substances which were adsorbed onto particles (e.g. PAH) were not desorbed to a significant degree. Moving particles were generally filtered out within the snowpack and, therefore, adsorbed substances were hardly leached by this way of transport. Frequent melt-freeze cycles and a deep snowpack lead to an enrichment of dissolved substances in the first melt water fractions and of substances adsorbed onto particles in the final fractions. A different macroscopic and microscopic spatial variation of ions within the snowpack results in different elution patterns during the snow melt. Since the PAH are predominantly adsorbed onto particles, approximately 90% of all PAH of a snow column were eluted with the last 20% of water during the snow melt. PAH with a high partition coefficient  $k_{ow}$  (e.g. benzo(a) pyrene, benzo(ghi)perylene) exhibited a stronger enrichment than fluoranthene with comparatively lower  $k_{ow}$ . Since the HCH isomers occur in dissolved as well as in adsorbed phase because of their low  $k_{ow}$  in melting snow, we observe an enrichment of the dissolved phase within the first fractions of melt water and of the adsorbed phase within the final fractions of melt water.

### **Introduction**

Snow contains a wide spectrum of pollutants, e.g. acid forming ions, free protons (Seip 1980), trace metals (Landsberger and Jervis 1985), and organic micropollut-

ants (Schrimppf *et al.* 1979), which all may be hazardous to the environment. These pollutants, which contaminate the snow originate from snowout and washout (Knutson *et al.* 1976, Junge 1977, Barrie 1985) and dry deposition (Gjessing 1977, Benarie and Munn 1980, Ibrahim *et al.* 1983). The pattern of snow contamination depends on nearby natural or anthropogenic sources or on long distance transport (Herrmann 1978, Bjørseth and Olufsen 1983).

Trace metals and ions, which have accumulated within the snowpack during winter, will be eluted with the first melt water fraction in spring (Johannessen *et al.* 1977, Johannessen and Henriksen 1978), thus causing an acid flush possibly followed by fish kill (Hagen 1973, Leivestad and Muniz 1976, Rosseland *et al.* 1986). These publications initiated intensive studies of preferential elution of ions out of melting snowpacks in recent time (Davies *et al.* 1982, Cadle and Muhlbaier Dasch 1984, Tsiouris *et al.* 1985, Brimblecombe *et al.* 1985, Tranter *et al.* 1986, Brimblecombe *et al.* 1986), the results of which reveal, e.g., that  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are washed out more quickly than  $\text{Cl}^-$ .

Studying the chemodynamics and transport behaviour of organic micropollutants during snow melt above karstic rocks, we (Simmleit *et al.* 1986) found some indications for preferential elution of nonpolar organic micropollutants as well.

The objective of this paper is to present and discuss controlled laboratory experiments and field work related to these experiments, by means of which we want to investigate the chemodynamics and transport of selected organic micropollutants during snow melt. In addition, we want to compare the behaviour of the organic micropollutants during the melting of a snowpack with the behaviour of the ions. We selected organic micropollutants with a wide range of physico-chemical properties (solubility, partition coefficient):  $\alpha$ - and  $\gamma$ -HCH, fluoranthene, 3,4-benzopyrene, benzo(ghi)perylene.

## Fundamentals

### Partition coefficients

We will discuss the partition coefficients  $k_d$  for ions

$$k_d = c_{si} c_{ei}^{-1}$$

$c_{si}$  – concentration of an ion in the solid phase (ice) at the interface between liquid and solid phase

$c_{ei}$  – concentration of an ion in the liquid phase (water), again at the interface

and  $k_{ow}$  for nonpolar organic micropollutants in an octanol/water mixture

$$k_{ow} = c_o c_w^{-1}$$

$c_o$  – concentration of an organic micropollutant in octanol

$c_w$  – concentration of an organic micropollutant in water.

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The coefficient  $k_d$  reflects the relative exclusion of ions out of the ice crystal during freezing. Because of this exclusion the concentration of the solutes will increase on the liquid side of the interface, which results in a concentration gradient in the water (Leung and Carmichael 1984). The solute weakens the bonds between the water molecules, increases the intermolecular distances and lowers the melting point temperature. Thus, the partition coefficient  $k_d$  is a measure for the distortion which the solute exerts on the crystal lattice of the ice. Hobbs (1974) reports for ions dissolved in water values of  $k_d \ll 1$ . For fluoride as the counterion, Gross (1968) found the following series of decreasing acceptance regarding ice:  $\text{NH}_4^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{H}^+$ .

However, dissolved organic compounds are equally and independently concentrated in the liquid phase during freezing; and finally suspended and not ionized organic substances are more strongly repulsed from ice than ions (Malo and Baker 1968). Thus, it is possible to enrich dissolved  $\gamma$ -HCH (Kammerer and Lee 1969) and polycyclic aromatic hydrocarbons (e.g. 3.4-benzopyrene, benzo(ghi)perylene or fluoranthene) in water by freezing.

Since organic micropollutants with high partition coefficients  $k_{ow}$  tend to be relatively enriched on particles suspended in water, and since, below a definite freezing rate, the progressing ice/water-interface is able to push these particles back into the liquid phase, these organic micropollutants will be further enriched on the waterside (Uhlmann *et al.* 1964). After a freezing and melting cycle, Nakamura and Okada (1976 a and b) observed that great coagulates ( $d = 50\text{-}600 \mu\text{m}$ ) had been formed from originally dispersed particles ( $d = 0.8\text{-}1.5 \mu\text{m}$ ). They put down this formation of coagulates to a decrease of space of the liquid phase between growing ice crystals which enabled van-der-Waal forces to act on the dispersed particles.

### Metamorphosis of Snow

After deposition the snowflakes change their form and become rounded as their grain size decreases and the density increases. De Quervain (1963) subdivided this process into a destructive metamorphosis which is caused by redistribution of snow material because of a thermodynamic instability of the crystal surfaces, a constructive metamorphosis which is caused by water vapour transport within the snowpack along temperature gradients and finally a melting/freezing metamorphosis.

Small ice particles exist at a lower equilibrium temperature than large ice particles. Thus heat flows from the large particles and rapidly melts the small particles. The result is the disappearance of the small particles and the subsequent growth of the medium and large particles. Within the funicular saturation regime (water saturation exceeds 14 per cent of the pore volume and the air occurs in discrete bubbles trapped between the ice particles) the growth of large crystals at the

expense of small ones is supported by a better heat conduction. At low water content the temperature differences between particles are reduced as well as the area of heat flow, and much lower rates of grain growth are observed (Colbeck 1975).

These processes change and subsequently reduce the surfaces of the snowflakes. The pollutants in the snow freeze out partly and are concentrated in dissolved or particulate phase within the liquid-like layer (Kuroiwa 1975) on the surface (Colbeck 1981). Then, the first melt water is able to carry off most of the dissolved pollutants.

### **Flow of Melt Water**

Colbeck (1978) and Wankiewicz (1979) comprehensively studied the melting of snow of different structures under a wide range of meteorological conditions, and they provided mathematical models of the physical processes of melting. Therefore, at this place, we only want to point out that because of the exponential increase of the permeability from an unsaturated to a saturated snowpack, increasing melt rates e.g. during sunrise cause higher flow velocities. Thus, in the morning, snow melts from the upper surface and the melt water percolates down the snow pack. Later during the day intense melt catches up with the early melt water and forms a so-called shock front. This front absorbs available ions so that with increasing snow depth the concentration of ions also increases (Marsh and Webb 1979, Supatashvili 1981).

Once contained within the percolating water, soluble impurities are transported with the melt water, but are also subjected to molecular diffusion and mechanical dispersion. In addition the percolation is not completely uniform as some impurities may be bypassed and only be picked up by subsequent flow. These transport characteristics cause the typical melt curves of ions (e.g. Fig. 2 and Hibberd 1984).

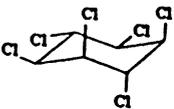
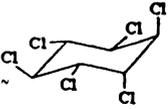
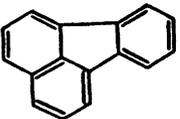
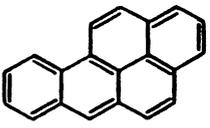
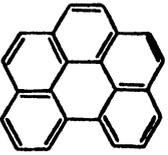
### **Physico-Chemical Properties of Selected Organic Micropollutants**

We studied the chemodynamics and transport behaviour of three different polycyclic aromatic hydrocarbons (PAH) and two isomers of HCH (hexachlorocyclohexane) which cover a wide range of solubilities and partition coefficients (Table 1).

Organic micropollutants with a high solubility in water are readily taken away with the melt water front whereas those with a high partition coefficient ( $k_{ow}$ ) which are adsorbed on particulate material, stay behind with that material in the snowpack. However, all of the selected hydrophobic organic micropollutants may be incorporated in micelles of dissolved organic substances (given as DOC). This is

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Table 1 - Physico-chemical properties of selected organic micropollutants.

	structural formula	molar mass g mol <sup>-1</sup>	solubility in water mg l <sup>-1</sup>	a) log k <sub>ow</sub>
γ-HCH		292	6 <sup>d)</sup>	4.1 <sup>e)</sup>
α-HCH		292	1.5 <sup>d)</sup>	3.6 <sup>f)</sup> - 4.1
Flour-anthene		202	0.20 <sup>b)</sup>	5.22 <sup>c)</sup>
Benzo(a)-pyrene		252	3.8 × 10 <sup>-3</sup> <sup>b)</sup>	6.5 <sup>c)</sup>
Benzo(ghi)-perylene		276	0.3 × 10 <sup>-3</sup> <sup>b)</sup>	7.10 <sup>c)</sup>

a) Octanol/water partition coefficient

b) Mackay and Shui (1977)

c) Walters and Luthy (1984)

d) Eichler (1983)

e) Korte (1980)

f) Kuntz and Warry (1983)

a process by which the solubility of trace organics can be increased. The solubility of hydrophobic organic micropollutants in water decreases considerably with decreasing temperature (May *et al.* 1978). Thus, at lower temperatures, a greater part of the organic micropollutants occurs in the adsorbed phase than at higher temperatures (Herbes 1977).

## **Laboratory and Field Experiments**

### **Laboratory experiments**

The main part of our laboratory experimental set up consisted of a double walled ( $d_o = 200$  mm,  $d_i = 144$  mm,  $h = 1045$  mm) glass cylinder (Fig. 1). We were able to control the snow temperature by passing a coolant through the double wall and induce melt/freeze cycles by appropriate radiation treatments. We used light bulbs as energy source which had a maximum emission within the infrared. Since the spectral albedo of snow decreases throughout the near infrared, the radiation of the lamps was for the most part absorbed. Further we thus avoided possible photochemical reactions of HCH and PAH which may occur in the ultraviolet. We controlled the melt rate by adjustment of the lamps and changing the number of lamps.

In order to observe the progression of the shock front and the melt process, we inserted tensiometers through sleeves into the snow column.

We constructed the snow tensiometers according to an advice given by Wankiewicz and De Vries (1978). The melt water passed a pH- and an electric conductivity-electrode which were placed below the snow column. By means of these electrodes and a balance which weighed the percolating melt water, we were able to continuously record pH, electric conductivity and melt water without disturbing the flow. Further, we were able to collect melt water samples for chemical analyses from below the column. We did not take melt water from the snow column before it reached the bottom. However, at the end of the second experiment we also took samples from the column.

With the exception of our 3rd laboratory experiment, the snow filled into the cylinder had the properties of a strongly metamorphosed, isotherm snow of spring-time. We collected the snow in March 1985 and January/February 1986 in the Fichtelgebirge (NE Bavaria) from homogeneous snow layers. This homogeneity was improved by mixing and controlled by measuring the electric conductivity and the turbidity. The mixing of snow resulted in a slightly higher density than that of the undisturbed snow.

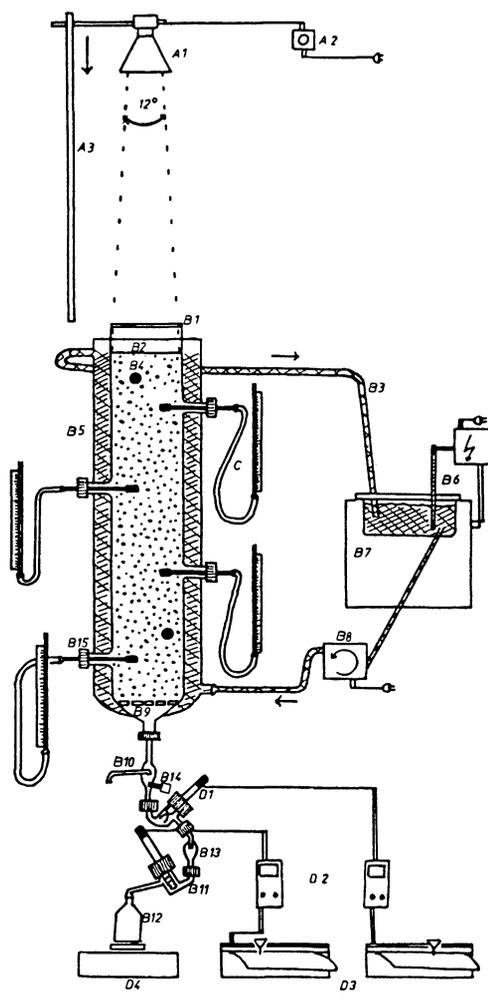
### **Field experiments**

By means of a snow lysimeter made out of plywood covered with aluminium foil, we collected melt water fractions, which were analyzed in the same way as those of the laboratory experiments.

### **Chemical analyses**

PAH and HCH isomers were liquid-liquid extracted from water with two additions of hexane (fraction I). This fraction, combined with a third extraction with dichloromethane, resulted in fraction II. HCH isomers were separated by capillary GC and detected by means of an ECD out of fraction I. PAH were separated by

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- A 1: radiation source  
(Phillips PAR 38, Economy,  
Spot 12°, 120 or 150 W)
- A 2: light control
- A 3: lamp support
- B 1: opening with glass cover
- B 2: snow surface
- B 3: PVC cooling-water hose
- B 4: sleeves for thermometers  $h \equiv$   
97 cm and 27 cm above the  
bottom
- B 5: jacket ( $\Delta W \equiv 2.8$  cm)
- B 6: temperature control unit  
( $\Delta \delta \equiv \pm 0.3^\circ\text{C}$ )
- B 7: cooler (Edwards)
- B 8: pump
- B 9: support plate ( $d \equiv 10$  cm,  
pore width  $\equiv 1.4$  mm, glass)
- B 10: outlet for discontinuous  
sampling
- B 11: continuous-flow vessel
- B 12: flask
- B 13: trickling vessel
- B 14: stopcock (Teflon)
- B 15: sleeves for tensiometers
- C : tensiometers
- D 1: electrodes
- D 2: amplifier
- D 3: chart recorder
- D 4: recording balance  
(Mettler PC 3300)

Fig. 1. Experimental set up in the laboratory, not to scale, column material: glass

HPTLC and detected by fluorescence spectrometry (Herrmann 1978) out of fraction II. The mean recovery rates were 90% for HCH and 85% for PAH, the detection limits  $c_{dl}$  (HCH) = 0.03 ng l<sup>-1</sup> and  $c_{dl}$  (PAH) = 0.15 ng l<sup>-1</sup>.

The concentrations of the anions were determined by ionchromatography. We measured the concentrations of alkaline earth metals and alkali metals by flame photometry and atomic absorption spectrophotometry. Finally, NH<sub>4</sub><sup>+</sup> was analyzed direct potentiometrically with a pNH<sub>3</sub> combined electrode (Orion, model 95-10).

In order to obtain a measure for adsorptive properties of melt water, we measured the extinction at  $\lambda = 420$  nm and 530 nm.

**Results and Discussion of Laboratory Experiments**

We will discuss the results of three experiments, the melting conditions of which are given in Table 2.

Table 2 – Melting conditions of laboratory experiments.

Experiment	I	II	III (s. Fig. 5)
State of metamorphosis	old snow, coarse snow particles	old snow, coarse snow particles	freshly deposited snow, hexagonal crystal structures (in the upper half of the snow core) fine-coarse granular snow (in the lower half)
Hight of snowpack (cm)	101	100	46
Density at beginning of melting ( $\text{g cm}^{-3}$ )	0.46	0.46	0.16 (average)
Mean melting rate ( $\text{mm h}^{-1}$ )	6.8	12.2	3.9
Comments		refreezing when the melt water front reached the lower third of the column	undisturbed column

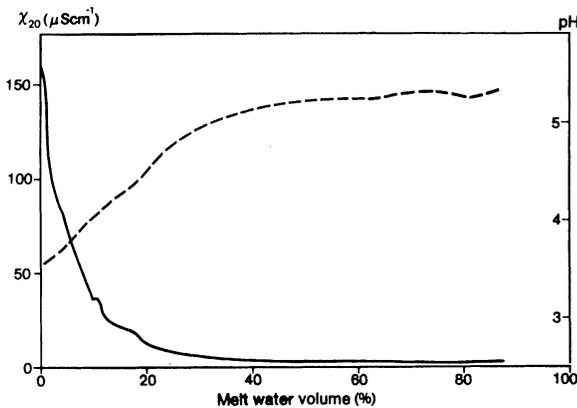


Fig. 2.  
Specific conductivity  $\chi_{20}$  (—) and pH (---) as a function of cumulative melt water flow.

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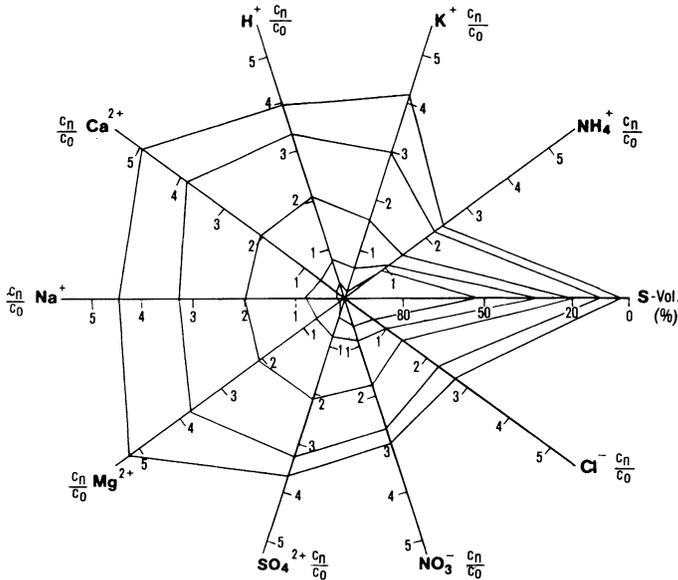


Fig. 3. Concentration ratios  $c_n/c_0$  of ions as a function of cumulative melt water flow ( $c_0$  = mean concentration of ions in snow before melting started,  $c_n$  = concentration related to the sum of percolated melt water, S-Vol. (%) = cumulative melt water flow), first experiment. Note: The cumulative volume of melt water (S-Vol. (%)) increases towards the mid of the diagram whereas the factors of concentration decrease.

### Elution of inorganic ions out of melting snow

By means of Figs. 2 and 3 we present the concentration of ions and the electric conductivity as a function of the drained melt water. The exponential drop of ion concentration in the melt water can be explained by the physical chemical processes during snow melt.

Following Gross (1968) we interpret the significantly slower elution of  $\text{NH}_4^+$  by the relatively higher partition coefficient which hinders strong enrichment of this ion within the liquid-like layer on the surface of the solid phase during snow metamorphosis. Contrary to chemicals which are washed out of the atmosphere,  $\text{Cl}^-$  is primarily incorporated in the crystals as condensation nucleus originating from sea spray. Thus,  $\text{Cl}^-$  and  $\text{NH}_4^+$  are enriched to a lesser degree than other ions within the liquid-like layer which results in a comparatively slower elution during snow melt. In contrast to maritime snow where  $\text{Cl}^-$  is also contained within the crystals,  $\text{Cl}^-$  elutes rapidly from continental snow where it is merely adsorbed on the crystal surface or solved within the liquid-like layer during wash out (e.g. in the USSR, Supatashvili 1981). The partition coefficients  $k_d$  of  $\text{Cl}^-$  and other anions are not known. However,  $k_d(\text{Cl}^-)$  should be lower than  $k_d(\text{F}^-)$  because  $k_d(\text{NH}_4\text{F}) > k_d(\text{NH}_4\text{Cl})$ .

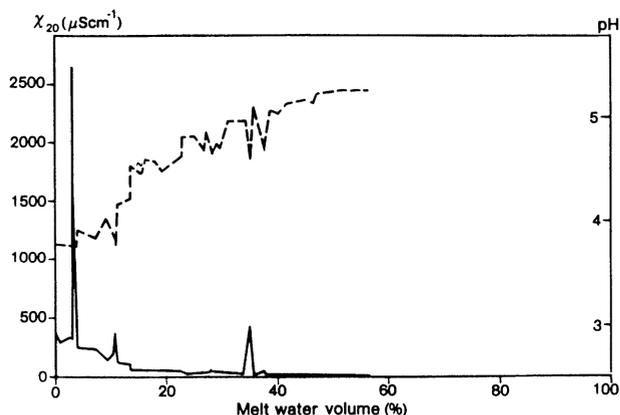


Fig. 4.  
Specific conductivity  $\chi_{20}$  (—) and pH (---) as a function of cumulative melt water flow second experiment.

In other field and laboratory experiments we could observe that during freezing cycles melt water was impounded above thin water tight ice layers. After melting of these layers short waves of melt water, enriched with ions (Fig. 4) passed the snow column. Within the first melt water of the third experiment we observed by far the lowest enrichment of ions. The ions were eluted irregularly. This might be explained by a low degree of metamorphosis, a low snow depth and the laminated structure of the snow pack which also favoured the formation of more or less vertical macropores. Thus, the ions on the crystals away from these macropores were not eluted. Since the melting process in this case is vertically and horizontally differentiated, an irregular elution of ions is the result.

#### Elution of organic micropollutants out of melting snow

In Fig. 5 we display the physical structure and the concentration of ions, extinction, and some organic micropollutants in an undisturbed snow core. The following Figs. 6 and 7 present the temporal variation of the concentration of trace organics in melt water. We ask the reader to notice that the second laboratory experiment (Fig. 7) was stopped when the column had shrunk to a height of  $h = 23$  cm. This column was divided into three parts (A: light top column with a few coarse particles on top; B: dense dark snow in the middle; C: clear densely packed layer of ice grains) and analysed as was the melt water.

The transport behaviour of nonpolar organic micropollutants follows clear rules which can be best observed during melting of homogenous deep snow columns (cf. Figs. 6 and 7):

- We find high concentrations of the HCH isomers in the first and the final melt water fractions. The melt water draining in between contains nearly no HCH.
- More than 90 % of the mass of PAH remains in the snow column and will only be released with final melt water, thus leading to high PAH concentrations.
- The extinction is slightly higher in the first draining melt water than in the

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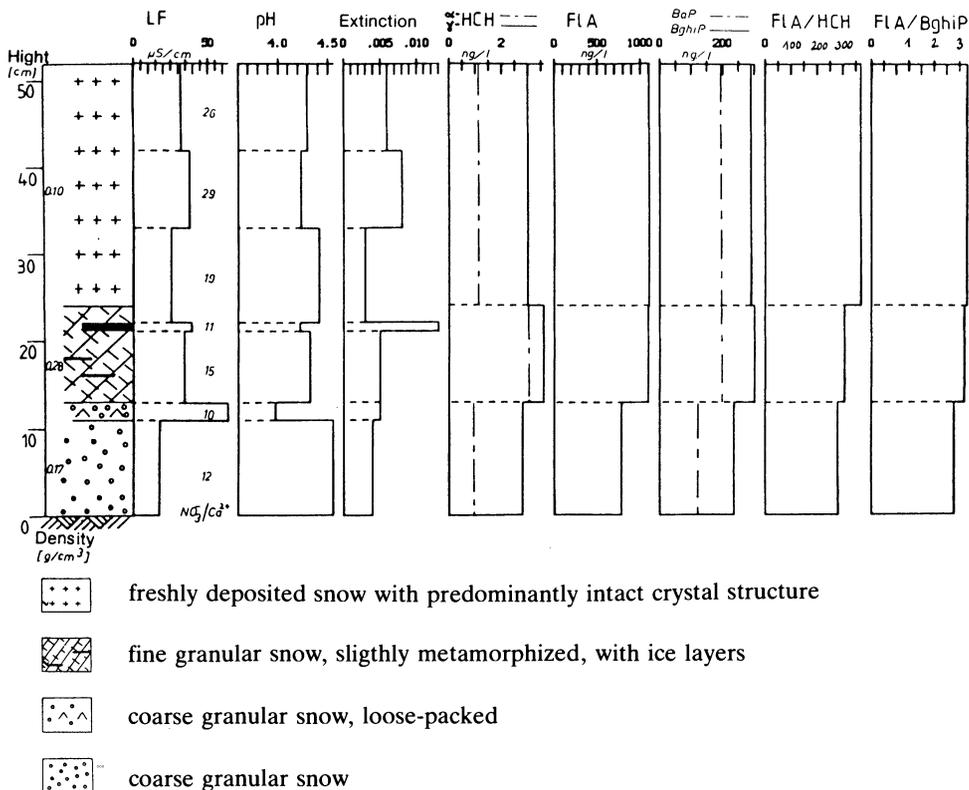


Fig. 5. Snow structure and vertical distribution of  $\kappa_{20}$  (LF), pH, extinction and concentrations of organic micropollutants as found in the field. The upper 6 cm of snow were discarded before the experiment began (third experiment).

following fractions. However, we observe a significant increase of extinction in the final fraction.

- Fluoranthene is enriched in respect to  $\gamma$ -HCH within the snow column during snow melt. The reverse is true in respect to benzo(ghi)perylene. Note that the maximum of this ratio appears when 20% of the melt water has drained.

Though snow matrix and melt conditions of the third experiment differ from those of the first and second experiment, and clearly influence the elution of ions, our above observations are equally confirmed in the third experiment.

The differences in transport behaviour of the organic micropollutants can be attributed to their physical-chemical properties, first of all to their solubilities and their partition coefficients (Table 1): At the low temperature  $\delta = 0^\circ\text{C}$  of melt water the higher ring PAH (e.g. benzo(a)pyrene, benzo(ghi)perylene) are predominantly adsorbed onto particles. Thus, their transport is governed by the transport of

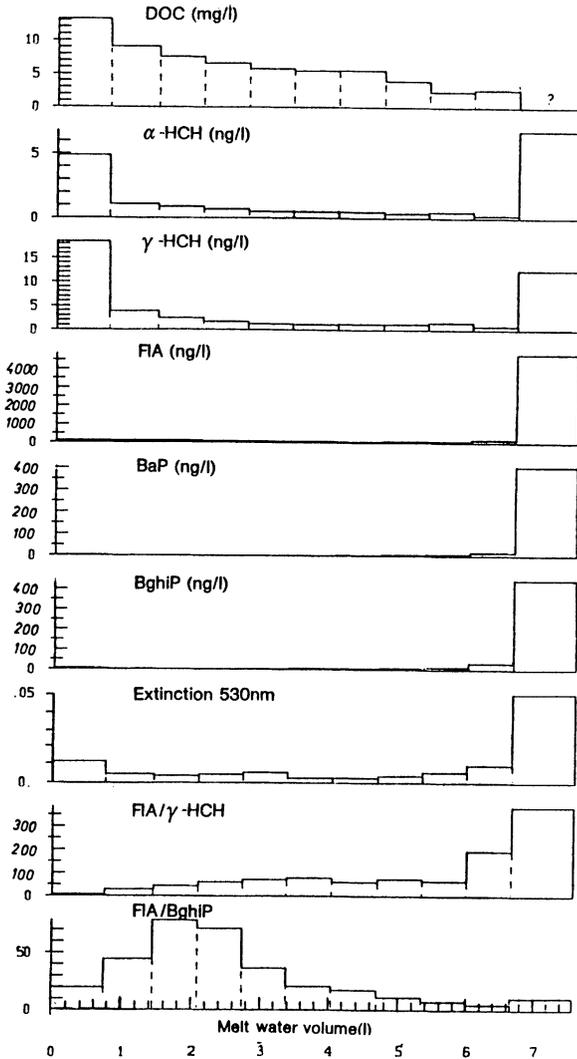
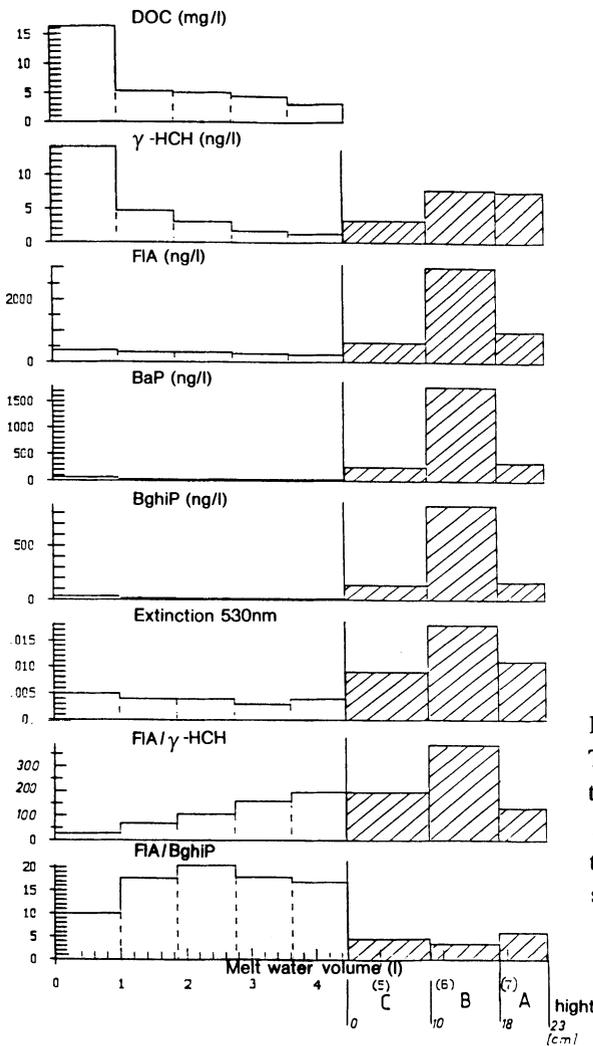


Fig. 6. Temporal variation of the concentration of organic micropollutants, DOC, extinction and concentration ratios during a melting process, first experiment.

particles within a melting snow column. We point to the high correlation between the extinction and the concentration of benzo(a)pyrene and benzo(ghi)perylene (Figs. 6 and 7).

The temporal variation of the concentration ratio fluoranthene/benzo(ghi)perylene in melting snow increases after an initial drainage of benzo(ghi)perylene adsorbed on particulate matter had diminished, and the higher proportion of dissolved fluoranthene leads to a higher ratio. Benzo(ghi)perylene is stronger adsorbed onto particles than fluoranthene. At the beginning of the melt experiments a relatively high amount of benzo(ghi)perylene adsorbed onto particles was washed out of the snow column. With increasing coagulation of particles retained

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**Fig. 7.** Temporal variation of the concentration of organic micropollutants, DOC, extinction and concentration ratios during a melting process, second experiment.

within the snow column, with decreasing permeability of the snow, and with an increase of the filter capacity by clogging particles within the capillary fringe above the bottom of the snow column, the flux of particle-bound benzo(ghi)perylene declines greatly and fluoranthene with a higher solubility is relatively more eluted. The decrease of the ratio at the end of the melt process might be explained as follows:

- dissolved fluoranthene is increasingly washed away from pore water and the surfaces of crystals, due to the rules that dissolved matter drains first in melting snow

- the transfer of fluoranthene from particulate matter into the surrounding melt water decreases since the portion of stronger bound fluoranthene (chemisorption and inclusion into coagulates) increases and, corresponding to the adsorption isotherms, less fluoranthene could be dissolved.
- The concentration of particulate matter with adsorbed benzo(ghi)perylene increased towards the end of the melting process.

We should expect an inverse temporal variation of the ratio fluoranthene/ $\gamma$ -HCH compared with that of fluoranthene/benzo(ghi)perylene. However, because of the relatively high portion of dissolved  $\gamma$ -HCH of the total HCH, the ratio reaches its peak only at the end of the melting process.

The HCH-isomers (Figs. 6 and 7) however, show a distinct ambivalence of their transport behaviour in a melting snow column: on the one hand they are washed away by percolating melt water from crystal surfaces, out of pore water and from surfaces of particles in truly dissolved phase or by the association with DOC, on the other hand they are enclosed into coagulates of smaller particles or are adsorbed on particulates which remained on the snow surface, and thus are concentrated in the final melt water. This behaviour explains the even distribution – contrary to the PAH – of HCH in the surface of the remaining snow column (Fig. 7, A) and above the impounding ice layer (Fig. 7, B).

The cumulative elution of ions and organic micropollutants related to the cumulative melt water flow clearly confirms the different transport behaviour of the selected substances (Fig. 8).

#### Field measurements of organic micropollutants in snow

In March 1986, seven days after the beginning of a melting period, along a wall of a highly metamorphized and partly wet snowpack (Figs. 9 and 10) we measured the concentrations of selected organic micropollutants. Correlating with the extinction, the HCH isomers show a higher concentration in the upper snow column than in

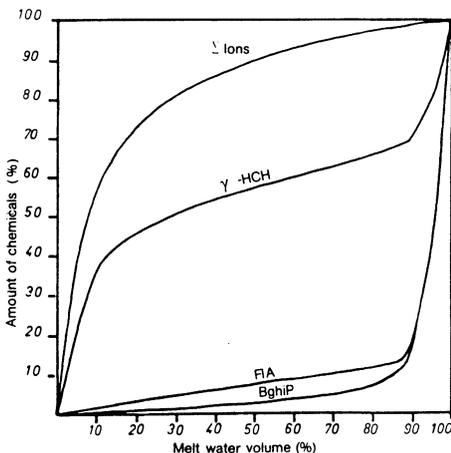


Fig. 8. Cumulative elution of ions and organic micropollutants as a function of cumulative melt water flow.

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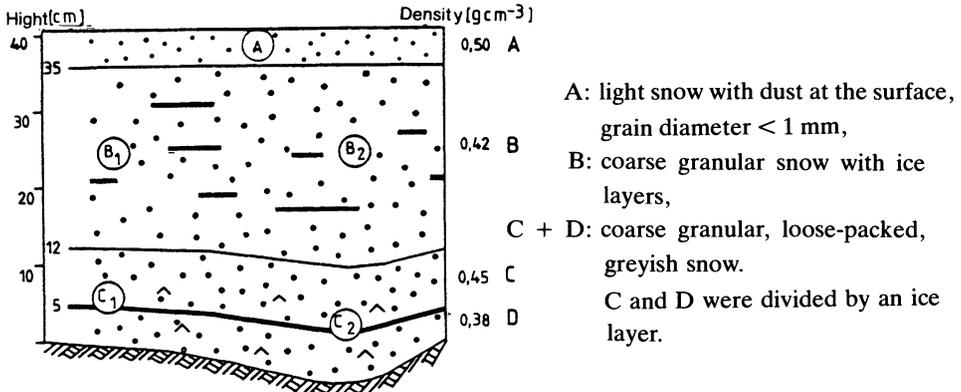


Fig. 9. Cross section of a snow pit. Positions of snow sampling are shown by A to C<sub>2</sub> (March 1986, Fichtelgebirge)

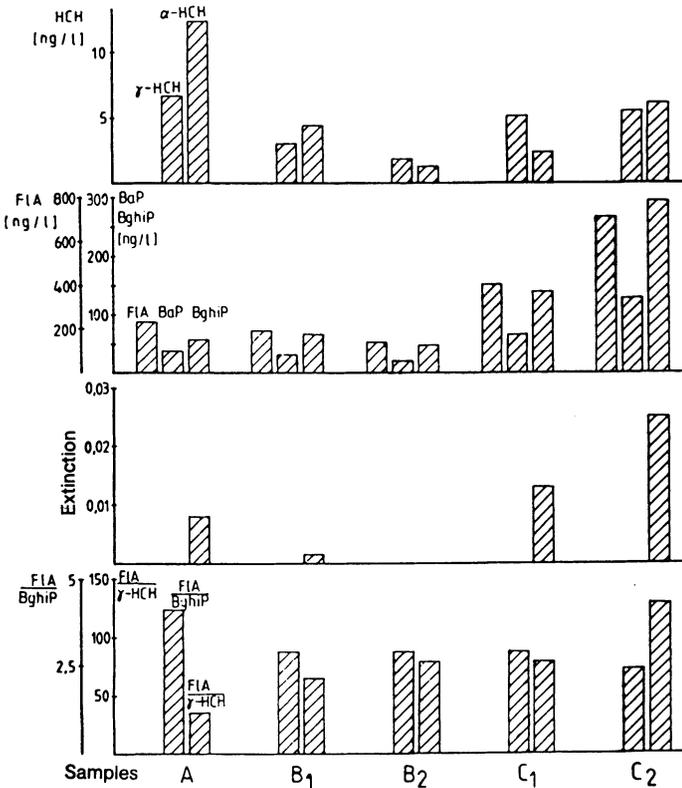


Fig. 10. Concentrations and concentration ratios of organic micropollutants in the cross section shown in Fig. 9.

the lower one. The PAH exhibit a reversed distribution pattern. We explain this behaviour by a stronger desorption of HCH from particulate matter in the lower snow column. Further, PAH with higher  $k_{ow}$  are relatively more enriched in the lower snow column than in the upper one. The retarding influence of the partition

coefficient on the distribution pattern is also clearly exhibited by the relation of fluoranthene to  $\gamma$ -HCH. During snow melt particulate matter is concentrated in the lower snow column by different physical processes (e.g. coagulation, transport by melt water flow along ice boundaries, velocity divergence, increasing filter capacity by accumulated particulate matter (O'Melia 1980), thus hydrophobic trace organics are accumulated in this lower zone.

#### **Transport behaviour of ions and organic micropollutants in a shallow snowpack**

In Fig. 11 we present the temporal variation of pH, electric conductivity and concentration of organic micropollutants during a rain-induced melt process of a shallow ripe snowpack ( $h = 10$  cm) near Bayreuth. The rain easily percolated through the snow column. Thus, the concentration of inorganic ions was diluted by a rain of low ion concentration. At the same time warm rainwater enlarged the pores and was able to flush fine particles from surfaces through the snow column. Hoekstra and Miller (1967) indicate that under these conditions particles can also be removed out of the ice. In addition to organic trace pollutants adsorbed on particles, dissolved trace organics from the liquid surface layer of the crystals can also be washed out. Baker (1969) found that contaminants on surfaces of ice blocks, which were formed after freezing of contaminated water, can be washed off by water. This process explained by Baker (1969) and a dissolution of organic matter from the particles may explain the response of DOC to the rainfall. Thus, the final melt water fraction did not show a higher concentration of organic micropollutants compared to the preceding fractions as was the case in deep melting snow.

High air temperatures, cloud cover, melting during the night, wind and rain exclude the formation of a melt water front, which causes a first flush of melt water with a high concentration of ions. In a shallow snow pack, of course, higher concentrations of ions in first melt water cannot develop.

#### **Conclusion**

Under the climatic conditions of Central Europe two extreme types of processes of snow melt mark the range of transport behaviour of ions and trace organics in melting snow:

- Shallow snowpacks in low altitudes predominantly melt already during the winter at times with rainfall. Under these conditions particles within the snow, which carry organic micropollutants, dependent on their partition coefficients, are washed out by percolating rainwater. Further, we also observe a more equal elution of dissolved trace organics and ions compared with the elution of these substances in deep snowpacks.

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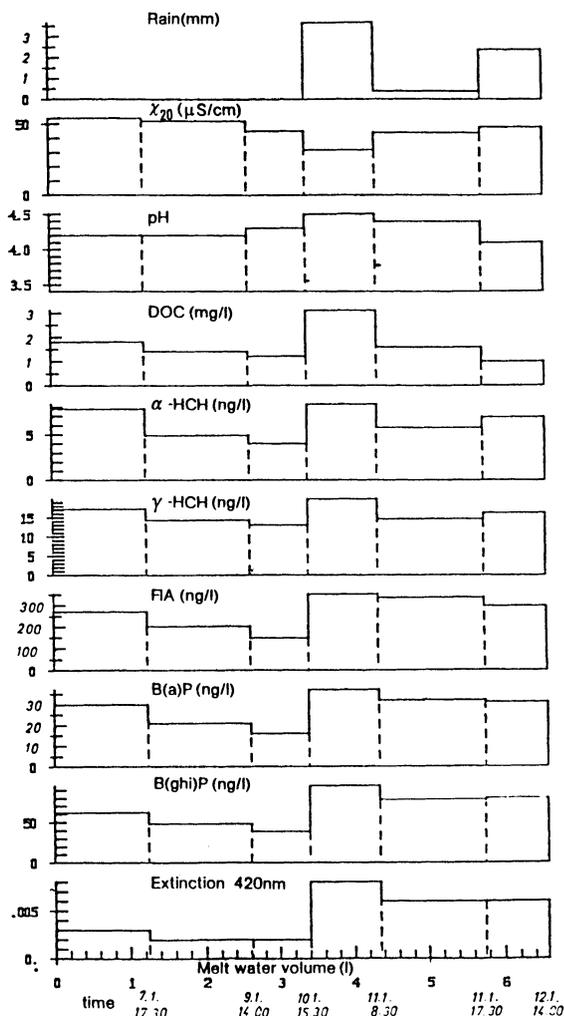


Fig. 11. Temporal variation of electric conductivity, pH, extinction, DOC and concentration of organic micropollutants during a rain induced snow melt of a shallow snow-pack.

- Deep snowpacks in higher altitudes generally melt in spring under the influence of strong radiation with frequent thaw and freeze cycles. This type of melt process is of great ecological importance since the pollutants which accumulate during winter, e.g. by long distance transport, are released in form of two shock waves at the beginning (dissolved pollutants) and at the end (adsorbed ones on particles). Further, in deep snowpacks the snow structure (e.g. ice layers and pipes) has an additional influence on the spatial and temporal distribution of organic micropollutants and ions.

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