THE BEHAVIOR OF HYDROPHOBIC, ORGANIC MICROPOLLUTANTS IN DIFFERENT KARST WATER SYSTEMS

I. *Transport of Micropollutants and Contaminant Balances during the Melting of Snow*

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Abstract. During and after the melting of snow, Karst groundwater of an agriculturally used and a wooded catchment area situated on a Dolomite plateau in Upper Franconia (F.R.G.) were investigated. Seventeen hydrochemical and hydraulic parameters were analyzed in the Karst water of two different springs in the course of the snow melting. Hydrograph analysis and the temporal variation of chloride concentrations were used to distinguish different types of Karst waters reaching the spring. Polycyclic aromatic hydrocarbons (benzo(a)pyrene, fluoranthene, benzo(ghi)perylene) and chlorinated pesticides (α-BHC, lindane) are transported in Karst waters adsorbed on suspended solids, dissolved in water and adsorbed on dissolved humic material. Most of the organic contaminants reach the groundwater level with conduit and trickle water. However, BHC-molecules also arrive at the spring with seepage water three weeks after the meltwater input. Using Karst springs as natural lysimeters for their catchment areas, pollutant input-output balances were calculated for PAHs and BHCs revealing that 87.5 to 99.7% of the atmospheric micropollutants released from the snow cover are retained in the Karst system. Potential pollutant sinks are proposed and discussed.

1. Introduction

Carbonate and Dolomite rocks which are susceptible to karstification form 4% of the geological bedrock of all continents (Europe 13.5%). In these terrains the hydrogeology is determined by the high secondary permeability of the karstic carbonate and dolomitic strata, which is responsible for short residence times of the Karst waters (Milanović, 1981). In addition, the high hydraulic conductivity of ambient soils causes fast percolation of soil water (Simpson and Cunningham, 1982). Therefore, Karst groundwaters are very susceptible to any kind of pollution (Atkinson, 1971; LeGrand, 1973; Maire, 1979). Being aware of the potential dangers, it is surprising that only a few studies deal with the pollution of Karst aquifers by inorganic contaminants (Adamek and Rauser, 1977; Murray *et al.*, 1981; Schrimpff, 1984) and their self-purification capacity (Preka, 1975).

In ealier times it was assumed that organic pollutants like pesticides can never reach the groundwater because of adsorption on organic soil material (Beran and Guth, 1965). However, other studies *in situ* demonstrated that hydrophobic micropollutants can also be transported in macropores (Thomas and Phillips, 1979) and crevices of soils (Bierl

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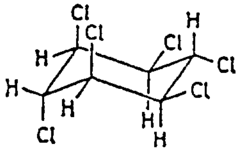
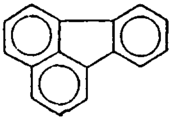
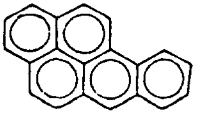
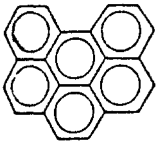
et al., 1984) and thus contaminate groundwater resources. It is known from soils of carbonate terrains that most of the soil water percolates rapidly in vertical flow channels (Simpson and Cunningham, 1978; Aley, 1977). Therefore Karst groundwaters can be substantially contaminated by organic contaminants due to a point source of pollution in a doline (Ruhe *et al.*, 1980). In contrast to that Schrimpff (1984) found low concentrations of polycyclic aromatic hydrocarbons (PAH) and chlorinated pesticides especially in waters of Karst aquifers under the influence of the same non-point contamination by wet and dry deposition. Unfortunately no other publications deal with the pollution of Karst waters by organic contaminants. For future assessments of drinking water quality in Karst areas, however, it is necessary to know more about input and behavior of organic micropollutants in Karst water systems (Yevjevich, 1981).

This study deals with the water quality of groundwater in a relatively nonpolluted Karst area and looks into the impact of deposition of air-borne organic contaminants. In this first section the aim was to investigate the behavior of organic micropollutants in different Karst systems during the melting of snow. By establishing pollutant input-output balances, the filtration capacity of Karst systems was to be deduced.

TABLE I

Organic micropollutants investigated

Compound	Structure	Molecular weight	Water solubility (25 °C, μmol L^{-1})
BHC		292	γ-BHC 24[a] α-BHC 10[b]
Fa		202	1.3[c] 5 °C 0.35[c]
BaP		252	0.015[d]
BghiP		276	0.00094[d]

[a] Industrieverband Pflanzenschutz (1982).

[b] Oehme and Manø (1984).

[c] May and Wasik (1978).

[d] McKay and Shiu (1977).

Three PAHs, benzo(a)pyrene (BaP), fluoranthene (Fa), and benzo(ghi)perylene (BghiP) as well as the α- and γ-isomer of hexachlorocyclohexane (BHC) were chosen as model substances (Table I). The PAHs are cancerogenic, relatively stable by-products of combustion processes and are found in every compartment of the environment (Neff, 1979; Edwards, 1983). Lindane (γ-BHC) was applied seasonally in North-East-Bavaria (F.R.G.) as a pesticide for combatting the bark beetle populations in forests. In the past both groups of chemicals were detected in the precipitation of the research area throughout the year (Herrmann, 1978; Schrimpff *et al.*, 1979; Thomas, 1981).

2. Materials and Methods

2.1. SAMPLING SITES AND SAMPLING PERIOD

Most of the hydrogeological data of the Karst terrain in Upper Franconia (F.R.G.) were collected from the Wiesentalb 40 km SW of Bayreuth, North-East-Bavaria (Kanz *et al.*, 1978). A simplified hydrogeological profile of the Wiesentalb is shown in Figure 1. The ambient Karst water resources are stored above water impermeable strata of clay or marl in the carbonate strata and former dolomite reefs of the Malm (Streit, 1971). Previously the hydrochemistry and hydrology of 30 springs which drain the Wiesentalb were investigated by Walayati (1978). Using the available hydrogeological and hydrochemical data, two perennial springs were selected for this study (Figure 1).

The contact spring in the Leipoldstal drains a small, woody watershed which is classified as a shallow Karst system (Apel, 1971), because the impervious layer is situated above the niveau of the River Leinleiter. This spring is only fed by the

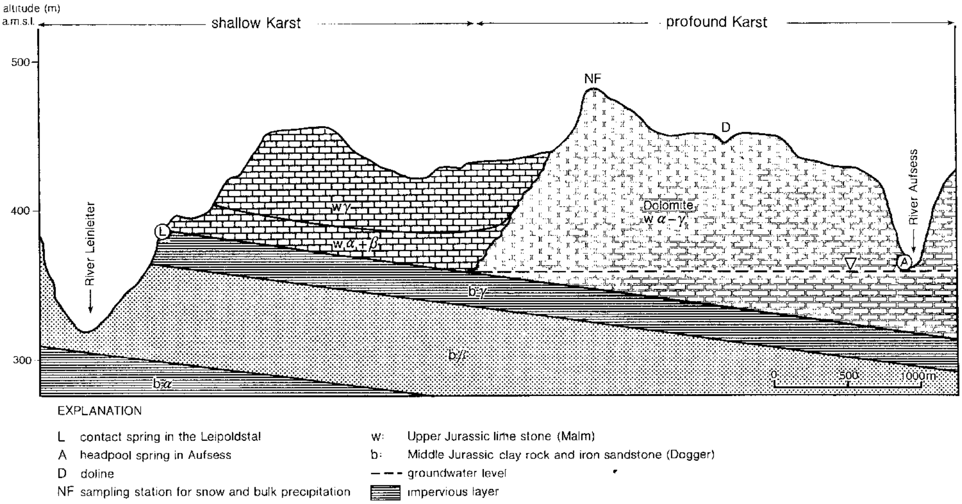


Fig. 1. Hydrogeological scheme of the Wiesentalb (F.R.G.).

percolating water of the vadose zone. The headpool spring in Aufsess drains a partly agriculturally used drainage area and is fed mainly by water from the phreatic zone. However, there is a direct connection between the spring and a doline (Figure 1) which causes high water flows within 24 hr after rainfalls due to conduit flow. Following Apel (1971) this Karst system is classified as the external zone of the profound Karst.

During February and March 1984 discharge (*Q*) was measured and water samples were taken from these springs in daily intervals and in hourly intervals during highwater flow.

During January snowfall caused a 24 cm high snow cover on the Wiesentalb. In February the air temperature rose above 0 °C and the snow began to melt. Then, in daily intervals bulk samples of snow were taken from station NF, a representative site on the plateau for both catchment areas (Figure 1). Furthermore, bulk precipitation was collected in weekly intervals at the same site using glass totalisators (Simmleit and Thomas, 1984).

Results about the release of hydrophobic micropollutants from the snow cover during the melting of snow have been reported recently (Simmleit *et al.*, 1986a). The period of melting was finished by a rainstorm (30 mm) in the night from 6 to 7 February. After that a cold and dry period followed, lasting five weeks.

2.2. ANALYSIS

Specific conductivity (Cond), water temperature (*T*) and hydrogen activity (pH) of rainwater and Karst water were measured *in situ* using a conductivity electrode (Metrohm EA 1070) and a temperature-corrected pH-electrode (Ingold 405–88). Suspended solids (SS) were determined gravimetrically by filtration of a water sample through a 0.45 μm membrane filter (Sartorius Type 41). The anions chloride, nitrate and sulfate were analyzed by direct injection of 100 μmL original water sample in an ion chromatograph with UV-detection (Gilson) according to the method of Cochrane and Hillmann (1982). The detection limits were determined for chloride as 0.5 mg L^{-1}, for nitrate as 1.1 mg L^{-1} and for sulphate as 1.3 mg L^{-1}. Total Ca and total Mg of Karst water samples were analyzed using flame photometry (Eppendorf). After acidification of filtered samples ($pH < 2$) with HCl the dissolved organic carbon (DOC) was determined with an automatic TOC-Analyzer (Maihaik TOCOR2). For the parameters Ca, Mg, and DOC the detection limits were determined as 0.3 mg L^{-1}.

For the analysis of organic micropollutants snow and rainwater samples (2 L) were liquid-liquid extracted three times with 50 mL distilled dichloromethane. The extracts were purified on a 3 g Al_2O_3-column (Bierl *et al.*, 1984) and then analyzed for PAHs by high performance thin layer chromatography (Herrmann, 1978) and for BHCs by capillary gas chromatography (Thomas, 1981). The determination of PAHs was carried out under following conditions:

DC-plates:	HPTLC-RP 18 (Merck),
solvent:	analytical grade acetonitrile,
scanner:	chromatogram-spectrophotometer MQ3 (Zeiss),

excitation: 366 nm,
filters: M436 for BaP and Fa, M 405 for BghiP,
recovery rates: Bap 94%, Fa 90%, Bghip 97%,
detection limits: BaP 0.1 ng L^{-1}, Fa 0.6 ng L^{-1}, BghiP 0.2 ng L^{-1}.

BHCs were quantified using aldrin as internal standard (Kirchner *et al.*, 1983):
instrument: gaschromatograph Varian Model 3700,
injection: 2 μL of concentrated extract, 260 °C,
split: 30 mL $\min^{-1}$,
column: 20 m OV 101; 180 °C 3 min, 4 °C $\min^{-1}$, 260 °C 10 min,
carrier gas: N_2, 35 cm s^{-1},
attitude: 64 10^{-12} mV s^{-1},
detection: ECD ^{63}Ni, 370 °C, make-up 37.5 mL $\min^{-1}$,
recovery rates: α-BHC 94%, γ-BHC 92%
detection limits: α-BHC 0.05 ng L^{-1}
γ-BHC 0.03 ng L^{-1}.

Using distilled hexane as solvent for the extraction of Karst water samples, the purification step was superfluous. Therefore, the original, concentrated hexane extract could be used for further analysis. Despite the slightly worse recovery rates of 80 to 89% for all compounds, the detection limits did not deteriorate.

2.3. DATA EVALUATION

For establishment of micropolluant balances, it is necessary to calculate proper input and output loadings. This is feasible by applying a cubic spline function which does not connect each measuring point but calculates a smoothed curve through the confidence intervals of each measuring point (Reinsch, 1967).

The confidence intervals were calculated by multiplying the standard deviation of the recovery rates with the appropriate student-t-distribution factors (95%) (Sachs, 1974). For all parameters analyzed the confidence intervals varied between 8 and 15% of the concentration measured.

Thus it was possible to calculate hourly discharge and concentration values on the basis of irregular measurements. These values were plotted against time and are shown in Figure 2. The temporal variation of hourly micropollutant loadings in the Karst springs is gained by multiplication of the hourly concentration with the corresponding discharge value. By adding the hourly pollutant loadings, it is possible to calculate daily loadings, monthly loadings and cummulative percentages of total pollutant loads and runoff. All these steps were put down in a self-made computer program written in FORTRAN 77 and performed on the computer (VAX-11/780) of the University of Bayreuth.

Furthermore multivariate, statistical methods (Veldman, 1967) were applied to reveal interrelationships between the 17 variables measured.

3. Results

3.1. HYDROGRAPH AFTER THE MELTING OF SNOW

The temporal variation of some selected parameters measured in the Karst spring of Aufsess during the melting of snow is shown in Figure 2. At the beginning of the melting

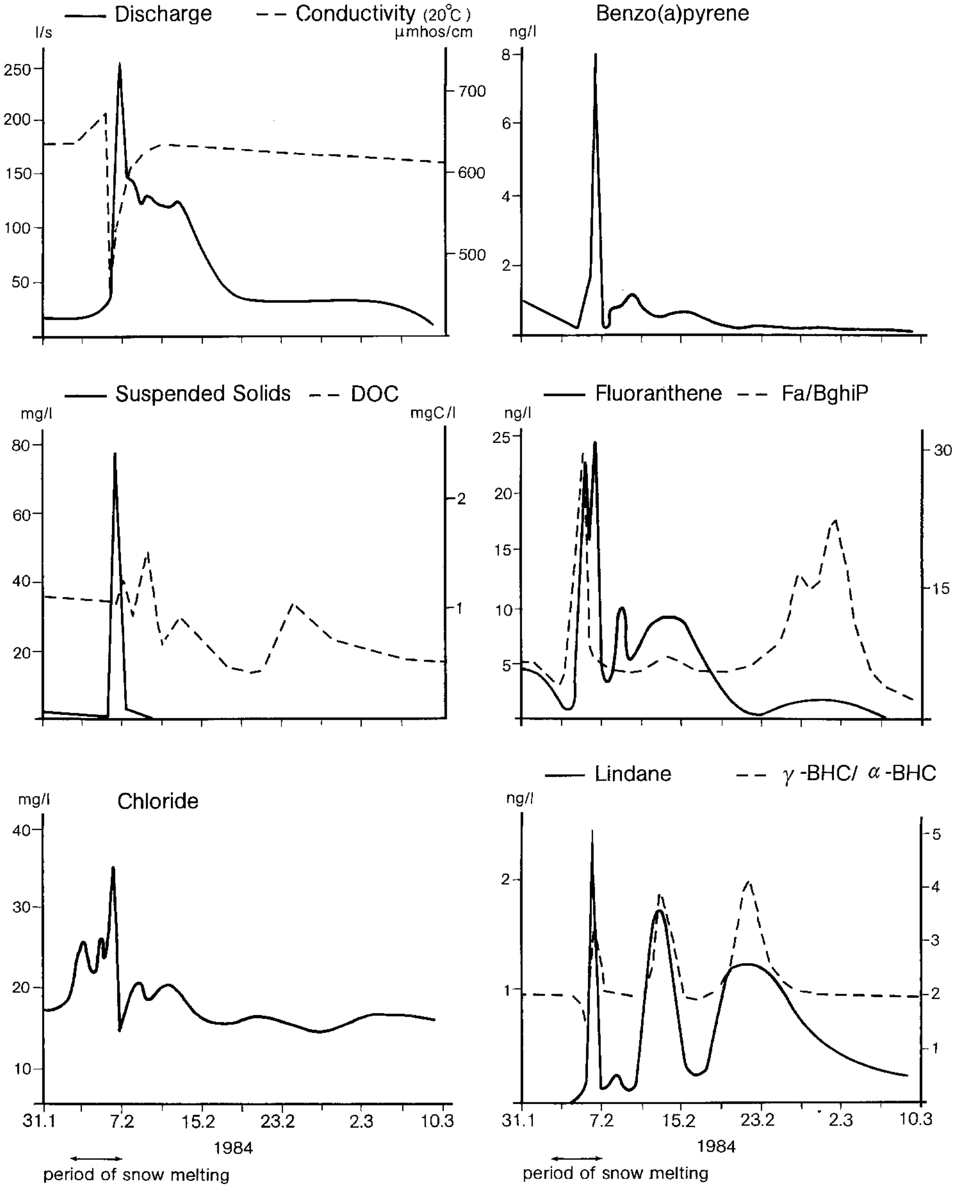


Fig. 2. Temporal variation of selected constituents of groundwater from the Karst spring in Aufsess during and after the melting of snow.

period, the spring was merely fed by groundwater from the phreatic zone and delivered 14 L s^{-1}. The first meltwater input caused an increase of the discharge only up to 25 L s^{-1}. But 24 hr after the rainstorm the delivery of the spring rose for some hours up to 260 L s^{-1} due to rapid conduit flow caused by infiltration of rainwater in the doline. After the rainfall ceased, discharge decreased and remained fairly constant on two levels at 130 L s^{-1} and 40 L s^{-1} until it reached again the initial base flow after 33 days. During the whole period the pH and the temperature of the Karst water remained fairly constant at pH 7.2 and 8.2 °C.

3.2. THE TEMPORAL VARIABILITY OF INORGANIC CONSTITUENTS

According to Udluft (1979), the conductivity of Franconian Karst water is fairly identical to the content of dissolved solids (TDS):

$$\mathrm{TDS}(\mathrm{mg\ L}^{-1}) = 1.04\ \mathrm{Cond.}(20\ ^\circ\mathrm{C}, \mu\mathrm{mhos\ cm}^{-1}).$$

As shown in Figure 2 the conductivity, respectively, the content of TDS in Aufsess augmented in the course of the snow melting reflecting the sudden release of ions from snow cover with the first fraction of meltwater (Simmleit *et al.*, 1986a). The Karst water was diluted substantially at the beginning of the rainstorm, but again reached its normal level of 640 mg L^{-1} TDS.

In winter the chloride concentration of these Karst springs is mainly due to the salting of roads in the catchment basins (Walayati, 1978). Chloride does not adsorb in the Karst system and therefore can be used as a tracer. Prior to maximal discharge, the chloride concentrations increased three times (Figure 2). During highwater flow the chloride concentration was diluted such as concentrations of every other constituent. Afterwards the chloride concentration increased again two times before finding its background level of 17 mg L^{-1}. Following the theory of Maillet, the declining part of a hydrograph caused by a single impulse of precipitation input can be separated in several expotential discharge phases (Schoeller, 1967). In Karst systems, these discharge phases are caused by different pathways of percolation, respectively, different reservoirs of Karst water such as conduit, trickle, seepage, and groundwater (Sweeting *et al.*, 1973). However, it is noteworthy that Gunn (1981) distinguished six different pathways of diffuse flow for water infiltrating in a sink-hole. Therefore, each chloride maximum can be explained by the arrival of a new wave of Karst water from one of the reservoirs and the simultaneous, constant discharge phases may be caused by overlapping of several waves of trickle and seepage water with different residence times (Wilcock, 1968).

3.3. THE TEMPORAL VARIABILITY OF ORGANIC CONSTITUENTS

The arrival of each new wave of infiltrated water caused an increase of DOC. The DOC in these groundwaters is presumably only due to water-soluble humic substances of the soils. As shown in Figure 2 the first relative increase of DOC is occasioned by conduit water infiltrated directly into the doline, the second and third relative increase of DOC is caused by trickle water which flows in larger fissures and the fourth relative increase corresponds to seepage water, which flows in smaller fissures and pores. The base level of 0.6 mg C L^{-1} is due to groundwater from the phreatic zone.

Karst water is usually free of suspended solids. The water investigated contained only during few hours of highwater flow suspended solids up to 80 mg L^{-1}. As shown in Figure 2, this load of particulate matter in conduit water was responsible for the sudden increase of micropollutant concentrations. Nevertheless the less hydrophobic, i.e. the more water soluble contaminants like Fa and γ-BHC reached the spring independently from the occurrence of suspended solids. They could also be transported adsorbed on humic materials as the comparison to the DOC curve shows. For benzo(a)pyrene the partition coefficient between water and aquatic humic substances is in the range of log 4.1 (Herrmann, 1981) and log 6.0 (Landrum *et al.*, 1984). Therefore, a certain part of PAHs has to be transported on dissolved humic material (DHM) as recently reported by McCarthy and Jimenez (1985). The molecular ratio between less hydrophobic and more hydrophobic substances, as an example Fa/BghiP (Figure 2) demonstrates, however, that a certain part of micropollutants was also transported dissolved in water. Otherwise this ratio would not have increased with the arrival of a new wave of Karst water together with the increase of DOC. In particular, FA molecules already reach the spring before highwater flow. This agrees with the observation that more water soluble organic constituents are released more rapidly from the snow cover than less water soluble organic contaminants (Simmleit *et al.*, 1986a). During highwater flow with its high content of suspended solids the ratio Fa/BghiP decreased again, because now most of the PAHs molecules were transported adsorbed on particles.

The BHCs were also transported independently from the occurrence of suspended solids and are partitioned between water, DHM and particulate matter. Recently Caron *et al.* (1985) showed that the content of DOC has no effect on the transport of lindane in a river system. This finding suggests that lindane is mostly transported in a dissolved state. As shown in Figure 2 the three relative maxima of the BHC concentrations are correlated with the arrival of conduit water, trickle and seepage water at the spring. The pollutant peaks become broader with time, indicating the impact of dispersion. The second relative increase of Fa and γ-BHC concentrations due to trickle water occurred three days after the corresponding relative increase of the chloride concentration. From kinetic studies it is known that adsorption of organic pollutants, e.g., on soil material is faster than desorption (Sharom *et al.*, 1980). Hence, the delay of the arrival of contaminants compared with the arrival of chloride ions can be explained by delayed desorption processes of organic contaminants.

4. Discussion

4.1. DISCHARGE PHASES

The hydrograph shown in Figure 2 is the result of the overlapping of several waves derived from various Karst water reservoirs with different residence times as already described in other studies (Schoeller, 1967; Ashton, 1968; Sweeting *et al.*, 1973). For

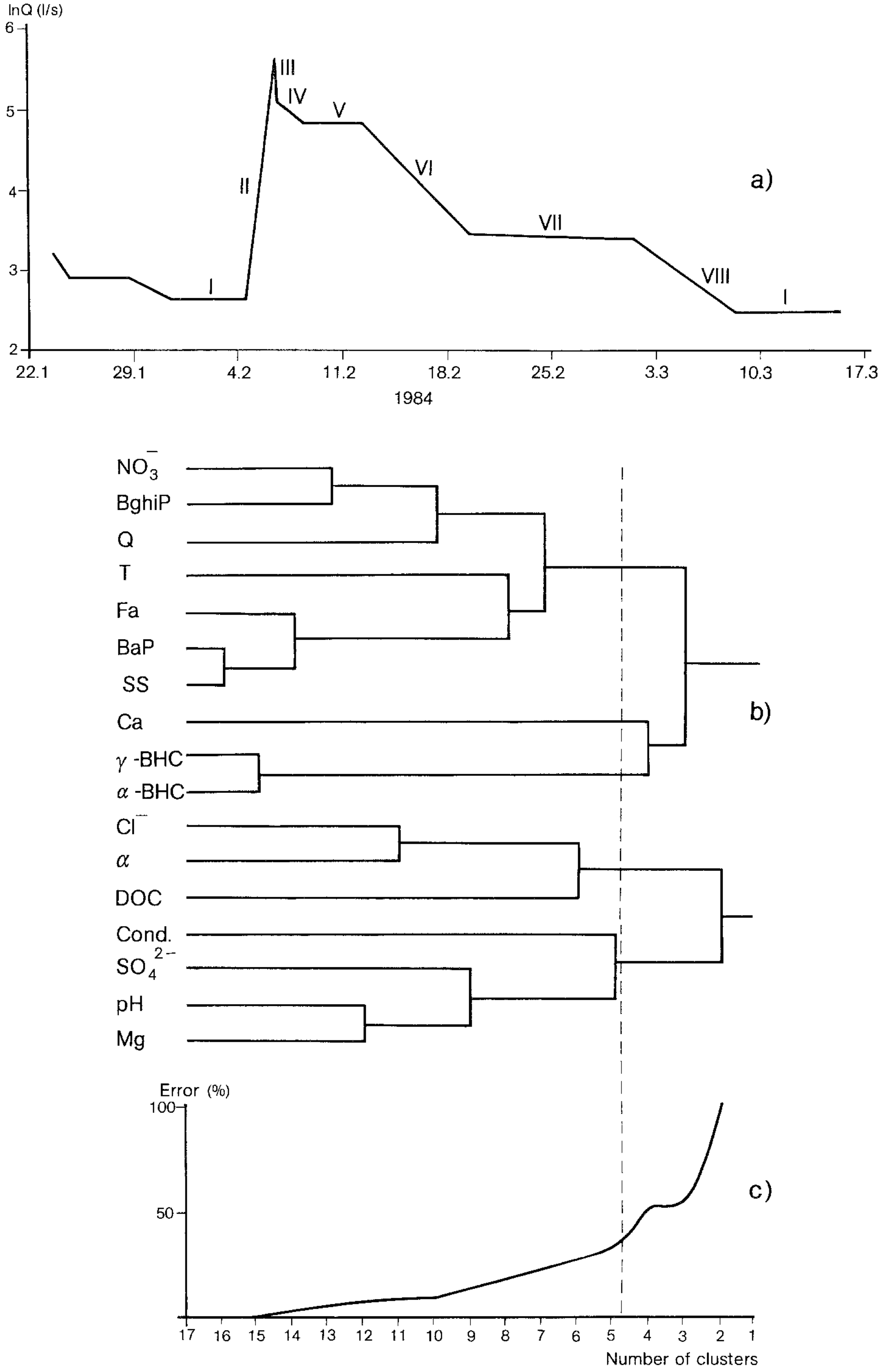


Fig. 3. (a) Logarithmic plot of the discharge of the Karst spring in Aufsess showing eight discharge phases (I–VIII). (b) Dendrogram of the hierarchical cluster analysis performed with standardized mean values of hydraulic and hydrochemical parameter which were calculated for eight discharge phases of the Karst spring in Aufsess during the melting of snow. (c) Diagram showing the increasing error due to the formation of clusters.

a detailed description of the interrelationsships between hydrochemical and hydrological parameters, we plotted the logarithmic hydrograph of the spring in Aufsess in Figure 3a. Defining discharge phases by time intervals with constant gradients α, we derived eight discharge phases I-VIII. The classical hydrograph analysis according to Schoeller (1967) was not conducted because it deals only with the declining part of the hydrograph. For every discharge phase arithmetic mean values of the variables measured were calculated. These hydrological and hydrochemical mean values were standardized and gathered to groups using a hierarchical cluster analysis based on an Euclidean distance matrix (Veldman, 1967). The different parameters are clustered according to their similarity in size and variation. The result of this cluster analysis is shown as a dendrogram in Figure 3b. In order to make a reasonable interpretation possible the cluster analysis is stopped when the error of clustering becomes too high (Figure 3c), which indicates a declining similarity within the groups. Therefore, the following five groups of parameters are discussed.

(1) Water temperature, discharge, nitrate, suspended solids, and PAHs showed a very similar behavior in course of the eight discharge phases. During rising discharge (II) all these parameters reached their highest mean concentrations. This includes nitrate which was not diluted during high water indicating substantial leaching of excess nitrate from agricultural 'Rendzinen' (Rendolls, U.S.D.A., 1975) during rainstorms (Simmleit and Hempfling, 1986). Before and after highwater flow these parameters show fairly constant mean concentrations.

(2) Compared with group one total Mg, pH, sulfate and specific conductivity show exactly the reflected behavior during the discharge phases. Before and after highwater flow they are also fairly constant, whereas during flood discharge dilution occurs, reducing their concentrations. The decreasing content of TDS, Mg and the declining pH during highwater flow show that dolomite dissolution is not in a state of equilibrium. In contrast to nitrate, sulfate which is also mainly due to anthropogenic input in this watershed (Walayati, 1978) is diluted, indicating stronger adsorption on soil material.

(3) The gradient of the logarithmic hydrograph, the content of dissolved organic carbon and the concentration of chloride showed an autonomous behavior. Concentrations of Cl^- and DOC are always very high when the discharge was changing rapidly.

(4) By reason of their very similar chemical structure the two BHC-isomers are clustered to one single group without any other member.

(5) The behavior of total Ca could not be correlated with the behavior of any other group because the mean concentration of Ca reached its maximum in the discharge phase IV after highwater flow. Calcium is also applied as a nutrient to the ambient agricultural soils (Walayati, 1978). In comparison with Mg, the increase of Ca is due to leaching from soils. But the bivalent charged Ca-ions are transported more slowly in the soil column than the monovalent charged nitrate ions, which already reached the spring with highwater flow.

4.2. THE BEHAVIOR OF KARST WATER CONSTITUENTS DURING HIGHWATER

Cluster analysis was also applied to the mean parameter values of the spring in the Leipoldstal leading to a very similar dendrogram. Combining all results, some general aspects can be deduced from the detailled analysis of hydrographs, pollutographs and dendrograms.

(1) Ions, which leach from soils (NO_3^-, Ca^{2+}) have their highest concentration during highwater. It seems that monovalent charged ions are not delayed as long as bivalent ions when being transported through the soil column. In both springs the maximal concentration of chloride arrived before that of nitrate. After the concentration rise of chloride and nitrate, the Ca content increased with the declining hydrograph.

(2) The content of ions which are derived only from the dissolution of dolomite (Mg^{2+}, HCO_3^- the main constituent of TDS) is diluted during highwater.

(3) Independently from the hydrogeological situation, the transport of organic micropollutants in Karst waters is mainly influenced by the occurrence of suspended solids and dissolved organic material. High concentrations of particulate matter occur either during the phase of rising discharge or during the phase of maximal discharge.

4.3. HOURLY POLLUTANT LOADINGS AND FIRST FLUSH EFFECT

For comparing the two springs investigated, we plotted hourly loadings of three selected, organic micropollutants against time (Figure 4). In Aufsess the highest loadings occur during highwater flow and with the largest content of particulate matter. Minor loadings of less hydrophobic micropollutants like Fa and γ-BHC were also observed with the arrival of trickle and seepage water.

During and after the melting of snow three maxima of contaminant loadings occured at the spring in the Leipoldstal (Figure 4). The first rise coincides with the maximal content of suspended solids (10 mg L^{-1}). This happened already in the phase of increasing discharge. The second and highest rise of pollutant loadings was caused by highwater flow (4 L s^{-1}). This spring is not connected with a sink-hole and although the residence time of the Karst water in the vadose zone is very short, the final rainstorm caused only a rise of discharge by the factor four. The third, minor increase of loadings of less hydrophobic contaminants is explained again by delayed desorption or various pathways of trickle water. The arrival of slowly percolating seepage water caused only a slight rise of contaminant loadings three weeks after the rainstorm.

Despite the different hydrogeological situation of the springs (Figure 1) the same pattern of transport of organic micropollutants in Karst water could be observed. Transient rises of pollutant loadings coincided with the increase of suspended solids or DHM. Obviously the transport of organic substances adsorbed on particulate matter is very important. This type of transport is also responsible for the first-flush effect, indicated by higher cummulative percentages of pollutant loads compared with runoff during highwater (Figure 4). Previously first-flush effects of hydrophobic micropollutants were already described for urban and rural catchment basins (Herrmann, 1981; Bierl *et al.*, 1984).

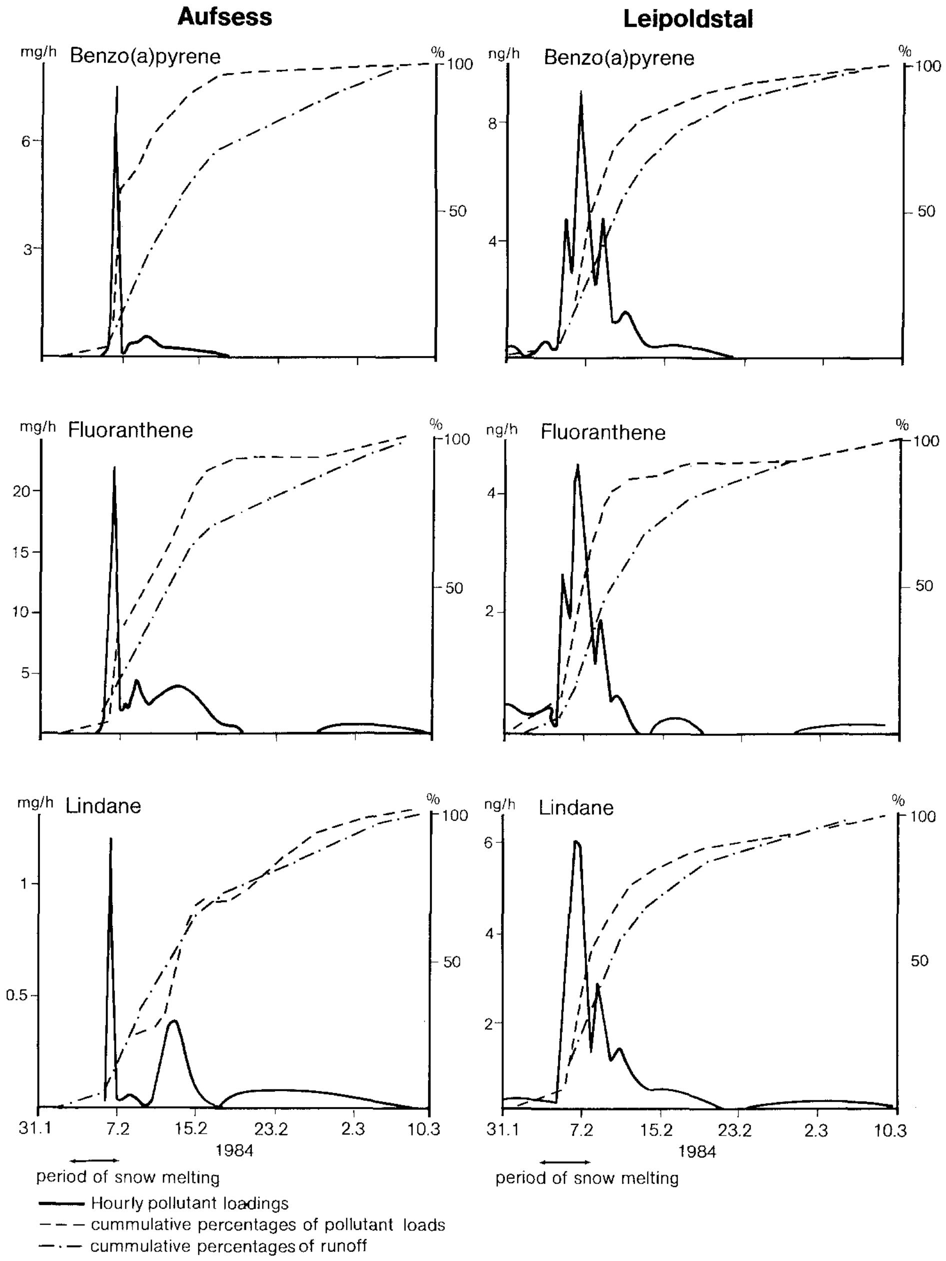


Fig. 4. Loadings of organic micropollutant at two Karst springs after the melting of snow.

4.4. MICROPOLLUTANT BALANCES

The filter capacity of Karst systems is considered to be very low due to their high permeability (Maire, 1979). A great deal of input of contaminants in Karst systems can be expected during rapid melting of snow because of the release of accumulated pollutants in the snow cover. Therefore, it was very interesting to look into the retention behavior of a Karst system during the melting of snow. For calculating micropollutant balances, however, it is necessary to know the size of the catchment areas. In Karst terrains, usually, it is not possible to determine the exact size of the drainage areas. We

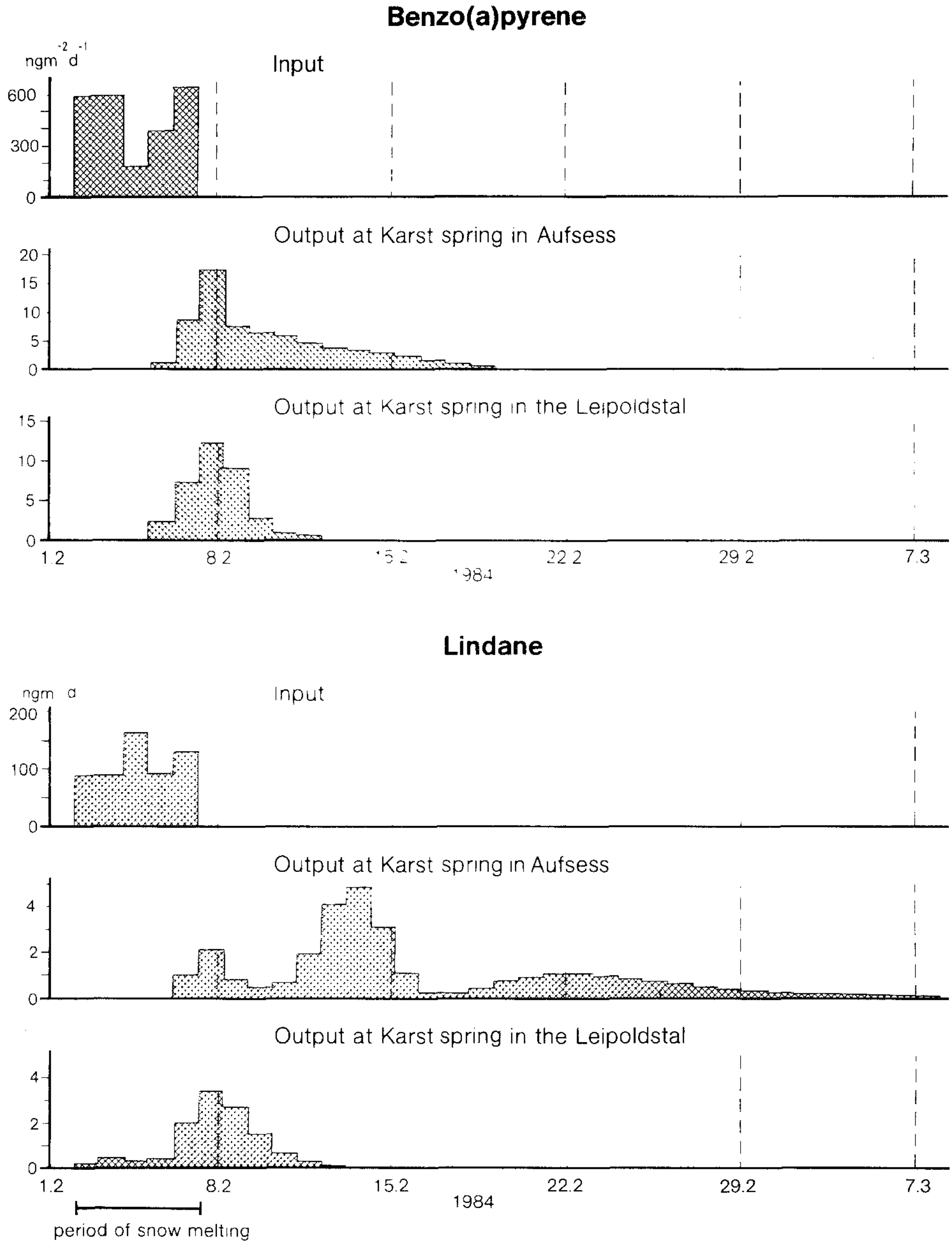


Fig. 5. Micropollutant balances for an agricultural and a wooded Karst catchment area after the melting of snow (ng m^{-2} d^{-1}) (input: daily input by meltwater and precipitation; output: daily pollutant loading at the Karst spring related to the size of the catchment area).

were lucky to record hydrographs which reached their initial base flow after three weeks. Assuming that in winter evapotranspiration is negligible and knowing the water content of the snow cover, the precipitation input and the base flow of the springs, it was possible to calculate the potential size of the catchment areas by integration of the hydrographs. Thus daily, area-related pollutant input-output loadings could be calculated as shown in Figure 5 for two selected organic micropollutants.

Since the start of the snow melting micropollutants were released fairly continuously from the snow cover and entered the Karst system (Simmleit *et al.*, 1986a). Primarily by the final rainstorm they were flushed through the Karst system and this resulted in maximal pollutant loadings within 24 hr after the rainstorm. The occurrence of high loadings of benzo(a)pyrene in the spring is directly connected to the occurrence of suspended solids in Karst water at this stage. With the exception of BHCs, as example lindane is shown in Figure 5, all loadings of other contaminants decline very rapidly within one week after the final input. The bulk of the more water soluble lindane, however, reaches the Karst spring in Aufsess one week and three weeks after the final input, indicating different pathways of diffuse flow as well as transport and delay mechanisms which have been already discussed.

Adding the daily input and output loadings, it becomes obvious that despite the fact that organic micropollutants can be detected in the Karst water after an input impulse, most of the contaminants are retained in the Karst system (Table II). In the agriculturally used Karst catchment area of the spring in Aufsess (*A*) 87.5 to 96.1% of the infiltrated micropollutants were retained in the Karst system and did not reach the spring. Even higher retention coefficients from 96.8 to 99.7% were calculated for the wooded Karst catchment area of the spring in the Leipoldstal (*L*), assuming the same area-related contaminant input. This again confirms the importance of forest ecosystems as a permanent sink for atmospheric pollutants (Matzner, 1984; Simmleit *et al.*, 1986b). As shown in Table II, no significant difference between PAHs and BHCs is observed.

TABLE II

Retention of organic micropollutants in two Karst systems during the melting of snow in February 1984

	BaP	Fa	BghiP	α-BHC	γ-BHC
Meltwater and precipitation input ($\mu g\ m^{-2}\ \Delta t^{-1}$)	1.3	12.3	3.3	0.27	0.33
Output at spring $A(\mu g\ m^{-2}\ \Delta t^{-1})$	0.01	0.66	0.13	0.01	0.04
Retention (%)	92.6	94.7	96.1	95.2	87.5
Output at spring $L(\mu g\ m^{-2}\ \Delta t^{-1})$	0.03	0.04	0.04	0.004	0.010
Retention (%)	97.6	99.7	98.9	98.6	96.8

Despite the high hydraulic permeability of the Karst system only few percent of the deposited load of organic micropollutants reached the Karst groundwater level. This result agrees with the annual measurements of Schrimpff (1984) who also reported such low breakthrough data for Karst watersheds mainly polluted by atmospheric deposition processes.

5. Conclusions

The detailed investigation of micropollutant loadings in snow, precipitation and Karst water showed that only a few percent of deposited contaminants reach the groundwater level. Obviously the hydrogeological situation is not as important as the occurrence of suspended solids and dissolved organic matter in the water. To the best of our knowledge no reports about sinks of organic contaminants are known for Karst systems. However, several potential sinks can be proposed:

(1) It is known that the organic micropollutants investigated adsorb rapidly on soil organic material and clay. PAHs as well as BHCs have very high partition coefficients i.e. in equilibrium most of the contaminants are in adsorbed state (Moreale and Bladel, 1978; Means *et al.*, 1980). Therefore one has to assume that a great part of deposited contaminants are adsorbed reversibly on the upper layer of ambient soils. In this part photodegradation and microbial action can transform the pollutants. However, desorption can also occur. This causes hydrophobic pollutants to migrate slowly through a homogenous soil column (Schwarzenbach and Westall, 1981). Yet, in zones of high hydraulic permeability rapid transport can take place in fissures and macropores (Thomas and Phillips, 1979).

(2) The transport of organic contaminants in Karst water can happen (a) in dissolved state. Thus the absence of potential carriers and the water temperatures with respect to water solubility is important. (b) In adsorbed state. As carriers dissolved humic material and suspended solids are suitable.

In carbonate waters more than 50% of DHM is neutralized by Ca^{2+}-ions and can be adsorbed on inorganic surfaces (Josephson, 1982). Therefore, the content of DHM, a potential carrier of micropollutants, in carbonate waters is very low (Stumm and Morgan, 1981). In the Karst water analysed we found DOC concentrations around 1 mg C L^{-1}. Furthermore, when calcium carbonate precipitation (sinter, tuff) occurs, micropollutants can be co-precipitated, because the crystallization of calcium carbonate starts preferably around organic molecules as crystallization nuclei (Kitano and Hood, 1965; Suess, 1970). In addition to these sinks, suspended solids can settle, e.g., in siphons.

All these potential pollutant sinks can cause the concentration of organic micropollutants in Karst water investigated to be very low. Further research is needed to examine these possibilities and first results will be reported in section II of this study (Simmleit and Herrmann, 1987).

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