

Seasonal biogeochemical cycles in riverborne groundwater

H. R. VON GUNTEN,^{1,3} G. KARAMEYAS,¹ U. KRÄHENBÜHL,¹ M. KUSLYS,^{1,*} R. GIOVANOLI,² E. HOEHN,³ and R. KEIL³

¹ Laboratorium für Radiochemie, Universität Bern, CH-3000 Bern 9, Switzerland

² Laboratorium für Elektronenmikroskopie, Universität Bern, CH-3000 Bern 9, Switzerland

³ Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

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Abstract—The behavior of dissolved ($<0.45\ \mu\text{m}$) inorganic species and changes in relevant properties of anthropogenically polluted river water were investigated during infiltration and movement in a hydraulically connected saturated aquifer. Water from the river and from several sampling wells was analyzed over 5 years for temporal and spatial chemical changes.

At the early stage of infiltration, a drastic decrease in pH and in the concentrations of O_2 and NO_3^- occurs. The gradients in these properties are most significant in the interstitial water of the river sediments. They are the result of the degradation of aquatic biota. The amount and grain morphology of river sediments varies seasonally and depends also on water flow conditions.

Temperature-related variations in microbiological activity in the river water and in the sediments of the riverbed induce pronounced annual cycles in the aquifer for several of the investigated properties. Each summer, under anoxic conditions, manganese (hydr)oxides dissolve, and trace metals (Cu, Zn, Cd) are mobilized. The main sources for manganese and other trace elements were found within the river sediments; degradation of algae and other aquatic biota and dissolution of calcite contribute to the observed effects. Higher winter concentrations of O_2 and NO_3^- result in precipitation of Mn and other redox sensitive elements in the aquifer. Zinc and Cd are retarded by interactions with the aquifer material, whereas Cu is mobile, probably as an organic complex.

INTRODUCTION

IN THE PERIALPINE BELT of central Europe and in geologically similar regions a large part of the groundwater is recharged from rivers and lakes (TRÜBB, 1977). This situation is uniquely suited to the study of chemical changes and processes during the infiltration of river water to a saturated aquifer. In contrast to the more general situation where rain or snowmelt percolates through an unsaturated zone, water samples can be taken without significantly disturbing the flow system, the sample size is not limited, and in addition the source term (the river water) can easily be analyzed.

The impact of contaminated rivers on groundwater quality is of major concern. Pollution of the groundwater can occur when toxic substances infiltrate either continuously or on a short time scale after an accident. For an estimation of the migration of contaminants in an aquifer and for efficient water management it is essential to understand the physical, chemical, and microbiological processes that lead to a retardation or remobilization of solutes.

The present study was performed to improve the knowledge of some of these processes. A study site was selected where infiltrating river water flows continuously through unconsolidated quaternary deposits and feeds the water-table aquifer. In a preceding paper (JACOBS et al., 1988) we discussed changes in important system properties, and of cation, anion, and trace element concentrations during the infiltration of river water to the shallow aquifer. We demonstrated that chemical changes in the infiltrating water can be approximated with a combination of a few simple stoichiometric

reactions, the most important being degradation of organic matter. In the present paper, we report mainly on seasonal changes of inorganic constituents along an infiltration flow path.

FIELD SITE

The study site is located in the lower River Glatt Valley near Zürich, in northern Switzerland (Fig. 1). The river and the adjacent aquifer have been extensively studied (ZOBRIET et al., 1976; GUJER et al., 1982; HOEHN et al., 1983; SCHWARZENBACH et al., 1983; AHEL et al., 1984; KULL, 1984; HOEHN and VON GUNTEN, 1985; VON GUNTEN and KULL, 1986; HOEHN and SANTISCHI, 1987; SANTISCHI et al., 1987; WABER et al., 1987; VON GUNTEN et al., 1988, 1988a; KUSLYS, 1988; HOEHN and VON GUNTEN, 1989; and WABER et al., 1990).

The small River Glatt (width 18 m, mean discharge rate $\sim 8\ \text{m}^3\ \text{s}^{-1}$) largely originates (40%) from Lake Greifen and recharges the aquifer at a rate of $0.4\text{--}0.8\ \text{m}^3\ \text{d}^{-1}$ per square meter of infiltration area (HOEHN and SANTISCHI, 1987). The direct contribution to the recharge of the aquifer from the vadose zone is negligible at the study site (precipitation $\sim 120\ \text{cm}\ \text{y}^{-1}$). Water from the river penetrates the uppermost part of the saturated aquifer and travels with an average flow velocity of $4\text{--}5\ \text{m}\ \text{d}^{-1}$ (HOEHN and SANTISCHI, 1987; HOEHN and VON GUNTEN, 1989). The river water is a typical calcium carbonate water ($\text{Ca}^{2+} \sim 1.8\ \text{mmol}\ \text{L}^{-1}$, alkalinity $\sim 4\ \text{meq}\ \text{L}^{-1}$), and it contains $\sim 15\%$ of water from several biological-mechanical sewage treatment plants located upstream of the field site.

The aquifer in the Glatt Valley consists of tightly packed glacio-fluvial outwash deposits (porosity ~ 0.2 , hydraulic conductivity $10^{-2}\text{--}10^{-4}\ \text{m}\ \text{s}^{-1}$) of poorly sorted gravel and interbedded layers of sand containing quartz (30–50%), calcite/dolomite (40–50%), and aluminosilicates (10–20%, micas, illites, chlorites, and feldspars). The cation exchange capacity is about $0.05\ \text{meq}\ \text{g}^{-1}$ for the size fraction $< 32\ \mu\text{m}$ and about $0.01\ \text{meq}\ \text{g}^{-1}$ for the coarser material (GRÜTTER et al., 1990).

Mixing is the main contribution to hydrodynamic dispersion. It has been measured in a local tracer experiment (uranine) and during an accidental release of a tritium pulse into the River Glatt and subsequent observations in the groundwater (HOEHN and SANTISCHI,

* Present address: Alpura Koreco AG, CH-3510 Konolfingen, Switzerland.

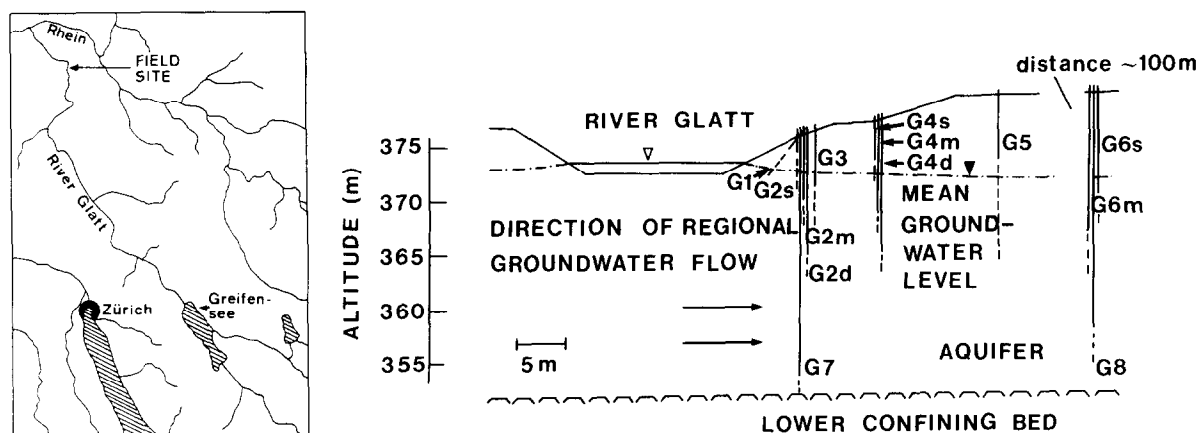


FIG. 1. Location and schematic layout of the study site (see also Table 1). Dashed lines: screened sections of pipes. Greifensee = Lake Greifen.

1987). These authors have evaluated longitudinal dispersivities to be about 10 m at Well G8 (100 m distance from the River Glatt). SCHWARZENBACH et al. (1983) have presented data on vertical concentration profiles in Well G8 for oxygen, DOC, and organic compounds. Their results suggest an admixture of about 10–20% deeper groundwater in agreement with mixing calculations using chloride (KUSLYS, 1988). Vertical mixing is reduced by the stratification of the aquifer.

The field site is equipped with a series of wells and pipes for sampling (Fig. 1). The wells were drilled at different distances from the river bank. The polyvinyl chloride pipes are screened with rows of slots which allow sampling at a fixed depth interval below the groundwater table (Table 1). Wells G2, G4, and G6 are “bundled piezometers” (CHERRY et al., 1983) reaching different levels in the groundwater.

Wells G7 and G8 sample deep groundwater. In this work we present data of samples taken in the river and in Wells G1–G3 and G5–G7.

METHODS

Sample Collection

Samples were collected from the river and from the groundwater wells between November 1984 and January 1990. Before 1987, sampling was in general monthly during summer, but was less frequent in winter. After 1987 sampling was less regular and only some results are reported here. There are considerable systematic daily variations in temperature, pH, and O_2 in the river, with largest amplitudes during summer (JACOBS et al., 1988). In order to minimize the variability

Table 1. Technical details of wells shown in Fig. 1. Sampling pipes are 2 inches in diameter (except G5). From Hoehn and von Gunten (1989).

Well No.	Linear distance from river bank to well, m	Upper and lower depth of screen, m above sea level	Remark
G1	2.5	374.0–372.1	inclined at 35°
G2s	5.0	373.8–370.8	shallow pipe of bundle
G2m	5.0	368.9–366.9	middle pipe of bundle
G2d	5.0	364.9–362.9	deep pipe of bundle
G3	7.0	370.7–367.7	
G4s	14	374.0–371.0	shallow pipe of bundle
G4m	14	369.0–367.0	middle pipe of bundle
G4d	14	365.0–363.0	deep pipe of bundle
G5	26	373.3–364.3	diameter 4 inch
G6s	100	370.5–367.5	shallow pipe of bundle
G6m	100	366.2–363.2	middle pipe of bundle
G7	5.0	354.3–351.3	deep well
G8	100	357.8–354.8	deep well

between different field trips, the samples from the river were collected between 10 and 12 am.

Water from the river and groundwater was collected with submersible polystyrene pumps from about 0.5 m below the water surfaces. In the groundwater this depth was chosen to ensure sampling of freshly infiltrated water. In the wells the sampling point was within the screened sections. Before sampling, 3–5 well volumes of water were removed. All samples were taken on the same day. Since the measured water flow velocity is about $4\text{--}5\text{ m d}^{-1}$, the sampling was in general not performed in a real-time mode, i.e., not the same water package was followed as it moved along an assumed infiltration line. In order to approximate a real-time sampling, values in Well G6 (100 m distance from the river) were compared with values in Wells G1/G2 from the sampling campaign one month before. A single one-week period of very frequent sampling allowed us to perform real-time measurements. The results of this sampling period agreed with the trends in chemical changes obtained by the usual sampling procedure. Further details on the sampling procedures are given by JACOBS et al. (1988).

Several water samples were recovered in summer 1988 from 5–10 cm depth within the river sediments using a buried small water collection chamber. This simple apparatus allowed us to investigate changes in water quality at the beginning of infiltration to the aquifer. Furthermore, interstitial water was extracted in 1989/90 by centrifugation of fine grained river sediments. These sediments were recovered from the riverbed at the location of the infiltration profile (KARAMETAXAS, 1991).

Sample Treatment and Analysis

Unfiltered water samples were collected for pH and O_2 determinations. The pH was measured either *in situ* or immediately after collection; O_2 was measured *in situ* or fixed for Winkler titrations within 2 minutes after sampling. Filtered ($0.45\text{ }\mu\text{m}$, nitrocellulose, sartorius) water samples were used to determine cations, anions, and DOC. Precautions were taken to minimize trace metal contamination: filters and materials were soaked for more than 24 hours in 2% HNO_3 (analytical grade), then thoroughly rinsed with double-distilled water. In the field, the filters and apparatus were rinsed with 100 mL of the respective groundwater before collection of samples. For cation analysis and DOC, the samples were acidified after filtration to pH 2 with ultrapure HNO_3 and stored at 4°C in cleaned 100 mL polyethylene bottles. Samples for the analysis of anions were frozen in the field (dry ice and propanol) to prevent chemical and biological changes. The analytical methods used in this work were given by JACOBS et al. (1988). In addition, ICP-AES was used to analyze the major cations.

In addition to the analysis of water samples, aquifer material ($<32\text{ }\mu\text{m}$) from drill cores was subjected to a leaching procedure (A. GRÜTTER, pers. comm.). CO_2 gas was bubbled through a suspension of the aquifer material in a synthetic water with a composition similar to groundwater. The slurry was centrifuged ($14'000\text{ g}$) and cation concentrations were determined. After replacement of the water, CO_2 was again bubbled through the suspension. The procedure was repeated several times. Metal concentrations were analyzed in each step.

RESULTS AND DISCUSSION

The river-groundwater infiltration system is inherently very complex. There are several variables influencing the measured properties:

Temperature

Temperature and the annual temperature variations of about 20°C are key parameters for the processes which occur during infiltration of river water to the aquifer. They control microbiological activity at the water/sediment interface in the river and influence solubilities of chemical compounds, e.g., CaCO_3 . Figure 2a shows the annual temperature variability in the river. The seasonal temperature changes are very similar each year; there are only minor differences in the amplitudes and small shifts on the time axis.

Daily variations of river water temperatures are reflected in Well G1 close to the river. At greater distances (Well G2 and farther) the diurnal variations disappear. The temperature gradient along the first 100 m of the infiltration path changes from a slight increase in winter to a decrease in summer. At a distance of 100 m (Well G6) and in the deep groundwater (Well G7) the temperatures are rather constant, namely (10.3 ± 2.2) and $(11.3 \pm 0.2)^\circ\text{C}$, respectively.

River Discharge

The discharge rate of the river varies due to seasonal changes in precipitation, snow melt, and storm events. Figure 2b shows the monthly means of the discharge for 1979

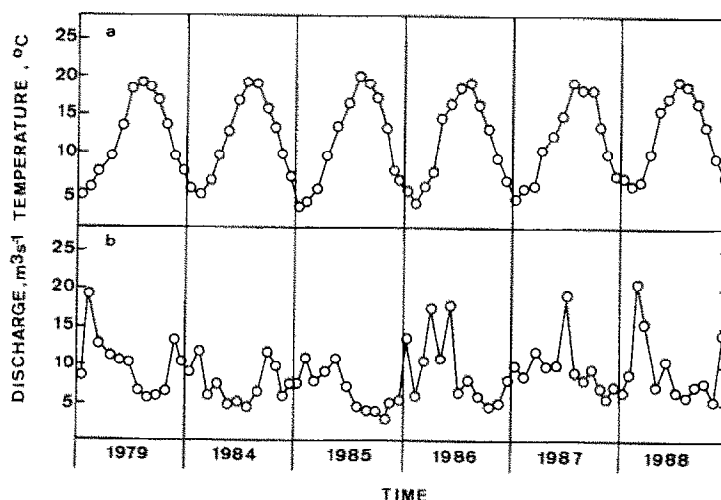


FIG. 2. Monthly means of temperature (a) and discharge rate (b) in the River Glatt for 1979, and 1984 to 1988. Values of 1979 from HOEHN et al. (1983).

(HOEHN et al., 1983) and for the period of 1984–88. These variations affect the water chemistry and the solid load of the river. They influence rates and flow paths of the infiltrating water by changing water levels, clogging, and erosion of the riverbed.

Water Levels

The groundwater table fluctuated due to variable recharge rates during the period of investigation (Fig. 3). Therefore, the water which was recovered from 0.5 m below the water table was not always in contact with the same part of the aquifer. Also, the residence times of the water in the aquifer vary with changing water levels in aquifer sections of a different hydraulic conductivity. These changes may influence the local chemical composition of the groundwater.

Anthropogenic and Biological Activities

The water composition is influenced by anthropogenic activities (e.g., industry, sewage treatment, road salt, agriculture) which lead to sudden changes in the concentrations of pollutants. Diurnal (i.e., photosynthesis and respiration) and seasonal variations in bio-activity (JACOBS et al., 1988) add to the complexity of the system. Bio-activity depends on water temperature (Fig. 2a), weather conditions, and sunlight. Sunlight enhances, in addition, photochemical reactions (WAITE et al., 1988; FULLER and DAVIS, 1989; SULZBERGER et al., 1989).

Despite this rather complicated situation at the site, which is governed by cyclic and stochastic processes, the properties of samples taken at corresponding months showed similar trends and patterns during all years of investigation. We present a set of selected data for several months of the year 1985 (Table 2), when sampling was most frequent and most elaborate. Complete data sets for 1984–1987 are given by KUSLYS (1988) and for 1988/89 by KARAMETAXAS (1991).

A few properties of the full period of investigation are shown in Fig. 4. Figure 5 shows the data of manganese for 1979 and the period 1984–87. Table 3 summarizes analyses of the interstitial water in the river sediments, and Table 4 gives additional average data for trace metals.

From Table 2 (and from the complete set of data) it is obvious that major changes of many properties occur between the river and Well G1, i.e., along the first 2.5 m of the flow path, corresponding to the first half day of infiltration. Furthermore, distinct seasonal concentration changes occur for several compounds. In Fig. 6 we summarize the observed effects for manganese.

pH, Oxygen, and Nitrate

Variations in space

In our earlier paper (JACOBS et al., 1988) we reported on diurnal cycles of pH and oxygen in the River Glatt, and on a significant decrease of pH, O_2 , and NO_3^- concentrations upon infiltration to the aquifer. The standardized sampling procedure of the present investigation (see previously) minimized the variability in the river water samples. The three-year mean of the pH [20 measurements (n)] was 7.91 ± 0.27 , of O_2 (322 ± 54) $\mu\text{mol L}^{-1}$ ($n = 34$), and of NO_3^- (358 ± 78) $\mu\text{mol L}^{-1}$ ($n = 40$).

Upon infiltration to the aquifer (i.e., between the river and Well G1, Fig. 1), the pH decreases in general by more than 0.5 units to 7.40 ± 0.13 ($n = 39$), O_2 by about 300 $\mu\text{mol L}^{-1}$ to 16 ± 11 $\mu\text{mol L}^{-1}$ ($n = 45$), and NO_3^- by about 100 $\mu\text{mol L}^{-1}$ to 250 ± 90 $\mu\text{mol L}^{-1}$ ($n = 20$).

KARAMETAXAS (1991) performed laboratory column experiments which simulated the situation in the field. His columns contained separated sections of river sediment and aquifer material. When river water flowed through the column the oxygen concentration fell below the detection limit of ~ 1 $\mu\text{mol L}^{-1}$ after passing through riverbed material of a

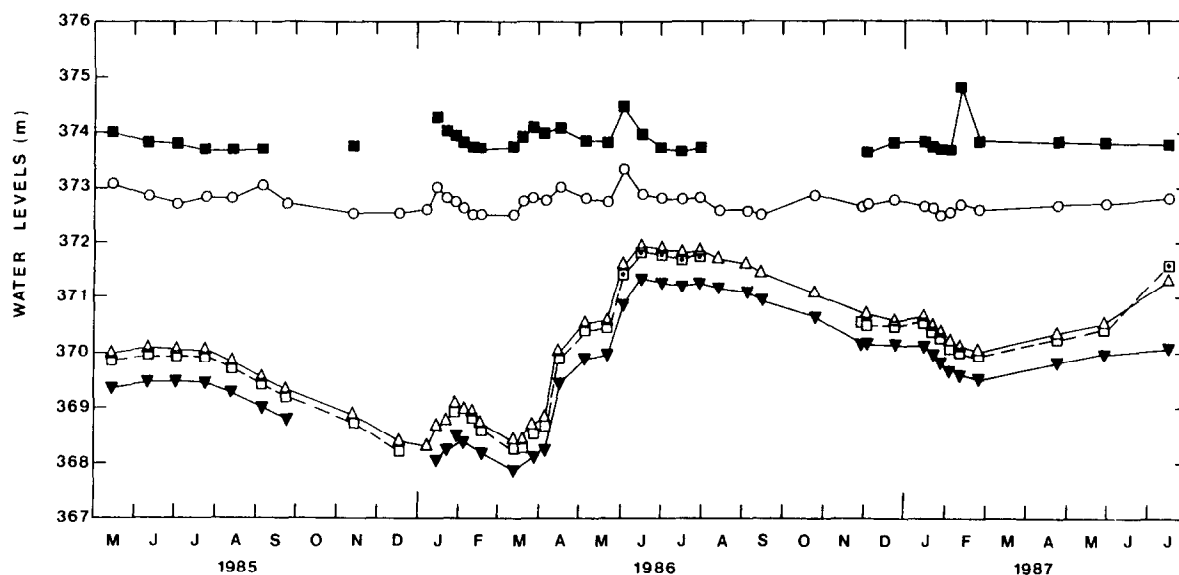


FIG. 3. Water levels in the River Glatt and in groundwater sampling wells for 1985 to 1987. River Glatt (■); Well G1 (○); Pipe G2m (□); Pipe G2s (△); Well G3 (△); Pipe G6s (▼); s = shallow, m = medium-depth wells.

Table 2 Selected properties and concentrations of water constituents in the River Glatt and in groundwater of the year 1985*.

N.D., not determined.

Date/Location	Temp. (°C)	pH	O ₂	NO ₃ ⁻	Mn	Cu	Zn	Cd
			(μmolL ⁻¹)	(nmolL ⁻¹)				
February								
River Glatt	4.2	7.90	400	310	220	47	200	0.9
G1	3.3	7.33	30	370	27	70	370	0.9
G2	4.3	7.34	190	330	4	35	77	0.4
G3	4.3	7.38	60	370	5	44	72	0.6
G6	9.8	N.D.	110	440	11	32	15	0.1
G7	10.9	7.23	230	410	5	12	87	0.2
April								
River Glatt	8.1	8.14	360	350	130	57	130	0.6
G1	8.1	7.41	20	370	N.D.	34	120	N.D.
G2	7.4	7.48	90	340	2	34	38	0.4
G3	7.9	7.37	100	370	64	41	43	0.6
G5	6.9	7.32	120	330	5	31	35	0.4
G6	8.3	7.36	220	470	27	29	17	0.3
G7	11.5	7.29	230	410	13	15	69	0.2
June								
River Glatt	13.9	8.00	310	310	110	83	150	0.3
G1	17.5	7.47	10	240	350	96	57	1.3
G2	N.D.	7.45	10	230	14	74	43	0.5
G3	17.0	7.84	20	320	27	93	43	0.5
G6	8.8	7.30	160	340	9	50	14	0.7
G7	11.4	7.25	230	430	5	14	28	0.1
July								
River Glatt	20.1	8.12	340	440	34	50	140	1.1
G1	21.0	7.50	10	310	1670	61	110	4.3
G2	19.7	7.46	10	200	5460	N.D.	470	5.5
G3	19.4	7.41	20	230	5680	83	50	2.8
G6	N.D.	7.33	60	220	5	77	12	0.4
G7	11.2	7.27	240	410	10	11	23	0.4
September								
River Glatt	18.5	7.97	260	380	44	83	240	2.1
G1	20.3	7.38	10	290	2350	76	90	3.4
G2	19.6	7.42	50	230	1640	110	34	1.5
G3	19.4	7.41	N.D.	230	4640	36	24	1.6
G6	13.9	7.25	120	330	N.D.	N.D.	58	0.9
G7	11.3	7.25	230	420	4	39	14	1.4
December								
River Glatt	6.6	7.97	340	340	180	49	240	0.2
G1	9.0	7.26	10	370	2180	43	146	0.4
G2	10.7	7.36	60	290	9	31	54	0.1
G3	11.1	7.36	160	320	13	29	57	0.1
G7	11.5	7.21	240	420	15	11	57	0.4

* For complete data sets of 1984–1989 see Kuslys (1988) and Karametaxas (1991).

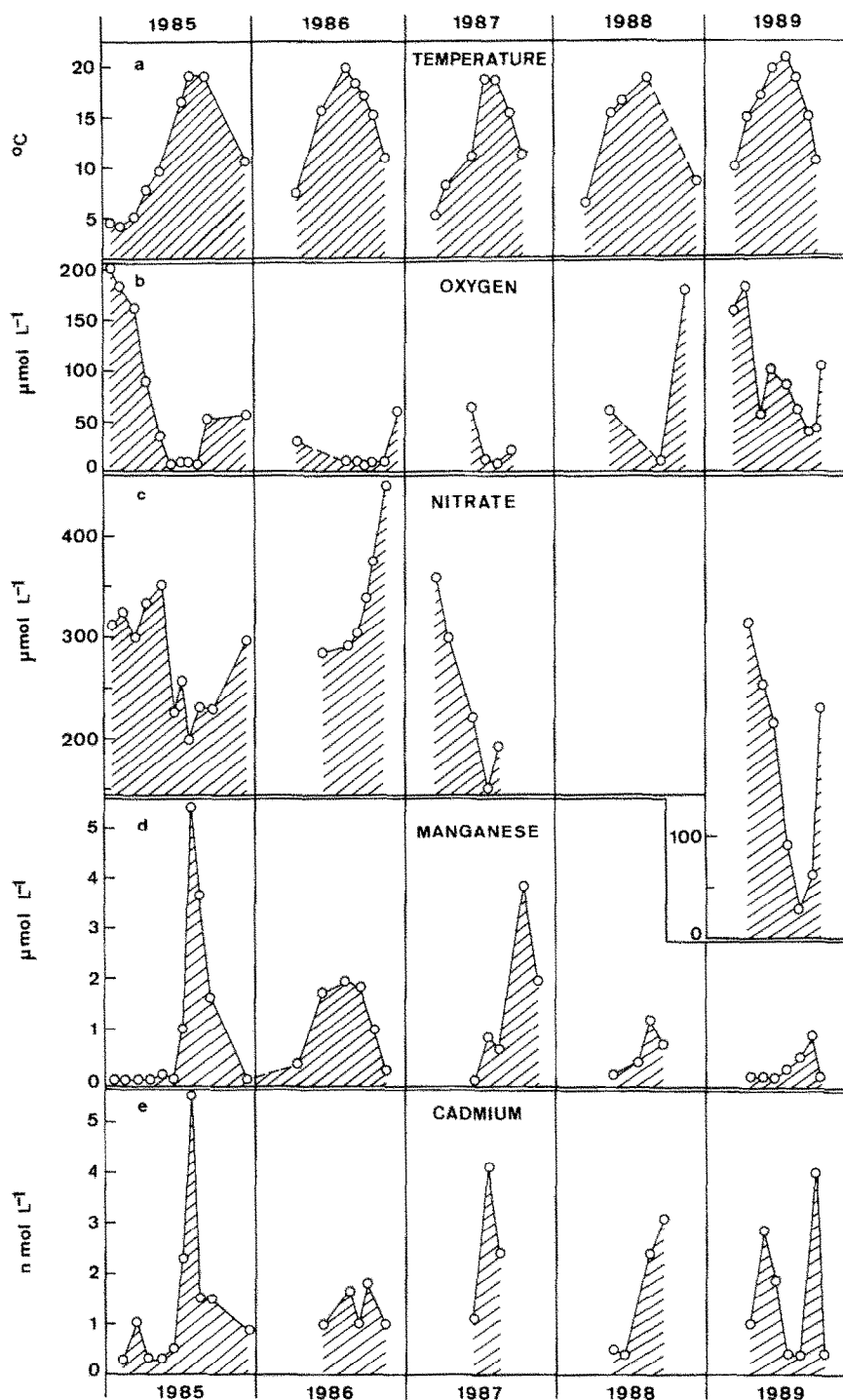


FIG. 4. Annual cycles of temperature, O_2 , NO_3^- , Mn, and Cd in Well G2. Notice different scale ($nmol\ L^{-1}$) for Cd.

few millimeters thickness, and NO_3^- disappeared completely after a few centimeters of flow.

In the field, the pH remains very constant (7.39 ± 0.12 , $n = 56$) between Wells G1 and G3 and along the farther flow path to Well G6 (100 m, mean pH 7.30 ± 0.07 , $n = 18$). The pH stability is due to the efficient buffering of the groundwater by calcite. In the deep groundwater (Well G7) the mean pH is 7.19 ± 0.08 , $n = 17$, in approximate agreement with calcite solubility at an assumed P_{CO_2} of 10^{-2} atm.

After passing Well G1, the oxygen and nitrate concentrations in the groundwater rise slowly along the infiltration path (Table 2). This is due to ingassing of atmospheric oxygen through the unsaturated zone of the aquifer and infiltration of liquid manure and synthetic fertilizer from the farmland on the test site area. Admixture of O_2 - and NO_3^- -rich deeper groundwater also contributes to the increasing concentrations. The deeper groundwater at this site contains more oxygen and nitrate because it originates from other locations and

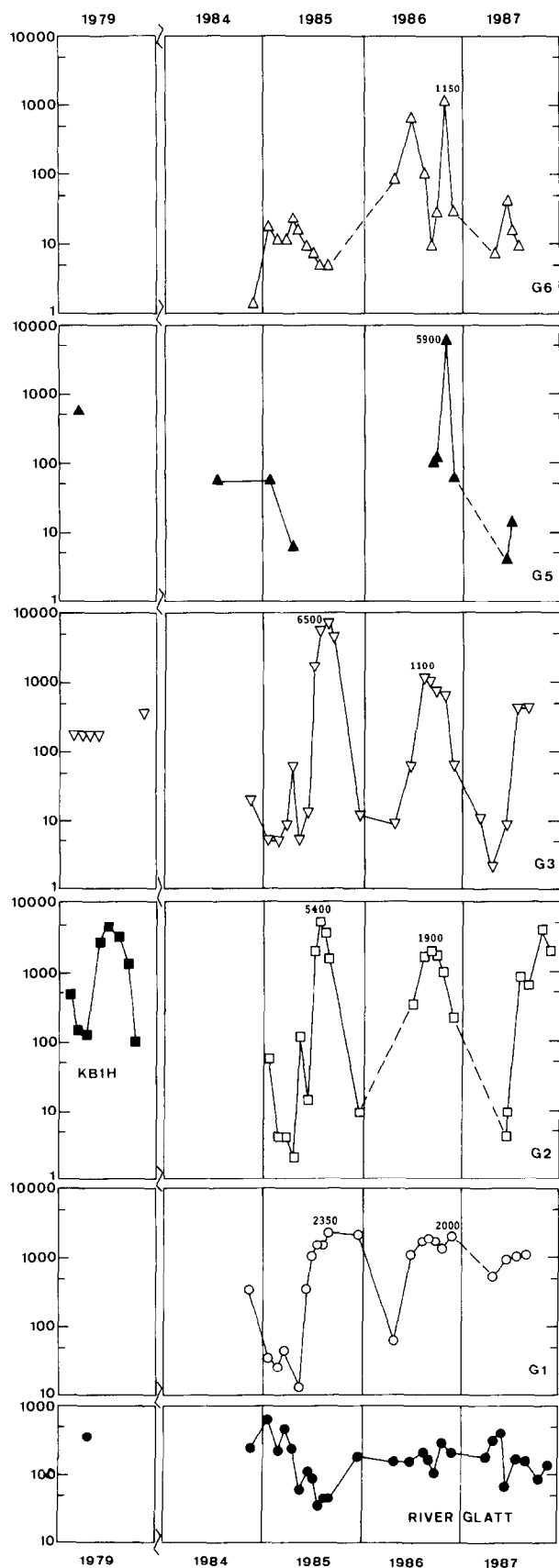
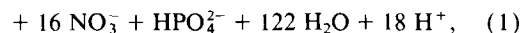


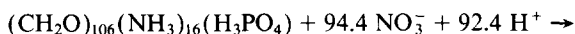
FIG. 5. Annual cycles of manganese. Manganese concentrations in the River Glatt and in Wells G1, G2, G3, G5, and G6. Values of

was subjected to different chemical processes than the fresh infiltrate. The somewhat higher oxygen and nitrate concentrations in the uppermost groundwater during part of the winter are probably produced by an inversion of the groundwater temperature (Table 2), which enhances mixing in the wells by density gradients.

The decrease in pH, O_2 , and NO_3^- at the river/aquifer interface is mainly due to bacteria-mediated degradation of organic matter (aquatic biota) according to the simplified equations:



and



The processes in the field are certainly much more complex than indicated by the stoichiometry of Eqns. (1) and (2), and for a successful material balance one has also to take into account nitrification and weathering reactions. But with these few reactions it is possible to reproduce the results of the field (JACOBS *et al.*, 1988).

NH_4^+ and NO_2^- were observed in the river and in Well G1 at very low concentrations. It is known that NH_4^+ is sorbed onto surfaces of aquifer materials (MURRAY *et al.*, 1978; SEITZINGER, 1988) and is thus not fully accessible for analysis.

Variations in time

The annual temperature cycles (Fig. 2a) influence biological processes. Bacteria-mediated degradation of organic matter proceeds at a faster rate in summer than in winter. Therefore one observes distinct annual cycles in the concentrations of oxygen and nitrates (e.g., Figs. 4b and 4c, for Well G2). The decrease of NO_3^- is observed only in summer (May to September) and is less pronounced than for O_2 , in agreement with redox potentials (STUMM and MORGAN, 1981) and the use of O_2 by heterotrophic organisms. The decrease in O_2 and NO_3^- during summer leads to an anaerobic and reducing environment in the river sediments and in part of the aquifer.

Implications

The cyclic variations of several important water properties and the sharp decrease of the pH and O_2 and NO_3^- concentrations at the river/aquifer interface have significant implications for the behavior of minor water constituents. For instance, the chemical changes in the river water and in the water of the adjacent aquifer are fully or partly responsible for the behavior of manganese and other trace constituents. Changes in nutrients and microbiological activity, in pH complexing agents (i.e., degradation products of aquatic biota), and in redox conditions influence speciation and solubilities and affect properties of mineral surfaces and the oxide/water interface. Surfaces and bacteria regulate the

1979 from HOEHN *et al.* (1983), measured in Well KB1H at 5 m distance from the river. (Unit of measure is $nmol L^{-1}$.)

Table 3. Comparison of water in River Glatt sediments with river water and groundwater.
Ca, NO_3^- (μmolL^{-1}); Mn (nmolL^{-1}); DOC (mgL^{-1}); N.D., not determined.

Date	River Glatt ¹⁾					River Sediments ¹⁾					Well G1				
	pH	Ca	Mn	NO_3^-	DOC ²⁾	pH	Ca	Mn	NO_3^-	DOC	pH	Ca	Mn	NO_3^-	DOC ³⁾
1988						Infiltration apparatus									
May	8.3	2230	65	N.D.	5	8.0	2230	1000	N.D.	N.D.	7.6	2100	960	N.D.	2
August	8.8	1585	65	420	5	7.8	1560	990	375	N.D.	7.5	1700	1260	230	2
(mean, n=4)															
1989						Interstitial water									
May	8.4	1560	30	470	5	N.D.	2260	16200	N.D.	N.D.	7.6	1760	1020	250	2
July	8.5	1540	60	390	5	N.D.	1830	25600	130	22	7.5	1595	1855	95	2
September	8.3	1475	60	275	5	N.D.	1620	22300	3	20	7.5	1515	3290	70	2
November	8.0	1855	160	390	5	N.D.	1880	5200	30	21	7.5	1870	2730	330	2
1990															
January	8.0	1900	275	530	5	N.D.	1950	1900	45	15	7.5	1980	3020	N.D.	2

¹⁾ O_2 in river water at $\geq 100\%$ saturation, in river sediments - 1% of saturation

²⁾ Mean of 1987 (4.6 ± 0.6) mgL^{-1} (n=7), excluding a storm event (14 mgL^{-1}), Waber et al. (1990).

Mean of 1991 (5.8 ± 1.3) mgL^{-1} (n=4) Ch. Lienert, personal communication.

³⁾ Mean of 1987 (2.0 ± 0.2) mgL^{-1} (n=6), Well G2, Waber et al. (1990).

Mean of 1991 (2.8 ± 0.8) mgL^{-1} (n=4) Ch. Lienert, personal communication.

Table 4

Comparison of the mean of selected heavy trace metal concentrations in the groundwater before and after 1985. In 1985 phosphates in detergents were replaced by NTA. Concentrations in nmolL^{-1} . In parentheses number of measurements.

Well	Cu		Zn		Cd	
	84/85	86/87	84/85	86/87	84/85	86/87
G1	71.6 \pm 22.0 (14)	92.4 \pm 26.0 (10)	160.6 \pm 71.9 (12)	154.4 \pm 56.6 (11)	2.2 \pm 1.2 (9)	2.5 \pm 0.7 (12)
G2	51.4 \pm 26.1 (11)	80.3 \pm 29.3 (9)	42.8 \pm 27.5 (9)	59.6 \pm 61.2 (7)	1.4 \pm 1.5 (10)	1.2 \pm 0.4 (7)
G3	59.1 \pm 19.8 (15)	92.0 \pm 35.7 (13)	55.0 \pm 38.2 (14)	65.7 \pm 30.6 (11)	1.1 \pm 0.9 (9)	1.6 \pm 0.7 (14)
G5	43.8 \pm 9.1 (4)	79.8 \pm 18.1 (8)	48.9 \pm 44.3 (4)	38.2 \pm 19.9 (7)	1) (4)	1.6 \pm 0.8 (8)
G6	49.6 \pm 17.5 (12)	65.7 \pm 16.5 (9)	48.9 \pm 35.2 (6)	16.8 \pm 7.6 (8)	1) (4)	1.2 \pm 1.1 (9)

¹⁾ Below detection

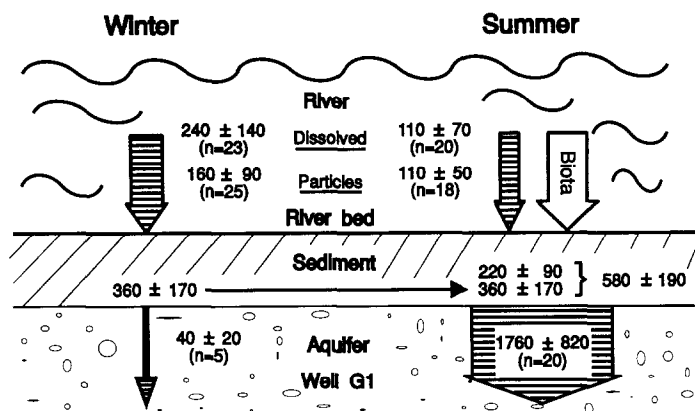


FIG. 6. Fluxes of manganese in winter and summer, in nmol L^{-1} . Mean semi-annual balances between river, river sediments, aquatic biota, and Well G1. Manganese is precipitated in the river sediments and in the aquifer during oxidizing winter conditions, and dissolved during reducing summer conditions. *Measured*: Concentrations of manganese in solution in the River Glatt and in Well G1, and in river particles; n = number of samples. Winter concentrations in Well G1 were measured between January and March of 1985/86. Concentrations of river particles are in part from LAURA SIGG (unpubl. data). The open arrow indicates unquantified contributions from aquatic biota.

concentrations of dissolved trace elements (JENNE, 1968, 1977; HEM, 1972, 1976; DREVER, 1982; MOREL, 1983; SPOSITO, 1984; LOVLEY and PHILLIPS, 1986, 1988, 1989; BOLT and VAN RIEMSDIJK, 1987; SCHINDLER and STUMM, 1987; SIGG, 1987; LOVLEY et al., 1990). While the concentrations of the main constituents (e.g., Ca^{2+} , O_2 , and NO_3^-) range from $\mu\text{mol L}^{-1}$ to mmol L^{-1} , those of trace constituents range from nmol L^{-1} to $\mu\text{mol L}^{-1}$. We focus our attention now on manganese and other trace metals.

Manganese

The chemical behavior of manganese in nature is complex and still not fully understood (e.g., SANTSCHI et al., 1990). In the following we describe its behavior in the River Glatt infiltration system and give information about seasonal variations, fluxes, sources, mobility, sinks, and possible processes which lead to the observations.

Seasonal variations in concentrations and fluxes

During the observation period the variability of dissolved manganese in the River Glatt (Fig. 5) was quite large ($180 \pm 130 \text{ nmol L}^{-1}$, $n = 43$). One notices differences between winter and summer (Fig. 6). The higher winter concentrations are produced by temperature inversions in Lake Greifen leading to transport of dissolved manganese from the anoxic hypolimnion of the lake (ANNETTE JOHNSON, pers. comm.). Recent measurements in the River Glatt by MÜLLER and SIGG (1990) and by KARAMEYAS (1991) support these results. The somewhat lower summer concentrations of dissolved ($<0.45 \mu\text{M}$) manganese are due to a smaller contribution from Lake Greifen and uptake of this essential element by growing aquatic biota in Lake Greifen and in the River Glatt.

In the groundwater and in the interstitial water of the river sediments one observes every summer between May and October a considerable increase in dissolved manganese (Tables 2 and 3, Figs. 4d and 5). During this period, the concentra-

tions in the groundwater reach the $\mu\text{mol L}^{-1}$ range; afterwards they decrease again. A qualitatively similar behavior was found by BOURG et al. (1989) for infiltrating river water from the Deûle River (France).

The seasonal and spatial variations in the concentrations of dissolved manganese are presented in Figs. 4 and 5. The latter includes data for the year 1979 from HOEHN et al. (1983). It appears that the summer peaks of manganese vary within a factor of four. The differences in the amplitudes and shapes of the peaks may be the result of the prevailing climatic conditions which influence microbiological activity and reaction rates, hence the redox conditions and/or the concentrations of complexing agents of the infiltrating water. Differences in amplitudes and shapes of the peaks could also result from: (1) varying amounts and changing composition of accumulated river sediment; (2) clogging of the riverbed; or (3) different flow paths due to changing groundwater levels. The amount of sediment is certainly influenced by flow conditions in the river (Fig. 2b) and by growth and decay of algae.

In Fig. 6 we present a simple model of the manganese fluxes during winter and summer in the River Glatt and in the aquifer. Fluxes and material balances suggest that manganese accumulates from infiltrating river water within the river sediments during more oxidizing winter conditions. These manganese deposits are then dissolved under reducing summer conditions, which leads to higher concentrations within the aquifer. This process accounts, however, only in part for the observed summer peaks. Possible additional manganese sources are discussed in the following paragraph.

Sources

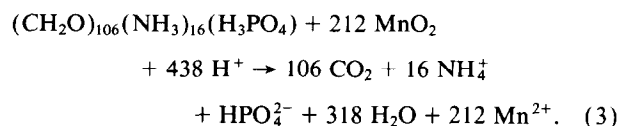
From the data in Table 2 and Figs. 5 and 6 it is evident that the concentrations of dissolved and particulate manganese in the river water cannot directly produce the summer peaks of manganese in the groundwater. The model presented in Fig. 6 proposes that the riverbed sediments retain and

release manganese in seasonal cycles. Measurements of riverbed sediments support this hypothesis. They contain about 1 mg Mn per g sediment. About 10% of the Mn is extractable by 10^{-3} M EDTA (KARAMETAXAS, 1991).

The results of Table 3 show that very large differences exist between river water and the interstitial water of the river sediments for the concentrations of Mn, O_2 , NO_3^- , and DOC, and the pH. The concentrations of Mn in the interstitial water reach summer values which are about ten times higher (i.e., about $25 \mu\text{mol L}^{-1}$) than those observed in the groundwater. The data of Table 3 indicate clearly that, in accordance with the model of Fig. 6, the summer peaks of manganese in the groundwater must result from dissolution of manganese deposits in the river sediments. From Fig. 6 it appears that only about 10% of the summer concentration infiltrates directly from the river; 20% may be produced by dissolution of winter deposits. The rest results probably from decomposition of aquatic biota which accumulates this essential element. KARAMETAXAS (1991) found similar concentrations of manganese in riverbed sediments and in the dry residues of decaying River Glatt algae. The river sediments are rich in organic carbon ($\sim 2\%$). He also measured high manganese concentrations (1%) in the excreta of small aquatic fauna feeding on these plants. If these decay products remain within the river sediments they contribute significantly to the observed high manganese concentrations in summer.

Processes

The dissolution of Mn starts in the warmer season when enhanced bio-degradation and oxidation of organic matter lead to a lower redox potential in the interstitial water of the river sediments. At the maximum of the microbiological activity the Eh in the interstitial water of the river sediments was so low that even SO_4^{2-} was reduced (i.e., $-200 < \text{Eh} < -100$ mV, STUMM and MORGAN, 1981). The bacteria-mediated dissolution of manganese is a process with relatively fast kinetics. The coupling of the degradation of aquatic organic matter with the dissolution of manganese can be approximated by the following simplified stoichiometric equation:



The speciation of the dissolved manganese is not known. Speciation calculations suggest 89% Mn^{2+} , 6% MnHCO_3^+ , and 4% MnCO_3^0 . Organic complexation was not assessed in these calculations, since the complexing agents and their concentrations are unknown. However, we found in the interstitial water of the river sediments DOC concentrations of up to 25 mg L^{-1} (Table 3), which could enhance the formation of metal complexes.

Recently it has been demonstrated that bacteria are directly involved in electron transfer reactions (LOVLEY and PHILLIPS, 1986, 1988, 1989; MYERS and NEALSON, 1988; LOVLEY et al., 1990). LOVLEY and PHILLIPS (1988) and MYERS and NEALSON (1988) have shown that microorganisms can completely oxidize organic compounds with Mn(IV) as the sole

electron acceptor and that this reaction can yield energy for microbial growth. Direct bacterial processes are very likely to mediate the reduction of manganese (hydr)oxides in the River Glatt/aquifer system; however, the present study does not give a direct proof for these biotic processes. The high concentrations of DOC in the interstitial water of the river sediments (Table 3) resulting from the degradation of organic matter may, in addition, enhance dissolution processes of metals (Mn, Cu, Cd) by complex formation.

Mobility and sinks

During the 1985–87 period the manganese concentrations in the groundwater increased in summer with flow distance in the aquifer (Fig. 5). The increase was observed at distances of up to 26 m (Well G5). We postulate that, between the river and Well G5, bacteria-mediated and/or reductive manganese dissolution occurs from surfaces of the aquifer material. Differences in the appearance and form of the peaks during different summers can result from changing groundwater levels in the aquifer. The very high peak in Well G5 in autumn 1986 and the irregularly shaped peaks of the same year in Well G6 could have been produced by the drastic increase in water table elevation of about 4 m (Fig. 3). During this period, additional manganese (hydr)oxides may have dissolved from grain surfaces freshly saturated with groundwater. To find out whether the 1986 peaks of Wells G5 and G6 are related to the 1985 peak in Well G3, we performed a simple estimation of possible retardation: from the groundwater flow velocity of $\sim 5 \text{ m d}^{-1}$, the apparent migration velocity of manganese between Wells G3 and G6 of 0.3 m d^{-1} (distance: $\sim 100 \text{ m}$; travel time: $\sim 300 \text{ d}$), a bulk density of the aquifer of about 2 g cm^{-3} and a porosity of ~ 0.2 , an apparent distribution ratio (R_D) between solid and liquid of about 2 mL g^{-1} results. This value for R_D is certainly too low (see later). Therefore, we conclude that the 1986 peaks in the more distant wells are not related to the 1985 peak in Well G3, but were produced locally.

At greater distances from the river, the concentrations of dissolved manganese decrease (Fig. 5). At 100 m they are usually negligible. The decrease is due to surface- and/or bacteria-catalyzed precipitation and sorption of manganese (hydr)oxides (DIEM and STUMM, 1984; SANTSCHI et al., 1990) resulting from ingassing of O_2 from the vadose zone and admixture of deeper groundwater.

In laboratory batch experiments, KARAMETAXAS (1991) measured under aerobic conditions a distribution coefficient (R_D) of $\sim 10^4 \text{ mL g}^{-1}$ for the sorption/precipitation of Mn in the presence of aquifer material. This value lies well within the range of R_D -values 10^3 – 10^6 mL g^{-1} given in the literature (e.g., SANTSCHI et al., 1990). In the laboratory sorption experiments equilibrium was reached after about 5 h.

In an attempt to collect fresh manganese precipitates we placed pans and teflon foils in some of the observation wells (similar procedure to BELZILE et al., 1989). After exposure during winter a black coating was found on the foils and pans (most probably the mineral birnessite, Fig. 7). The amount of material was, unfortunately, too small for an unambiguous identification by XRD but it contained high concentrations of manganese. The precipitation and plating of birnessite and

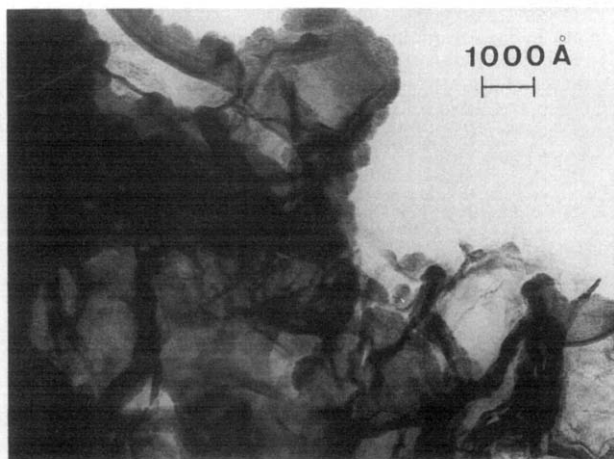


FIG. 7. Transmission electron micrograph of manganese deposits from traps in Well G2. The aggregations of platelets (some standing on edge) consist probably of the mineral birnessite.

amorphous manganese (hydr)oxides is expected to be part of the manganese source in the aquifer for the dissolution cycle of the following year.

Every year, in autumn or early winter, the concentrations of dissolved manganese in river sediments and in the groundwater begin to decrease (Tables 2 and 3; Figs. 4d and 5) and the travel distances of dissolved manganese become smaller. The decrease in the concentrations of Mn in the fall has probably three reasons: (1) Reduced microbiological activity due to falling ambient and water temperatures. This leads to a higher redox potential and/or less complexing conditions and to a smaller rate of (bacteria-mediated) manganese dissolution, which becomes finally negligible. (2) The manganese deposits in the river sediments start to be exhausted. (3) Decaying algae and sediments are swept away from the riverbed. The riverbed has now a clean appearance, and smaller quantities of sediments are observed. The morphology of the sediments changes from a sludge with particle sizes of $\sim 20 \mu\text{m}$ radius to a "clean" sand ($\sim 100 \mu\text{m}$). An exception to this general behavior was found in January 1990 (Table 3), when exceptionally high temperatures led to an unusually high bioactivity. This is also reflected in the strong reduction of NO_3^- in this period.

Anthropogenic Trace Metals

Several anthropogenic trace metals (i.e., Cr, Cu, Zn, Cd, Pb, and Hg) were measured in our investigation. Here we report on Cu, Zn, and Cd; the complete data are published by KUSLYS (1988) and KARAMEYAS (1991).

Copper

Copper results from the decomposition of organic matter in the riverbed (JACOBS et al., 1988). Copper is known to form strong complexes with organic ligands (e.g., FÖRSTNER and WITTMANN, 1981). During the time of observation, copper concentrations were in general somewhat higher in summer than in winter. Copper shows a high mobility in the aquifer. The average concentrations do not change much

along the infiltration path (Table 4). The decrease in concentrations with flow distances corresponds roughly to the effect of mixing. This mobility reflects the stability of the organic Cu complexes. Complex formation may be governed by degradation of organic matter in the river sediments. THURMAN (1985) has estimated that 1 mg humic carbon per liter can complex $1 \mu\text{mol L}^{-1}$ of Cu. Calcium will compete with Cu for binding sites. The binding strength for Ca is 100–1000 times less (MANTOURA, 1981). Thus, if we assume that the 2 mg L^{-1} of DOC (Table 3) are humic substances, then $\sim 1.8 \text{ mg}$ of it would be tied by Ca (using the reduced binding strength of 1000). The remaining DOC could then still complex 200 nmol L^{-1} of Cu. The assumption of a 100%-humic DOC is certainly an over-estimate, but the rough calculation shows that complexation by DOC could produce the observed concentrations of dissolved Cu. In addition, the River Glatt carries high concentrations of DOC released from sewage treatment plants. It is therefore likely that degradation products of aquatic biota and releases from sewage treatment plants contribute considerably to the mobilization and migration of copper.

Complexes can also form with EDTA and NTA, which were measured in concentrations of $1\text{--}200 \text{ nmol L}^{-1}$ and $10\text{--}40 \text{ nmol L}^{-1}$, respectively, in the river and groundwater at this site (GIGER, 1986; HOURIET, 1990). EDTA is mainly released by industry. Speciation calculations (JACOBS et al., 1988) indicate that in the groundwater at Glattfelden only about 14% of the total dissolved copper is expected to form an EDTA complex (for a mean EDTA concentration $\sim 20 \text{ nmol L}^{-1}$). NTA was recently introduced in detergents as a replacement for phosphates. The differences of about 30% in average copper concentrations between 1984/85 and 1986/87 (Table 4) may be due to this change in the composition of detergents in 1985.

Zinc

In contrast to manganese and copper, which result mainly from river sediments and from the decomposition of organic matter, the source for zinc is the river water itself, which receives this metal from industrial sources. The zinc concentrations were generally at a maximum in late summer, but annual cycles are not clearly observed. The infiltration behavior of zinc remains unchanged during the year. One notices a rapid decrease in concentration at the beginning of infiltration and a somewhat slower decrease farther along the flow path (Tables 2 and 4). We explain this decrease of a factor of 4–10 between Wells G1 and G6 by sorption processes on the aquifer material (WEGMÜLLER, 1987).

Cadmium

Generally, the cadmium concentrations are much higher in the groundwater than in the river. Cadmium, like manganese, shows significant annual concentration cycles (Fig. 4e). The cadmium peaks are not or only partly related to the manganese peaks and exhibit a different time behavior. The highest concentrations during summer are found between Wells G2 and G3 (2.5–7 m). At Well G1 cadmium results to a large extent from the decomposition of organic matter in the river sediments (JACOBS et al., 1988). Its further in-

crease along the flow path to Well G2 is probably related to the desorption of CdCO_3 from the aquifer. Sequential laboratory leaching experiments (see methods) with aquifer material ($<32 \mu\text{m}$) from the site at Glattfelden have demonstrated that cadmium resides at or very close to the surfaces of aquifer grains (A. GRÜTTER, pers. comm.). Its leaching behavior differs considerably from that of calcium. The cadmium concentrations obtained were close to saturation for CdCO_3 .

The decrease in cadmium concentrations beyond Well G3 is probably due to sorption on calcite surfaces and/or precipitation as CdCO_3 (FULLER and DAVIS, 1987; DAVIS et al., 1987) when alkalinity increases. Our batch laboratory experiments demonstrated that cadmium is not coprecipitated with manganese hydroxides. In a very recent paper COWAN et al. (1991) showed that cadmium is also sorbed on amorphous iron oxyhydroxide. Calcium was found to compete with Cd for accessible surface sites. The redox chemistry of Fe(hydr)oxides could, besides the dissolution of CdCO_3 , contribute to the observed annual cycles of Cd. KARAME-TAXAS (1991) observed considerable dissolution of iron within the river sediments in late summer.

The results in Table 4 indicate a decrease in the Cd concentrations of about a factor of 2 for 100 m flow distance. This slow decrease suggests the formation of quite strong Cd complexes or neutral species. In contrast to the results for Cu, one notices no difference in the concentrations since the use of NTA in detergents (Table 4).

CONCLUSIONS

- 1) Distinct annual cycles are observed for several parameters in the investigated river/groundwater system. These cycles are induced by variations of the ambient temperature which influence microbiological activities, the growth and decay of aquatic biota, and solubilities of chemical compounds.
- 2) The enhanced degradation of organic matter during the summer period produces a considerable decrease in pH, O_2 , and NO_3^- concentrations, and redox potential during infiltration of river water to the aquifer, and affects directly the concentrations of trace elements.
- 3) The most pronounced annual changes in water chemistry occur in the interstitial water of the sediments of the riverbed and in the groundwater close to the river. Here, one observes a strong mobilization of manganese and other trace elements during summer. More oxidizing conditions in winter lead to a precipitation of manganese within riverbed sediments and the aquifer. These (amorphous) Mn deposits may dissolve in the summer of the following year.
- 4) Cadmium is mobilized in summer in the riverbed and from aquifer material close to the river, but is then slowly removed in the farther aquifer, probably by adsorption and/or precipitation processes.
- 5) Copper resulting from degradation of river sediments and aquatic biota is mobile in the aquifer due to formation of organic complexes.
- 6) Zinc results directly from the river water, in contrast to manganese, copper, and cadmium, but is rapidly removed by sorption to surfaces of aquifer material.

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