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Behavior of Heavy Metals, Nutrients, and Major Components during Roof Runoff Infiltration

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The behavior of heavy metals (Cd, Cu, Zn, Cr, Pb), nutrients (organic C, P, and N parameters), and major ions was investigated during percolation of roof runoff water through an artificial infiltration site. The concentrations of the various components were determined in rainwater, roof runoff, and infiltrating water at various depths in the soil. The concentrations of most parameters in roof runoff were highest during the "first flush" at the beginning of rain events. Despite rapid infiltration caused by strong preferential flow, differences were still observed in infiltration behavior between individual compounds. Cl^- , NO_3^- , SO_4^{2-} , ortho-phosphate, and the major part of DOC behaved essentially conservatively during infiltration, whereas NH_4^+ concentration decreased probably as a consequence of nitrification. The concentrations of Ca, Mg, Na, K, and alkalinity were regulated by dissolution of soil material. The change in concentrations of Cu, Cd, and Cr during infiltration was mostly due to the concentration dynamics of roof runoff inflow water with only limited retention by soil, indicating the high mobility of these metals in the unsaturated zone. In the short term, Pb and Zn showed the opposite behavior with strong retention in the upper soil layers as determined by the large decrease in their concentrations measured in the lysimeters compared with those in the runoff water. However, in the long term, zinc and lead were also transported through the deeper soil layers of the unsaturated zone. The high mobility of Cu and Cd can be attributed to complexation by ligands in solution, and of Cr to the presence of Cr(VI) species. The artificial infiltration site used in this study was designed according to recommended standards for water infiltration; nevertheless its design turned out to be sub-optimal for the retention of heavy metals and for some of the organic and inorganic compounds.

Introduction

Urban stormwater runs first over sealed surfaces such as roads and roofs. It frequently contains contaminants, including heavy metals and organic pollutants washed off from these surfaces. Typically, urban stormwater is collected within the municipal sewer system and transported to wastewater treatment plants, where it dilutes household wastewater

with large volumes of relatively clean water. To avoid such a dilution effect, recent Swiss legislation (Swiss Water Pollution Control Law 1991, Article 7) has required that, where possible, unpolluted wastewater such as urban stormwater be infiltrated into the ground (1, 2). Enhancement of groundwater recharge would be an additional advantage. However, the contaminants in stormwater may then reach the groundwater by infiltration.

The aim of the present study was to evaluate the behavior of roof runoff constituents during infiltration through soil. This was studied at a field site with a technically designed infiltration pit fully equipped for monitoring and sampling. Heavy metals were of particular interest because of their potential toxic effects on groundwater used for drinking water, while infiltration of nutrients could increase bacterial growth and development of anoxic conditions.

There are several sources of pollutants in roof runoff. Atmospheric pollutants accumulate on the roofs as dry deposition as well as being washed out of the atmosphere in rain (wet deposition). In addition, the roof materials themselves may be a source of some metals, such as copper from the dissolution of copper gutters and drain pipes (1).

Previous studies have investigated the composition of roof runoff and determined the concentration range of contaminants in roof runoff from several types of roofs (tile, polyester, and gravel) (1–5). The results of these studies identified various groups of pollutants, such as pesticides and heavy metals (1–5). Heavy metal concentrations ranging from 20 to 324 $\mu\text{g/L}$ Cu, 8 to 63 $\mu\text{g/L}$ Zn, 2.6 to 20 $\mu\text{g/L}$ Pb, and 0.1 to 1 $\mu\text{g/L}$ Cd were determined in some examples of roof runoff. Initial, "first flush" concentrations were considerably higher than later during a rain event (1, 4). Copper and cadmium were found mostly in the dissolved form while 20% of Zn and most of the Pb were present as particulates. Voltammetric techniques demonstrated that dissolved Cu, Zn, and Cd were very labile (as free aqua ions or weak inorganic complexes) (3). Runoff dynamics of the different compounds studied (heavy metals, triazines) depended on the characteristics of the element and on the nature of the roof (4).

Transport of metals in soils is governed by a number of factors, such as physical and chemical soil properties, pH, and redox conditions (6–9). Metals may be retained in soils by adsorption reactions on the surfaces of soil minerals and organic matter and by precipitation reactions. In addition, microbial processes in the soil influence redox potential, soil pH, and CO_2 concentrations and thereby can mobilize or immobilize heavy metals. Mobilization of certain metals in soils can also occur as a result of complexation with dissolved organic ligands that originate from soil or roof runoff, a process which competes with sorption processes.

In the field system studied here, roof runoff from a large roof area of a building complex located in an industrial zone was collected and infiltrated in an infiltration pit. At this location, the contribution of a petrol station and of a solid waste incinerator in the immediate vicinity of the infiltration site needs to be considered. The hydraulic behavior at this site has been described elsewhere (10, 11). The infiltration behavior of heavy metals (Cd, Cu, Zn, Cr, Pb) and of nutrients (organic C, P, and N parameters) is examined in the present study. The composition of infiltrated water with respect to pH, alkalinity, and ionic strength will influence the behavior of heavy metals. The dynamics of major ions give insights into the chemical interactions of infiltrating water with the soil matrix. A parallel study has reported on the behavior of pesticides and nitrophenols at the same site (5).

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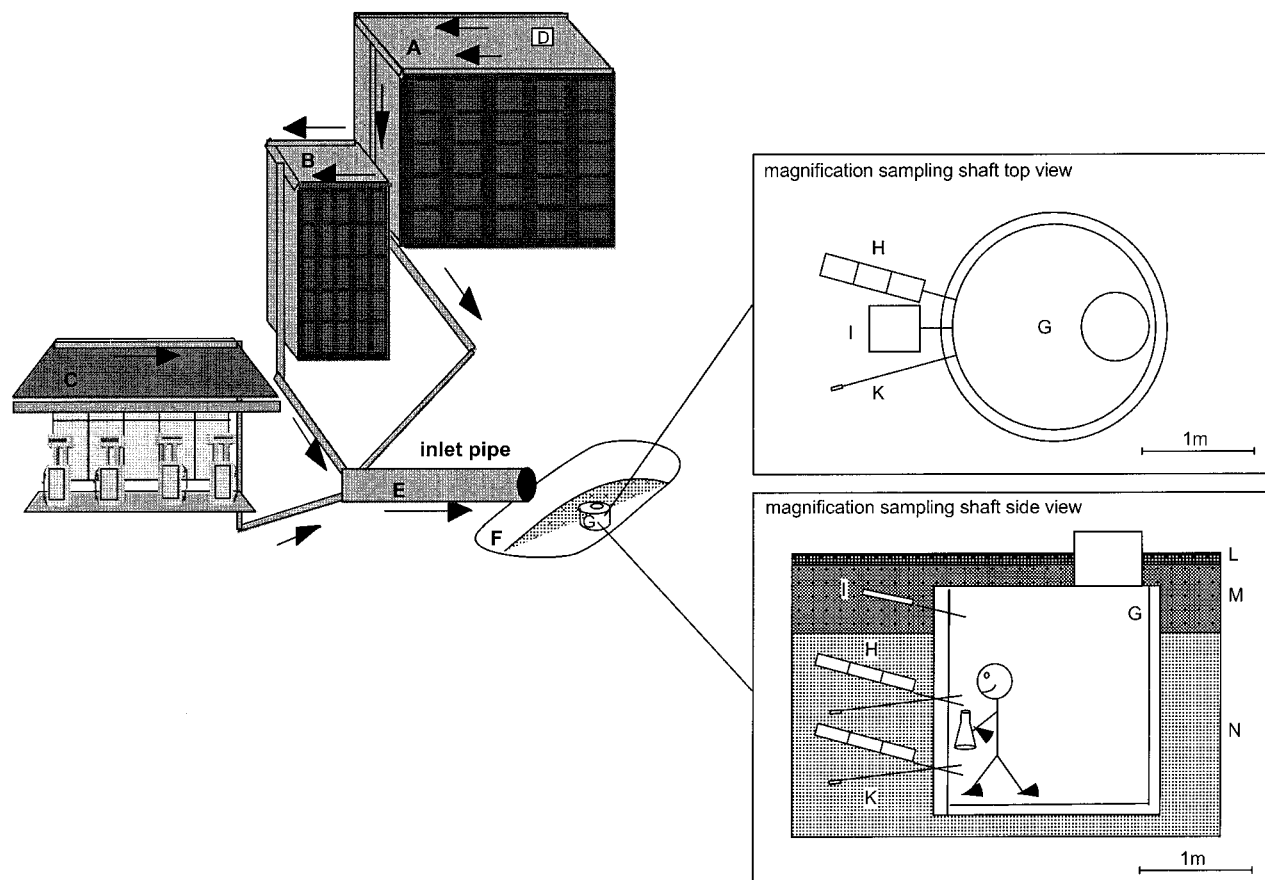


FIGURE 1. Scheme of the roof runoff infiltration site, with magnified sampling shaft: A, flat gravel roof; B, flat gravel roof with top humus layer; C, plastic roof; D, dry/wet deposition sampler; E, common drainage pipe; F, infiltration pit; G, sampling shaft; H, three semicircular tube lysimeters positioned at a -130° , 0° , and $+130^\circ$ angles toward the inlet pipe at a depth of -1.0 m (A, B, C) and three at -1.6 m (D, E, F); I, three tube lysimeters all at 0.40 m depth; K, three suction cups in the same orientations and depths as the lysimeters; L, humus layer $5-15$ cm thick mixed with medium-sized stones; M, drainage gravel layer 0.60 m thick; and N, natural aquifer sediment of fluvio-glacial gravel.

The objectives of this study are to determine the sources and concentration range of heavy metals, nutrients, and other components in roof runoff and to study how these contaminants are affected by the infiltration process. For the evaluation of the potential risk of contamination of the underlying groundwater, it was necessary to examine the degree of retention of these chemical components in the top organic-rich soil layer, and the extent of mobility through the unsaturated zone. This work also seeks to examine the accumulation of metals in soil over longer periods of time and to determine the potential for breakthrough.

Experimental Section

Field Site

The study site encompassed a large building complex at the industrial zone (Grüze) of the city of Winterthur (Switzerland). Roof runoff was collected from three types of roofs spanning a total area of 5350 m^2 (see Figure 1). The highest and largest roof (3913 m^2 , 73% of total area) was a gravel-covered flat roof (Figure 1A), a smaller (968 m^2 , 18% of total area) flat gravel roof covered with a humus layer (Figure 1B) and a third, (471 m^2 , 9% of total area), inclined plastic roof covering a gasoline station (Figure 1C). An assemblage of drainage pipes collected the water from the roof into a single (PVC) pipe (Figure 1E) that channeled the combined roof runoffs into an infiltration pit (Figure 1F) with an area of 106 m^2 , a depth of $3-4$ m, and an approximate retention volume of 150 m^3 .

At this site the top $5-15$ cm of soil material was composed of humus (organic-rich) material mixed with medium-sized stones (12). The layer beneath (2.9 m thickness) consisted of some clay, sandy gravel that contained small stones, and gravel-silt soil material. The sand content was between 20% and 50%. From 2.9 to 15 m there was a third layer of a quaternary glacial-fluvial washout origin. The groundwater level in this permeable aquifer (10) was at approximately 12 m and could rise to $6.5-7.5$ m in the event of floods. The soil material of the unsaturated zone contained carbonate (30–60%), with a relatively small clay content but with a high specific surface area, approximately 0.1–1% organic matter, and 10–20% silt ($1/256-1/16$ mm). The soil at this site was under oxic conditions. Drinking water is drawn from this aquifer from a well located about 400 m downstream from the pit (10).

In the middle of the infiltration pit a 2 m diameter and 2 m high concrete shaft (Figure 1G) was built for sampling purposes. Various soil water samplers were installed in a symmetrical radial manner in the direction of roof runoff inflow from within the sampling shaft. These extended into the surrounding soil at depths of 0.4 , 1 , and 1.6 m of the unsaturated zone. To sample macropore water, we placed six semicircular lysimeter pipes made of polyethylene with a 15° slope which provided free flow of soil water (Figure 1). Each lysimeter was 0.9 m long and was divided into three compartments (600 cm^2 each) from which an individual polyethylene tube transferred water into collection containers placed in the shaft.

TABLE 1. Hydrological Parameters for Three Rain Events

	1st event May	2nd event June	3rd event July
dry period length (days)	2.3	7.6	10.8
rain duration (days)	2.5	4.2	2
total rain over this event (mm)	21.4	54.8	
cumulative inflow (L) whole event	57180	146742	94811
cumulative inflow (L) "first flush" ^a	1039	476	591

^a "first flush" is the initial volume of roof runoff water (liters) up to the point where concentration changes of metals and other components measured get minimal, for example, the knee point in the washout curve.

In addition three polyethylene tub-shaped containers (1800 cm² each) were placed immediately below the top humus soil layer at a depth of 0.4 m. Further details on construction and hydrogeology of the infiltration pit are given elsewhere (10, 11).

Rain Events

Rain intensities (mm/min) were measured and digitally recorded on the highest roof and in the infiltration pit using tipping bucket rain gauges with a 0.25 mm-resolution/tip.

The rain events (May 25–27, June 20–24, and July 23–24, 1996) were characterized by the duration of the dry period preceding these rain events and by other parameters as given in Table 1. Sampling of each rain event included dry deposition that preceded the rain event, wet deposition (rain without roof contact), roof runoff (inflow to the infiltration site), and percolating water (soil water) through the unsaturated zone.

Sampling

Materials. Among various materials tested for lysimeters and subsurface tub samplers, polypropylene and polyethylene turned out to be the most suitable ones, since neither release of metals from these materials nor adsorption onto them was observed. Therefore, soil samplers, tubing, collecting bottles, and storage bottles for trace metal analysis were all made of polypropylene or polyethylene. Sampling bottles for trace metal analysis were soaked in 1 M HNO₃ Suprapur and subsequently rinsed with NANOpure water; bottles for major elements and nutrients analysis were rinsed twice with NANOpure water.

A **dry/wet deposition** collector described in detail elsewhere (13) was placed on the highest and largest roof. It essentially consisted of a rainwater sampler and a water surface as a receptor of dry deposition. Measurements of these samples provided the overall input to the roofs of dissolved and particle-bound components. Loads in dry and wet depositions were calculated according to 13.

The quantity of roof runoff inflow to the infiltration site was determined from automated water level measurements (every two minutes) in a siphon connected to the pit inlet pipe. Combined roof runoff was sampled from the infiltration pit inflow using a Sigma auto sampler. At certain intervals, programmed to span over the entire rain event, roof runoff water (800–1000 mL) was transferred into a polypropylene bottle. To calculate loads of components in the inflow, we integrated the water flow [Q in L/min] over time *t* [min] resulting in the volume [L] of influent water (Table 1). The cumulative amounts [μg or mg] of components were obtained by integrating concentrations [μg/L] over the cumulative volume [L] that entered the infiltration pit.

Samples of percolating water were collected from three different depths (0.4, 1.0, and 1.6 m; Figure 1) using lysimeters (1 and 1.6 m) and subsurface tub collectors (0–0.4 m). *Discrete*

samples of 2 L volume were taken when a continuous flow of percolating water took place. *Continuous samples* were collected when the percolating water flow was much less intense, that is, a trickle of water. The collection duration was registered in both cases.

Soil Material of the Infiltration Site. To investigate accumulation of components on soil material, we sampled the solid soil material three times: (1) At the beginning of operation of the site (Nov. 94), providing background levels at the site, three soil profiles (0–1.5 m) were taken. (2) Four months later, three pooled soil samples each taken from 16 points uniformly distributed over the surface (0–0.1 m). (3) Sixteen months later (Feb. 96) during installation of the lysimeters, three soil samples which were dug out were taken from 1.0 m and three samples from 1.6 m.

Sample Handling and Preparation for Analysis

All samples were kept in the dark at 4 °C and filtered after arrival in the laboratory (0.45 μm, Sartorius cellulose nitrate filters, precleaned by boiling in 1 M HNO₃ Suprapur for heavy metal analysis and by boiling in deionized water for all other components). For heavy metal analysis the filtrate was acidified to 0.1 M HNO₃ Suprapur.

The particulate metal fraction was collected from a known volume on the filter membrane and was acid-digested in a microwave oven (MLS 1200 Mega, Microwave Laboratory Systems) with 4 mL of 65% HNO₃ Suprapur and 1 mL of 30% H₂O₂ pro analysis. The digested samples were then diluted (1:10) with NANOpure water.

Soil material was dried at 80 °C for 24 h; 3–8 replicates of each sample were taken, ground with a pestle and mortar, homogenized, weighed, and acid-digested (4 mL of 65% HNO₃ Suprapur and 1 mL of 30% H₂O₂ p.a.) in a microwave oven. The digested samples were then diluted (1:10) with NANOpure water.

Analytical Methods

Major matrix elements (Ca, Mg, Na, K, detection limit = 0.01 mg/L) were determined by ICP-OES on a Spectroflame instrument (Spectro Analytical Instruments). The metals Cr, Cu, Zn, Cd, and Pb were measured by ICP-MS on a ELAN 5000 (Perkin-Elmer/Sciex) with an internal standard (50 μg of Rh/L) and detection limits of 0.05 μg/L for Cu and Zn and 0.01 μg/L for Cr, Pb, and Cd.

Ammonium concentrations were obtained from filtered samples by the NH₃ gas diffusion method in a FIA instrument. Alkalinity was determined by automatic titration (Titriprocessor 670, Metrohm). Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured by the high-temperature (680 °C) catalytic pyrolysis instrument Shimadzu TOC-500 using potassium phthalate for calibration. Concentrations of Cl[−], NO₂[−], NO₃[−], SO₄[−], acetate, formate, and oxalate were determined by anion-exchange separation using an OH[−] gradient (1–25 mM) with an AG11/AS11 column and analyzed by a DX-300 ion chromatograph (Dionex, Olten) with suppressed (ASRS) background conductivity detection.

For total nitrogen content the raw samples (including suspended solids) were digested by K₂S₂O₈ at 120 °C, 1 bar, for 2 h. Nitrate was then determined according to standard procedures by an air segmented continuous flow analyzer (Technicon). Soluble reactive phosphate was determined according to standard procedures on an air segmented continuous flow analyzer (Technicon).

Results and Discussion

Dry/Wet Atmospheric Depositions and Roof Runoff

To determine the possible sources of contaminants in roof runoff, that is, atmospheric deposition (dry plus wet) and/or

TABLE 2. Dry and Wet Atmospheric Deposition for Two Rain Events and Mass Balance for Input to Infiltration Site

element	sampled event	atmospheric deposition				input to infiltration site	
		dry deposition rate ($\mu\text{g m}^{-2} \text{d}^{-1}$)	wet deposition rate ($\mu\text{g m}^{-2} \text{d}^{-1}$)	dry deposition amount/event (mg)	wet deposition amount/event (mg)	cumulative inflow (mg)	cumulative inflow dry + wet depositions
Cr	May	2.1	3.4	26.1	48	32	0.43
	June	2.0	2.1	83	50	93	0.70
Cu	May	8.7	6.0	108.5	87	92	0.47
	June	18.0	6.7	732	161	370	0.41
Cd	May	0.6	1.0	7.7	13.7	11.8	0.55
	June	0.2	<0.1	6.9	<0.1	1.6	0.24
Zn	May	26.8	34.6	334	497	193	0.23
	June	44.7	200.0	1813	4780	1190	0.18
Pb	May	4.0	9.4	50	136	12	0.07
	June	5.2	15.2	211	364	56	0.10
Ca	June	500	5230	20408	117500	2491452	18.0
Mg	June	300	3170	12380	71260	214574	2.56
Na	June	160	1170	6620	26390	185765	5.6
K	June	110	390	4580	8800	377056	28.2
DOC	June	-	6990	-	293180	686163	
Cl	June	250	2600	10184	58636	177685	2.6
N(NO ₃ + NH ₄)	June			30347	217540	103742	0.42
N(NO ₃)	June	140	1960	5601	43977	92954	1.9
N(NH ₄)	June	610	7720	24746	173563	10788	0.05

roof structures, we calculated the mass balance of total atmospheric deposition and total cumulative inflow to the infiltration site for the June '96 event (Table 2). The dynamics of roof runoff flow rate, and the behavior of heavy metals and major components in this water are shown in Figures 2 and 3.

Calculations were performed on the water inflow to the infiltration pit (10, 11) as a function of rain intensities, and roof runoff from the three types of roofs with different water retention capabilities. These model calculations showed that roof runoff water from the smooth steep plastic roof was the first (residence time <10 min) to reach the infiltration pit constituting a "first flush" of water containing high pollutant concentrations, whereas roof runoff water from the gravel roofs appeared later, with the rainwater first filling the pores in the roof material prior to flushing. During the June event 7.4 L/m² rain was needed and a residence time of 31 h was observed until runoff onset.

Major Components. The ratios of the cumulative inflow to the sum of dry and wet depositions (Table 2), as well as the comparison of the concentrations in rainwater and roof runoff (Table 3) indicate that the roof material was a significant source of Ca, Mg, Na, K, and Cl in the roof runoff. The largest contribution to these elements was most probably provided by contact of rainwater with the gravel-covered roofs. The large differences in the concentrations of Ca, Mg, Na, K, and alkalinity between the first flush and subsequent samples (Figure 2, Table 3) were likely due to wash down of dust from the nonporous plastic roof. The pH range (7.0–7.6) and the substantial alkalinity in the roof runoff indicate rapid neutralization of the acid depositions by carbonate dissolution on the roofs.

The ratios of Na to K concentrations in the roof runoff were in the range 1.0–1.7, indicating relatively high K concentrations. In addition, the ratio of dry to wet deposition was larger for K than that for Na, Ca, and Mg (Table 2). K in dry deposition may be enriched in comparison to other elements due to contributions by waste incinerators (14). The waste incinerator located in the vicinity of the infiltration site (750 mW) may thus provide an additional K source.

Nutrients. DOC made up over 90% of total organic carbon (TOC) in the roof runoff. Acetate, formate, and oxalate were

the most abundant low molecular weight organic acids, which could act as complexing ligands for metals. The first flush contained the highest concentrations of these acids that were probably derived from processes occurring on the roofs (bacterial decomposition of organic compounds) since subsequent levels found matched those in the rain (Table 3).

NH₄⁺ was the predominant nitrogen species in the wet and dry depositions (Table 2), but only a small fraction (5%) of NH₄⁺ reached the infiltration pit. The mass balance indicates that NO₃⁻ increased on the roofs. Differences between NH₄⁺ and NO₃⁻ concentrations revealed that nitrification occurred on the gravel-covered roofs with the longer residence times. In runoff from the plastic roof ("first flush") NH₄⁺ and NO₃⁻ concentrations were found at similar concentrations. In contrast, in later samples the ammonium concentration diminished to much lower levels (0.003–0.02 mM) than nitrate (Table 3). The lowest concentrations occurred during the highest water flux (> 130 L/min) coming almost exclusively from gravel-covered roofs. From the sum of NH₄⁺ and NO₃⁻ it is apparent that only about half of the nitrogen from atmospheric depositions finally reached the infiltration pit. The larger part of this missing inorganic nitrogen was most probably retained as organically bound nitrogen, which regularly accounted for 20–50% of total nitrogen.

Soluble reactive phosphate (SRP) corresponding to the bioavailable phosphate was mostly below 1–2 μM in roof runoff, whereas total phosphate was 2–9 times higher.

Heavy Metals. The metals Cr, Cd, Pb, Zn, and Cu were monitored. During the studied rain events, average wet deposition rates of all metals (except Cu) were higher than the corresponding dry deposition rates. For all metals, the total (dry plus wet) atmospheric deposition exceeded the total metal load in roof runoff inflow (Table 2). The ratio of metal content in the cumulative inflow to the metal content in combined dry and wet deposition suggests that only a fraction of the metals deposited on the roof was washed off by the rain. For instance, only 42–67% Cr, 39–45% Cu, 18–23% Zn, 22–54% Cd, and 6–9% Pb were washed off the roof in the three rain events studied. These findings suggest that the gravel on the largest roof and the humus layer

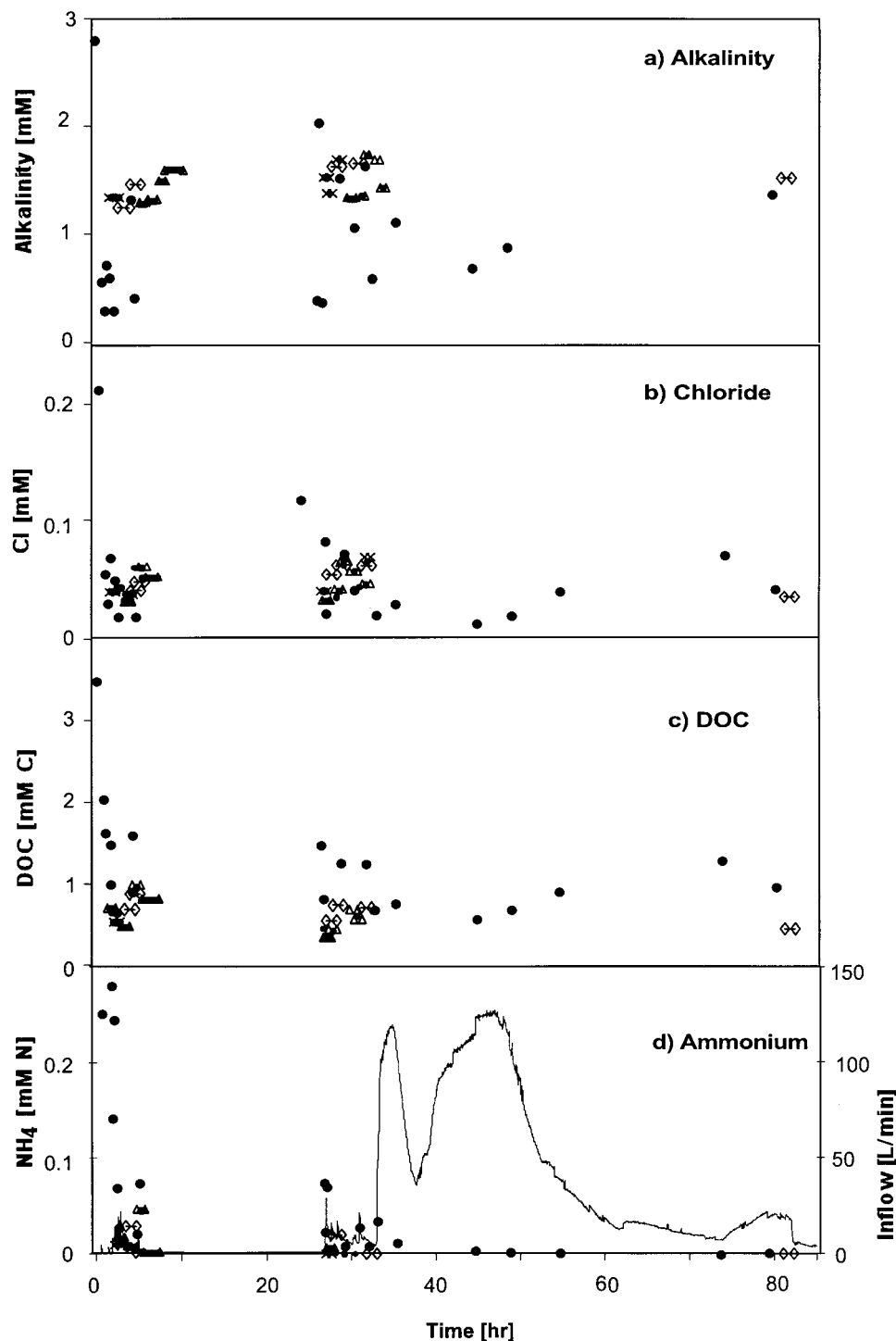


FIGURE 2. Dynamics of roof runoff inflow (—) and of concentrations of selected parameters in the inflow (●) and in lysimeters A (—1 m, ◇—◇), C (—1 m, △—△), and E (—1.6 m, ×|||||×) during the June rain event. Horizontal bars indicate sampling duration. Three types of processes are represented: (a) alkalinity depicts geochemically controlled parameters; (b) chloride and (c) DOC represent the behavior of conservative parameters; and (d) diminishing concentrations of ammonium in the lysimeter water indicate biological transformation despite preferential flow.

covering the smaller gravel roof retained the metals probably by sorption, precipitation, and complexation processes.

The results do not conclusively show whether the main source of heavy metals in the roof runoff was from atmospheric deposition or from metal structures (gutters, etc.) located on the roof. The latter is likely if there was very strong retention of heavy metals in the gravel/humus layers on the roofs. However, the contribution of the two sources remains to be determined.

Each rain event differed in duration, length of the preceding dry period, and volume of water entering the infiltration site during the first few minutes. Examination of the metal load in wet and dry deposition with respect to the length of the dry period preceding the sampled rain event and the duration of the rain event itself suggests that different metals were influenced to different degrees by the two parameters.

The dissolved Cr load in wet deposition was not affected by longer rain duration, whereas the corresponding dry

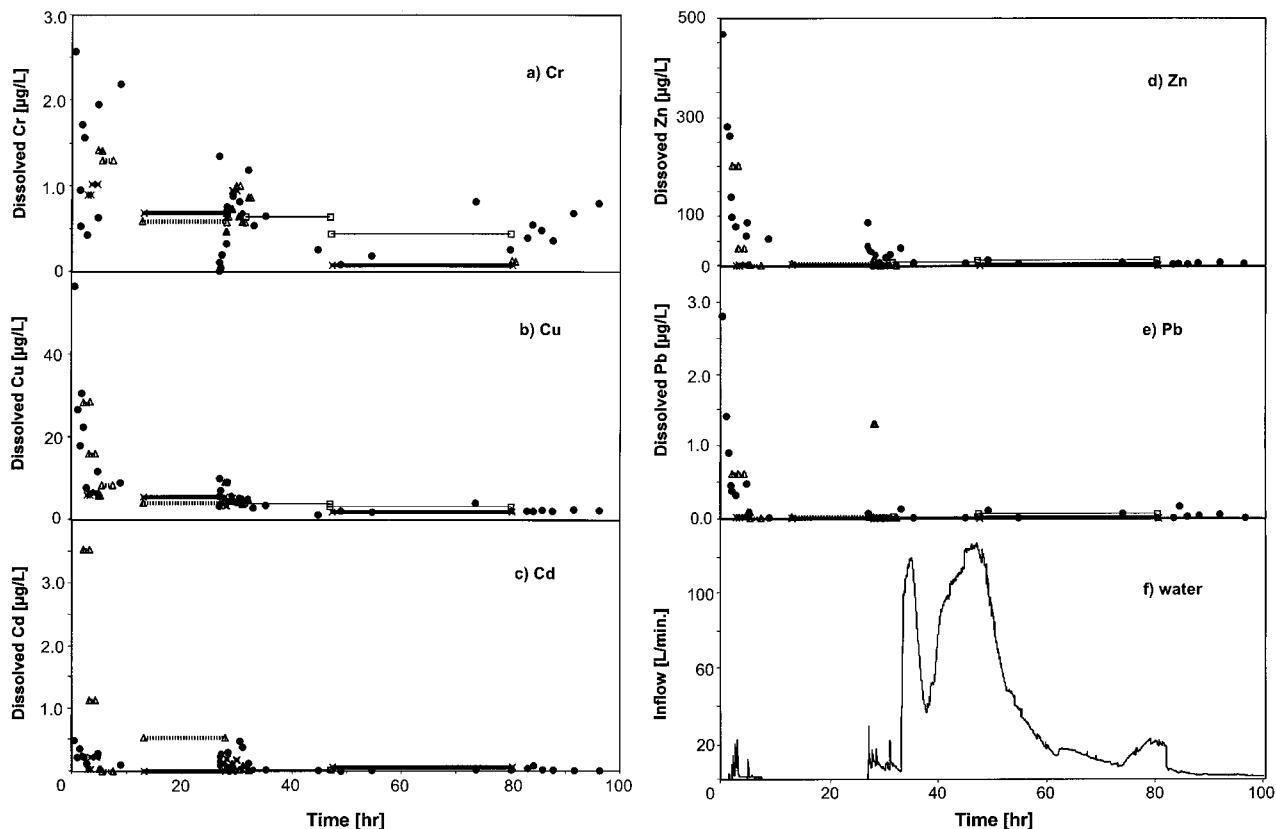


FIGURE 3. The concentrations of dissolved chromium (a), copper (b), cadmium (c), zinc (d), and lead (e) ($\mu\text{g/L}$) in roof runoff inflow and in the unsaturated zone (lysimeters) as a function of time and the dynamics of roof runoff flow rate (f) to the infiltration pit, Q (L/min) (—), as a function of time (h) for the June rain event: metals in the roof runoff inflow water (●); metals in the top humus layer collected in tub samplers (□—□); metals in soil at a depth of 1 m sampled by lysimeter C (Δ — Δ); and metals in soil at a depth of 1.6 m sampled by lysimeter E, (\times |||| \times).

TABLE 3. Concentration Ranges of Major Components in Rain (June) and Roof Runoff Water (Input to the Infiltration Pit) and in the Water Collected in Lysimeters at 1.0 and 1.6 m below Ground

parameter	rain	roof runoff		lysimeter	
		first flush	after first flush	A, C 1.0 m	E 1.6 m
pH	6.9	7.0–7.6	7.0–7.6	7.3–7.6	7.5–7.7
Ca^{2+} (mM)	0.06	0.4–1.3	0.1–0.5	0.63–0.93	0.68–0.88
Mg^{2+} (mM)	0.01	0.06–0.44	0.01–0.04	0.04–0.14	0.1–0.14
Na^{+} (mM)	0.02	0.22–0.56	0.02–0.20	0.09–0.15	0.11–0.15
K^{+} (mM)	0.01	0.10–0.35	0.02–0.10	0.06–0.10	0.08–0.15
NH_4^{+} (mM)	0.14	0.14–0.29	0.02–0.07	0–0.04	0–0.01
alkalinity (mM)	0.08	0.7–2.8	0.3–0.6	0.8–1.7	1.3–1.7
Cl^{-} (mM)	0.01	0.06–0.22	0.02–0.06	0.01–0.06	0.03–0.06
SO_4^{2-} (mM)	0.04	0.1–0.2	0.01–0.1	0.01–0.1	0.01–0.10
o-P (μM)		1–2	0.1–1.0	0.06–1	
NO_3^{-} (mM)	0.06	0.29–0.64	0.02–0.20	0.05–0.20	0.09–0.14
N_{tot} (mM)		0.50–1.2	0.07–0.30	0.20–0.30	0.14–0.21
DOC (mM)	0.6	1–3	0.5–1.0	0.42–0.83	0.42–0.83
acetate (μM)	20	40–135	8–20	2–14	2–14
formate (μM)	40	35–62	0–18	0–2	0–2
oxalate (μM)	3	10–17	3–10	1–5	1–5

deposition fraction increased with increasing duration of the preceding dry period (Tables 1 and 2). In contrast, the Cd load in dry deposition was not affected by the increased duration of the preceding dry period.

The loads of dissolved copper and zinc and the total (dissolved plus particulate) lead increased with the increased length of the rain period as well as with the increased length of the preceding dry period.

These data suggest that the length of the dry period preceding the rain and duration of rain had an impact on both the extent of retention processes on metal concentra-

tions from roof origin and on metal concentrations in dry and wet atmospheric depositions.

The metal loads in inflow water are summarized in Table 2, and the dynamics are shown in Figure 3a–f, where metal concentrations [$\mu\text{g/L}$] in the inflow water and the roof runoff flow rate (Q) as monitored at the point of discharge into the infiltration site [L/min] are presented for the June event. Two metal fractions need to be distinguished: the first metal fraction, which was found in the “first flush” water, spanned a short period of time (i.e., the first few minutes after the beginning of the rain) but registered the highest metal

concentrations. Most of this water originated from the steep, plastic roof above the petrol station. The second metal fraction, which extended over a much longer period of time 2–4 days, consisted of water originating from all of the roofs.

“First Flush” Effect. In general, the metal concentration pattern in the inflow water followed the flow rate trend (Table 4, Figure 3). The magnitude of metal concentrations in the “first flush” influent followed the order June > July > May, whereas the total volume of roof runoff water followed exactly in the reverse order May > July > June. The highest metal contents were thus concentrated in the smallest volume of roof runoff water.

Very high concentrations at the beginning of the rain event were observed for Cr, Cd, Pb, Zn, and Cu. However, the concentrations of dissolved copper, lead, and zinc (Figure 3b,d,e) subsequently decreased, indicating a “first flush” effect. This effect could be accounted for by approximately 1 mm (480 L) of rain which was needed to rinse the plastic roof (Figure 1C). The small increase in concentration of dissolved copper, lead, and zinc after 23 h can be attributed to the renewal of rain after it stopped on the first day. Dissolved cadmium, chromium, and particulate lead (Figure 3a,c), however, exhibited a large increase in concentration on the second day, which can be explained by the release of large amounts of these metals from the gravel roofs. Unlike the other metals studied, the concentrations of chromium remained relatively high for a long period of time.

Infiltration Processes

To assess how the heavy metals, major components, and nutrients were affected by the infiltration process, we compared their concentrations in soil water collected by lysimeters at various depths to those in the roof runoff inflow to the infiltration site. The June rain event was selected to be shown in detail because the largest variations in concentrations of all components were observed and the dynamic behavior of pollutants could be exemplified. The concentrations of major components and of nutrients are reported in Table 3 for this event only, whereas heavy metal results are compared in Table 4 for the May, June, and July events. Figures 2 and 3 refer only to the June event.

At the discharge point from the inlet pipe in the infiltration pit, uneven distribution of the water occurred as a result of shortcomings in the configuration of the infiltration site. Though improvements were made including covering the soil around the discharge point with a polyethylene sheet, the contact between the water and the top humus layer remained insufficient (10). In addition, the soil structure between the inlet pipe and the lysimeters resulted in preferential flow directing the infiltrating water via a “short circuit”. As a result the tub samplers that were installed in the top soil layer (0.4 m) filled only after 6 h. This suggests that the tubs were filled also by direct rain as well as by percolating water, and therefore, these water samples may not be solely representative of infiltration processes.

Conservative Parameters

The concentrations of chloride, sulfate, nitrate, and SRP (Table 3, Figure 2) in lysimeter water followed the concentration fluctuations of those components in roof runoff water, where highly concentrated small volumes of water during first flush were later diluted either by soil water and/or by large volumes of runoff from the gravel roofs (Table 3). The concentrations of chloride, sulfate, nitrate, and SRP did not change substantially during soil infiltration, indicating the lack of an efficient retention mechanism for these compounds in soil. Due to the conservative behavior of Cl^- and SO_4^{2-} during infiltration, they can be considered as internal tracers.

A major part of dissolved organic carbon exhibited a similar conservative behavior with approximately the same

TABLE 4. Dissolved and Particulate Concentrations of Cadmium, Copper, Chromium, Zinc, and Lead ($\mu\text{g/L}$) in Roof Runoff (inflow water), Top Soil Tub Sampler, Lysimeter C at 1.0 m and Lysimeter E at 1.6 m for Three Rain Events

	rain event	inflow dissolved			inflow particulate			tub sampler at 0.4 m		lysimeter C at 1 m		lysimeter E at 1.6 m	
		“first flush”	after “first flush”	after “first flush”	“first flush”	after “first flush”	after “first flush”	dissolved	particulate	dissolved	particulate	dissolved	particulate
Cd ($\mu\text{g/L}$)	May	0.02–0.06	0.05–0.25	<0.01	<0.01	<0.01–0.06	<0.01	<0.01	<0.01	0.02–0.09	<0.01–0.03	0.02–0.16	<0.01–0.01
	June	0.12–0.48	<0.01–0.47	<0.01–0.07	<0.01–0.03	<0.01–0.03	<0.01	<0.01–0.02	<0.01	<0.01–1.10	<0.01–0.07	0.04–0.23	<0.01–0.02
	July	<0.01–0.15	<0.01–0.12	0.04–0.11	<0.01–0.07	<0.01–0.07	<0.01	0.14	<0.01	0.07–0.03	<0.01	<0.01–0.27	<0.01
Cu ($\mu\text{g/L}$)	May	2.0–3.5	1.2–3.1	0.2–0.4	0.1–0.6	0.1–0.6	2.1	2.1	0.3	2.4–3.3	0.2–1.5	1.7–2.9	<0.05–1.1
	June	7.3–56	1.0–11.6	0.7–6.9	0.1–3.0	0.1–3.0	3.1–3.7	3.1–3.7	0.2	2.2–28.1	0.2–1.1	1.9–6.7	<0.05–2.1
	July	2.2–14.2	1.7–4.0	2.8–13.8	0.2–14.7	0.2–14.7	2.8–4.2	2.8–4.2	0.4–1.3	2.4–3.3	0.1–0.9	1.9–3.1	0.3–0.8
Cr ($\mu\text{g/L}$)	May	0.3–0.4	0.3–0.7	0.2–0.3	0.1–0.2	0.1–0.2	0.3	0.3	0.8	0.4–0.6	0.2–2.0	0.4–0.7	0.2–1.7
	June	0.4–2.6	0.2–2.2	0.3–1.6	0.1–0.6	0.1–0.6	0.4–0.6	0.4–0.6	0.3–0.4	0.1–4.6	0.2–2.2	0.1–1.0	0.2–2.0
	July	0.2–0.8	0.3–0.7	0.9–9.6	0.3–4.0	0.3–4.0	0.8–0.8	0.8–0.8	0.7–1.9	0.5–1.2	0.3–1.3	0.3–0.6	0.3–0.8
Zn ($\mu\text{g/L}$)	May	8.4–29	0.4–10.8	3.4–5.6	0.2–2.4	0.2–2.4	5.6	5.6	0.7	2.2–4.4	<0.05–2.2	0.4–3.1	<0.05–5.1
	June	78–468	1.4–87	3.1–45	<0.05–24	<0.05–24	4.8–9.1	4.8–9.1	2.5–3.9	<0.05–202	<0.05–10.5	<0.05–1.6	<0.05–7.2
	July	65–153	<0.05–79	12.7–98	0.9–54	0.9–54	0.9–1.6	0.9–1.6	0.8–6.3	5.7–17.6	0.9–4.3	0.8–3.8	1.0–1.6
Pb ($\mu\text{g/L}$)	May	0.06–0.08	<0.01–0.34	0.33–0.51	0.04–0.38	0.04–0.38	<0.01	<0.01	0.60	0.02–0.11	0.08–1.70	<0.01–0.13	<0.01–0.92
	June	0.32–2.73	0.02–0.47	1.02–5.43	0.12–4.56	0.12–4.56	0.02–0.06	0.02–0.06	0.26–0.27	<0.01–1.31	0.07–0.72	<0.01–0.02	0.05–1.73
	July	0.09–0.58	<0.01–0.09	2.61–29.9	0.04–16.7	0.04–16.7	<0.01–0.03	<0.01–0.03	0.48–2.04	<0.01–0.08	0.13–0.93	<0.01	<0.37–0.91

concentration of dissolved organic carbon in the inflow water as in the lysimeters, indicating that only small amounts of DOC were retained by the soil. The same behavior was found for the pesticide atrazine at this site (5). It can be postulated that, as with chloride, sulfate, nitrate, and SRP, the initial large concentrations of DOC during first flush were diluted upon infiltration either by soil water or by large volumes of runoff from the gravel roofs. The major fraction of DOC was presumably refractory to biological degradation, and due to relatively weak attraction of DOC to solid soil surfaces, its transport would occur by preferential flow.

Geochemical Processes

The concentrations of Ca, Mg, alkalinity, Na, and K in the infiltrating water were within narrow ranges (Table 3, Figure 2), with average concentrations (arithmetic mean calculated from 26 individual lysimeter samples) of 0.73 ± 0.14 mM Ca, 0.11 ± 0.02 Mg, 1.4 ± 0.2 mM alkalinity, 0.16 ± 0.07 mM Na, and 0.08 ± 0.02 mM K. The ratio of Ca to Mg was on average 6.7 ± 0.5 . These concentrations indicate that the infiltrating water has reacted with the soil matrix. The contact of water during infiltration with carbonate rocks (calcite and dolomite) can explain the increase of Ca and carbonate content in unsaturated roof runoff water, whereas higher concentrations decreased by dilution or precipitation. Calcium and alkalinity measured in the lysimeter water were close to equilibrium concentrations of water with calcite. Despite the short contact time of the water with the soil matrix, the major ion composition thus approached the typical composition of water in contact with carbonate rocks.

Biological Processes

Much lower ammonium concentrations were found in infiltrating water collected by lysimeters compared to those found in roof runoff (Figure 2). NH_4^+ concentrations clearly decreased as a function of the infiltration path length. Highest NH_4^+ concentrations were found for the shortest infiltration path (lysimeter A, -1.0 m). The water collected in lysimeter C, at the same level but further away from the inlet pipe, had lower concentrations whereas the lowest concentrations occurred in samples from the lysimeter E located deeper (-1.6 m). The disappearance of ammonium can be attributed to nitrification occurring in soil, and possibly also to the adsorption of ammonium onto a negatively charged surface of soil material by ionic interaction. These processes were sufficiently rapid to take place even with relatively short contact time.

The decrease in concentrations of acetate, formate, and oxalate in infiltrating water as compared to their concentrations in the inflow indicates microbial uptake of specific carbon substrates. These low molecular weight organic acids represent, however, only a small part (about 10%) of the dissolved organic carbon.

Behavior of Heavy Metals during Infiltration

The infiltration behavior of dissolved Cr, Cu, Cd, Zn, and Pb was followed during the June rain event from inflow water to top soil sampler (0.4 m) to a soil depth of 1 m (lysimeter C) and even deeper (1.6 m) in the unsaturated zone (lysimeter E) in Figure 3a–e. Dissolved and particulate metal fractions in the inflow water and in the soil lysimeters are summarized for the three rain events in Table 4. However, the dissolved metal fraction (which may include colloids $<0.45 \mu\text{m}$) is of primary interest with regard to the transport of metals in pore waters, since it is assumed that particulate-bound metals will be mostly retained by the soil. Furthermore, the origin and significance of the particulate fraction in the lysimeters was not clear. Whereas Cr, Cu, Zn, and Cd were found mainly in the dissolved form, particulate lead represented a sig-

TABLE 5. Comparison of the Metal Content in Soil Layers at Different Depths between the Years 1994 and 1996 ($\mu\text{g/g}$)

	0–0.05 m (4 months)		1.0 m (16 months)		1.6 m (16 months)	
	1994	1995	1994	1996	1994	1996
Zn	27.7	49.5	6.6	13.0	30.9	13.0
Pb	28.7	34.1	3.6	4.5	9.2	4.5
Cu	18.0	22.3	5.7	9.9	18.9	7.1
Cr	55.2	46.1	35.5	23.5	55.0	23.5
Cd	0.02	0.6	0.2	0.18	0.03	0.18

nificant part of the total lead, and therefore, the behavior of particulate lead is reported in more detail.

Heavy Metals in Soil Water in Top Soil Layers. Metal concentrations determined in the top soil layers were much lower compared with metal concentrations collected deeper in the soil, at 1 and 1.6 m, an observation which indicates that a significant part of Cr, Cu, Zn, Cd, and Pb migrated downward in the unsaturated zone. The low concentrations determined in the top soil were probably caused by dilution of percolating roof runoff by direct rainfall as well as by uneven water distribution in the infiltration pit resulting in insufficient contact of inflow water with top soil layers.

Heavy Metals in Soil Water in the Unsaturated Zone. Two types of metal behavior were identified in the unsaturated zone. The first concerned the concentrations of Cu, Cd, and Cr (Figure 3a–c) in soil water which followed their trend in the inflow water; that is, high metal concentrations were observed in inflow water, followed by similarly increased concentrations in soil at the beginning of the rain event, and a subsequent decrease in the inflow water was followed by a similar decrease of metal concentration in the infiltrated water. Cr, Cu, and Cd were only partly retained by the soil, and a significant fraction was transported by soil water downward through the unsaturated zone therefore remaining mobile. The second type of behavior was seen for Zn and Pb (Figure 3d,e) which did not follow the trend observed in the inflow water. The concentrations of Zn and Pb in infiltrated water rapidly decreased even though their concentrations in inflow water were still high. This behavior indicates that in the short term, retention of these metals took place in the soil.

The hydrological factors, especially the strong preferential flow and the insufficient contact of the infiltrating water with the top humus layer, certainly contributed to metal transport in the unsaturated zone. However, the different behavior of Zn and Pb, in comparison to Cu, Cd, and Cr, indicates that chemical factors also play an important role in the retention versus mobilization of metals in the unsaturated zone.

Heavy Metal Accumulation in Soil. Metal behavior in infiltrating roof runoff water was also determined indirectly from the metal content in the solid soil material for soil depths of 0–0.05, 1, and 1.6 m over a 2-year period (Table 5).

The results reveal that, during the first 4 months of operation of the infiltration site, the concentrations of all metals except Cr increased in the top soil layer. The increase of Zn and Cd was greater than for Cu and Pb. This result indicates retention (even if only transiently) of Zn, Cu, Pb, and Cd in the top soil layers. A 0–1.6 m soil profile from 1994 showed that the metals were distributed unevenly between the various layers with higher metal concentrations in the deeper (1.6 m) soil layer than in the more shallow (1 m) soil layer. However, 16 months later, in 1996, metals were evenly distributed between these two layers.

Zn, Pb, and Cu concentrations increased two-fold at a soil depth of 1 m between 1994 and 1996, whereas Cd concentration remained similar and Cr concentration decreased in the same time frame. In contrast, at a depth of 1.6

m, the concentrations of Zn, Pb, and Cr all increased by a factor of 2 during this time period.

These results indicated a temporary accumulation of some of the metals in the top soil and at 1 m depth. In later years the results strongly suggest downward migration of metals out of the deeper soil layer. These observations also indicate that chromium was the most mobile metal among the metals studied, while transport of Cu, Zn, and Pb was slower.

Role of Physicochemical Processes in Retention Versus Mobilization of Heavy Metals during Infiltration

Zinc and lead showed two types of behavior: a short-term strong retention as was evident by their rapid disappearance from soil water and accumulation in the upper soil layers. However, longer term, as indicated from their decrease in deeper soil layers, they were transported downward in the unsaturated zone. The short-term behavior indicates that Zn and Pb were more reactive toward the soil material than Cu, Cd, and Cr. The retention of metals in this system may take place on one hand by retention of particulate material to which the metals are bound (including particles in the colloidal range), and on the other hand by adsorption of dissolved metals onto soil surfaces such as clay minerals and oxides, or by precipitation. Precipitation is, however, less likely to occur in this system because of relatively low metal concentrations. The metal cations of Zn(II), Pb(II), Cu(II), and Cd(II) are known to adsorb strongly on oxide and (oxy)-hydroxide surfaces, for example, Mn, Al, and Fe oxides (7, 15, 16). The affinity of these cations to oxide surfaces decreases in the order Pb(II) > Cu(II) > Zn(II) > Cd(II). The pH range in the infiltrating water was favorable for binding of these metals to surfaces. The retention of Pb and Zn may thus have taken place either by adsorption or by retention of particulate metals. Since a large fraction of lead in roof runoff entered the soil already as particulate matter, it is likely that the soil material served as a filter in retaining particulate lead. Dissolved lead is highly particle reactive and may be rapidly removed from solution by adsorption (17). Zn may also have been partly present in small particles retained by the soil material but has been more likely bound by adsorption.

Complexation by organic ligands in solution may compete with the adsorption of dissolved metals onto solid surfaces such as iron oxides. Among the metals considered in our study, Cu(II) has the highest affinity to organic ligands, whereas Zn(II) is usually only weakly complexed. Complexing ligands typically increase the dissolved metal concentration and therefore the metal mobility (9, 18–20).

Organic ligands in solution in this system included the low molecular weight acids acetate, formate, and oxalate of atmospheric origin as well as other components of the DOC in the roof runoff that were presumably nonbiodegradable and were not retained by the soil material thus behaving conservatively. Humic and fulvic acids from soil origin probably also played an important role. Speciation calculations (data not shown) with representative concentrations of metals and of the small organic acids indicated that, among the measured organic acids, only oxalate can significantly act as a ligand for Cu, Zn, and Cd. According to these calculations, a significant part of Cu in the infiltrating roof runoff water would be bound to oxalate. The effect of fulvic acid has not been assessed quantitatively, but it is likely that soluble copper–fulvic acid complexes are also formed. Therefore, the high mobility of Cu in this system may be attributed to complexation by ligands in solution. This hypothesis may also apply to Cd, which is only weakly bound to mineral surfaces. The strong mobility of chromium suggests that Cr occurs mostly as Cr(VI) species which are soluble and therefore mobile. The transport of metals bound

to colloids is another mechanism for metal transport in soil water that might play a role over longer time periods and could account for the long-term behavior of Pb (17). Thus the different behavior of the metals may be understood on the basis of their chemical interactions.

Consequences for Design of Artificial Infiltration Sites

The artificial infiltration site studied here was designed according to normal standards for water infiltration sites, but it turned out to be suboptimally designed with respect to the retention of heavy metals and some of the nutrients. Immediate percolation of roof runoff at the point of discharge to the infiltration pit, together with strong preferential flow, resulted in insufficient contact time between the infiltrating roof runoff water and the top soil layer. As a result, only minor retention of the metals Cu, Zn, Pb, Cr, and Cd by the top organic-rich humus layer took place. Metals, in particular Cu, Cd, and Cr, as well as DOC and nitrate were transported in soil water downward through the unsaturated zone and could finally reach groundwater. This case illustrates that an infiltration site should be optimized with regard not only to rapid water flow but also to the retention of pollutants in the top soil layers.

Artificial infiltration may have some advantages with regard to groundwater recharge and to decreased dilution of sewage. It must, however, be considered that artificial infiltration of roof runoff could lead to accumulation of heavy metals in the soil layers, and probably in many cases to increased contamination of groundwater with heavy metals.

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