

# New Device and Method for Flux-Proportional Sampling of Mobile Solutes in Soil and Groundwater

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The importance of monitoring the transport of organic contaminants in soil and groundwater, and the pros and cons of existing sampling methods, are outlined. A new, alternative sampling method is proposed, using a passive sampler that functions as a water-permeable, semi-infinite sink for passing solutes of interest. Tracers integrated in the device store information on the volume of water passing through the sampler during the installation period. The conceptual basis of the sampling method is described. This device enables flux-proportional monitoring of the concentrations of mobile contaminants in the soil and groundwater.  $^{14}\text{C}$ -labeled phenanthrene (PHEN) and glyphosate (GLY) are used as case study compounds in laboratory experiments. The sorption capacities and uptake kinetics of 13 adsorbents are screened and compared, as well as the dissolution kinetics of three tracer salts: calcium citrate, calcium fluoride ( $\text{CaF}_2$ ), and calcium hydrogen phosphate ( $\text{CaHPO}_4$ ). The application of the passive sampler is then demonstrated in long-term laboratory experiments, using large soil columns under steady-state hydraulic conditions. The accumulated flux of PHEN was sampled with an accuracy of 3.6%–17.8%, using graphitized carbon, hexagonal mesoporous silica, and cross-linked polymers as adsorbents. The accumulated flux of GLY was sampled with an accuracy of 12.4%, using  $\gamma$ -alumina as an adsorbent. The advantages and limitations of this new environmental monitoring method are discussed.

## Introduction

Monitoring of contaminant transport in soils and sediments has numerous applications in environmental sciences. It is essential, for example, for the remediation of hazardous waste sites (1, 2), but also in the assessment of organic and inorganic components in agriculture and in drinking water production (3). Leaching studies in the unsaturated zone are often used to determine the risk of groundwater and surface water pollution, as well as contaminant fate and exposure studies (4, 5). Our increasing understanding of the environmental and health impact of numerous chemicals (6) is prompting

the development of new monitoring and analysis methods. These include direct and indirect observation methods, using chemical tests, sensors, or spectroscopic techniques (7).

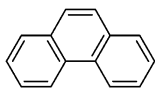
The most widespread method in environmental analysis is the “grab sampling” of contaminated soil or sediment, to determine total concentrations. This method is applicable to all contaminants and is a prerequisite for determining their presence and spatial distribution. It is tried and reliable, but also costly and labor-intensive. Furthermore, analysis of a soil sample gives only a static picture of the contaminants, reflecting the concentrations at the time of the sampling. It can only give information about contaminant mobility if other parameters are known and a predictive model is applied. This disadvantage could be overcome by taking and analyzing a very large number of samples over time; however, this is seldom done, because of the high analysis costs and the worker-hours involved in taking and storing large numbers of samples (8).

The most common devices used to monitor mobile contaminants in the unsaturated zone are fixed-tension lysimeters (9). The method is proven for different solutes; however, the pore water concentrations measured are not flow-proportional, and a water-balance model is necessary to estimate solute fluxes (10). A direct estimate of the soil water drainage flux is given by improved lysimeters that adjust the suction in the lysimeter in response to the tension in the surrounding soil (11–13). Both methods require an on-site vacuum control system. In contrast, passive capillary wick samplers rely on the capillary suction from a fiberglass wick. This suction is related to the wick material, length, and diameter, and it withdraws capillary-bound water and solutes from the soil (14–16). A common feature of these devices is that they break the capillary continuity of the water-flow path, so that flow divergence around the sampler may occur. The installation, in some cases, involves backfilling of the soil above the sampler device (16). In groundwater monitoring, the method used most often is well-purging followed by pumping or bailing of a sample, as described in the United States Environmental Protection Agency (USEPA) regulations (17). This method gives “snapshot” concentrations in time. Because concentrations may strongly vary with time, repeated sampling is necessary to obtain a representative picture.

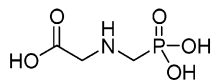
In this paper, we introduce a new device and method for in situ sampling of mobile dissolved solutes and/or colloids (18). The method potentially covers a wide range of solutes, including pesticides, phosphates, and hydrophobic organic contaminants (HOCs). The device is essentially a passive “smart filter”—a water-permeable porous sampler that is in continuous capillary contact with its surroundings and functions as a semi-infinite adsorptive sink for the solutes of interest. Tracers integrated in this filter store information on the volume of water that has passed the sampler during the installation period. The advantage of this new method is that it enables continuous sampling over a long time period, without the need for costly and time-consuming operations (no vacuum systems, pumping, or servicing). Unlike grab sampling, this method can account for concentration dynamics, because it gives a flow-proportional weighted average that is representative of the entire sampling period.

The aim of this paper is to present the concept behind this new sampling device and method, and describe its general principles and potential applications. We chose phenanthrene (PHEN) and glyphosate (GLY) as case study compounds. These compounds have very different electronic and molecular properties. Phenanthrene is a common hydrophobic organic contaminant, that is highly apolar.

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PHEN



GLY

Glyphosate [*N*-(phosphonomethyl)-glycine, which is also known by the tradename RoundUp], on the other hand, is a widely used herbicide (19) that represents a class of very polar and potentially ionic (pH-dependent) compounds (20). Therefore, the development of an efficient sampler for these compounds would demonstrate the applicability of the concept to two diverse groups of molecules.

### Theory

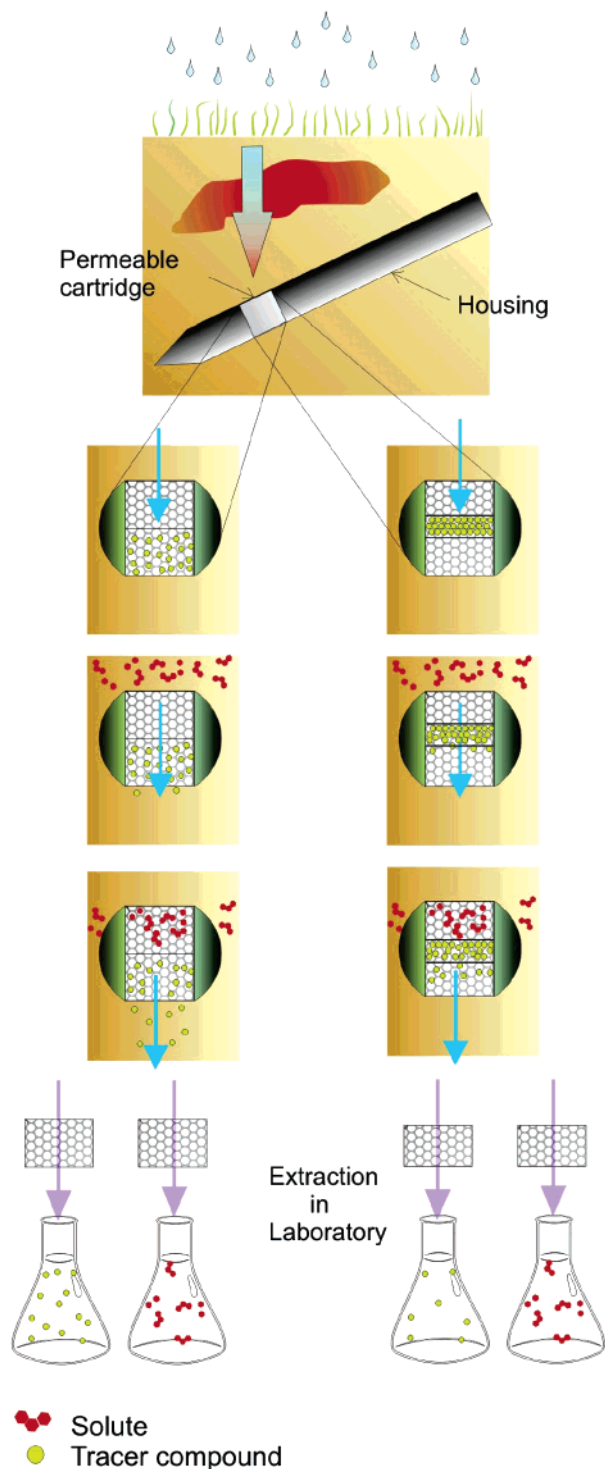
**Sampler Design and Installation Mode.** The sampler consists of a housing that contains one or more cartridges that are permeable to water (Figure 1). The sampler is installed for a certain period in the soil/groundwater. When water passes through the sampler, the cartridge adsorbs the solutes of interest and simultaneously releases a tracer compound into the water. After a given period, the cartridge is removed and the adsorbed solute mass and tracer loss are quantified using standard laboratory methods. The tracer displacement is dependent on the volume of water that passes through the cartridge during the installation period. Together with the adsorbed solute mass, it gives a flow-proportional solute concentration for the installation period.

The sampler may be installed either at an angle or perpendicular to the flow direction. Both the “upstream” and “downstream” interfaces of the cartridge should be in capillary contact with the surrounding soil. The cartridge must have good wetting and draining properties, as well as an unsaturated hydraulic conductivity that is at least as high as that of the surrounding soil. The hydraulic gradient in the soil then governs the flow of water and solutes through the cartridge.

As an example, the cartridge may have two compartments: the upstream compartment, which contains an adsorbent, and the downstream compartment, which contains the tracer. The adsorbent should display a high sorption capacity for the solutes and/or colloids of interest (the sorption capacity is defined as the volume of water that can pass through the cartridge without significant breakthrough of the solute, e.g. <1% of total incoming mass). This capacity is empirically determined in the laboratory. The cartridge’s capacity must be sufficiently high to ensure that no breakthrough will occur under field-test conditions. This means that the testing of the sorption properties should be performed under high flow conditions to simulate a worst-case scenario. If several different solutes are sampled simultaneously, the capacity should be defined following the least-sorbing solute, i.e., the sampler should function as a semi-infinite sink for all of the solutes measured. The sampler can be installed for long time periods, as long as two conditions are met: (i) the sorption capacity for the least-sorbing solute should not be exceeded, and (ii) the tracer should not be completely dissolved.

**Back Calculation of Solute Flux and Pore Water Concentration.** The sampling method may be used to calculate the mass flux density: the accumulated solute mass,  $M_s$ , is divided by the area of the filter intercepting the aqueous flow. Ideally, the volumetric flux density through the cartridge should be similar to that of the surrounding soil. However, if there is divergence or convergence of water and solute flow around the sampler, no direct estimate of the solute flux can be derived. In this case, a flow-proportional concentration is sampled by the use of tracer substances.

In the case shown in Figure 1 (left), the tracer ions leach out of the sampler cartridge when pore water passes through



**FIGURE 1.** Cartoon showing the sampler design, mode of installation, and sampling principle. Left: Two-compartment cartridge, with an adsorbent in the upstream compartment that sequesters the solute, and a tracer compound in the downstream compartment that leaches out in proportion to the volume of water passing (eluviation measurement). Right: three-compartment cartridge, with an upstream compartment that sequesters the solute, a center compartment that contains a semi-infinite source of tracer compound, and a downstream compartment that sequesters the tracer ions that leach out of the center compartment in proportion to the volume of water passing (illuviation measurement).

(tracer eluviation measurement). In this case, the accumulated mass of solute ( $M_s$ ) and the remaining mass of tracer ( $M_t$ ) are eluted and quantified using standard methods (e.g., high-performance liquid chromatography (HPLC)). The

water volume passing through the cartridge during installation is then given by eq 1:

$$V = \frac{M_{t,o} - M_t}{C_{t,max}} \quad (1)$$

where  $V$  is the water volume passing through the sampler,  $M_{t,o}$  the initial tracer mass,  $M_t$  the final remaining tracer mass after installation, and  $C_{t,max}$  the concentration of the tracer ion in solution. The average flux concentration of the solute,  $\bar{C}_s$ , is then given by eq 2:

$$\bar{C}_s = \frac{M_s}{V} \quad (2)$$

The volume of water passing through the cartridge is most accurately measured if 20%–80% of the initial amount remains after the installation period. This means one must estimate the order of magnitude of the cumulative water flux during the installation period. Furthermore, it is possible to use a combination of tracer salts with different  $K_{sp}$  values and/or different initial amounts, so that the uncertainty can be reduced and the optimal range of measurement can be expanded.

Alternatively, the tracer can be placed in the center section of the porous cartridge (Figure 1, right). Instead of measuring the tracer that remains in the cartridge, one can measure the increase of the tracer in the downstream compartment (tracer illuviation measurement). This lower section is filled with an adsorbent that can sequester the tracer released in the downstream compartment, either as the cation, anion, or both. In this case, the volume of water passing through the sampler is given by eq 3:

$$V = \frac{M_t}{C_{t,max}} \quad (3)$$

where  $M_t$  is the molar mass accumulated downstream from the tracer source.  $\bar{C}_s$  may be calculated from eq 2. The calculation is not dependent on the exact initial tracer mass prior to installation, and the center compartment acts as a semi-infinite source.

This configuration has another important advantage: It can compensate for tracer displacement due to diffusion under low flow conditions by measuring both upstream and downstream displacement (see Supporting Information for details). Another possibility to account for diffusive loss of the tracer is to install cartridges perpendicular to the flow direction. In this case, no convective transport of water through the cartridge would occur, and the mass loss of tracer during an installation period is the result of diffusive mass transfer.

**Choosing the Right Tracer Compound.** The tracer should (a) be nontoxic, (b) dissolve to give a instantaneous constant concentration in the passing fluid, and (c) be effectively retrieved after the installation and quantified using standard analytical techniques.

A good tracer compound is only partially soluble in water—it is partially displaced through and/or leached out of the sampler, in proportion to the volume of water that passes through the cartridge. The ideal case is when there is a linear relationship between the water volume and the amount of tracer displaced. For this, the dissolved tracer concentration should be constant, irrespective of the water flow rate. Sparingly soluble salts make good tracers, because they dissolve to a maximum concentration governed by their solubility products ( $K_{sp}$ ). In this study, three classes of tracers are distinguished (note that it is possible also to use a combination of tracers of different classes).

**TABLE 1. First-Screening Ranking of Adsorbent Materials for PHEN**

adsorbent <sup>a</sup>	$K_{d,PHEN}$ (L/kg)	extraction recovery (%)
<b>A</b>	$9.56 \times 10^4$	85.0
<b>B<sup>b</sup></b>	$1.38 \times 10^4$	113.5
Lewatite EP-63, cross-linked polystyrene	$1.24 \times 10^4$	112.8
<b>C</b>	$9.94 \times 10^3$	113.0
silica gel		
grade 10180 <sup>b</sup>	$2.02 \times 10^3$	105.5
grade 7754 <sup>b</sup>	$1.7 \times 10^3$	115.4
Carbotrap, graphitized carbon black	$1.79 \times 10^5$	7.9
Carboxen 569, carbon molecular sieve	$1.34 \times 10^5$	<1
active carbon zeolite	$3.88 \times 10^3$	<1
Molsieve 13X	4.82	115.2
Molsieve 5A	4.64	117.8
Al <sub>2</sub> O <sub>3</sub>		
<b>D</b>	0.62	119.0
fused	0.50	

<sup>a</sup> Codes for the adsorbents were as follows: **A**, Carbotrap C, graphitized carbon black; **B**, molybdenum-substituted hexagonal mesoporous silica (HMS); **C**, Amberlite XAD-7, polymeric beads; and **D**, Al<sub>2</sub>O<sub>3</sub>, activated, acidic. <sup>b</sup> PHEN sorbing to the glass accounts for the mass balance of >100%. <sup>c</sup> Adsorbent sample calcinated at 700 °C.

**Class A:** Tracers based on sparingly soluble inorganic salts (e.g., BaSO<sub>4</sub>). The  $K_{sp}$  values of inorganic salts are well-known and change only slightly over the range of temperatures in the soil and groundwater. Another advantage is that these salts are not affected by microbial degradation.

**Class B:** Tracers based on hybrid organic/inorganic salts (e.g., calcium benzoates). Here, the tracer contains an organic anion and an inorganic cation, or vice versa. The advantage of these hybrid salts over inorganic salts is that the potential pool of compounds increases dramatically. Therefore, it is relatively easy to find organic ions that are not present in the soil and meet the other criteria defined previously.

**Class C:** Tracers based on organic/organic salts. Here, an organic cation (e.g., [Bu<sub>4</sub>N]<sup>+</sup>) is coupled to an organic anion (e.g., acetate, pivalate, benzoate, etc.).

The solubility product of the tracers should be relatively independent of the ionic composition of the water passing through the sampler. In practice, tracers should be chosen with the macrochemical composition of the sampled water in mind. For example, Ca<sup>2+</sup> is often the predominant cation in natural soil and groundwater. Hence, co-ions will affect the solubility of calcium salts above a certain threshold concentration. To avoid this, the solubility of calcium salts should be well above this threshold value. Alternatively, ions may be chosen that are rarely present in the soil environment (e.g., La<sup>3+</sup>), or organic cations (such as tetrabutylammonium) may be selected, provided that such ions are nontoxic.

## Experimental Section

A detailed description of the materials synthesis procedures and the saturated hydraulic conductivity measurements is given in the Supporting Information.

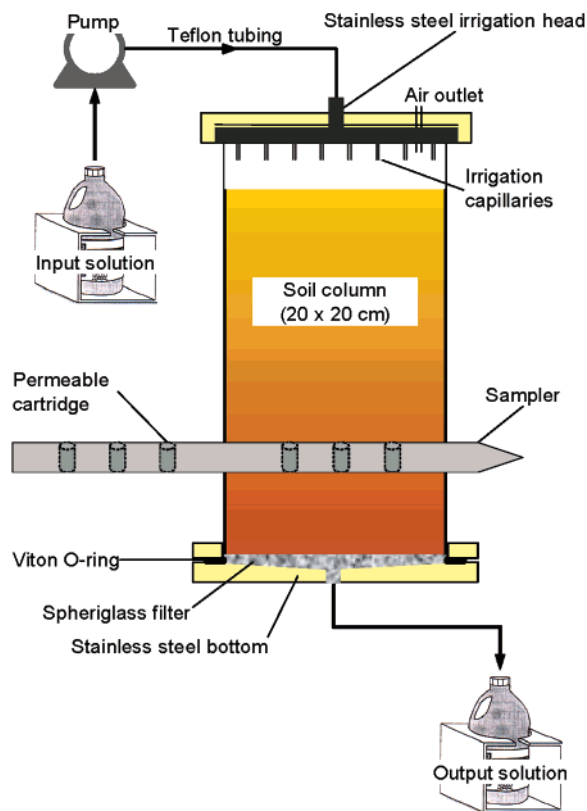
**Procedure for Batch Sorption Experiments.** A quantity (50 mg) of PHEN was dissolved in 200 mL of methanol. A volume of 0.04 mL of this solution was then mixed with 0.20 mL of a stock solution that contained 10 mCi/L of <sup>14</sup>C-labeled PHEN and brought to a volume of 1.00 L with demineralized water. The working solution had a total PHEN concentration of 33.8 μg/L, with a <sup>14</sup>C activity of  $2.0 \times 10^{-3}$  mCi/L. Adsorbent material ( $0.100 \pm 0.002$  g; see Table 1 for the list of adsorbents), was weighed into 10-mL glass centrifuge tubes with Teflon-

lined lids (each experiment was performed in triplicate). A portion (10.00 mL) of the working solution was then pipetted into the centrifuge tubes. The tubes were manually shaken for 10 s to ensure a homogeneous suspension, and then shaken end-over-end for 1 h, using a mechanical shaker. Control experiments (blanks) were performed by pipetting 10.00 mL of the working solution into empty tubes that were further treated in a manner identical to that of other samples. After shaking, the tubes were centrifuged for 5 min at 200 g, and 3.00 mL of the supernatant was pipetted into 20-mL scintillation vials. An aliquot (17.00 mL) of scintillation cocktail (Ultima Gold, Packard) was added, and the  $^{14}\text{C}$  activity was measured using a liquid scintillation counter (Packard 2250 CA, 0.5% counting precision). The amount of PHEN adsorbed was calculated from the difference between the  $^{14}\text{C}$  activity of the blank samples and the supernatant of the adsorbent-containing samples.

To measure the extraction efficiency, another 6.00 mL of the supernatant was removed, and 9.00 mL of ethyl acetate was pipetted into the centrifuge tubes. The tubes were closed, shaken overnight, and then centrifuged for 5 min at 200 g. A portion (3.00 mL) of the resulting supernatant was then pipetted into a scintillation vial, and the  $^{14}\text{C}$  activity was measured as described previously. The sorption distribution coefficient was calculated as  $K_d = C_s/C_w$ , (where  $C_s$  denotes the concentration of PHEN adsorbed to the solid phase and  $C_w$  represents the concentration of PHEN in the aqueous supernatant). The extraction efficiency was calculated from the amount recovered in ethyl acetate and the total amount remaining in the centrifuge tubes after removal of the 9 mL of the aqueous supernatant.

**Precolumn Saturated Flow Experiments Using  $^{14}\text{C}$ -Labeled PHEN.** The input solution had a total PHEN concentration of  $100.0 \mu\text{g/L}$ , with a  $^{14}\text{C}$  activity of  $2.0 \times 10^{-3}$  mCi/L. The input solution was pumped (Constametric 3200 HPLC pump) and split, via a stainless-steel cross, into three separate stainless-steel capillaries. These capillaries were connected to three parallel semi-prep guard columns (Upchurch Scientific, Oak Harbor, WA; internal volume of  $0.78 \text{ cm}^3$ , cross section of  $0.78 \text{ cm}^2$ ). In each experiment, the three guard columns each contained a different adsorbent (A, B, and C; see Table 1). The experiment was performed three times, so that a triplicate measurement was obtained. The solution was pumped overnight at a flow rate of  $0.2 \text{ mL/min}$ , to ensure constant input concentrations. Before the start of the actual experiment, 3 mL of the input solution was taken, and the  $^{14}\text{C}$  activity was measured as described previously. The flow rate was then set at  $0.48 \text{ mL/min}$ , the precolumns were attached, and the effluent from each precolumn was sampled every 20 min (for a total of 15 samples). The sampling time and the sample volume were measured so that the outflow rate for each column could be calculated. The average flow rate calculated for all experiments was  $0.159 \pm 0.026 \text{ mL/min}$ . PHEN concentrations were calculated from the  $^{14}\text{C}$  activity of each effluent sample, measured as described previously, while accounting for the actual volume of each effluent. Another sample of the feed concentration was measured for comparison at the end of each experiment.

**Procedures for Tracer Salt Dissolution Experiments.** A special apparatus was constructed for parallel measurement of the salt dissolution kinetics. Fluid pumped using an HPLC pump (Constametric 3200) was split in a T toward two manifolds (Valco Instruments, model Z10M1). These manifolds further split the fluid in 20 steel precision capillaries (30 cm in length, 0.13 mm inner diameter (ID)), each connected to a precolumn holder (Upchurch Scientific, model C1000). Triplicate samples of six different salts were placed in 18 of the precolumns, and 2 precolumns were left empty (blanks). Demineralized water was then pumped through the system at a rate of  $3.35 \text{ mL/min}$ . At  $t = 1 \text{ h}$ , effluent



**FIGURE 2.** Schematic of the soil column experimental setup used to measure the sequestering of phenanthrene (PHEN) and glyphosate (GLY).

samples were collected and weighed, and the flow rate was switched to  $1.67 \text{ mL/min}$ . Similar effluent sampling and changes of flow rate were performed at  $t = 3 \text{ h}$  ( $0.84 \text{ mL/min}$ ),  $t = 7 \text{ h}$  ( $0.20 \text{ mL/min}$ ),  $t = 25 \text{ h}$  ( $0.14 \text{ mL/min}$ ),  $t = 49 \text{ h}$  ( $0.84 \text{ mL/min}$ ), and  $t = 53 \text{ h}$  ( $1.67 \text{ mL/min}$ ). After 55 h, the final effluent samples were collected and weighed. The precise flow rate for each effluent sample was calculated from the elapsed time and the weight of the effluents. Calcium concentrations were then measured for each sample using atomic adsorption spectroscopy (AAS). All AAS measurements were performed in duplicate.

**Soil Column Experiments with PHEN and GLY.** Each experiment was performed using a stainless-steel column (20 cm in height  $\times$  20 cm in diameter). Two holes were drilled 15 cm from the top of each column, so that the samplers could be installed through the column (Figure 2; see also the detailed technical description and photograph of this setup in the Supporting Information). The columns were hand-packed with Voldby sand at a bulk density of  $1.50 \text{ g/cm}^3$ . The Voldby sand is fine-textured (45% fine sand, 49% medium sand, and 1% coarse sand), having an  $f_{oc}$  fraction of  $0.01 \text{ g/g}$  and a saturated hydraulic conductivity of  $590 \text{ cm/day}$ .

In a pre-equilibration period, the sampler cartridges were filled with the Amberlite resin (adsorbent C, PHEN experiment) and with  $\gamma$ -alumina (adsorbent D, GLY experiment), and each column was placed on a stainless-steel funnel that was filled with Spheriglass beads (Grade 2227, 75–180  $\mu\text{m}$ , Potters-Ballotini, Germany). This funnel was connected, with polytetrafluoroethylene (PTFE) tubing, to a 5-L collection bottle. The effluent sampling bottle connected to the PHEN column was pre-filled with 200 mL of methanol, to avoid the sorption of PHEN to the bottle. The outlet of the hanging water column, as formed by the tubing, was 35 cm below the bottom of the soil columns. The columns were then irrigated with a background feed solution ( $10 \text{ mg/L HgCl}_2$ ,  $3 \text{ mM CaCl}_2$ ) for 14 days at a rate of  $0.87 \text{ mL/min}$  ( $40 \text{ mm/day}$ ).

**TABLE 2. Long-Term Soil Column Experiments with PHEN and GLY**

sampling period	start (day)	finish (day)	input flow rate (mm/day)	effluent flow rate (mm/day)	adsorbent <sup>a</sup>
<b>PHEN Solute</b>					
1	0	28	40.0 ± 2.5	41.8 ± 1.8	A/B/C
2	28	35	40.3 ± 0.1	41.3 ± 0.3	A/B/C
3	35	42	39.8 ± 0.6	40.8 ± 0.3	A/B/C
4	42	49	37.6 ± 1.4	38.9 ± 2.7	A/B/C
5	49	56	38.1 ± 0.7	32.2 ± 10.7	A/B/C
6	56	77		5.3	A/B/C
7	77	91	36.4 ± 9.6	38.3 ± 8.8	A/B/C
8	91	104	35.3 ± 3.8	35.2 ± 8.5	B/B/B
9	104	106	38.2 ± 0.7	41.3 ± 0.7	B/C/C
10	106	111	39.8 ± 0.5	40.5 ± 1.7	B/C/C
11	111	113	36.4 ± 5.1	38.8 ± 1.1	A/C/C
12	113	118	40.0 ± 0.1	39.7 ± 2.9	A/C/C
13	118	132	37.8 ± 2.1	36.4 ± 5.2	B/C/C
<b>GLY Solute</b>					
1	0	28	38.0 ± 8.6	36.5 ± 7.9	D/D/D
2	28	42	38.7 ± 0.8	29.5 ± 9.5	D/D/D
3	42	56	38.4 ± 0.8	34.0 ± 6.5	D/D/D
4	56	77		7.8	D/D/D
5	77	104	41.6 ± 6.0	38.5 ± 2.9	D/D/D
6	104	111	34.1 ± 5.7	30.8 ± 7.6	D/D/D
7	111	120	39.8 ± 1.0	36.7 ± 4.2	D/D/D
8	120	139	39.9 ± 2.3	35.7 ± 7.2	D/D/D

<sup>a</sup> Adsorbent codes are as follows: **A**, Carbotrap C, graphitized carbon black; **B**, molybdenum-substituted hexagonal mesoporous silica (HMS); **C**, Amberlite XAD-7, polymeric beads; and **D**, Al<sub>2</sub>O<sub>3</sub>, activated, acidic.

Input solutions were prepared in 10-L batches and contained 10 mg/L HgCl<sub>2</sub>, 3 mM CaCl<sub>2</sub>, and either 100 μg/L PHEN or 5 μg/L GLY. PHEN was applied as a mixture of <sup>12</sup>C- (0.094 mg/L) and <sup>14</sup>C-labeled molecules (6 μg/L, 5 × 10<sup>-4</sup> mCi/L). GLY was applied as pure <sup>14</sup>C-labeled molecules (8.6 × 10<sup>-4</sup> mCi/L). At *t* = 0, the pumps were connected to these input solutions. The input flow was kept constant at 0.87 mL/min (40 mm/day) until day 56. The flow was then decreased to 0.29 mL/min (13 mm/day). A power failure occurred on day 73 (December 30), and the power was restored on day 77. After day 77, the flow was resumed at a rate of 40 mm/day until the end of the experiment (132 days for PHEN and 139 days for GLY). On every weekday, the input <sup>14</sup>C concentration and the input flow rate of the two columns were measured as follows: ca. 3 mL of solution was taken in a scintillation vial, using a three-way valve between the pump and the irrigation head. The sample was weighed, and the time and the <sup>14</sup>C activity were recorded. A triplicate 3-mL sample was taken on weekdays also from the effluent bottles, and the <sup>14</sup>C activity was measured and the effluent flow rates were calculated based on the weight of the effluent bottles and the elapsed time.

The samplers were moved back and forth, to alternately expose three of the six adsorbent cartridges to the soil. By doing this, disturbance to the soil was minimized. The adsorbent scheme and sampling periods are given in Table 2. Adsorbents were weighed in the steel cartridges and pre-wetted in demineralized water before installation. After exposure to the soil, PHEN or GLY were extracted from the adsorbent by shaking extraction (16 h) and centrifuging (20 mL of ethyl acetate for PHEN, 30 mL of 0.2 M KOH for GLY). Aliquots (3.00 mL) were then analyzed for <sup>14</sup>C activity.

After the irrigation of the columns was stopped, the soil was extracted from the 0–4, 4–8, 8–12, 12–16, and 16–20 cm depth layers for determination of the GLY and PHEN soil resident concentrations. Soil from each layer was transferred into a preweighed metal tray and thoroughly mixed. From each tray, three subsamples of ~20 g of moist soil were

weighed (with an accuracy of two decimal places) and placed into preweighed 100-mL Duran glass bottles. PHEN was extracted from the soil with 50 mL of ethyl acetate and GLY was extracted with 50 mL of 0.2 M KOH. The suspensions were shaken overnight in an end-over-end shaking apparatus. The bottles were then left overnight, to allow the soil particles to settle. The <sup>14</sup>C activity in the supernatant of the extraction bottles were measured in duplicate, as described previously. The remaining soil was dried at 105 °C for 24 h and weighed again, to measure the gravimetric soil water content.

## Results and Discussion

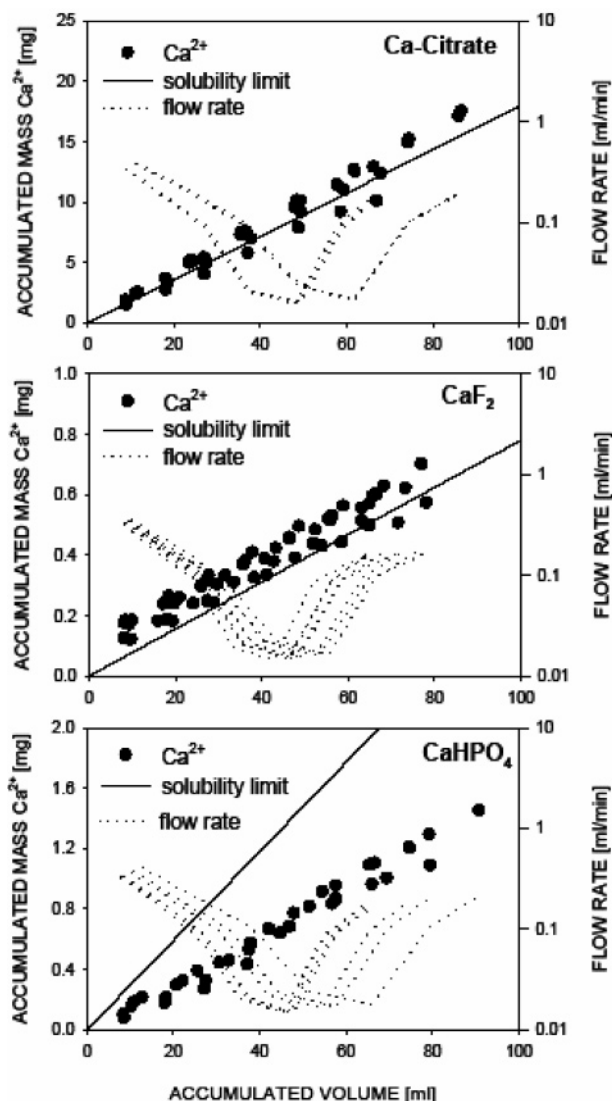
To monitor mobile solutes in soil and groundwater, the sampler should fulfill three basic requirements. It should enable (a) an ideal solubilization of the tracer compound, yielding constant tracer concentrations regardless of flow rate; (b) strong sorption of the solute to the adsorbent in the field, with full recovery after extraction in the laboratory; and (c) hydraulic equilibrium with the surrounding soil, or sediment, and minimization of flow disturbances.

In this section, we test the application of the sampler in a laboratory-scale mass flux assessment of PHEN and GLY and discuss the pros and cons of using various tracers and adsorbents, in relation to the three basic requirements defined above.

**Tracer Dissolution Studies.** The dissolution kinetics of three different tracers were studied: calcium citrate (2-hydroxy-1,2,3-propanetricarboxylic acid calcium salt 2:3), calcium fluoride (CaF<sub>2</sub>), and calcium hydrogen phosphate (CaHPO<sub>4</sub>). Figure 3 shows the dissolution curves (cumulative mass) for these tracers, as a function of the cumulative water volume. The effluent flow rate is also shown. The linear dissolution curves indicate that constant concentrations were reached, irrespective of the flow rate (5–128 mm/h). Thus, if maximum solubility is reached within this flow range, it will certainly be reached for lower flow rates. The dotted lines show the tracers' saturation limit. Calcium citrate and CaF<sub>2</sub> both conform to the solubility products of the two salts (21). [The solubility of calcium citrate at 25 °C is 0.85 g/L. The *K*<sub>sp</sub> values for CaF<sub>2</sub> and CaHPO<sub>4</sub> are 5.3 × 10<sup>-9</sup> and 1.0 × 10<sup>-7</sup>, respectively.] CaHPO<sub>4</sub> is slightly below this limit. For calcium citrate, it has been demonstrated that nonkinetically restricted solubilization holds for crystallites of different sizes (22).

Tracers should be selected for minimal interference of background electrolytes. Ca<sup>2+</sup>, for example, is usually the predominant cation in soil and groundwater. Solubilization properties are additive under a certain threshold value, but co-ion effects will interfere with the dissolution of calcium citrate above this threshold. In this case, measurement of tracer eluviation (Figure 1, left) is preferred over tracer illuviation (Figure 1, right), because, in the latter, there would always be extra Ca<sup>2+</sup> adsorbed from the background. As long as the solubility product is not affected, and the residual amount of remaining tracer is high enough, the background Ca<sup>2+</sup> will not interfere with the quantification of *V* (eq 1). The biodegradability of the tracer compounds should also be considered. For example, citrate is biodegradable under aerobic conditions (23). Further experiments (outside the scope of this paper) are needed to document these properties under various geochemical conditions.

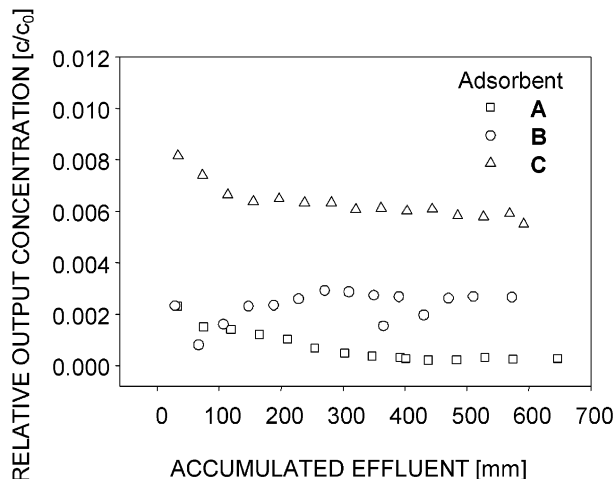
**Choosing the Right Adsorbent.** For sampling soluble contaminants, the adsorbent should meet the following criteria. First, it should enable the free passage of pore water. Second, it must display a high sorption capacity, combining a strong affinity to the solute with fast uptake kinetics. For biodegradable solutes, nanoporous adsorbents are preferred to shield the solute from micro-organisms. Third, it should enable the recovery of the solute in the laboratory.



**FIGURE 3.** Dissolution curves for calcium citrate (top),  $\text{CaF}_2$  (middle), and  $\text{CaHPO}_4$  (bottom). The broken lines indicate the theoretical dissolution limits based on the  $K_{sp}$  values of the salts.

Alumina **D** was used as the adsorbent for GLY, based on previous studies. GLY is strongly adsorbed by alumina, and the sorption coefficient of alumina **D** was  $K_d = 2.31 \times 10^3$  L/kg. GLY is effectively extracted from this alumina by 0.2 M KOH (94.6% extraction recovery). To choose the adsorbent for PHEN, we screened 13 different commercial and in-house synthesized materials in batch sorption experiments. The materials were ranked according to a combination of two criteria: their sorption coefficient ( $K_d$ ) and their recovery efficiency (see Table 1). Recovery was performed by extraction with ethyl acetate, which is an environmentally friendly solvent. Based on this preliminary screening, we chose three candidates: graphitized carbon **A** (Carbotrap C), molybdenum-substituted hexagonal mesoporous silica **B**, and an ion-exchange resin XAD-7 (Amberlite, **C**).

The batch-experiment  $K_d$  values reflect fast adsorption uptake (the adsorbents were exposed to PHEN only for 1 h). The results are sufficient to rank the adsorbents, relative to each other. However, the real test for an adsorbent's dynamic sorption capacity should be done under "worst-case" flow conditions. These conditions were mimicked using pre-column saturated flow experiments with PHEN at a high flow rate of  $\sim 0.16$  mL/min (123 mm/h) and a high input concentration of  $100 \mu\text{g/L}$  of PHEN (Figure 4). Under these



**FIGURE 4.** PHEN effluent concentrations from pre-column saturated flow experiments with three selected adsorbents performed under "worst case" conditions: input concentration of  $100 \mu\text{g/L}$ , flow rate of 123 mm/h.

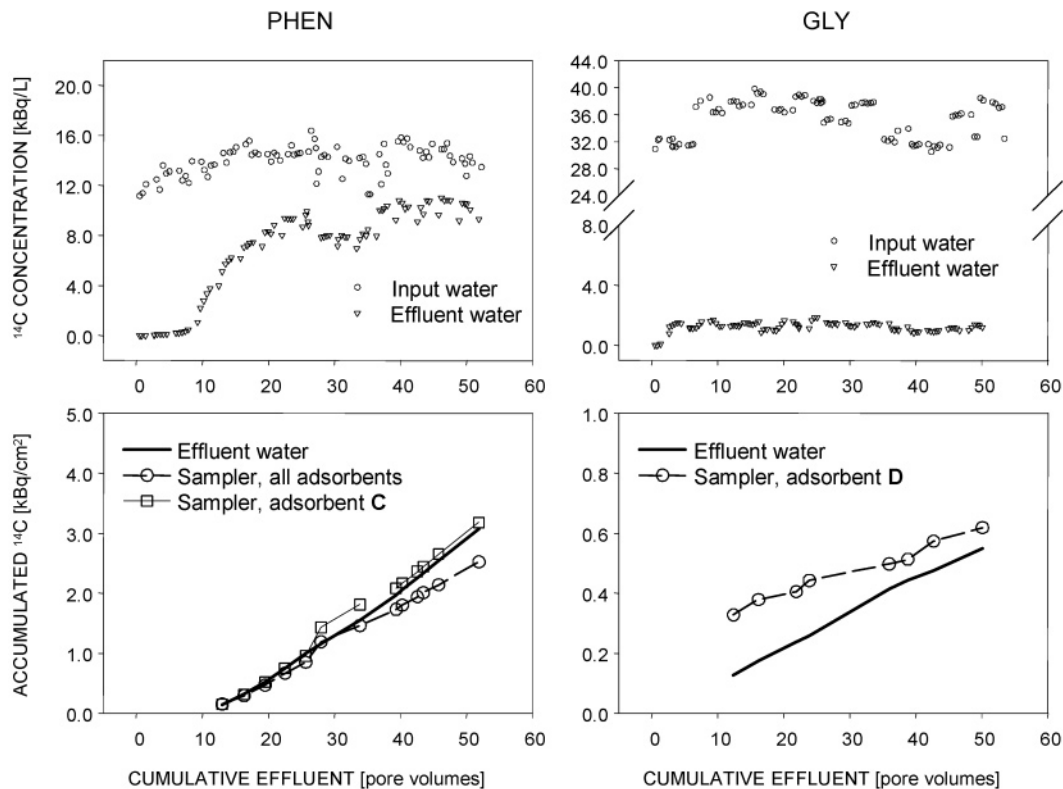
worst-case conditions, the average residence time of water in the precolumns was only 2 min.

Despite the short residence time of the water in the precolumns,  $>99\%$  of the PHEN was sorbed! The outlet concentrations decreased in the following order:  $C > B > A$ . The water volume corresponded to  $\sim 500$  mm of water, more than approximately one year of groundwater recharge in temperate climates (24). This means that, as far as sorption capacity is concerned, any of the three adsorbents would be suitable for installation for up to one year in soil, under normally encountered flow conditions.

Free passage of pore water through the cartridge occurs when the hydraulic conductivity is higher than the surrounding soil. Here, we use the saturated conductivity ( $K_{sat}$ ) as an indicative measure of the cartridge flow properties under unsaturated conditions (vide infra). The  $K_{sat}$  values of cartridges filled with adsorbents **A** and **C** ( $5450 \pm 640$  and  $6190 \pm 730$  cm/day, respectively) were much higher than that of Voldby sandy soil ( $663 \pm 76$  cm/day). The  $K_{sat}$  value of cartridges filled with adsorbent **B**,  $78 \pm 9$  cm/day, was  $\sim 10$  times lower than that of the soil. We suspect this may cause a diverging flow path around the sampler, both under saturated and unsaturated conditions. For pore water sampling in light-textured soil, larger **B** particles may solve this problem. However, more-detailed studies on unsaturated flow properties of the cartridges are needed to predict flow behavior and design cartridges for use under various saturated conditions.

**Soil Column Experiments with PHEN and GLY.** The previously mentioned four adsorbents were then tested using large unsaturated soil columns (see Figure 2). The sampler tests in the PHEN column (adsorbents **A**, **B**, and **C**) were conducted in 13 sampling periods, and those in the GLY column (adsorbent **D**) were run in eight sampling periods (see Table 2).

Input concentrations were maintained stable throughout the measuring period (Figure 5, top). The PHEN breakthrough curve (BTC) was asymmetric, which is typical for sorption-retarded transport (25) (Figure 5, top left). Effluent concentrations started to increase after approximately seven pore volumes (day 16). The steepest increase was observed after 12 pore volumes, and by the end of the experiment, the effluent concentrations approached the level of the input concentrations, reflecting that the system approached steady-state conditions. The GLY breakthrough showed a completely different pattern (Figure 5, top right). The  $^{14}\text{C}$  concentration in the effluent increased sharply in the beginning of the



**FIGURE 5.** Results from column experiments with PHEN (left) and GLY (right). The top graphs show the measured input and effluent concentrations. The bottom graphs show the accumulated solute flux-density as measured on the effluent (solid lines) and as recovered from the sampler (open circle (○) and square (□) symbols).

experiment, becoming stable already after three pore volumes at a level of  $\sim 1.5$  kBq/L ( $0.22 \mu\text{g/L}$ ). This low and steady concentration level was maintained throughout the entire measuring period.

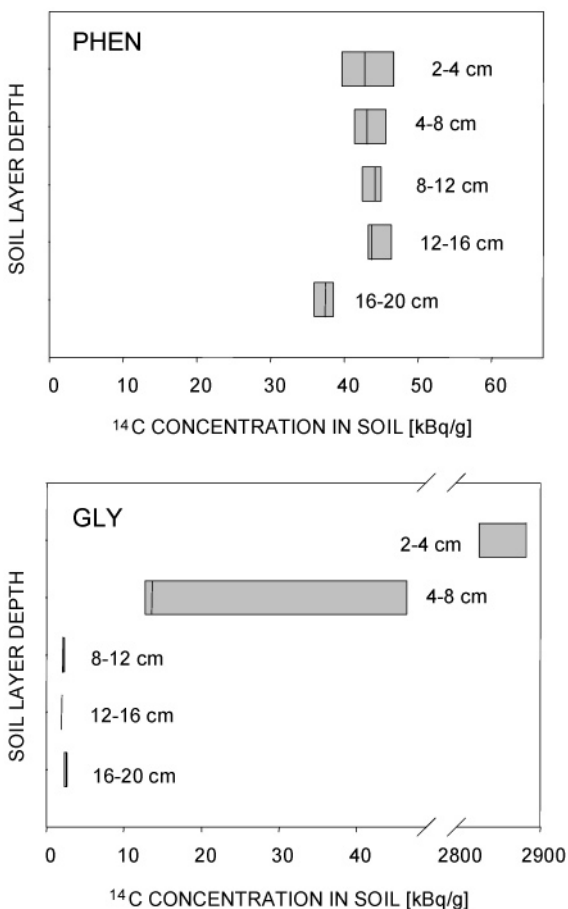
If we compare these data to the concentrations of PHEN and GLY that were recovered at the end of the experiment from different layers of the soil, we observe a similar pattern (Figure 6): Soil concentrations of PHEN were almost constant with depth, indicating that pore-water and soil concentrations were approaching equilibrium by the end of the experiment. By contrast, almost all of the sorbed GLY remained in the upper 2 cm of the soil column, and only traces of <sup>14</sup>C were observed in all of the other soil layers. Almost 50% of PHEN was recovered in the effluent, compared to only 3.3% of GLY. The rapid breakthrough of GLY at trace concentrations may be due to colloid-facilitated transport (26).

We chose steady-state hydraulic conditions to facilitate the comparison between solute flux at the bottom of the column (effluent) and the solute flux intercepted by the sampler. A steady water flux was maintained in almost all sampling periods, except for the period in which the flow interruption occurred (see Table 2). Moreover, the GLY effluent stagnated at the end of sampling period 1, possibly because of entrapped air. After replacement of the bottom filter, the steady state was restored. The gravimetric water content of the soil columns at the end of the experiments was  $0.25 \pm 0.015 \text{ cm}^3/\text{cm}^3$  (this value is the average of the two columns, for five soil layers). The estimated porosity in the column was  $0.43 \text{ cm}^3/\text{cm}^3$ , assuming a particle solid-phase density of  $2.65 \text{ g}/\text{cm}^3$ . Hence, the experiments were conducted under unsaturated conditions.

To compare the <sup>14</sup>C activity from the effluent and the sampler, we divided the effluent mass by the area covered by the soil columns ( $314 \text{ cm}^2$ ) minus the total area covered by the filters of the sampler cartridges ( $3 \times 1.58 \text{ cm}^2 = 4.74 \text{ cm}^2$ ). The mass accumulated in the cartridges was divided

by the sampler filter area. Figure 5 (bottom left) shows the average cumulative flux density for all three adsorbents (denoted by open circle (○) symbols) as well as for adsorbent C only (denoted by open square (□) symbols). The fit of the adsorbent C cartridges to the PHEN effluent data was excellent ( $R^2 = 0.993$ ). There are some small deviations directly after the flow interruption, probably due to nonequilibrium of the water transport and sorption into the soil (vide supra). This means that (i) water flowed unhindered through the adsorbent C cartridges; (ii) all the PHEN passing through the cartridges was adsorbed, regardless of concentration level or installation time; and (iii) all the sorbed PHEN was recovered in the extraction with ethyl acetate. If we consider all three adsorbents, the slope of the cumulative curve deviates after 30 pore volumes. This means that, for adsorbents A and B, either water flow through the cartridges was hindered, the extraction recovery was incomplete, or both. The last explanation is not expected for adsorbent B (see Table 2), so we suggest that its lower hydraulic conductivity caused a divergence of the water flow around the B-filled cartridges. For adsorbent A, we believe that incomplete recovery may explain the deviation in the slope (see Table 2). The mean standard deviation from the three cartridges was 23.3% for all 14 installation periods. This variation includes real flux variations, as well as flow disturbance and variations in the extraction recovery of PHEN. The final difference between the cumulative flux captured in the sampler and the effluent was 3.6% for the C-filled cartridges and 17.8% for all adsorbents combined.

GLY fluxes were measured in triplicate, using only adsorbent D. Nevertheless, the mean standard deviation from the three cartridges was higher than that for PHEN, with an average of 34.8% for eight installation periods. The deviations between effluent flux and sampled fluxes were also higher than for PHEN, notably in the first sampling period, where the sampled flux was more than twice the effluent flux (Figure



**FIGURE 6.** Amounts of recovered  $^{14}\text{C}$ -labeled PHEN (top) and  $^{14}\text{C}$ -labeled GLY (bottom) extracted from different layers of the soil columns at the end of the experiment.

5, bottom right). Because the sampler was installed at a depth of 15 cm, and the effluent was sampled from the 20-cm-depth plane, such behavior is theoretically expected initially, when the concentration increases sharply in the 15–20-cm depth plane. Also, nonequilibrium hydraulic conditions may have added to this effect, as indicated by the unstable effluent flow rates. From the second sampling period and onward, the cumulative mass captured in the sampling device approached the cumulative mass sampled in the effluent. At the end of the experiment, the deviation of cumulative mass was reduced to 12.4%.

#### Comparison with Other Passive Sampling Devices.

Several passive sampling devices have emerged as an alternative for repeated grab sampling (27). The methods can be compared according to the parameters needed to back-calculate ambient (pore) water concentrations from the sampled solute mass. Existing methods use solute-specific equilibrium sorption constants (27, 28) and/or kinetic diffusion parameters (29–31). The temperature and concentration effects on these parameters are solute-specific (30, 32). In contrast, the method demonstrated here does not use solute-specific parameters, and this makes the back-calculation procedure robust and simple (see eqs 1–3, given previously). The only information required is the dynamic sorption capacity for the least-sorbing solute, plus the solubility product of the tracer compound(s).

Most passive samplers capture solutes by diffusive exchange. Therefore, only free dissolved molecules are sampled from the aqueous phase. Thus, their strength lies in the quantification of the bioavailable fraction (27, 29). However, it has been shown that mobile colloids can also

facilitate the transport of solutes in soils and sediments (33). The sampling device presented in this study has the potential for capturing mobile colloids with minimal disturbance to the flow pattern. This means, for example, that reactive humic substances could, in principle, be trapped with metal oxides (34, 35), resins (36), and carbons (37). In principle, it should be possible to distinguish colloid-facilitated transport from free-solute transport through the use of different adsorbents and/or extraction techniques.

Unlike diffusive devices, passive samplers that are in hydraulic contact with the surrounding medium display flow-proportional capturing of convectively transported solutes (18, 38, 39). This is particularly relevant when discharge varies with time. For example, discharge and solute concentrations are very dynamic in the unsaturated zone and the upper groundwater. Moreover, the relationship between solute/colloid concentration on one hand and flow rate on the other hand is extremely complex (25, 40–42).

The sampling method presented here has limitations: It gives point measurements, determined by the area of the cartridge exposed to the soil, and the detection limit is dependent on the volume of water passing through the cartridge, similar to a liquid sample. This means that the filter size must be optimized with the required detection limit and installation time in mind. Another limitation is that it is difficult to make repeated measurements at the same location when the method is applied in the unsaturated zone. To try to overcome some of these these limitations, we are developing passive samplers for a range of different applications, under realistic intermittent flow regimes, and we will also work on identifying adsorbents for an increased range of solutes.

In summary, passive samplers offer unique benefits over conventional grab sampling techniques. The device shown here has the potential to (i) operate under a wide range of dynamic flow conditions in soils and sediments and (ii) monitor a broad group of solutes and colloids. The feasibility of the basic physical/chemical principles underlying the method has been demonstrated for the case of PHEN and GLY transport in unsaturated soil. This new method enables a sampling strategy that integrates in situ hydraulic flow and concentration dynamics over long installation periods, without expensive infrastructure or repetitive site visits.

#### Supporting Information Available

Detailed description of the chemicals and instrumentation used in this study, the synthesis procedure for adsorbent **B**, the procedures for saturated hydraulic conductivity measurements, and the derivation of the differential equations describing the tracer transport and the effects of diffusion (PDF). This material is available via the Internet at <http://pubs.acs.org>.

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