

Suction cup sampler bias in leaching characterization of an undisturbed field soil

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Abstract. An accurate assessment of leaching losses in the vadose zone requires measurement of both solute and water flux to compute flux concentrations (C_F). Leachate collected at a depth of 1.2 m in 32 passive capillary samplers (PCAPS), which sample soil-pore water continuously at tensions of 0–50 cm H₂O was compared to that collected in 32 suction cup samplers operated under a falling head vacuum of 530-cm H₂O over a 2-year period. There was evidence that PCAPS collected C_F and suction cup samplers collected resident concentrations (C_R) as shown by the earlier breakthrough of a bromide tracer in the PCAPS as compared to the suction cup samplers. C_R was up to 100% lower than C_F during the rising branch of Br tracer breakthrough and up to 78% greater during the declining branch of breakthrough. Br content and water flux into PCAPS were correlated with correlation coefficients changing from positive to negative values with the advancement of the tracer breakthrough peak through the profile indicating the declining importance of preferential flow on Br transport. C_R and C_F differed significantly ($P < 0.05$) for 35% of the sampling events for NO₃, but seasonal means were mostly insignificantly different for this regularly applied and therefore more uniformly distributed anion. The early breakthrough of Rhodamine WT and Brilliant Blue FCF, which was applied with the Br, was very low with 0.15% and 0.08% of the initial concentration C_0 , respectively, with C_R differing from C_F by up to –100%. For all tracers, mass leached using C_R is therefore prone to bias for short-term (<0.6 pore volumes) monitoring.

Introduction

An accurate monitoring scheme of water flow and solute transport in the vadose zone relies on a thorough understanding of the characteristics at the site of interest. It is now widely recognized that the concept of a uniform displacement of the solute is not valid for most soils. *Flury et al.* [1994] came to the conclusion that preferential flow is the dominant form of water flow in a good portion of Swiss soils. Preferential flow, such as funneling in layered, sandy soils [*Kung*, 1990], unstable, fingering flow in homogeneous sandy soils [e.g., *Selker et al.*, 1992], or macropore flow in structured soils [*Shaffer et al.*, 1979; *White*, 1985; *Priebe and Blackmer*, 1989; *Jabro et al.*, 1991] can lead to a concentration of flow in a small portion of the soil. Often, the percolating water bypasses the greater portion of the soil matrix [*Thomas and Phillips*, 1979; *Magid et al.*, 1992].

Since the bypassing water is not at equilibrium with the less mobile water, in general, it will have a different solute concentration. *Kreft and Zuber* [1978] therefore defined the flux concentration C_F , which is the mass of solute per unit volume of fluid passing through a given cross section at a given time

interval, and the resident concentration C_R , which is the mass of solute per unit volume of fluid contained in an elementary volume of the system at a given instant. Which of these concentrations should be detected depends on the research goal. For leaching studies a measurement of C_F is appropriate. When the main concern is the available amount of nutrients, C_R should give a good estimate.

The concentration mode to be measured dictates appropriate sampling technology. Large weighing monolith lysimeters are effective for measuring leachate and thus C_F [*Parker and van Genuchten*, 1984] but are limited by constructional and maintenance costs and a long stabilization period [*Keeney*, 1986]. Soil coring is the best method to determine C_R , since it gives the amount of solute contained in a representative volume at a given instant of time. However, it is destructive, requires a large number of samples, and does not allow for repetitive measurements at the same point, thus limiting its usefulness when monitoring changes over time.

The solute content collected by the suction cup sampler depends upon the mode of operation. When used in a falling head mode, where the time of soil sample extraction is short in comparison to the time between sampling events, the sampler detects C_R [*Magid and Christensen*, 1993]. Even under these conditions, it is only an approximation of C_R , because for the suction cup, when operated under a falling head, (1) soil-pores

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Table 1. Organic Carbon Content, pH, Bulk Density, Particle Size Distribution, and Saturated Hydraulic Conductivity (K_{sat}) of Willamette Loam Soil

Depth, cm	Organic Carbon*			pH†			Bulk Density‡			Particle Size Distribution				K_{sat} §		
	Mean, g kg ⁻¹	CV, %	n	Mean	CV, %	n	Mean, Mg m ⁻³	CV, %	n	Clay, %	Silt, %	Sand, %	n	Mean, μm s ⁻¹	CV, %	n
13	12	13	16	6.2	7	11	1.24	4	4	16.8	50.0	33.2	1	60	72	3
64	1.9	51	14	5.7	3	11	1.35	1	4	27.3	46.8	25.9	1	7	115	3
114	0.8	42	9	5.8	2	12	1.29	2	4	17.4	38.7	43.9	1	0.7	83	3

*Organic carbon content was measured with a Dohrmann carbon analyzer.

†A 1:2 solution of soil and distilled water.

‡Determined from soil cores.

||Determined according to *Gee and Bander* [1986].

§Determined from soil cores using constant head in a tempe cell following *Klute and Dirksen* [1986].

<5 μm are not sampled, since typically the vacuum applied is <60 kPa [*American Society for Testing and Materials*, 1992]; (2) the sampled volume is not known [*England*, 1974]; and (3) the measurement is not instantaneous; i.e., it typically takes place over several hours to days, depending on the moisture content of the soil. When the suction cup is operated under a constant head equal to the tension at which water is moving in the soil, it represents an approximation of C_F , since it does not sample over a defined area.

Zero tension pan samplers collect the soil-pore water over a defined area and period of time, in principle collecting C_F . However, the usefulness of this device in collecting C_F is limited because of the disturbance of the native flow. Water must arrive at the sampler surface at positive pressure prior to sample collection. Usually, this requires not only a saturated condition but the development of a capillary fringe above the device. This typically leads to a diversion of flow away from the sampler due to a gradient in matrix potential, resulting in low collection efficiencies (45% to 58%) [*Jemison and Fox*, 1992].

Combining the ideas of applying tension to the soil-water and intercepting a large area of flow by a pan, *Brown et al.* [1986] introduced the wick pan lysimeter termed the passive capillary sampler (PCAPS). PCAPS have proven to give superior results to existing soil-water samplers in terms of long-term mass balance of water and chemical loading [*Brown et al.*, 1986; *Holder et al.*, 1991; *Boll et al.*, 1992; *Brandi-Dohrn et al.*, 1996]. The wetted wick acts as a hanging water column and develops a suction of 0 to 5 kPa in the soil-water depending on the flux, requiring no external application of suction. The sampler works continuously without any dedicated machinery [*Boll et al.*, 1992].

It is apparent that it is difficult to obtain samples of the water flux and its solute content without disturbing the native flow [*Parker and van Genuchten*, 1984]. Probably the most reliable measurement of C_F , besides large weighing monolith lysimeters, can be obtained using PCAPS, since this device introduces minimal disturbance to the native flow regime. The matric potential at the top of the wick can be matched to the expected matric potential in the soil as a function of the flux by applying the design equation by *Knutson and Selker* [1994]. The length and the diameter of the wick and the sampling area will be adjusted to achieve the closest possible match. Dispersivity values of fiberglass wicks are much lower than those observed in many soils [*Boll et al.*, 1992; *Knutson and Selker*, 1996], and thus solute breakthrough characteristics are retained.

The objective of this study is to compare the estimate of the mean concentration of the soil solution as obtained by PCAPS

to that obtained by the traditional suction cup sampler under the assumption that the first yields C_F and the latter C_R .

Materials and Methods

Experimental Site

The experiment was carried out at the North Willamette Research and Extension Center (NWREC), Aurora, Oregon. The soil, which is of glaciolacustrine genesis, is a Willamette loam (fine-loamy mixed mesic Pachic Ultic Argixeroll). Some basic properties of the soil are listed in Table 1. According to the U.S. Department of Agriculture classification scheme, the soil texture was classified as a loam/silt loam at the 13 cm depth, as a loam/clay loam at 64 cm, and as a loam at 114 cm. During the summer months (May to October), evapotranspiration is generally higher than the mean monthly precipitation of 44 mm. The wet winter months show a mean monthly rainfall of 128 mm.

From 1982 to 1989 the area was in a uniform wheat/fallow rotation. In 1989, a cover crop/crop rotation study was established on the 0.9 ha site. The experimental design is a randomized complete block split plot, with cropping system as main plot and N rate as the subplot and with four replications. The subplots received either a zero (N0), medium (N1), or recommended (N2) rate of urea. One PCAPS was installed in each N1 and N2 replication and two PCAPS and four suction cup samplers in each N0 replication, for a total of 32 PCAPS and 32 suction cup samplers. The number and position of the samplers were dictated by the requirements and financial constraints of the ongoing agronomic trials at this location.

Instrumentation

PCAPS were constructed from custom made epoxy-coated fiberglass boxes (32 × 85.5 × 62 cm) supporting a stainless steel panel (1 mm thick, 31 × 84.5 cm) with a 0.5-cm edge. The panel was subdivided into three 31 by 28-cm sections, each containing one wick and one collection vessel, thus establishing three sampling units within each sampler. The collection vessels were 3.78-L glass jars connected to the soil surface by high-density polyethylene (HDPE) tubing. The wicks employed were 2.93-cm OD Amatex fiberglass wicks (braided medium-density 1-inch fiberglass wick, #10-863KR-08, Amatex Co., Norristown, PA) with a maximum fiber length of 70 cm. (Use of trade names does not constitute endorsement by Oregon State University.) The first 22 cm of the wicks were separated into single filaments, and the material was cleaned according to *Knutson et al.* [1993] by combustion in a kiln at

400°C for 12 hours. At installation, the wick filaments were spread out radially on the top panel and glued down at the edge of the stainless steel pan with one drop of silicone sealant at the end of each strand. The construction and installation of the PCAPS is described elsewhere in greater detail [Brandi-Dohrn *et al.*, 1996].

High-flow porous ceramic cups (5 cm OD, 6-cm length, 1 bar air entry pressure) from Soilmoisture Equipment, Santa Barbara, California (653X01.B1M3) were used to construct the 32 suction cup samplers. A 15-cm long, ID 4.4-cm polyvinyl chloride (PVC) pipe was glued with epoxy to the porous cup. The top of the sampler was sealed with a rubber stopper. Two 3.175-mm ID HDPE tubings were used as sampling and vacuum tubings. All sampling tubing extended to the bottom of the cup to prevent dead volume.

The PCAPS were installed from trenches 2.3 m long, 1.2 m wide and 2.7 m deep dug with a back hoe. Perpendicular to the trench, 1.2-m-long tunnels were excavated such that the roof of the tunnel was at a depth of 1.2 m below surface, which is the depth where soil solution samples were collected. The roofs of the tunnels were leveled and smoothed, avoiding smearing pores with clay by carefully scraping with a serrated blade. The top panels of the samplers were filled with sieved, slightly compacted native soils and another layer of sieved soil put on top to fill in any small gaps. The samplers were elevated with wedges to bring them into very firm contact with the roof of the tunnel. The samplers were hydraulically isolated from the trench by packing a 4-cm-thick dry bentonite seal between sampler and trench. One suction cup sampler was installed 30 cm from each side of every other PCAPS, at the same depth as the PCAPS (1.2 m). Suction cup sampler installation was done according to Parizek and Lane [1970]. The trenches were re-filled in two lifts, compacting each lift with a back hoe mounted hydraulic compactor. Sampler installation was completed by September 25, 1992.

Using a vacuum pump, samples were extracted from the glass jars in the PCAPS via the HDPE access tubing to the soil surface into 2000-mL graduated cylinders. The sample retrieval procedure did not impose any suction on the soil-pore water in the soil, since air could enter about the wick. Samples were taken after 2 cm of precipitation. Thus, for the critical leaching time November through April, samples were taken on average every 10.6 days. Sample collection covered the time period from September 25, 1992, to November 1, 1994. Precipitation was recorded daily with a nonrecording gauge at the nearby (500 m) Oregon Climate Service weather station. Time domain reflectometry (TDR) measurements of soil moisture content were made at five different plots using a Tektronix 1502 C TDR by inserting a 25-cm-long probe attached to a long handle into the soil at three depths (0–25 cm, 50–75 cm, 90–115 cm) as accessed through a freshly augered hole. Also, each NO site was fitted with a tensiometer located at the height of the PCAPS (1.2 m), which was read weekly during the winter.

Suction cup samplers were operated under a falling head of 53 kPa which was sufficient to collect ample volume and reliably obtained using the electric vacuum pumps employed in this study. The tension was applied to each sampler on the sample date prior to sample collection.

Tracers and Sampling

Three tracers were applied on November 4, 1992: (1) Bromide as a conservative tracer which moves approximately at

the same speed as water; (2) Brilliant Blue FCF (C.I. 42090) as a nonconservative tracer to model the movement of compounds which sorb to soil clays and organic matter; and (3) Rhodamine WT as a backup to Brilliant Blue FCF, since analytical procedures are fairly simple for fluorescent tracers. Further reasons for selecting these tracers were their low background concentrations, their high solubility, and their low toxicity to the environment [e.g., Flury and Papritz, 1993]. Brilliant Blue FCF with a reported retardation factor of 5.6 has been cited as a surrogate for atrazine [Andreini and Steenhuis, 1990]. Tracers were mixed with an electric mixer in 11.34 L of tap water at concentrations of 29.6 g L⁻¹ (bromide), 67.9 g L⁻¹ (Brilliant Blue FCF), and 27 mg L⁻¹ (Rhodamine WT). This tracer solution was applied to neighboring pairs of PCAPS across a rectangular area of 3 by 7.5 m using a 3-m wide pesticide bicycle sprayer in eight passes. The 0.5-mm depth of application of tracer solution was easily taken up by the soil with the exception of two plots, which were partially flooded with water at the time of tracer application. There was a trace of precipitation on the two days following the application. On the third day, 3.5 mm of precipitation was recorded, on the fourth day 4.5 mm. The initial concentration C_0 was calculated as mass of tracer applied divided by water content of the first 8 cm, assuming an 8-cm mixing zone. The water content was estimated to be 0.44 volumetric based on a 2.2-kPa value using the data obtained from a moisture retention study of the 0–25 cm surface soil.

A Dionex 2000i ion chromatograph (Dionex Corp., Sunnyvale, California) with a Dionex AS4A-SC separator column and an AG4A-SC guard column was used to determine anion concentrations. Samples were diluted 1:1 and poured into vials and frozen at -12.7°C until analysis which was done in less than a week after sampling. Rhodamine WT concentrations were determined at room temperature using a Turner Filter Fluorometer Model 111 (Mountain View, California) and Brilliant Blue FCF using a Milton Roy Spectronic 20 (Rochester, New York) spectrophotometer. Because of optical interference between Brilliant Blue FCF and Rhodamine WT, the fluorescence reading had to be corrected according to the following empirical relationship:

$$C_{\text{Rhod}} = k_1 F \exp(k_2 C_{\text{Blue}}^{k_3}) \quad (1)$$

where C_{Rhod} is the concentration of Rhodamine WT, C_{Blue} the concentration of Brilliant Blue FCF, F the measured fluorescence, and k_1 , k_2 and k_3 coefficients to be determined by non-linear regression. The regression coefficients at the used aperture ($\times 30$) and in the presence of 0–10 mg L⁻¹ Brilliant Blue FCF were found to be $k_1 = 0.0054$, $k_2 = 0.019$, and $k_3 = 1.87$ ($R^2 = 0.98$). The absorbance of Brilliant Blue FCF was recorded at a wave length of 630 nm. Sample bottles were washed, rinsed twice with distilled water, and air dried before reuse in the field. The sample bottles did not absorb any detectable amounts of dye.

Statistics

To assess whether a sample was drawn from the normal distribution, the probability plot correlation coefficient test (PPCC) was used, since it is conceptually easy and marginally more powerful for symmetric and skewed longer-tailed samples than other test statistics for normality, for example, Shapiro-Wilks test statistic [Filiben, 1975]. The PPCC is given by

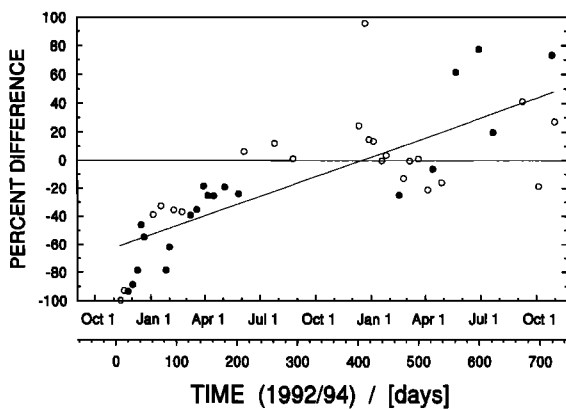


Figure 1. Median of relative differences in Br concentration between arithmetic mean of the two suction cup samplers compared to its corresponding PCAPS and linear trend ($R^2 = 0.596$). Solid circles mark significant ($P < 0.05$) deviations. Day 0 corresponds to tracer application (November 4, 1992).

$$PPCC = \frac{\sum (x_i - \bar{x})(w_i - \bar{w})}{\left[\sum (x_i - \bar{x})^2 \sum (w_i - \bar{w})^2 \right]^{0.5}} \quad (2)$$

where x_i denotes the ordered observations and w_i the corresponding fitted quantiles according to $w_i = N^{-1}(1 - q_i)$, where $N(q)$ is the cumulative distribution function of the normal distribution and q_i the plotting position for each x_i with $q_i = (i - 3/8)/(n + 1/4)$, $i = 1, \dots, n$, and n the size of the sample. Essentially, the PPCC gives an assessment of the linearity of the probability plot, with values close to 1 suggesting that the observations could have been drawn from a normal distribution. Critical values for the PPCC are given by *Filiben* [1975].

Data sets with data points less than the detection limit (censored data) were treated as follows: Data sets with more than 12% censored data were not considered. In that case, the missing data points will introduce too much uncertainty into the process of finding the underlying distribution. For data sets with less than 12% censored data, only the data above the detection limit were correlated to the fitted quantiles as determined from the complete data set.

For nonnormal data sets, nonparametric tests for the H_0 hypothesis that the distribution of the dependent variable y does not change with the explanatory variable x include the Spearman rank correlation coefficient and the Kendall correlation coefficient. We used the latter [Kendall, 1938], since it is equally or more powerful than the first [Alvo et al., 1982]. The correction for censored data was employed [Hirsch et al., 1993].

Results and Discussion

Bromide

Following the assumption from our objective, we will refer to the concentration measurements made by the PCAPS as C_F and to those by the suction cup sampler as C_R . When comparing C_F and C_R , we were interested in (1) the comparison of the two concentration modes per se, i.e. on a small scale, which was in our experiment approximately 1 m², and (2) the comparison of the means of the two concentration modes on a 1-ha field scale. For the first comparison, we compared the arith-

metic mean Br concentration of the two suction cup samplers with its corresponding PCAPS and plotted the median of those 16 relative differences in Figure 1. C_R is up to 100% less than C_F shortly after tracer application, approximately the same as C_F during peak breakthrough, and up to 78% greater (June 29, 1994) on the declining branch of the tracer breakthrough curve. The trend for the discrepancy in C_R to increase in time is highly significant ($P < 0.001$), as represented with a linear relationship. The earlier breakthrough of C_F compared to C_R matches the theoretical findings of *Parker and van Genuchten* [1984], thus confirming our assumption that PCAPS collect C_F and suction cup samplers C_R .

These differences can be explained by the following concept. In the Willamette Variant loam the 28-cm-thick Ap horizon constitutes a mixing horizon at times of high moisture content, since any macropore system has been destroyed by plowing. At the time of the bromide pulse application, the upper profile was close to saturation after 82 mm of precipitation in the preceding 5 days. Preferential flow paths beginning in the B horizon, establish a shortcut from the mixing zone, the Ap horizon, to greater depths of 160 cm and more. The existence of preferential flow paths in most of the soils has been described numerous times [e.g., *Andreini and Steenhuis*, 1990; *Jabro et al.*, 1991; *Flury et al.*, 1994]. At this site, the observed light gray, gleyed areas which extend like fingers down to greater depths, constitute these flow paths, since many more fine and very fine roots and pores were observed in the mottles than in the soil matrix. During the installation procedure these gray mottles could not only be observed in vertical crosssections as fingers on the trench walls, but also in horizontal crosssections as oval to round shaped gray mottles on the roof of the tunnels. From infiltration experiments with stained water in the upper B horizon we additionally know that the contact area between soil aggregates serves as preferential flow path. Besides the preferential flow, the water flow in the dark brown soil-matrix will be termed matrix flow.

The solute content of the preferential flow is governed by two systems. The first system is the mixing horizon, from where the water penetrates the preferential flow system. The second system is the surrounding soil matrix with mass transfer by diffusion. The importance of the second system depends on the velocity of the preferential flow, which governs the time available to reach equilibrium between solute content of the preferential flow and matrix flow. Because of the generally much higher velocities of preferential flow [e.g., *Biggar and Nielsen*, 1976; *Thomas and Phillips*, 1979], the first system should be more important. Therefore the Br concentration of the preferential flow will be high compared to that of the matrix flow shortly after tracer application. With the advancement of the tracer peak through the profile, the Br concentration of the preferential flow component will decrease compared to that of the matrix flow, since (1) the Br supply for the preferential flow system, the Ap horizon, will eventually be depleted; and (2) the Br distributes increasingly by diffusion into the finer soil matrix, especially after the period June through November 1993, when virtually no percolation was observed. Therefore, when the tracer peak has moved well beyond the depth of the samplers, preferential flow will contain much less Br compared to the matrix flow.

PCAPS, collecting water moving at tensions from 0 to 50 cm H₂O, presumably collect both preferential and matrix flow. Because of the generally higher percolation volumes of preferential flow and because of the small velocity of matrix flow,

the solute content of the preferential flow greatly influences the solute content of the sample collected.

Suction cup samplers also collect both preferential and matrix flow. However, we found that the vacuum in the suction cup samplers declined by 50% within 4.5 hours in the field, when the soil had a volumetric moisture content of 43% at the same depth as the suction cup samplers as measured with TDR. Typically, the water content of the soil was greater than 43% as determined with tensiometers and comparing to laboratory water retention curves made on cores from this elevation [Brandi-Dohrn *et al.*, 1996]. Therefore the vacuum in the suction cup samplers may have dropped even faster. As a conservative estimate, the suction cup samplers sampled about one day out of the average ten days sampling period, or 10% of the time. Due to this short collection window and the smaller size of the sampling area of this device, the suction cup sampler collects preferential flow to a lesser extent. The leading edge of the Br breakthrough was observed earlier in PCAPS than the suction cup samplers. Four percent of suction cup samplers had concentrations >3 times the native $0.014 \text{ mg Br L}^{-1}$ background 8 and 15 days after tracer application, and 32% were 3 times background after 21 days. In comparison, the percentage of the 32 PCAPS, which collected Br concentrations three times higher than the background concentration, was 12% 8 days after tracer application, 14% after 15 days, and 77% after 21 days. Since only 71 mm of water (0.14 pore volumes) had fallen on the site over this period, tracers captured by the samplers could only be explained as being preferentially transported through soil macropores. Hence C_F is mainly affected by preferential flow, whereas C_R reflects mainly the slow moving matrix solute content. In connection with a one-time Br pulse application, this allows us to distinguish between the two concentration modes as shown in Figure 1.

Similar results were obtained by Magid and Christensen [1993]. Using a pan sampler with a 10-cm wick at a depth of 60 and 90 cm as well as ceramic suction cup samplers, they found that the solution chemistry in the pan samplers is more influenced by either the rainwater or the upper fertilized plow layer as compared to the solution in the suction cup device. The difference between the soil solutions as sampled by the two different devices was significant for a variety of solutes. Especially for chloride, where high concentrations are expected in the plow layer in fall, the flux concentrations were higher than the resident concentrations during the beginning of the drainage season, and lower for the rest of the time.

Regarding the second comparison, i.e. comparing the estimates of the field averages of C_F and C_R , one has to take into account that for C_F , a flow-weighted mean of concentration measurements is preferred to taking a simple arithmetic mean, since it is defined as [Kreft and Zuber, 1978]

$$C_F = J/q \quad (3)$$

where J is the solute flux [$M T^{-1} L^{-2}$] and q the water flux [$L^1 T^{-1}$]. When using suction cup samplers (i.e., C_R), the mean solute concentration must be estimated by the arithmetic mean of sample concentrations, since the sampled soil volume and its water content is unknown.

Field-averaged C_R was less by as much as 97% (19 Nov. 1992) than field-averaged C_F in the early part of the breakthrough curve, and greater by as much as 71% (28 Oct. 1994) on the declining branch of the tracer breakthrough curve (Figure 2). The pattern of the discrepancy in C_R was similar to that in Figure 1.

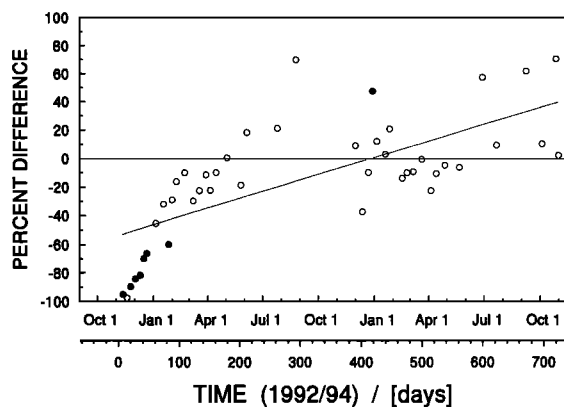


Figure 2. Discrepancy in Br concentrations between field-averaged C_R (suction cup samplers) and C_F (PCAPS) and linear trend ($R^2 = 0.501$). Filled circles mark significant ($P < 0.05$) differences. Day 0 corresponds to tracer application (November 4, 1992).

The calculation of a flow-weighted mean of C_F as compared to an arithmetic mean of C_F increased the absolute value of the discrepancy by on average 5%. Therefore the discrepancy between field-averaged C_R and C_F is composed of (1) the difference between the two concentration detection modes, i.e. the difference on the 1-m^2 scale; and (2) the difference between the two estimators for a mean value on the 1-ha field scale.

A small fraction of the difference between C_F and C_R is due to the timing of sample collection. Since the suction cup samplers sample for only one day after applying the suction, they capture the tracer breakthrough roughly at time $t_{i-1} + 0.5$, where t_i is the sample collection date in [d]. Yet the PCAPS collect a sample between sampling dates (Δt_i in days), and thus capture the tracer breakthrough curve at about $t_{i-1} + \Delta t_i/2$.

Dependence Between Br Content and Water Flow

Since preferential flow is associated with greater percolation volumes than matrix flow, the initially greater Br content of the preferential flow compared to the matrix flow is reflected in a positive correlation between Br content and volume collected in PCAPS shortly after tracer application (Figure 3). The increasing importance of matrix flow in transporting Br is reflected in the decreasing correlation coefficients between Br content and volume. Once the peak has moved well past the samplers, there is a negative correlation between Br content and volume. The decreasing trend of the correlation coefficients with time is highly significant ($P < 0.001$). The data thus demonstrate that the PCAPS collected tracer from both preferential flow, as it is evident from the positive correlations between volume collected and tracer content, and matrix flow, as shown by the negative correlations between volume collected and tracer content. The ability of PCAPS to collect preferential flow is further evidenced by high concentration early breakthrough (Figure 4) and the ability to collect matrix flow by the peak in Br obtained centered on one pore volume of sample collected (January 20, 1994 = one pore volume, Figure 4).

Statistical Distribution of Bromide Concentrations Over Time

The over-time changing influence of preferential and matrix flow on Br transport can also be demonstrated by the statistical

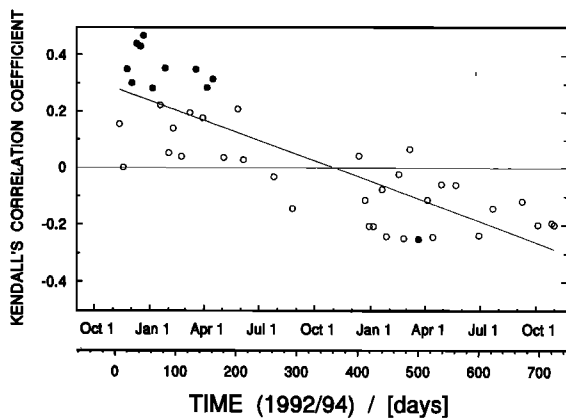


Figure 3. Kendall's correlation coefficient r between volume collected and bromide concentrations as collected by PCAPS and linear trend ($R^2 = 0.672$, $P < 0.001$). Filled circles mark significant ($P < 0.05$) correlations. Day 0 corresponds to tracer application (November 4, 1992).

distribution of the Br concentrations. A first assessment of the underlying distribution can be made using a box plot (Figure 4). On the rising branch of the tracer breakthrough curve, Br concentrations were positively skewed (e.g., mean > median), whereas during tracer peak breakthrough, the distributions were fairly symmetrical. The Filiben test reveals that Br concentrations in PCAPS followed the lognormal distribution shortly after tracer application ($P < 0.01$), and the normal distribution ($P < 0.01$) while the Br peak was passing the PCAPS (Figure 5). The lognormal distribution reflects the initial influence of the preferential flow high in Br. With time, matrix and preferential flow became equally important for Br transport, resulting in a symmetrical, i.e., normal distribution. Toward the declining branch of the tracer breakthrough, there is no clear trend since the matrix flow high in Br content becomes diluted in the sample bottles by large volumes of

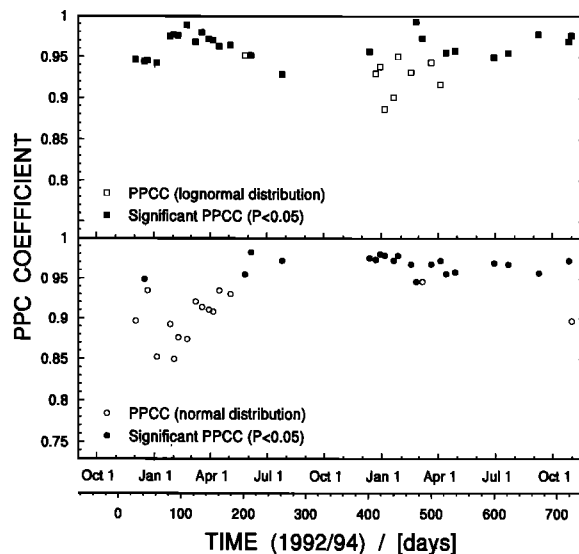


Figure 5. PPC for the normal and lognormal distribution for the Br breakthrough curves as observed by 32 PCAPS. Day 0 corresponds to tracer application (November 4, 1992).

preferential flow now low in Br. For the suction cup samplers, however, there is a clear trend back to the lognormal distribution ($P < 0.01$) toward the declining branch of the tracer breakthrough curve (Figure 6). This is because (1) the high vacuum applied to the suction cup sampler empties finer pores, which are high in Br due to diffusion, as compared to the PCAPS; and (2) the large percolation volume of preferential flow does not dilute the Br concentration in the suction cup sampler, because it fails to accurately represent the frequency and magnitude of preferential flow. Shortly after tracer application, the Br concentrations in the suction cup sampler also follow the lognormal distribution ($P < 0.01$). Here the influence of preferential flow is less pronounced as can be seen

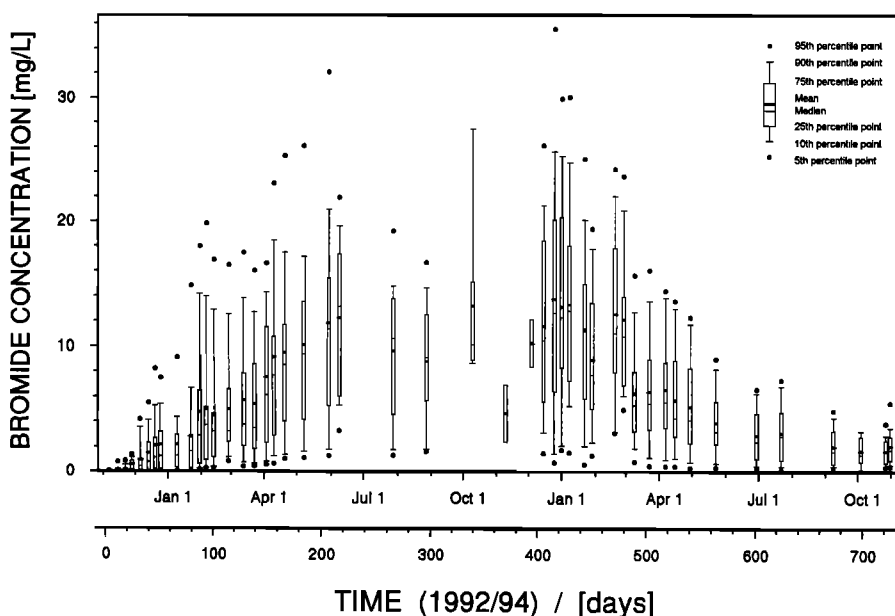


Figure 4. Boxplot of Br concentrations as observed by 32 PCAPS. Day 0 corresponds to tracer application (November 4, 1992).

from the better correlation to the normal distribution. The PPCC for the normal distribution is significant ($P < 0.01$) by day 163 (April 16, 1993) for the suction cup samplers, whereas not until day 204 (May 27, 1993) for the PCAPS.

Estimation of Mean Br Mass Leached

The estimation of the vertical flux of a contaminant is of primary concern in many studies where the quality of groundwater recharge is to be estimated. Typically, a mass flux is computed using suction cup sampler in conjunction with an estimate of the water flux. An assessment of this approach is given by comparing the cumulative Br mass leached calculated from the product of field-averaged suction cup sampler concentrations (i.e., C_R) and field-averaged water fluxes with the observed Br mass leached obtained by field-averaging Br fluxes obtained using PCAPS (i.e., C_F).

The observed cumulative Br mass leached increased approximately twice as quickly as the suction cup estimated value in the first winter (Figure 7). This reflects the importance of preferential flow in the early part of the tracer breakthrough. The increasing contribution of matrix flow to bromide transport in time corresponds to an increasing fraction of the tracer being carried as C_R through the course of the experiment. However, it did not compensate the stronger increase of the cumulative Br mass leached using the exact solution in the first winter. The bias in cumulative Br mass leached as calculated using C_R decreased from -57% after 3 months (0.58 pore volumes) to -28% after 12 months (0.95 pore volumes). After 24 months (1.83 pore volumes), a difference of -14% (6.6 kg/ha) remained. Possibly, this difference will decrease further and become negligible with time. Similarly possible is an increased mass transfer by diffusion from the soil matrix to the preferential flow system during the declining branch of the tracer breakthrough. These results indicate that for short periods or single sampling dates the mean flux of dissolved constituents as calculated from suction cup sampler concentration measurements and water flux estimates can be severely biased.

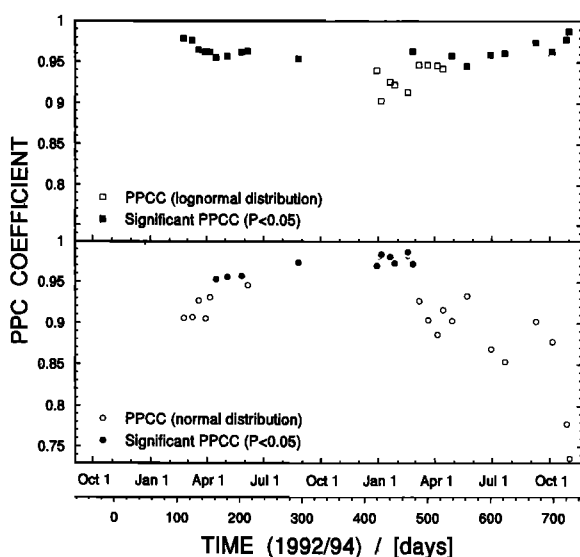


Figure 6. PPCC for the normal and lognormal distribution for the Br breakthrough curves as observed by 32 suction cup samplers. Day 0 corresponds to tracer application (November 4, 1992).

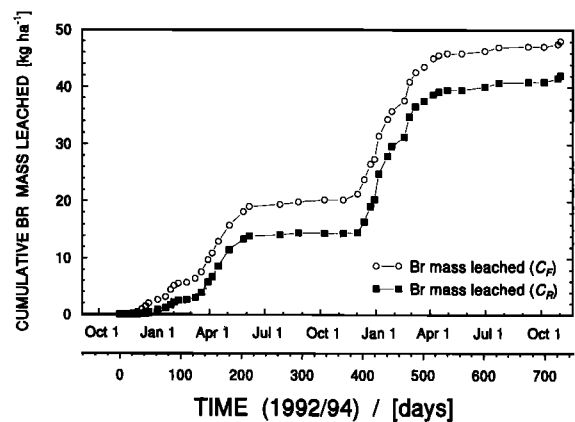


Figure 7. Cumulative bromide mass leached as estimated from field-averaged bromide fluxes (C_F) and from the product of field-averaged water fluxes and field-averaged C_R . Day 0 corresponds to tracer application (November 4, 1992).

Note that for degrading compounds the early time breakthrough dominates, which would further accentuate this bias.

This also demonstrates that for tilled soils, the downward flux of a solute can be accelerated, if the location of the solute is in the Ap horizon, and decelerated if its location is in the strata not disturbed by agricultural activities [Steenhuis *et al.*, 1994]. Factors affecting this process are the degree of preferential flow, the antecedent water content, the hydraulic conductivity in the soil matrix, the rate of diffusion between the mobile and less mobile soil-water, and the contact area between preferential flow paths and soil matrix [White, 1985].

The importance of the proper calculation of the solute flux by field averaging the solute flux in comparison to taking the product of field-averaged C_F and field-averaged water fluxes has been questioned by Richter and Jury [1986]. Using 0.126-m² microlysimeters and a bromide tracer, they found that the difference between the two methods of calculating the solute flux differed by up to 100% for individual drainage events, but averaged out to a negligible difference for a time period of 100 days. In the present study, the product of field-averaged C_F and field-averaged water fluxes differed by up to -95% from the field-averaged solute flux. Over the course of 728 days, this difference averaged out to -4% when comparing the cumulative Br mass leached (data not shown). Therefore we agree with Richter and Jury [1986] that the traditional calculation of the solute flux by multiplying the field-averaged concentration with the field-averaged water flux is for longer time periods, i.e. >3 months, in good agreement with the proper calculation of the solute flux by field-averaging the solute flux. However, our data can not corroborate the conclusion of Richter and Jury [1986] that there is no correlation between solute concentration and water flux (Figure 3). Since correlation coefficients change from positive to negative values over the course of the breakthrough of a pulse applied tracer, its effects on the proper calculation of the solute flux average out for longer periods.

Nitrate

Field-averaged $\text{NO}_3\text{-N}$ concentrations in the suction cup samplers were on average 0.38 mg L^{-1} ($+8\%$) higher ($P = 0.952$) than in the PCAPS for year 1 (November 4, 1992 to November 8, 1993), and 0.09 mg L^{-1} (-2%) lower ($P = 0.795$) in year 2 (November 9, 1993 to November 1, 1994).

Table 2. Difference Between PCAPS (C_F) and Suction Cup Samplers (C_R) in Estimating Nitrate-N Mass Leached in Winter Fallow Versus Winter-Cover Cropped Plots

	PCAPS		Suction Cup Sampler		Difference	
	Amount, kg NO ₃ -N ha ⁻¹	Percent Change Due to Cover Crop, %	Amount, kg NO ₃ -N ha ⁻¹	Percent Change Due to Cover Crop, %	Amount, %	Percent Change Due to Cover Crop, %
			<i>Year 1</i>			
Winter fallow	24.8	-59	24.0	-53	-3	-10
Winter-cover crop	10.1		11.2		+11	
			<i>Year 2</i>			
Winter fallow	20.3	-44	19.4	-59	-4	+36
Winter-cover crop	11.5		7.9		-31*	

*Significant difference (paired t-test, $P < 0.05$).

This insignificant and relatively small bias in comparison to bromide is due to the more uniform distribution of the nitrate ion throughout the soil matrix. However, on single sampling events the deviations of the field-averaged suction cup sampler mean from the PCAPS mean ranged from -48% to +190%, and were for 35% of the sampling events significant ($P < 0.05$). It appears that for long-term monitoring schemes of NO₃ leaching, C_F and C_R are not significantly different. For short-term monitoring (i.e. <0.05 pore volumes), there can be a significant difference.

Biggar and Nielsen [1976] suggested using the suction cup sampler only to estimate relative differences instead of absolute values of the solute flux due to the lognormal distribution of the pore-water velocity. Since the evaluation of NO₃ leaching under different management practices is of interest in many studies, we compared the two sampling devices, i.e. concentration detection modes, in estimating the NO₃ mass leached under winter-cover cropped plots and winter-fallow plots receiving no fertilizer (Table 2). NO₃ mass losses estimated using PCAPS were computed from averaged NO₃ fluxes, and for suction cup samplers from the product of average NO₃ concentrations (C_R) and average water flux as estimated by PCAPS. Only in year 2 for the winter-cover cropped plots, the suction cup sampler estimate of NO₃ mass leached was significantly different than the PCAPS estimate ($P < 0.05$). The greatest bias of the suction cup sampler in estimating NO₃ mass losses, however, was found in the relative difference between winter fallow and winter-cover cropped plots for year 2. Although this difference appears to be due to random variations ($P = 0.314$), it casts doubt on the conclusion to use suction cup samplers to monitor relative differences. Further

evidence is necessary from a wider range of soils to conclusively prove this point.

Rhodamine WT and Brilliant Blue FCF

Pesticide contamination of ground water is of significant contemporary concern. Chemical compounds with strong sorptive behavior, such as pesticides or the dyes used in this experiment, are most susceptible to leaching via macropores shortly after application at times of large infiltration, due to irrigation or strong precipitation events [Andreini and Steenhuis, 1990]. Macropores, such as cracks or burrows, are most pronounced in heavy soils under dry conditions, but essentially all soils contain some macropores [Beven and German, 1982].

Upon installation, macropores were observed through visual inspection of the upper soil surface prior to PCAPS installation just above the samplers at an average rate of 0.8 macropores per sampler with a diameter ranging from 0.5 to 1 cm. Since these macropores are too small for mice and too big for earth worms, they probably originate from root activity. Old roots and one old tree trunk found in the profile support this hypothesis. We assume that the soil was near saturation in the upper part of the profile because of high amounts of precipitation (82 mm) 5 days before tracer application. Extrapolating measured matric potential at the depth of the samplers [Brandi-Dohrn et al., 1996] indicates that the soil moisture content in the lower part of the profile was still fairly low.

Observed dye concentrations were very low with a maximum observation of 0.15% of C_0 of Rhodamine WT (day 21) and 0.08% of C_0 of Brilliant Blue FCF (day 37). This implies that just after application preferential flow paths were not active. Several reasons might explain this fact. While backfilling and

Table 3. Difference Between PCAPS (C_F) and Suction Cup Samplers (C_R) in Estimating Field-Averaged Rhodamine WT and Brilliant Blue FCF Concentrations

Date	Days Since Tracer Application	PCAPS, % C_0		Suction Cups, % C_0		Difference, %	
		Rhodamine WT	Brilliant Blue	Rhodamine WT	Brilliant Blue	Rhodamine WT	Brilliant Blue
Nov. 12, 1992	8	1×10^{-2} (1×10^{-2})*	4×10^{-3} (2×10^{-3})	2×10^{-2} (5×10^{-3})	2×10^{-3} (6×10^{-4})	46	-58
Nov. 19, 1992	15	3×10^{-3} (2×10^{-2})	2×10^{-5} (4×10^{-4})	4×10^{-3} (2×10^{-3})	0 (0)†	37	-100
Nov. 25, 1992	21	2×10^{-2} (6×10^{-3})	4×10^{-3} (2×10^{-3})	1×10^{-3} (4×10^{-4})	7×10^{-4} (3×10^{-4})	-95‡	-85‡
Dec. 3, 1992	29	1×10^{-2} (5×10^{-3})	5×10^{-3} (2×10^{-3})	3×10^{-3} (1×10^{-3})	1×10^{-3} (5×10^{-4})	-73	-80

*Number in parenthesis is standard error.

†For Rhodamine WT and Brilliant Blue FCF concentrations smaller than the detection limit were taken as zero.

‡Significant difference (paired t-test, $P < 0.05$).

twice compacting the trench with a back hoe, the inherent soil structure might have been damaged by the vibration. This is unlikely given the firm to very firm consistence of the soil. A more likely explanation is that the Ap horizon, which was close to saturation at the time of application, served as a mixing zone for the tracers, because tillage destroyed preferential flow paths in that layer. Thus the tracers were exposed to a much greater surface area and to longer residence times before reaching subsoil preferential flow-paths. Greater surface area and longer residence times both greatly enhance sorption thus explaining the very low early breakthrough of the tracers.

In the second year, virtually no Brilliant Blue FCF or Rhodamine WT was observed. Maximum concentrations were typically 0.009% and 0.01% of C_0 for Brilliant Blue FCF and Rhodamine WT, respectively. We believe that most of the Brilliant Blue FCF is degraded. Tonogai et al. [1978] found that Brilliant Blue FCF at a concentration of 0.3 of that applied in the present study diminished by 25% within 6 days under anaerobic conditions when mixed with 750 mL of sludge.

Field-averaged Rhodamine WT concentrations in suction cup samplers deviated by -95% to +46% as compared to the PCAPS for November 12 to December 3, 1992 (four sample dates after tracer application), when significant amounts of Rhodamine WT were observed (Table 3). A significant ($P < 0.05$) deviation was observed only on November 25, 1992 (-95%).

Field-averaged Brilliant Blue FCF concentrations were consistently lower by 100% to 58% in the suction cup samplers as compared to the PCAPS for November 12 to December 3, 1992 (Table 3). The deviation was significant ($P < 0.05$) only on November 25, 1992. These numbers indicate that for sorbing compounds a lower mean concentration in the suction cup samplers is to be expected due to preferential flow phenomena. Further research at different sites is necessary to establish wider evidence.

Conclusion

Our assumption that suction cup samplers operated under a falling head vacuum detect C_R while PCAPS detect C_F has been confirmed by the early breakthrough of C_F as compared to C_R , which matches the theoretical findings of Parker and van Genuchten [1984]. This resulted in an underestimation of true leaching losses of a bromide tracer as long as the Br peak is above the sampler, and an overestimation as soon as it moved past the sampler. For longer time periods, i.e., >2 pore volumes, the overall bias might average out to a negligible difference. For shorter time periods (i.e., <0.6 pore volumes), the suction cup sampler will provide a severely biased estimate of Br mass leached. For a more evenly distributed anion such as NO_3^- , which is applied many times a year over many years rather than in a single pulse, the bias appears to be most pronounced at short timescales (<0.05 pore volumes) but can in addition be significant at time scales of seasonal averages (i.e. 0.9 pore volumes). The typical early breakthrough of sorbing compounds due to macropores, which apparently is under-sampled by suction cups, is underestimated using suction cups due to the importance of preferential flow on C_F .

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