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Assessment of vadose zone sampling methods for detection of preferential herbicide transport

N. P. Peranginangin[1,*], B. K. Richards[1], and T. S. Steenhuis[1]

[1]Department of Biological & Environmental Engineering, Cornell University, Ithaca, New York, USA
[*]now at: Syngenta Crop Protection Inc., North Carolina, USA

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Abstract

Accurate soil water sampling is needed for monitoring of pesticide leaching through the vadose zone, especially in soils with significant preferential flowpaths. We assessed the effectiveness of wick and gravity pan lysimeters as well as ceramic cups

5   (installed 45–60 cm deep) in strongly-structured silty clay loam (Hudson series) and weakly-structured fine sandy loam (Arkport series) soils. Simulated rainfall (10–14 cm in 4 d, approximately equal to a 10-yr, 24 h storm) was applied following concurrent application of agronomic rates ($0.2\,g\,m^{-2}$) of atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) and 2,4-D (2,4-dichloro-phenoxy-acetic acid) immediately

10   following application of a chloride tracer (22–$44\,g\,m^{-2}$). Preferential flow mechanisms were observed in both soils, with herbicide and tracer mobility greater than would be predicted by uniform flow. Preferential flow was more dominant in the Hudson soil, with earlier breakthroughs observed. Mean wick and gravity pan sampler percolate concentrations at 60 cm depth ranged from 96 to $223\,\mu g\,L^{-1}$ for atrazine and 54 to $78\,\mu g\,L^{-1}$

15   for 2,4-D at the Hudson site, and from 7 to $22\,\mu g\,L^{-1}$ for atrazine and 0.5 to $2.8\,\mu g\,L^{-1}$ for 2,4-D at the Arkport site. Gravity and wick pan lysimeters had comparably good collection efficiencies at elevated soil moisture levels, whereas wick pan samplers performed better at lower moisture contents. Cup samplers performed poorly with wide variations in collections and solute concentrations.

20 ## 1 Introduction

Leaching of agricultural chemicals can be accelerated by the presence of preferential flowpaths in the vadose zone (Beven and Germann, 1982; Wildenschild et al., 1994; Flury, 1996; Jaynes et al., 2001; Kladivko et al., 2001). Preferential flowpaths in structured soils (Lawes et al., 1882; Beven and Germann, 1982) consist of macropores

25   caused by worm holes, root channels, cracks, animal burrows, etc., while in coarse unstructured soils, unstable wetting fronts lead to rapid finger flow (Hill and Parlange,

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1972; Glass et al., 1989). As noted by Kohne et al. (2009a), strong soil structure (and resulting macroporosity) can adversely impact the "filtering" function of the vadose zone. As a result, water and solutes can rapidly bypass the bulk of the soil matrix, such that a small fraction of soil media participates in most of the flow, allowing much faster transport of water and solutes due to minimal soil interaction and rapid water velocities. Although preferential flow has been well-documented in the research literature for several decades, practitioner awareness has lagged (e.g. Richards et al., 2003) until more recently.

Both atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) and 2,4-D (2,4-dichloro-phenoxyacetic acid) have relatively low adsorption coefficients with Koc values ranging from 40 to 394 mL/g for atrazine (Giddings et al., 2005) and 31 to 471 mL/g for 2,4-D (Industry Task Force II). According to the mobility classification developed by McCall et al. (1981), both of these compounds are considered as moderately to highly mobile. Atrazine aerobic soil half-life ranges from 20 to 146 d (Giddings et al., 2005), whereas 2,4-D has a relatively short aerobic soil half-life of 1.7 d (Industry Task Force II), indicating that this compound is easily biodegraded (Hamaker, 1972; Willems et al., 1996); herbicide degradation rates may be enhanced in soils receiving regular annual applications (Jenks et al., 1998). In view of these environmental fate properties (sorption and/or biodegradation), it was initially thought that neither compound would migrate significantly to groundwater through the soil profile. Nevertheless, it has been shown that due to preferential flow phenomena, these compounds may be transported as rapidly as non-adsorbed tracers, albeit at lower concentrations (Steenhuis et al., 1990; Kladivko et al., 1991; Flury, 1996). Therefore, soil water sampling methods need to be able to detect the transport of low levels of herbicides, especially that occurring via preferential flowpaths.

Various sampling methods are used to collect soil water from the vadose zone (Weihermüller et al., 2007), involving the acquisition of water drained either by the force of gravity (i.e. gravity pan samplers, agricultural tile lines, pipe lysimeters, and shallow wells) or by applying suction, either passively (wick pan samplers) or actively (porous

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cups, tension lysimeters). Like wells and agricultural drain lines, gravity pan samplers can only collect water from pores that are saturated (Barbee and Brown, 1986; Holder et al., 1991), often allowing water to bypass the pan sampler in high conductivity soils under unsaturated conditions. Wick pan samplers (also known as passive capillary samplers) use wicks to apply a continuous capillary suction (Holder et al., 1991; Boll et al., 1992; Knutson and Selker, 1994, 1996), allowing the collection of soil water from both saturated and unsaturated pores. Solute travel times and dispersion in wicks are very small compared to soil, as is the adsorption of organic and inorganic components to the fiberglass wicks (Boll et al., 1992; Poletika et al., 1992; Holder et al., 1992; Pivetz and Steenhuis, 1995). However, flow divergence can result in over- or undersampling, depending on soil moisture status relative to wick suction and capacity (Rimmer et al., 1995). Control tubes can minimize such flow divergence but require disturbance of the sampled area above the sampler (Gee et al., 2002, 2009). Recent modifications include incorporation of integral flow measurement resulting in fluxmeter functionality (Gee et al., 2002, 2009) and remote datalogging (Jabro et al., 2008) − both also applicable to gravity pan samplers. Integration of granular activated carbon sorbents with wicks allow collection of hydrophobic compounds (McNamara and Luthy, 2005). Far simpler and cheaper than pan lysimeters are porous cup vacuum samplers. However, there are limitations with this method: large networks of cups are typically necessary to account for heterogeneity (Liator, 1988); suction cup samplers installed in unsaturated soils above the capillary fringe are unsatisfactory for collecting representative samples since the samplers draw water from smaller soil pores while missing rapidly leaching water (Shaffer et al., 1979; Bailey, 1990; Boll et al., 1991; also Liator, 1988). Similarly, BrandiDohrn et al. (1996a) suggested that cup samplers collected resident water but were less effective at detecting flux concentrations. Modifications to the design have been made such as time domain reflectometry (TDR) combined with porous cups in order to try to assess flow and thereby solute flux conditions (Caron et al., 1999; Hart and Lowery, 1997), and the passive porous ceramic pan (Barzegar et al., 2004) which represents an interesting hybrid that provides greater collection efficiency

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and source area definition than porous cups but which similarly requires a vacuum source and has the complex installation requirements of pan lysimeters. Recent developments to reduce over/undersampling (as summarized by Weihermüller et al., 2007) include automated sensing of ambient matric potentials, with a matching tension then applied to the suction plate.

Our objective was to assess the relative capability three soil water sampling methods – gravity pan lysimeters, passive wick pan lysimeters and porous cups – to detect herbicide transport in two soil series in which preferential flow is known to occur.

2 Materials and methods

2.1 Overview

Experiments were carried out in Ithaca, New York at two field sites which were instrumented with a range of soil water samplers. A reasonable worse-case scenario was performed by applying simulated rain storms (10 to 14 cm total over 4 d – cumulative rainfall amount represents a 10-yr, 24 h storm) following herbicide application at typical agronomic rates. Two commonly used herbicides – atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) and 2,4-D (2,4-dichloro-phenoxyacetic acid) – were chosen as model compounds, representing strongly adsorbed and rapidly degradable herbicides, respectively. A non-reactive chloride tracer (KCl) was used to determine the spatial and temporal breakthrough curves for water and non-adsorbed solutes which allowed determination of the retardation of herbicide movement.

2.2 Soil descriptions

Both field sites were located on long-term grass sods which were regularly mowed or grazed. Earlier experiments, including blue dye tracers to visualize preferential flow paths, have shown well-defined macropore networks and preferential flow for the soils

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at both of these sites (Steenhuis et al., 1994; Ogawa et al., 1999; Richards et al., 1998, 2000; Akhtar et al. 2003a,b). The first site (denoted as the Hudson site) was located on mowed sod within the Cornell University Orchards on Hudson silty clay loam (fine, illitic, mesic Glossaquic Hapludalf) soil. The soil is moderately well-drained, with moderate to moderately slow conductivity in the surface and subsurface layers (40–120 cm d^{-1} for the upper 25 cm) and slow to very slow in the lower subsoil and substratum (between 1 and 40 cm d^{-1} for depths of 25–110 cm; Neeley, 1965). Conductivities become much greater during the summer due to macropores formed by partial drying of the soil (Merwin et al., 1994). Surface-connected cracks as wide as 10+ mm were observed during testing.

The second site (denoted as the Arkport site) was located about 0.3 km from the Orchards in a lightly-grazed horse pasture on Arkport fine sandy loam soil (coarse loamy, mixed, mesic, active, mesic Lamellic Hapludalf). This series is well drained and has a high content of fine sand in the surface layers but with heavier, finer textures at depth. The soil at the test plot consisted of 6 distinct layers: dark brown medium fine sand with many fine roots and some fine gravel (0–20 cm), light tan fine sand with many root channels as well as both fine and large earthworm holes present as well as many distinct lamellae of the overlying soil (20–50 cm), fine loamy sand with a weak subangular blocky structure (50–80 cm), silt loam/silty clay loam with a moderate subangular blocky structure (80–130 cm), clay loam (130–155 cm), and silty clay (>155 cm). The thickness of these soil horizons are average values, varying considerably across the pit due to the fluvial origins. Hydraulic conductivity for the top 60 cm ranged from 40–400 cm d^{-1}, with rates between 120 and >400 cm d^{-1} for 60–90 cm depths (Neeley, 1965). The conductivity of the clay loam/silty clay subsoil layers was very low, with lateral water flow atop these horizons noted during sampler installation.

2.3 Samplers and installation

Passive wick pan lysimeters followed the general design of Boll et al. (1991), consisting of an enclosed box (34×34 cm, 1 m tall) with an anodized aluminum plate (33×33 cm)

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mounted at the top, to which were attached 25 thin stainless steel plates (6.3×6.3 cm, 5×5 plate array), each supported by a compression spring. A fiberglass wick (9.5 mm diameter×0.8 m long, previously baked to remove organic binders; Pepperell Braiding Co.) was attached to each plate. Wicks were fed through corresponding holes in the

5 stainless steel plate and the aluminum wick plate and were suspended vertically in the sampler, encased in 13 mm (i.d.) clear PVC (polyvinyl chloride) tubing. The 0.8 m vertical suspension enabled the wicks to exert a capillary matric potential (suction) on the soil in contact with the tops of the wicks. The bottoms of the wicks were grouped into 4 HDPE (high density polyethylene) collection bottles at the base of the sampler.

10 These bottles were evacuated periodically by vacuum applied to HDPE sampling lines from the soil surface.

Gravity pan lysimeters differ in that there are no wicks exerting suction on the sampled soil and thus collect soil water only when the subsoil above the sampler is saturated, allowing free drainage. An anodized aluminum plate (identical to that used in the

15 wick pan lysimeters but without wicks or springs) served as the pan, with a layer (4- to 6-cm deep) of small glass beads (2- to 4-mm dia.) placed on the plate support the subsoil over the sampler. PVC tubing connected the 25 holes in the gravity pan with four HDPE collection bottles.

Porous cup samplers used a ceramic cup (48-mm diameter, Soil Moisture Inc.) ce-

20 mented to a 40- to 50-cm long PVC pipe sealed with two-hole stopper. Plastic tubing was installed through the stopper holes, with a shorter length for applying the vacuum to the cup, and a longer section for sample retrieval.

Sampler installation was similar to that detailed by Richards et al. (1998). Pits were excavated by backhoe adjacent to and down gradient from the test plots to facilitate

25 sampler installation. Vertical soil profiles were described and sampled across the face of the pit. Samplers were installed at each site in a plot area of approximately 2.4 m×6.6 m (16 m^2) and 3.6 m×6.9 m (26 m^2) for Hudson and Arkport sites, respectively (Fig. 1). At each plot, two wick pan lysimeters and a gravity pan lysimeter were installed 1 m apart, 0.6 m below the soil surface in horizontal tunnels excavated lat-

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erally under the test plot. The samplers were pressed upward against the exposed face of undisturbed subsoil using wedges and blocks. Five suction cup lysimeters were installed at the Hudson site at 60 cm depth. Six cup lysimeters were installed at the Arkport site at textural boundaries (at 50–60 cm). Each sampler was installed through

5 an augered hole backfilled with a slurry of the original soil, and holes were sealed with a 25 cm layer of expanding foam to prevent direct infiltration from the surface. Underdrains (perforated PVC tubing, 5-cm dia) were installed under the samplers at depths of 95 to 105 cm to prevent potential sampler flooding. Drains were connected to HDPE pails or bottles that were periodically sampled via a HDPE vacuum line. All

10 sampling lines were grouped into standpipes for protection and were capped to prevent contamination. Samples were evacuated using a vacuum pump and a 2-L or 4-L glass vacuum flask. The total sample volume was recorded before sub-samples were transferred to certified precleaned amber glass bottles (Environmental Sampling Supply, Oakland, CA) as per APHA/AWWA/WEF (1998) standard procedures.

15 Samplers were designed and constructed to avoid the use of materials that may adsorb herbicides. Contact materials for wick samplers included fiberglass wicking, stainless steel wick support plates, silicone glue used to attach wicking to the plates, flexible PVC tubing loosely encasing wicks, and HDPE bottles and evacuation tubing. Contact materials unique to the gravity pan lysimeters included glass beads, fiberglass

20 screening for retaining the glass beads, and the anodized aluminum support plate. Suction lysimeters had ceramic cups and PCV pipe. All of these contact materials had been thought to be non-reactive (Papiernik et al., 1996; Koskinen et al., 1999). Suction lysimeters had PVC pipe and ceramic cups that rapidly equilibrate within a small amount of collected sample (Perrin-Ganier et al., 1993, 1994). However, subsequent

25 to our experiments, others have indicated greater potential herbcide reactivity with ceramic porous cups (e.g. Domange and Gregoire, 2006).

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2.4 Tracer, herbicide and rain application

2.4.1 Hudson site

Approximate steady-state soil moisture conditions were established by applying artificial rain (irrigation) at $2\,cm\,d^{-1}$ for 4 consecutive days. In order to determine baseline
5 control data, leachate was collected from each sampler on the first day of the experiment (13 August 2002) prior to herbicide and chloride (Cl^-) applications. Immediately thereafter, Cl^- tracer solution was applied (with a manual sprayer) to the $16\,m^2$ plot area on 13 August 2002 at a rate of $44.1\,g\,Cl^-\,m^{-2}$. Atrazine and 2,4-D were then applied at typical agronomic rates of $0.2\,g\,m^{-2}$ by a certified applicator using a hand-pump back-
10 pack sprayer. Multiple passes with the sprayer were used to ensure even distribution across the plot. Shortly following herbicide application, irrigation was applied with two sprinklers. During the first 4 d, 2.5 to 2.8 cm of rain was applied daily at a rate of 1.5 to $1.7\,cm\,h^{-1}$. Water samples were collected immediately after rainfall simulation ceased, and again on the next day before resuming irrigation. After the fourth day (10.4 cm
15 of cumulative rain), the rain was applied every 2 to 4 d at similar intensity and durations. When natural rainfall occurred, the irrigation amount was reduced accordingly to achieve 2.5 to 2.8 cm of total rain per application. Percolating water was collected the morning following application. Irrigation was applied only until September 24 (56 cm of cumulative rain), during this irrigation period the total natural rainfall was 14 cm. After
20 12 September (38 cm of cumulative rain depth), it was observed that the peak solute concentrations had already occurred. Therefore, subsequent water samples were collected every one to four weeks, depending on the occurrence of natural rain events. Final samples were collected on 20 November, cumulative rain and irrigation totaled 75 cm, of which 31 cm was natural rainfall.

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2.4.2 Arkport site

Steady state flow conditions were established by daily irrigations in June 2002. On 28 June, baseline water samples were collected from samplers except for porous suction cup lysimeters. The Cl^- tracer was applied at $21.5\,g\,m^{-2}$ to the $26\,m^2$ experimental plot.
5 Atrazine and 2,4-D were applied as previously described at rates of $0.2\,g\,m^{-2}$. Immediately after herbicide application, irrigation was initiated. Due to unexpectedly erratic irrigation water supplies, this site received a different simulated rainfall pattern than the Hudson site. Total rain depths of 1.3 to 2.1 cm were applied daily for 3 d at rates of 0.26 to $0.35\,cm\,h^{-1}$ using two sprinklers. On the fourth day (1 July), the artificial rain was
10 applied at $5.5\,cm\,h^{-1}$ for 1.5 h. Natural rainfall was then used throughout the rest of the experiment, with cumulative rain and irrigation totaling 53 cm. Leachate was collected daily during the first 4 d, and then twice per week to monthly thereafter, depending on the occurrence of rain events. Final samples were collected on 26 November.

2.5 Analytical procedures and soil sampling

15 Each leachate sample was analyzed for chloride with a Buchler Instruments Model 442-5000 digital chloridometer. All initial samples were analyzed for herbicides, with periodic analyses thereafter when concentrations were on the declining phase of the breakthrough curves. Atrazine and 2,4-D analyses were carried out using enzyme-linked immunosorbent assay (ELISA) kits (Strategic Diagnostics Inc., Newark, DE).
20 Minimum detection limits were 0.05 and $0.7\,\mu g\,L^{-1}$ for atrazine and 2,4-D, respectively. Concentrations were determined spectrophotometrically ($450\,\mu m$) in a dedicated RPA-1 spectrophotometer. Standard regression correlations (r^2) were 0.994 to 0.998, stronger than required correlations of >0.990. A small number of percolate samples were forwarded to the New York Department of Environmental Conservation for confir-
25 matory analysis via HPLC, which resulted in a mean ELISA/HPLC ratio of 0.95 (data not shown).

Soil core samples were collected from both plots two days after the cumulative rain

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levels reached 63 (Hudson) and 45 cm (Arkport sites). Three replicate soil cores were extracted from each plot to a depth of 90 cm, with samples subdivided at soil depths of 15, 30, 45, 60, and 90 cm. Additionally, three replicate soil cores were extracted from outside the plots for background data. After determining soil moisture content gravimetrically, 10 g of each dried sample was ground using a mortar, then mixed with 25 mL distilled water and shaken for 16 h. The suspensions were allowed to settle for 1 h, after which supernatants were analyzed for chloride in order to calculate a mass balance of applied chloride.

Laboratory measurements of bulk dry density from two different locations inside and outside the plots area were also performed. The samples were taken on 9 October and 29 October for Hudson and Arkport sites, respectively. In each location, undisturbed soil samples were taken at 0–15 cm and 30–45 cm below the soil surface, using stainless steel cylindrical rings (7.2 cm dia., 6.7 cm tall).

Collection efficiencies were determined for the wick and gravity pan by dividing the mass collected (equal to mean concentration times total volume) by the mass applied to the nominal contributing surface area ($0.116 \, m^2$) above the samplers.

2.6 Statistical analysis

Whenever applicable, the variability of water and solute collection and measured concentrations among similar samplers was analyzed by determining mean coefficients of variation (CV), which was the average of CVs of all collected volume, solutes, or measured concentrations at every sampling interval. Variation was assessed among the multiple subsample bottles within each wick pan or gravity pan lysimeter. The CVs and their respective 95% confidence intervals were calculated by standard procedures using SAS software (SAS Institute) version 8.02.

3 Results

Breakthrough curves (BTCs) for chloride and herbicides are presented, followed by mass balances and collection efficiencies. Solute concentrations presented are corrected for background (baseline) levels (except cup lysimeters at the Arkport site, where background levels were not available). At the Hudson site, background concentrations were 0.6 to 2.2 mM Cl$^-$, 0.1 to 0.3 μg L^{-1} atrazine, and less than 0.7 μg L^{-1} 2,4-D. Background levels at the Arkport site were 1.0 to 1.5 mM Cl$^-$, less than 0.05 to 0.8 μg L^{-1} atrazine, and less than 0.7 μg L^{-1} 2,4-D.

3.1 Chloride breakthrough

3.1.1 Hudson site

Chloride BTCs for the Hudson site are shown in Fig. 2. Initial breakthrough occurred immediately after application (2.6 cm of cumulative rain) for all samplers other than wick pan lysimeter 1 (W1). Peak concentrations for wick pan lysimeter 2 (W2) were substantially greater compared to other samplers (Fig. 2). W1 showed a delayed peak concentrations, arriving at cumulative rain application of 10 cm (Fig. 2), 3 d after pulse application.

The mean Cl$^-$ BTC of porous cup samplers (Fig. 2) showed high variability, with a mean coefficient of variation (CV) of 81% compared to wick sampler CVs of 46%. Two porous cups had Cl$^-$ peaks immediately after pulse application, suggesting that these particular cups were sampling preferential flowpaths. A third cup peaked the day after application, but the two remaining cups indicated little if any form of a chloride peak.

The soil moisture profiles collected from the Hudson site showed soil moisture contents of 0.26 to 0.37 (Fig. 3). At these moisture contents, the rainfall intensity of 2.5 cm d^{-1} would conventionally be expected to result in pore water velocities of 7 to 10 cm d^{-1} if uniform matrix flow is assumed. Accordingly, if all water and solute moved

with the average velocity, initial solute breakthrough would be observed 6 to 9 d after pulse application, or at 15–22.5 cm of cumulative rainfall. Clearly, this was not the case for the Hudson soil, where solute was observed at 2.6 cm of cumulative applied rain and immediately after the tracer was surface applied, confirming the dominant influence of preferential flow.

3.1.2 Arkport site

In the Arkport site, peak chloride concentrations appeared for most samplers after a cumulative rain of 13 cm (Fig. 4) and at substantially lower peak concentrations. These results indicated a smaller preferential flow component and a correspondingly greater tendency towards matrix flow than at the Hudson site. The pattern of results from sampler W2 (Fig. 4) similarly reflect this finding. The initial peak (at 13 cm cumulative rain) indicated the effect of preferential flow paths, followed by matrix flow, especially as indicated by the delayed jump at the end of the experiment (53 cm cumulative rain). Little percolate was collected during the natural rainfall period, likely due to the coarse sandy layer at 50 cm depth, which could divert flow laterally when the soil moisture was low, thereby bypassing the wick sampler.

Results for the six porous cup samplers showed considerable variability, with peak concentrations of various cups occurring at differing cumulative rain applications. All samplers did not collect water for several days during the experiment because the flow may have bypassed the suction cup locations (Shuford et al., 1977; Steenhuis et al., 1990; Bailey, 1990) or the bubbling pressure was lower than the applied suction. Only one cup sampler had a peak concentration on the first day of application. Despite the high spatial and temporal variability in BTCs, the calculated mean CV (78%) for measured concentrations showed that the observed concentrations were moderately variable relatively to other samplers (43–101%, Fig. 4). However, these CVs should be interpreted with caution because for most sampling periods, there were 1 to 4 (out of 6) cups "missing" due to no water available for collection.

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3.2 Herbicide breakthrough curves

3.2.1 Hudson site

Atrazine BTCs at the Hudson site closely followed those observed for chloride (Fig. 5), indicating rapid preferential transport. Peak soil percolate atrazine concentrations coincided with chloride peaks for samplers W1 and W2, with mean concentrations within each sampler ranging from 195 (W1) to 1200 (W2) $\mu g\,L^{-1}$, with concentrations in W2 again substantially greater than other samplers. For the gravity pan lysimeter, atrazine peaked at 300 $\mu g\,L^{-1}$ occurring on the day following chloride peaks and again after ~10 cm cumulative rain. Variation among subsample bottles within the gravity pan lysimeter was marked (CV=69.5%), typical of that observed with preferential flow. Small secondary/tertiary atrazine peaks occurred at 19 cm of water application except for the W2 sampler and are highly associated with the matrix flow component.

Suction cup samplers again showed high variability, as reflected by a CV of 100% (Fig. 5). The range of atrazine concentrations from single cup was 1 to 570 $\mu g\,L^{-1}$ with the peak single cup atrazine concentration of 570 $\mu g\,L^{-1}$ coinciding with the peak chloride concentration on day 2 (5 cm cumulative rain), attributed to the existence of macropores around the sampler. Interestingly, the peak of a second cup (57 $\mu g\,L^{-1}$) occurred on the second day, much earlier than its chloride peak, suggesting some small scale heterogenity of application of tracer vs. herbicides. Delayed atrazine peaks (compared to chloride) were observed for three cups, with peak concentrations ranging from 80 to 250 $\mu g\,L^{-1}$.

BTCs for 2,4-D were initially similar to those of atrazine (Fig. 5). Breakthroughs for all samplers, except for porous suction cups, were in the same order as atrazine and occurred either on the day of or the day following application. The concentrations of 2,4-D from a single cup ranged from 0 to 2500 ppb, with single peak concentrations of 190 to 2500 $\mu g\,L^{-1}$, similar to those of atrazine. Observed 2,4-D concentrations declined more rapidly after the initial breakthroughs, likely due to the rapid biodegradation that has been observed to occur in macropores (e.g. Pivetz and Steenhuis, 1995). After

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10 cm of cumulative rain, 2,4-D ceased to be detected in some samplers (W2), and was not detected in any sampler after 30 cm of cumulative rain.

For most suction cups, 2,4-D tended to appear only during the greatest flow event shortly after application (i.e. the first 10 cm of rain application at the rainfall intensity of 2.5 to 2.8 cm d^{-1}, Figs. 3 and 5). BTCs for the majority of cups lysimeters showed similar shape and breakthroughs occurred either on the first or second day after application, ranging from 25 to 250 μg L^{-1}. For most cup lysimeters 2,4-D soon fell below the detection limit after about 10 cm of cumulative rain application. The exception was one cup which had an extraordinarily high initial peak of 3700 μg L^{-1} which, like chloride and atrazine, gradually returned to baseline. This sampler may have intersected a flowpath or area where an initial pulse of tracer and herbicide accumulated, and the gradual decline may have been due to the fact that sample volumes for cup lysimeters were smaller than for the other samplers, thus taking longer to attenuate the pulse.

3.2.2 Arkport site

Similar to chloride, atrazine breakthroughs for all samplers at the Arkport site occurred at cumulative rain applications of 13 cm (Fig. 6). Atrazine concentrations and patterns among the pan and wick lysimeters were similar, with peak mean concentrations ranging from 10 to 30 μg L^{-1}. Several cup lysimeters had early peaks near 10 cm, although most had peak concentrations coinciding with the other samplers. For all samplers at the Arkport site, 2,4-D typically reached the 45–60 cm sampling depth only after 13 cm of cumulative rain and at relatively low concentrations, with peak levels up to 18 μg L^{-1} (Fig. 6). Unlike the Hudson site, cup samplers had markedly lower levels of 2,4D detection than atrazine at the Arkport site, likely due to the greater matrix flow component which afforded greater opportunities for degradation. The greatest concentrations were traceable to two subsample bottles each within the W2 and G samplers. 2,4-D was barely detected after the peak, suggesting rapid biodegradation.

3.3 Mass balances and collection efficiencies

3.3.1 Hudson site

At the Hudson site, it was observed that all pan (wick and gravity) samplers collected water at rates greater than the amount of rain applied to the sampler nominal sampling area of 0.116 m^2, especially during the intensive artificial rain applications. This "overcollection" has been observed with samplers in this and similar strongly-structured soils (Rimmer et al., 1995). As the soil profile of the silty clay loam becomes wetter and saturated, water movement was highly influenced by the gravitational potential gradient which caused the surrounding soil water to not only flow vertically but also drain laterally into the pan samplers as the easiest pathway for outflow. Extrapolating this overcollection to the solute movement on the entire plot area would be erroneous, so collection efficiency and mass balance calculations were adjusted to assume that the "actual" water volume collected was equal to the amount of applied rain multiplied by the sampler's nominal surface area. This assumption was derived from the fact that steady state flow conditions had been established prior to the experiment.

Chloride and herbicide relative cumulative masses plotted as a function of cumulative rain (Fig. 7) reflect the initial rapid transport, especially of chloride. Cumulative chloride recovered in samplers increased rapidly within the first 10 cm (14%) of total rain applied, with cumulative masses ranging from 24% to 65% of applied. Interestingly, cumulative chloride percolating to W2 during the first 5 cm (7% of total rain application) was 44% of that applied, more than twice that of other samplers, indicating greater preferential flow contributions to W2. The lower relative amounts of atrazine and 2,4-D collected within the same period reflect herbicide adsorption and/or degradation.

Analysis of soil collected on 9 October (cumulative applied rain of 63 cm) showed that the amount of chloride still stored in the top 15 cm of soil was 10% of applied, with no chloride found between 15 cm and 90 cm (Table 1). Mass balance results indicated that collected chloride exceeded that applied (to each sampler's nominal application area) by up to 18% for the Hudson plot.

The first efficiency assessment of water collection was conducted as of 22 cm of cumulative rain (27 August), the last day of continuous herbicide analysis. Samplers G and W2 collected nearly all water applied (Table 2), but the amount of chloride recovered from the leachate ranged from 62% to 81% of surface-applied chloride. The discrepancy between water and chloride collection may be attributed to some chloride bypassing the samplers and/or diffusing laterally as well as the chloride subsequently shown to be remaining in the soil above the samplers. The collections of 9 to 30% of applied atrazine reflects expected soil adsorption (Flury, 1996; Gidding et al, 2005) of the bulk of applied herbicide, as well as some degradation and any potential effects of sampler bias. Inferred degradation of 2,4-D (Sirons et al., 1982; Industry Task Force II) reduced potential for transport, with collections ranging from 5 to 11% of applied 2,4-D. As of the end of experiment (75 cm of total cumulative rain, 20 November), total water collection (69–91%) was lower than that for chloride (96–115%, Table 2), likely related to the increased degree of bypass flow later in the study when most chloride had already leached.

3.3.2 Arkport site

Given the high conductivity of this soil, nearly all percolate was able to move through the soil matrix except when the soil was very wet. Hence, water and solutes tended to flow more uniformly and slowly than at the Hudson site, resulting in significantly more chloride remaining in the surface of the soil. Based on the soil sampling performed on November 1 (45 cm cumulative applied rain), the amount of chloride stored in the top 60 cm of soil was 50% of applied mass, with none found below 60 cm. Total in-soil plus collected chloride indicated shortfalls of 11 to 24% compared to the applied chloride (Table 1). Accordingly, herbicides experienced more interaction with the soil matrix and had greater time for adsorption and degradation to occur, resulting in lower collection efficiencies in the Arkport soil, as inferred from Fig. 7.

As of the last day of continuous herbicide analysis (30 July, 20 cm of cumulative rain application), water collections were 55 to 85% of total water applied (Table 2), and

chloride collection efficiencies were 17 to 33%. Atrazine collections were 0.6 to 2.0% of the total applied, and 2,4-D collections ranging up to only 0.2% of total applied.

By the end of the experiment (53 cm of cumulative rain), the sampler water collection efficiencies were nearly the same as those for chloride, ranging from 29% to 37% for pan lysimeters. As mentioned earlier, wick lysimeter 2 was unable to collect water for several days during the natural rainfall period due to a coarse lens above the sampler (50–55 cm depth) that diverted percolate flow laterally when the soil was below field capacity. The gravity sampler initially collected more water than wick samplers, but by the end of the experiment (when lower natural rainfall rates left the soil below field capacity) their efficiencies were nearly the same.

3.4 Sampler variation

The four bottles within each wick and gravity samplers unit allowed variability to be assessed among the bottles within each sampler as well as between sampler units. The variation among bottles within each sampler (Table 2) in total water and chloride collected tended to be lower for the gravity pan lysimeter (CV 23 to 52%) than for wick pan lysimeters (42 to 71%). More significant in a practical sense is the variability among samplers of each type in collecting water and solutes at each sampling interval. Table 3 shows that wick samplers had the least variation between samplers (mean CV=32 to 121%), with cup samplers showing the greatest variability (mean CV=60 to 204%). In comparison, the variability in herbicide concentrations among bottles in each gravity sampler closely mirrored the between-sampler variability of the wick pan lysimeters.

4 Discussion

It should be remembered that the context of this experiment was agronomic applications of both herbicides on established grass sod, closely followed by significant (but by no means unrealistically extreme) rainfall, totaling 10 (Hudson) to 14 (Arkport) cm of

rainfall in the 4 d following application. This cumulative rainfall amount is approximately equal to a 10-yr, 24 h storm (the 24 h storm with a 10% probability of occurring in any given year), which would yield a cumulative rainfall of 4 in (derived from isohyetal maps of Hershfield, 1961 using Weather Bureau data, reproduced in Dunn and Leopold, 1978). The first day rainfall intensities were less than or equal to a 2-yr, 1 h storm (ca. 2.7 cm for Ithaca NY), again indicating that the rainfall regime used was a reasonable test case. (In contrast, applying a total of 10 cm in only 6 h would have simulated a far less probable 100-yr, 6 h storm).

Preferential flow occurred in both soils, being more dominant in the Hudson silty clay loam soil. As shown in sequential images documenting blue dye penetration into Hudson soil (supplementary material, see: http://www.hydrol-earth-syst-sci-discuss.net/6/7247/2009/hessd-6-7247-2009-supplement.zip, Peranginangin et al., 2003), a uniform dye color was observed along the distribution layer (plow layer), below which the dye branched into many fine structural cracks and continuous earthworm channels, as observed previously at this field site (Richards et al., 1998) and later in undisturbed soil columns extracted from this site (Akhtar et al. 2003a,b). Similar tests showed that the dye path through the Arkport soil was more uniformly distributed than it was at the Hudson site (Peranginangin et al., 2003; Akhtar et al. 2003a) and that Arkport soils showed less tendency for preferential breakthrough (Akhtar et al. 2003b).

Peak percolate concentrations of 2,4-D and atrazine (as well as chloride tracer) occurred shortly after application, consistent with previous reports of herbicide mobility following application (e.g. Smith et al., 1990; Kladivko et al., 1991; Gish et al., 1991; Ghodrati and Jury, 1992). Edwards et al. (1993) similarly reported that the greatest potential for significant preferential transport followed intense rainfall events that occurred shortly after atrazine application. Malone et al. (2004) found that preferential flow similarly accelerated the transport of four herbicides regardless of sorptive properties, with the majority of losses occurring within 1.1 d of application. Shipitalo et al. (2000) similarly concluded that intense precipitation events shortly after surface herbicide application can transmit up to several percent of applied herbicide to the subsoil irrespective

of the chemical's adsorptive affinity.

Herbicide concentrations in the well-structured Hudson silty clay loam were greater than those observed in the sandy loam soils at the Arkport site (Table 4), and breakthrough occurred at higher cumulative rain in the Arkport soil than in the Hudson soil, both consistent with observations of more extensive preferential flow paths in the Hudson soil. In concord with our results, Sadhegi et al. (2000) found greater herbicide leaching in a finer silt loam soil (due to macroporosity likely arising from greater aggregate stability) than in a sandy loam soil. Montoya et al. (2006) concluded that intrinsic soil properties had greater effects on atrazine transport than did tillage practices applied to each soil. Tsegaye et al. (2007) found that switchgrass roots promoted preferential atrazine transport in both fine loamy and clayey Hapludult soils, and Siczek et al. (2008) recovered more than 1% of applied atrazine in leachates from both conventionally-tilled and untilled soil columns.

Table 4 shows that the observed percolate concentrations were caused by the transport of a small fraction (M/M_0) of the applied herbicide mass. For example, the Hudson site W1 wick sampler had a volume-weighted mean concentration of 96 μg L^{-1} over the course of the study, which represented 0.31 mg atrazine, which was 1.4% of the 21.6 mg atrazine applied to the nominal 1080 cm^2 sampling area. As noted by Boesten (2008), while many pesticide leaching models can account for the bulk of applied compounds, even low levels of "unaccounted losses" (less than 1% of applied pesticide) could potentially cause relatively high leachate concentrations (Steenhuis and Parlange, 1990). The lower the concentration of concern, the more important becomes the impact of preferential flowpaths. As such, pesticide transport models for structured soils that can account for preferential flow yield more realistic results than do "chromatographic" (matric) flow models (Kohne et al., 2009b). Although leachate is to be distinguished from groundwater, in some instances close connection between macropores and drains (e.g. Fox et al., 2007) or shallow aquifers could hasten transport to surface or ground water with reduced opportunity for contaminant adsorption.

In terms of sampler performance, under relatively high rainfall (irrigation) rates, the

collection efficiencies of wick and gravity pan samplers were comparable, but the efficiency of the gravity pan samplers decreased under decreased soil moisture, as observed elsewhere (Boll et al., 1991). The hydraulic conductivity of the Hudson clay loam matrix was very low, thus macropores were the primary transport path in that soil. Water flows through these macropores under zero matric tension and the suction applied by the fiberglass wick provides no additional sampling capability, resulting in similar results between gravity and wick lysimeters where each captured preferential flow (as previously mentioned, saturated flow in macropores similarly favors sampler overcollection when the sampler is the easiest flow destination available). Unsurprisingly, the wick samplers had an advantage over gravity driven samplers when the soil moisture content was below field capacity. Overcollection and other flow divergence due to stratification (e.g. BrandiDohrn, 1996b) or textural gradients (as found over the Arkport W2 sampler) can lead can result in significant lateral movement that complicates determination of areal-based mass fluxes. In contrast, leachate concentrations are less affected, and the mean herbicide concentrations over the experimental period showed reasonable agreement among wick and gravity pan samplers, with ranges of 96 to 223 μg L^{-1} for atrazine and 54 to 78 μg L^{-1} for 2,4-D at the Hudson site, and 7 to 22 μg L^{-1} for atrazine and 0.5 to 2.8 μg L^{-1} for 2,4-D at the Arkport site (Table 4).

Suction cup lysimeters performed far less consistently than pan samplers, producing erratic BTCs with both soil types. Similar performance has also been found in previous studies (Boll et al., 1991; Bailey, 1990) indicating that these measurements were much more sensitive to small-scale variations in the soil profile. With variable and difficult to define sampling/extraction domains (Weihermüller et al., 2007), rapidly leaching water may only be captured by chance (Shaffer et al., 1979), resulting in high variability in water and solute collection as compared to other samplers (Table 3). This variability may be partially compensated for with larger numbers of samplers, with probabilistic approaches suggested to achieve given levels of confidence (e.g. BrandiDohrn et al., 1996b). Wick and gravity pan samplers, while better suited to detecting preferental flow (this study; Weihermüller et al., 2007) involve a tradeoff of far greater cost and

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installation requirements.

In sum, we have shown that preferential flow mechanisms were present in both soils tested, a reasonable test case scenario of agronomic application of herbicides followed by rain events led to significant percolate herbicide concentrations at up to 60 cm sampling depth, and soil water samplers differed in their ability to detect preferential transport of herbicides. Gravity and wick pan lysimeters had comparably good collection efficiencies at elevated soil moisture levels, whereas wick pan samplers performed better at lower moisture contents. Cup samplers performed poorly with wide variations in collections and solute concentrations.

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Table 1. Chloride mass balances for Hudson and Arkport plots. All values expressed as percent of total chloride applied.

Site and sampler	Collected in leachate (%)	Stored in soil 0–60 cm (%)	Stored in soil 60–90 cm (%)	Total (%)	Shortfall/ excess (%)
Hudson *(as of Oct 9; 63 cm cumulative rainfall)*					
Wick 1 (W1)	90	10	0	100	0
Wick 2 (W2)	106	10	0	116	+16
Gravity (G)	108	10	0	118	+18
Arkport *(as of Nov 1; 45 cm cumulative rainfall)*					
Wick 1 (W1)	39	50	0	89	−11
Wick 2 (W2)	26	50	0	76	−24
Gravity (G)	34	50	0	84	−16

Table 2. Cumulative water, chloride and herbicide collections in samplers (as percent of applied mass) at two timepoints.

Site and Sampler	Total collected as of the end of continuous ELISA analysis (percent of applied)				Total collected as of the end of experiment (percent of applied)			
	Water	Chloride	Atrazine	2,4-D	Water	CV (%)	Chloride	CV (%)
Hudson								
	at 22 cm cumulative rain				at 75 cm cumulative rain			
Wick 1 (W1)	77.8	49.0	9.12	5.6	68.6	42.4	95.7	64.5
Wick 2 (W2)	99.1	80.5	29.6	10.7	90.6	62.7	109	71.5
Gravity (G)	96.0	61.5	20.9	6.6	77.1	42.4	115	23.2
Arkport								
	at 20 cm cumulative rain				at 53 cm cumulative rain			
Wick 1 (W1)	54.8	31.9	1.00	0.03	32.4	55.0	38.9	70.7
Wick 2 (W2)	67.4	17.2	0.56	0.10	29.4	44.2	25.8	64.2
Gravity (G)	85.2	33.2	2.02	0.22	37.3	22.6	33.5	52.1

Table 3. Mean coefficients of variation (among replicate samplers) for water volume and chloride and herbicide concentrations. For each sampler type, the mean CV was determined by averaging CVs (among replicate samplers) of the measured concentrations at every sampling event. Gravity CV's are calculated from variability among bottles within the single sampler at each site.

Sampler	Water	Chloride	Atrazine	2,4-D
Hudson				
Wick	32.1	37.2	53.6	70.5
Gravity	–	–	69.5	82.9
Cup	63.4	117	135	204
Arkport				
Wick	83.5	102	43.6	121
Gravity	–	–	40.2	123
Cup	175	76.1	104	130

Header: CV (%)

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Table 4. Percolate chloride, atrazine and 2,4-D: peak and volume-weighted mean concentrations, cumulative mass collected, cumulative mass as fraction of applied (M/M_0).

Site and sampler	Chloride Peak (mM)	Mass (g)	M/M_0	Atrazine Mean $(\mu g\,L^{-1})$	Peak $(\mu g\,L^{-1})$	Mass (mg)	M/M_0	2,4-D Mean $(\mu g\,L^{-1})$	Peak $(\mu g\,L^{-1})$	Mass (mg)	M/M_0
Hudson											
Wick 1 (W1)	5.37	0.43	0.09	95.8	181	0.31	0.01	55.5	255	0.44	0.02
Wick 2 (W2)	14.2	1.40	0.29	223	1214	3.38	0.14	78.4	533	1.48	0.06
Gravity (G)	4.41	0.44	0.09	181	285	0.78	0.03	53.8	194	0.53	0.02
Arkport											
Wick 1 (W1)	2.44	0.67	0.29	13.8	26.6	0.21	0.01	0.54	0.85	0.01	0.00
Wick 2 (W2)	0.86	0.38	0.17	7.42	9.61	0.12	0.01	1.66	1.92	0.02	0.00
Gravity (G)	1.38	0.07	0.03	21.6	27.6	0.42	0.02	2.8	3.44	0.05	0.00

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Top View

Legend
- Wick sampler
- Pan sampler
- Suction cup sampler
- Tile drain
- Sample lines
- Standpipe

Excavated & backfilled area   Application area

Section View

Sample lines   Poly film barrier

Standpipe   Application area
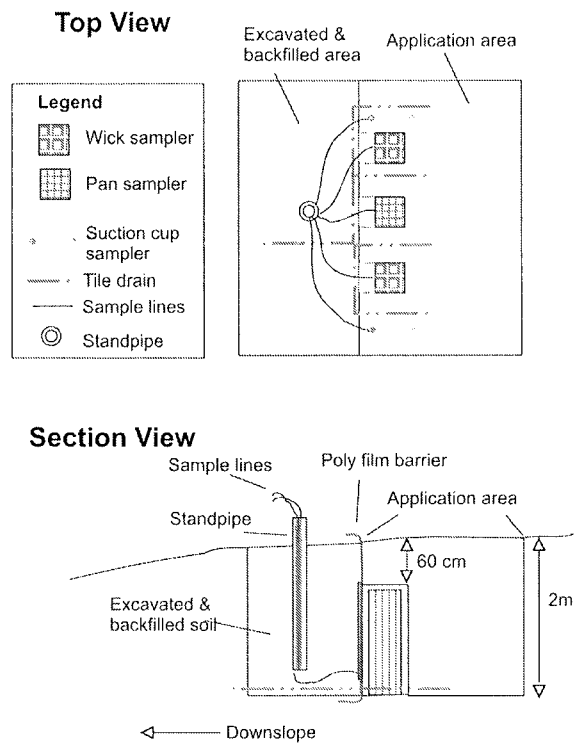
60 cm

2m

Excavated & backfilled soil

◁——— Downslope

Fig. 1. General layout and section view of sampler installation beneath undisturbed soil profiles.
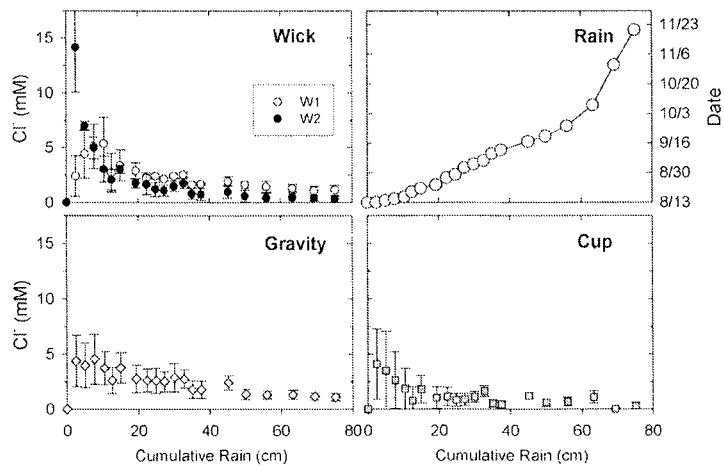
Fig. 2. Hudson site chloride breakthrough curves: chloride concentrations (mM) as a function of cumulative rain (irrigation plus natural rainfall). Plot in upper right shows date (2002) vs. cumulative rain.
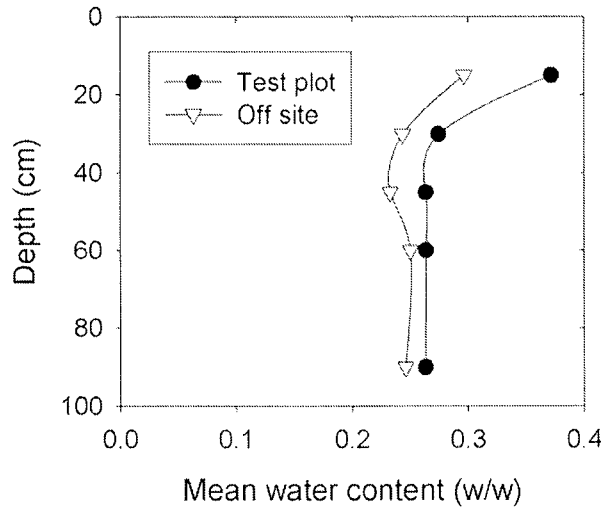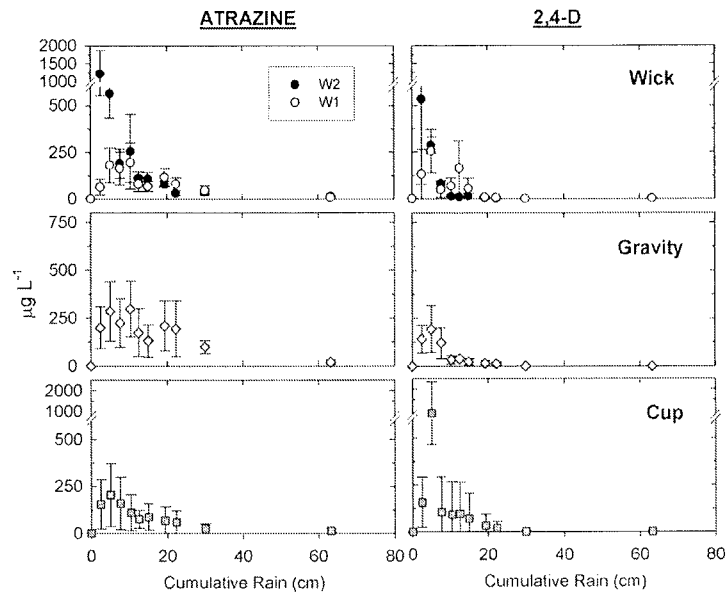
Fig. 3. Hudson site soil moisture as a function of depth both on the experimental plot as well as nearby.
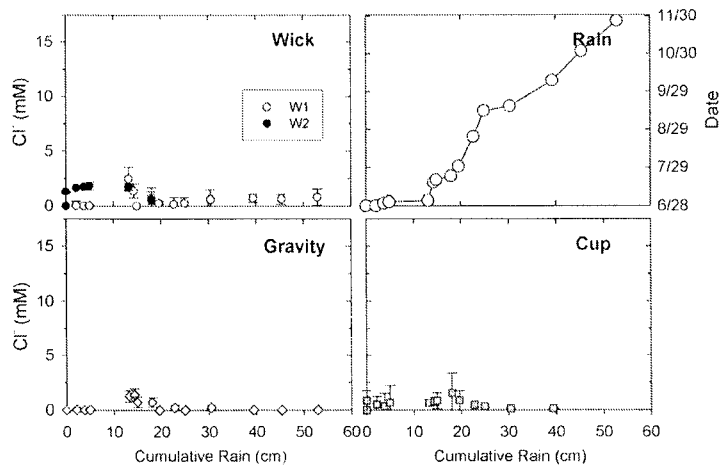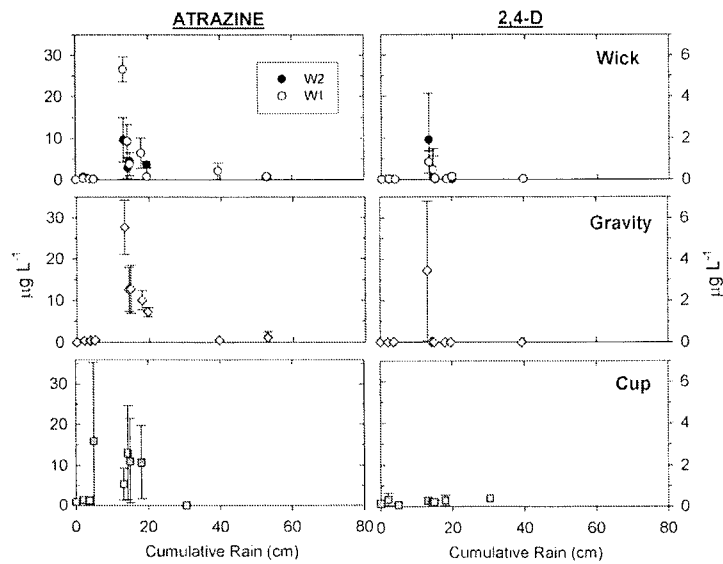
Fig. 4. Arkport site chloride breakthrough curves: chloride concentrations (mM) as a function of cumulative rain (irrigation plus natural rainfall). Plot in upper right shows date (2002) vs. cumulative rain.
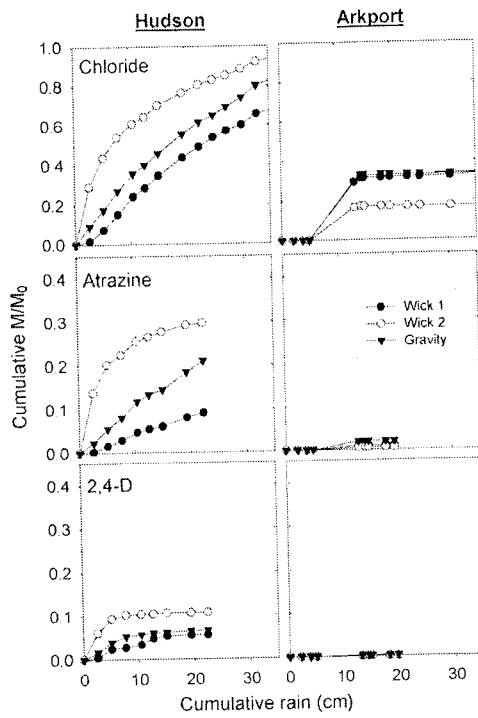
Fig. 5. Hudson site herbicide breakthrough curves: atrazine and 2,4-D concentrations (μg L^{-1}) as a function of cumulative rain (irrigation plus natural rainfall).

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Fig. 6. Arkport site herbicide breakthrough curves: atrazine and 2,4-D concentrations (μg L^{-1}) as a function of cumulative rain (irrigation plus natural rainfall).

Fig. 7. Relative cumulative mass of chloride, atrazine and 2,4-D leached and collected (expressed as M/M_0) for various samplers as a function of cumulative rain (irrigation and natural rainfall).

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