

Hydrologic flowpaths influence inorganic and organic nutrient leaching in a forest soil

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Received: 29 November 2005 / Accepted: 24 May 2006 / Published online: 5 September 2006
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Abstract Hydrologic pathways through soil affect element leaching by determining the relative importance of biogeochemical processes such as sorption and decomposition. We used stable hydrogen isotopes of water (δD) to examine the influence of flowpaths on soil solution chemistry in a mature spruce–hemlock forest in coastal Oregon, USA. Soil solutions (50 cm depth, $n = 13$) were collected monthly for 1 year and analyzed for δD , major ions and dissolved organic carbon (DOC) and nitrogen (DON). We propose that the variability of δD can be used as an index of flowpath length and contact time. Throughfall variability in δD was much greater than soil solution variability, illustrating that soil solution integrates the variation in inputs. Lysimeters with greater variation in δD presumably have a greater proportion of flow through rapid flowpaths such as macropores. The variation in soil solution δD

for individual lysimeters explained up to 53% of the variation in soil solution chemistry, and suggests that flowpaths influence leaching of some constituents. Soil solutions from lysimeters with greater δD variation had higher DOC and DON ($r^2 = 0.51$ and 0.37 , respectively), perhaps because transport via macropores reduces interaction of DOM with the soil matrix. In contrast, nitrate concentrations were highest in lysimeters with a small variation in δD , where long contact time and low DOC concentrations may yield higher net nitrification. Our results demonstrate the utility of stable isotopes to link flowpaths and soil solution chemistry, and illustrate how the spatial complexity of soils can influence ecosystem-level nutrient losses.

Keywords Soil solution · Throughfall · Dissolved organic nitrogen · Dissolved organic carbon · Nitrate · Cations · Hydrogen isotopes · Lysimeters · Flowpaths · Contact time

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Introduction

Soil solution chemistry can be quite variable over space and time (Avila et al. 1995), and this variability can be attributed to patterns in element inputs to the soil surface, hydrological flowpaths, and biogeochemical processing along those flowpaths. Conceptual models suggest that hydrologic

factors are as important as geochemical factors that affect nutrient leaching in forest soils (Qualls 2000), but few studies address the importance of flowpaths for biogeochemistry. In the past, it has been difficult to study interactions between hydrology and biogeochemistry due to methodological limitations in following water movement through the complex soil environment. Recent studies have used dye, chemical and isotopic tracers to characterize soil water movement. Hagedorn et al. (1999) characterized preferential flow paths in soil using a high density of very small lysimeters in combination with dye and chemical tracers that allowed them to compare the chemistry of soil solutions in rapid versus slow flowpaths. Their work suggested that flow paths are coated with C- and N-rich biofilms that have higher rates of N mineralization than the soil matrix.

Stable isotopes of water (δD and $\delta^{18}\text{O}$) also are useful tracers to detect the flowpath and ages of water in soil (Stewart and McDonnell 1991; Asano et al. 2002) and represent an advantage to other tracers that could influence, or be influenced by, soil biogeochemistry. The variation of water isotopes in soil solution across time and space may provide insights into hydrologic flowpath characteristics. Individual rain events can vary tremendously in $\delta^{18}\text{O}$ and δD over time because of storm tracks and weather patterns, but this variation is dampened in soil solution over time (Stewart and McDonnell 1991). The dampening occurs through mixing of throughfall with pre-existing soil water during infiltration to the sampling location within the soil. Previous studies have used this dampening to determine flowpaths and contact times of water in soil (Stewart and McDonnell 1991; Lindstrom and Rodhe 1992; Asano et al. 2002). Although temporal patterns indicate mixing of the water isotopes in lysimeter solutions, spatial patterns, represented by differences among lysimeters, could provide insight into flowpath characteristics.

Our study evaluates heterogeneous water movement in forest soil using natural abundance isotopes of water, to examine the effect of flowpath length and contact times on concentrations and fluxes of nutrients in soil solution. We examined the variability in the hydrogen isotope

ratios of the water in soil solutions, to create an index of flowpath length and contact time for these solutions. We propose that the variability in isotopes for each lysimeter is inversely related to flowpath length and soil contact time. Using this index of flowpath length, we focus on the effect of heterogeneous water movement on transport of DOC and DON, NO_3^- , cations and silica in soil solution.

Methods

Site description

This study was conducted in a mature sitka spruce–western hemlock (*Picea sitchensis*–*Tsuga heterophylla*) forest along the Oregon Coast. The study area is in Cascade Head Experimental Forest, part of the Siuslaw National Forest (45°02′50″ N, 123°54′21″ W), approximately 2 km north of Otis, OR, USA, and 7 km from the Pacific Ocean. Elevation is 210 m above sea level, and the mean annual temperature is 10°C. Mean annual bulk precipitation is 2,500 mm, most of which falls as rain between October and June (US EPA, unpublished data). The slope is approximately 12%. These forests are in the sitka spruce zone of Franklin and Dyrness (1988), a highly productive, coastal zone generally a few kilometers in width. The stand is dominated by sitka spruce, western hemlock and scattered Douglas-fir (*Pseudotsuga menziesii*), originating after the stand-replacing Nestucca fire of the mid-1800s (Harcombe et al. 1990; Greene et al. 1992). Soil is classified as the Tolovana soil series (USDA 1997), isomesic Typic Fulvudands formed in colluvium from sandstone. These are deep, well-drained soils with a loam texture at the surface.

Precipitation and soil solution sampling

We collected bulk precipitation in a large canopy opening approximately 2 km from the study site, at Cascade Head Experimental Forest research station. Bulk throughfall collectors were placed at seven locations within the 100 m radius area of our lysimeter plots. Collectors consisted of a funnel with glass wool in the neck to prevent

contamination and reduce evaporation, connected to a collecting bottle via tygon tubing. Precipitation and throughfall were collected every 2 weeks from October 2002 to December 2003.

We installed 19 tension lysimeters at 50 cm soil depth during fall 2001. The lysimeters (super quartz lysimeters; pore size 2 μm , dimensions 21 \times 95 mm; Prenart Equipment ApS, Denmark) were installed from an approximately 45° angle by driving a solid steel rod into the ground, then inserting the lysimeters at 50 cm depth from the soil surface after removing the steel rod. This method avoids creating and backfilling a large hole, and also means that the soil above the lysimeter is undisturbed. A small amount of silica flour slurry was used to ensure contact with the surrounding soil. Solutions were collected once per month from October 2001 to December 2002, using acid-washed bottles for each sample period. A 15 mm Hg vacuum was placed on the lysimeters, and the resulting solution collected after 3 days. Soil solutions collected from January to December 2002 were used for the analysis, after an initial adjustment period. We did not sample during the dry summer months of August and September.

Chemical and isotope analyses

Lysimeter solutions were analyzed chemically and for hydrogen isotopes as described below. Throughfall samples were analyzed only for volume and isotopes, in order to compare with the soil solution data. Lysimeter solutions were filtered in the lab within 24 h of collection (0.25 μm polycarbonate membrane; Whatman Inc., Newton, MA, USA) and analyzed for NH_4^+ , NO_3^- , PO_4^{3-} and SiO_2 using automated colorimetric continuous flow autoanalyzer (US EPA 1983; Lachat Instruments, Milwaukee, WI, USA). Total dissolved N was determined using persulfate digestion followed by automated colorimetric analysis for NO_3^- as described above (US EPA 1983). We calculated DON as total dissolved N minus NO_3^- -N and ammonium. Samples were re-analyzed if DON was negative by $>0.005 \text{ mg N l}^{-1}$; if DON was negative by $<0.005 \text{ mg N l}^{-1}$, the value was set to zero. DOC was determined

by automated UV-persulfate oxidation followed by infrared spectrophotometry (US EPA 1987; Dohrmann TOC analyzer, Teledyne Tekmar, Mason OH). Dissolved major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were determined in HNO_3 acidified aliquots using flame atomic absorption spectrophotometry (US EPA 1987; Perkin–Elmer Instruments, Norwalk, CT, USA). Concentrations of Cl^- and SO_4^{2-} were determined by ion chromatography (US EPA 1987; Dionex Corporation, Sunnyvale, CA).

Filtered lysimeter and throughfall samples were analyzed for hydrogen isotope ratios after storage at 4°C in air-tight HDPE bottles. Tests indicated that neither filtering nor storage affected sample δD . Isotope ratios of hydrogen (δD) were determined at EPA's Integrated Stable Isotope Research Facility (ISIRF) by Finnigan MAT Delta Plus XL Isotope Ratio Mass Spectrometer using high temperature conversion elemental analyzer (TC/EA) on the front end (Thermo Electron Corporation, Waltham, MA). Duplicate analyses of each sample were used to produce the δD relative to the Vienna standard mean ocean water (VSMOW). Repeated analyses of the same laboratory reverse osmosis water across 11 runs gave a mean and standard deviation of -65.98 ± 1.35 for δD .

For some sample dates and lysimeters, the volume of sample collected was not sufficient to conduct all analyses. Stable isotope analyses were conducted for 13 of the 19 lysimeters, using samples collected on January, March, April, June, November and December in 2002. For consistent comparison of the chemical and isotope patterns in soil solutions, we use data only from these 13 lysimeters.

Calculations and statistical analyses

In order to determine whether lysimeter properties varied more with time than across space, we calculated integrated measures of both spatial and temporal variation for the soil solution chemistry, isotopes and volume. Spatial variation was determined by first calculating the coefficient of variation (CV) among lysimeters for each sample time period. The CV for each time period represents spatial variation, which was then

averaged across all time periods to produce an integrated measure of spatial variation in the solution properties. Temporal variation was determined by first calculating the CV of all solutions collected by an individual lysimeter. The CV for an individual lysimeter represents temporal variation; CVs for each lysimeter were then averaged to produce the integrated temporal variation of soil solution properties. These CVs were then compared for each property, in order to determine whether each constituent was more variable over space or over time. Calculations and linear regressions of relationships between soil solution properties were conducted using Microsoft Office Excel 2003.

We used two approaches to calculate element fluxes, in order to account for the possible effects of preferential flowpaths. Precipitation volume was measured using a tipping bucket rain gauge from an open site at the Cascade Head Experimental Forest headquarters, approximately 2 km southeast of the lysimeter plots (US EPA, unpublished data). We used stream data from nearby Toketa Creek (<0.5 km from lysimeters) to estimate water fluxes from the soil. In the year 2000, precipitation was 1,252 mm and runoff was 1,132 mm at Toketa Creek (Compton et al. 2003), yielding an annual evapotranspiration (ET) loss of 120 mm. This year had very low rainfall (nearly half the mean of 2,500 mm), and 90% of precipitation came as runoff. Both precipitation and ET appear to be variable from year to year for a given site in this region, in contrast to the relatively constant ET found by Bormann and Likens (1994) for Hubbard Brook, New Hampshire. In the Olympic peninsula of Washington, runoff varied from 54% to 89% of precipitation (mean = 78%), and ET spanned a 4-fold range from 36 mm to 150 mm (Edmonds et al. 1998). We consider the Olympic climate to be more representative of our near-coastal site than the Oregon Cascades HJ Andrews site, where runoff is 70% of precipitation (Sollins et al. 1980). In order to calculate soil solution fluxes in 2002, we use 78% of the precipitation amount in 2002 to calculate runoff. We assume that little evapotranspiration occurs between 50 cm and the stream, such that the estimated runoff is approximately equivalent to leaching from 50 cm depth.

We calculated soil solute fluxes per unit area in two ways: (1) the arithmetic average concentration of all lysimeters multiplied by the runoff value, and (2) the volume-weighted averages multiplied by the runoff value, which takes into account the rate of water movement past each lysimeter. In the second approach, lysimeters with greater water flux will have more influence on the total rate of solute loss. We were unable to calculate a true variance for these flux estimates, since there is no error associated with the value for runoff in 2002 as calculated. Precipitation in coastal Washington varied from 1,750 to 3,470 in an 8-year record (Edmonds et al. 1998), and thus our fluxes could vary by 100% from year to year.

Results

Isotope ratios in throughfall and soil solutions

The δD of throughfall was more variable than soil solution δD over time when the record overlaps (Fig. 1). Mean δD in throughfall decreased from -32.8 to -84.7 from November 2002 to January 2003; the mean δD in soil solution decreased only slightly from -46.7 to -53.2 during this same period (Fig. 1b). This variation in soil solution

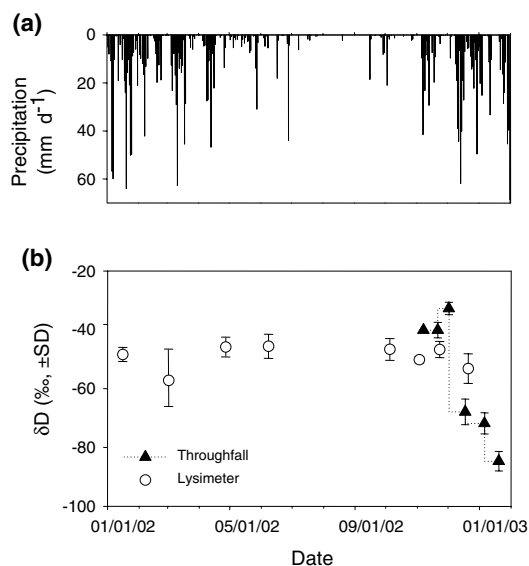


Fig. 1 Precipitation rate (a) and δD in throughfall and soil solution (b) over time

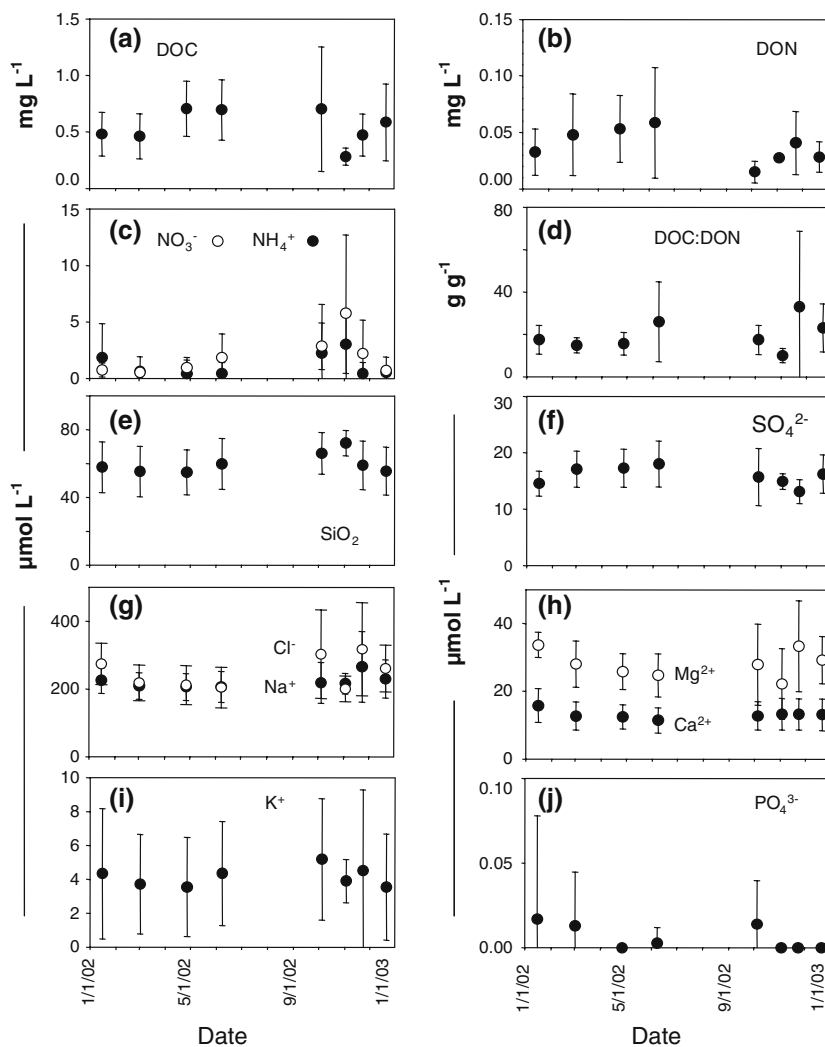
was only 23% of throughfall variation during the same time period. The highest δD value in lysimeter solution we measured was in October (mean -46.7) and the lowest in February (mean -57.2), revealing a weak seasonal pattern.

Soil solution was generally more variable over space than throughfall. Standard deviation of δD of throughfall on each sampling date ranged from 2.1 to 4.3 ($n = 7$), whereas the standard deviation of lysimeter solutions ranged from 2.4 to 8.1 (calculated from dates with $n > 7$ measurements). In addition, the standard deviation (SD) of each lysimeter δD during the observed period varied widely (± 1.1 to 10.9), which illustrates that some lysimeters have nearly constant δD and others are much more variable.

Temporal and spatial patterns in soil solution chemistry

Some solute concentrations were strongly variable over space and time, while others were more constant (Figs. 2, 3). These patterns provide insight into the biogeochemical processes operating along these flowpaths. Important plant nutrients such as NO_3^- , ammonium and phosphate had low concentrations that tended to be more variable with space and time (CVs $\geq 100\%$). Concentrations of ammonium and NO_3^- increased with the onset of fall rains (Fig. 2). Silica, Cl^- and SO_4^{2-} were less variable (CVs $< 50\%$). Dissolved organic C and N were intermediate in terms of spatial and temporal

Fig. 2 Mean solute concentrations in soil solutions over time (\pm SD)



variability (CVs = 50–100%). The relationship of Na^+ to Cl^- concentrations varied slightly over the year; higher ratios in the spring and summer indicate a biotic influence. Silica and SO_4^{2-} concentrations were relatively constant over time. Potassium concentrations were constant over time, but highly variable among lysimeters.

Soil solution chemistry was consistently more variable in space than over time, since mean CV by site was greater than mean CV by time, except for ammonium (Fig. 3). This is somewhat surprising, given the strong seasonality of rainfall in this region. Spatial patterns appear to have a larger imprint on soil solution chemistry and leaching losses than seasonal patterns.

Effect of flowpath on solute concentration in soil solution

To examine how flowpaths influenced soil solution chemistry, we plotted the mean solute concentrations of each lysimeter across all time periods against the SD of δD (Fig. 4). This variation in δD is our proposed index of flowpath length and contact or residence time. We propose that when the flowpath of water to a lysimeter is dominated by more preferential type flow (i.e., mean flow path length and mean contact time is short), then the δD of this lysimeter solution is more closely related to precipitation input and thus would be more variable over time. In contrast, when the flow-

path of water is dominated by more matrix type flow (i.e., mean flow path length and contact time is long), then the δD of this lysimeter is more dampened and constant over time. The temporal variation of δD then appears to be inversely related to the mean flow path length and contact time with soil.

An inverse relationship between the SD of δD and the volume of water collected for each lysimeter ($r^2 = 0.28$, $P < 0.1$; data not shown) indicates that lysimeters with long flowpaths retain and supply water at a more consistent rate. The variability in δD only explains 28% of the relationship, and thus other factors must play a role as well. The relationship might be influenced by our sampling approach; we would expect a different relationship if more samples were collected during rainstorms, during which time we would expect more water movement through rapid flowpaths. The significant relationship between the SD of δD and lysimeter water volume also supports the above proposal that variation in δD can be an index to characterize the hydrologic flowpath for each lysimeter.

The index of flowpath length (SD of δD) provides insight into soil biogeochemical processes influencing soil solution chemistry. Mean DOC, DON and SO_4^{2-} concentrations increased significantly with SD of δD , while SiO_2 and NO_3^- concentration decreased with increase in SD of δD (Fig. 4). Thus flowpath characteristics appear to affect the spatial variation of those solutes. In contrast, concentrations of other constituents (Cl^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ and PO_4^{3-}) were independent of the variation of δD , indicating that flowpaths have little influence on the concentrations of those solutes.

Discussion

Variation in δD of soil solutions: a proxy for flowpath length?

Temporal variation of δD in soil solution was much smaller than variation in throughfall (Fig. 1), which illustrates that mixing with soil water reduces temporal variation (Stewart and

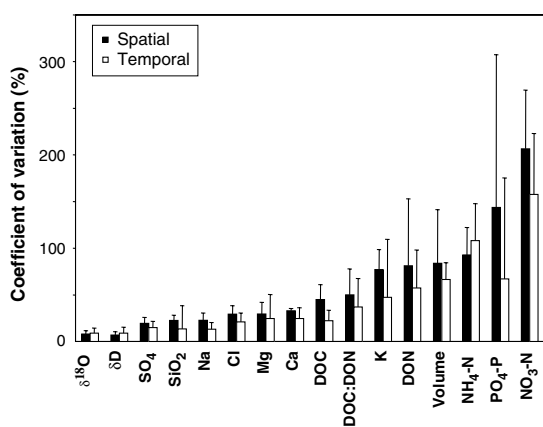
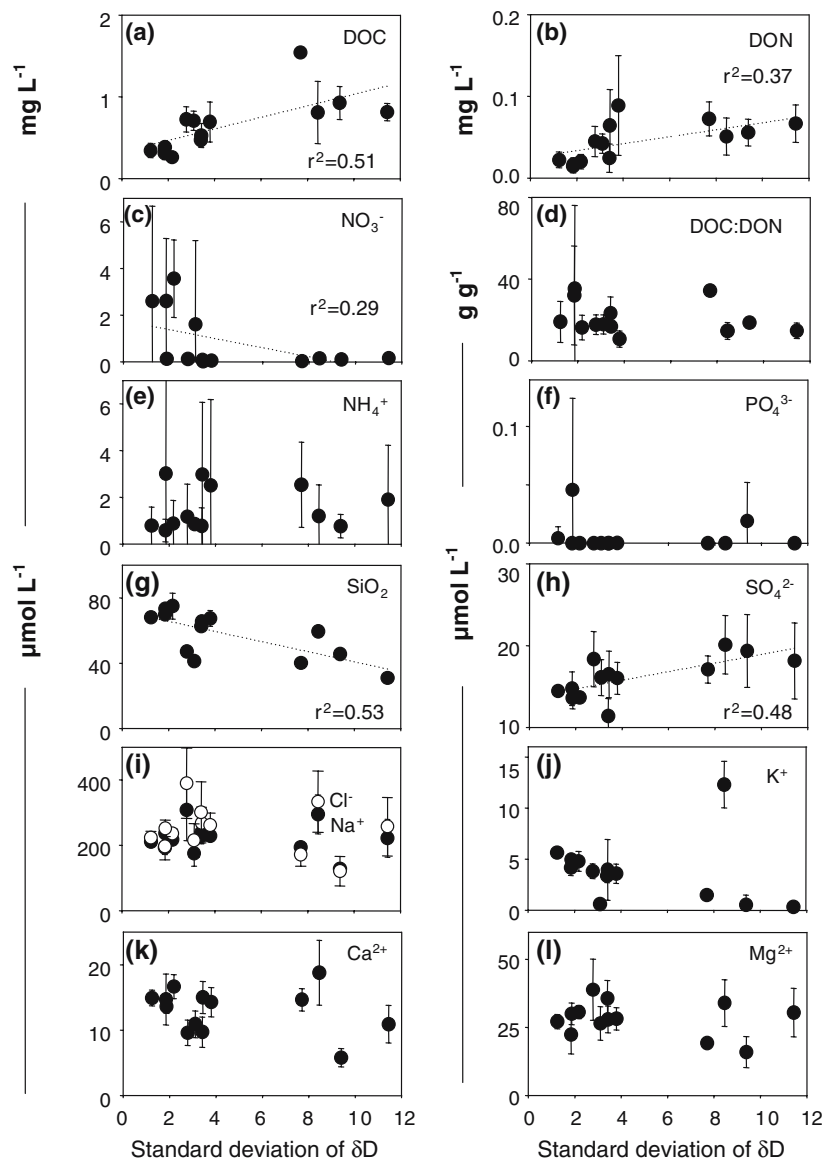


Fig. 3 Mean coefficient of variation of lysimeter solution concentrations, oriented from low to high spatial variation

Fig. 4 Relationship between SD of δD and mean solute concentrations. Significant linear regressions are shown ($P < 0.10$). Error bars are SD of concentrations



McDonnell 1991; Lindstrom and Rodhe 1992; Asano et al. 2002). Spatial differences also provide information about flowpath characteristics of individual lysimeters. We found slightly greater spatial variability of δD in lysimeter solutions than in throughfall (Fig. 1b), opposing the expectation that variation in isotope signal in throughfall should decline in soil solution due to mixing with pre-existing soil water during infiltration. We suggest that the large spatial variation in lysimeter δD is derived not from variability in

throughfall inputs, but rather from variations in flowpath to each lysimeter.

The variation of δD in soil solution provides insight into the characteristics of hydrologic flowpaths, and we use this measure as an index of flowpath length and contact time (Fig. 4). Hagedorn and Bundt (2002) demonstrated that preferential flow paths in a structured forest soil are persistent for decades. Therefore we propose that the SD of δD in soil solution could serve as an index of long-term mean flowpath length and

contact times of water. The variation in δD can also provide insights into element leaching, since it explained up to 53% of the variation in the solute concentrations. Flowpaths clearly influence some solutes but are less important for others; in addition, the nature of the relationship between the variation in δD and the solute concentrations (Fig. 4) can provide insights into the behavior of these constituents. These insights are developed in the following sections.

Solutes that decrease with flowpath length:
DOC, DON and sulfate

Dissolved organic matter (DOM) increases in concentration as water moves through the vegetation canopy and organic horizon, then disappears from soil solution during infiltration into deeper layers via mechanisms such as adsorption, decomposition and precipitation (Aitkenhead-Peterson et al. 2003). Sources of DOM in forests include precipitation, throughfall, root exudates, microbial byproducts, and litter and soil organic matter. Qualls (2000) proposed that hydrological and geochemical soil factors determine the rate and extent of DOM adsorption. Our work illustrates the influence of hydrologic flowpaths on soil solution DOM concentrations. The positive relationship we observed between SD of δD and DOC and δD and DON (Fig. 4) indicates that for long contact times and flowpath lengths, dissolved organic matter has more opportunity to be removed from soil solution by microbial activity and sorption. Hydrologic losses of DON through rapid flowpaths are thought to contribute to biologically “uncontrollable” losses of N from N-limited forests (Perakis 2002).

The C:N ratio is used as an index of soil organic matter for microbial activity, and this perspective could also apply to the C:N of DOM. Although DOM concentrations decreased in longer flowpaths, the ratio of DOC:DON was not influenced by flowpath length and contact time over the time scale of our study (Fig. 4d). There was a clear positive relationship between DOC and DON for each lysimeter ($y = 0.059x + 0.0018$, $r^2 = 0.50$, $P < 0.001$). In addition, the C:N could provide insights into the relative sorption of DOC versus DON along flowpaths. The ratio of DOC:DON

has been shown to decrease as soil solution moves through the profile, since N concentrations are higher in hydrophilic DOM whereas hydrophobic components of DOM are sorbed preferentially (Kaiser and Zech 1998). Results for individual sites have suggested a decline in DOC:DON ratios with soil depth (Qualls and Haines 1991), yet two reviews have shown no pattern of DOC:DON ratios with depth across a wide range of sites (Michalzik et al. 2001; Aitkenhead-Peterson et al. 2003). Our findings suggest that adsorption does not preferentially remove DOC from soil solution as DOM moved through the soil profile since flowpath length did not influence DOC:DON. Flowpaths could still influence the quality of DOM transported through the soil. Litter leachate may be more bioavailable than mineral soil DOM (Cleveland et al. 2004), and thus surface DOC with a high proportion of bioavailable DOM may bypass deeper soils through rapid flowpaths.

Sulfate is strongly influenced by both geochemical and biotic processes, regulated by interactions with soil minerals, microbes and vegetation in forest ecosystems (e.g., Johnson and Lindberg 1992; Likens et al. 2002). Similar to the behavior of DOM, SO_4^{2-} concentrations decreased with contact times and flowpath lengths. This positive relationship between SO_4^{2-} and the SD of δD indicates that SO_4^{2-} in solution had more opportunity to be sorbed to soils and/or incorporated by organisms for the lysimeter solution with longer flowpath length and contact times. These soils are classified as Inceptisols with andic properties (USDA 1997), and thus have strong phosphate and sulfate sorption potential. Considering the importance of sorption in sulfate dynamics (Sollins et al. 1988), it is very likely that longer flowpaths allow for more contact time and increase the proportion of sulfate sorbed to soils.

Solutes that increase with flowpath length:
silica, nitrate

Silica in soil solution is derived from dissolution of primary and secondary minerals (White 1995) and biogenic sources such as phytoliths (Derry et al. 2005). Therefore, geochemical equilibrium and

hydrologic transport can influence SiO_2 concentrations in soil solution (Stonestrom et al. 1998; Gerard et al. 2002). It has been difficult, however, to separate the influence of those two factors. Mean dissolved SiO_2 concentrations increase with flowpath length and soil contact time (Fig. 4g), although the SD of SiO_2 concentrations for individual lysimeters was relatively small (Fig. 4). This indicates that SiO_2 concentrations of each lysimeter are constant throughout the observation period, which spans large variations in precipitation inputs and presumably water contact time. This constancy suggests that SiO_2 concentrations are specific to individual lysimeters across the year, independent of presumed differences in contact time. We cannot discount, however, the possibility that this temporal constancy may be influenced by our use of SiO_2 flour to promote soil contact when we installed the lysimeters.

If contact time is not the explanation for higher SiO_2 concentrations for long contact lysimeters, our results then suggest that SiO_2 concentrations depend on the contacting mineralogy and biogeochemical processes along the flowpath to the lysimeter. This supports previous work showing that contact times have only a small effect on the determination of SiO_2 concentration in soil solution (e.g., Kennedy 1971; Asano et al. 2003). It is possible that lysimeters with a small SD of δD collect solutions that pass through the mineral soil matrix with high SiO_2 availability, whereas lysimeters with more variable δD may collect soil solution that passes through the forest floor and then through preferential flowpaths that historically have flushed more water and thus are depleted in SiO_2 . Preferential flowpaths can have organic matter coatings (Bundt et al. 2001) that would prevent SiO_2 dissolution, and thus solutions passing through preferential flowpaths then might be expected to have lower SiO_2 concentrations.

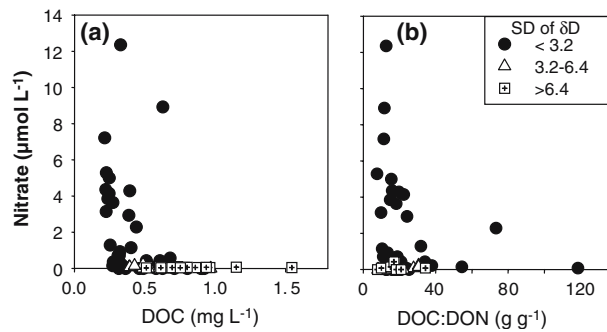
Our data provide insights into hydrologic and biogeochemical mechanisms related to nitrate retention. Nitrogen is a fundamental but limiting nutrient in temperate forests (Vitousek and Howarth 1991). Nitrogen leaching overall was quite low in these forests, especially in comparison to nearby alder and mixed conifer-alder

stands (Binkley et al. 1992). Effective use of nitrogen generally results in very low rates of NO_3^- loss in undisturbed temperate forests with low N status, and the predominant form of N loss is as DON (Hedin et al. 1995). DON also dominated lysimeter N losses for this mature spruce forest with low N leaching and deposition, as observed for other mature conifer forests in the Pacific Northwest (Sollins et al. 1980). Nitrate was detected only in lysimeters with SD of δD less than 3.2 (Fig. 4c), suggesting that longer flowpaths and contact time increase NO_3^- mobility. This is in contrast to DON concentrations, which were inversely related to apparent flowpath length. Our work reinforces the idea that DON and NO_3^- losses are controlled by different mechanisms (Hedin et al. 1995).

Differences in flowpaths and DOM availability could explain the increase in NO_3^- concentrations with contact time and flowpath length. Nitrate concentrations were affected by quantity (DOC concentration) and composition (DOC to DON ratio) of dissolved organic matter (Fig. 5). Low DOC concentrations were associated with longer flowpath and contact time. The inverse relationship between DOC or DOC:DON and NO_3^- concentrations in soil solutions could be related to microbial activity and/or hydrologic flowpaths. The lysimeters with longer flowpaths had lower DOC and higher NO_3^- concentrations (Figure 5a). Although the majority of soil solution DOC is not biodegradable (Qualls and Haines 1992; Yano et al. 2000), some DOC can be a substrate for microbial growth (Meyer et al. 1987). Lower DOC concentrations in long flowpaths then could yield less immobilization and thus higher NO_3^- concentrations. Hart et al. (1994) showed that NO_3^- took some time to build up in soil microcosms, and demonstrated the importance of immobilization in controlling net NO_3^- production. In addition, flowpaths may have increased microbial activity and immobilization since they have higher soil carbon than the surrounding matrix (Bundt et al. 2001). At fine spatial scales, similar mechanisms may explain the positive relationship between contact time and NO_3^- leaching we observed in soil solution.

Our work also supports previous work suggesting that the C:N ratio of DOM influences

Fig. 5 Soil solution nitrate concentration as a function of the concentration of DOC (a) and the ratio of DOC:DON (b). Points are classified by the SD of δD



NO_3^- loss (Goodale et al. 2000). Although our work cannot elucidate the mechanisms to explain the influence of DOM on NO_3^- , it does demonstrate that hydrologic flowpaths influence this interaction (Fig. 5b).

Solutes that are independent of δD variation:
chloride and cations

Solute concentrations not influenced by δD variation likely are controlled by factors other than flowpath characteristics. The relationship between variation of δD and concentrations of Cl^- , Na^+ , Ca^{2+} and Mg^{2+} in soil solution indicated that the direct effect of flowpath on these solutes was small (Fig. 4i, k, l). With the exception of one lysimeter, there was an inverse relationship between the SD of δD and K^+ concentration (Fig. 4j), indicating that potassium concentrations increase with flowpath length and contact time, similar to SiO_2 . Both K^+ and SiO_2 appear to have an important weathering component.

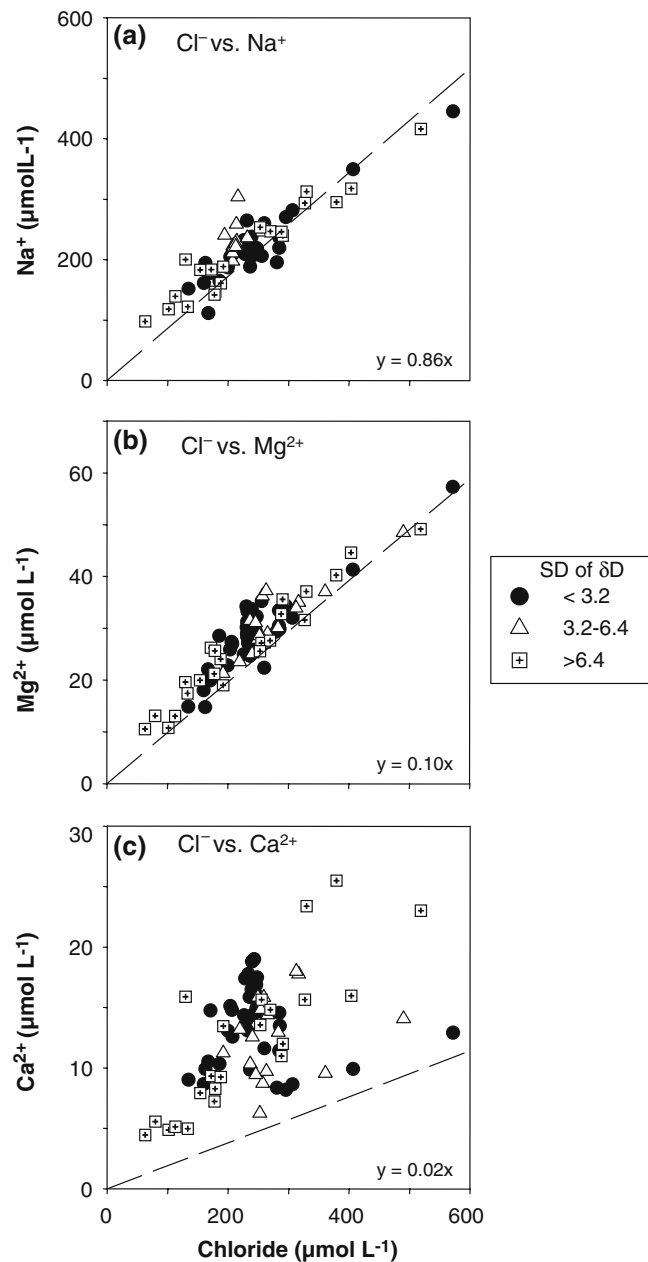
We use the sea salt ratios as a basis for deciding whether variation of Cl, Na, Ca and Mg concentrations are derived from the variation in atmospheric input, because in this near-coastal site, sea salt appears to influence nutrient leaching from catchments (Compton et al. 2003). Figure 6a shows the clear relationship between Na^+ and Cl^- concentrations, and the slopes of this relationship (0.88 and 0.89 for different flowpaths) were similar to seawater (0.86; Holland 1978). A similar relationship was also observed for Mg^{2+} and Cl^- (Fig. 6b, Table 1). Atmospheric input is the

dominant source of Cl, Na and Mg in lysimeter solutions, derived from sea salt.

Weathering inputs appear to be more important for Ca than for Na and Mg. A significant positive relationship between Ca^{2+} and Cl^- was observed only for lysimeters with the largest SD of δD (Fig. 6c). However, the slope of this relationship (0.05) was 2.5 times greater than that of sea water Ca to Cl ratios (0.02, Table 1). Further, Ca^{2+} to Cl^- ratios in soil solutions were much higher than the ratio in sea water, implying that Ca was not only derived from sea salt but also from other sources such as mineral weathering in the soil. The importance of non-sea salt Ca also was noted in near coastal areas in this basin, where sea salt contributions to streamwater Na, Mg and potassium were high (85, 55 and 45%, respectively), but were very low for Ca (<10%; Compton et al. 2003).

Our results differ from Burns et al. (1998), who demonstrated that base cation concentration is significantly lower in pipeflow than in matrix flow from their trench study at Panola Mountain Research Watershed in Georgia, USA. They suggested that variation in base cation concentrations of ephemeral subsurface flow across the trench face was inversely related to flushing frequency, that is, flowpaths that pass greater volumes of water result in the leaching of a greater mass of base cations, and lower base cation concentrations. The explanation for our contrasting results is likely that since the near coastal area studied here receives high sea salt inputs, the effect of flowpaths on most cations

Fig. 6 Relationships between chloride and sodium, magnesium and calcium concentrations. Dashed lines represent sea salt ratios



may be small. In areas receiving lower cation deposition, flowpaths may play a more important role.

Flowpath influences on solute leaching fluxes

Including information about preferential flow had a small effect on the areal rates of solute leaching

(Table 2). We conducted volume-weighting over space (considering the differences in volume of individual lysimeters), and volume-weighting over time (considering the big differences in water flux over the course of the year). The SD of δD is marginally related to the average volume of collected soil solution ($P < 0.1$), which indicates that lysimeters that collected more water had

Table 1 Regression analyses for Na⁺, Mg²⁺ and Ca²⁺ versus Cl⁻ concentrations in soil solution

	SD of δD (‰)	m	r^2	P	n
Cl ⁻ to Na ⁺	<3.2	0.89	0.99	<0.001	40
	3.2–6.4	0.88	1.00	<0.001	16
	>6.4	0.88	0.98	<0.001	21
Cl ⁻ to Mg ²⁺	<3.2	0.12	0.96	<0.001	39
	3.2–6.4	0.11	0.99	<0.001	17
	>6.4	0.11	0.98	<0.001	22
Cl ⁻ to Ca ²⁺	<3.2	0.05	0.87	0.8	39
	3.2–6.4	0.04	0.91	0.4	17
	>6.4	0.05	0.94	<0.001	22

$C = m[\text{Cl}]$ where C is Na⁺, Mg²⁺ or Ca²⁺ concentration and $[\text{Cl}]$ is Cl⁻ concentration in $\mu\text{mol l}^{-1}$ and m is the fitted slope

longer flowpaths and presumably more constant delivery of water. Thus preferential flowpaths delivered less water during the time periods we sampled.

DOC and DON losses were 22% and 20% lower when we considered the differences in volume across the lysimeters. Since nitrate concentrations were higher and water volume collected was greater through slow flowpaths, nitrate-N losses were 36% higher with volume-weighting. We sampled at regular intervals, independent of the weather conditions, and assume that we captured roughly average conditions over 1 year for each lysimeter plot. The time period of sampling is important: for solutes influenced by flowpaths, continuous sampling likely would yield a different answer than sampling for a few days at a time during rain events or at regular intervals. Moreover, since lysimeters that collected little water or only very few samples were omitted from this analysis, we may not have captured average conditions over that area. Lysimeters that collected little water may sample more preferential flowpaths, such as animal burrows or large macropores, which would only transport water during storms. Since leaching of some solutes in soil solution varies by contact time and flow-path length, our findings indicate that estimates of solute fluxes using lysimeters could be refined by taking preferential flowpaths into account.

Table 2 Fluxes of inorganic and organic dissolved nutrients below 50 cm, calculated using different methods. Runoff was 1,590 mm, calculated as 78% of precipitation. VW = volume-weighting

	DOC (kg ha ⁻¹)	DON (kg ha ⁻¹)	TDN (kg ha ⁻¹)	NO ₃ -N (kg ha ⁻¹)	NH ₄ -N (kg ha ⁻¹)	PO ₄ -P (g ha ⁻¹)	Ca (kg ha ⁻¹)	Cl (kg ha ⁻¹)	K (kg ha ⁻¹)	Mg (kg ha ⁻¹)	Na (kg ha ⁻¹)	SiO ₂ (kg ha ⁻¹)	SO ₄ (kg ha ⁻¹)	
No VW	8.84	0.61	1.2	0.3	0.4	2.9	8.3	141	2.6	10.9	81.6	57.3	24.4	
VW over time	9.09	0.63	1.1	0.2	0.3	2.8	8.3	141	2.5	11.1	81.8	55.7	24.7	
VW over space	6.90	0.48	1.0	0.4	0.2	2.4	8.0	137	2.6	10.3	76.3	60.4	23.1	
VW over space & time	7.19	0.50	1.0	0.4	0.2	2.2	8.6	138	2.6	10.4	77.3	60.1	23.1	
Change between time only and space & time	-22%	-20%	-16%	36%	-52%	-16%	-4%	-3%	2%	-6%	-7%	5%	-5%	

Conclusions

This study used stable isotopes of water to examine the influence of heterogeneous water movement on variation in organic and inorganic constituents in soil solution. The results showed that the use of stable isotopes can link hydrological flowpaths and soil solution chemistry. The SD of δD for each lysimeter was inversely related to flowpath length and contact time of water, and thus can be used as an index of these properties. Spatial variation of DOC, DON, SO_4^{2-} , SiO_2 and NO_3^- concentrations were related to δD variation, indicating these solutes are directly affected by hydrologic flowpaths in soil. Concentrations of DOC and DON decreased as flowpath length increased, indicating that DOM transport occurs preferentially through rapid flowpaths. Nitrate showed the opposite trend, and the mechanism may involve contact time or interactions with DOC. Calcium concentrations were controlled indirectly by flowpath, with different mechanisms operating at long versus short flowpaths. In contrast, concentrations of Cl^- , Na^+ , Mg^{2+} , K^+ , NH_4^+ and PO_4^{3-} were independent of the variation of δD , indicating that flowpaths had little effect on those solutes. Consideration of variability in hydrologic flowpaths could improve flux estimates for those solutes influenced by contact time. Identifying the effect of flowpath helped interpret the soil solution chemistry, and provided insight into complex ecosystem processes such as DON and nitrate loss.

Acknowledgements A Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists allowed the first author to work in the United States. We thank Warren Evans, Toni Hoymann and Gail Heine for field assistance, and the Willamette Research Station staff for water chemistry analyses. Jacqueline Aitkenhead-Peterson and two anonymous reviewers provided many valuable suggestions for improving this paper. Renée Brooks, William Griffis and Warren Evans conducted the stable isotope analyses. We also thank Taro Uchida and Steven Perakis for valuable discussions. The U.S. Forest Service Pacific Northwest Research Station provided field site access. Climate data were provided by the Western Ecology Division, Office of Research and Development, National Health and Environmental Effects Research Laboratory, United States Environmental Protection Agency. The information in this article has been funded by the U.S. Environmental Protection Agency and approved for publication as an EPA document.

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