Hydrological controls on chemical export from an undisturbed old-growth Chilean forest

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Abstract

Stream water chemical concentrations from an undisturbed, temperate, old-growth Chilean forest were analyzed to gain insights into hydrological controls on watershed-scale losses of different nutrients and chemical elements. Our goal was to understand how hydrological and biogeochemical processes interact to control patterns of export of dissolved chemicals from these types of forested watersheds. The study is unique in that the monitored watershed lies in a part of the world that receives very little anthropogenic influence and this is the first study of its type in this part of the world. A small, densely forested, montane watershed was continuously monitored for stream discharge and precipitation and was sampled biweekly for stream-, precipitation-, and soil-water chemistry. Three different forms of hydrological controls were used to describe how concentrations of different elements changed as a function of increased stream water discharge: *dilution* of elements due to decreased relative contributions by baseflow sources, increased concentration due to *enhanced hydrological access* to elements in to shallow soil horizons, and no net effect, i.e. *hydrologically constant*. A hyperbolic relationship was used to describe element concentration as a function of stream discharge to quantify the variations for major ions, cations, and organic forms of nutrients. In general, this hydro-biogeochemical system showed the most distinct dilution and enhanced hydrological access for chemicals with large concentration differences between deep and shallow soil water. Deep soil water sources were most distinct for Ca^{2+} and Si, both of which demonstrated dilution. In contrast, variations in H^+ concentrations resembled enhanced hydrological access indicating shallow soil sources, coupled with the consumption of acidity by weathering or cation exchange in deeper soil layers. Rainwater sometimes enhanced and sometimes tempered the observed trends. Potassium was the least hydrologically variable element (hydrologically constant) in this study, possibly due to strong biological mechanisms internal to the watershed. The approach used here is a simple method to identify the importance of hydrologic variations in controlling streamwater chemistry relative to internal biogeochemical sources and processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The link between streamwater chemistry and hydrology has historically been used to understand how different sources and mechanisms control the export of nutrients and chemicals at the watershed scale (Zesker, 1963; Voronokov, 1963; Toler, 1965; Knuckle, 1965; Johnson et al., 1969; Newbury et al., 1969; Pinder and Jones, 1969; Sklash et al., 1976;

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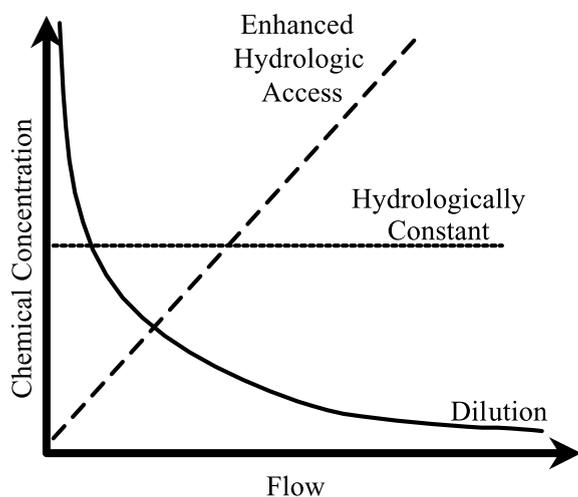 *E-mail address:* mtw5@cornell.edu (M.T. Walter).

Fig. 1. Schematic of chemical responses to hydrological controls for the study system. Concentration decreases hyperbolically with increasing flow for dilution control, remains constant for hydrologically constant control, and will increase under enhanced hydrologic contact; note: the shape of the enhanced hydrologic contact control curve is uncertain.

Pilgrim et al., 1979; Kennedy et al., 1986; DeWalle et al., 1988; Christophersen et al., 1990; Hill, 1990; Hooper et al., 1990; Eshleman et al., 1993; Ogunkoya and Jenkins, 1993; Cassie et al., 1996; Elsenbeer and Lack, 1996). Such studies have developed insights into processes such as anthropogenic deposition of mineral acids (Peters and Driscoll, 1986; Schnabel et al., 1993), cation exchange in upper soil horizons, weathering release of elements (Johnson et al., 1969), and production of organic forms of chemicals within soils (Boyer et al., 1996,1997). However, many of these studies were conducted in watersheds subject to strong human effects on soil and surface water chemistry, either from atmospheric deposition or from forest cutting and other land use effects.

The objective of this investigation was to identify and compare how hydrological variability influences the export of major dissolved elements in a small and unimpacted watershed in southern Chile. The hydrological controls were generalized and idealized for simple comparison among the different chemical constituents. One unique aspect of this project is that anthropogenic chemical inputs in the study watershed are among the lowest measured worldwide, and that the forest has not been subject to cutting or other major human disturbances (Hedin et al., 1995).

This means that the study offers an opportunity to understand the interactions of hydrological and biogeochemical processes without the bias of human perturbation. In addition, this type of investigation helps identify spatial and temporal regimes of particular biogeochemical variation and sensitivity.

2. Theoretical approach

The idealized approach used in this study allowed direct comparison of how different chemical elements varied as a function of hydrology. Hydrological controls on streamwater chemical concentrations were assumed to exhibit one of the three general trends with respect to stream discharge: *dilution*, *hydrologically constant*, or *enhanced hydrological access* (Fig. 1).

Dilution occurs whenever the net increase in water delivery to the stream is greater than the increase in chemical delivery. This type of relationship is expected for chemicals with a strong internal watershed source that does not increase in magnitude as a function of increased hydrologic throughput. Examples of this type of relationship include deep soil weathering, which can be an important source of Si or Ca^{2+} relative to the more dilute inputs that occur from the atmosphere. If the rate of weathering supply remains relatively unchanged during precipitation events, we expect these elements to be diluted by the enhanced throughput of water.

A balance between changes in water delivery and chemical delivery characterizes hydrologically constant controls. This relationship is expected for elements that are delivered with precipitation water to the watershed, but that lack significant internal production or consumption processes. In the strictest sense, such idealized hydrological constancy may be rare since evapotranspiration provides a mechanism for concentrating solutes in deeper soil waters, and thus may impart differences in the delivery of chemicals and water depending on soil water flow paths. Some form of constancy may also be expected for elements that are chemically buffered within soils (e.g. via cation exchange reactions), but only if rates of hydrologic throughput remain low enough to maintain some form of equilibrium between soils and soil solutions. This is not likely to occur in most natural
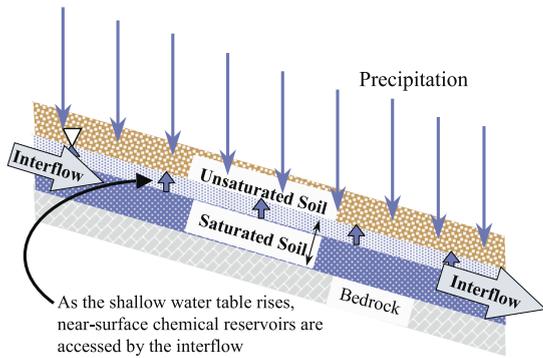
Fig. 2. Schematic of Enhanced hydrological access. The vadose zone transmits water at the precipitation rate resulting shallow, perched soil water. The shallow water table rises when rates of precipitation and up-slope interflow are greater than down-slope interflow. This, in turn, results in the saturated soil water coming in contact with chemicals residing in near-surface soil.

soils that experience variable hydrologic inputs over time.

Enhanced hydrological access refers to controls that exhibit increasing chemical concentration with increasing discharge. The most common enhanced hydrological access is for chemicals found in areas of a watershed that are only hydrologically active during periods of high flows. For example, in the case of elements produced in the surface soil horizons, as the region of subsurface flow deepens, i.e. as the saturated soil boundary approaches the soil surface, the flowing water increasingly accesses these elements (Fig. 2). In recent years, this hydrological process has often been referred to as 'piston flow'.

3. Study site

Our study site is located in southwestern Chile on the western slope of the Cordillera de Piuchue in Chiloe National Park (42°22′S, 74°03′W). The 1.2 ha, remote forested watershed ranges in elevation from 650 to 700 m above sea level (Zarin et al., 1998). The watershed's upland region is relatively flat moorland, which rapidly changes to steep slopes and dense forest to the east (Fig. 3).

The forest soils are provisionally classified as Inceptisols of Folists based on the lack of well-defined mineral horizons (Vann et al., 2001). Underlying the soil is highly weathered, impermeable, Paleozoic
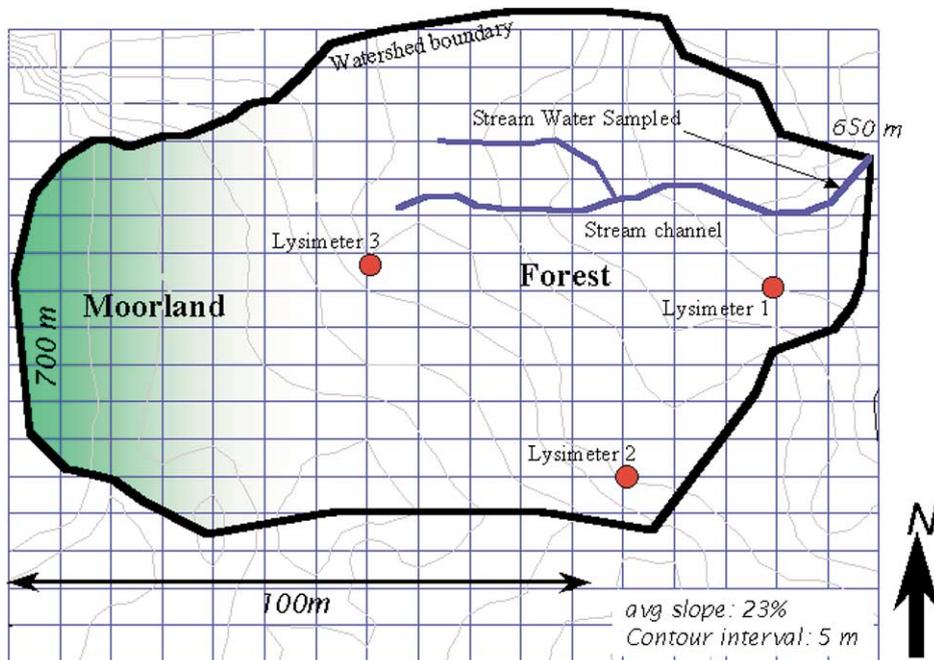

Fig. 3. Map of the study watershed, CP2 showing location of lysimeters used to collect soil water and location of stream water sampling. Stream discharge was measured at the watershed outlet.
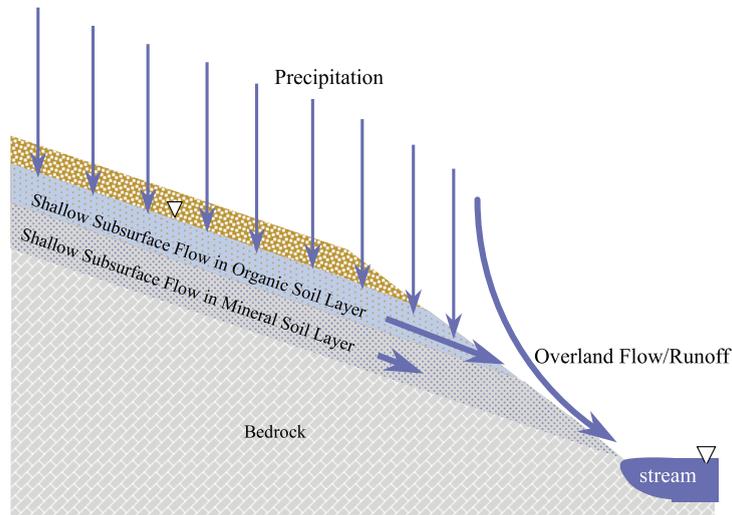
Fig. 4. Schematic of the watershed's hydraulics; the fastest water source is runoff, shallow flow through the organic matter is an intermediate source, and lateral flow through the deeper mineral soil is the most delayed flow.

micaschist (Holdgate, 1961; Pérez et al., 1991; Ruth-satz and Villagrán, 1991) containing mostly quartz and albite feldspar. The bedrock also contains some chlorite and muscovite, with minor amounts of sphene, apatite, magnetite and tourmaline (Watters and Fleming, 1972). The soils are shallow and on an average range between 40 and 60 cm depth (Pérez et al., 1998). Throughout most of the watershed, the top 10 cm of soil are highly organic (~50% C_t) (Pérez

et al., 1998) with an average bulk density of 0.07 g cm^{-3} (Zarin et al., 1998). The soil becomes increasingly mineral with greater depth, and average bulk density below 10 cm depth is 0.17 g cm^{-3}. In the Moorland, the soils have somewhat higher bulk densities ranging from 0.12 g cm^{-3} for the top 10 cm and 0.58 g cm^{-3} at depth. Using the method developed by Brutsaert (1993), the average catchment-scale hydraulic conductivity is 5 m day^{-1}. The deeper
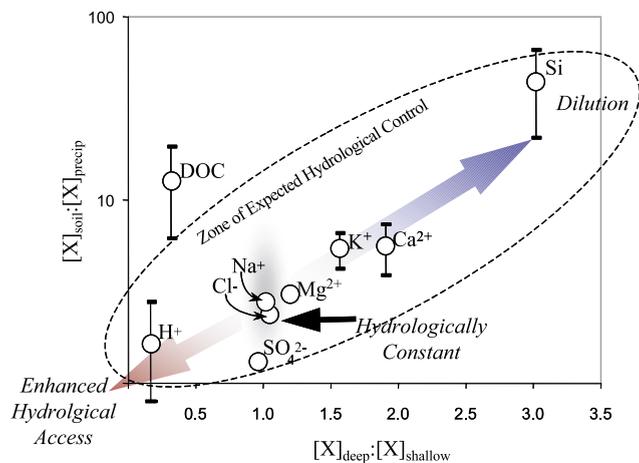

Fig. 7. Summary of expected hydrological control results. The outlined area (dashed line) shows the region where concentration ratios typically result in obvious hydrologically controlled behavior. The shaded area represents a zone of Hydrologically Constant behavior. Error bars are +/− one standard deviation; missing error bars indicate error is less than the symbol diameter.

mineral soil has a lower hydraulic conductivity, 0.1 m day^{-1}, determined using Hvorslev piezometer test (Freeze and Cherry, 1979). Soils are acidic (pH < 5) with low base-cation content, average of 15 cmol$_c$ kg^{-1} of soil of exchangeable calcium (Pérez et al., 1998).

The climate is humid and temperate and the temperature ranges from -1 to 28°C (Pérez et al., 1998). Over 3 years of study, the average annual rainfall was 588 cm (September 1995–September 1998). The longest observed period without rain was 16 days. However, the average period between discrete rainfall events is less than 1 day. Measurable streamflow was persistent everyday except during extended dry periods.

The physical description of the watershed fits the classic example of an area hydrologically controlled by variable source area processes with shallow subsurface lateral flow (a.k.a. interflow) dominating the hydrograph (Dunne and Leopold, 1978). The annual water balance indicates that the stream and evapotranspiration are the only water losses from the watershed. The periodic dry-up of the stream during summer periods suggests no significant deep groundwater reservoir; this seems especially valid given the relatively high annual precipitation. A linear reservoir analysis suggests three distinct reservoirs. This is consistent with the physical, qualitative observations of the watershed, namely a deep (10–20 cm) and relatively slow hydrological regime dominated by flow through mineral soil, a shallower hydrological regime dominated by flow through very permeable organic soils, and surface runoff through forest litter. In Fig. 4, the hypothesized hydraulics of this three-reservoir system is shown. The deep mineral soil is the slowest or most delayed flow, thus comprising the 'baseflow' for this system. Direct rainfall-runoff or through-debris-flow from saturated areas is the quickest flow in the system. Flow through the shallow, organic soil is the intermediate source.

4. Methods

Precipitation was continuously measured in a clearing adjacent to the watershed using a Belfort rain gage. The gage was checked and reset approximately every two weeks. Chart recorder data were digitized and converted to spreadsheet format using a method detailed in Walter et al. (1999). Precipitation samples were collected for chemical analyses every time the gage was reset.

Two Parshall flumes were installed in series at the outlet of the basin; one high and one low capacity permitting measures between 100 and 0.1 l s^{-1} (the capacity of the largest flume was never exceeded). Stage measurements were recorded continuously using a Stevens recorder on a 16 day time scale. Stage–discharge relationships for each flume were validated using periodic manual stream discharge measurements. Digitized stage heights were converted to spreadsheet format, similar to precipitation charts. Two pressure transducers were also installed at each flume for back-up use during chart-recorder malfunctioning. A short distance ($\sim$5 m) upstream of the flumes, biweekly stream samples were collected for chemical analyses.

Three low vacuum suction lysimeter sites in the watershed (Fig. 3) provided biweekly information on soil solution chemistry. Deep (20 cm) and shallow (10 cm) samples were taken at each site. Soil solution samples were collected by applying a 30 cm Hg vacuum over a 1–2 day period. The sampling apparatus was completely closed to minimize contamination due to opening of the seal of the vacuum bottles. All removable components of the sampling apparatus were acid washed and/or leached with copious amounts of deionized water, and we randomly tested rinsed bottles and plasticware for trace-level contamination. Water samples were immediately filtered through a pre-rinsed Gelman A/E glass fiber filters (<1 μm nominal pore size, tested in our lab), stored in thoroughly rinsed clean HDPE bottles, kept on ice for up to 6 h, and subsequently refrigerated. Samples were collected in duplicate, with high-pressure-liquid-chromatography-grade chloroform (0.5% of final volume) added as a preservative to one of the two samples. Samples were shipped by refrigerated air express to our laboratory at Cornell University for analysis.

All water samples from stream water, precipitation, and lysimeters were analyzed for sulfate (SO_4^{2-}), chloride (Cl^-), dissolved organic carbon (DOC), hydrogen ions (H^+), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+), calcium (Ca^{2+}), and silica (Si). Occasionally, there was not enough sample
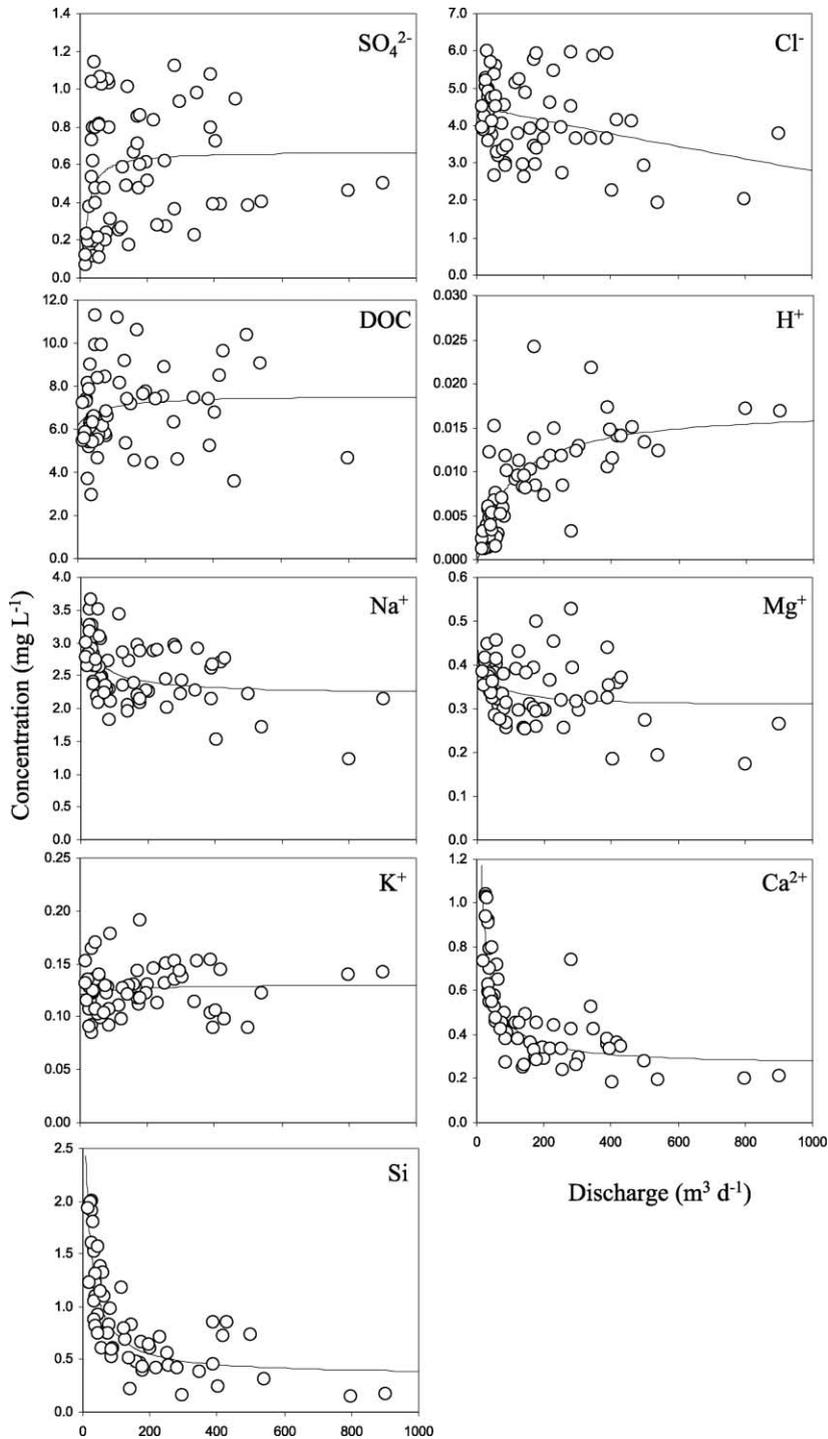
Fig. 5. Concentration–discharge relationships for the chemical constituents. The symbols show observed values and the lines show the best-fit relationship using Eq. (1) and the associated constants shown in Table 1. The dashed line for Cl⁻ corresponds to Eq. (1) fit through all points except those marked.

volume to analyze all these constituents and in these cases SO_4^{2-}, Cl^-, H^+ and DOC were given preference over the cations and Si. Analytical methods for dissolved elements were: SO_4^{2-} and Cl^- by Dionex chemically suppressed ion chromatography; H^+ by potentiometry using a Ross electrode; DOC by Shimadzu 5000 high-temperature (850°C) platinum catalyst combustion; Na^+, Mg^{2+}, K^+, and Ca^{2+} by Perkin–Elmer Flame Atomic Absorption Spectrophotometry; and Si, by Alpkem automated colorimetry. Method detection limits were: $SO_4^{2-} < 0.1$; $Cl^- < 0.01$; DOC < 0.05; $Na^+ < 0.1$; $Mg^{2+} < 0.01$; $K^+ < 0.005$; $Ca^{2+} < 0.01$; and Si $< 0.05 \, mg \, l^{-1}$. For concentrations below these detection limits, we assigned a value of half the detection limit.

Trends in the chemical concentration verses discharge relationships were characterized using a general hyperbolic dilution equation similar to the commonly used model developed by Johnson et al. (1969):

$$C = \frac{\alpha_1}{1 + \alpha_2 Q} + \alpha_3 \qquad (1)$$

where C is the concentration of a chemical in the streamwater, Q is the stream discharge, and α_1, α_2, and α_3 are constants for a particular chemical. Because Johnson et al.'s (1969) original parameter descriptions are difficult to determine physically (Lawrence and Driscoll, 1990), no attempt was made to mechanistically quantify the equation. Instead, general trends were compared to the three hydrological control mechanisms discussed earlier. Mathematically, $\alpha_1 > 0$ corresponds to a dilution-type curve and $\alpha_1 < 0$ to a curve characteristic of enhanced hydrological access. The α_2 parameter controls the curvature of the function; a large α_2 indicates sharp curvature and a low α_2 indicates straight line linear behavior. Non-significant correlation between Eq. (1) and the data is an indicator of hydrologically constant behavior.

5. Results and discussion

Fig. 5 and Table 1 summarize the concentration-discharge results for our study watershed, fitted mathematically according to Eq. (1), above, and Table 2 summarizes the median, mean, and standard devia-

Table 1
Hyperbolic model parameters and correlation coefficients for data (italic values correspond to the dashed line in Fig. 5)

	α_1	α_2	α_3	R^2
SO_4^{2-}	− 634.1	10000×10^{-5}	0.670	0.14[a]
Cl^-	22.02	0.01×10^{-5}	− 17.52	0.10
	4.273	*0.01×10^{-5}*	*0.100*	*0.003*
DOC	− 1.421	1.90×10^{-5}	7.586	0.03
H^+	− 0.018	1.30×10^{-5}	0.017	0.60[a]
Na^+	1.210	3.16×10^{-5}	2.212	0.24[a]
Mg^{2+}	0.132	3.43×10^{-5}	0.306	0.12[a]
K^+	− 0.010	1.00×10^{-5}	0.131	0.01
Ca^{2+}	2.209	13.0×10^{-5}	0.260	0.70[a]
Si	3.67	10.0×10^{-5}	0.345	0.70[a]

[a] Significant correlation, $\alpha < 0.01$.

tions for concentrations of all dissolved nutrients and elements in shallow and deep soil water, and in precipitation. For consistency, the discussion utilizes median values, though similar conclusions can be drawn from concentration means. Fig. 6 displays the relative median concentrations among the three water sources, precipitation, shallow soil water, and deep soil water, and relevant concentration ratios among the sources.

Inspection of the shape of changes in concentrations with increased stream water flow (Fig. 5) and of the sign and strength of parameter α_1 in Eq. (1) (Table 1) showed that Si and Ca^{2+} displayed the most pronounced dilution-type variations. The relative concentrations of the different water sources (Fig. 6) combined with the physical hydraulics of the system (i.e. Figs 2 and 3) agree with the idea that internal weathering was the predominant source for both Si and Ca^{2+}. At low stream flows, concentrations of these elements will be dominated by deep soil water which is characterized by relatively high concentrations of weathering-produced Si and Ca^{2+}, e.g. $[X]_{deep} : [X]_{shallow} \geq \sim 2$. At higher discharges, both deep and shallow soil water reservoirs will contribute to stream concentrations, with the low concentrations of shallow soil water acting to dilute the chemical contribution from the deeper reservoir. At very high discharges, there will be an increased contribution of direct rainfall to streamwater concentrations that, for both Si and Ca^{2+}, will even further dilute the soil water concentrations; $[X]_{soil} : [X]_{precip} \geq \sim 5$. Both Si and Ca^{2+} show concentration ratios of at least

Table 2
Median and mean water concentrations and standard deviation (mg l^{-1}) (N = number of samples)

	Deep soil water				Shallow soil water				Precipitation			
	Median	Mean	St. dev.	N	Median	Mean	St. dev.	N	Median	Mean	St. dev.	N
SO_4^{2-}	0.578	0.573	0.105	126	0.600	0.658	0.405	107	0.448	0.508	0.395	118
Cl^-	4.925	4.901	0.611	128	4.710	4.785	1.601	107	2.019	2.692	2.966	118
DOC	2.139	4.261	4.843	121	6.745	9.166	6.442	87	0.347	0.540	1.203	127
H^+	0.002	0.003	0.002	79	0.014	0.014	0.009	35	0.005	0.006	0.0045	90
Na^+	3.035	3.024	0.306	99	2.976	3.00	0.752	77	1.083	1.462	1.545	108
Mg^{2+}	0.448	0.445	0.051	101	0.373	0.373	0.102	78	0.135	0.186	0.190	112
K^+	0.317	0.343	0.119	101	0.202	0.247	0.143	77	0.048	0.063	0.068	111
Ca^{2+}	0.379	0.411	0.172	101	0.198	0.236	0.138	77	0.051	0.065	0.059	120
Si	1.661	1.644	0.217	96	0.549	0.634	0.262	79	0.025	0.036	0.260	111

two among the three main stream flow sources, deep soil water, shallow soil water, and precipitation with a consistent diluting trend from deep to shallow to precipitation (Fig. 6).

Similar, but much less pronounced, dilution-type changes in concentrations occur for Na^+ (especially for low flows) and Mg^{2+} with stream discharge variations (Table 1; Fig. 5). The relative weakness of these relationships appears to be due to the greater relative contributions of Na^+ and Mg^{2+} in atmospheric sea-salt aerosols than Si and Ca^{2+}; i.e. Na^+ and Mg^{2+} have significant sources outside the watershed that are delivered via precipitation. These two chemicals showed much smaller concentration ratios between their respective soil water reservoirs ($[X]_{deep}$: $[X]_{shallow} \sim 1$), and between soil and precipitation water ($[X]_{soil}$: $[X]_{precip} \sim 2$–3), when compared to Si and Ca^{2+} (Fig. 6). For flows above 200 m^3 d^{-1}, Na^+ and Mg^{2+} appear to follow the hydrologically constant model, which corroborates the relatively high atmospheric contributions of these elements and homogenous distribution in the soil.

In contrast to these results for Si, Ca^{2+}, Na^+, and Mg^{2+}, the strongest evidence of enhanced hydrological access occurred for H^+ (Table 1 and Fig. 5). This result is corroborated by the relative concentration differences in Fig. 6. The shallow soil, which contributes at higher discharges, has the highest concentration ($[H^+]_{shallow}$: $[H^+]_{deep} \sim 5$), presumably due to high concentration and production of organic acids in the organic horizons near the soil surface. In contrast, the deep reservoir (which dominates during low discharge) consistently displayed only low

concentrations of H^+, most likely due to consumption of H^+ by processes of weathering (c.f., Ca^{2+} and Si, above) and cation exchange. Precipitation had an intermediate concentration (Fig. 6), which may explain why the concentrations associated with the two highest discharges are not the two highest concentrations (Fig. 5); i.e. at very high flows, the added contribution of direct rainfall may act to further dilute high concentrations in shallow soil water. Thus, the internal source of H^+, associated with shallow organic soil horizons, is accessed by water flow only during high flow events, leading to enhanced hydrological access of H^+ with increasing flow.

Although DOC displays a strongly negative α_1, visual inspection of Fig. 6 does not support the model of enhanced hydrologic access across the entire range of flow values. DOC showed a distribution of soil water concentrations similar to H^+ (Fig. 6); i.e. the deep soil water is much more dilute than the shallow soil water ($[DOC]_{shallow}$: $[DOC]_{deep} \sim 4$). The lack of clear enhanced hydrologic access across discharge appears to be due to the fact that (in contrast to H^+) the DOC concentration in precipitation was proportionally much lower relative to the soil water ($[DOC]_{soil}$: $[DOC]_{precip} \sim 6+$) and, therefore, dilution by precipitation may offset any enhanced hydrological access behavior during strong precipitation events. To test this hypothesis, we considered only the dry months, December–March, for which the extent of surface saturation (i.e. area generating direct rainfall-runoff) is relatively small and, therefore, streamwater is dominated by soil water. For these months, the model–data correlation was significant
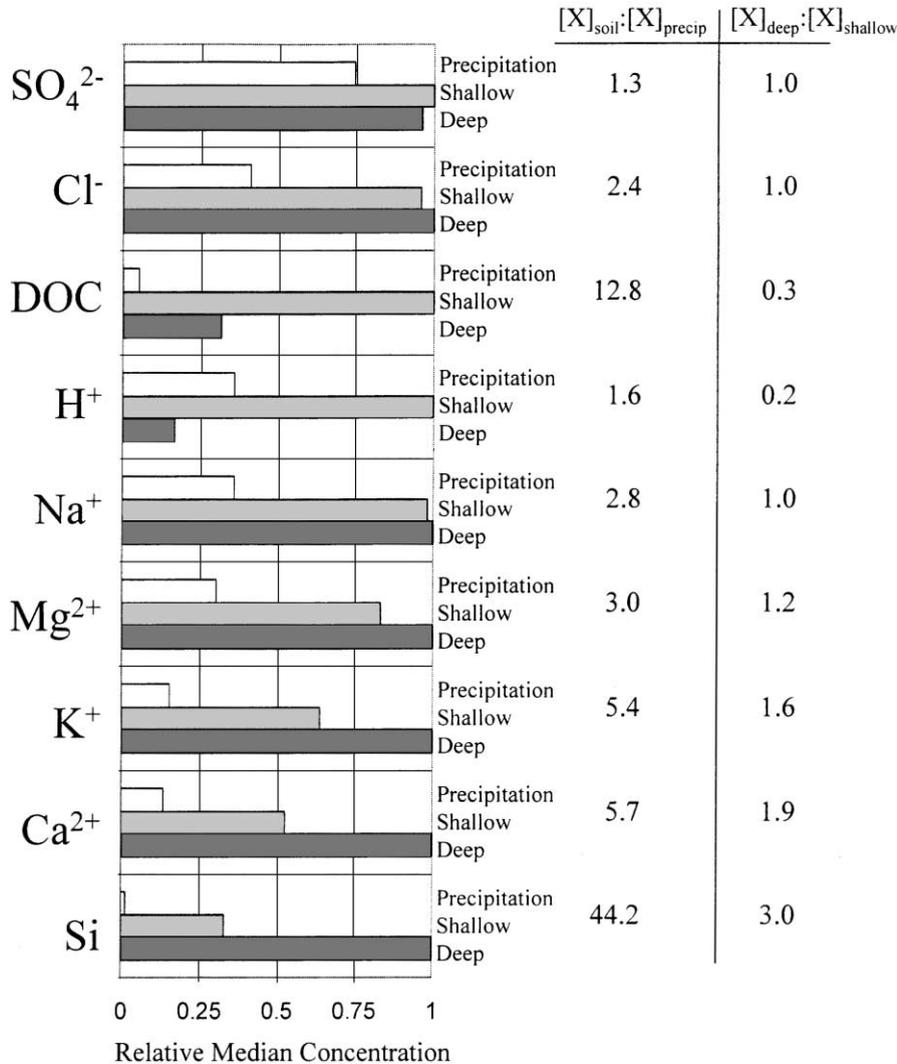
Fig. 6. Relative median concentrations among streamwater sources. Concentrations are shown as fractions of the largest member for each element.

($\alpha < 0.01$) and $R^2 = 0.25$, and it displayed the expected shape for enhanced hydrological access. This further suggests rain dilution is offsetting enhanced hydrological access within the soil. Note that DOC is extremely variable within the soil when compared to the other chemicals (Table 2) and, therefore, presumably may also experience internal biogeochemical dynamics that offset the hydrological controls. In addition, the $[X]_{shallow}:[X]_{deep}$ ratio is somewhat less pronounced for DOC than for H^+ probably because there are less consumptive processes in

the deep soil for DOC than for H^+ (e.g. weathering). The data-sampling interval was too large to compare our results with recent DOC work by Boyer et al. (1996,1997).

Although the model parameters for SO_4^{2-} suggest slight enhanced hydrological access (Table 1), the low correlation coefficient, lack of significant correlation (Table 1), and generally flat relationship over a large range of flows (Fig. 5) are more representative of hydrologically constant behavior. Indeed, Fig. 6 shows only relatively small differences between the

concentrations in the soil reservoirs ($[SO_4^{2-}]_{deep}$: $[SO_4^{2-}]_{shallow} \sim 1$). The concentration in the rain water is similar to the soil water ($[SO_4^{2-}]_{soil}$: $[SO_4^{2-}]_{precip} \sim 1.3$), which means that direct dilution from rain (as observed for Na^+ and Mg^{2+}) is likely to be of limited importance.

Our results suggest that K^+ appears to conform most closely to the hydrologically constant model (Fig. 5). This is not an intuitively obvious result based on the large differences observed between soil and rainwater concentrations (Fig. 6). K^+ exhibits a concentration distribution among deep soil, shallow soil, and precipitation waters that suggests a hydrological dilution control should be present, yet this is not observed (Fig. 5). While not as pronounced as for Ca^{2+} and Si, the ratio between soil water concentrations is relatively large ($[K^+]_{deep}$: $[K^+]_{shallow} \sim 1.6$). Additionally, the rain concentration is much lower than the soil water concentrations ($[K^+]_{soil}$: $[K^+]_{precip} \sim 4$–6), similar to Ca^+ (Fig. 6). This lack of a clear dilution relationship is similar, but more strongly expressed, than that previously discussed regarding Na^+ and Mg^{2+}.

An additional internal watershed process must act to modulate the expected changes in K^+ concentration as a function of different hydrologic regimes, especially when the watershed is very wet and ion mobility enhanced. One such possibility is biological uptake and recycling of K^+, which may maintain an internal source due to the rapid loss of K^+ during the leaching of soil litter (Aber and Melillo, 1991). Though it is only speculative, it is possible that such a mechanism increases the supply of K^+ with increasing water flow, and that this supply of K^+ is large enough to counteract the expected dilution with increasing flow rates. Thus, the watershed-scale control on K^+ remains unresolved, at present. Johnson et al. (1969) also noted unusual K^+ behavior.

The model correlation with Cl^- was low ($R^2 = 0.1$), relatively insignificant (Table 1), and uniquely linear with flow (Fig. 5; note the relatively small α_2 in Table 1), all of which suggest hydrologically constant controls. This is corroborated by the strong likelihood that rain water is the primary source of Cl^- for this system. Hydrological constancy is supported by the soil concentrations ($[Cl^-]_{deep}$: $[Cl^-]_{shallow} \sim 1$). The concentration ratio between soil and precipitation water was relatively low, suggesting minimal dilution

from direct rain water. The fact that $[Cl^-]_{soil}$: $[Cl^-]_{precip}$ was higher than one (Fig. 6) suggests the presence of some concentrating effect from evapotranspiration. The downward sloping line in Fig. 5 (solid line) was developed using all the data. Because large storms often flush aerosol Cl^- from the atmosphere, the model was fit to data with the elimination of data points likely to be influenced by this phenomena (four points marked in Fig. 5) and the result is the horizontal dashed line (Fig. 5). Comparing these two curves, it is probable that any occasional dilution effects during high flow events was due to such atmospheric aerosol dilution effects.

6. Conclusions

Though the export of some of the studied elements appears to be dominated by processes other than simple watershed-level combinations of three source pools, the observed variations in streamwater chemistry generally corroborated the existence of three dominant types of hydrologic control at the watershed scale. Fig. 7 summarizes these controls as an idealized hydro-biogeochemical system. Dilution was strongest for chemicals with strong internal generation (e.g. weathering) for which the ratio of soil water concentrations ($[X]_{deep}$:$[X]_{shallow}$), and soil to precipitation concentrations ($[X]_{deep}$:$[X]_{shallow}$), were relatively high, as in the case of Si and Ca^{2+}. Enhanced hydrological access only occurred for chemicals with low $[X]_{deep}$:$[X]_{shallow}$ and reasonably low $[X]_{soil}$:$[X]_{precip}$, as in the case of H^+. Chemicals with little concentration difference among the soil reservoirs and rainwater generally exhibited hydrologically constant controls — in fact, SO_4^{2-}, Cl^-. Mg^{2+} and Na^+ had concentration distributions similar to Cl^- (Fig. 7), and though they were hydrologically constant over a large range of flow, they occasionally experienced significant dilution, probably due to aerosol washout effects in precipitation.

Despite the strong concentration differences that existed for K^+ among the various water sources (Fig. 7), the differences did not translate into the predicted pattern of dilution control. This observation suggests that, while a coarse-scale analysis of watershed source pools can help to define the overall expected relationships between stream concentrations

and hydrologic flow, additional watershed processes may modulate the exact nature of this relationship. In the case of K^+, the difference between observed and expected variations suggests the existence of a yet unknown process with an impact at the watershed scale. The coarse-scale approach adopted here can then be used to define broad hydro-biogeochemical patterns, and to identify cases in which unknown factors intrude on the expected controls at scales of entire watersheds.

Acknowledgements

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