Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients

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[1] Many processes lead to variability of catchment concentration-discharge relationships, but exports of geogenic (weathering derived) solutes and nutrients (nitrogen and phosphorus species) from agricultural basins display relatively constant concentrations despite large variations in streamflow. These "chemostatic" responses are hypothesized to arise when a large mass store, the parent material for geogenics or chemically recalcitrant legacies of fertilization in agricultural catchments, buffers concentration variability. This hypothesis implies that (1) chemostatic behavior should be a general response to elevated external inputs to a catchment and (2) chemostatic behavior should be predictable from theory. Data- and model-based analyses were used to explore these hypotheses. We evaluated concentration variability relative to discharge (expressed as the ratio of the coefficients of variation of concentration and flow, or CV_C/CV_Q) across a gradient of increasing exported load, as a proxy for an external impact gradient. The CV_C/CV_Q of multiple solutes declined with increasing exported load. Exceptions included the geogenic solutes, which showed chemostatic responses for all sites, phosphorus, and some nitrogen species. Nitrate showed a suggestive pattern in CV_C/CV_Q with export, but further data are needed to confirm its generality. A simple model of runoff generation and solute export suggested that the decline in CV_C/CV_Q arises if the internal mass store is distributed homogeneously in space and there is sufficient time for mass transfer to reach steady state between runoff events. Export from catchments may become more predictable in impacted watersheds, simplifying water quality prediction but inducing strong hysteresis in recovery and making restoration efforts challenging.

1. Introduction

1.1. Background

[2] Hydrochemical studies addressing the behavior of dissolved solute species in response to fluctuations in stream discharge have a long history [*Edwards*, 1973; *Foster*, 1979; *Foster and Walling*, 1978; *Glover and Johnson*, 1974; *Walling and Foster*, 1975], which has contributed to improved understanding of runoff generation in catchments [*Kirchner*, 2003; *McDonnell*, 2003; *Pinder and Jones*, 1969], the development of end-member mixing techniques for hydrograph partitioning [*Burns et al.*, 2001; *Hooper et al.*, 1990], and a proliferation of studies that mechanistically link biogeochemistry and hydrology in both theoretical and experimental contexts [*Asano et al.*, 2009; *Burt and Pinay*, 2005; *Haygarth et al.*, 2005; *Kohler et al.*, 2009; *Ocampo et al.*, 2006; *Seibert et al.*, 2009; *Uchida et al.*, 2005]. Consistent relationships between concentration and discharge simplify the prediction of water quality impairment in receiving water bodies, associated with, for example salinization [*Kaushal et al.*, 2005], eutrophication [*McDowell et al.*, 2001; *Rabalais et al.*, 2002], chronic or acute toxicity [*Ying et al.*, 2002]. Long-term patterns in hydrochemistry also provide valuable records of catchment condition and response to external forcing, such as the depletion of base cations following acid deposition [*Lamontagne et al.*, 2000; *Likens et al.*, 1998; *Pastor et al.*, 2003; *Valett et al.*, 2002]. Understanding the dynamics and drivers of in-stream export from catchments is therefore of ongoing importance.

[3] A broad range of responses of solute concentrations to fluctuations in streamflow have been observed, varying between sites, solute species and specific storm events [*Butturini et al.*, 2006; *Edwards*, 1973; *Hill*, 1993; *Kirchner*, 2003; *Rademacher et al.*, 2005; *Temnerud et al.*, 2007; *Walling and Foster*, 1975]. Catchment-specific studies have identified numerous factors driving these differences, including ante-

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cedent wetness conditions [*Creed and Band*, 1998; *Biron et al.*, 1999], multiple solute sources [*Anderson et al.*, 1997; *Deboer and Campbell*, 1990; *Evans and Davies*, 1998], fluctuations in rainfall and through fall concentration [*Burt*, 1979; *McDowell*, 1998], seasonality in rainfall and thus flushing of soils [*Butturini and Sabater*, 2000; *Pinol et al.*, 1992], snowpack influences [*Ahearn et al.*, 2004; *Brooks and Williams*, 1999; *Brooks et al.*, 1999], and seasonal controls on plant uptake or microbiological cycling [*Rusjan and Mikos*, 2010]. While these complicated process controls could confound the predictability of hydrochemistry, recent studies have found commonalities across a broad range of sites. *Godsey et al.* [2009] showed a highly damped variability in the concentrations (C) of geogenic solutes (Ca^{2+}, Mg^{2+}, SiO_2^{2-}, Na^+) relative to discharge (Q) across 59 pristine US watersheds (6 km^2 to 6000 km^2 in area), in which concentrations were approximately constant. Observing near-constant concentrations of weathering products in streamflow is not new [*Ahearn et al.*, 2004; *Edwards*, 1973; *Walling and Foster*, 1975], but the synthesis of data over a large range of parent materials, climate, vegetation and catchment scales suggests that chemostatic responses may be widespread for geogenic solutes.

[4] Also using a data synthesis approach, *Basu et al.* [2010a] showed that patterns of total nitrogen (TN) and total phosphorus (TP) export from agricultural basins worldwide were also characterized by near-constant flow-weighted concentrations at annual time scales. However, such trends are uncommon outside of agricultural basins, as testified by the literature on nitrogen [*Ahearn et al.*, 2004; *Band et al.*, 2001; *Bernhardt et al.*, 2005; *Brooks and Williams*, 1999; *Creed and Band*, 1998; *Hedin et al.*, 1995; *Rusjan and Mikos*, 2010; *Vanderbilt et al.*, 2003] and phosphorus species [*Fiorentino et al.*, 2003; *Haygarth et al.*, 2004; *Lamontagne et al.*, 2000; *Valett et al.*, 2002].

1.2. Conceptual Models Proposed to Explain Chemostatic Responses

[5] The results presented by *Godsey et al.* [2009] and *Basu et al.* [2010a] are somewhat paradoxical, since it is not apparent why the dynamics of N and P exports from agricultural sites should resemble those of weathering products. Existing conceptual models that attempt to explain the emergence of chemostatic responses are reviewed below as a starting point to addressing this paradox. These conceptual models treat chemostatic behavior as a special case of a hypothesized power law $C - Q$ relationship of the form $C = aQ^b$, where chemostatic responses correspond to the case where $b = 0$.

[6] *Godsey et al.* [2009] suggested that if permeability (k), pore aperture (p) and porosity (ϕ) all decreased exponentially with soil depth then chemostatic behavior would arise if $\lambda_\phi^{-1} - \lambda_p^{-1} = \lambda_k^{-1}$, where λ is a shape factor describing an exponential decline with depth. This model assumes that solutes are uniformly available through time (i.e., ignoring variable biogeochemical dynamics), and has the appealing result that the derived values of b are determined solely from soil properties, potentially explaining the ubiquity of chemostatic behavior for weathering products. The highly specific covariation in k, p and ϕ needed to predict $b = 0$ in the model can be explored using the Carman-Kozeny equation to derive the covariation of k, p and ϕ geometrically. This analysis (see Appendix A for details) suggests,

positively, that b values should be highly constrained in the range -0.5 to -1.5, but did not generate $b \approx 0$ for realistic parameter choices. Obviously the *Godsey et al.* [2009] model, developed explicitly for weathering products in natural systems, does not directly apply to emergence of chemostatic responses for N and P.

[7] Considering dissolved organic carbon and the $C = aQ^b$ relationship, *Seibert et al.* [2009] derived $b = \lambda_Q^{-1} (\lambda_c + \lambda_Q) - 1$. Again λ is a shape factor quantifying exponential declines with depth of hydrologic fluxes (λ_Q) and solute concentrations (λ_C). Chemostatic behavior arises if the distribution of exchangeable solutes is near-constant relative to the vertical hydrological flux variation, that is if $\lambda_Q \gg \lambda_C$. *Basu et al.* [2010a] focused on a statistical description of covariance between hydrologic fluxes and chemical sources, accounting for the spatial correlation between random fields representing saturation, flow generation and concentration of exchangeable constituents. In this conceptual model, chemostatic behavior arose where these fields were uncorrelated. Both the *Seibert et al.* [2009] and *Basu et al.* [2010a] models suggest that homogeneous spatial distributions of solutes promote chemostatic responses, although neither approach quantitatively addresses temporal variations in water or concentration fluxes.

[8] *Basu et al.* [2010a] suggested that anthropogenic inputs of N and P at agricultural sites are so large that they exceed loss mechanisms and thus accumulate in an immobile 'legacy' mass store (potentially consisting of sorbed P and organic N [*Behrendt and Boekhold*, 1993; *Whalen and Chang*, 2001; *Addiscott*, 1996]). These stores were hypothesized to provide a near uniform mass input to water moving through the saturated zone, large enough to overwhelm the signal of natural fluctuations in exported concentration. The large geological mass store associated with weathering products is analogous to this legacy store for nutrients. This hypothesis could therefore explain both the consistently chemostatic behavior of geogenic export dynamics, and the near-chemostatic export behavior of nutrients in agricultural catchments.

1.3. Study Goals

[9] This study aims to explore the *Basu et al.* [2010a] hypothesis that chemostatic responses reflect the presence of internal mass stores: the parent material in the case of geogenic solutes, or a legacy store developed following a history of elevated exogenous inputs. If this proposed mechanism is general then we hypothesize that:

[10] 1. Chemostatic behavior should emerge as a consequence of increased solute mass stores in a catchment. Where these stores are not intrinsic, they should arise following persistent external inputs to a catchment. Chemostatic behavior should not be specific to particular solutes or land uses;

[11] 2. Simple theoretical approaches should be able to predict the emergence of chemostatic behavior as a consequence of a large internal solute store, whether naturally occurring (geogenic) or arising as a consequence of external input (legacy),subject to modification by biological and chemical processes.

[12] The first hypothesis is tested using data from 31 small intensively studied watersheds (0.1–22 km^2) contained within long-term ecological research sites (LTERs) and experimental forests in the USA. The second hypothesis is
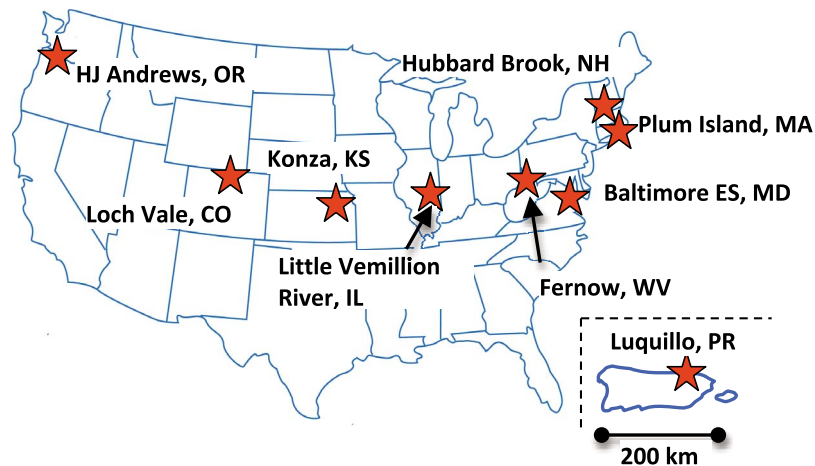
Figure 1. Location of the nine experimental watersheds included in this study.

addressed using a simple theoretical model. Section 2 describes the sites, the metrics and analytical approaches used to investigate hypothesis 1, and develops the physical and chemical transport model used to address hypothesis 2.

2. Methods

2.1. Empirical Approaches

2.1.1. Research Sites

[13] Discharge and concentration data were obtained from nine experimental watersheds in the continental US and Puerto Rico (Figure 1). To simplify the analysis and reduce the effects of confounding factors, only control watersheds were included in the data set, leaving a set of 31 sub-watersheds for consideration. Note that the data set includes sites impacted by natural disturbances such as hurricanes at Luquillo [*McDowell et al.*, 2001; *Schaefer et al.*, 2000], and burned sites at Konza Prairie [*Hayes and Seastedt*, 1989]. Summary data for the studied sites are provided in Table 1. The sites are mesic-humid catchments with mean annual precipitation ranging from 835 mm at Konza Prairie (KS) to 3300 mm at Luquillo (PR). All sites are small, lower-order watersheds, ranging from 0.1 to 22 km^2 in area, thus minimizing the effects of spatial averaging on the hydrochemistry. The sites span multiple land use types: (1) agriculture at the Little Vermillion River (IL) and McDonogh (MD) Watersheds, (2) urban in the Baltimore Ecosystem Study (MD) and the Plum Island Ecosystem Study (MA) watersheds, (3) managed prairies in the Konza Prairie LTER (KS), and (4) numerous forests including Luquillo (PR), H. J. Andrews (OR), Loch Vale (CO), Fernow Forest (WV), Hubbard Brook Forest (NH) and urban forests in the Baltimore Ecosystem Study (MD) (Baltimore Ecosystem Study, http://www.beslter.org/; Fernow Experimental Forest Study, http://www.fs.fed.us/ne/parsons/webdata/index.htm; HJ Andrews Long Term Ecosystem Research Study, http://andrewsforest.oregonstate.edu/data/mastercatalog.cfm?topnav=97; J. Campbell, Instantaneous streamflow by watershed, Hubbard Brook Ecosystem Study, http://www.hubbardbrook.org/data/dataset.php?id=1; G. E. Likens, Chemistry of streamflow at HBEF WS-1 through WS-9, Hubbard Brook Ecosystem Study, http://www.hubbardbrook.org/data/dataset.php?id=3; Loch Vale Watershed Study, http://co.water.usgs.gov/lochvale/data.html; Luquillo Long Term Ecosystem Research Study, http://luq.lternet.edu/data/ltercata.html; Plum Island Long Term Ecosystem Research Study, http://ecosystems.mbl.edu/Pie/data.htm; and P. K. Kalita, Stream chemistry and discharge of the Little Vermillion River, IL, unpublished data, 2005). The sites also span a climatic gradient from tropical through temperate.

[14] The catchments range from highly impacted to near pristine in terms of land use and the magnitude of external input fluxes. For example, Hubbard Brook and Fernow Forest historically received some of the highest concentrations of N and S in rainfall in the US, leading to acidification and nitrogen enrichment [*Likens et al.*, 2002; *Adams et al.*, 1993; *Bernhardt et al.*, 2005]. Conversely, H. J. Andrews and Luquillo forests receive minimal N deposition [*McDowell et al.*, 1990; *Vanderbilt et al.*, 2003], and N inputs to the agricultural Little Vermillion River and McDonogh watersheds are dominated by fertilizer [*Groffman et al.*, 2004; *Algoazany*, 2006]. Elevated N inputs also arise in suburban areas in Baltimore [*Groffman et al.*, 2004]. Input loads of salts vary with distance from the ocean and with urbanization, the latter due to the application of deicing salts to urban roads [*Jackson and Jobbagy*, 2005]. A site like Luquillo, which is amongst the most impacted in terms of chloride input due to sea salt episodes, is amongst the least impacted in terms of nitrogen input. Similar variability occurs throughout the data set, reflecting differences in geographical location, land use and land management. The quality of data available to estimate mass inputs into the sites is highly variable so that it is not generally possible to close nutrient or solute mass balances. Indicative inputs of solutes in wet deposition, fertilization estimates and estimates of road salt inputs, as well as the annual exported load per unit area, are summarized in Tables 2, 3, 4, and 5. While these data are indicative of the external impacts on the catchments, their precision, completeness and accuracy are uncertain.

2.1.2. Available Data

[15] All sites had daily sampling of flow and daily to monthly sampling of nitrate over at least a 3 year period. Other solutes measured varied between sites and are listed in the metadata table (Table 1). To ensure that disparities in discharge and concentration sampling frequencies did not bias the data record, we compared the discharge range during concentration sampling with the full flow duration curves for

Table 1. Metadata for the Study Watersheds[a]

Site	Watershed	Q Frequency	C Frequency	Period of Record	Solutes	Elevation (m)	Land Use	Area (ha)	P (mm)	Q (mm)
HJ Andrews	GS Mack (Mack)	daily	daily	1980–2008	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, TSS, NH_3/NH_4, PO_4^{2-}	765–1626	forest	580	1030	2040
	GSWS02 (WS2)	daily	daily	1953–2008	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, TSS, NH_3/NH_4, PO_4^{2-}	530–1070	forest	60	2180	1570
	GSWS08 (WS8)	daily	reported 3-weekly	1964–2008	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, TSS, NH_3/NH_4, PO_4^{2-}	955–1190	forest	21.4	1980	1370
	GSWS09 (WS9)	daily	reported 3-weekly	1969–2008	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, TSS, NH_3/NH_4, PO_4^{2-}	425–700	forest	8.5	1230	1730
Fernow	WS4	daily	weekly	1980–2007	Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4	740–865	forest	38.7	1440	670
Luquillo	Espiritu Santo (ES)	daily	fortnightly	2003–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, NH_3/NH_4, PO_4^{2-}, TSS	740–865	forest	2233	3300	800
	Mameyes at Sonadora (MS)	daily	fortnightly	1989–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, NH_3/NH_4, PO_4^{2-}, TSS	390	forest	1782	3300	980
	Sabana (Sa)	daily	fortnightly	2003–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, NH_3/NH_4, PO_4^{2-}, TSS	114	forest	1026	3300	560
	Sonadora (So)	daily	fortnightly	1983–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, NH_3/NH_4, PO_4^{2-}, TSS	101	forest	262	3300	860
	Icacos (Ic)	daily	fortnightly	1983–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, Cl^-, SO_4^{2-}, NO_3^-, NH_3/NH_4, PO_4^{2-}, TSS	375	forest	326	3300	1350
Hubbard Brook	WS1	daily	daily, reported monthly	1963–2005	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	616	forest	11.8	1340	850
	WS3	daily	daily, reported monthly	1963–2006	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	488–747	forest	42.4	1340	850
	WS6	daily	daily, reported monthly	1963–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	527–732	forest	13.2	1440	920
	WS7	daily	daily, reported monthly	1995–2005	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	549–792	forest	77.4	1470	970
	WS8	daily	daily, reported monthly	1995–2006	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	619–899	forest	59.4	1480	950
	WS9	daily	daily, reported monthly	1995–2007	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	610–905	forest	68.4	1570	1000
Loch Vale	Loch Outlet (LO)	daily	fortnightly	1983–2004	Ca^{2+}, Mg^{2+}, Na^+, SiO_2, SO_4^{2-}, Cl^-, NO_3^-, NH_3/NH_4, PO_4^{2-}	685–910	alpine	660	1100	360
Little Vermillion River	B1	continuous	weekly (low flow)	1991–2000	NO_3^-, PO_4^{2-}	150	corn-soy	48.6	930	190
	B2	continuous	weekly (low flow)	1991–2000	NO_3^-, PO_4^{2-}	150	corn-soy	33.4	930	200
weekly (low flow)		NO_3^-, PO_4^{2-}	150	corn-soy	33.4	930	200			
	H1	continuous	<daily (high flow)	1993–2000	NO_3^-, PO_4^{2-}	150	corn-soy	68	830	160
	M1	continuous	<daily (high flow)	1991–2000	NO_3^-, PO_4^{2-}	150	corn-soy	75.6	830	170
Plum Island	Cart Creek (CC)	15 min	daily	2001–2009	TN, TP, NO_3^-	sea level	mixed suburban forest	39.6	1180	390
	Cedar Swamp (CS)	15 min	daily	2005–2008	TN, TP, NO_3^-	sea level	mixed suburban forest	14	1180	1290
	Sawmill Brook (SB)	15 min	daily	2001–2009	TN, TP, NO_3^-	sea level	urban	41	1180	480
Konza Prairie	1 year	daily	1–3 weekly	1985–1997	NO_3^-, NH_4^+, TN, PO_4^{2-}, TP	320–444	prairie	121	830	170
	2 year	daily	1–3 weekly	1985–1997	NO_3^-, NH_4^+, TN, PO_4^{2-}, TP	320–444	prairie	119	830	180
	4 year	daily	1–3 weekly	1985–1997	NO_3^-, NH_4^+, TN, PO_4^{2-}, TP	320–444	prairie	135	830	210
	20 year	daily	1–3 weekly	1993–1997	NO_3^-, NH_4^+, TN, PO_4^{2-}, TP	320–444	prairie	84	830	90
Baltimore Ecosystem Study	McDonogh (MD)	daily	weekly	1999–2009	Cl^-, NO_3^-, TN, TP, PO_4^{2-}, SO_4^{2-}	0–260	agriculture	8	1090	370
	Baisman Run (BR)	daily	weekly	1998–2009	Cl^-, NO_3^-, TN, TP, PO_4^{2-}, SO_4^{2-}	0–260	80% forest/suburban	381	1090	470
	Glyndon Falls (GF)	daily	weekly	1998–2009	Cl^-, NO_3^-, TN, TP, PO_4^{2-}, SO_4^{2-}	0–260	suburban	96	1090	420
	Pond Branch (PB)	daily	weekly	1998–2009	Cl^-, NO_3^-, TN, TP, PO_4^{2-}, SO_4^{2-}	0–260	urban forest	41	1090	510

[a] Note that natural disturbances, including fire, hurricanes, and landslips, are included, but isolated experimental manipulations have been excluded. Significant temporal trends arose at Hubbard Brook (see Figure 2 for trend analysis). The finding that $P < Q$ for the GSMack site is attributable to precipitation spatial heterogeneity in this large mountainous watershed.

Table 2. Summary of Measures of Concentration Variability for the Geogenic Species[a]

Species	Site	Subwatershed	Input (g m⁻² yr⁻¹)	Export (g m⁻² yr⁻¹)	CV_C/CV_Q	Error	$L-Q\ r^2$	b	$b\ r^2$	p
Mg[b]	Luquillo	ES	1.32	1	0.14	<0.01	0.75	−0.3	0.4	0
		MS	1.32	0.72	0.19	<0.01	0.96	−0.2	0.19	0
		So	1.32	0.41	0.13	<0.01	0.94	−0.1	0.17	0
		Sa	1.32	0.59	0.12	<0.01	0.99	−0.3	0.59	0
		Ic	1.32	0.52	0.17	<0.01	0.99	−0.2	0.27	0
	HJA	Mack	0.23	0.09	0.35	<0.01	0.79	−0.1	0.37	0
		WS2	0.23	0.06	0.24	<0.01	0.83	−0.1	0.29	0
		WS8	0.23	0.05	0.11	<0.01	0.89	−0.1	0.45	0
		WS9	0.23	0.05	0.24	<0.01	0.69	−0.1	0.21	0
	Loch Vale	LO	0.02	0.01	0.26	0.01	0.77	−0.1	0.48	0
	HB pre 75	WS3	0.05	0.32	0.14	0.01	0.78	−0.1	0.29	0
		WS6	0.06	0.3	0.12	0.02	0.87	−0	0.12	0
	HB post 75	WS3	0.03	0.23	0.21	0.01	0.7	−0.1	0.45	0
		WS6	0.03	0.22	0.21	0.02	0.59	−0.1	0.3	0
		WS7	0.03	0.28	0.21	0.02	0.95	−0.1	0.7	0
		WS8	0.03	0.27	0.19	0.02	0.95	−0.1	0.59	0
		WS9	0.03	0.19	0.2	0.03	0.98	−0.1	0.44	0
	Fernow	WS4	0.01	0.08	0.08	<0.01	0.88	0.01	0.01	0
Ca[c]	Luquillo	ES	2.06	1.89	0.12	<0.01	0.55	−0.2	0.36	0
		MS	2.06	**2.7**	0.17	<0.01	0.96	−0.2	0.11	0
		So	2.06	0.69	0.14	<0.01	0.89	−0.1	0.13	0
		Sa	2.06	1.14	0.13	<0.01	0.94	−0.3	0.46	0
		Ic	2.06	1.45	0.18	<0.01	0.99	−0.2	0.29	0
	HJA	Mack	0.71	0.22	0.14	<0.01	0.94	−0.1	0.41	0
		WS2	0.71	0.25	0.09	<0.01	0.99	−0.1	0.53	0
		WS8	0.71	0.22	0.11	<0.01	0.87	−0.1	0.34	0
		WS9	0.71	0.26	0.11	<0.01	0.9	−0.1	0.31	0
	Loch Vale	LO	0.18	0.05	0.26	<0.01	0.71	−0.1	0.51	0
	HB pre 75	WS3	0.19	1.44	0.14	0.01	0.76	−0	0.08	0
		WS6	0.2	1.22	0.14	0.02	0.86	0.01	0.01	0.2
	HB post 75	WS3	0.1	0.93	0.2	<0.01	0.52	−0.1	0.13	0
		WS6	0.11	0.79	0.21	<0.01	0.4	−0	0.04	0
		WS7	0.11	0.91	0.12	0.01	0.94	−0.1	0.57	0
		WS8	0.11	0.74	0.16	0.01	0.95	−0.1	0.56	0
		WS9	0.11	0.56	0.18	0.01	0.95	−0.1	0.5	0
	Fernow	WS4	0.05	0.17	0.14	<0.01	0.91	0.01	0.01	0
SiO₂[d]	Luquillo	MS	3.71	5.92	0.19	<0.01	0.77	−0.3	0.12	0
		So	3.71	2.43	0.18	<0.01	0.79	−0.2	0.12	0
		Sa	3.71	5.56	0.1	<0.01	0.89	−0.2	0.23	0
		Ic	3.71	**7.8**	0.22	<0.01	0.99	−0.4	0.19	0
		Mack	0.32	0.64	0.1	<0.01	0.96	−0.1	0.49	0
	HJA	WS2	0.32	0.67	0.04	<0.01	1	−0	0.28	0
		WS8	0.32	0.57	0.14	<0.01	0.5	−0	0.02	0
		WS9	0.32	0.62	0.11	<0.01	0.7	−0	0.04	0
	Loch Vale	LO		0.07	0.28	<0.01	0.85	−0.1	0.17	0
	HB pre 75	WS3	0.09	5.27	0.15	<0.01	0.88	−0.1	0.53	0
		WS6	0.1	3.61	0.18	<0.01	0.87	−0.1	0.67	0
	HB post 75	WS3	0.09	4.26	0.17	<0.01	0.92	−0.1	0.7	0
		WS6	0.09	3.45	0.19	<0.01	0.92	−0.1	0.7	0
		WS7	0.08	4.31	0.22	<0.01	0.92	−0.2	0.79	0
		WS8	0.08	4.49	0.24	<0.01	0.93	−0.2	0.71	0
		WS9	0.09	4.37	0.3	<0.01	0.95	−0.2	0.6	0

[a]The columns relate to the annual mass input per unit of the solutes in wet deposition (or anthropogenic fertilization, where measured), the annual export per unit area, the ratio of coefficients of variation of concentration and discharge, the associated measurement error in this ratio, the coefficient of determination of an annualized linear fit to the load-discharge relationship, the exponent b of the best power law fit to a $C = aQ^b$ relationship, the coefficient of determination of the power-law C-Q relationship (b, r^2), and the significance of the power-law C-Q relationship (p). The site with the highest annual exported load, used for normalization, is given in bold for each solute. Abbreviations for the subwatersheds are defined in Table 1.

[b]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 0.2 and 0.1; 0.9 and 0.1, −0 and 0.1, 0.4 and 0.2, and 0 and 0, respectively.

[c]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 0.2 and 0, 0.8 and 0.2, −0 and 0.1, 0.3 and 0.2, and 0 and 0, respectively.

[d]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 0.2 and 0.1, 0.8 and 0.1, −0 and 0.1, 0.4 and 0.3, and 0 and 0, respectively.

each site. For all data, the flow regimes associated with chemical sampling spanned over 90% of the full flow regime. For 98% of sites and chemical species, more than 99% of the flow variability was sampled. The length of the data records are therefore sufficient to avoid bias between flow and concentration sampling.

[16] The Hubbard Brook watersheds displayed a significant long-term trend due to reduced atmospheric sulfate inputs since the institution of the Clean Air Act in 1970. We attempted to recognize this distinction by partitioning the data set at the year 1975, viewing data from pre-1975 as primarily reflecting the pre-Clean Air Act regime, and data from post-1975 as being indicative of the site under post-Clean Air Act sulfate loading. This split was based on inspection of the annual load data for nutrients and base

Table 3. Summary of Measures of Concentration Variability for the Exogenous Inorganic Species[a]

Species	Site	Subwatershed	Input (g m^{-2} yr^{-1})	Export (g m^{-2} yr^{-1})	CV_C/CV_Q	Error	$L - Q\,r^2$	b	$b\,r^2$	p
SO$_4^{2-}$[b]	Luquillo	ES	5.45	0.2	0.08	<0.01	0.97	−0	0.02	0.03
		MS	5.45	0.4	0.2	<0.01	0.99	−0.1	0.01	0.05
		So	5.45	0.2	0.23	<0.01	0.95	0.03	0.01	0.03
		Ic	5.45	0.1	0.4	0.01	0.95	0.05	0.01	0.24
	HJA	Mack	0.24	0	0.26	0.02	0.75	−0.1	0.09	0
		WS2	0.24	0	0.18	0.01	0.51	−0.1	0.08	0
		WS8	0.24	0	0.38	0.06	0.6	−0.1	0.02	0.12
		WS9	0.24	0	0.21	0.02	0.68	0	0	0.99
	Loch Vale	LO	0.52	0.1	0.29	<0.01	0.51	−0.1	0.38	0
	HB pre 75	WS3	3.76	**6.5**	0.11	<0.01	0.97	−0	0.05	0.1
		WS6	3.94	5.4	0.08	<0.01	0.97	−0	0.21	0
	HB post 75	WS3	2.5	4.4	0.16	<0.01	0.68	−0.1	0.18	0
		WS6	2.63	4.3	0.16	<0.01	0.66	−0.1	0.2	0
		WS7	2.04	3.8	0.09	<0.01	0.96	−0.1	0.57	0
		WS8	2.03	3.7	0.08	<0.01	0.95	−0	0.18	0
		WS9	2.07	3.8	0.13	<0.01	0.93	−0	0.2	0
	Fernow	WS4	0.62	0.5	0.1	<0.01	0.96	0	0	0.83
	Baltimore ES	BR	1.62	0.2	0.4	<0.01	0.87	0.25	0.4	0
		PB	1.62	0.1	0.73	<0.01	0.9	0.18	0.1	0
		MD	1.62	0.6	0.08	<0.01	0.99	−0.1	0.08	0
		GF	1.62	1	0.06	<0.01	0.96	−0.1	0.19	0
Na[c]	Luquillo	ES	6.61	2.3	0.1	<0.01	0.96	−0.2	0.23	0
		MS	6.61	**2.4**	0.13	<0.01	0.97	−0.1	0.1	0
		So	6.61	1.4	0.11	<0.01	0.96	−0.1	0.11	0
		Sa	6.61	2	0.08	<0.01	1	−0.1	0.45	0
		Ic	6.61	2.3	0.12	<0.01	0.99	−0.1	0.29	0
	HJA	Mack	1.87	0.1	0.13	<0.01	0.99	−0.1	0.62	0
		WS2	1.87	0.2	0.09	<0.01	0.99	−0.1	0.65	0
		WS8	1.87	0.2	0.08	<0.01	0.97	−0.1	0.39	0
		WS9	1.87	0.2	0.13	<0.01	0.95	−0.1	0.38	0
	Loch Vale	LO	0.02	0	0.35	<0.01	0.67	−0.2	0.61	0
	HB pre 75	WS3	0.08	0.2	0.63	<0.01	0.84	−0.1	0.68	0
		WS6	0.08	0.2	0.44	0.01	0.78	0.14	0.7	0
	HB post 75	WS3	0.06	0.1	0.68	<0.01	0.38	−0.1	0.77	0
		WS6	0.06	0.2	0.56	<0.01	0.46	−0.2	0.75	0
		WS7	0.06	0.2	0.29	0.01	0.83	−0.2	0.86	0
		WS8	0.06	0.2	0.24	0.01	0.85	−0.2	0.84	0
		WS9	0.06	0.2	0.38	0.01	0.4	−0.2	0.74	0
	Fernow	WS4	0.01	0	0.15	<0.01	0.91	−0.1	0.33	0
Cl[d]	Luquillo	ES	12	3	0.09	<0.01	0.95	−0.1	0.16	0
		MS	12	2.8	0.14	<0.01	0.94	−0.1	0.04	0
		So	12	1.9	0.12	<0.01	0.96	−0	0.03	0
		Sa	12	2.6	0.11	<0.01	1	−0.1	0.23	0
		Ic	12	2.8	0.14	<0.01	1	−0.1	0.07	0
	HJA	Mack	1.62	0.1	0.55	<0.01	0.51	−0	0.02	0
		WS2	1.62	0.1	0.12	<0.01	0.81	−0	0	0.27
		WS8	1.62	0.1	0.37	0.01	0.81	−0	0	0.55
		WS9	1.62	0.1	0.35	<0.01	0.61	−0	0	0.3
	Loch Vale	LO	0.07	0	0.32	0.01	0.57	−0.1	0.16	0
	HB pre 75	WS3	0.81	0.5	0.21	0.02	0.62	0	0	0.89
		WS6	0.51	0.5	0.18	0.01	0.58	−0	0.01	0.33
	HB post 75	WS3	0.27	0.4	0.21	0.01	0.68	−0	0.04	0
		WS6	0.29	0.4	0.23	0.01	0.69	−0	0.04	0
		WS7	0.26	0.4	0.2	0.02	0.86	−0	0.01	0.23
		WS8	0.26	0.4	0.25	0.02	0.82	−0	0.02	0.15
		WS9	0.27	0.4	0.34	0.02	0.76	−0.1	0.04	0.03
	Fernow	WS4	0.03	0.1	0.1	<0.01	0.86	−0	0.01	0
	Baltimore ES	BR	0.24	1.3	0.56	<0.01	0.8	−0	0	0.15
		PB	0.24	0.1	0.19	<0.01	0.99	−0	0.02	0
		MD	0.24	0.2	0.08	<0.01	0.99	−0	0.04	0
		GF	0.24	**4.8**	0.41	<0.01	0.83	−0.1	0.05	0

[a]The site with the highest annual exported load, used for normalization, is given in bold for each solute. See Table 2 for definition of the columns.
[b]Mean and standard deviation for CV_C/CV_Q, $L - Q\,r^2$, b, $b\,r^2$, and p are 0.2 and 0.2, 0.8 and 0.2, (none) and 0.1, 0.1 and 0.2, and 0.1 and 0.3, respectively.
[c]Mean and standard deviation for CV_C/CV_Q, $L - Q\,r^2$, b, $b\,r^2$, and p are 0.3 and 0.2, 0.8 and 0.2, (none) and 0.1, 0.5 and 0.3, and 0 and 0, respectively.
[d]Mean and standard deviation for CV_C/CV_Q, $L - Q\,r^2$, b, $b\,r^2$, and p are 0.2 and 0.1, 0.8 and 0.2, (none) and 0, 0.1 and 0.1, and 0.1 and 0.2, respectively.

cations, which have evident differences in their means and temporal trajectories before and after 1975 (see Figure 2). As a result of this split there are two data points used for Hubbard Brook Watersheds 3 and 6, reflecting the pre- and post-1975 export dynamics.

[17] No data were available to quantify the magnitude of solute stores at the sites, largely due to the challenges of

Table 4. Summary of Measures of Concentration Variability for the Nitrogen Species[a]

Species	Site	Subwatershed	Input (g m⁻² yr⁻¹)	Export (g m⁻² yr⁻¹)	CV_C/CV_Q	Error	$L - Q\ r^2$	b	$b\ r^2$	p
NH₄⁺[b]	Luquillo	ES	0.7	0	0.6	<0.01	0.43	0.06	0.01	0.3
		MS	0.7	0.01	1.52	<0.01	0.01	−0	0	0.7
		So	0.7	0	1.19	<0.01	0.02	−0.1	0.02	0
		Sa	0.7	0	0.64	<0.01	0.8	−0	0	0.7
		Ic	0.7	0.01	1.23	<0.01	0.49	0.23	0.03	0
	HJA	Mack	0.2	0	0.65	0.01	0.11	−0.1	0.01	0.03
		WS2	0.2	0	0.44	0.01	0.7	0.02	0	0.41
		WS8	0.2	0	0.39	0.02	0.06	0	0	0.9
		WS9	0.2	0	0.6	0.01	0.35	0.02	0	0.3
	Loch Vale	LO	0.1	0	0.62	<0.01	0.57	−0	0.02	0
	HB pre 75	WS3	0.2	0.02	0.42	0.05	0.31	0.02	0	0.8
		WS6	0.2	**0**	1.33	0.03	0.02	−0.1	0.03	0.1
	HB post 75	WS3	0.2	0.01	0.64	0.04	0.08	0.01	0	0.6
		WS6	0.2	0.01	0.69	0.04	0.06	−0	0	0.8
		WS7	0.2	0.01	0.79	0.11	0.55	−0.1	0.02	0.1
		WS8	0.2	0.01	0.73	0.12	0.63	−0.1	0.02	0.2
		WS9	0.2	0.01	0.96	0.12	0.65	0	0	0.9
TN[c]	Baltimore ES	BR	0.9	0.07	0.26	<0.01	0.98	0.08	0.08	0
		PB	0.9	0.01	2.51	0.06	0.73	−0.3	0.03	0
		MD	11	**0.2**	0.35	<0.01	0.91	−0	0	0.2
		GF	2.3	0.08	0.09	<0.01	0.91	−0	0.02	0
	Konza Prairie	Konza 1 year	0.5	0	0.34	<0.01	0.48	0.08	0.02	0
		Konza 2 year	0.5	0.01	0.48	<0.01	0.91	0.08	0.01	0.1
		Konza 4 year	0.5	0.01	0.53	<0.01	0.87	0.18	0.06	0
		Konza 20 year	0.5	0.05	0.39	<0.01	–	0.09	0.06	0.1
	Plum Island	CC	0.4	0	0.16	<0.01	0.64	−0.3	0.07	0.1
		CS	0.4	0.02	0.29	<0.01	0.05	−0.1	0.07	0
		SB	0.4	0.01	0	<0.01	0	0.08	0.02	0.1
NO₃⁻[d]	Luquillo	ES	0.3	0.02	0.28	<0.01	0.87	0	0	1
		MS	0.3	0.03	0.49	<0.01	0.49	0.21	0.02	0
		So	0.3	0.03	0.32	<0.01	0.62	−0.1	0.04	0
		Sa	0.3	0.03	0.16	<0.01	0.96	0.01	0	0.9
		Ic	0.3	0.05	0.31	<0.01	0.86	0	0	1
	HJA	Mack	0.2	0.01	0.39	<0.01	0.47	0.07	0.03	0
		WS2	0.2	0	0.43	0.04	0.68	−0.1	0.02	0.02
		WS8	0.2	0	0.99	0.03	0.05	0.09	0.02	0.03
		WS9	0.2	0	1.35	0.04	0.12	0.03	0	0.4
	Loch Vale	LO	0.2	0.05	0.35	<0.01	0.42	0.01	0	0.3
	HB pre 75	WS3	0.5	0.55	0.83	<0.01	0.15	0.27	0.09	0.02
		WS6	0.5	0.38	0.94	<0.01	0.35	0.53	0.26	0
	HB post 75	WS3	0.5	0.13	1.34	<0.01	0	0.03	0	0.65
		WS6	0.5	0.14	1.57	<0.01	0.01	0.27	0.03	0
		WS7	0.4	0.1	1.27	<0.01	0.15	0.39	0.08	0
		WS8	0.4	0.1	1.1	<0.01	0.09	0.12	0.01	0.29
		WS9	0.4	0.07	1.46	<0.01	0	0.21	0.02	0.08
	Fernow	WS4	0.1	0.09	0.16	<0.01	0.7	0.07	0.2	0
	Baltimore ES	BR	0.9	0.07	0.26	<0.01	0.98	0.12	0.12	0
		PB	0.9	0	1.42	<0.01	0.83	−0.4	0.13	0
		MD	11	0.19	0.14	<0.01	0.84	−0.1	0.02	0
		GF	2.3	0.08	0.09	<0.01	0.95	−0.1	0.07	0
	Konza Prairie	Konza 1 year	0.2	0	0.64	<0.01	0.81	0.09	0.01	0.1
		Konza 2 year	0.2	0	1.12	<0.01	0.6	0.28	0.1	0
		Konza 4 year	0.2	0	0.97	<0.01	0.76	0.15	0.03	0
		Konza 20 year	0.2	0.01	1.09	<0.01	0.04	0.22	0.05	0.2
	LVRW	B1	12	**3**	0.27	<0.01	0.95	−0.1	0.02	0
		B2	13	2.32	0.21	<0.01	0.97	−0	0	1
		H1	13	2.32	0.21	<0.01	0.97	−0	0.01	0.1
		M1	9.3	1.2	0.27	<0.01	0.92	0.06	0.04	0
	Plum Island	CC	0.3	0	0.45	<0.01	0.23	0.5	0.14	0
		CS	0.3	0	0.75	<0.01	0.6	0.08	0	0.3
		SB	0.3	0.01	0.08	<0.01	0.02	0.09	0.01	0.2

[a]The site with the highest annual exported load, used for normalization, is given in bold for each solute. See Table 2 for definition of the columns.
[b]Mean and standard deviation for CV_C/CV_Q, $L - Q\ r^2$, b, $b\ r^2$, and p are 0.79 and 0.34; 0.3 and 0.3, (none) and 0.1, 0 and 0, and 0.4 and 0.4, respectively.
[c]Mean and standard deviation for CV_C/CV_Q, $L - Q\ r^2$, b, $b\ r^2$, and p are 0.49 and 0.69, 0.7 and 0.4, (none) and 0.2, 0 and 0, and 0.1 and 0.1, respectively.
[d]Mean and standard deviation for CV_C/CV_Q, $L - Q\ r^2$, b, $b\ r^2$, and p are 0.67 and 0.48, 0.5 and 0.4, 0.10 and 0.2, 0.1 and 0.1, and 0.2 and 0.3, respectively.

Table 5. Summary of Measures of Concentration Variability for the Phosphorus Species[a]

Species	Site	Subwatershed	Input (g m⁻² yr⁻¹)	Export (g m⁻² yr⁻¹)	CV_C/CV_Q	Error	$L-Q\ r^2$	b	$b\ r^2$	p
PO_4^{2-}[b]	Luquillo	ES	0.12	0.001	0.44	0.01	0.98	0.04	0	0.48
		MS	0.12	0.003	5.39	0.01	0.4	−0.13	0.01	0
		So	0.12	0.001	0.72	<0.01	0.89	0	0	0.81
		Sa	0.12	0.002	0.2	0.01	0.9	−0.1	0.03	0.01
		Ic	0.12	0.002	0.61	0.01	0.82	−0.15	0.02	0.01
	HJA	Mack	0.03	0.001	0.2	0.01	0.86	−0.11	0.16	0
		WS2	0.03	0.002	0.08	<0.01	0.98	−0.05	0.16	0
		WS8	0.03	0.001	0.13	<0.01	0.86	−0.06	0.14	0
		WS9	0.03	0.002	0.15	<0.01	0.93	−0.06	0.15	0
	Loch Vale	Loch Vale	−	0.002	4.85	0.03	0.69	−0.05	0.02	0.15
	HB Pre 75	WS 3	0.01	0.003	0.58	0.05	0.77	−0.15	0.08	0.07
		WS6	0.01	0.003	0.45	0.05	0.5	0	0	0.98
	HB Post 75	WS3	0.02	0.003	0.72	0.02	0.09	−0.08	0.02	0.01
		WS6	0.02	0.003	0.82	0.02	0.04	−0.03	0	0.32
		WS7	0.01	0.002	1	0.06	0.01	−0.07	0.03	0.04
		WS8	0.01	0.002	0.49	0.03	0.32	−0.04	0.01	0.26
		WS9	0.01	0.006	0.66	0.01	0.01	0.02	0	0.73
	Baltimore ES	BR	−	0	0.96	0.06	0.62	0.12	0.04	0
		PB	−	0	1.01	0.06	0.78	0.07	0.02	0
		MD	−	0.001	0.38	<0.01	0.79	0.02	0	0.63
		GF	−	0.001	0.39	<0.01	0.9	−0.13	0.03	0
	Konza Prairie	Konza 1 year	−	0	0.93	<0.01	0.6	0.16	0.05	0.04
		Konza 2 year	−	0	1.27	<0.01	0.09	0.29	0.18	0
		Konza 4 year	−	0	0.92	<0.01	0.93	0.1	0.03	0.04
		Konza 20 year	−	0.002	1.61	<0.01	−	2.14	1	0
	LVRW	B1	7.40	0.016	2.19	<0.01	0.52	0.44	0.05	0
		B2	5.60	**0.02**	3.39	<0.01	0.61	0.34	0.05	0
		H1	5.60	0.02	3.39	<0.01	0.61	0.34	0.19	0
		M1	4.40	0.01	1.65	<0.01	0.49	0.23	0.06	0
TP[c]	Baltimore ES	BR	−	4E-04	2.64	0.06	0.47	0.14	0.02	0
		PB	−	5E-04	1.84	0.03	0.83	−0.05	0	0.3
		MD	−	0.002	0.51	<0.01	0.65	−0.05	0.01	0.09
		GF	−	0.001	0.28	<0.01	0.76	−0.02	0	0.63
	Konza Prairie	Konza 1 year	−	1E-04	0.36	<0.01	0.54	−0.01	0	0.8
		Konza 2 year	−	2E-04	0.28	<0.01	0.99	0	0	0.93
		Konza 4 year	−	5E-04	0.3	<0.01	0.98	0	0	0.96
		Konza 20 year	−	0.002	0.59	<0.01	−	0.01	0	0.91
	Plum Island	CC	−	1E-04	0.3	<0.01	0.23	−0.18	0.02	0.22
		CS	−	**0**	0.48	<0.01	0.79	−0.22	0.05	0
		SB	−	2E-04	0.1	<0.01	0.29	0.18	0.02	0.07
TSS[d]	Luquillo	MS	−	2.14	3.31	0.2	0.02	1.04	0.08	0
		So	−	1.58	1.22	0.1	0.09	0.24	0.17	0
		Sa	−	2.25	0.61	0.07	0.81	0.54	0.06	0
		Ic	−	6.26	2.23	0.09	0.42	1.02	0.33	0
	HJA	Mack	−	**7.06**	5.21	0.07	0.11	0.38	0.01	0.06
		WS2	−	2.97	3.92	0.16	0.4	0.33	0.07	0
		WS8	−	1.05	0.97	0.24	0.69	0.34	0.04	0
		WS9	−	0.59	1.65	0.17	0.05	0.25	0.15	0

[a]The site with the highest annual exported load, used for normalization, is highlighted for each solute. See Table 2 for definition of the columns.

[b]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 1.2 and 1.4, 0.6 and 0.3, 0.11 and 0.42, 0.1 and 0.2, and 0.2 and 0.3, respectively.

[c]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 0.7 and 0.8, 0.7 and 0.3, −0.02 and 0.12, 0 and 0, and 0.5 and 0.4, respectively.

[d]Mean and standard deviation for CV_C/CV_Q, $L-Q\ r^2$, b, $b\ r^2$, and p are 2.4 and 1.6, 0.3 and 0.3, 0.52 and 0.33, 0.1 and 0.1, and 0 and 0, respectively.

gathering these data [*MacDonald and Bennett*, 2009] [but see *Bruland et al.*, 2006; *Behrendt and Boekhold*, 1993; *Tsykin and Slessar*, 1985].

2.1.3. Metrics of Impact

[18] The exported mass loads in streamflow were taken as being the most robust available metric of the biogeochemical status of the studied watersheds, given the lack of stored mass estimates and the uncertainties in the magnitude of external inputs to the catchments. This flux is intensively and extensively sampled, and represents an integrated measure of the watershed behavior. Mass balance studies suggest that stream export is correlated to the degree of external impact on a catchment [*Aber et al.*, 1995; *Behrendt and Boekhold*, 1993; *Fenn et al.*, 1998; *Howarth et al.*, 1995; *Kahl et al.*, 1993], making it a viable proxy for the presence of a legacy store. To

allow variability in load to be compared between multiple solutes, however, a normalization is needed. We normalized the exported loads by the peak exported load (g m⁻² yr⁻¹) of each solute across all studied sites in the pooled data set. The normalizing values used are highlighted in Tables 2–5.

2.1.4. Metrics of Chemostatic Response

[19] Several different metrics have been proposed to quantify chemostatic behavior. *Godsey et al.* [2009] studied the exponent b in the relationship $C = aQ^b$, and defined chemostatic response as $b \approx 0$. *Basu et al.* [2010a] argued that chemostatic behavior implied near linearity in the annual load (L_T)–discharge (Q_T) relationship ($L_T = C_f Q_T$), as measured by the correlation coefficient (r^2). Both metrics are informative but are subject to limitations: first, the absence of a dependence of concentration on discharge (as indicated by,
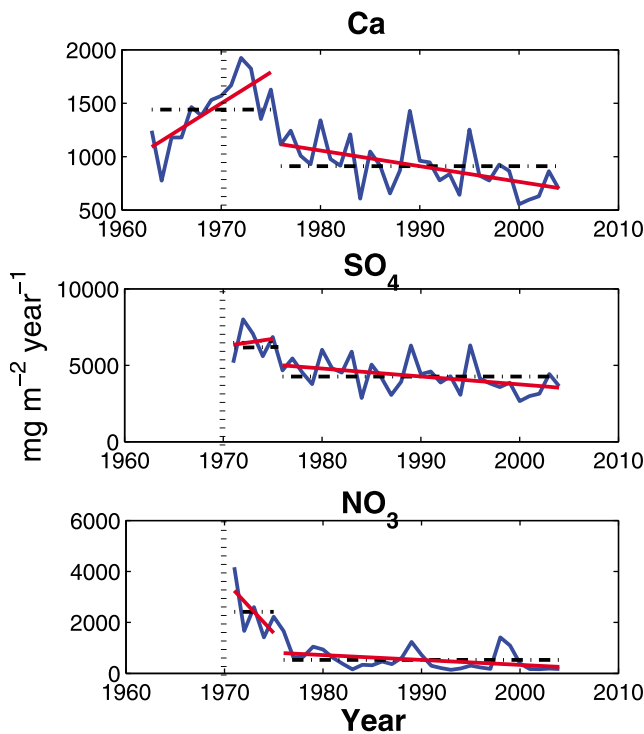
Figure 2. Trends in annual export of nitrogen species, sulfate, and calcium (as a representative base cation) from Hubbard Brook. Annual export is shown in blue, the dash-dotted black line indicates the mean annual export pre- and post-1975, and the time trajectory of export (linear trend) for the pre- and post-1975 periods is shown in red. Passage of the Clean Air Act in 1970 is indicated by the vertical dotted line. Although declining linear trends persist after 1975, the overall trend in the mean is smaller than interannual variability over the 1975–2005 time period.

e.g., $b \approx 0$) is not evidence that the variability in concentration is small, and second, conventional metrics regarding the goodness of fit of power law $C - Q$ responses with an exponent near zero (such as the r^2 value or the significance of the fit as measured by the f statistic) become uninformative as b approaches zero. Finally, the definition of load as $L_T = C_f Q_T$ complicates the interpretation of the $L_T - Q_T r^2$ value as a measure of linearity, due to the construction of L_T as a linear function of Q_T [but see *Basu et al.*, 2010a]. An alternative, nonparametric, measure of chemostatic response can be defined as the ratio of the coefficients of variation of concentration and discharge, where the coefficient of variation (or CV) is the standard deviation σ of a variable normalized by its mean μ. The proposed metric is the ratio

$$\mathrm{CV}_C/\mathrm{CV}_Q = \frac{\mu_Q}{\mu_C}\frac{\sigma_C}{\sigma_Q}. \tag{1}$$

[20] *Godsey et al.* [2009] proposed a simple null hypothesis that in-stream concentrations should reflect dilution of a fixed mass available for export (i.e., $C = aQ^{-1}$). A propagation of variance analysis from flow to concentration implies that for this null hypothesis, $\mathrm{CV}_C/\mathrm{CV}_Q = 1$. Chemostatic behavior could then be considered a case where the variability in concentration was highly buffered compared to this null hypothesis, i.e., $\mathrm{CV}_C/\mathrm{CV}_Q \ll 1$. Note that if $C = aQ^0$ (the

Godsey et al. [2009] criterion for chemostatic behavior), then $\mathrm{CV}_C/\mathrm{CV}_Q = 0$. It follows directly from $\mathrm{CV}_C/\mathrm{CV}_Q \ll 1$ that the variation in exported load is driven primarily by the variation in flow. This conclusion recovers the *Basu et al.* [2010a] criterion that for chemostatic conditions, load dynamics should be predictable from discharge variability. Similarly, the CV ratio approximates the ratio of the standard deviations of log(C) and log(Q), a metric used, but not presented, by *Godsey et al.* [2009]. Thus, $\mathrm{CV}_C/\mathrm{CV}_Q$ is consistent with previous metrics, but more general in its construction. Describing a condition of low $\mathrm{CV}_C/\mathrm{CV}_Q$ as chemostatic behavior, however, should not be overinterpreted. This use of the term chemostatic does not imply that concentrations are truly invariant, or uncorrelated with variations in flow. Nor is it intended to negate the importance of small variations in concentration in many contexts (e.g., for inference of hydrological travel paths, the short-term dynamics of source depletion, or prediction of in-stream habitat quality) [*Evans and Davies*, 1998; *McDonnell et al.*, 1991; *Rose*, 2003; *Walling and Foster*, 1975].

[21] Having identified appropriate metrics, we can define a quantitative test of hypothesis 1: that the mean and between-site variability of the ratio $\mathrm{CV}_C/\mathrm{CV}_Q$ for sites characterized by high normalized mass flux exports will be less than that for sites with low normalized flux exports.

2.1.5. Data Analysis

[22] For each subwatershed we obtained the time series of discharge and in-stream solute concentrations. Solute records with a large fraction (>10%) of data at the limit of detection were excluded from the analysis. We computed the ratio of the coefficients of variation for the full data record of each solute at each site. This ratio was plotted as a function of the normalized exported load of each solute. The normalizing loads used were the peak annual loads for each solute across the range of sites analyzed, as shown in Tables 2–5. To check the sensitivity of the results to the normalization factor, the analysis was repeated using the median annual loads. We grouped the plots according to the dominant sources for each solute type: geogenic solutes, primarily derived from mineral weathering within a catchment; deposition derived solutes which, despite having geogenic sources, rise to elevated levels in catchments primarily because of elevated inputs in wet or dry deposition; nitrogen species, which, although they may be associated with deposition, biological fixation and internal cycling, generally reach their highest concentrations due to fertilization; and phosphorus species, whose concentrations are also elevated by fertilization but which have substantially different reactivity and transport behavior from N.

2.1.6. Error Analysis

[23] A potential difficulty with using the coefficient of variation is its sensitivity to small changes in standard deviation if the mean (μ) of the sample is low. Thus there could be high uncertainty associated with the CV values, particularly if the limit of detection of the samples is close to the mean concentration μ. We used a propagation of uncertainty analysis to assess the effects of measurement error on the estimates of the mean and standard deviation of the sample ($u(x)/\sqrt{N}$ and $u(x)/\sqrt{2(N-1)}$, respectively, where $u(x)$ is the measurement error). The propagation of error rule

$$u(A \cdot B) = A \cdot B \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(B)}{B}\right)^2} \tag{2}$$
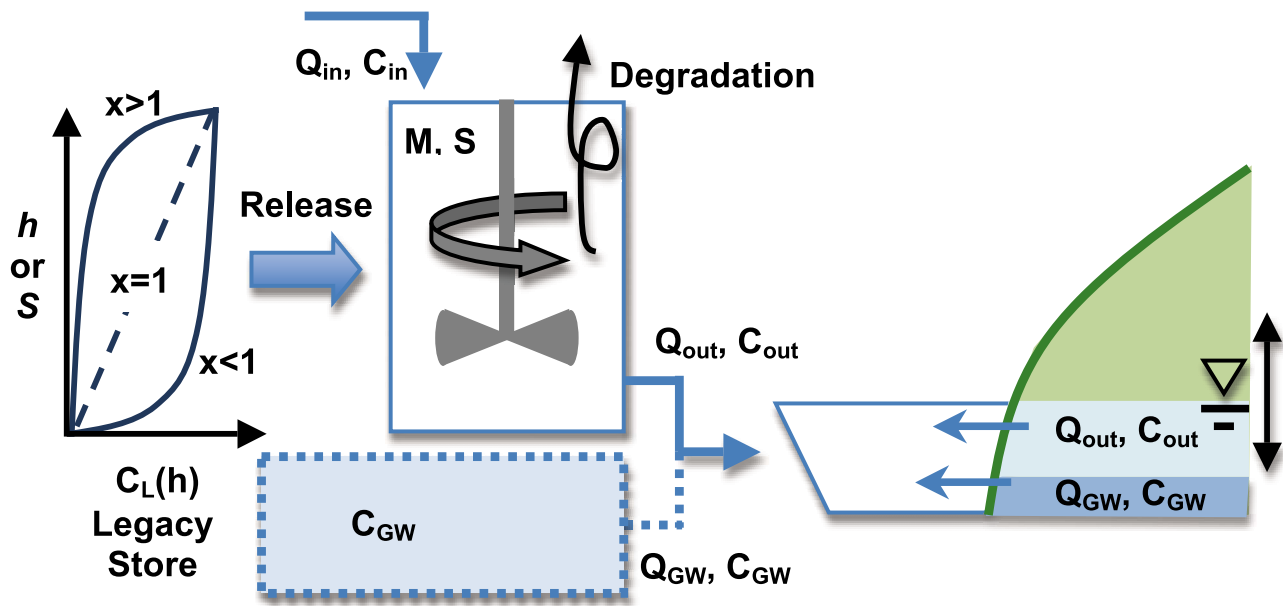
Figure 3. Conceptual diagram showing the saturated soil zone as a simple, continuously stirred reactor. The assumed power law distribution of stored mass with depth h of the saturated zone ($C_L(h) = vh^x$) is shown at the left. The two boxes in the conceptual model broadly correspond to a decomposition of subsurface water stores into a fluctuating zone with storage S and mobile mass M responsible for the generation of interflow and with low residence times and a permanent water table responsible for the generation of base flow. Water fluxes Q and associated concentrations C are also indicated.

was then applied recursively to estimate the uncertainty in the CVs and their ratio [*Graham et al.*, 1994]. To facilitate comparison with previous studies we also computed the linear $L - Q$ r^2 values, the b exponents for the best power law fit between C and Q, and the p value of this fit [*Fox*, 2008].

2.2. Theoretical Development

[24] To proceed at a similar level of complexity to the models proposed by *Godsey et al.* [2009], *Seibert et al.* [2009] and *Basu et al.* [2010a], but to account for temporal variation, we modeled streamflow discharge as the output of a continuously stirred linear reactor (CSTR) (shown schematically in Figure 3). This reactor represents the fluctuating component of the water table that responds to rainfall and generates interflow. Although the contribution of base flow is not explicitly simulated, adding relatively uniform base flow volumes and concentrations to the interflow contribution would dampen concentration variability. The derivation of the equations for the fluctuating component of the water table modeled by the reactor are provided in Appendix B. Briefly, the model consists of two coupled mass balance equations for water storage and mobile solute mass, in chemical exchange with the legacy store. Recharge is approximated as a Poisson process [*Botter et al.*, 2007a, 2007b], and concentrations of solute in recharge are treated as uniformly distributed random variables. The model assumes a linear storage-discharge relationship, perfect mixing, and a vertical distribution of mass in the legacy store (compare to *Seibert et al.* [2009]). The legacy store is assumed to be sufficiently large that the release dynamics from the store to the mobile phase can be approximated by a zeroth-order release. Finally, linear uptake/degradation kinetics are assumed to govern solute remove from the mobile phase, by,

e.g., biological uptake or degradation. The resulting model equations are

$$\frac{dS}{dt} = Q_{in} - \beta S \tag{3}$$

$$\frac{dM}{dt} = Q_{in} C_{in} - \beta M + \alpha_1 v S^{x+1} - \frac{k}{R} M, \tag{4}$$

where Q_{in} $[L/T]$ is the specific recharge volume, β $[T^{-1}]$ is the inverse hydraulic residence time, and S $[L]$ the volume of water stored in the saturated zone per unit area and is assumed linearly proportional to the depth of the water table h; that is, $S = Ah$; M $[M]$ is the mobile solute mass, C_{in} $[M/L^3/L^2]$ is the concentration in the recharge (taken, for simplicity, as being uniformly distributed between 0 and an arbitrary value C_{max}; note that since all model output is expressed in proportional terms, the value of C_{max} does not change the dynamics), α_1 $[T^{-1}]$ is proportional to the mass transfer rate from the legacy store to the mobile phase, C_L $[M/L^3/L^2]$ is the concentration available from the legacy store, distributed according to a depth profile $C_L(h) = vh^x$, where x represents the vertical distribution of solute and v is a constant determining the magnitude of the mass store with units that depend on x. Note that the use of a power law distribution for the vertical solute profile is primarily for analytical flexibility by allowing concentrations to increase or decrease at different rates with depth. k $[t^{-1}]$ is a rate constant representing linear uptake or degradation and R is the retardation factor.

[25] Nondimensionalizing these equations for the case where $x = 0$ (uniform vertical mass distribution) (see Appendix B) produces three control parameters for the system, given by the ratios of the legacy mass transfer rate to the inverse residence time: $\gamma^* = \alpha_1 v/\beta$, the ratio of the degradation rate to the inverse residence time, $k^* = k/R\beta$ and
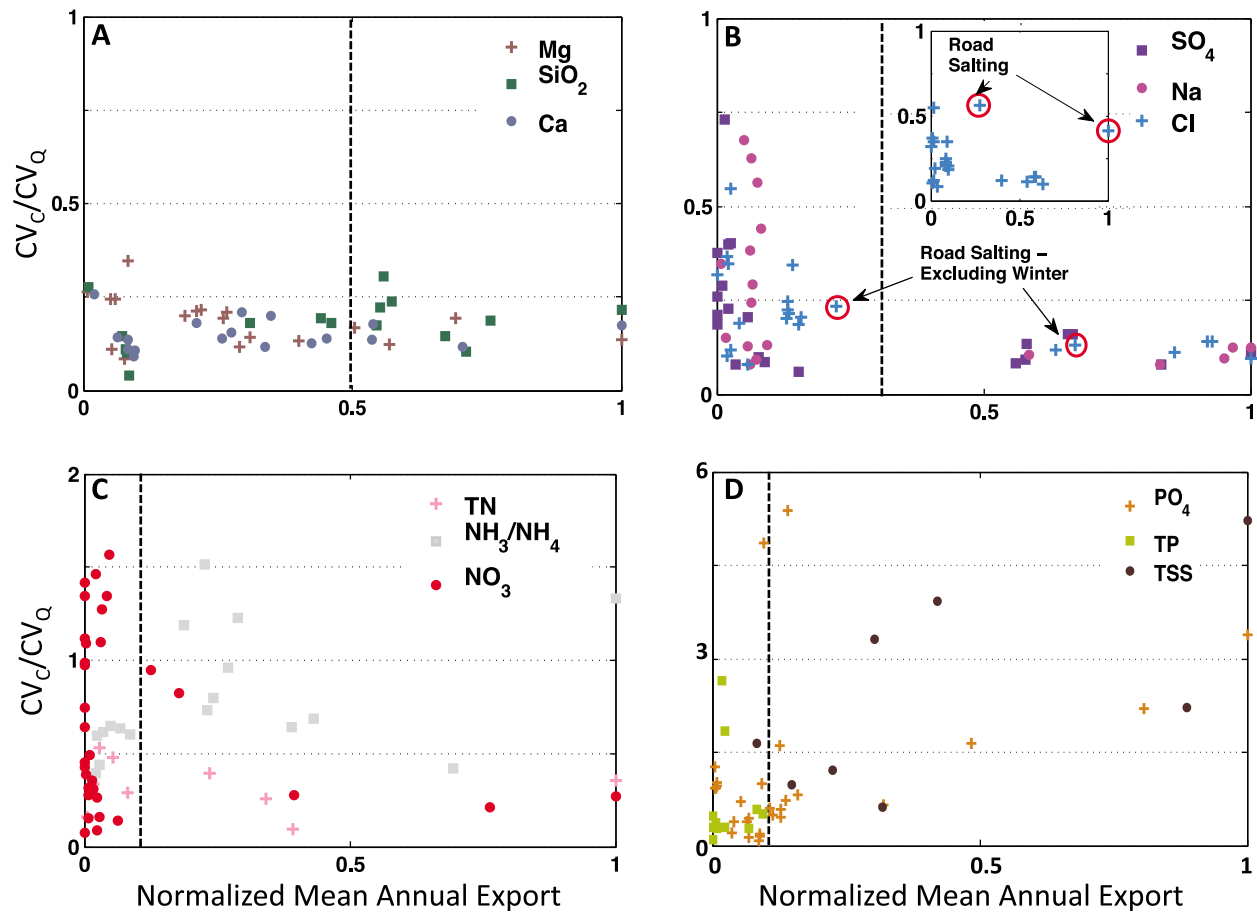
Figure 4. Pattern in the coefficients of variation of concentration and flow for (a) geogenic species, (b) exogenous inorganic salts, and (c) nitrogen species with increasing mean annual exported load across the sites. (d) The same pattern in the CV ratio for phosphorus species and total suspended solids (TSS). The inset in Figure 4b shows the pattern in chloride export if the full annual chloride export from the Baltimore Ecosystem Study sites was retained. The data in Figure 4b show this pattern if winter chloride export, which is impacted by large spikes of chloride from road salting, is excluded. Vertical dashed lines indicate the point at which the data set was (visually) divided into high- and low-export watersheds for statistical analysis.

the ratio of the recharge frequency λ to the inverse residence time $\lambda^* = \lambda/\beta$. The emergence of these time constants as control parameters is consistent with stochastic formulations for saturated zone export dynamics [*Botter et al.*, 2006]. Conceptually this formulation is comparable to that adopted by *Seibert et al.* [2009] in that the model primarily treats the fluctuating depth of the water table in the unsaturated zone as the driver of streamflow discharge and solute export.

[26] We used this simple representation of storage, mass release, mass uptake and mixing to explore the dependence of fluctuations in the concentration leaving the reactor, C_{out} (i.e., $\beta M/S$) relative to fluctuations in the discharge (i.e., βS) on the control parameters describing the recharge frequency, the degradation/uptake rate, and the rate of mass transfer from the legacy store to the mobile phase.

3. Results

3.1. Empirical Results: CV_C/CV_Q With Changing Exports

[27] Plots of the CV_C/CV_Q ratio with normalized export for four categories of solute (geogenic, exogenous inorganics,

nitrogen species and phosphorus species) are provided in Figure 4. The error in the CV_C/CV_Q ratio as computed in equation (2) was included in the plots, but is generally too small to be visible behind the data points. The error values, the computed CV_C/CV_Q ratio, and other metrics of chemostatic response are listed for reference in Tables 2–5.

3.1.1. Geogenic Solutes

[28] For the geogenic species, the exported loads spanned approximately 2 orders of magnitude ($\approx$0.01–1 g m^{-2} yr^{-1} for Mg^{2+}, $\approx$0.05–2.7 g m^{-2} yr^{-1} for Ca^{2+}, and $\approx$0.07–7.8 g m^{-2} yr^{-1} for silicate). As shown in Figure 4a, the mean CV_C/CV_Q was 0.17 (range 0.15–0.19) with standard deviation 0.06 (range 0.04–0.07), i.e., uniformly well below 1. Furthermore there was no trend in the mean value of the CV_C/CV_Q ratio across the 2 orders of magnitude of variation in exported loads in the data set. Reanalyzing the data using median rather than mean annual export values had no effect on the observed trends. The additional metrics of chemostatic behavior shown in Table 2 reflect the results presented by *Godsey et al.* [2009] with low CV_C/CV_Q, high $L - Q$ r^2, and low, negative b exponents (mean -0.14 and standard deviation of 0.08) for all solutes. That is, for

geogenic solutes all metrics were consistent with each other and pointed to near-chemostatic responses. These values can be taken as a reference case to compare the other solutes against. We define a chemostatic CV ratio as being within two standard deviations of the mean geogenic CV_C/CV_Q, that is ≈ 0.3.

3.1.2. Inorganic Solutes With Exogenous Sources

[29] Exported loads of exogenous salts ranged over 2–3 orders of magnitude (≈ 0.007–6.5 g m^{-2} yr^{-1} for SO$_4^{2-}$, ≈ 0.02–2.4 g m^{-2} yr^{-1} for Na$^+$ and ≈ 0.006–3 g m^{-2} yr^{-1} for Cl$^-$). As shown in Figure 4b, a pattern of high CV_C/CV_Q occurred for sites with low exported loads, with lower CV_C/CV_Q for the sites with high loads. We visually divided the sites according to the observed trend in variability. For sites characterized by low exported loads, the CV_C/CV_Q ratio ranged between $\ll 0.1$ and 0.8 (mean 0.27) and was variable between sites (standard deviation 0.17 (range 0.12–0.2) for all solutes). As shown in Figure 4b this variability was considerably reduced for samples in the top 50% of export conditions. In this group, the CV_C/CV_Q was more consistent between sites and solutes, and was constrained between 0 and 0.2, with a mean of 0.11 (the means of the three solutes individually ranged from 0.1–0.12), with a standard deviation of 0.03 (range 0.02–0.035). The variability of in-stream concentrations of Na$^+$, Cl$^-$ and SO$_4^{2-}$ at sites with high export was comparable to the variability in the concentrations of geogenic constituents. Two sites appeared to act as exceptions to this trend, exhibiting CV_C/CV_Q ratios of >0.4 for chloride despite having large exported loads (the statistics quoted above exclude these sites). These two sites, from the Baltimore Ecosystem Study, are both impacted by surface road salting for deicing purposes, resulting in large pulses of salt during snowmelt events, and elevating the CV_C/CV_Q ratio. The impact of this salting persists beyond the winter snowmelt periods, however, and if the Baltimore data are analyzed for the spring-fall months only, export remains elevated, but the CV_C/CV_Q values are greatly reduced. Figure 4b shows the modified Baltimore records (spring-fall data only) and the raw chloride data as an inset. The additional metrics of chemostatic behavior shown in Table 3 were again generally consistent across the solutes, with low CV_C/CV_Q being associated with high $L - Q\ r^2$, and low and negative b exponents, and vice versa. Some exceptions, with high CV_C/CV_Q in spite of low b values and high $L - Q\ r^2$ values, arose, including Na$^+$ concentrations in Hubbard Brook Watershed 3, SO$_4^{2-}$ concentrations in the Pond Branch Watershed, or Cl$^-$ concentrations at Baisman Run. These exceptions reflect the greater sensitivity of the CV_C/CV_Q metric to within-year variation than the b and $L - Q\ r^2$ metrics, as (1) $b \approx 0$ does not imply low variability in the C time series, and (2) while episodes of unusually high concentration (such as the snowmelt pulses in Baisman Run) may greatly increase σ_C, unless they also contribute substantially to the annual loads, they may be insufficient to disrupt a near-linear $L - Q$ relationship.

3.1.3. Nitrogen Species

[30] The pattern of the CV ratio for exported nitrogen species with normalized export varied with the nitrogen species considered (Figure 4c). The range of exported loads was also variable (0.0005–0.02 g m^{-2} yr^{-1} for ammonium, 9×10^{-5} to 3 g m^{-2} yr^{-1} for nitrate and 0.001–0.08 g m^{-2} yr^{-1} for TN). There was limited overlap between sites providing NO$_3^-$ data and sites providing TN data. For ammonium, the

CV_C/CV_Q was high (mean 0.79) and variable (standard deviation 0.34). Some sites had $CV_C/CV_Q > 1$, implying that the relative variability in ammonium concentrations exceeded the variability in stream discharge. Although the CV_C/CV_Q ratios were variable across the sites (and in practice, the highest ratios occurred at the Luquillo sites, likely reflecting the effect of hurricanes in releasing large pulses of ammonium in these sites [Schaefer et al., 2000]), the CV_C/CV_Q across all sites were consistently larger than observed in either geogenic or inorganic species. By contrast, the overall relationship between nitrate export and variability resembled that of the exogenous inorganic species, where sites that exported smaller loads were characterized by large CV_C/CV_Q ratios (mean 0.70, standard deviation 0.49) that decreased as export increased, albeit less abruptly than in the case of the exogenous salts. The lowest values of CV_C/CV_Q for NO$_3^-$ were in the range of 0.2–0.4, comparable to the geogenic species. Although suggestive, the data at high export levels remain scarce. The trends were robust to a change in the normalization to median values. Given the restricted range of sites where TN data were available, determining any trend in TN with export was not possible. The difficulty in relying on the power law exponent b as a measure of chemostatic response was well illustrated by the behavior of the nitrogen species shown in Table 4. Numerous sites displayed $b \approx 0$, but nonetheless exhibited a wide range of variability as measured by CV_C/CV_Q, and a similarly wide range of $L - Q\ r^2$ values.

3.1.4. Phosphorus Species

[31] Phosphorus CV_C/CV_Q ratios, as shown in Figure 4d, were globally larger than those observed for any of the other species under consideration (mean 1.22, standard deviation 1.4). The mean annual loads ranged from 9×10^{-5} to 0.02 g m^{-2} yr^{-1} for phosphate and 7×10^{-5} to 0.02 g m^{-2} yr^{-1} for TP. Discerning a trend in the CV_C/CV_Q ratios with increasing mean annual exported load was not possible based on the available data (Figure 4d). While legacy stores of phosphorus species are known to accrue [Bruland et al., 2006], the export dynamics of phosphate and TP are influenced by the sorption of phosphorus onto soil particles, including those from the streambed sediments [Sharpley, 1995]. High mean annual export may therefore reflect the both the presence of a legacy store and the likelihood of large sediment transport events. For this reason we compared the phosphorus CV ratios to those of total suspended solids, which are also expected to be strongly related to stochastic erosion events. TSS exhibited similarly high CV_C/CV_Q values to P species. The P and TSS analyses were also stable if the analyses were repeated with median annual exports. As with nitrogen, the power law exponent b proved an inconclusive measure of chemostatic responses when compared with the CV_C/CV_Q ratio and the $L - Q\ r^2$ (Table 5).

3.1.5. Statistical Analysis of Observed Patterns

[32] The data presented in Figures 4b and 4c and Tables 3–4 show a common pattern: that beyond a threshold in the normalized export, determined by inspection of the data, (1) the variability and (2) the mean of the CV_C/CV_Q ratios declined. By contrast, this pattern is absent in Figure 4a (Table 2), and less clear in Figure 4d.

[33] Two statistical tests were applied to assess these claims. The decline in the variability of the CV_C/CV_Q ratios was assessed using Bartlett tests for homogeneity of variance (where $p > 0.05$ is taken as implying homogeneous variance between two groups of samples). The decline in the

Table 6. Summary Statistics From the Analysis of the Patterns in CV Ratio With Export[a]

		Low Export			High Export					
	Threshold	Low n	Mean CV_C/CV_Q	Standard Deviation CV_C/CV_Q	High n	Mean CV_C/CV_Q	Standard Deviation CV_C/CV_Q	Bartlett Test p	One-Way t Test p	Two-Way t Test p
Mg	50%	9	0.21	0.07	9	0.16	0.04	0.24	0.06	0.06
SiO$_2$	50%	8	0.15	0.07	8	0.2	0.06	0.23	0.07	0.2
Ca	50%	10	0.1524	0.0509	10	0.1481	0.0316	0.24	0.7	0.84
Geogenics	50%	27	0.17	0.06	27	0.18	0.05	0.5	0.56	0.65
SO4	30%	15	0.29	0.18	7	0.12	0.03	**0.005**	**1.00E-05**	**0.02**
Na	30%	13	0.32	0.21	5	0.11	0.02	**0.003**	**1.00E-05**	**0.04**
Cl	30%	14	0.25	0.12	8	0.12	0.02	**6.00E-04**	**1.00E-05**	**0.02**
Exogenous Salts	30%	42	0.27	0.15	20	0.12	3.00E-02	**5.00E-11**	**1.00E-15**	**1.00E-04**
NO$_3$	10%	27	0.7	0.5	6	0.46	0.33	0.42	0.13	0.26
	20%	29	0.71	0.48	4	0.24	0.03	**0.0007**	**1.00E-03**	0.06
TN	20%	9	0.61	0.85	4	0.3	0.13	0.8	**1.00E-02**	0.45
NH$_3$	20%	10	0.64	0.23	9	0.92	0.36	0.24	0.08	0.08
P means	10%	27	1.0121	1.3239	13	2.2562	1.1723	0.77	0.06	0.07
TSS means	20%	4	1.79	1.05	4	3	2	0.32	0.33	0.32
TSS medians	20%	4	3.5	1.5	4	1.25	0.7	0.24	**0.007**	**0.03**

[a]Threshold indicates the normalized export value at which the sites were divided into low-export and high-export groups; n indicates the number of sites in each group and p values are provided for the Bartlett and t tests. For the Bartlett test a low p value indicates significant differences in the variance between high and low export, while for the t tests a low p value indicates a significant difference in the mean CV ratios between high and low export. Bold indicates that the low- and high-export watersheds had significantly different CV ratios at a 5% significance level. Mean and standard deviations of the CV ratios for each group are also provided.

mean of the CV_C/CV_Q ratios was assessed using t tests for difference on the mean. First, a two-way t test, which determined if the two sample means were significantly different, was used. For comparison, one-way t tests, which repeat this analysis but neglect the uncertainty in the estimation of the mean CV ratio of the sites with low export, were also performed. Given the high variability in the CV ratios at low export, both tests were considered informative. The most robust indicator of difference in the mean would be indicated by a low p value obtained with the two-way test. The most robust indication that the means were unchanged would be indicated by high p values obtained by the one-way test. Mixed results suggest that further investigation of the variation of the CV ratio with export would be warranted. The results of the statistical analysis are provided in Table 6. They demonstrate that there is no significant change in mean or variance of the CV ratio with export for geogenics, and that there are statistically significant reductions in both mean and variance with increasing export for the exogenous inorganic species. The statistics are less clear for N species: if the threshold is selected at 20% of the peak loads then statistically significant differences in both mean and variance are found for NO_3^-. This metric effectively divides the agricultural sites from other sites, and suggests that their export dynamics are significantly different. If the urban sites are included with the agricultural sites (equivalent to dividing the population at 10% of the peak loads), however, then the differences are no longer significant. No significant trends with export were found in the TN or NH_3/NH_4 data. P and TSS data remain exceptional in showing no consistent CV_C/CV_Q behavior (i.e., they do not behave like the geogenics, exogenous inorganics or nitrate). We attribute this to the threshold-driven nature of sediment transport (meaning that large export events occur episodically) and the dependence of P export on sediment movement. While the trends in N are suggestive, further data at high export sites will be needed to allow robust statistical analysis of these trends.

3.1.6. Comparison With Other Measures of Chemostatic Behavior

[34] Tables 2–5 show that $b \approx 0$ did not imply low CV_C/CV_Q or high $L - Q\ r^2$, and that the occurrence of b exponents that differed greatly from zero was very low. Only $\approx 20\%$ of all the samples taken, (and $\approx 25\%$ and $\approx 30\%$ of nitrogen and phosphorus species, respectively) had $|b| > 0.2$, outside the range of chemostatic behavior defined by *Godsey et al.* [2009]. By comparison, 45% of the samples, and 75% of N and P species, had CV ratios exceeding the threshold of $CV_C/CV_Q = 0.3$ determined with respect to the geogenic solutes, suggesting that the CV ratio offered additional capacity to discriminate chemostatic behavior. Of all the sites that did have $|b| > 0.2$, for only five samples, that is 11% of sites with $|b| > 0.2$ or approximately 3% of the total data set, did a power law explain more than 40% of the variance in the concentration. The remaining sites with $|b| > 0.2$ displayed weak positive or negative trends in C with Q, suggesting that explanations for concentration variation beyond trends in discharge must be sought. The CV ratio of course does not explain any of the variance in C, but avoids making any assumptions about an underlying C-Q relationship, which appears to be appropriate given these results. Linear load-discharge relationships prevailed for geogenic and inorganic solutes ($r^2 \approx 85\%$), and were less frequent for nitrogen, phosphorus and suspended solids ($r^2 \approx 0.5$–0.65). Linear load-discharge relationships for nitrogen species were found in urban and agricultural sites. The r^2 of the $L - Q$ relationships for phosphorus in agricultural sites were low (0.5–0.6) when compared to observations made at much larger agricultural sites ($r^2 \approx 0.8$–0.9 [*Basu et al.*, 2010a]), potentially reflecting spatial-scale dependence in phosphorus export behaviors.

3.2. Model Output

[35] The continuously stirred reactor model introduced in section 2.2.1 was used to investigate the legacy store hypothesis and changing CV_C/CV_Q behavior in simple theoretical terms. Figure 5 shows representative model
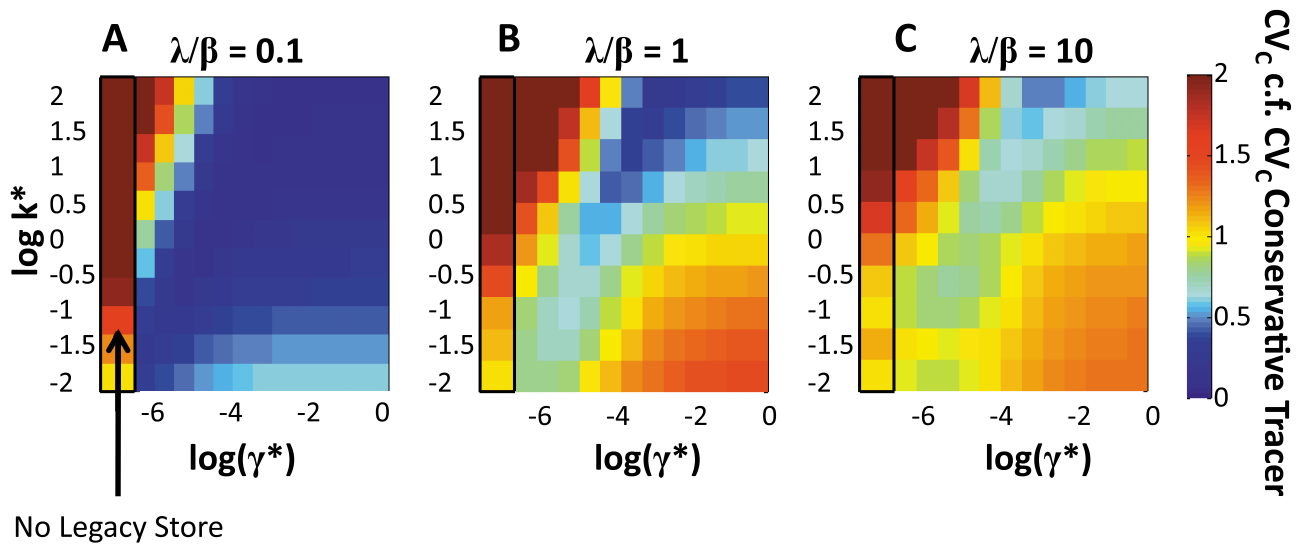
Figure 5. Variations in the CV_C/CV_Q ratio relative to that of a conservative tracer as a function of the scaled time constants for removal processes ($k^* = k/R\beta$), source processes ($\gamma^* = \alpha_1 v/\beta$), and rainfall interarrival time (λ/β). Thus, k^* or $\gamma^* \ll 1$ imply that chemical processes occur more slowly than physical transport in the reactor, while k^* or $\gamma^* \gg 1$ imply rapid chemistry relative to physical residence times. Black boxes show a reference case with zero mass transfer from the legacy store (shown separately because $\log(\gamma^* = 0) = -\infty$). The CV_C/CV_Q ratio for the conservative tracer was 0.5 for all cases, with variability in C driven by stochastic concentrations in the recharge. The role of a legacy store in buffering concentrations was most evident where the recharge interarrival time is comparable to or greater than the residence time in the reactor (i.e., $\lambda/\beta \leq 1$).

output as a function of the control parameters for $x = 0$, with $\beta = 0.01$ and k, α and λ (and their ratios) varying over several orders of magnitude (note that the axes are presented on log scales). Other values of x are discussed below. The specific choice of β does not alter the model behavior, as output will be shown in terms of rate parameters normalized to β. The model outputs are shown as the proportional increase or decrease in CV_C/CV_Q for a reactive tracer relative to a conservative tracer (for which CV_C/CV_Q is approximately 0.5 in all cases, because of the uniform distribution of incoming concentrations in rainfall). The plot essentially shows $CV_C/CV_{Ctracer}$ since the flow dynamics are identical in each case. Where recharge is infrequent or comparable in time scale to flow generation (that is, $\lambda/\beta \leq 1$, Figure 5a), the presence of the mass store reduces the CV_C/CV_Q of streamflow relative to a conservative tracer for a range of parameters describing a curve in (k^*, γ^*) space approximately described by the line $k^*/\gamma^* \approx 5$. Relative values of k^* and γ^* divide the phase space into three broad domains. Domain 1 lies above the $k^*/\gamma^* \approx 5$ line. Within this regime, depletion dynamics dominate, the catchment is solute limited and CV_C/CV_Q is large compared to a conservative tracer (reminiscent of, e.g., nitrogen dynamics in the N-limited sites of Luquillo or H. J. Andrews). Domain 2 lies in the bottom right of the plots, where large mass inputs from the legacy store are not buffered by uptake or back reactions, leading to large CV_C/CV_Q ratios. CV_C/CV_Q ratios are minimized where a chemical steady state can be defined by the combination of mass release and degradation processes, which is achieved in domain 3 in the center of the plots. This steady state occurs most readily where the residence time in the reactor is long compared to the frequency of flushing (i.e., a low λ/β ratio), implying that there is

sufficient time for the steady state conditions to arise. As λ increases relative to β (Figures 5b and 5c), the efficacy of the chemical controls in stabilizing concentration is reduced and the range of values of k^* and γ^* over which chemostatic conditions can be achieved is narrower (the narrow blue band in Figure 5b). This observation is analogous to the requirement in the *Seibert et al.* [2009] model that residence times within the riparian zone must be long enough for chemical equilibrium to occur. Furthermore, repeating the analysis with $x \neq 0$ (not shown) showed that chemostatic behavior couldn't be recovered unless $x \approx 0$, recapitulating the *Seibert et al.* [2009] requirement of spatial homogeneity for chemostatic responses to occur. Where $\lambda \gg \beta$ the CV_C/CV_Q ratios resemble those of a conservative tracer for a wide range of k^* and γ^* values, which simply reflects the dominant role of rainfall in determining the in-stream concentrations. Note that $\lambda/\beta = 10$ represents an upper bound on the plausible range of λ/β [*Botter et al.*, 2007a, 2007b, 2010].

4. Discussion

4.1. Hypothesis 1: Emergence of Chemostatic Behavior

[36] The empirical component of this study was motivated by the hypothesis that chemostatic behavior should emerge as a general phenomenon as the magnitude and frequency of external inputs to a catchment increase, and should not be specific to particular solutes or land uses. We argued that this hypothesis translated quantitatively into the prediction that as normalized exported loads increased across multiple catchments, the ratio CV_C/CV_Q would decline in the mean and become more consistent between sites. The empirical results here are broadly consistent with this hypothesis: as the normalized exported loads increased, streamflow solute

concentrations become less variable with respect to discharge (as reflected in the low CV_C/CV_Q), the differences in CV_C/CV_Q ratios between catchments were less pronounced, and the CV_C/CV_Q values approached those of geogenic constituents. This convergence was most obvious and statistically significant for chloride, sodium and sulfate, while suggestive patterns were also seen for nitrate species. These patterns were preserved using median annual exported loads instead of the mean, thereby damping the effect of extreme events on the export behavior. The emergence of similar trends across different sites and for different solutes supports the hypothesis that a common mechanism is involved in reducing the CV ratio.

[37] The exceptions to the observed pattern of reducing CV ratios were highly reactive species such as ammonium [*Patrick and Reddy*, 1976], total suspended sediments and sediment bound solutes such as phosphate and TP. These exceptions had elevated CV_C/CV_Q ratios compared to other species and did not display obvious trends with the normalized export. These exceptions, however, may still be consistent with the legacy storage mechanism. For instance typical half lives for ammonium in shallow soils are on the order of 13 days [*DeSimone et al.*, 1996], compared to decades for soil organic N [*Addiscott*, 1996], suggesting that no legacy store is likely to be present at all for ammonium species. The high CV ratios seen for P species may be due to the association of strongly sorbing P species with episodic exports [*Hart et al.*, 2004], elevating the CV of concentration. Similar nonchemostatic behavior was observed by *Basu et al.* [2010a] for pesticides such as atrazine at annual time scales. Many pesticides are also strongly sorbing species with transport primarily occurring during large storm events [*McGrath*, 2007]. Mean annual export may therefore not prove to be the most informative metric of impact for elucidating the potential effects of a legacy store on P species.

4.2. Hypothesis 2: Theoretical Predictability of Chemostatic Behavior

[38] We assessed whether the presence of legacy stores would promote chemostatic behavior using a simple model. The model results suggested that slow mass release from legacy stores reduces CV_C/CV_Q ratios by comparison to conservative tracers. Reductions in CV_C/CV_Q arose where removal processes, associated with formation of the legacy store or with secondary transformations such as N uptake or denitrification, were fast compared to the rate of mass release from the legacy store, so that chemical steady states were reached, but not so rapid that the system became solute limited. Similarly, the model suggested that as exports were increasingly dominated by mass introduced in rainfall, the efficacy of the legacy store as a chemostatic buffer was reduced. The model also implied that chemostatic responses were associated with spatially homogeneous distributions of mass (i.e., that $x \approx 0$), consistent with the predictions of *Basu et al.* [2010a] and *Seibert et al.* [2009]. If the presence of a legacy store corresponds to increased total mass exchange, then the model predictions were also consistent with the reduction in variability in species such as nitrate from low- to high-N sites (assuming similar uptake kinetics k^*): for low mass release rates (γ^*) the variability in concentration was high relative to flow, while for high γ^* this variation was substantially damped.

[39] Given the plausibility of the legacy storage mechanism for promoting chemostatic responses, is it possible that such legacy stores were present at the studied sites with low CV_C/CV_Q ratios and high exported loads? In the case of nitrogen, leaching from impacted watersheds is associated with a saturation of N stores [*Aber et al.*, 1995; *Fenn et al.*, 1998], which has been linked to reductions in the variability of nitrogen export in streamflow at several sites [*Kahl et al.*, 1993; *Ohrui and Mitchell*, 1997; *Ohte et al.*, 2001]. In agricultural settings, organic nitrogen stores have been estimated at 1410 kg/ha [*Addiscott*, 1996], suggesting that the build up of large internal mass stores of N is certainly possible. The development of large mass stores of phosphorus in agricultural catchments is also well documented [*Behrendt and Boekhold*, 1993; *Reddy et al.*, 2005; *Whalen and Chang*, 2001]. Similarly, elevated soil sulfate stores [*Adams et al.*, 1997] are known to accrue in watersheds subject to prolonged acid deposition, with the store likely to be associated with pH-dependent ion exchange [*Mitchell et al.*, 1992]. In Hubbard Brook these stores are distributed in a near-uniform fashion, and annual sulfate export is spatially homogeneous in the lower-order watersheds [*Likens et al.*, 2002]. Mechanisms for developing a recalcitrant store of sodium and chloride are more questionable given the high solubility of these ions. Storage processes could feasibly involve cation and anion exchange, with the latter being most feasible in catchments like Luquillo with tropical, volcanic soils containing iron and aluminum oxides [*Silver et al.*, 1994], although storage of divalent ions (calcium, magnesium, sulfate) would be more likely than storage of monovalent sodium or chloride. More generally, stores of mobile sodium or chloride in groundwater may be responsible for increased exports and reduced variability of export of these salts [*Howard and Haynes*, 1993]. Thus both physical constraints, such as long residence times in groundwater, and chemical constraints, such as storage of solutes in a chemically recalcitrant form, may reduce the flushing of solute from the system and can be associated with the formation of a legacy store [*Brusseau and Rao*, 1990; *Rao et al.*, 1974, 1980]. Although a wide range of processes are linked to the variability of exported concentrations in both impacted and pristine catchments [*Likens et al.*, 2002; *Lischeid*, 2001; *Shanley and Peters*, 1993], in the presence of a legacy store the concentration fluctuations they induce may represent a comparatively smaller proportion of the exported concentrations [cf. *Gbondo-Tugbawa et al.*, 2002], reducing the overall CV of concentration. The consistency of chemostatic responses in geogenic solutes [*Godsey et al.*, 2009; *Walling and Foster*, 1975], nutrients in agricultural catchments [*Basu et al.*, 2010a], sulfate in catchments with a history of acid deposition [*Adams et al.*, 1997; *Likens et al.*, 2002], and sodium and chloride ions in high-input catchments [*Howard and Haynes*, 1993] is suggestive of a general mechanism reducing the CV_C/CV_Q. The results here are consistent with the hypothesis that it is the presence of a large, spatially homogeneous and recalcitrant mass source that reduces the relative variability of concentration in stream discharge.

5. Conclusions

[40] Prediction of watershed biogeochemical responses to variation in climatic forcing is a challenging task in many

watersheds due to the wide range of processes that can influence the availability and mobility of solutes in runoff [*Anderson*, 1995; *Elofsson*, 2010; *Hamilton*, 2010; *Justic et al.*, 2007; *Porcal et al.*, 2009]. Consequently, detailed runoff generation models must be coupled to complex biogeochemical cycling models (e.g., RHESSys [*Band et al.*, 2001], MAGIC [*Hruska et al.*, 2002], SWMM [*Borah et al.*, 2006], SWAT [*Santhi et al.*, 2001]) in order to predict streamflow concentration dynamics at high frequencies. In many impacted catchments, however, the primary goal of prediction is to determine the magnitude of chemical loads exported from the catchment to a receiving water body [*Borsuk et al.*, 2002; *Karr and Yoder*, 2004]. As indicated by the low CV_C/CV_Q ratios for certain solutes (e.g., nitrate) in heavily impacted catchments, concentrations often do not vary significantly in time, and thus loads can be predicted as a simple function of discharge [*Basu et al.*, 2010b; *Borsuk et al.*, 2004]. As a further implication of these findings, chemostatic responses could be used as tractable indicators of the presence of large mass stores within catchments, with important implications for the time scales of restoration and recovery of impacted catchments.

[41] The results from the data analysis suggest that, for exogenous inorganic species and potentially nitrate, CV_C/CV_Q ratios declined as mean biogeochemical impacts increased, with CV_C/CV_Q ratios under conditions of high impact approaching the more uniform behavior of geogenic solutes. Exceptions to this trend, specifically ammonia/ammonium species and phosphorus species, may be linked to rapid reaction rates and sediment-bound transport properties, respectively. A decline in CV_C/CV_Q ratio with the presence of an internal mass store was supported by the CSTR model which suggested that as mass release rates from such a store increased, the variability of in-stream concentrations declined relative to a conservative tracer. The model suggests that chemical transformations in the subsurface can promote chemostatic responses under certain circumstances. The buffering of concentration variability, however, appears to be a function of the biogeochemical rate constants and transport mechanisms, the site hydrology and the climatic forcing. Given the simplicity of model used (comparable to the conceptual models of *Seibert et al.* [2009], *Godsey et al.* [2009], and *Basu et al.* [2010b]), elaborating on its mechanistic formulation could allow further investigation of these processes. Although chemostatic responses appear to be a pseudo steady state feature of impacted catchments, the factors that determine the time scales and trajectories at which these pseudo steady states are reached remain unclear. Studies of watershed response to acidification indicate that land use history, vegetation dynamics and initial soil concentrations alter the magnitudes of solute storage in a catchment [*Aber and Driscoll*, 1997; *Goodale and Aber*, 2001]. Strong hysteresis in catchment biogeochemistry suggests that recovery of impacted catchments to unimpacted states is likely to be very long term for many solutes and sites [*Behrendt and Boekhold*, 1993; *Bruland et al.*, 2006; *Hill et al.*, 2002; *Whalen and Chang*, 2001]. Spatial variability in the sensitivity of catchment hydrochemistry to land use change is not well understood, but the importance of specific landscape features (e.g., the riparian zone) in controlling stream fluxes suggests that spatial variation on subwatershed scales may prove impor-

tant for the trajectories of change [*Aber and Driscoll*, 1997; *Goodale and Aber*, 2001]. Similar spatial dependencies are seen in the efficiency of revegetation for dryland salinity management [*Hajkowicz and Young*, 2002]. However, in general, we lack the theory to determine how the spatial patterns of development or restoration activities in a catchment affect the development or depletion of a legacy store, or the emergence of lower CV_C/CV_Q ratios. Longer-term, spatially explicit numerical and field experiments addressing the generation and depletion of legacy stores are needed to further understand the emergence of biogeochemical simplicity in response to exogenous loading.

Appendix A: Carman-Kozeny Equation Analysis

[42] The Carman-Kozeny (CK) equation for flow around spheres is given by [*Chapuis and Aubertin*, 2003]

$$k = C \frac{g}{\mu_W \rho_W} \frac{e^3}{S^2 D_R^2 (1 + e)}, \qquad (A1)$$

where k is the hydraulic conductivity; e is the void ratio (V_v/V_s), where V_v is the volume of voids and V_s is the volume of solids in a porous material; g is the gravitational acceleration; μ_W and ρ_W are the dynamic viscosity and density of water, respectively; S is the specific surface area of the solid fraction (m²/kg); and D_R is the specific weight (ρ_s/ρ_W) of the solids. Although an idealization of real soils, the CK equation is often found to predict soil properties reasonably well [*Chapuis and Aubertin*, 2003]. To apply the *Godsey et al.* [2009] model the CK equation must be reexpressed in terms of the porosity and pore aperture. First, assuming sphere packing, the specific surface area can be taken as

$$S(d) = 6/d\rho_s \qquad (A2)$$

where d is the grain diameter. For sphere packing, a linear relationship exists between the grain diameter d and the pore aperture p, so that we can rewrite $S(d) = 6/\omega p \rho_s$, where ω varies with packing geometry. The void ratio e can then be expressed in terms of the porosity (ϕ) by noting that $\phi = V_v/(V_v + V_s)$ and therefore $e = \phi/(1 - \phi)$. This allows equation (A1) to be rewritten as

$$k = C \frac{g\rho_s^2}{36\omega^2 \mu_W \rho_W D_R^2} \frac{p^2 \phi^3}{(\phi - 1)^2}. \qquad (A3)$$

[43] Following *Godsey et al.* [2009], the depth dependence of the porosity and pore aperture can be expressed as exponential declines from their surface values p_o and ϕ_o as follows:

$$\phi = \phi_o \exp[-z/\lambda_\phi]$$
$$p = p_o \exp[-z/\lambda_p]. \qquad (A4)$$

And thus, factoring out all constants, the depth dependence of k has the form

$$k \propto \frac{(\exp[-z/\lambda_p])^2 (\exp[-z/\lambda_\phi])^3}{(\phi_o \exp[-z/\lambda_\phi] - 1)^2}. \qquad (A5)$$

Again following *Godsey et al.* [2009], we assumed that k also had an exponential profile

$$k = k_o \exp[-z/\lambda_k]. \qquad (A6)$$

[44] We allowed λ_p and λ_ϕ to vary factorially in the range 0 to 10 for a range of ϕ_o values, computed a k profile, and determined λ_k by fitting this profile. The k profiles were very well approximated as exponentials (r^2 of >0.95 for all cases). Having fitted λ_k, we then computed b using $b = \lambda_k/\lambda_\phi - \lambda_k/\lambda_p - 1$ [*Godsey et al.*, 2009, equation A11]. The results provide mixed support for the proposed model: positively, b was highly constrained, ranging from -1.5 to -0.5 with a median of -1, for all choices of ϕ_o made. This certainly suggests that the proposed mechanisms could contribute to the homogeneity in behavior of weathering product export seen across multiple sites. Less positively, we could not identify a set of parameters (except if porosity or pore aperture increased with depth), which produced chemostatic responses in the sense that $b \approx 0$. Evidently this is an idealized analysis, and by accounting for alternative grain sizes, variable tortuosity and cementing, it may be possible to show that $b \approx 0$ in real soils.

Appendix B: Dynamic Model Formulation

[45] The model describes the unsaturated zone of a catchment in which the water table fluctuates above its minimum long-term value in response to rainfall and generates interflow. The height of these fluctuations h $[L]$ is treated as being linearly proportional to a stored volume S $[L^3]$; that is, we assume the hillslope can be approximated as planar. Water mass balance in this unsaturated region is driven by stochastic recharge Q_{in} $[L^3/T/L^2]$, modeled as a marked Poisson process [*Botter et al.*, 2007a, 2007b], and discharge is assumed to be linearly proportional to the stored volume in the unsaturated zone [*Nash*, 1957; *Schilling and Helmers*, 2008]:

$$\frac{dS}{dt} = Q_{in} - \beta S. \qquad (B1)$$

[46] We thus assume a single recession constant β $[T^{-1}]$, not a general assumption, but a tractable starting point and likely to be reasonable for many of the study sites in this data set (flashy mountainous headwaters, tile drained agricultural sites, and urban areas) [*Kalita et al.*, 2007; *Schellekens et al.*, 2004; *Johnson et al.*, 2000; *Hogan and Blum*, 2003; *Reinhart et al.*, 1963]. The solute mass balance is driven by a mass flux M_{in} $[M/T]$ associated with a stochastic concentration C_{in} $[M/L^3/L^2]$ in the recharge, uniformly distributed between 0 and an arbitrary maximum value C_{max}, such that $M_{in} = Q_{in} \times C_{in}$. The reactor is assumed to be perfectly stirred, so that the mass flux leaving the reactor is $M_{out} = Q_{out} \times M/S = \beta M_s$, where M_s $[M]$ represents the mass store in the mobile phase. Within the reactor, we assume that mass release occurs from a legacy store with a vertical spatial distribution of available concentration $C_{store} = C(h)$ $[M/L]$ and a mass transfer rate α $[T^{-1}]$. We assume $C(h) = vh^x$ where v is a scaling constant whose units vary with x. The concentration of solute in the mobile phase is assumed to be spatially uniform. Thus

the mean rate of (reversible) mass release from the legacy store in the unsaturated zone with variable storage S over depth h_m is given by

$$\begin{aligned} release &= \alpha \int_0^{h_m} \left[vh_m^x - \frac{M_s}{S} \right] dh \\ &= \alpha \left[\frac{vh_m^{x+1}}{x+1} - \frac{M_s}{S} h_m \right]. \end{aligned} \qquad (B2)$$

[47] If h_m is linearly proportional to S, then, release $= \alpha_1 v S^{x+1} - \alpha_2 M_s$ where α_1 and α_2 are constants. As one further assumption, we assume that the transfer of mass from the mobile phase to the store can be neglected or accounted for via an appropriate choice of α_1 such that release $= \alpha_1 v S^{x+1}$; that is, a zeroth-order approximation for mass release can be applied. Finally, we assume linear kinetics for uptake (and/or degradation) and write

$$uptake = \frac{k}{R} M_s, \qquad (B3)$$

where k $[T^{-1}]$ is a linear reaction rate and R $[]$ is the retardation factor for the solute under consideration: this formulation assumes uptake occurs in the dissolved phase. Overall:

$$\frac{dM_s}{dt} = Q_{in}C_{in} - \beta M_s + \alpha_1 v S^{x+1} - \frac{k}{R} M_s. \qquad (B4)$$

[48] If equations (B1) and (B4) are nondimensionalized for the case where $x = 0$ (corresponding to a linear distribution of stored mass with depth), we recover the dimensionless equations and parameters:

$$\frac{dS^*}{dt^*} = Q^* - S^* \qquad (B5)$$

$$\frac{dM^*}{dt^*} = \frac{Q_{in}^* C_{in}^*}{S} - M^* + \gamma^* - k^* M^*, \qquad (B6)$$

where $S^* = S/S_{max}$, $M^* = M_s/C_{store}S$, $C_{in}^* = C_{in}/v$, $t* = t/\beta$, $Q^* = Q/\beta S_{max}$, $\gamma^* = \alpha_1 v/\beta$, $k^* = k/R\beta$, where S_{max} is a peak storage. Simulations of these equations were initialized with $S^* = 0.5$ of its maximum value, and $M = 0$. As is typical for processes with a Markovian driver such as this stochastic recharge, the "memory" of the initial condition does not persist in the time series.

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