Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity

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[1] Complexity of heterogeneous catchments poses challenges in predicting biogeochemical responses to human alterations and stochastic hydro-climatic drivers. Human interferences and climate change may have contributed to the demise of hydrologic stationarity, but our synthesis of a large body of observational data suggests that anthropogenic impacts have also resulted in the emergence of effective biogeochemical stationarity in managed catchments. Long-term monitoring data from the Mississippi-Atchafalaya River Basin (MARB) and the Baltic Sea Drainage Basin (BSDB) reveal that inter-annual variations in loads (L_T) for total-N (TN) and total-P (TP), exported from a catchment are dominantly controlled by discharge (Q_T) leading inevitably to temporal invariance of the annual, flow-weighted concentration, $\overline{C_f} = (L_T/Q_T)$. Emergence of this consistent pattern across diverse managed catchments is attributed to the anthropogenic legacy of accumulated nutrient sources generating memory, similar to ubiquitously present sources for geogenic constituents that also exhibit a linear L_T-Q_T relationship. These responses are characteristic of transport-limited systems. In contrast, in the absence of legacy sources in less-managed catchments, $\overline{C_f}$ values were highly variable and supply limited. We offer a theoretical explanation for the observed patterns at the event scale, and extend it to consider the stochastic nature of rainfall/flow patterns at annual scales. Our analysis suggests that: (1) expected inter-annual variations in L_T can be robustly predicted given discharge variations arising from hydro-climatic or anthropogenic forcing, and (2) water-quality problems in receiving inland and coastal waters would persist until the accumulated storages of nutrients have been substantially depleted. The finding has notable implications on catchment management to mitigate adverse water-quality impacts, and on acceleration of global biogeochemical cycles. **Citation:** Basu, N. B., et al. (2010), Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity, *Geophys. Res. Lett.*, *37*, L23404, doi:10.1029/2010GL045168.

1. Introduction

[2] Nutrient export from intensively managed catchments has been implicated in chronic coastal hypoxia in the Gulf of Mexico, the Baltic Sea, and several other coastal sites [*Aulenbach et al.*, 2007; *Diaz and Rosenberg*, 2008; *Helsinki Commission* (*HELCOM*), 2009; *Osterman et al.*, 2009; *Rabalais et al.*, 2010]. Observed temporal dynamics of the spatial extent and severity of such hypoxic zones are correlated to, among other factors, temporal fluctuations in nutrient loadings from the contributing drainage basins [*Kemp et al.*, 2009; *Rabalais et al.*, 2009]. Thus, understanding the intra- and inter-annual patterns and dominant processes controlling nutrient loading from diverse catchments is essential for predicting and mitigating associated adverse ecological impacts [*Diaz and Rosenberg*, 2008; *Osterman et al.*, 2009].

[3] We present the synthesis of long-term (ten to thirty years) monitoring data for export of two major nutrients (TN and TP) from twenty-one large (10^4 to 10^6 km^2), intensively managed catchments in the Mississippi-Atchafalaya River Basin (MARB) [*Aulenbach et al.*, 2007] and fourteen (10^2 to 10^5 km^2) catchments in the Baltic Sea Drainage Basin (BSDB) [*HELCOM*, 2009] (Table S1 of the auxiliary material).[1] This primary analysis is supplemented with data (Section S1 of Text S1) for the export of key geogenic and anthropogenic constituents from: (1) the twenty-one large MARB catchments; (2) thirty-one smaller (10^1–10^3 km^2), forested catchments located in the continental U.S. and Puerto Rico (J. Campbell, Instantaneous streamflow by watershed, Hubbard Brook Ecosystem Study; G. Likens, Chemistry of streamflow at HBEF WS 1–9, Hubbard Brook Ecosystem Study; Loch Vale Watershed Data Portal; all data accessed November 2009); (3) three managed catchments that drain into Lake Okeechobee, Florida (South Florida Water Management District (SFWMD), Environmental Database, accessed November 2009); and (4) two catchments within the Swan River Basin, Western Australia (Department of Water, Water Information Provision Section, Perth,

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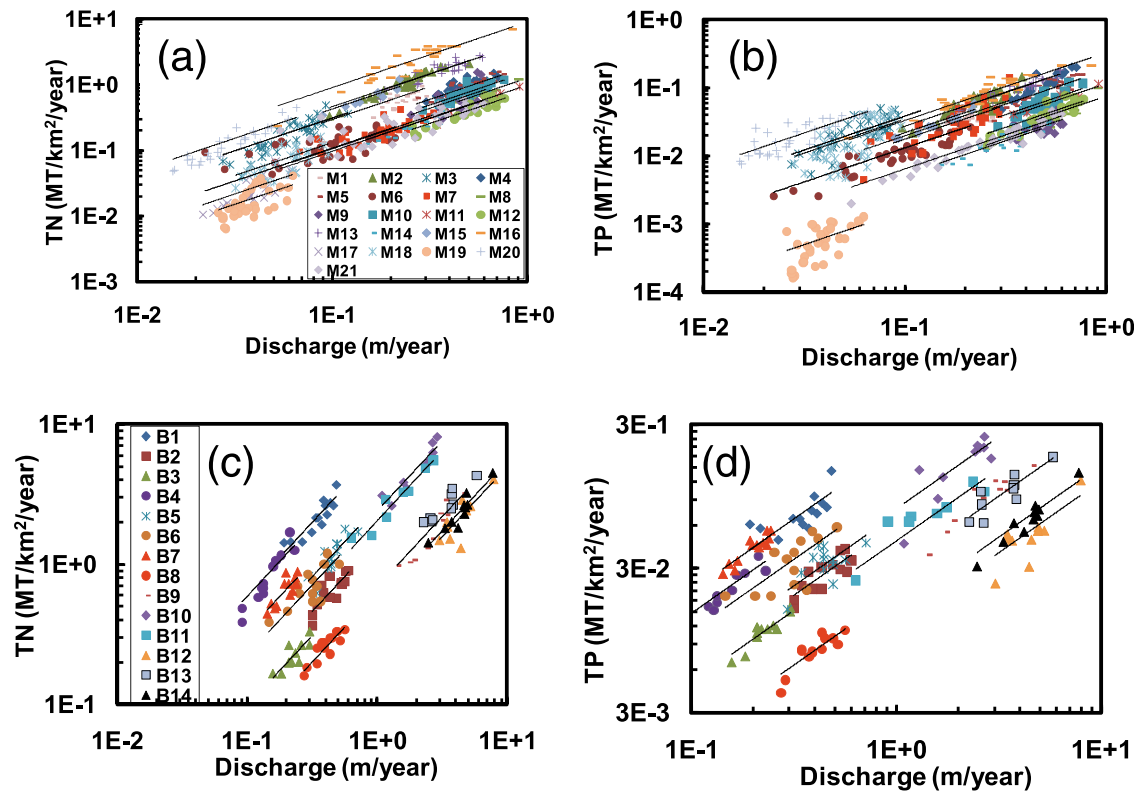
Figure 1. Dominance of hydrologic forcing on inter-annual variations in total-N (TN) and total-P (TP) loads exported from selected basins in MARB and BSDB. Annual loads (L_T; MT/km^2/year) of TN and TP are plotted against annual discharge (Q_T; m/year) (a and b) for the MARB catchments and (c and d) for the BSDB sub-basins. The plots are presented on a log-log scale for visual clarity; however, zero-intercept linear regression fits are shown as solid lines. Slopes and coefficients of determination (R^2) for fits are presented in Table S1 in the supplementary material.

Western Australia, Australia, Hydstra Database: Time-series data, 2009, Water Information (WIN) Database: Discrete sample data, 2009). The origin of the sector studies databases lie in trans-national efforts to find efficient nonpoint source controls for large-scale watershed nutrient loads to receiving inland and coastal water bodies.

2. Patterns in Long-Term Monitoring Data

[4] Constant daily concentrations, C (M/L^3), in spite of orders of magnitude variations in daily discharge, Q (L/T), have been reported for five geogenic solutes exported from 79 small (10^1 to 10^2 km^2), pristine catchments in the U.S. [*Godsey et al.*, 2009]. Such a chemostatic response leads directly to a linear dependence of load, L (=QC, M/L^2/T), on discharge at all time scales [*Godsey et al.*, 2009]. However, non-chemostatic responses are typical of nutrient (TN and TP) export from managed catchments in the MARB and BSDB (Figures S1 and S2). Notwithstanding non-chemostatic response at the daily or monthly time scales, we find consistent linear relationships ($R^2 = 0.7 \pm 0.2$) between annual exported nutrient loads, L_T, and annual discharge, Q_T (Figure 1). Linear L_T-Q_T relationships also characterize silicate and chloride export from MARB (Figure S3), and have been reported for bicarbonate loads [*Raymond et al.*, 2009]. The annual flow-weighted concentration $\overline{C_f} = (L_T/Q_T)$ (ML^{-3}) exhibits temporal invariance (Figure 2), even with significant (~1.5 times) increase in nutrient inputs over the last three decades in the MARB [*McIsaac et al.*, 2001;

Aulenbach et al., 2007]. For the BSDB, concerted efforts to decrease nutrient inputs towards a target level of ~50% have failed to show positive results [*HELCOM*, 2009]. The low inter-annual variability in $\overline{C_f}$ implies that each catchment may be characterized with a constant, mean annual, flow-weighted concentration (slope of the linear fit in Figure 1), $\overline{\overline{C_f}}$ (ML^{-3}), as a useful index for "effective biogeochemical stationarity". Thus, while human interferences and climate change may have contributed to the demise of hydrologic stationarity [*Milly et al.*, 2008], our synthesis shows that anthropogenic impacts have also resulted in the emergence of effective biogeochemical stationarity in managed catchments. In the following, we offer an explanation based on a conceptual model for the emergence of such effective stationarity at the larger spatiotemporal scales, and examine the practical significance of these patterns.

3. A Conceptual Model for the Observed Patterns

[5] A power function ($C=AQ^b$) is commonly used [*Haygarth et al.*, 2004; *Vogel et al.*, 2005] as an empirical model to describe the relationship between concentration, C, and discharge, Q, in small catchments at fine temporal resolution (daily or monthly). Recent work [*Godsey et al.*, 2009; *Siebert et al.*, 2009] has demonstrated that such relationships can be derived by assuming specific functional forms for the dependence of access to the vadose-zone sources with temporal fluctuations in water-table depth. We provide a more general process conceptualization, by con-
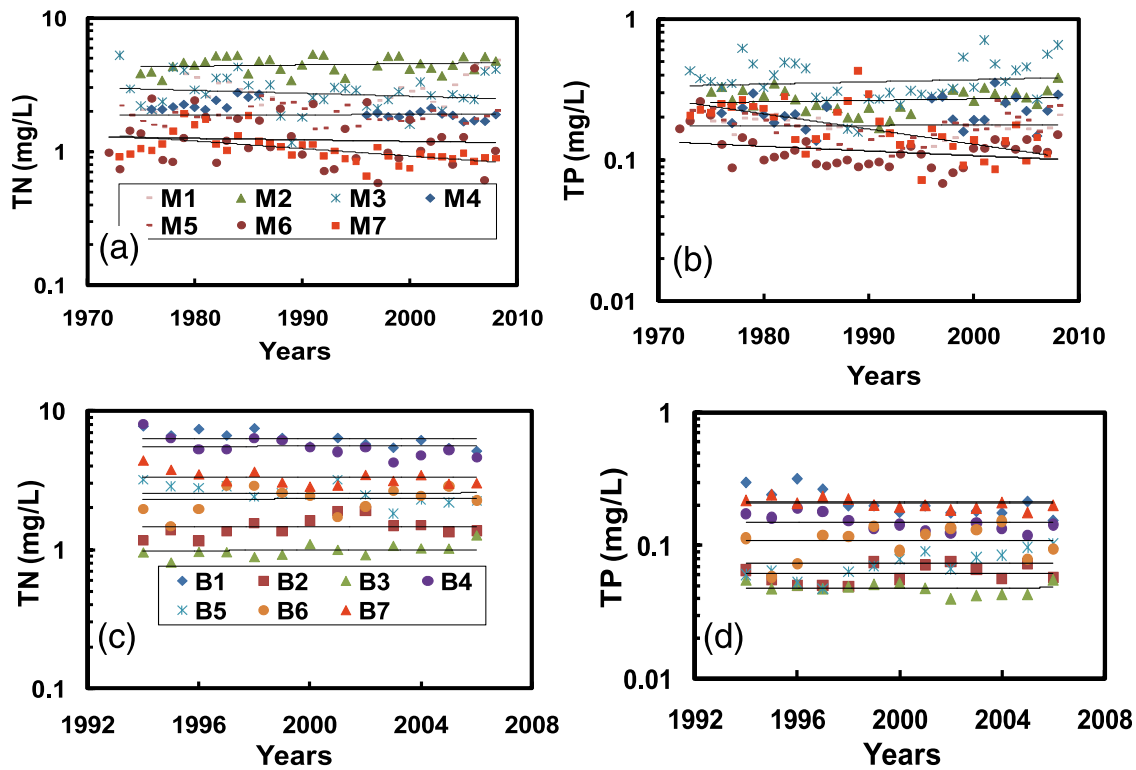
Figure 2. Annual flow-weighted concentration, $\overline{C_f}$ (mg/L), of TN and TP does not change significantly over time, despite one and a half times increase in fertilizer application in MARB (1976–2000) and decrease in inputs for BSDB (1992-2008). (a and b) TN and TP data for the MARB catchments and (c and d) the corresponding data for the BSDB catchments.

sidering the source zones and the flow-generating zones to also vary laterally.

[6] The observed C-Q patterns are assumed to arise from interactions between temporally varying "flow-generating zones" mobilizing nutrients from spatially distributed contaminant "source zones". Two dimensionless terms, $R(t)$ and $S(t)$ describe the fraction of the watershed contributing to discharge and solute loads, respectively. The nonlinear correlation between S and R is represented by $S=aR^b$, where a and b are empirical constants, and the C-Q relationship can be derived from this correlation (Section S2 of Text S1). The model provides a physical basis for b as the index that explains the deviation from chemostatic behavior ($b \neq 0$), while a represents the fraction of the watershed that contains the solute sources. Furthermore, starting with the C-Q power function, the load-discharge relationship at the annual scale can be represented as: $L_T = AmQ_T^{(b+1)}$ (Section S3 of Text S1). Here, the catchment properties (hydrograph recession constant) and stochastic rainfall characteristics (e.g., effective rainfall frequency and depth)) are reflected in the eqpuvcpv *m'']*Botter et al.*, 422: _0*

4. Analysis and Interpretation of Model Parameters

[7] We fitted daily water-quality monitoring data for MARB catchments to the C-Q power function, and the resulting b values had a mean (μ_b) of -0.02 and a standard deviation (σ_b) of 0.25 (Figure S4). The near zero clustering of this data suggests an overall chemostatic response for these constituents. The distribution of b values for the geogenic

constituents (Type I: $\mu_b = -0.1$, $\sigma_b = 0.2$) was statistically different (Kruskal-Wallis $p = 4.36 \times 10^{-13}$) from that of the anthropogenic constituents (Type II: $\mu_b = -0.09$, $\sigma_b = 0.3$). Compilation of b values for forested sites in the U.S. and Puerto Rico, and managed catchments in Sweden, Florida and Australia, reaffirms our observation of zero or slightly negative correlation for the geogenic constituents, and mostly positive correlation for the anthropogenic constituents (Table S2). However, linear fits to the L_T-Q_T relationship are judged adequate ($R^2 > 0.8$) for a range of b values ($-0.4 < b < 1.4$) (Section S4 of Text S1), and would suggest effective geochemical stationarity at the annual timescale. This criterion is satisfied for all observed b values for Type II constituents and 90% of the b values for Type I constituents. Researchers have previously noted linear correlations between nutrient exports and discharge [*Goolsby et al.*, 2000; *Donner et al.*, 2002, 2004; *Vogel et al.*, 2005] and argued that (a) it is expected given the lower variability of C relative to Q, and (b) it is a spurious correlation since discharge is a component of load calculation. In the following section, we address the issue of spurious correlation, and offer an explanation for the more fundamental process-based question: why does C vary less than Q?

5. Role of Legacy in Biogeochemical Stationarity

[8] Biogeochemical stationarity (low variability in concentration) might be expected for geogenic constituents that have large, ubiquitous source mass distributed within the catchment. Similar outcome noted here for nutrients in managed catchments is surprising, given their infrequent
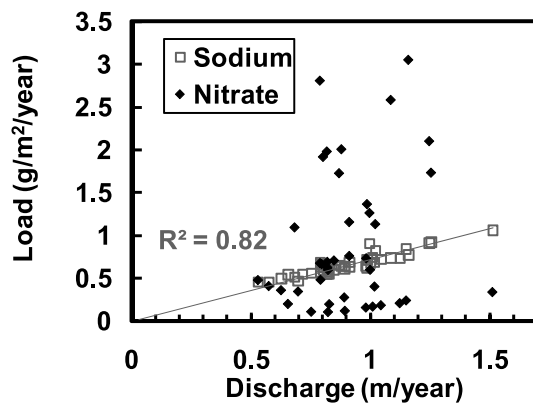
Figure 3. Relationship between annual load and discharge for sodium (Na) and nitrate (NO$_3$) in the Hubbard Brook (HB) Catchment (Likens, 2009; Campbell, 2009). The L_T-Q_T relationship is strongly linear for Na, while there is a lack of any correlation between load and discharge for NO$_3$. Absence of large legacy nutrient stores in forested catchments like HB is attributed to poor correlation.

inputs and various sinks (e.g., transformations; uptake). However, nutrient sources can accumulate within the landscape elements—as a legacy of excessive fertilizer applications over several decades of intensive land management [*Haag and Kaupenjohann*, 2001]—which then provide the long-term memory to buffer the expected biogeochemical variations. Previous studies examining individual constituents in single, managed catchments provide supporting evidence for such build-up of subsurface nutrient memories [*Baresel and Destouni*, 2005; *Darracq et al.*, 2008]. Trends in nitrate concentration data in MARB [*Aulenbach et al.*, 2007] indicate stable concentrations after 1975, in contrast to increasing trends in the previous 25 years (1950–1975). This is concurrent with the period of rapid expansion of intensive crop management and fertilizer use, and suggests that after a lag time to accumulate legacy nutrient sources, nitrate concentrations stabilized. The observed patterns indicate that nutrient export from managed catchments is transport- rather than supply-limited, such that contemporary distributed and point sources have lesser influence on inter-annual fluctuations in stream nutrient concentrations.

[9] This is in contrast to supply-limited systems that exhibit considerable scatter in the L_T-Q_T relationship. We provide two such examples: (a) pesticide loads from managed catchments, and (b) nutrient loads from "less-managed" catchments. Pesticides exhibit supply-limited responses, because short half-lives (e.g., 1 to 100 days for pesticides [*Wauchope et al.*, 1992]) preclude the buildup of legacy sources from annual applications [*Kladivko et al.*, 1991]. Our analysis of data from the Hubbard Brook (US) catchment showed that, under conditions of minimal anthropogenic influence, and resulting low nitrate concentrations, the L_T-Q_T relationship lacked any significant correlation. At the same site, however, the geogenic constituent sodium exhibited significant linear correlation (Figure 3). Thus, despite the spuriousness of the L_T-Q_T relationship, lack of correlation in the two examples of supply-limited systems lends support to our argument that biogeochemical stationarity for nutrients in impacted catchments arises from anthropogenic legacy of management. In contrast, for the geogenic constituents,

catchment geologic legacy is the primary controlling factor, and thus its linearity is independent of anthropogenic impacts.

6. Implications

[10] The ubiquity of effective geochemical stationarity constitutes an important advance by providing a process-based understanding of biogeochemical responses observed in diverse managed catchments located across continents. Attribution of legacy as the dominant driver of stationarity helps enhance our understanding the domain of applicability of such empirical relationships, and identify exceptions (e.g., Figure 3). Based on the persistence of linear L_T-Q_T, annual nutrient loads can be robustly estimated as $L_T = Q_T \overline{\overline{C_f}}$, where the hydro-climatic controls (e.g., precipitation, evapotranspiration) are manifested in Q_T, and the anthropogenic drivers (e.g., land-use; nutrient inputs) are reflected in $\overline{\overline{C_f}}$. Emergent effective biogeochemical stationarity indicates that annual stream discharge can serve as a reliable surrogate for estimating annual loads of geogenic and anthropogenic constituents exported from managed catchments at diverse spatial scales. This parsimonious, process-based approach offers as an alternate to empirical regression analyses to forecast the implications of land- and climate-change on nutrient export, and associated water-quality impairment and ecosystem-health impacts. It should be noted however, that, under land-use change scenarios, the timescale over which the assumption of stationarity is valid is a function of the accumulated legacy stores and their rate of depletion.

[11] Our analysis also suggests that water-quality problems in receiving freshwater and coastal waters will persist until the legacy sources are substantially depleted. Pollution abatement policies and management strategies have focused primarily on controlling contemporary nutrient input reductions [*Pickaver*, 2002; *Destouni and Darracq*, 2009]. While these are necessary long-term strategies, the ubiquity of legacy sources that we report suggests that broader range of tactics is needed. Downstream measures (e.g., buffer strips, constructed wetlands, etc.) implemented at various spatial scales to intercept and attenuate nutrient loads exported from catchments [*Mitsch et al.*, 2001; *Pickaver*, 2002] would provide immediate benefits to ecosystems. Long-term strategies should focus on understanding the magnitude and spatial distributions of the accumulated legacy stores, and factors controlling their depletion rates to predict the temporal lags expected between source-reduction and changes in the catchment biogeochemical signatures.

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