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HIERARCHICAL REGULATION OF NITROGEN EXPORT FROM URBAN CATCHMENTS: INTERACTIONS OF STORMS AND LANDSCAPES

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Abstract. In urban catchments of arid central Arizona, we investigate how the export of mineral and organic nitrogen (N) in storm runoff is regulated by interactions between local landscape characteristics and broader scale storm features. First, we test whether N export is more a function of (1) processes that affect N concentration in runoff or (2) the propensity of the catchment to convey rainfall as runoff. With data pooled across catchments, the mass of N in export (load) is determined by processes regulating runoff N concentration. There are exceptions when catchments are examined individually, where N load from some catchments is determined by the hydrologic responsiveness of the catchment. Second, we investigate the relationship between N export and catchment features. Loads per catchment area were greater from more impervious catchments, probably because impervious catchments held more N in a mobilizable phase and conveyed more rainfall as overland flow. Loads per area were lower from larger catchments, possibly owing to more N-retention hot spots in larger catchments. Catchments with the greatest N exports were those with commercial land use, and loads decreased as development became less prevalent or as residential replaced industrial land use. Third, we investigated how catchment features moderated direct responses of N export to storms. Export was less correlated with storm features in catchments that were larger, more pervious, and less industrial. Results support an "N build and flush" hypothesis, which purports that there is little biotic processing of N deposited to arid, urban surfaces with little organic matter. The rate and duration of deposition determine the size of the mobile N pool. Any amount of rainfall capable of generating overland flow would entrain nearly all mobilizable N and export it from the catchment. Nonetheless, these results suggest that, even with daunting seasonal and interannual variability in storm conditions, material export can be reduced by managing intrinsic catchment features.

Key words: Arizona; impervious cover; land use; path analysis; Phoenix; runoff; scale; Sonoran Desert; southwest; storms; urban ecosystem; watershed.

Introduction

The export of nitrogen (N) in stormwater runoff poses several threats to environmental and human health and consumes a large share of public resources (Parker et al. 2000, NRC 2001). From the perspective of the receiving ecosystem, upflow catchments are point sources of pollution. Thus, catchments that drain to waters of the United States are subject to the Clean Water Act, and a pollution discharge permit must be obtained. Developing solutions to this problem requires applying—and affords furthering—basic principles of ecology and biogeochemistry. These include issues of scale and of material transport.

Globally pervasive changes are simultaneously occurring both within (land-use change) and across (climate change) most ecosystems. Unfortunately, the cross-scale interactions (after O'Neill et al. 1986) between intrinsic and broad-scale drivers of ecosystems remain poorly understood. Like ecological phenomena associated with populations and communities, ecosystem functions are governed by processes operating at multiple scales (Levin 1992). They are influenced by intrinsic features of an ecosystem such as size, geomorphology, patch structure, and community structure (Schindler et al. 1997, Fisher et al. 1998, 2004, Gold et al. 2001, Peterson et al. 2001, Schade et al. 2001) and by broader scale drivers such as climate and hydrology, nutrient deposition, species invasions, and surrounding landscape context (Grimm and Fisher 1992, Hedin et al. 1995, Reed-Andersen et al. 2000, Sponseller and Benfield 2001).

To investigate the response of ecosystem functions to multiple drivers, we focus on material export from catchment ecosystems. Material export both reflects the capacity of an ecosystem to retain material and represents a subsidy, or cross-boundary flux, of resources and pollutants to recipient ecosystems (Correll et al. 1992, Grimm et al. 2003). Thus, the export term in

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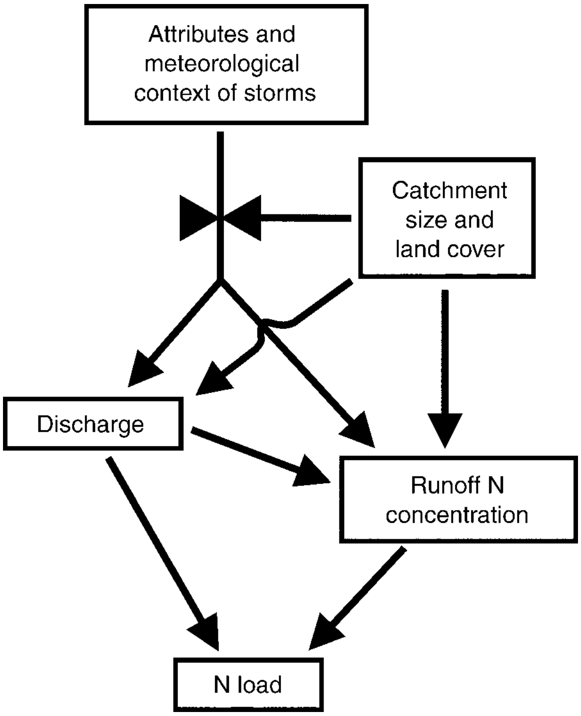

FIG. 1. Hierarchical model of material export. The model describes how N export from catchments is regulated by interactions between storm and catchment features, and their effects on N concentration and runoff.

ecosystem budgets has figured prominently in the development of theories of ecosystem maturity, succession, and nutrient limitation (Odum 1969, Vitousek and Reiners 1975, Grimm 1987, Perakis and Hedin 2002) and of ecosystem response to disturbance (Bernhardt et al. 2003, Watmough and Dillon 2003).

The issue of material export from an ecosystem centers on two general principles, as N exemplifies. First, N export depends on the amount (pool size) of N that is potentially mobile. This pool size is governed initially by the amount imported to the ecosystem, and subsequently by retentive processes (or lack thereof) acting on N within the ecosystem. Such processes include those that transform N in transit (Welter et al. 2005) and those that capture N, such as biochemical stabilization in the organic matter of hyporheic zones and soils (Grimm and Fisher 1984, Kaye et al. 2002). Second, export requires that potentially mobile material actually gets mobilized. Mobilization depends on the openness of the ecosystem to transport vectors such as water (Lewis et al. 2006*b*). These two principles shed light on N exported from a catchment ecosystem in stormwater runoff. The mass of N exported, or load, is calculated as the concentration of N in runoff water integrated over the total volume of runoff from the storm. The concentration of N in runoff is determined by a combination of the processes that retain and liberate N, and by the volume of water carrying the mobile fraction.

These principles are important in urban, arid settings. In cities, rates of material deposition are high and many surfaces are impervious. And, in arid biomes, dry periods may be protracted. With these conditions in concert, materials will accumulate in a mobilizable phase over weeks or months and then be rapidly exported by overland stormwater runoff.

We identify three questions regarding N export from catchment ecosystems.

1) What is the relative importance for N export of the processes that affect N concentration in runoff vs. the propensity of a catchment to convey runoff?

2) For the export of N and water, what is the importance of land use and land cover?

3) How are N and water export influenced by the interaction of storms and climate systems (broad-scale drivers) and land use and land cover (intrinsic catchment features)?

We developed a conceptual model to combine these issues of scale and material transport (Fig. 1). This model depicts a hierarchy of factors governing N export from urban catchments in central Arizona, USA, which is arid, so channels flow only in response to discrete rainstorms. Load (the mass of N exported in runoff) will be influenced by the N concentration in runoff and by discharge (the volume of runoff). We also point out the possible positive (scour) and negative (dilution) influences of discharge on N concentration. Storm and catchment features may directly influence discharge and N concentration in stormwater runoff. Additionally, catchment features may mediate the relationship between storm features and the consequent discharge and N concentration.

Hypotheses

We evaluate support for three suites of hypotheses about the factors that regulate N load. The first suite examines the roles of N biogeochemistry and hydrology:

H1-a: N load is influenced by the processes that affect N concentration in runoff.

H1-b: N load is influenced by the hydrological responsiveness of the catchment.

The second suite comprises three nonexclusive hypotheses about the roles of land use and land cover:

H2-a: Imperviousness increases both the pool size of potentially mobile N (by preventing N uptake and binding in soils and biota) and the conveyance of rainfall as overland runoff.

H2-b: Larger catchments tend to encompass a greater number of retentive hotspots.

H2-c: Deposition from human activities increases the pool size of potentially mobile N.

The third suite is one general hypothesis about factors that interact across scales:

H3: Catchment features mediate the relationship between storm attributes and N load.

TABLE 1. Features of urban catchments in arid central Arizona, USA.

No.	Catchment	Events	Area (km^2)	Impervious cover (%)	Land use percentage: Residential	Industrial	Commercial	Undeveloped
1	Salt River at 40th Street, Phoenix	38	0.49	74	0	100	0	0
2	Salt River at 35th Avenue, Phoenix	37	5.52	54	21	42	18	19
3	Salt River at 27th Avenue, Phoenix	30	0.18	15	6	94	0	0
4	Salt River at 67th Avenue, Phoenix	12	19.18	15	13	26	0	61
5	Salt River tributary in South Mountain Park, Phoenix	2	4.53	1	0	0	1	99
6	Indian Bend Wash at 40th Street, near Cactus Road, Phoenix	45	2.47	37	78	0	11	11
7	Peoria Avenue and 43rd Avenue, Phoenix	32	0.01	94	0	0	97	3
8	Box culvert at 48th Street drain, south of West University Drive, Tempe	27	0.16	80	0	85	8	7
9	Horne and 6th Street, Mesa	52	0.78	63	100	0	0	0
10	Broadway and Lindsay, Mesa	45	0.59	26	98	0	0	2
11	Falcon Field Airport at Fighter Aces Drive north of McKellips Road, Mesa	59	0.69	65	0	100	0	0
12	Horne and Grandview Street, Mesa	43	0.46	51	100	0	0	0
13	Broadway and Dobson, Mesa	38	0.26	89	0	0	100	0
14	Olive Avenue and 67th Avenue, Peoria	26	0.07	60	100	0	0	0
15	Agua Fria River at Youngtown	6	0.33	33	90	0	10	0

Notes: "Events" shows the number of runoff episodes recorded in the catchment, though the actual number of events with N-load data may be less for some N species. Catchments are listed in the numerical sequence referred to elsewhere in the paper.

To investigate support for these hypotheses, we analyzed the export of N in runoff from multiple storm events from each of 15 catchments. Nitrogen species we examined included nitrate (NO_3^-), ammonium (NH_4^+), organic N, and total N.

METHODS

The catchments are in the central Arizona–Phoenix (CAP) metropolitan area and are diverse in terms of size, impervious land cover, and land use (Table 1). CAP is a metropolis of 4.2 million people (1 July 2007 estimate) inhabiting 31 municipalities and 43 unincorporated areas within the arid biome of the northern Sonoran Desert. From 1975 to 2000, CAP increased in spatial area 3.4-fold and in population 2.5-fold (data from CAP Long-Term Ecological Research program, Arizona State University). CAP experiences two rainy seasons, generating 19.6 cm mean annual precipitation. Summer monsoons originate in the Gulfs of Mexico and California, occur between July and October, and account for 40–45% of annual rainfall. Winter cold fronts originate in the Gulf of Alaska, occur between November and March, and account for about 50% of annual rainfall. The remaining rainfall, between April and June, can derive from either storm system (data from Phoenix Sky Harbor airport).

Database

We aggregated data from the United States Geological Survey (USGS) and the Flood Control District of Maricopa County (FCDMC), Arizona, USA. The database contains information specific to individual storms monitored at 15 catchments during the period from October 1991 to February 2005. Rain was recorded on 148 days from varying numbers of catchments per day, yielding 394 runoff events ("event" refers to runoff from a single catchment during a single storm). Storm attributes, runoff hydrology, and runoff chemistry were separately recorded for each event. The three storm attributes were total precipitation, number of rain-free (dry) days preceding the storm, and the season in which the storm occurred (storms during April, May, and June were of unknown climatic system type, and were excluded from analyses of season). Each catchment is described by six landscape characteristics: contributing area, the proportion of area with impervious land cover, and the proportions of area under residential, commercial, industrial, and undeveloped land use.

The data set includes export of each of the four N species (NO_3^-, NH_4^+, organic N, and total N) in multiple runoff events from each of the 15 catchments for 60 N species × catchment combinations. Sample size for each combination equals the number of storms in which the export of that N species from that catchment was observed, and varies among the 60 combinations from $n = 2$ events to $n = 50$ events. We will describe the process of selecting catchments, quantifying precipitation and hydrology, and collecting and analyzing water samples. Several original source documents describe how these methods were developed and used in these catchments. Principal documents include Rantz (1982), Kennedy (1984), Fishman and Friedman (1989), Lopes et al. (1995), Oblinger Childress (1999), and Fossum et al. (2001).

Catchment selection.—The catchments were selected to span a range of land-use types. Classification was based on aerial photographs and ground truthing by walking each catchment. Portions of a catchment that did not contribute to runoff were not included in contributing area. The channels flowing out of the bases of these urban catchments are made of impervious paving material. These "streambeds" are thus concrete canals and roadway curbsides. This channel structure means that channel features are easily measured (e.g., channel cross sections are simple polygons) and do not erode, shift, or otherwise change substantially over the decadal time scale of this study. Additionally, because they comprise paved material above and at the point of catchment exit, the entire outflow channel of any catchment is a flow-control structure in its own right. The installation of control structures such as V-notch weirs was unnecessary.

Precipitation and hydrology data.—At each catchment, a tipping-bucket rain gage was used to measure precipitation. While runoff efflux was occurring, an instantaneous measurement of discharge (L/s) was made every 60 s. The mean of two consecutive measurements was multiplied by 60 s for an estimate of discharge for each minute. Total runoff was obtained by summing across all minute-specific estimates of discharge.

Our acquisition of instantaneous discharge data needs to be considered in two steps. First, a stage-discharge rating curve was developed for the outflow channel of each catchment. Such a curve shows the relationship between stage (i.e., water depth above the channel bottom) and discharge. To develop the rating curves, stage and discharge were estimated independently at several levels of discharge. Stage was measured using either a float and tape system or a thermally insulated pressure transducer that was calibrated to stage ±0.6 cm. Discharge was either directly measured using Price Type AA and Pygmy current meters (USGS Hydrologic Instrumentation Facility, Stennis Space Center, Mississippi, USA) or was calculated from the Manning equation based on the slope-conveyance method of setting rating curve shape (Rantz 1982, Kennedy 1984). The Manning equation describes discharge as a function of channel cross-sectional area and the factors that influence flow velocity (slope, roughness, and area-to-perimeter ratio of the wetted cross section). The parameters for the Manning equation were uniquely determined for each catchment, and were either established via survey (e.g., of slope and cross section) or taken from commonly accepted values (roughness coefficients of 0.012–0.018 for concrete; Arcement and Schneider 1989). These parameters were assumed not to change over the time span of the study, given that catchment outflow channels were made of consolidated paving materials (e.g., concrete). Rating curves fit well to the stage and discharge data used in building them ($r = 0.99$; Lopes et al. 1995).

The second step is the acquisition of discharge data in the actual runoff events for which we report runoff chemistry in this study. After the rating curve had been developed for any given catchment, discharge in subsequent runoff events (those reported here) could be estimated by measuring stage. In events for which we report N load and concentration in the present study, stage was measured with a pressure transducer that signaled a datalogger. The datalogger, in turn, was programmed with the rating curve for its respective catchment, so instantaneous measures of pressure (stage) were converted into instantaneous estimates of discharge (Lopes et al. 1995).

Load calculation and runoff sampling.—Load is a computed variable, where load (mass N/catchment area) = concentration of N in runoff (mass N/L discharge) multiplied by the area-corrected amount of discharge during the storm (L discharge/contributing catchment area). During an event, up to 24 discrete water samples were collected by automated pumping through an intake tube fixed to the channel bed in the center of flow at the efflux point where discharge was measured. Other than the intake tube, water samples were only in contact with glass, polytetrafluoroethylene (PTFE), and stainless steel. Samples from this tube were representative of the whole water column, as confirmed with manually collected, depth-integrated samples (Lopes et al. 1995).

A new, discrete sample was pumped into its own 1-L, PTFE-lined polyethylene bottle every time a specified volume of runoff had passed the collection point. Discrete samples were then combined into a composite by mixing equal volumes of each. The concentration of each N species in the composite sample is defined as the event-mean concentration. Here, load is the product of this event-mean N concentration and discharge during the period when the 24 discrete samples were collected, divided by catchment contributing area.

Composite samples were analyzed at the USGS National Water Quality Laboratory (Denver, Colorado, USA) following methods in Fishman and Friedman (1989). Chain of custody was documented during sample transport. Field and laboratory blanks were analyzed for sample contamination, spiked samples were analyzed for interferences, and duplicate samples were analyzed for precision. Results from these quality controls confirmed that sample collection, handling, and analysis produced reliable water chemistry data (Lopes et al. 1995). All N species were analyzed colorimetrically with an automated-segmented flow system. Concentrations of nitrite (NO_2^-) + NO_3^- (hereafter, NO_3^-) were determined with cadmium reduction-diazotization (USGS method I-4545-85). Concentrations of NH_4^+ were determined with a salicylate-hypochlorite technique (USGS method I-4522-85). Concentrations of reduced N (NH_4^+ + organic N) were determined by digesting organic compounds with sulfuric acid in the presence of mercuric sulfate and potassium sulfate and then analyzing for NH_4^+ with the salicylate-hypochlorite technique (USGS method I-4552-85). For this paper, we calculated organic N as reduced N minus the independent measure of NH_4^+, and we calculated total

N as $NO_3^- + NH_4^+$ + organic N. Method detection levels were determined for all analytes (Oblinger Childress et al. 1999) and were subject to change during the >13-yr study period as quality controls improved.

The volume of discharge required to trigger the pumping of a new sample was set to divide runoff into 24 discharge-equivalent (as opposed to time-equivalent) periods. Discharge-weighting accommodates pulsed runoff, which occurs owing to transient storage zones within the catchment (in the sense of Thomas et al. 2003) or to fluctuations in rainfall intensity. The "sample-trigging" volume was specific to each catchment (i.e., catchments with typically more runoff need larger "sample-triggering" discharge). When discharge was greater than expected, water sampling stopped after the 24th sample, and the tailing end of the runoff was not sampled. We assumed that by the 24th sample, all potentially mobile material would have been exported from the catchment; thus, missing the tailing end of runoff was inconsequential for estimating load. Conductivity data (not shown) from discrete runoff samples support this assumption.

Data analyses

To determine how N load was influenced by (H1-a) processes that affect N concentration in runoff and (H1-b) the openness of the catchment to hydrologic flux, we analyzed data in two ways. First, we determined whether N load was more highly correlated with the N concentration of runoff water or with discharge. We compared the Pearson correlation coefficient between N load and the N concentration in the sampled runoff (hereafter, N concentration) with the correlation coefficient between N load and the volume of the sampled runoff (hereafter, Q). These correlations were calculated (1) with data from all catchments pooled and (2) with data from each catchment separately. For analyses of individual catchments, we then determined whether these Pearson coefficients were correlated with catchment land-cover and land-use features. Second, we used path analysis, with hypothesized paths from Q to N concentration and N load, and a path from N concentration to N load. These paths were part of a larger path analysis (described later) that included paths from catchment and storm features.

Comparing the N load–N concentration relationship with the N load–Q relationship is a useful way to ascertain which factor most generates variability in N load and to determine the relative support for H1-a vs. H1-b. We acknowledge that when examining the relationships that N load bears with N concentration and Q we are correlating a computed variable with the factors from which it was computed (an A × B vs. A relationship). Though this practice has pitfalls (Brett 2004), our application of it is warranted. As a means of teasing apart two hypotheses (H1-a vs. H1-b), we wish to see which of N load's two factors (N concentration and Q) is a more important for generating variability in N load. That is, we are less interested in the A × B vs. A relationship, per se, and rather more interested in comparing the A × B vs. A relationship against the A × B vs. B relationship as a means of hypothesis discrimination. Additionally, any effects of storm attributes and catchment features on load are levied through storm and catchment effects on N concentration and Q (Fig. 1). As subsequent analyses will show, it is conceptually informative to retain N concentration and Q in analyses that examine how N load responds to storm and catchment characteristics.

We also investigated relationships between N and water export and land use and cover. For H2-a, we fit regressions of N load, N concentration, and Q against the proportion of the catchment with impervious cover. For H2-b, we fit regressions of N load, N concentration, and Q against the contributing area of the catchment. In these regressions, the analysis was of mean load (averaged across storms) for each catchment vs. the impervious cover or area of the catchment. Thus, sample size was, conservatively, the number of catchments. Regressions were weighted, with the weight of each catchment equal to the number of storm runoff events observed from that catchment. In these regressions, some of the correlation that N load might have with either impervious cover or catchment size might be indirect, owing to correlations between load and one of its factors (Q and N concentration) and then between one or both of these factors and the catchment attributes. To account for possible indirect correlations between N load and catchment attributes, we calculated both an R^2 and a partial R^2. Partial R^2 is the R^2 of load and catchment feature (impervious cover or area) when Q and N concentration are fixed (given that Q and N concentration exhibit a correlation with the catchment feature in question). Partial $R^2 = [t/(t^2 + \mathrm{rdf})^{0.5}]^2$, where t is the t statistic of the catchment feature in a multiple regression of load on the catchment feature and on Q and N concentration, and rdf is the residual degrees of freedom.

For H2-c, we used two analyses to investigate N load as a function of the degree and type of development. First, we used ANOVA to compare N loads among catchments of different predominant land use. Analyses were weighted, as previously described, so sample size equaled 15 catchments. The land use category (industrial, commercial, residential, and undeveloped) assigned to each catchment was the land use that occupied a majority or plurality of the area (Table 1). Second, we plotted N load against percentage of catchment that was undeveloped. Because there were many catchments with 0% undeveloped area, among which development type varied, these data precluded straightforward statistical analyses, so the analyses were qualitative.

We used two analytical approaches to investigate whether and how catchment features mediate the effect of storms on N load (H3). The first is path analysis. Path analysis is a form of structured equation modeling,

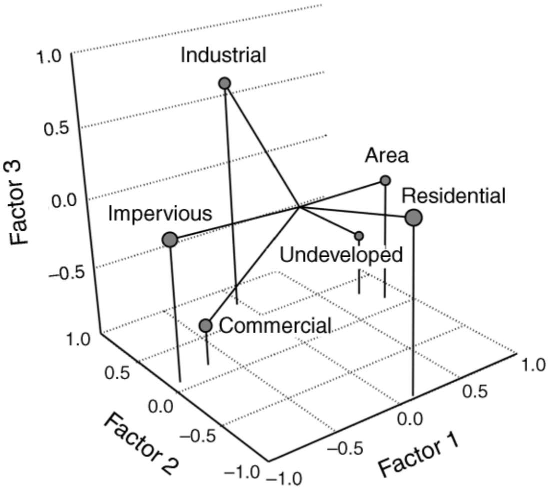

FIG. 2. Loadings of six catchment features reduced to three axes using factor analysis.

where the user explicitly draws the hypothesized causal pathways, often conceptualized in a box-and-arrow diagram. Regression analysis is conducted for each variable as a function of other variables identified as its causes. One then obtains path coefficients for these arrows (which indicate strength of association) and confidence intervals for the coefficients. Path analysis is well suited for this study because (1) N concentration and Q are simultaneously drivers (of N load) and responses (to storm and catchment features) and (2) we wanted to discriminate direct and indirect effects, and identify spurious effects, among variables.

We fit a path model to each N species, with data from all catchments pooled. We hypothesized direct paths from storm features, catchment features, and storm feature × catchment feature interactions to Q, N concentration, and N load; direct paths from Q and N concentration to N load; and a direct path from Q to N concentration. To reduce the set of possible path models, we reduced the number of catchment characteristics using factor analysis with no rotation and a correlation matrix for extraction. With a minimum eigenvalue of 1.0, we reduced the six catchment characteristics to three "land factors," LF1, LF2, and LF3 (Fig. 2).

We developed a "build and reduce" protocol for identifying the best-fit path model (Box 1). We considered H3 supported if the final best fit model included any storm feature × LF interaction terms. This is a conservative approach biased to *not* find support for H3 because many potentially important storm feature × LF interaction terms were never examined. We examined only storm feature × LF interaction terms for combinations of storm features and LFs that had already been identified as each having a first-order relationship with the same dependent variable (Q, N

Box 1. Protocol for identifying best-fit-path models of N load from catchment ecosystems.

1) Fit the full "storm features only" model, Model A:
   (season, precipitation, dry days) → Q
   (season, precipitation, dry days, Q) → N concentration
   (season, precipitation, dry days, Q, N concentration) → N load.

2) Remove all insignificant paths, i.e., those paths for which $0 \in$ 90% confidence interval of the path coefficient.
   Refer to this model as Model B.

3) Test effects of land factors (LF1, LF2, and LF3) on N load.
   To Model B, add paths (LF1, LF2, LF3) → N load, and fit model.
   Remove all insignificant LF → N load paths; refer to this model as Model B1.

4) Test effects of land factors (LF1, LF2, and LF3) on N concentration.
   To Model B1, add paths (LF1, LF2, LF3) → N concentration, and fit model.
   Remove all insignificant LF → N concentration paths; refer to this model as Model B2.

5) Test effects of land factors (LF1, LF2, and LF3) on discharge.
   To Model B2, add paths (LF1, LF2, LF3) → Q, and fit model.
   Remove all insignificant LF → Q paths; refer to this model as Model C.

6) Test effects of land factor × storm feature interactions.
   In Model C, note all instances in which an endogenous variable (N load, N concentration, and Q) receives a path both from a storm feature (S_i) and from a land factor (LF_j). In all such instances, add the $S_i \times LF_j$ interaction term to the relevant endogenous variable. Then, fit the model and remove all insignificant ($S \times$ LF) → endogenous variable paths. Refer to this model as the best-fit model.

concentration, or N load). It is possible that some storm features and LFs did not exhibit first order relationships with any export variables (N load, N concentration, or Q) owing to the very fact that they *did* have significant interactive effects.

Our path analyses employed covariance matrices using the maximum Wishart likelihood method of estimation. In the original cases-by-variables matrix, from which the covariance matrix was calculated, we created the storm feature × LF interaction variables by multiplying storm features by LF terms. In the path models, we pointed latent error variables, with path coefficients fixed at 1.0, to N load, N concentration, Q, and precipitation (variables for which measurement error was likely). Variance paths, with free parameters, were applied to these latent error variables and to variables for which measurement error was less likely (season, preceding dry days, and LF1-3). Where storm feature × LF interaction terms were considered, a latent error variable with path fixed at 1.0 was pointed to the interaction term if the storm feature was precipitation, and a free variance path was used otherwise.

In our second analysis regarding H3, we examined data from each catchment separately. We fit regression models of the concentration of each N species and Q as functions of all three storm features and their interactions. F statistics were calculated with partial (Type II) sum of squares. For each independent variable (first-order storm feature terms and their higher order interaction terms), we calculated a semi-partial R^2. Semi-partial R^2 is the amount of variability in the dependent variable (Q or concentration of an N species) explained by the independent variable in question, while holding all other independent variables constant. Thus, a term with a high R^2 might have a low semi-partial R^2 if it covaries with another independent variable in the model. Semi-partial R^2 is the decline in R^2 that results when the indicated storm feature is removed from a regression model, while all other terms of equal or lesser order are retained in the model. From the regression results, we classified catchments into groups based on which storm attributes were correlated with N concentration and Q. For each storm feature, catchments were placed into "yes" and "no" groups according to whether that storm feature was a significant ($\alpha = 0.10$) predictor of N concentration or Q. We then used ANOVA to determine whether catchment landscape features differed between the "yes" and "no" groups.

In all analyses, Q, N concentration, and N load were natural-logarithm transformed to meet assumptions of normality and to avoid heteroskedastic residuals. By design, most catchments were dominated by one land use. Thus, proportions land use (p) were poorly distributed, being clustered near 1.0 and 0.0. To improve the distribution of p for statistical analyses, we transformed land use proportions as $2 \times \sin^{-1}(p^{0.5})$. Proportion catchment under impervious cover was similarly transformed for the factor analysis to produce LFs, but was untransformed for other analyses.

RESULTS

Relations of N load with N concentration and discharge

With all catchments pooled, the loads of all N species exhibited stronger positive relationships with concentration than with Q, as revealed both by Pearson correlations (Figs. 3 and 4) and by direct effects in path analysis (Fig. 5, Table 2). Though Figs. 3 and 4 suggest a strong correlation between concentration and load, some portion of this apparent correlation may be spurious because both concentration and load are responding to third variables, such as Q, season, and precipitation (Fig. 5, Table 2). And, while Q exerted a positive direct effect on load, it also exerted a negative indirect effect on the loads of NO_3^-, organic N, and total N. This negative indirect effect derived from a negative direct correlation between Q and concentration coupled with a positive direct correlation between concentration and load (Fig. 5). Of the Q effects on organic N load, the negative indirect effect was of greater magnitude than the positive direct effect (Table 2).

When catchments were analyzed separately, loads exhibited correlations with concentration, Q, both, or neither, depending on the catchment (Fig. 6). Organic N loads were correlated more strongly with concentration than with Q in most catchments. For all N species, land use and cover did not explain whether load was best correlated with concentration or Q (with $n = 15$ catchments, $P > 0.05$ for one-way ANOVA that compares any land use/cover variable L between the two varieties of catchment classified by "load relationships," load best predicted by N concentration vs. load best predicted by Q). Land use and cover also did not explain the degree to which load was correlated with either N concentration or Q ($P > 0.05$ for regression vs. L of the Pearson coefficients of the N load–N concentration and N load–Q correlations).

Relations of N and water export with land use and cover

The relationship between N load and impervious cover varied among N species (Fig. 7). Organic N load exhibited no correlation with the proportion of catchment cover that was impervious. Loads of NO_3^-, total N, and NH_4^+, in that order, exhibited increasingly greater R^2 and steeper slopes. Discharge (Q) per unit area was positively related to impervious cover. The concentration of NH_4^+ in runoff water was correlated with impervious cover ($P = 0.016$, $R^2 = 0.37$), while the concentrations of NO_3^-, organic N, and total N were not (plots of concentration vs. proportion impervious and vs. contributing area; not shown). Because load was correlated with area-corrected Q, and area-corrected Q was related to impervious cover, some of the load–impervious cover correlation was indirect. So, we calculated partial R^2 values for the effect of impervious

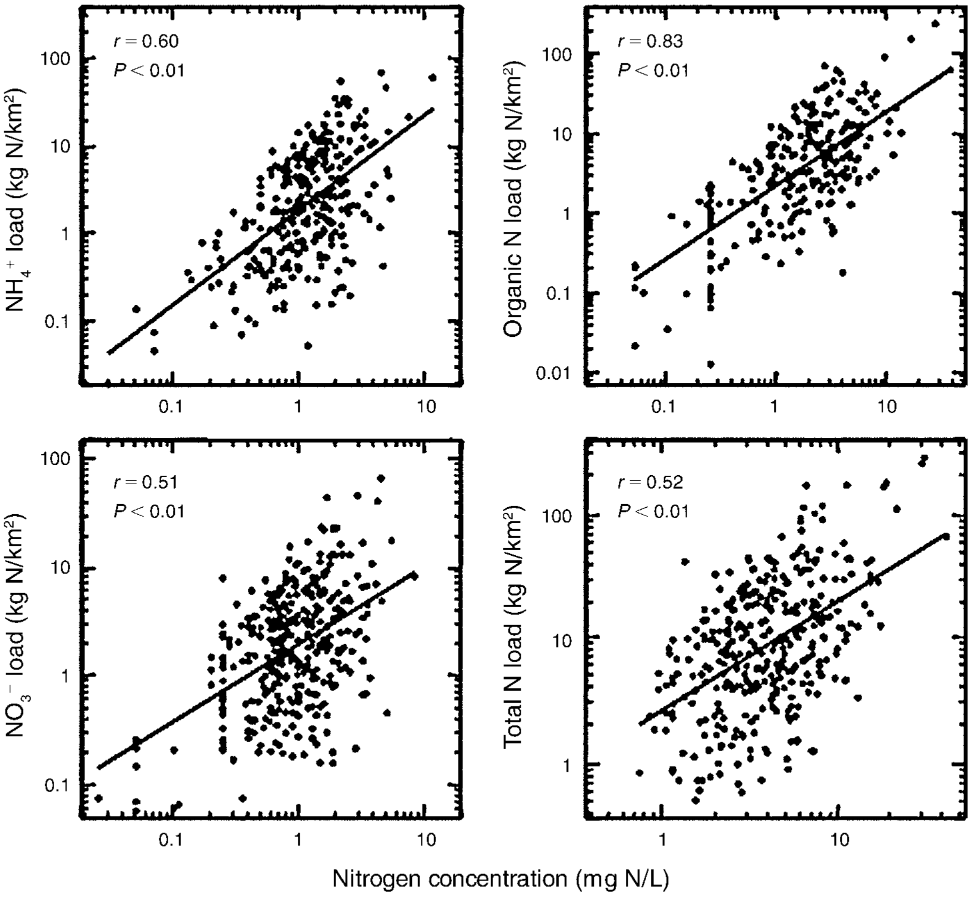

FIG. 3. Scatter plots of the loads (kg N/km^2 contributing catchment area) of four N species plotted against their concentrations. Data are pooled from multiple storm events from each of 15 catchments. Note the log scaling of both axes.

cover on load, given *Q* (and for NH$_4^+$ load, given both *Q* and NH$_4^+$ concentration). Partial R^2 values were much less than R^2, indicating that most of the relationship between load and impervious cover was a consequence of the response of load to area-corrected *Q* (and for NH$_4^+$, to concentration) and of *Q* and concentration to impervious cover.

Larger catchments exported less N per unit contributing area (Fig. 7). Load per area declined with catchment size at about the same rate for all N species. The volume of water exported per unit contributing area was also less for larger catchments. Owing to this *Q*–catchment area relationship, the correlations between N loads and catchment area were 24–63% indirect. The concentration of each N species was not correlated with catchment size.

Loads of N were related to catchment land use (Fig. 8). Loads of NH$_4^+$, NO$_3^-$, and (marginally) total N were greater from catchments under commercial land use than from those under undeveloped land use. Loads of NO$_3^-$, total N, and (marginally) NH$_4^+$ from commercial catchments were also greater than from residential catchments. Organic N loads exhibited similar trends, but were not statistically different among land-use types.

Loads of N tended to be lower in catchments with a greater proportion of land cover that was undeveloped (Fig. 9). There was, however, still a great deal of variability in load among catchments that were highly developed. For these highly developed catchments, loads tended to be highest when that development was commercial.

Interactions of catchment and storm features

NH$_4^+$.—Path analysis indicated that NH$_4^+$ load was positively correlated with precipitation and was influenced by season (Fig. 5). The season effect was such that loads were greater in summer monsoons than in winter cold fronts. Load was also indirectly related to several storm and catchment features through their direct relationship with concentration coupled with the direct path from concentration to load. Concentration was positively correlated with the number of dry days preceding the storm and with LF2 (which indicates industrial use at the expense of residential use; Fig. 2). Concentration was also greater in runoff from monsoons than from cold fronts. The total effect of season on load is the sum of its direct effect (season → load path coefficient) and its indirect effect through concen-

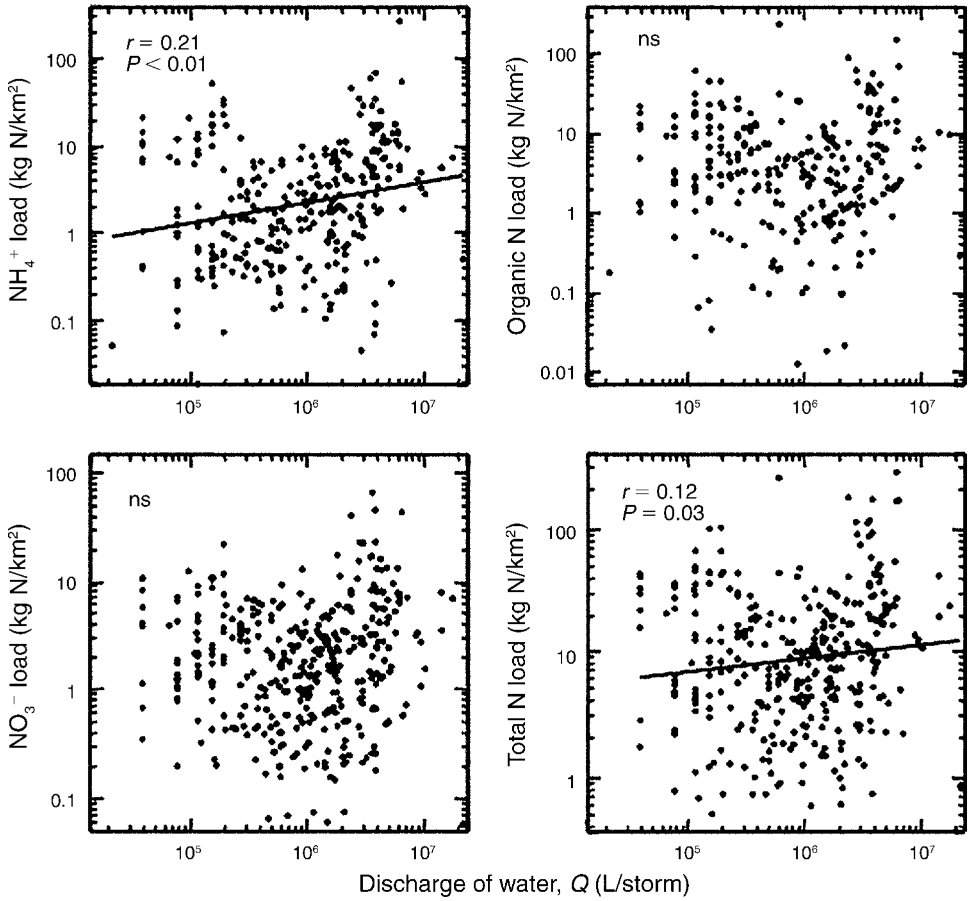

FIG. 4. Scatter plots of the loads (kg N/km^2 contributing catchment area) of four N species plotted against discharge. Data are pooled from multiple storm events from each of 15 catchments. Note the log scaling of both axes. Nonsignificant regressions are indicated by "ns."

tration (the product of season → concentration → load path coefficients). The concentration of NH_4^+ was also correlated with the LF2 × dry days and LF2 × season interaction terms. The interaction terms indicated that the positive effect of LF2 on concentration was relatively exacerbated for monsoon storms and following long periods without storms. The path analysis identified no direct effects of land factors on load.

To consider what might influence *Q* and concentration (whose effects are then transmitted to load) at the level of individual catchments, we regressed them against storm features. Across all catchments, there were three, storm feature × storm feature interactive effects on runoff NH_4^+ concentration (Table 3). The positive "$p \times d$" interaction in catchment 2 indicates that the positive effect of total precipitation on runoff NH_4^+ concentration was more pronounced in storms following long dry periods than in those following short dry periods, suggesting that storm size—small or large—is irrelevant for runoff NH_4^+ concentration if there has been insufficient pre-storm time for mobilizable material to accumulate in the catchment.

There were many more correlations between concentration and first-order storm feature terms. There were marked differences among catchments as to which, if any, of the storm feature terms were correlated with concentration (Fig. 10). Catchments that exhibited a season effect on NH_4^+ concentration (at the $\alpha = 0.1$ level) tended to be relatively small ($n = 7$ catchments), while the catchments for which season did not effect concentration were relatively large ($n = 7$; Fig. 11). The difference in mean size between these two groups of catchments is significant (ANOVA $P = 0.007$). Similarly, catchments for which precipitation was correlated with NH_4^+ concentration were smaller ($n = 3$) than catchments for which precipitation was not correlated with NH_4^+ concentration ($n = 11$; $P = 0.025$).

NO_3^-.—Path analysis (Fig. 5) indicated that NO_3^- load was directly, positively correlated with precipitation, was greater in monsoons than in cold fronts, and was greater with the multivariate land use features associated with the negative end of the LF3 axis (Fig. 2). There were no direct correlations of storm features or land factors on *Q*. There were no significant paths from

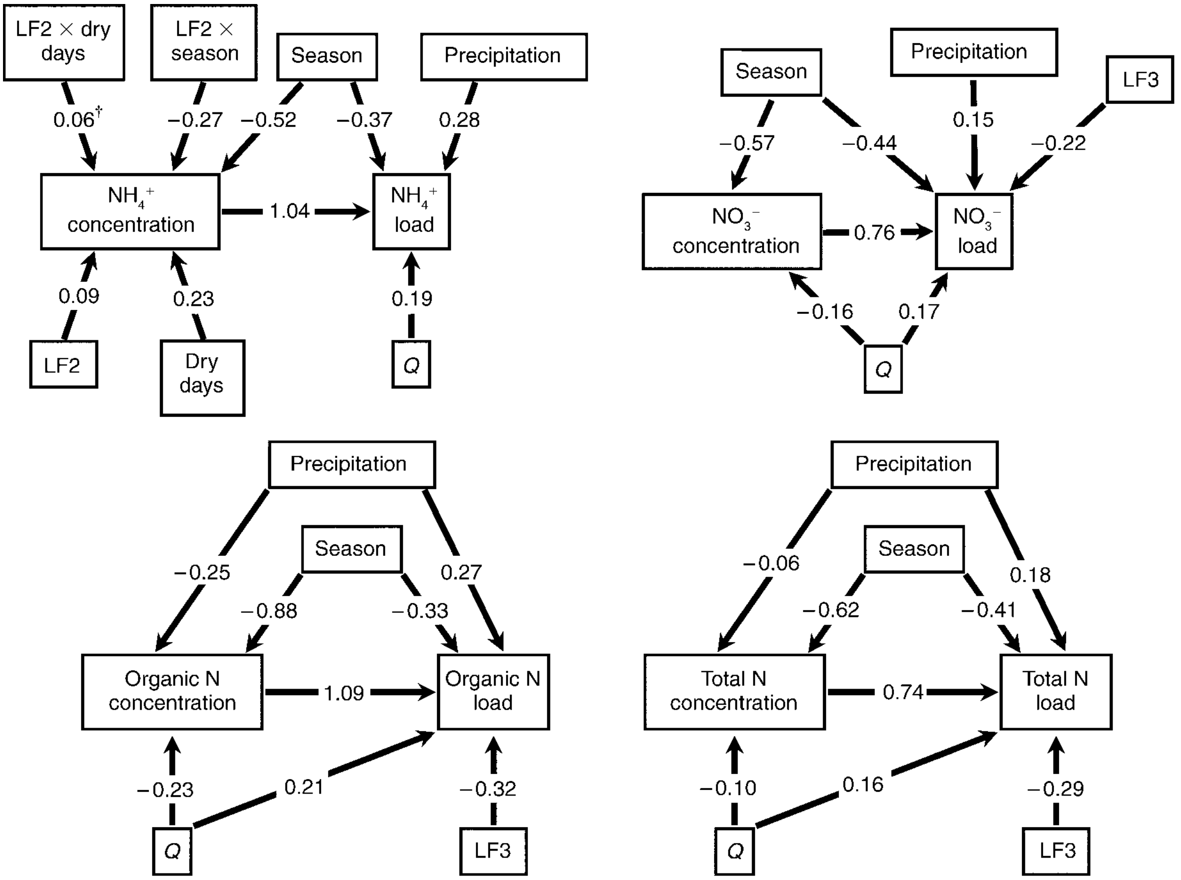

FIG. 5. Best-fit path models obtained following the protocol in Box 1. Numbers on arrows are path coefficients and represent direct effects; the dagger (†) indicates a 90% confidence range (−0.009, 0.128). Abbreviations: Q is discharge (volume of runoff); LF indicates "land factor." Negative coefficients for season indicate higher values for monsoons than for cold fronts.

LF × storm feature interactions to Q, NO_3^- concentration, or NO_3^- load.

There were differences among catchments in the influence of first-order storm feature terms on NO_3^- concentration (Fig. 10). Catchments that exhibited a significant season effect on NO_3^- concentration tended to relatively more impervious (69% ± 6%, mean ± SE; $n = 8$) than catchments for which season did not effect NO_3^- concentration (33% ± 8%; $n = 6$; $P = 0.004$; Fig. 11). As with NH_4^+ concentration, there were a small number of multi-storm feature interactions affecting runoff NO_3^- concentration (Table 3). The three-way interactive effect in catchment 6 indicates that there is a positive "$p \times d$" effect like the one previously described, but that it applies more in the monsoon than in the cold-front season.

Organic N.—Organic N loads, according to path analysis, were positively correlated with precipitation, were higher for monsoon than for cold-front storms, and were higher among land-use compositions associated with the negative end of the LF3 axis. Organic N concentration was negatively correlated with precipitation and was greater in monsoon than in cold-front storms. No storm feature × LF interaction terms were retained in the best-fit-path model.

In regression analyses of organic N, relative to other N species, there were few instances of concentration exhibiting correlation with storm features (Fig. 10). Organic N concentration exhibited a tendency to be more responsive to season than to precipitation or preceding dry days. There were no land use or cover differences between catchments that did vs. did not exhibit correlations between storm features and organic N export. Again, we observed a small number of multi-storm features interactive effects on runoff organic N concentration. Interestingly in catchment 6, the three-way effect had a different sign for organic N than for NO_3^- (the reason why is unclear), indicating that the "$p \times d$" effect was more applicable to the cold-front season (Table 3).

Total N.—The structure of the best-path model for total N was identical to that for organic N. The coefficients, while being of different values, bore the same signs.

As with other N species, total N concentration behaved differently in different catchments (Fig. 10). It

TABLE 2. Decomposition of effects of discharge (Q) and N concentration (Conc.) on the load of each N species.

N species source	Effect types				
			Spurious		
	Direct	Indirect	Via Q	Via season	Via precip.
NH_4^+					
Q	0.19	0		0	0
Conc.	1.04		0	0.19	0
NO_3^-					
Q	0.17	−0.12		0	0
Conc.	0.76		−0.03	0.25	0
Organic N					
Q	0.21	−0.25		0	0
Conc.	1.09		−0.05	0.29	−0.07
Total N					
Q	0.16	−0.07		0	0
Conc.	0.74		−0.02	0.25	−0.01

Notes: For a direct effect, the value shown is the coefficient for the path from the source to the load of the indicated N species (Fig. 5). For an indirect effect, the value is the product of the coefficients for the paths $Q \rightarrow$ Conc. and Conc. $\rightarrow$ load. Indirect effects of concentration on load were not possible owing to the a priori structure of the model (Fig. 1). For a spurious effect, the value is the product of coefficients for the paths $X_i \rightarrow$ Conc. and $X_i \rightarrow$ load (where X_i is a mutual effect [Q, season, or precipitation] on both concentration and load). Spurious effects of Q on load via season and precipitation were possible but were not detected.

was correlated with zero, one, two, or three storm features, depending on catchment; and when it was correlated with just one storm feature, the identity of that feature varied depending on catchment. The catchments for which total N concentration was correlated with precipitation were smaller ($n = 3$) than the catchments for which it was not correlated with precipitation ($n = 10$; $P = 0.012$; Fig. 11). Similarly, catchments for which total N concentration was influenced by precipitation were more impervious (81% ± 12%; $n = 3$) than catchments for which N concentration was not influenced by precipitation (50% ± 6%; $n = 10$; $P = 0.045$). Imperviousness was also marginally greater ($P = 0.087$) for catchments in which season did correlate with N concentration (65% ± 7%; $n = 9$) than for catchments in which it did not (40% ± 11%; $n = 4$). Of the few multi-storm feature-interactive effects on total N concentration, catchments 7 and 10 exhibited positive “$s \times d$” effects. These indicate that the importance of long pre-storm “material accumulation” periods for producing high runoff N concentrations is more evident during the cold-front season than during the monsoon season (Table 3).

Q.—Path analyses do not indicate any effects of storm features or land factors on Q (Fig. 5). In contrast to the path analyses, the multiple regressions do indicate a response of Q to storm features. Discharge was correlated with interactive storm feature terms in several catchments. In catchment 12, a “$p \times d$” effect on Q had a negative direction (Table 3), suggesting that Q was more responsive to high precipitation after a *shorter* dry period, which could result if soil saturation, from a recent storm, reduces infiltration and generates overland runoff. Consistent with this interpretation are the negative “$s \times p$” effects on Q in catchments 7 and 13, indicating that the tendency for high precipitation to generate high discharge applies more in the monsoon season than in the cold-front season. Monsoon storms are short, intense cloudbursts than can deliver as much precipitation in 15 minutes that a cold front storm delivers in several hours. Thus, owing to the rate of rain delivery, monsoon storms can quickly saturate surface soils and start producing runoff, whereas most precipitation from cold fronts has an opportunity to infiltrate any pervious ground surface. Precipitation (compared to dry days and season) was the first-order-storm feature most often correlated with Q (Fig. 10). The catchments in which Q was correlated with precipitation tended to be smaller ($n = 9$) than the catchments in which Q was not correlated with precipitation ($n = 5$; $P = 0.013$; Fig. 11)

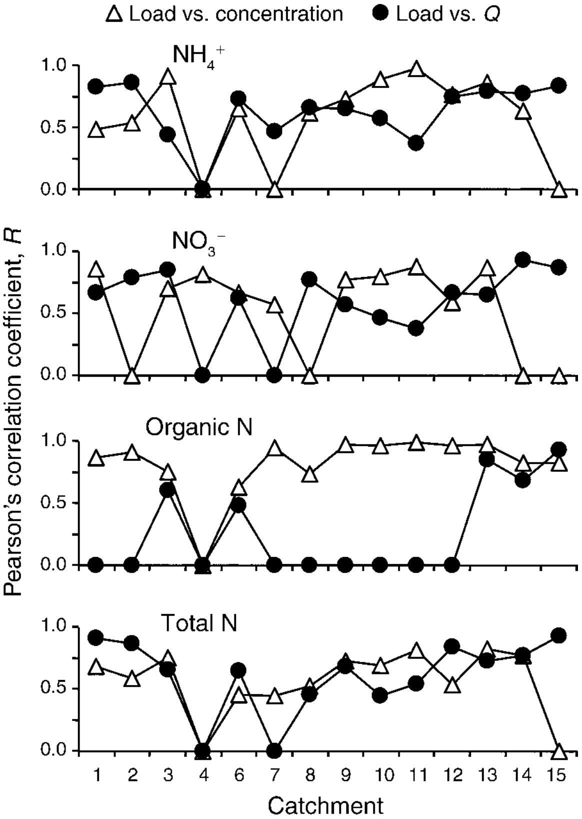

FIG. 6. Coefficients of correlation between N load and the N concentration of runoff (open triangles), and of correlation between N load and discharge, Q (solid circles), of each N species from each catchment. Each point depicts a single correlation coefficient calculated from multiple storm events in the catchment indicated on the x-axis. Coefficients are set to 0 where the correlation was not significant at the $\alpha = 0.05$ level. Coefficients were not calculated for catchment 5, where $n = 2$ events.

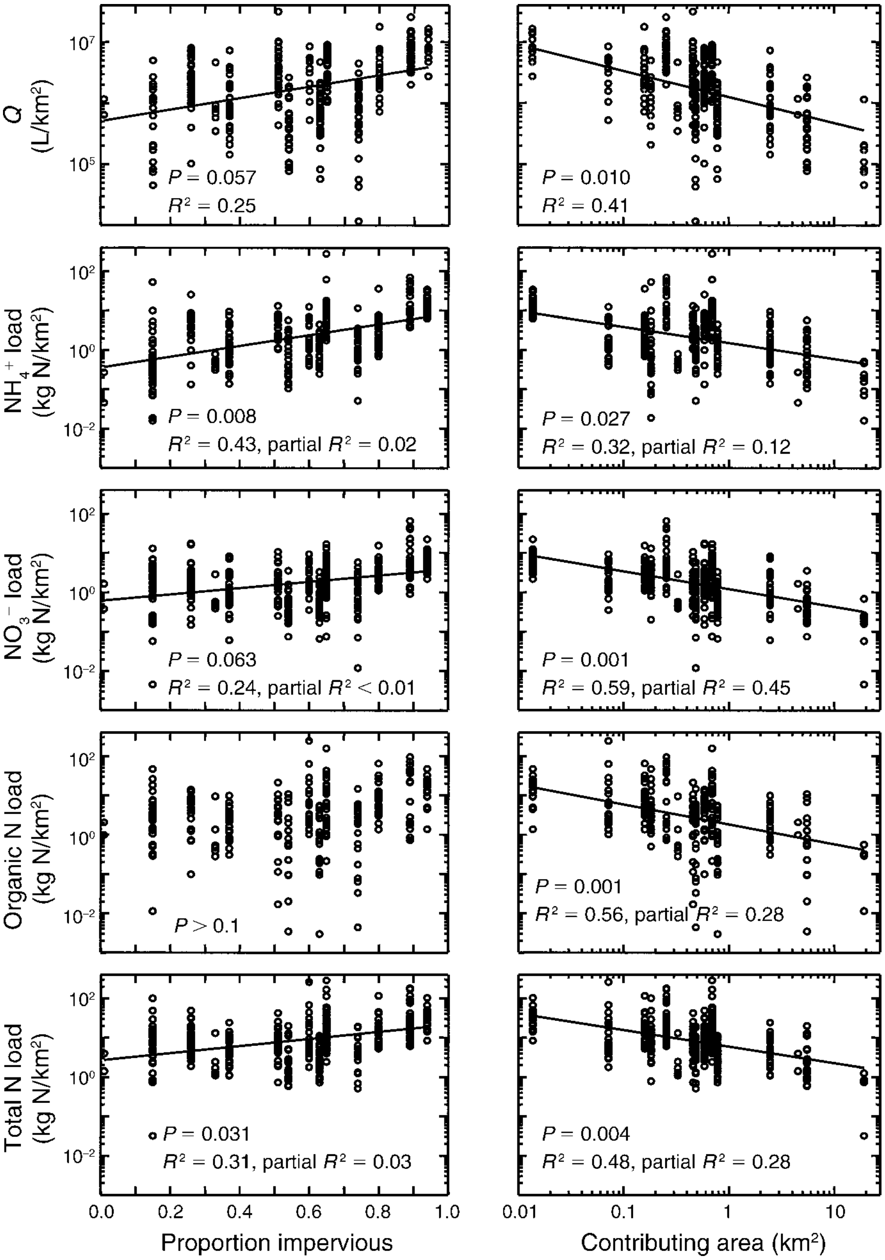

FIG. 7. Plots of Q and N loads (kg N/km^2 contributing catchment area) per storm against the proportion of catchment with impervious cover and against catchment size. All data are shown on $\log_{10}$ axes so they can be presented clearly and their variability can be demonstrated. However, the P, R^2, and partial R^2 values are from weighted regressions with $n = 15$ catchments using natural-log-transformed data (except for proportion impervious, which was not transformed).

DISCUSSION

Nitrogen transport through ecosystems and across their boundaries is an issue that focuses basic ecological and biogeochemical principles on a pervasive environmental problem. In urban (and desert) catchments in the arid Southwest United States, stormwater runoff is one of the prominent vectors of N transport. To better understand N runoff from catchments, we asked three questions.

Controls on N export—N biogeochemistry vs. hydrology

Our results indicate that across the CAP metropolitan region, N load was more a function of the processes that affect runoff N concentration (H1-a) than of the propensity of a catchment to convey precipitation as overland runoff (H1-b). We draw this conclusion from two lines of evidence. First, N load exhibits a stronger positive correlation with runoff N concentration than with Q, as both Pearson correlations and path coeffi-

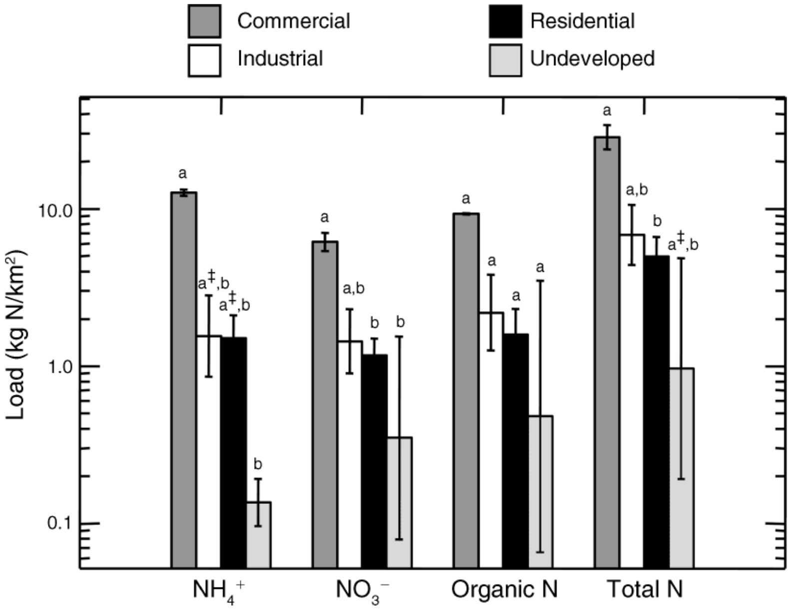

FIG. 8. Load (mean ± SE) among catchments in each land use type. For an N species, different letters indicate land use types with statistically different load ($\alpha = 0.05$). Land use types denoted by "a‡" differed from land uses denoted by "a" at the level of $\alpha = 0.10$. Note the log scaling of the *y*-axis.

cients demonstrate (Figs. 3 and 4). Second, this result holds even after accounting for spurious and indirect effects (Table 2). The spurious effect of N concentration on N load (resulting from a direct effect of *Q* on both) was of much smaller magnitude than the direct positive effect of N concentration on N load. Furthermore, the N concentration effect on N load is strong enough to overcome what might be a "masking" effect of *Q*. Path

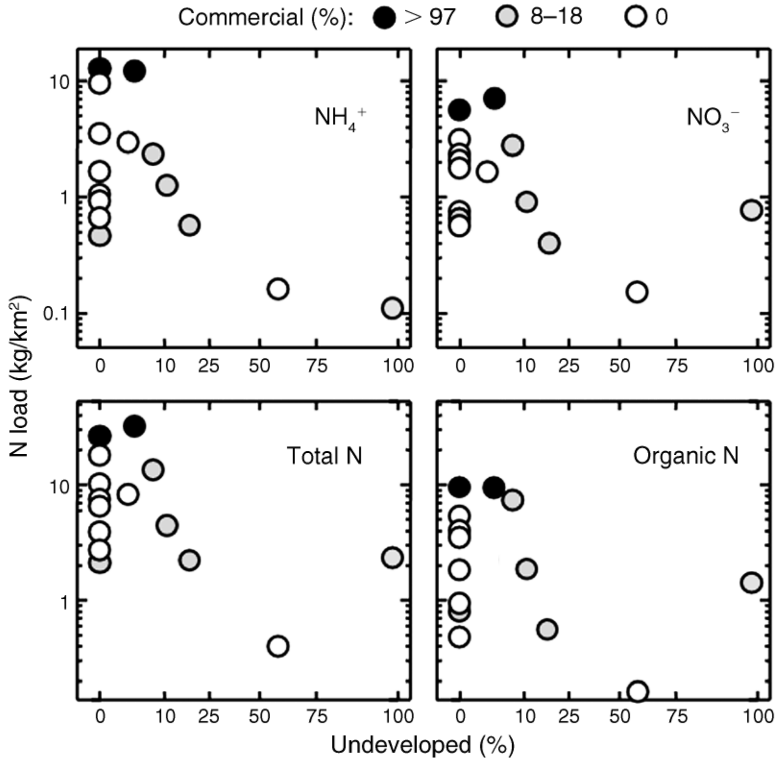

FIG. 9. Plots of N load against percentage of catchment that is undeveloped. Symbol shading reflects the percentage of the catchment under commercial use, with darker shading indicating more commercial use. Note the log scaling on both axes.

TABLE 3. Significant ($\alpha = 0.05$) storm feature interactions on N concentration and Q.

Material	Catchment no.	Interaction	Sign of coefficient	Semi-partial R^2
NH_4^+	2	$p \times d$	positive	0.22
NH_4^+	6	$s \times p \times d$	positive	0.14
NH_4^+	12	$s \times d$	positive	0.32
NO_3^-	6	$s \times p \times d$	negative	0.15
NO_3^-	8	$p \times d$	positive	0.17
NO_3^-	8	$s \times d$	negative	0.12
NO_3^-	14	$p \times d$	positive	0.14
Organic N	6	$s \times p \times d$	positive	0.33
Organic N	7	$s \times p \times d$	positive	0.13
Organic N	7	$p \times d$	positive	0.16
Organic N	7	$s \times d$	positive	0.19
Total N	2	$p \times d$	positive	0.17
Total N	7	$s \times d$	positive	0.06
Total N	10	$s \times d$	positive	0.14
Q	7	$s \times p \times d$	positive	0.11
Q	7	$s \times p$	negative	0.11
Q	10	$p \times d$	positive	0.19
Q	12	$p \times d$	negative	0.17
Q	13	$s \times p$	negative	0.14
Q	14	$s \times p \times d$	negative	0.15

Notes: Season is represented by "*s*," precipitation by "*p*," and dry days by "*d*." When season is one of the interactive terms, a positive coefficient favors cold fronts and a negative coefficient favors monsoons.

coefficients show that Q is directly, positively correlated with load (a volume phenomenon, whereby more water flux simply means more N flux) and that Q is also directly, *negatively* correlated with N concentration. This negative relationship between runoff N concentration and runoff volume presumably results from dilution. Thus, increasing Q simultaneously produces higher N load and lower N concentration, from which we would expect an inverse relationship between N load and N concentration. But instead, we observe a positive N load–N concentration relationship. This masking effect may actually work in another manner. For organic N, and nearly for NO_3^-, the indirect negative effect of Q on load (levied via high $Q \rightarrow$ low N concentration $\rightarrow$ low N load) swamps out the direct positive signal of Q on load.

Thus, we conclude that at the scale of the whole metropolitan area, the mass of N exported in stormwater runoff is determined by the processes that govern runoff N concentration. Runoff N concentration is determined by a combination of the processes that retain and liberate N and by the volume of water carrying the mobile N fraction. Since the effect of water volume on N concentration is negative, however, we can dismiss Q as a mechanism underlying the positive N load–N concentration relationship. If we conduct a thought experiment and hold Q constant, what are the processes that could concentrate N in runoff, thus leading to greater N mass flux in export? We suggest that an "N build and flush" hypothesis provides one such mechanism. According to this model, there is a general *lack* of biological processing of atmospherically and intentionally deposited N on arid-land urban surfaces, such as roadways and low organic matter lots and xeriscaped yards. Thus, variation in the rate and time span of deposition determines the accumulation of the potentially mobile N pool on the ground surface. Any amount of rainfall capable of generating overland flow would entrain nearly all mobilizable N and export it from the catchment. This reasoning has the important implication that relatively high loads of N could be exported by small discharge events, suggesting that water quality and pollution discharge management should focus on all events, not just the "big" ones.

This support for H1-a is less clear when catchments are considered separately. In many catchments, N loads are correlated with Q, supporting H1-b. When patterns change with the spatial extent of analysis, drivers specific

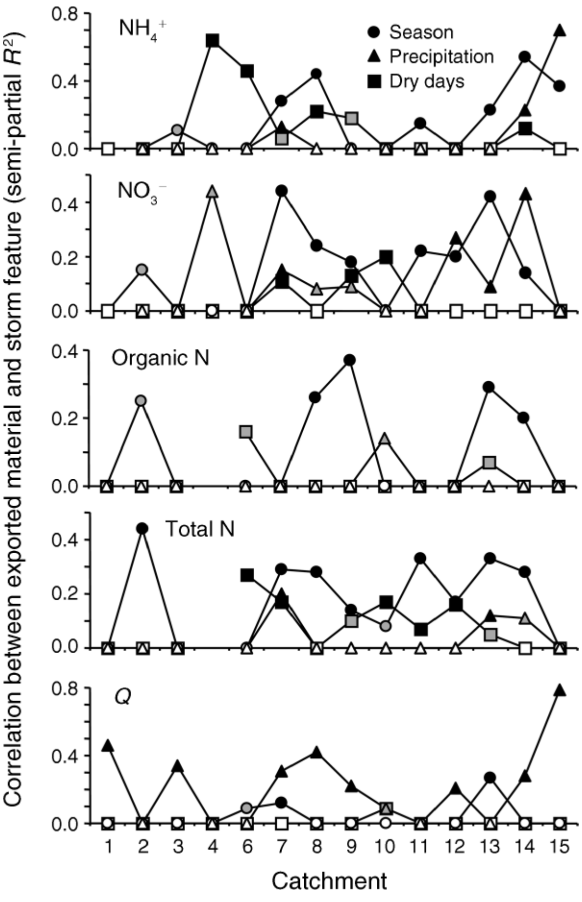

FIG. 10. Semi-partial R^2 between the variable named in the panel and the storm feature identified by the symbol, as observed in runoff from the catchment indicated on the x-axis (catchment 5 excluded). Nitrogen variables are concentration (mass N/volume runoff). Circles depict correlations with season, triangles with precipitation, and squares with dry days. Solid symbols denote correlations significant at $\alpha = 0.05$, and shaded symbols denote those significant at $\alpha = 0.10$. Semi-partial R^2 is set to 0 (open symbols) for storm features that were not significant (at $\alpha = 0.10$). The correlations with season are such that exports are greater from summer monsoons than from winter cold fronts, with the one exception in catchment 7, where Q exhibited the opposite response to season.

to each scale often need to be considered (Levin 1992). In our case, it is tempting to suspect that there is some feature of catchments that occasionally obscures the metropolis-wide relationship between runoff N concentration and N load. There was, however, no consistency among N species *within* a catchment as to whether their load was more correlated with Q or with N concentration. And, there were no systematic differences in land use and cover between the catchments exhibiting an N load–N concentration relationship and the catchments exhibiting an N load–Q relationship. Thus, we cannot identify which, if any, attributes of catchments or N molecular types render load sensitive to Q.

Regulation of N export by land use and cover

We also asked how land use and cover influenced the masses of N and water exported from catchments. We hypothesized (H2-a) that impervious cover increases both the pool size of potentially mobile N and the conveyance of rainfall as runoff. Impervious cover should increase potentially mobile N by preventing infiltration of N into soil, where it would be physically stored, bound with soil minerals and organic matter, and taken up by biota. Impervious cover should also increase the hydrologic responsiveness of the catchment by forcing runoff over land (Jennings and Jarnagin 2002). For NH_4^+, NO_3^-, and total N, we interpret the positive relationship between impervious cover and load as support for H2-a and as further basis for the "N build and flush" hypothesis. For NO_3^- and total N loads, the mechanism is certainly that impervious cover increases hydrological responsiveness. The direct correlations of NO_3^- and total N loads with impervious cover were almost entirely indirect owing to the correlation of impervious cover with Q and of Q with load (where Q is area corrected). Impervious cover probably increases NH_4^+ load via both mechanisms. The correlation of NH_4^+ load with impervious cover was also nearly wholly indirect, and area-corrected Q and NH_4^+ concentrations were each responsible for about half the difference between R^2 and partial R^2 of the NH_4^+ load-impervious cover correlation.

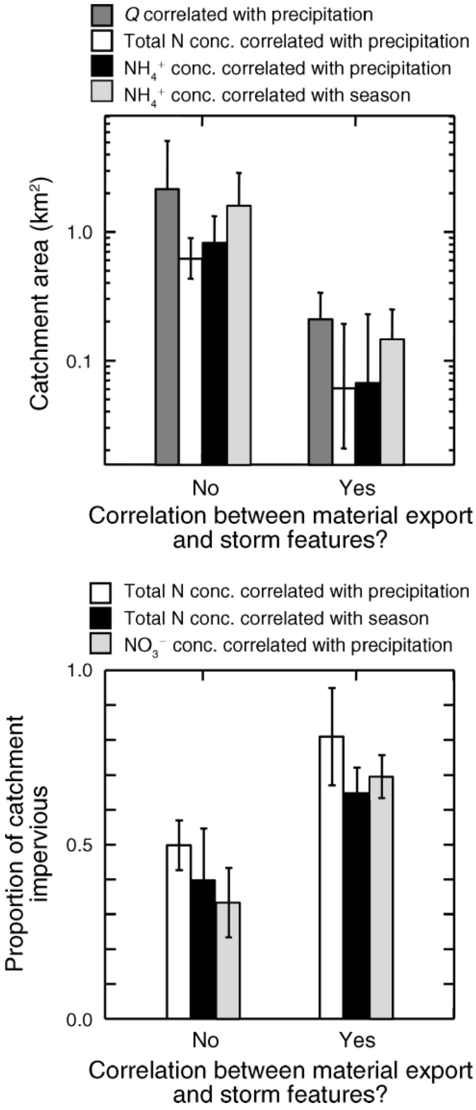

FIG. 11. Mean area (log scale) and impervious cover of catchment classified into groups depending on whether they exhibited a relationship between export (Q or N concentration in runoff) and a storm feature. Seven such export–storm feature relationships are considered, as indicated by different bar shadings in different panels.

We also hypothesized (H2-b) that more retention hot spots would be present in larger catchments than in smaller ones. We interpret the inverse relationship between the load of all N species and catchment area as supporting this hypothesis. Roughly half the load–area relationship could be explained by the combination of load–Q and Q–area relationships. Thus, about half of the improvement in N retention that comes with catchment size cannot be explained by the retention of water. Stormwater detention basins may underlie these results. In urban areas prone to flooding (e.g., the CAP metropolis), stormwater detention basins are mandated landscape features in new building developments. Though not designed with N retention in mind, they are archetypal N retention hot spots as they host some of the highest denitrification rates reported in the literature (Zhu et al. 2004). Hot spots are small areas with disproportionately high reaction rates (after McClain et al. 2003). They are thus relatively rare on the landscape and may be absent by chance from small areas. Even with similar proportions of catchment area occupied by retention hot spots, larger catchments, by virtue of having more actual numbers of hotspots, should retain more N (if retention by a hot spot is not a scalar but rather some function of input to it). While retention basins retain some N simply by capturing water, microbial processes within retention basins also act directly on the N being delivered.

We further proposed that human activities increase the pool size of potentially mobile N (H2-c). Anthropogenic N inputs to urban areas derive from many sources, including unintentional deposition (e.g., NO_x produced by combustion engines) and intentional imports of food, groundwater, and fertilizer (Baker et al. 2001). In CAP, metro-wide mean rates of fertilizer input to residential yards are about 11.2 g $N \cdot m^{-2} \cdot yr^{-1}$, which is six- to ninefold greater than the rate of soil N accumulation, 1.2–1.9 g $N \cdot m^{-2} \cdot yr^{-1}$ (Lewis et al. 2006*a*), suggesting that most of this anthropogenic input is mobile and subject to export in runoff. We interpret the greater rates of N export from more developed catchments as support for hypothesis H2-c. Commercial land use, in particular, is associated with the highest rates of export. Generalization of these results will benefit from a greater sample size of catchments under different predominant land uses.

Path analyses also indicate land use effects on load. Load of NH_4^+ was positively (and indirectly) related to LF2, an industrial–residential land use trade-off. Loads of NO_3^-, organic N, and total N were all negatively correlated with LF3. Interpreting these LF3 results as support of H2-c, however, is not straightforward. The multivariate nature of LF3 (Fig. 2) precludes viewing the correlation between load and LF3 as any simple proxy for a correlation between load and some land use metric.

Interactive effects of catchment and storm features on N export

Our third major question regarding N export was how it responded to multiple drivers that interact across scales. We hypothesized (H3) that intrinsic catchment characteristics mediate the response of N export to storms (Fig. 1).

In support of H3, path analysis suggests that the replacement of industrial land use with residential land use dampens the responsiveness of NH_4^+ export to storm features. With relatively more industrial land use (positive end of the LF2 axis), NH_4^+ export is more responsive to the number of antecedent dry days and exhibits a stronger season effect (where export from monsoons is greater than export from cold fronts). While catchments differ in responsiveness of load to storm features, they also differ in terms of which storm feature NH_4^+ load is even correlated with. In particular, NH_4^+ load is correlated with season and precipitation when catchments are relatively small. Smaller catchments may have fewer retentive hot spots or other complex geomorphic and biogeochemical features to buffer the simple response of export to meteorological drivers. This suggestion agrees with findings from a scaling study showing that a greater number of factors regulates elemental budgets in larger catchments than in smaller ones (Sponseller and Fisher 2006).

Path analyses of NO_3^-, organic N, and total N do not support H3. They identify no storm feature × land factor interactive effects on load, concentration, or *Q*. In support of H3, conversely, catchments differed in terms of which storm feature these loads were most correlated with. As with NH_4^+, these other N species were correlated with season (monsoon > cold fronts) in relatively more catchments and were correlated with precipitation and dry days in relatively fewer catchments. However, there were catchments in which loads of these N species were correlated solely with precipitation and solely with dry days. Unlike N species, *Q* exhibited less variation among catchments in terms of the storm variable with which it was correlated; when it was correlated with any storm feature, it was usually precipitation. Like total N and NH_4^+ loads, catchment size seemed to influence whether *Q* was correlated with precipitation. Overall, in larger catchments with more pervious surface, N and water export were both (1) lower per unit size of catchment and (2) less sensitive to season and storm size.

At a continental extent, catchment features interact with broader scale drivers like climate. Our data permit comparisons of fluvial N loss between urban catchments with an arid climate and pulsed runoff events and urban catchments with a humid climate and perennial stream flow (Baltimore, Maryland, USA; Groffman et al. 2004). Across three years, six catchments in the Baltimore region produced NO_3^- export of 290–700 kg $N \cdot km^{-2} \cdot yr^{-1}$ (median 540 kg) and total N export of 450–1140 kg $N \cdot km^{-2} \cdot yr^{-1}$ (median 670 kg). In our study, median NO_3^- export = 1.9 kg $N \cdot km^{-2} \cdot storm^{-1}$ and 7.4 kg $N \cdot km^{-2} \cdot yr^{-1}$. Median total N export = 9.2 kg $N \cdot km^{-2} \cdot storm^{-1}$ and 38.2 kg $N \cdot km^{-2} \cdot yr^{-1}$. (Our estimates of annual loads were calculated by summing across all storms in each year for each catchment and taking the median of all year-by-catchment values. These values will slightly underestimate actual annual N load if any small storms beneath the runoff-triggering level did, in fact, generate a small amount of runoff that was not sampled.) Thus, annual N export from catchments in the Baltimore region (U.S. mid-Atlantic coastline) exceeds per-storm N export from catchments in the Phoenix region (>3200 km away in the intermountain U.S. Southwest) by roughly 280-fold for NO_3^- and 70-fold for total N. In a median year, the arid catchments of Phoenix probably export roughly 1% of the NO_3^- and 5% of the total N that humid catchments of Baltimore export. Also, export from the Baltimore catchments is dominated by NO_3^- and export from the Phoenix catchments is dominated by organic N. These differences between Baltimore and Phoenix in the amount *and* form of exported N have implications for the ecological functioning (e.g., primary production, heterotrophic microbial respiration) and thus service provision (e.g., carbon sequestration) of recipient systems.

Management implications

In the arid CAP metropolis, recipient systems are often dry streambeds, yet are nonetheless classified as protected "waters of the United States." Pollutant export from catchments is generated by storms, which are exogenous forces not subject to management. As a consequence, an important management question is whether material export can be minimized by managing intrinsic catchment features. Our results suggest that the answer is yes, on two accounts. First, intrinsic catchment features can directly govern material export. Reducing the prevalence of impervious cover within a catchment could probably facilitate material capture, particularly if the pervious cover were strategically located near the catchment outflow (Groffman et al. 2003, Walsh et al. 2005). Second, intrinsic catchment features might also reduce export indirectly, by moderating the sensitivity of N and water mobilization to various storm features. Our study certainly demonstrates that N load does not respond to storm attributes the same way for any two catchments, indicating that load–storm relationships bear the stamp of the catchment in which they play out. Our initial results from 15 catchments suggest that the responsiveness of export to storm features may be governed by catchment size, imperviousness, and land use composition. Additionally, if our "N build and flush" hypothesis is right, N export in stormwater runoff could be minimized by interrupting the N accumulation process, perhaps by washing impervious surfaces (including rooftops) after long dry period *and* directing wash water to pervious areas like grassy swales and yards (not to storm drains).

This study begins to unravel the complex, cross-scale interactions of intrinsic catchment features and broader-scale meteorological forcing (Fig. 1). We have demonstrated that these interactions, coupled with continental scale drivers, regulate N export from ecosystems. Much remains to be learned however, about fluxes of N and other elements. Biogeochemical responses to multiscale drivers thus remains a promising, and societally important, research frontier.

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