

Stoichiometry and load of nutrients and metals discharged from urban catchments by storms

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Abstract

I investigated factors influencing the chemistry of storm water runoff in cities. I analyzed data collected from water discharged from instrumented, delimited hydrologic catchments. Six hypotheses were formulated regarding the roles of storm characteristics and urban demography on the chemistry runoff. The first two were that the (1) stoichiometry and (2) load of constituents in runoff are influenced by features of storms. Within a contiguous metropolitan area (i.e., Phoenix, Arizona, USA), no features of storms explained variation in the ratios total nitrogen (TN) : total phosphorus (TP) or inorganic N (iN) : organic N (oN). Among 102 storms, the median TN : TP ratio = 17.5 (st. dev. = 27.2); the median iN : oN ratio = 0.92 (st. dev. = 2.38). Loads of TN, TP, and metals, exhibited a positive relationship with storm intensity (maximum precipitation / 5 minutes), but not with storm duration or total rainfall. Among storms, load of all constituents was log-normally distributed. In runoff from single events, median TN load = 123.2 g / ha (st. dev. = 205.7); median TP = 16.3 g / ha (st. dev. = 33.6); and median metals load = 10.4 g / ha (st. dev. = 25.3). My third and fourth hypotheses addressed temporal variation in deposition of material flushing rates. They predicted (3) that load of material in runoff would be positively correlated with the number of dry days prior to a storm, and (4) that runoff chemistry would differ between summer and winter storm systems. These hypothesis were unsupported, as I observed no systematic temporal variation in runoff chemistry. From the final two hypotheses, regarding the relationship between runoff chemistry and population density, I predicted (5) that the TN : TP ratio and (6) that TN and TP loads were correlated with housing density (housing units / hectare). Among 12 municipalities in the Phoenix metropolitan area, the TN : TP ratio and TN load (but not the TP load) both increased with housing density. Among 13 municipalities across the United States, TN : TP ratio and TN load also increased with population density, but the relationship was much weaker than among municipalities within the Phoenix metropolitan area. These findings can inform management efforts concerned with influence of water discharged from urban catchments on recipient systems.

Introduction

The export of material and energy from ecosystems presents a problem of both ecological and social significance. With inputs and internal cycling, export constitutes one of the three major features of any ecosystem budget. Such budgets are often critical for testing predictions from the basic theories that describe how ecosystems might accrue, retain, and export nutrients.

Policy issues further demand a comprehensive understanding of nutrient export. Out of concern for the status of recipient systems, regulatory interests have long focused on pollutant discharge from point and, increasingly, non-point sources. The loading of excessive nutrients and other pollutants into recipient systems often generates controversy over the responsible sources. These arguments particularly develop between agricultural and urban advocates. Solutions to these disputes, in addition to the development of basic ecosystem budgets and the crafting of effective management

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policies, will benefit from focused research on the factors responsible for nutrient export from ecosystems. In this paper, I test several hypotheses regarding the factors influencing the stoichiometry and load of constituents in storm water discharged from urban catchments.

By transporting material and triggering biogeochemical processes, storms provide potentially effective vectors of nutrient export from ecosystems. Understanding is far from complete, however, about how storms initiate transport and about the amount of material they transport. This knowledge gap derives from the difficulty in quantifying storms and runoff from start to finish, and in determining the area over which runoff integrates material. I overcame these problems by analyzing runoff from well-delimited catchments instrumented with auto-sampling devices. This small watershed approach facilitates an understanding of ecosystem biogeochemistry by defining the spatial bounds of an ecosystem as those of a hydrologic catchment.

I employ the small watershed approach in urban ecosystems to investigate spatial and temporal variability in the concentration and load of constituents transported by storm water runoff. Much of this research focuses on the desert metropolis centered around Phoenix, Arizona, USA. Arid cities provide models for studying the interactive roles of storms and landscape management in the biogeochemistry of ecosystems. In these ecosystems, material accumulates during protracted dry periods on an impermeable landscape, only to be rapidly mobilized by intense, flashy storms. These conditions, in addition to intense management and rapid growth, place arid cities near the extreme end of Earth's ecosystem types, thus recommending them as study units potentially informative to ecosystem science.

The last thirty years have witnessed a growing public awareness that human activities on land influence freshwater resources. The implementation of the Clean Water Act reflects this awareness. In accordance with the Clean Water Act, the U.S. Environmental Protection Agency oversees the National Pollutant Discharge Elimination System (NPDES). The NPDES requires permits for the discharge of pollutants from point sources. Amendments to the Clean Water Act, in 1987, recognize municipalities as point sources. Consequently, cities must now receive permits for the discharge of storm water runoff. This permitting process entails monitoring the load of constituents in storm water runoff. These monitoring activities, in turn, provide data for addressing my basic question.

Most generally, I ask: what controls the stoichiometry and load of constituents in storm water discharged from cities? To begin answering this question, I test predictions deriving from several specific hypotheses about how discharge is influenced by storm characteristics and demography. Storm characteristics examined include total precipitation, precipitation intensity, storm duration, number of dry days preceding the storm, year in which the storm occurred, and season in which the storm occurred (summer monsoon or winter cold front). Precipitation intensity equals the amount of rain to fall during the most intense 5-minute period of the storm, or maximum cm / 5 min. The demographic feature examined for each city is housing density (housing units per hectare). I list the specific hypotheses below.

Hypotheses

For brevity in this conference abstract, I only list the hypotheses and predictions. The line of reasoning underlying each hypothesis is fully explicated in a manuscript currently being edited.

My first hypothesis is that in arid cities, storm activity influences the stoichiometry of runoff. Specifically, I predict an inverse relationship of both total nitrogen (TN) : total phosphorus (TP) and inorganic N (iN) : organic N (oN) ratios with storm activity, measured as duration and as total rainfall. The predictions from an alternative hypothesis are that no relationship exists of either TN : TP or iN : oN ratios with storm activity.

My second hypothesis is that storm characteristics influence the load of constituents in storm water runoff. Specifically, I predict a positive relationship of constituent loads with storm duration, total rainfall, and storm intensity. Alternatively, the load of material in runoff bears no relation with storm duration, with total rainfall, or with storm intensity. Rather, most material is discharged at the

threshold storm size required to generate runoff. From this alternative, I predict (1) no relationship of load with storm characteristics, and (2) that most material will be in the observed in the first flush of runoff, with little exported in the hydrologic runoff occurring thereafter.

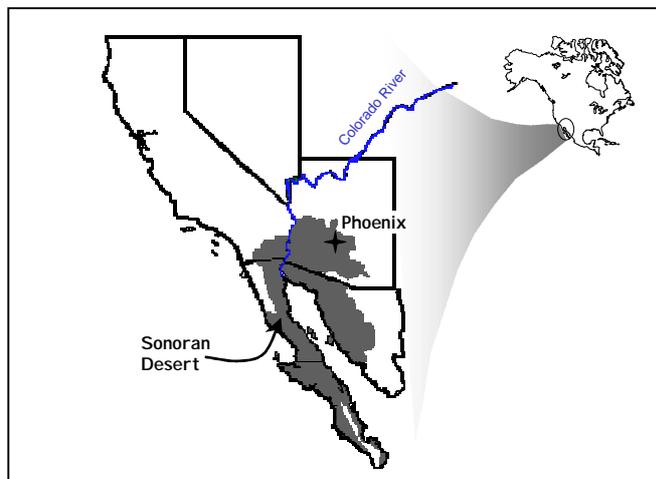


Figure 1. Locations of the Sonoran Desert, in northwestern Mexico and southwestern USA, and of Phoenix, Arizona, USA.

seasons. Monsoons, occurring between July and October, are typically brief, intense thunderstorms that originate in the Gulfs of Mexico and California. Cold fronts, occurring between November and March, are typically protracted, gentler rainfalls that originate in the Gulf of Alaska. From this hypothesis, I predict that load and stoichiometry of runoff should differ between summer monsoons and winter cold fronts. An alternative hypothesis predicts that load and stoichiometry of runoff will not differ between summer monsoons and winter cold fronts.



Figure 2. Location of 13 municipalities, across the USA, used to evaluate the relationship between runoff chemistry and housing density.

hypothesis predicts no relationship of runoff stoichiometry with housing density.

My sixth hypothesis is that denser aggregations of people generate greater deposition of material capable of being mobilized by storms. I thus predict a positive relationship of constituent load in storm water runoff with the housing density of cities. This relationship will be tighter among municipalities within Phoenix than among municipalities across the U.S. An alternative hypothesis,

My third hypothesis is that the rate of dry deposition that occurs between storms is uniform through time, and all storms are equally effective at transporting material stored on the ground surface. Thus, I predict a positive relationship of constituent load in storm runoff with the number of dry days prior to a storm. From the alternative hypothesis, that deposition rates are not uniform through time, and that not all storms are equally effective at removing material stored on the surface, I predict no relationship of load in runoff with the number of dry days prior to a storm.

My fourth hypothesis is that, in the northern Sonoran Desert, where Phoenix is located (Fig. 1), factors influencing runoff chemistry differ seasonally. The northern Sonoran desert experiences two distinct rainy

My fifth hypothesis is that population density disproportionately generates greater deposition of storm-mobile N, relative to storm-mobile P. From this hypothesis, I predict a positive relationship of TN : TP with housing density. I also predict that this relationship will be stronger (i.e., greater R^2) among municipalities within the metropolitan area surrounding Phoenix than among municipalities across the United States (Fig. 2). One alternative hypothesis is that population density disproportionately generates greater deposition of storm-mobile P, relative to storm-mobile N. From this hypothesis, I predict an inverse relation between TN : TP ratio and population density. Again, I add the prediction that this relationship will be stronger among municipalities within Phoenix than among municipalities across the United States. An additional alternative



Figure 3. Locations, within CAP, of catchments from which runoff chemistry and storm data were collected by the USGS. Data for six catchments, circled, are analyzed in this paper.

that the density of human aggregations does not influence the deposition of mobile material, predicts no relationship between load of constituents in runoff and housing density.

Study Area

I analyzed storm runoff data collected from hydrologic catchments within the greater metropolitan area of Phoenix, Arizona, USA (hereafter referred to as the Central Arizona – Phoenix, or CAP, ecosystem). CAP rapidly grew from a population of 50,000 residents in the mid-1940s to approximately 3 million people presently living in nearly 30

municipalities. This urban ecosystem sits 300 – 400 m above sea level in a broad valley that is part of the Basin and Range province of the American Southwest. CAP experiences a hot, dry climate. From 1968-1998, the maximum mean monthly temperature, in July, was 40.7 C, and the minimum mean monthly temperature, in January, was 5.3 C. For the years 1954-1990, mean annual rainfall was 19.5 cm. As described above, two weather patterns account for 90% of this precipitation.

I analyzed storm runoff collected from 15 drainage basins, 1.4 – 1918.2 ha in size, within the CAP ecosystem (Fig 3). Data for six representative catchments are presented here. Drainage basins consisted of both mixed and homogenous land uses, including residential, industrial, commercial, and undeveloped. The proportion of drainage area comprising impervious surface varied among the basins from 0.01 – 0.94. Flow emanates from these catchments only as storm runoff. Other than storm runoff, no stream flow discharges from these catchments.

We also analyzed estimates of constituent load discharged from the entire spatial extent of 24 municipalities. Twelve of these were located within the metropolitan area surrounding Phoenix. Thirteen of these, including Phoenix, were located throughout the United States (Fig. 2)

Methods

I obtained data on precipitation and on the physical and chemical attributes of runoff from each catchment for storms occurring during 1991-1998. Precipitation and runoff data were only collected for rainfall events that persisted for a minimum duration and delivered a minimum amount of rainfall. These criteria varied seasonally. The United States Geologic Survey (USGS) and the Flood Control District of Maricopa County (FCDMC) collected and analyzed samples. Storm water runoff was channelized into stream flow at the outlet of each catchment. Dataloggers were used to measure precipitation and the stage (depth of flow) of runoff, and to activate automatic pumping samplers. Precipitation (cm of rainfall) was measured every minute using tipping-bucket rain gages. Stage of runoff was measured every minute using a pressure regulator system, and then converted to discharge ($L s^{-1}$) using rating curves.

I investigated factors that influenced the load of constituents ($mass ha^{-1}$). Load was calculated as event-mean concentration ($mass / L$) x runoff (L) x surface area of catchment⁻¹ (ha^{-1}). The USGS and FCDMC obtained event-mean concentrations by collecting flow-weighted discrete samples. Using this method, a specified volume of water is pumped from the centroid of flow every time a

specified volume of runoff has discharged past the collection point. Discrete samples are aggregated into a single composite sample for chemical analysis.

Some of my hypotheses require estimates of runoff from the entire spatial extent of 24 municipalities. To estimate loads for each municipality, load per hectare was first modeled for various land use categories and storm conditions. Second, these model estimates were scaled up to an entire municipality based on the area of the city comprised of each land use category and on the mean storm

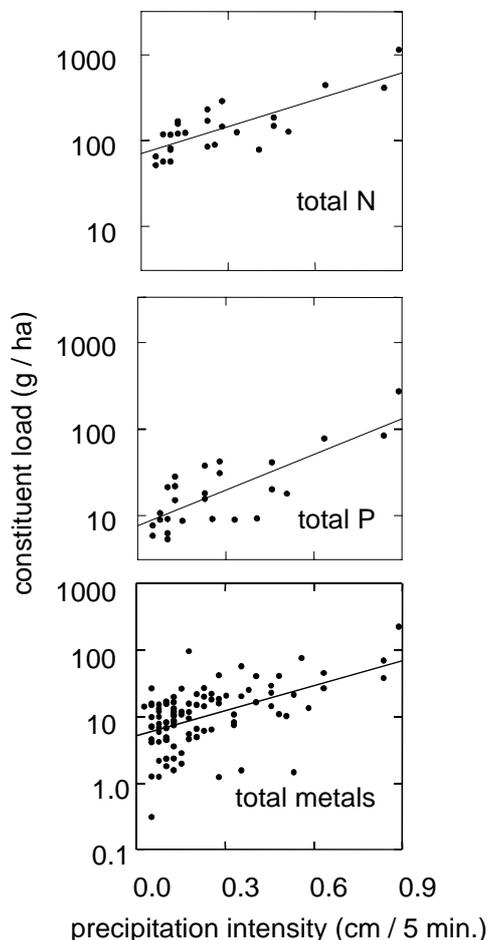


Figure 4. Relationships between load and storm intensity. Each point represents one storm. For TN and TP, data are presented from a single, representative catchment. Data from all catchments are presented for total metals. Total metals equals the sum of arsenic, cadmium, chromium, copper, lead, nickel, and zinc. Similar relationships were observed for individual metal species in individual catchments. In all cases, $p < 0.05$.

TN:TP ratio increased with population density. This relationship was stronger among 12 municipalities in CAP than among 13 municipalities across the U.S. Total P did not exhibit a relationship with housing density (Fig. 5)

Discussion

Storm characteristics and demographic features both influence the chemistry of storm water runoff from urban ecosystems. I developed various hypotheses as to how storm features and

conditions for each season (summer monsoon, winter cold front, and spring with mixed systems). This approach provides estimated load of constituents in storm runoff from entire cities for each season and for the whole year. I obtained demographic features of cities, such as housing density, from the U.S. Census Bureau.

Data were analyzed using general linear models, including regression and ANOVA. Prior to all analyses, nutrient data were log-transformed to normalize variance.

Results

Storm water runoff chemistry was characterized from 102 storm events occurring in 6 catchments in CAP. The TN : TP ratio was log-normally distributed around a median value of 17.5. The iN : oN ratio was log-normally distributed, as well, around a median value of 0.92. Neither ratio correlated significantly with any storm characteristic or differed between monsoon and cold front storms. The loads of TP, TN, and metals all correlated with storm intensity (Fig. 4). Loads did not correlate with storm duration, total rainfall, or antecedent dry days, and did not differ between monsoon and cold front storms.

Runoff chemistry was correlated with housing density in cities. Both TN load (Fig. 5) and the

population density may influence runoff. Below, I evaluate the support for these hypotheses provided by data in this paper, and I briefly comment on some implications of these findings for management of storm runoff in cities.

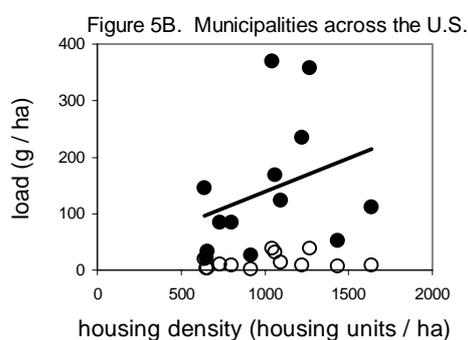
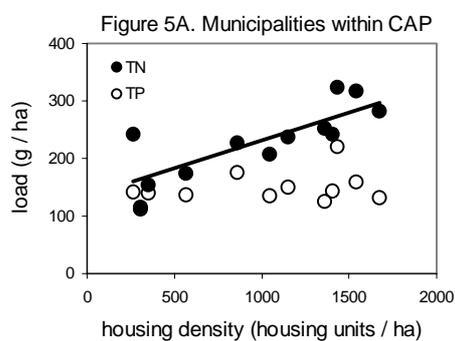


Figure 5. Relationship between estimated annual load from the entire spatial extent of municipalities and housing density. In both panels, $p < 0.05$ for TN and $p > 0.05$ for TP.

From my first hypothesis, that storm activity influences the stoichiometry of runoff, I predicted an inverse relationship of both TN : TP and iN : oN ratios with storm activity, measured as duration and as total rainfall. My data provided no support for this hypothesis, as these predictions were wrong. There are several reasons why storm activity may have little influence on the stoichiometry of runoff. First, alteration of nutrient ratios may require that biotic processes, such as denitrification, operate for several days. The short duration of storms, typically < 24 hours, may induce an insufficient magnitude of microbial processing to substantially alter nutrient ratios. Second, even if storms stimulate enough microbial processing to alter nutrient ratios, it may only matter that the ground is wet. That is, any microbial processing that does occur may be triggered by some threshold amount of moisture. Once the ground is wet, additional rainfall beyond this threshold has an unappreciable impact on nutrient processing. Consequently, nutrient ratios will not change along a gradient of rainfall amount. Third, even if biotic processing changes along a gradient of storm activity, the wet conditions caused by storms may facilitate similar magnitudes of countervailing biotic processes. For instance, N-fixation, nitrification, and denitrification may all exhibit similar increases with greater storm activity. This phenomenon would leave N : P and inorganic N : organic N ratios virtually unchanged. These possibilities all represent post-hoc hypotheses suitable for evaluation in future studies.

From my second hypothesis, that storm characteristics influence the load of constituents in storm water runoff, I predicted a positive relationship of constituent loads with storm duration, total rainfall, and storm intensity. Loads of TN, TP, and metals increased with increasing storm intensity, but not with other features of storms. Load may have increased with intensity owing to the nature of urban land cover. Mobile material accumulates on available surfaces. Thus, on the rugose surfaces of asphalt and concrete, most mobile material accumulates in fine fissures, cracks, and dimples. This material will be mobilized by the scrubbing action of intense storms. Long storms, if they are gentle, will not necessarily generate greater loads. Additionally, large volumes of total precipitation will not necessarily generate greater loads. Once a sufficient amount of rainfall has occurred to initiate hydrologic runoff, there may be no influence of additional water on the ground.

An alternative hypothesis suggests that this relationship between load and storm intensity is spurious. It is possible that storm intensity does not generate load. Rather, storm intensity merely covaries with the time of year (summer) exhibiting the highest rates of interstorm deposition, and interstorm deposition underlies variation in load. For this hypothesis to be supported, however, load would have to be greater during summer storms than during winter storms. Such a pattern, however, was not observed, thus undermining this alternative and further supporting the hypothesis that constituent load in urban runoff derives from storm intensity.

From my third hypothesis, that deposition is uniform through time, and all storms are equally effective at transporting material, I predicted a positive relationship of constituent load in storm runoff with the number of dry days prior to a storm. Again, my data provided no support for this hypothesis,

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as TN, TP, and metals were all unrelated to antecedent dry days. There may have been at least two reasons why load did not exhibit a positive relationship with antecedent dry days. First, the rate of deposition (mass / day) may have varied among interstorm dry periods. Second, there may have been differential flushing among storms. After a long period of great material accumulation, a relatively gentle storm may export only small amounts of material, leaving great amounts of material available for export by the subsequent storm. An intense storm, occurring quickly thereafter may export most of the material deposited over several prior interstorm dry periods.

From my fourth hypothesis, that factors influencing runoff chemistry differ seasonally, I predict that load and stoichiometry of runoff should differ between summer monsoons and winter cold fronts. No data supported this hypothesis. The lack of seasonal difference in runoff chemistry suggests that there is no seasonal difference in the factors influencing runoff chemistry. For instance, the relationship between load and storm intensity, coupled with the purported difference in intensity between monsoons and cold fronts, collectively suggest that loads should differ between monsoons and cold fronts. No such difference was observed. It is possible, that despite stereotypes and popular intuition, storm intensity did not differ between summer and winter in these particular catchments during the years these data were collected.

From my fifth hypothesis, that population density disproportionately generates greater deposition of storm-mobile N, relative to storm-mobile P, I predicted a positive relationship of TN : TP with housing density. My results support this hypothesis that more people add more N faster than they add more P. Enhanced TN : TP in storm load may derive from enhanced N, but not enhanced P, deposition. Through industrial processes and automotive combustion, people fix large quantities of atmospheric N₂ gas. Human activities, such as land clearing and the exposure of clay and rock in building materials, may enhance weathering and deposition of P, as well. Compared to the strong influence of humans on the gaseous N cycle, and owing to a lack of a gaseous P cycle, this increased deposition of P may be relatively small. This change in the TN : TP ratio with population density derives from the influence of people on individual nutrient cycles.

From my sixth hypothesis, that denser aggregations of people generate greater deposition of mobile material, I predicted a positive relationship of TN and TP with housing density. I also predicted that any relationships of runoff chemistry with housing density will be stronger at a finer spatial scale (among municipalities within CAP) than at a broader spatial scale (among municipalities across the United States). As suggested above, TN, but not TP, increased with housing density. This increase likely reflects the unique influence of people on the gaseous N cycle. These correlations are weaker at broader spatial scales, however. Additional climatic and geologic drivers, which do not vary among municipalities within CAP, likely vary at a broader scale.

Research on storm water can inform management efforts concerned with discharge permitting and the influence of urban catchments on recipient systems. Urban management can impose no direct or immediate control over the climatic forces that dictate storm frequency, origin, and intensity. Once the role of storms in generating discharge is understood, however, landscape management decisions can incorporate that knowledge. If storm intensity generates runoff, management can reduce the effective storm intensity on load-bearing surfaces, and reduce the actual amount of load-bearing surface. For instance, load reductions might result from maintaining well-paved streets with minimal interstitial fissures; by frequent street sweeping (as street sweepers behave like intense storms); and by constructing narrow streets with overarching canopies. In addition to reducing the amount of impervious surface, narrow streets can be completely overarched by tree canopies. An overarching canopy that intercepts rainfall destined for an impervious surface may reduce the impact of rain drops. Such a landscape design may provide additional, conspicuous ecological services for urban dwellers. Narrow, shaded streets will generate less of a heat-island effect, thus cooling neighborhoods in intense climates like Phoenix. Shade trees on parking strips may aesthetically complement the structural diversity of yards with other forms of xeric or mesic landscaping, perhaps facilitating animal diversity and human-nature interactions in habitats most familiar to people, their own yards, parks, and neighbourhoods.

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