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Relationships among nutrients, chloride and biological indices in urban Maryland streams

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Abstract Using a spatially extensive urban database constructed from the Maryland Biological Stream Survey (MBSS), we describe the relationships of nutrients in small-order streams to eight defined categories of percent catchment urbanization, correlations between chloride and conductivity in urban streams, and relationships between nutrients and chloride with two Maryland-specific indices of biotic integrity for benthic macroinvertebrates and fish assemblages. Stream nutrients become elevated with increasing percent catchment urbanization, followed by increases in all four measured nitrogen species and total phosphorus at catchment urbanization levels greater than 10%. There was a strong collinear relationship (r^2=0.90) between chloride and conductivity (trimeans) across all eight urbanization classes, where Cl (mg/L)=−0.397+0.188*conductivity (μS/cm). Critical values for all water quality parameters with the two Maryland biological indices were derived using quantile regression, with significant regressions developed for 11 of 16 water quality parameters and the two biotic indices. For nitrate (NO_3-N), the critical thresholds between fair and poor stream quality for the two Maryland biological indices were 0.83 mg/L (benthic macroinvertebrate assemblages) and 0.86 mg/L (fish assemblages). Increasing stream nutrient and chloride levels, associated with widespread catchment urbanization intensity, now affect many small streams in Maryland, with implications for decreasing water quality in major tributaries and the Chesapeake Bay.

Keywords Stream · Nutrients · Chloride · Urbanization · Indices

Introduction

Urbanization effects on stream communities have been reported worldwide (Forman and Alexander 1998; Forman et al. 2003; Paul and Meyer 2001; Walsh et al. 2005b). Urbanization is a major disruptive force to stream ecosystems, presenting symptoms of the

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"urban stream syndrome" when human population density reaches a critical limit within a catchment (Groffman et al. 2005; Klein 1979; Meyer et al. 2005; Paul and Meyer 2001). Urban and periurban land conversion modifies stream structure and function, often resulting in degraded physiochemical conditions with associated biotic changes (Gergel et al. 2002; Meyer et al. 2005; Paul and Meyer 2001; Roth et al. 1999; Walsh et al. 2005a). Paul and Meyer (2001) note that urbanization is second only to agriculture as a primary agent of stream degradation in the US. Once catchments are urbanized, both intermittent and perennial streams display altered hydrologic regimes, elevated nutrient and contaminant concentrations, and degraded biotic assemblages. These effects may be difficult to mediate or reverse (Booth 2005; Groffman et al. 2003; Paul and Meyer 2001; Walsh et al. 2005b).

Over the last 400 years, nutrient loading in many small stream systems has increased, resulting from anthropogenic influences such as agricultural runoff, wastewater discharge, atmospheric deposition, and urban/suburban point and non-point sources (Brabec et al. 2002; Galloway et al. 2003). Increased sediment loading and elevated stream temperatures, as anthropogenic effects from urbanization, have been observed in aquatic ecosystems throughout the world (Allan 1995; Paul and Meyer 2001; Waters 1995).

Another attribute of water quality well documented in the urban literature is stream conductivity (Herlihy et al. 1998; Paul and Meyer 2001). Increased urban stream ion concentrations, especially chloride, are a consequence of runoff over impervious surfaces, passage through pipes, and exposure to other anthropogenic infrastructure (Hatt et al. 2004; Rose 2002). Chloride has emerged as an important stressor to urban stream quality due to road deicing practices (Kaushal et al. 2005). Although previously found in high levels in urban areas (Bryan 1971), the widespread use of salt to deice roadways has led to regionally elevated chloride levels up to 25% of the chloride concentration in seawater during winter, and remaining high throughout the summer even in less urbanized watersheds due to long-term accumulation in ground water over decades (Kaushal et al. 2005).

Using a spatially extensive urban data base for small streams derived from the Maryland Biological Stream Survey (MBSS), including data from over 2,000 streams, we describe (1) the relationship of nutrients (four nitrogen and two phosphorous species) to catchment urbanization in Maryland, (2) the correlation between chloride and conductivity relating to urban intensity, and (3) the association among nutrients, chloride and conductivity with two biotic integrity indices developed specifically for Maryland.

Materials and methods

Design

Patterns between urbanization intensity, stream nutrients, chloride and biological indices were examined using the MBSS database. This statewide stream survey was conducted by the Maryland Department of Natural Resources (MDDNR), Versar, Inc., and the University of Maryland between 1995 to 1997 (Round One—3 years) and 2000 to 2004 (Round Two—5 years). Initially, the MBSS was designed to assess acidic deposition and other anthropogenic effects on the biotic integrity of fish and benthic macroinvertebrates within specific regions of Maryland (Roth et al. 1999; Kazyak 2000). Both MBSS rounds together comprise a large dataset (with over 2,000 sites sampled) that may be used to assess nutrient and chloride concentrations under spring baseflow conditions (spring index period) across Maryland, and to relate these to biological indices (summer index period). Although a complete understanding of stream nutrient dynamics requires intensive data collected over time (i.e., taken over multiple years and seasons, and usually at a smaller number of fixed stations), the MBSS water chemistry results provide a "snapshot" of nutrient and chloride concentrations is streams that may be compared among watersheds statewide.

The MDDNR initially implemented a hierarchical probability-based sampling design as a cost-effective way to characterize Maryland stream resources (Heimbuch et al. 1999). By randomly selecting sites, the MBSS allows quantitative inferences about characteristics of more than 19,000 km of Maryland non-tidal streams. The Round One MBSS design began with the Maryland Synoptic Stream Chemistry Survey sampling design (Knapp and Saunders 1987; Knapp et al. 1988), and was modified during the 1993 pilot and 1994 demonstration phases (Vølstad et al. 1995, 1996). The final design allowed robust estimates at the level of stream size (Strahler orders 1, 2, and 3), large watershed (17 river basins), and statewide (map scale=1:250,000).

MBSS Round Two was a modified design allowing unbiased estimates at a smaller watershed level (85 individual or combined Maryland 8-digit watersheds using a 1:100,000-scale base map). In order to achieve the necessary sample target density (each watershed having greater than ten sample sites), Round Two took 5 years to complete rather than the 3 years of Round One. Round Two includes all non-tidal stream reaches of fourth-order and smaller, with exclusion of non-wadeable impoundments or substantially altered riverine reaches. Fourth-order streams were included to expand statewide coverage and to ensure that all the streams classified as third order by the 1:250,000 map scale in Round One were also covered in the 2000–2004 MBSS. Of 134 watersheds, 79 contained less than 160 non-tidal stream km. These were combined into 29 "super-watersheds," each containing between two and seven constituent 8-digit watersheds. When combined with the 55 remaining watersheds, 84 watersheds were identified as discrete primary sampling units (or PSUs) for Round Two. Any bias resulting from differences between Round One and Two were correctable by limiting analyses to stream populations overlapping the two sampling frames.

Specific water quality parameters were determined for first (N=845), second (N=265) and third-order (N=140) streams sampled in Round Two (2000–2004). Only 39 fourth-order sites were sampled and were excluded from subsequent analyses. Round One sampled 325 first-order, 332 second-order, and 297 third-order streams for water quality; however, the only nutrient measured was nitrate (NO_3-N).

Water quality analyses and biological indices

All water quality measurements were performed at the Appalachian Laboratory. Grab water samples were collected using EPA-approved techniques and delivered to AL for analysis (USEPA 1987). Closed pH samples were collected in gas-tight 60 cc syringes and analyzed in the laboratory (USEPA 1987). Specific conductance and acid neutralizing capacity (ANC) were measured on unfiltered samples collected in pre-cleaned, polyethylene bottles (USEPA 1987). Total nitrogen (TN) and phosphorus (TP) were also measured on unfiltered samples collected in pre-cleaned, polyethylene bottles. Inline UV-assisted persulfate digestion techniques followed by flow injection colorimetry were used to determine TN and TP (APHA 1998). Nutrients, dissolved organic carbon (DOC), and anions were measured on filtered (0.45 μm) samples. Chloride, nitrate-N, and sulfate were analyzed by ion chromatography (USEPA 1987). Nitrite-N (NO_2-N), ammonia-N (NH_4-N) and orthophosphate (OP) were analyzed by flow injection colorimetry (USEPA 1999; APHA

1998). DOC was measured using a UV-assisted persulfate technique (USEPA 1987). A total of 2243 streams were sampled over 8 years in both MBSS rounds.

Two Maryland-specific biological indices-the benthic index of biotic integrity (BIBI) and the fish index of biotic integrity (FIBI)-were determined for each MBSS site (Stribling et al. 1998; Roth et al. 1999). Benthic macroinvertebrates were collected during the Spring Index period and fish during the Summer Index period using standardized techniques and protocols (Roth et al. 1999; Kazyak 2000). In addition, a rigorous QA/QC program supported the MBSS program (Roth et al. 1999; Kazyak 2000).

For each water quality parameter, except for the TN:TP ratio, estimates were made of critical values for the Maryland BIBI and the FIBI in the urban data set, using the Maryland biocriteria IBI breakpoint of 3.0 (Roth et al. 1999; Vølstad et al. 2003). Although this 3.0 breakpoint serves as an indicator for MBSS reference conditions statewide (an IBI of 3.0–3.9 falls within the 10th–50th percentile for reference sites), it is also the breakpoint between fair (IBI=3.0–3.9) and poor (IBI=2.0–2.9) stream biotic conditions, with a very poor score (IBI=1.0–1.9) indicating severe stream degradation. An IBI score of 4.0–5.0 represents sites with minimal impacts, typically above the 50th percentile for reference sites (Roth et al. 1999).

Landscape classification

MDDNR quantified land use patterns of the upstream catchment for each MBSS site using GIS (1:62,500 scale) and landuse/landcover data (Federal EPA Region III Multi-Resolution Land Characteristics, 30×30 m resolution). All catchments with >30% agricultural landuse (mean=28.6%, 95% confidence interval=27.7–29.6%) were eliminated to reduce confounding effects of current agricultural practices; however, this may not account for any historical agricultural practices. A total of 934 MBSS sites met the criterion for site selection and comprised the primary urban data set for subsequent statistical analyses-these were classified into eight discrete groups based on the calculated % catchment urbanization (CU: 0–9.9%, 10–19.9%, 20–29.9%, 30–39.9%, 40–49.9%, 50–59.9%, 60–69.9% and >70%).

Statistical analyses

Medians, means and standard errors were calculated (Statistica, Version 7.1, StatSoft, Tulsa, OK), for each water quality parameter based on the % catchment urbanization classification (Table 1). Tukey's trimean was determined for each analyte in order to increase robustness of each parameter estimate and were used for graphical presentation (Gilbert 1987). Quantile regression (STATA 9, StataCorp LP, College Station, TX) was used to examine relationships among selected water quality parameters and the two MBSS indices of biological integrity (Cade and Noon 2003; Roth et al. 1999).

We encountered two problems with the statistical distributions for several analytes. One problem was the large N associated with the lowest % catchment urbanization (0–9.9%) for every analyte. For example, NO_3-N in the 0–9.9% class contained 620 observations while the next highest class contained 71 observations. This large difference in sample size per urban class possibility created the second problem of significant Levene and Brown-Forsythe tests for homogeneity of variances in preliminary ANOVA—a problem not solved by variable transformation (Steel and Torrie 1960). Consequently, we employed a non-parametric Kruskal-Wallis test, followed by a multiple comparison test. However, we were not interested in comparisons among all urbanization classes, but only the single comparison of each percent catchment urbanization (CU) class to the lowest class of 0–9.9%, representing the lowest catchment urbanization intensity.

Results

Nitrogen species

All four nitrogen species (NO_3-N, NO_2-N, NH_3-N and TN) measured in MBSS Round One and Round Two increased with increasing urbanization intensity (Table 1 and Fig. 1). For NO_3-N, all percent catchment urbanization (CU) classes over 20% were significantly elevated ($p \leq 0.05$) from the reference class of <9.9% CU (Table 1), with median NO_3-N concentrations ranging from 0.84 to 1.39 mg/L over 20% CU, or approximately 2–3 times higher than the reference class. This same general pattern was observed for NO_2-N (Table 1 and Fig. 1) except that there was a significant increase versus the reference class in the 10–19.9% CU, and five of the other classes. The 20–29.9% CU NO_2-N was elevated but the median value was not significantly different from 0–9.9% CU. Mean MBSS NO_2-N levels were low, ranging from 0.0012 to 0.010 mg/L across all CU classes. However, the highest NO_2-N values were approximately eight times greater than the CU reference class.

In contrast to NO_2-N, NH_3-N was elevated in all 7 CU classes greater than 10%, ranging from 0.016 to 0.034 mg/L, versus the reference CU of 0.0090 mg/L (Table 1 and Fig. 1), although median values were only significantly different from the reference for 4 CU classes (Table 1). The highest levels of NH_3-N were over 3.5 times greater than the reference value of 0.56 mg/L NH_3-N. For TN (Table 1 and Fig. 1), five of the CU classes were significantly different from the reference CU—all five were at a CU>30% and ranged from 1.20 to 1.60 mg/L NH_3-N. Overall, nitrate contributed the most nitrogen to the TN values. All four nitrogen species displayed a general pattern of elevated concentrations with increasing CU, especially at CU levels greater than 10–20%.

In order to place the urban nitrogen data set into perspective with the entire statewide MBSS data set of 2,190 NO_3-N measurements made in both MBSS rounds, only 0.87% ($N=19$) exceeded the EPA Maximum Contaminant Level of 10 mg/L of NO_3-N (EPA criteria for ground water and drinking water). The highest stream NO_3-N measured was 53 mg/L (in Round One—a site in a heavily farmed catchment), with an overall mean of 2.0 mg/L (SE=0.053). In 1,140 NO_2-N measurements made in the second MBSS round, no stream samples exceeded the EPA Maximum Contaminant Level of 1 mg/L for NO_2-N (criteria for ground water and drinking water). The highest stream NO_2-N measured was 0.15 mg/L with an overall mean equal to 0.0078 mg/L (SE=0.00035). Of 1212 NH_3-N measurements, the highest stream NH_3-N value measured was 2.8 mg/L, with a mean ammonia of 0.049 mg/L (SE=0.0045). The highest TN measured in the second MBSS round was 16 mg/L with an average TN of 2.0 mg/L ($N=1211$, SE=0.059).

Phosphorus species

TP, over all CU classes, increased with escalating urbanization intensity, with median concentrations ranging from 0.017 to 0.026 mg/L in the 7 CU classes versus the CU reference of 0.012 mg/L (Table 1 and Fig. 2). Although not all higher CU classes were significantly different from the CU reference, the overall median TP in these classes was

Table 1 Median, mean, standard error (SE) and trimean (TM) values for selected water quality measurements taken during Round One and Round Two MBSS index periods

Percent Catchment Urbanization									
Parameter	Statistic	0–9.9	10–19.9	20–29.9	30–39.9	40–49.9	50–59.9	60–69.9	>70
NO_3-N	Median	0.42	0.47	0.84*	0.86*	1.39*	1.04*	1.18*	1.38*
	Mean	0.54	0.60	0.97	0.94	1.28	1.63	1.40	1.41
N=899	SE	0.020	0.051	0.13	0.10	0.095	0.28	0.19	0.12
	TM	0.43	0.50	0.85	0.89	1.32	1.22	1.21	1.37
NO_2-N	Median	0.0012	0.0038*	0.0034	0.0095*	0.010*	0.0083*	0.0069*	0.010*
	Mean	0.0022	0.0044	0.0036	0.010	0.015	0.0095	0.010	0.012
N=512	SE	0.00016	0.00057	0.00087	0.0018	0.0036	0.0021	0.0027	0.0014
	TM	0.0014	0.0041	0.0031	0.0098	0.011	0.0080	0.0068	0.012
NH_3-N	Median	0.0090	0.028*	0.026	0.016	0.022*	0.034*	0.026	0.034*
	Mean	0.28	0.039	0.041	0.16	0.18	0.072	0.042	0.12
N=544	SE	0.26	0.0051	0.011	0.13	0.067	0.019	0.011	0.067
	TM	0.010	0.031	0.034	0.023	0.038	0.050	0.033	0.044
TN	Median	0.56	0.59	0.59	1.22*	1.41*	1.20*	1.42*	1.60*
	Mean	0.70	0.75	0.90	1.39	1.66	1.72	1.46	1.60
N=575	SE	0.027	0.069	0.16	0.18	0.17	0.27	0.15	0.19
	TM	0.59	0.69	0.69	1.2	1.5	1.3	1.4	1.5
TP	Median	0.012	0.026*	0.021	0.017	0.025*	0.017	0.018	0.023*
	Mean	0.022	0.038	0.032	0.030	0.068	0.026	0.032	0.036
N=575	SE	0.0019	0.0057	0.0063	0.0092	0.023	0.0087	0.0075	0.0084
	TM	0.014	0.029	0.024	0.020	0.031	0.018	0.023	0.024
OP	Median	0.0013	0.0033	0.00070	0.0019	0.0032	0.00070	0.0011	0.0038
	Mean	0.0058	0.0044	0.0025	0.0034	0.0065	0.0019	0.0034	0.011
N=550	SE	0.0014	0.00072	0.00087	0.00097	0.0014	0.00065	0.0014	0.0067
	TM	0.002	0.003	0.001	0.002	0.004	0.001	0.002	0.004
TN:TP	Median	43	22	30	66	65	82	68	62
N=575	Mean	62	35	48	92	73	140	76	66
	TM	48	23	39	67	62	80	68	64
Cl	Median	7.4	27.9*	29.5*	63.0*	58.8*	93.1*	84.1*	95.5*
	Mean	16.4	37.2	55.0	73.4	64.6	96.1	89.4	117.9
N=575	SE	1.75	4.93	11.3	11.7	6.27	9.24	8.71	14.9
	TM	7.9	32.2	39.6	64.5	58.3	100.6	83.4	102.2
Conductivity	Median	87	156*	180*	313*	331*	416*	474*	560*
	Mean	131	212	283	336	389	467	566	839
N=927	SE	6.2	18	42	31	29	44	75	120
	TM	92	173	206	304	339	420	492	593

Median values marked with an asterisk are significantly different from the lowest % catchment level (0–9.9%) at ρ=0.05 (Kruskal-Wallis multiple comparison test). All units are in mg/L except for conductivity (μS/cm) and the TN:TP ratio (only median, mean and trimean reported; the TN:TP ratio was not tested with the Kruskal-Wallis test)

almost double the reference CU level (Table 1). In contrast to TP, OP levels in the higher CU classes (although median levels were elevated in 3 CU classes) were not significantly different from the reference CU class of 0.0013 mg/L (Table 1). Trimean OP values (range= 0.001–0.004 mg/L) were remarkably constant over all CU classes (Fig. 2), even though median and mean values varied over all CU classes (Table 1). High OP concentrations (median=0.0038 mg/L and mean=0.011 mg/L) were observed in the highest CU class

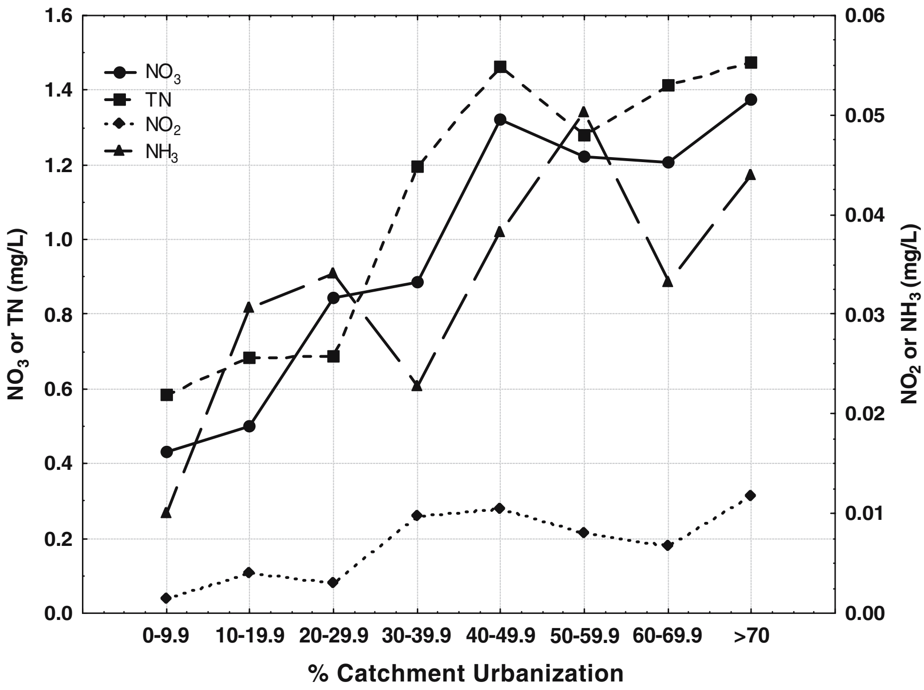

Fig. 1 Trimean concentrations of four nitrogen species (NO_3-N, NO_2-N, NH_3-N and TN) measured in the MBSS Round One and Round Two as a function of % catchment urbanization

(Table 1). Median TN:TP ratios varied between 22 and 82 over all CU classes, and were higher (ratio>60) than the reference CU (ratio=43) at urbanization intensities greater than 30% (Fig. 2). The sharp TN:TP decline at a CU of 10–19.9% was a function of an increase in TP (Fig. 2) with little increase in TN versus the reference CU class, thus driving the ratio downward (Fig. 1).

Again, to put the urban phosphorus data into perspective with the entire statewide MBSS data set, the highest TP value measured in the second MBSS round was 1.5 mg/L (N= 1266), with an overall mean TP of 0.041 mg/L (SE=0.0023). Of 1,232 OP measurements made in the second MBSS round, the highest value measured was 1.2 mg/L, with an overall mean OP of 0.012 mg/L (SE=0.0015).

Chloride

Both chloride and conductivity significantly increased over 7 CU classes versus the reference CU class (Table 1). For trimeans from this urban MBSS data set (Table 1), the relationship (r^2=0.90, ρ=0.0003) between both parameters from the lowest CU class of 0.9–9% to the highest CU class of greater than 70%, is explained by a set of simple linear regression equations:

$$Chloride\,(mg/L) = -0.397 + 0.188^{*}\,Conductivity\,(\mu S/cm) \tag{1}$$

$$Conductivity\,(\mu S/cm) = 35.4 + 4.78^{*}Chloride(mg/L) \tag{2}$$

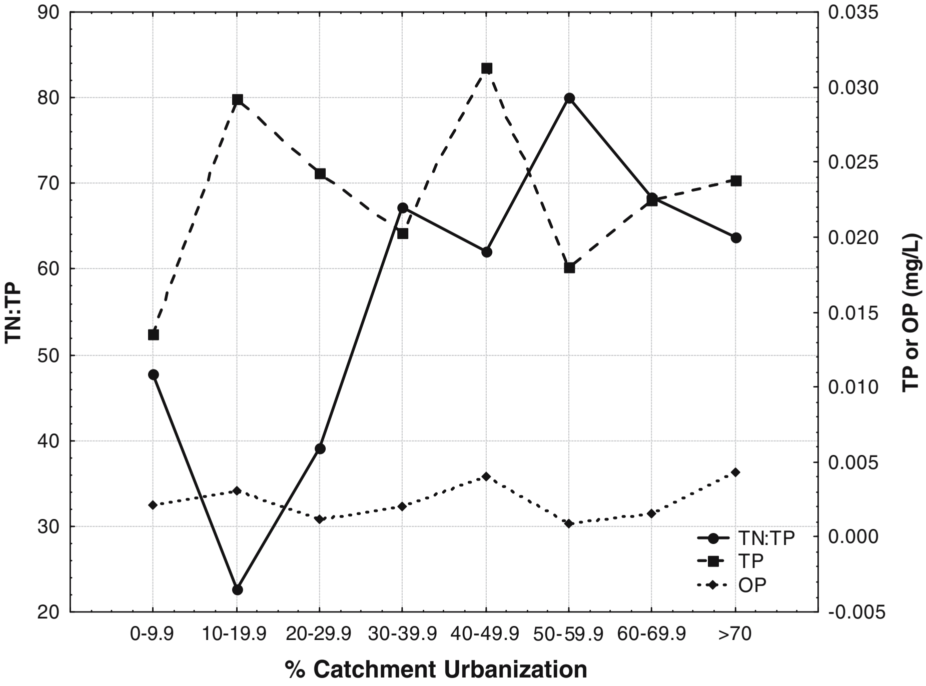

Fig. 2 Trimean concentrations of TP and OP and the ratio TN:TP measured in MBSS Round One and Round Two as a function of % catchment urbanization

Given that conductivity is easily measured in the field, an estimate may be made of chloride concentrations in urban dominated streams using Eq. 1. For all MBSS sites in both rounds, an alternative equation (Chloride $= -14.8 + 0.203^{*}$conductivity; r^2=0.81, $p<$ 0.0000) may be used for any site in Maryland, except for a small number of streams dominated by either organic acidity or acid mine drainage. Median chloride was low (7.4 mg/L) in the reference CU class and increased to 96 mg/L in the highest CU class (Table 1). The concomitant increases in stream conductivity in urban streams were driven by chloride sources (Table 1); in the highest CU class (>70%), conductivity was greater than 550 μS/cm.

To put the urban chloride and conductivity data into perspective with the entire statewide MBSS data set, the highest chloride value measured in the second MBSS round was 1,195 mg/L (N=1266), with an overall mean of 31 mg/L (SE=1.5). Of 2,220 conductivity measurements made in both MBSS rounds, the highest value measured was 4,077 μS/cm, with an overall mean of 220 μS/cm (SE=5.3).

Biological indices

Critical values were derived for eight water quality parameters sampled in the MBSS program based on the 3.0 IBI score for the urban data set (Table 2). Significant quantile (50th) regression equations were developed for the BIBI (all eight parameters), but only three significant regressions for the FIBI. Water quality measurements, greater than these critical values, indicate potential detrimental effects on the biotic assemblage, including

Table 2 Critical values and quantile regressions for water quality parameters versus both MBSS benthic (BIBI) and fish (FIBI) indices (Stribling et al. 1998; Roth et al. 1999)

Parameter	Critical Value-BIBI	Critical Value-FIBI
NO_3-N	0.86	0.83
(mg/L)	BIBI=3.2973–0.3456(NO_3-N)	FIBI=3.2765–0.3351(NO_3-N)
NO_2-N	0.005	–
(mg/L)	BIBI=3.3936–78.723(NO_2-N)	NS, ρ=0.65
NH_3	0.18	–
(mg/L)	BIBI=3.2224–1.2094(NH_3)	NS, ρ=0.57
TN	1.3	–
(mg/L)	BIBI=3.4528–0.3523(TN)	NS, ρ=0.39
TP	0.043	–
(mg/L)	BIBI=3.3775–8.7500(TP)	NS, ρ=0.72
OP	0.052	–
(mg/L)	BIBI=3.2230–4.2758(OP)	NS, ρ=0.077
Cl	50	17
(mg/L)	BIBI=3.4116–0.008192(Cl)	FIBI=3.06445–0.003823(Cl)
Conductivity	247	171
(μS/cm)	BIBI=3.4110–0.001665(COND)	FIBI=3.1833–0.001070(COND)

For estimation of critical values, the breakpoint of 3.0 for the Maryland stream BIBI and FIBI, above which is considered to meet MBSS reference conditions, was employed (Vølstad et al. 2003). All listed regression equations have significant levels of $\rho \leq 0.01$ for the water quality parameter

effects on both benthic and fish assemblages. For example, the BIBI NO_3-N breakpoint was 0.86 mg/L and the FIBI 0.83 mg/L; consequently, stream NO_3-N levels greater than these values may be an important indicator of degraded urban water, with the IBI scoring potentially less than 3.0. To expand on the NO_3-N example, a value greater than 3.8 mg/L would potentially indicate BIBI scores between 2.0 and 2.9, and a value of 6.6 mg/L BIBI scores from 1.0 to 1.9. For chloride, the critical value of 50 mg/L for the BIBI and 17 mg/l for the FIBI were surprisingly low. Field conductivity measurements in urban catchments may be an important simple indicator of biotic assemblages, since conductivity and chloride were highly correlated (Eqs. 1 and 2).

Discussion

Urbanization and nutrients

We observed that catchment urbanization elevates stream nutrients, with the most substantial increases in both nitrogen and phosphorus species at lower urbanization levels between only 10–30%, and greater. Although water quality is sampled primarily during the spring baseflow period (Spring Index), the MBSS program presents a comprehensive picture of first to third order non-tidal streams in Maryland, with excellent spatial coverage. We observed both elevated NH_4-N concentrations, along with NO_3-N, during the MBSS Spring Index period. In part, the constancy in nitrogen species in highly urbanized catchments may be correlated to declines or changes in home fertilizer usage (Kaye et al. 2006).

The phosphorus response was not as strong as what we observed for the nitrate species, especially for orthophosphate. Trimean TP never exceeded 0.035 mg/L, and orthophosphate did not exceed 0.005 mg/L. Consequently, this opens the question as to whether phosphorus cycling itself is greatly compromised in urban streams, or whether phosphorus simply moves through the system rapidly.

Stream nutrient dynamics are of particular interest in urbanizing areas because of the linkage between headwater systems (first and second order) and the upper tidal reaches of the Chesapeake Bay, which is important to consider in managing fluxes of organic and inorganic materials in the Chesapeake Bay (Gomi et al. 2002; Peterson et al. 2001). Small undisturbed streams, the first and second order streams that comprise 76% of Maryland stream km (Roth et al. 1999), are responsible for the most rapid uptake and transformation of inorganic nitrogen (Peterson et al. 2001).

Either the disturbance, or the complete loss of nutrient processing, in small urban streams may result in an increased nutrient delivery to freshwater tidal and estuarine systems and changes in runoff patterns (Hayward et al. 2006). Phosphorous often occurs at high concentrations in urban streams (Brett et al. 2005; Hatt et al. 2004; Paul and Meyer 2001). Brett et al. (2005) discovered that urban streams had 95% higher TP and 122% higher soluble reactive phosphorous than forested streams. Sources of phosphorous in urban watersheds come from fertilizers, wastewater effluent, and the soil capacity to retain phosphorous in areas with a high density of septic tanks (LaValle 1975; Gerritse et al. 1995). Thus, evidence from studies of instream carbon, nitrogen, and phosphorous demonstrates that ecosystem function does appear to be altered in urban stream networks (Gergel et al. 2002; Groffman et al. 2003; Groffman et al. 2004; Meyer et al. 2005; Paul and Meyer 2001; Schoonover et al. 2005; Walsh et al. 2005a,b; Wollheim et al. 2005). Results from our analyses indicate that key functions in Maryland urban streams have been compromised through urbanization effects.

Both TN and TP figure prominently in future strategies to reduce nutrient loadings (Dodds and Welch 2000; King and Richardson 2003; Pinay et al. 2002; USEPA 2000a,b,c), especially since the EPA is responsible for setting nutrient criteria for streams, rivers and lakes as part of the Clean Water Action Plan. There is a significant body of literature for stream and lakes that examines TN:TP ratios, and serves as a model to examine nutrient limitations (Allan 1995; Dodds 2002). The concept of a 16:1 TN:TP ratio has been discussed extensively and stands as a lentic nutrient paradigm, though there are questions as to its overall utility in lotic systems (Allan 1995; Dodds 2002). In Maryland urban systems, it appears that OP is being highly conserved, but both TN and TP are leaking into coastal waters, with most springtime TN in the form of NO_3-N.

In December 2000, the USEPA published ambient water quality criteria recommendations (TP, TN, chlorophyll a, and turbidity) for rivers and streams in Nutrient Ecoregions, a series of aggregated ecoregions within the United States. There are three Nutrient Ecoregions associated with Maryland (USEPA 2000a, 2000b, 2000c). Nutrient Ecoregion IX is the Southeastern Temperate Forested Plains and Hills (equivalent to sections of the western Coastal Plain and the entire Piedmont), Nutrient Ecoregion XI is the Central and Eastern Forested Uplands (equivalent to the Blue Ridge, Ridge and Valley, and Allegheny Plateau), and Nutrient Ecoregion XIV is the Eastern Coastal Plain (equivalent to the Coastal Plain on the Eastern Shore, and a section of the western Coastal Plain). The TN criterion for Nutrient Ecoregion IX is 0.69 mg/L, XI 0.31 mg/L, and XIV 0.71 mg/L. Using the USEPA Aggregate Ecoregion approach for Maryland rivers and streams, the TN:TP ratio for Ecoregion IX is 19, for XI 31, and for XIV 23. Most highly urbanized catchments in Maryland (>30% CU) far exceed these ecoregion threshold ratios (Table 2).

Urbanization and chloride

Chloride has emerged as an important potential stressor to urban stream quality due to increasing road deicing practices (Kaushal et al. 2005). We derived a strong empirical relationship (see Eqs. 1 and 2) between chloride and conductivity for Maryland streams, as well as increasing mean chloride levels with increasing CU (Table 1). With continual urbanization occurring within Maryland catchments, especially periurban development in the Piedmont, there is a strong potential for future chronic and acute toxicity to stream biota from chloride, with subsequent changes in the stream biotic assemblages (Kaushal et al. 2005). We observed that low levels of stream chloride significantly affected both the BIBI and FIBI, although mechanisms are not known, and may involve sublethal effects that are typically not quantified.

Urbanization and biological indices

Stressor relationships (cause–effect) with stream biotic components, and their derived indices, are often difficult to partition from complex temporal–spatial data sets such as the MBSS, primarily because of the potential array of multiple stressors working at the reach to landscape level in small streams (Helms et al. 2005; Miltner et al. 2004; Morgan and Cushman 2005; Tong 2001, 2003; Vølstad et al. 2003). However, we were able to develop a series of quantile regression equations that describe the relationship of urban water quality to the BIBI and FIBI, although both chloride and conductivity are highly correlated and only one of these should be used in a predictive model. In this paper, we do not attempt to understand the potential mechanisms for these relationships; however, the utility of these equations, especially with the BIBI, is in the ability to predict potential decreases in stream biota based on synoptic water quality sampling (Spring Index). However, these analyses may need to be extended to the entire MBSS data set, rather than the trimmed urban data set.

Species assemblages, as measured by biological indices, respond strongly to urban effects. Miltner et al. (2004) noted that the Ohio Index of Biotic Integrity (OIBI) decreased significantly if impervious surface was greater than 14%, and that OIBI decreases were observed in urbanizing watersheds as low as 4%. Morgan and Cushman (2005) found significant changes in fish assemblages when urban land cover was greater than 25%. However, Helms et al. (2005) did not observe a strong linkage between fish assemblages and impervious surface, suggesting that these fish assemblages respond to an interplay of complex stressors. Thus, responses of species assemblages to urban effects may be complex, and difficult to discern unless there is a robust data set.

Conclusions

Using a spatially extensive urban data base, we described nutrient, chloride, and conductivity relationships among eight defined levels of urbanization, as well as the relationship of water quality to two Maryland-specific indices of biotic integrity for benthic and fish assemblages. We found a significant increase in nutrient concentration with increasing percent catchment urbanization in all four measured nitrogen species and total phosphorus at catchment urbanization levels occurring between only 10–30%, and greater (up to 70%). There was a strong collinear relationship between chloride and conductivity (trimeans) across all eight urbanization classes in Maryland.

Critical values for all water quality parameters with the two Maryland biological indices were derived using quantile regression, with significant regressions developed for 11 of 16 water quality parameters and the two biotic indices. Using these equations, it may be possible to predict critical water quality concentrations and develop water quality criteria necessary to protect Maryland stream biota. Increasing stream nutrient and chloride levels in many Maryland streams, driven by increasing catchment urbanization intensity, may ultimately have effects on freshwater tidal and estuarine water quality in Chesapeake Bay.

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References

Allan JD (1995) Stream ecology: structure and function of running waters. Chapman and Hall, London, England

APHA (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, Washington, DC

Booth DB (2005) Challenges and prospects for restoring urban streams: a perspective from the Pacific Northwest of North America. J North Am Benthol Soc 24:724–737

Brabec E, Schulte S, Richards PL (2002) Impervious surfaces and water quality: a review of current literature and its implications for watershed planning. J Plan Lit 16:499–514

Brett MT, Arhonditsis GB, Mueller SE, Hartley DM, Frodge JD, Funke DE (2005) Non-point-source impacts on stream nutrient concentrations along a forest to urban gradient. Environ Manag 35:330–342

Bryan EH (1971) Quality of stormwater drainage from urban land. Water-Resour Bull 8:578–588

Cade BS, Noon BR (2003) A gentle introduction to quantile regression for ecologists. Front Ecol Environ 1:412–420

Dodds WK (2002) Freshwater ecology. Academic Press, San Diego, CA

Dodds WK, Welch EB (2000) Establishing nutrient criteria in streams. J North Am Benthol Soc 19:186–196

Forman RTT, Alexander LE (1998) Roads and their major ecological effects. Ann Rev Ecolog Syst 29:207–231

Forman RTT, Sperling D, Bissonette JA, Clevenger AP, Cutshall CD, Dale VH, Fahrig L, France R, Goldman CR, Heanue K, Jones JA, Swanson FJ, Turrentine T, Winter TC (2003) Road ecology: science and solutions. Island Press, Washington, DC

Galloway JN, Aber JD, Erisman JW, Seitzinger SS, Howarth RW, Cowling EB, Cosby BJ (2003) The nitrogen cascade. BioScience 53:341–356

Gergel SE, Turner MG, Miller JR, Melack JM, Stanley EH (2002) Landscape indicators of human impacts to riverine systems. Aquat Sci 64:118–128

Gerritse RG, Adeney JA, Dommock GM, Oliver YM (1995) Retention of nitrate and phosphate in soils of the Darling Plateau in Western Australia: implications for domestic septic tank systems. Aust J Soil Res 33:353–367

Gilbert RO (1987) Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold, New York, NY

Gomi T, Sidle RC, Richardson JS (2002) Understanding processes and downstream linkages of headwater systems. BioScience 52:905–916

Groffman PM, Bain DJ, Band L E, Belt KT, Brush GS, Grove JM, Pouyat RV, Yesilonis IC, Zipperer WC (2003) Down by the riverside: urban riparian ecology. Front Ecol Environ 1:316–321

Groffman PM, Law NL, Belt KT, Band LE, Fisher GT (2004) Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7:393–403

Groffman PM, Dorsey AM, Mayer PM (2005) N processing within geomorphic structures in urban streams. J North Am Benthol Soc 24:613–625

Hatt BE, Fletcher TD, Walsh CJ, Taylor SL (2004) The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environ Manag 34:112–124
Hayward BW, Grenfell HR, Sabaa AT, Morley MS, Horrocks M (2006) Effect and timing of increased freshwater runoff into sheltered harbor environments around Auckland City, New Zealand. Estuaries Coasts 29:165–182
Heimbuch DG, Seibel JC, Wilson HT, Kazyak PF (1999) A multiyear lattice sampling design for Maryland-wide fish abundance estimation. J Agric Biol Environ Stat 4:443–455
Helms BS, Feminella JW, Pan S (2005) Detection of biotic responses to urbanization using fish assemblages from small streams of western Georgia, USA. Urban Ecosyst 8:39–57
Herlihy AT, Stoddard JL, Johnson CB (1998) The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region, U. S. Water Air Soil Pollut 195:377–386
Kaushal SS, Groffman PM, Likens GE, Belt KT, Stack WP, Kelly VR, Band LE, Fisher GT (2005) Increased salinization of fresh water in the northeastern United States. Proc Natl Acad Sci 38:13517–13520
Kaye JP, Groffman PM, Grimm NB, Baker LA, Pouyat RV (2006) A distinct urban biogeochemistry? Trends Ecol Evol 21:192–199
Kazyak PF (2000) Maryland biological stream survey sampling manual. Monitoring and non-tidal assessment division. Maryland Department of Natural Resources, Annapolis, MD
King RS, Richardson CJ (2003) Integrating bioassessment and ecological risk assessment: an approach to developing numerical water-quality criteria. Environ Manag 31:795–809
Klein RD (1979) Urbanization and stream quality impairment. Water-Resour Bull 15:948–963
Knapp CM, Saunders WP (1987) Maryland synoptic stream chemistry design report. Prepared by International Science and Technology, Inc., Reston, VA, for the Maryland Department of Natural Resources, Power Plant Research Program, Annapolis, MD (Report # AD-87-5)
Knapp CM, Saunders WP, Heimbuch DG, Greening HS, Filbin GJ (1988) Maryland synoptic stream chemistry survey: estimating the number and distribution of streams affected by or at risk from acidification. Prepared by International Science and Technology, Inc., Reston, VA, for the Maryland Department of Natural Resources, Power Plant Research Program, Annapolis, MD (Report # AD-88-2, NTIS No. PB88-213996/AS)
LaValle PD (1975) Domestic sources of stream phosphates in urban streams. Water Resour 9:913–915
Meyer JL, Paul MJ, Taulbee WK (2005) Stream ecosystem function in urbanizing landscapes. J North Am Benthol Soc 24:602–612
Miltner RJ, White D, Yoder C (2004) The biotic integrity of streams in urban and suburbanizing landscapes. Landsc Urban Plan 69:87–100
Morgan RP, Cushman SF (2005) Urbanization effects on stream fish assemblages in Maryland, USA. J North Am Benthol Soc 24:643–655
Paul MJ, Meyer JL (2001) Streams in the urban landscape. Ann Rev Ecolog Syst 32:333–365
Peterson BJ, Wollheim WW, Mulholland PJ, Webster JR, Meyer JL, Tank JL, Marti E, Bowden WB, Valett HM, Hershey AE, McDowell WH, Dodds WK, Hamilton SK, Gregory S, Morrall DD (2001) Control of nitrogen export from watersheds by headwater streams. Science 292:86–90
Pinay G, Clement JC, Naiman RJ (2002) Basic principles and ecological consequences of changing water regimes on nitrogen cycling in fluvial systems. Environ Manag 30:481–491
Rose S (2002) Effects of urbanization on streamflow in the Atlanta area (Georgia, USA): a comparative hydrological approach. Hydrol Process 15:1441–1457
Roth NE, Southerland MT, Mercurio G, Chaillou JC, Kazyak PF, Stranko SS, Prochaska AP, Heimbuch DG, Seibel JC (1999) State of the streams: 1995–1997 Maryland biological stream survey results. Monitoring and Non-Tidal Assessment Division. Maryland Department of Natural Resources, Annapolis, MD
Schoonover JE, Lockaby BG, Pan S (2005) Changes in chemical and physical properties of stream water across an urban-rural gradient in western Georgia. Urban Ecosyst 8:107–124
Steel RGD, Torrie JH (1960) Principles and procedures of statistics. McGraw-Hill, New York
Stribling JB, Jessup BK, White JS, Boward DM, Hurd MK (1998) Development of a benthic index of biotic integrity for maryland streams. Prepared by Tetra Tech, Inc., Owings Mills, MD and Maryland Department of Natural Resources, Monitoring and Non-tidal Assessment Program. (Report # CBWP-MANTA-EA-98-3)
Tong STY (2001) An integrated exploratory approach to examining the relationships of environmental stressors and fish responses. J Aquat Ecosyst Stress Recovery 9:1–19
Tong STY (2003) Relationships among environmental stressors and fish community composition and health: case study of Chesapeake Bay. In: Rapport DJ, Lasley WL, Rolston DE, Nielsen NO, Qualset CO, Damania AB (eds) Managing for healthy ecosystems. Lewis, Boca Raton, FL, pp 413–428

USEPA (1987) Handbook of methods for acid deposition studies: laboratory analyses for surface water chemistry. Office of Acid Deposition, Environmental Monitoring and Quality Assurance, USEPA, Washington, DC

USEPA (1999) Methods and guidance for analysis of water. EPA 821-C-99-004. Office of Water, Office of Science and Technology, USEPA, Washington, DC

USEPA (2000a) Ambient water quality criteria recommendations: rivers and streams in nutrient Ecoregion IX. EPA-822-B-00-019, USEPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division, Washington, DC

USEPA (2000b) Ambient water quality criteria recommendations: rivers and streams in nutrient ecoregion XI. EPA-822-B-00-020, USEPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division, Washington, DC

USEPA (2000c) Ambient water quality criteria recommendations: rivers and streams in nutrient ecoregion XIV. EPA-822-B-00-022, USEPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division, Washington, DC

Vølstad JH, Southerland MT, Chaillou JC, Wilson HT, Heimbuch DG, Jacobson PT, Weisberg SB (1995) The Maryland biological stream survey: The 1993 pilot study. Prepared by Versar, Inc., Columbia, MD for Maryland Department of Natural Resources, Chesapeake Bay Research and Monitoring Division, Annapolis, MD (Report # CBRM-AD-95-3)

Vølstad JH, Southerland MT, Weisberg SB, Wilson HT, Heimbuch DG, Seibel JC (1996) Maryland biological stream survey: The 1994 demonstration project. Prepared by Versar, Inc., Columbia, MD, for Maryland Department of Natural Resources, Monitoring and Non-Tidal Assessment Division, Annapolis, MD (Report # CBWP-MANTA-EA-95-9)

Vølstad JH, Roth NE, Mercurio G, Southerland MT, Strebel DE (2003) Using environmental stressor information to predict the ecological status of Maryland non-tidal streams as measured by biological indicators. Environ Monit Assess 84:219–242

Walsh CJ, Fletcher TD, Ladson AR (2005a) Stream restoration in urban catchments through redesigning stormwater systems: looking to the catchment to save the stream. J North Am Benthol Soc 24:690–705

Walsh CJ, Roy AH, Feminella JW, Cottingham PD, Groffman PM, Morgan RP (2005b) The urban stream syndrome: current knowledge and the search for a cure. J North Am Benthol Soc 24:706–723

Waters TF (1995) Sediment in streams. American Fisheries Society Monograph 7, American Fisheries Society, Bethesda, MD

Wollheim WM, Pellerin BA, Vörösmarty, Hopkinson CS (2005) N retention in urbanizing headwater catchments. Ecosystems 8:871–884