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Long-term trends in nitrate and chloride in streams in an exurban watershed

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Abstract

The lines between natural areas and human habitats have blurred as urbanization continues, creating a need for the study of ecosystems at all levels of development. This need is particularly acute for exurban environments, which have low population density but are rapidly changing and have a dynamic mix of natural and human-dominated features. We examined long-term (1998–2018) trends in nitrate and chloride concentrations and fluxes in forested and exurban streams in Baltimore County, Md USA. Concentrations and fluxes of nitrate and chloride were an order of magnitude higher in the exurban stream than the forested stream and were increasing even though snowfall and road salt use did not increase over the study period. In the forested stream, concentrations and fluxes of chloride increased from 1998 to 2008, but decreased from 2008 to 2018 due to unquantified factors. Concentrations of nitrate decreased in the forested stream, likely due to decreases in atmospheric deposition. These decreases in atmospheric deposition, and efforts to reduce fertilizer use by county governments, do not appear to have affected nitrate concentrations and fluxes in the exurban watershed. Any efforts to reduce the concentrations and fluxes of chloride and nitrate in exurban streams will likely benefit substantially from further understanding of the mechanisms underlying the temporal patterns.

Key terms Nitrate · Chloride · Salt · Exurban · Watershed · Long-term

Introduction

Urban land use affects watershed dynamics and stream water quality in complex ways. The addition of impervious surfaces and drainage infrastructure alters the way water moves from the land to streams, and the use of fertilizers, deicing agents and other chemicals alters the chemistry of that water. Urbanization also affects the ability of soils, plants and other ecosystem components to process water and chemicals, creating enormous complexity in the watershed dynamics of cities (Walsh et al. 2005). Unraveling this complexity has been facilitated by long-term studies that apply the watershed approach (Likens 2013). In the Baltimore Ecosystem Study (BES), a component of the U.S. National Science Foundation funded the Long Term Ecological Research (LTER) network, the watershed approach has been used as a platform to examine differences among forest, agricultural and urban, suburban and exurban areas within the Baltimore, Maryland metropolitan area (Fig. 1) (Groffman et al. 2019).

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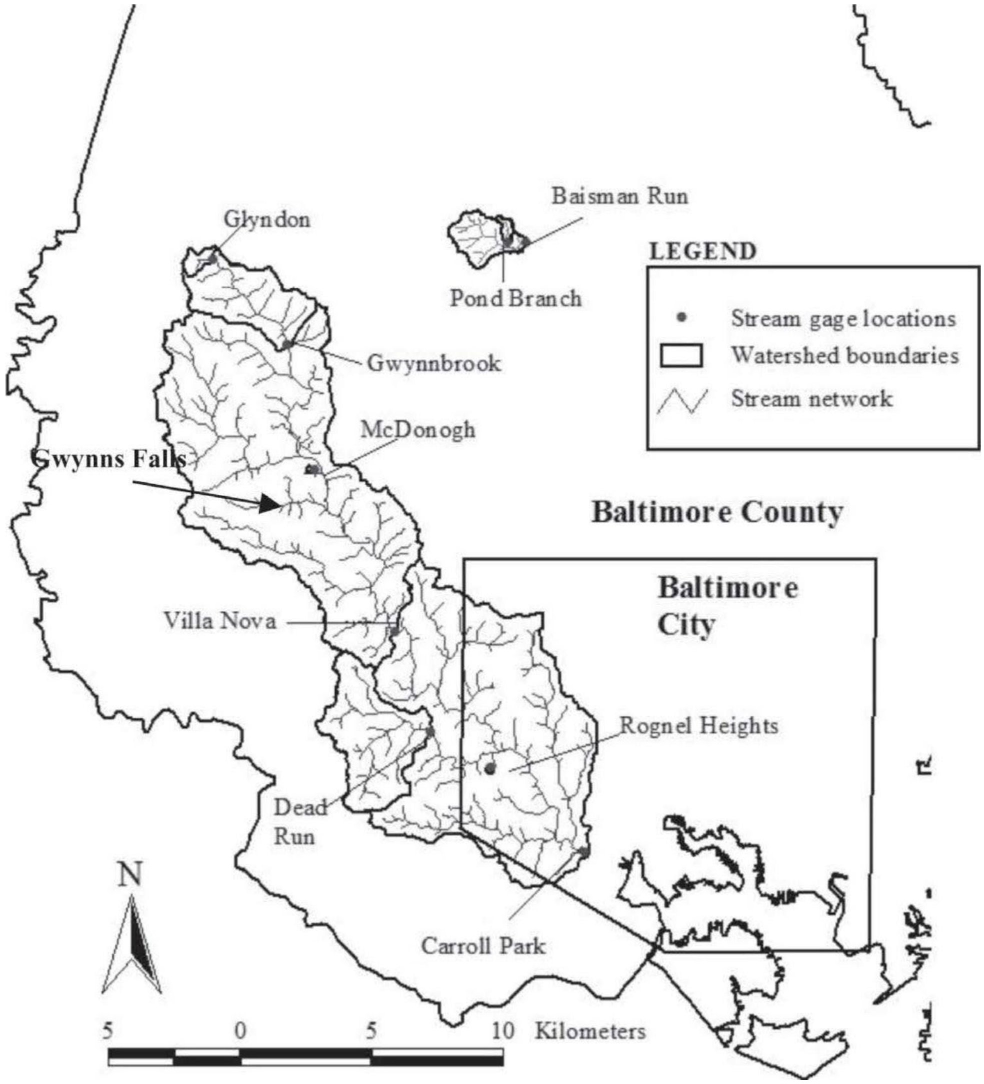
Fig. 1 The Baltimore Ecosystem Study watersheds and stream network for the Gwynns Falls, Baisman Run, and Pond Branch watersheds in the Baltimore metropolitan area



Urbanization exists on a spectrum, ranging from heavily populated and infrastructurally dense urban core areas to low density exurban areas with extensive areas of unmanaged ecosystems (Hale et al. 2016; Moore et al. 2017; Blaszczak et al. 2019). Exurban areas have received less attention than dense urban, suburban, or rural ecosystems despite the fact that they are rapidly growing and their dynamics are affected by a complex mix of anthropogenic and natural factors (Hansen et al. 2005; Newburn and Berck 2011; Lopez 2014). The interaction of these factors is particularly important in exurban watersheds where natural plant, soil, and microbial processes can strongly influence water and nutrient dynamics that are also affected by human activities. Previous BES watershed studies have focused more on urban and suburban watersheds than on exurban watersheds with a focus on interactions between climate, especially extreme events (Kaushal et al. 2008; Bettez et al. 2015), land use (Groffman et al. 2004), and changes in green and grey infrastructure (Reisinger et al. 2018). Here we focus on how changes in climate, atmospheric chemistry, and human use of road salt and fertilizer interact to affect water quality in the low density exurban and forested reference BES watersheds.

Two solutes, nitrate and chloride, are of particular concern to the water quality of exurban watersheds. Nitrate is the most common and mobile form of reactive nitrogen, acting as a drinking water pollutant and cause of eutrophication in coastal waters, including the Chesapeake Bay (Boesch et al. 2001). The dominant sources of nitrate in urban watersheds are fertilizers and sewage (Hobbie et al. 2017; Byrnes et al. 2020). The dominant source of chloride in watersheds in areas with frozen winter precipitation is the salt used to mitigate icy road conditions in colder months (Kaushal et al. 2018). The chloride from road salt is transported to streams and aquifers by surface runoff and groundwater flow, harming aquatic life, damaging infrastructure, and contaminating drinking water (Findlay and Kelly 2011).

Previous work in urban watersheds has identified complexities and uncertainties around nitrate dynamics. Results from several cities have found significant retention of nitrogen in urban watersheds, i.e., inputs/sources greater than exports (Baker et al. 2001; Bettez et al. 2015; Hobbie et al. 2017). Nitrogen dynamics in the Baltimore area are further complicated by three co-occurring long-term changes. First, atmospheric nitrogen deposition has been declining in the Chesapeake Bay region since implementation of the 1990 Clean Air Act Amendments, which limits NOx emissions (Eshleman and Sabo 2016). Second, nitrate concentrations in the Baltimore environment are likely affected by efforts to reduce nitrogen fertilizer use and nitrogen exports from septic systems and municipal sewer systems (Birch et al. 2011; Wainger 2012; Reisinger et al. 2018). Third, increases in the volume and intensity of precipitation reduce ecosystem nitrogen retention and result in increased N export to downstream water bodies (Kaushal et al. 2008; Bettez et al. 2015).

Similar to nitrate, research has identified complexities and uncertainties associated with chloride concentrations in urban, suburban and exurban streams (Kaushal et al. 2018; Rossi et al. 2022). While high concentrations of chloride are expected following snow events and the associated application of road salt in winter, salty winter snowmelt water recharges groundwater, the primary source of water for low flows (base flow), giving rise to elevated salt concentrations at base flow year round (Gelhar and Wilson 1974; Kaushal et al. 2005; Blaszczak et al. 2019). This recharge creates a "legacy" source of chloride that can last for decades (Kelly et al. 2019). These complex interactions are further affected by increases in the amount and intensity of precipitation in ways that are not clear. There is an expectation that chloride concentration in streams should decline as climate warming should decrease snow events and the subsequent need for road salt application. In addition, efforts to improve the efficiency of road salt use should reduce overall mass loading of salt, resulting in lower chloride concentrations in streams.

This study focused on changes in nitrate and chloride concentrations from 1999 to 2018 in two long-term study watersheds in BES; Pond Branch (POBR) which is forested and serves as a reference site for BES and Baisman Run (BARN) to which POBR is a tributary. BARN, which is characterized by exurban land use in the upper third of the catchment, and is otherwise forested, is part of the Gunpowder Falls basin, drains into one of Baltimore's three major water supply reservoirs (Law et al. 2004). The forested and exurban watersheds are ideal for exploring how effects of climate, land management (fertilizer and road salt application), and atmospheric chemistry interact as these watershed dynamics are not dominated by sewage and stormwater infrastructure, although BARN has 120 houses with septic systems (Law et al. 2004).

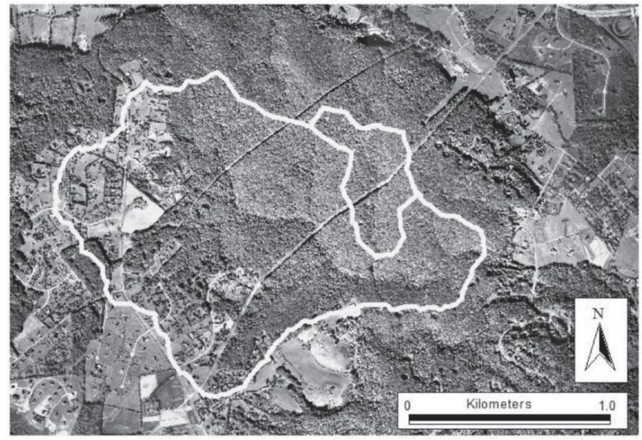


Fig. 2 Aerial image of the Baisman Run (420 ha) and Pond Branch (40 ha) study watersheds from (October 1999). Pond Branch is the smaller subwatershed in the northeast corner of Baisman Run. From Law et al. (2004)

We tested four hypotheses: H1) Chloride concentrations will decline over time in the exurban watershed and the driver of this will be (H2) decreased snowfall and associated road salt use due to climate warming. H3) Nitrate concentrations will decline in both watersheds over time and the drivers of this change will be (H4) declines in atmospheric deposition as facilitated by the 1990 Clean Air Act Amendments and efforts to reduce fertilizer use such as the introduction of the 2013 Maryland Lawn Fertilizer Law (https://mda.maryland.gov/Pages/fertilizer.aspx). Alternatively, nitrate and chloride concentrations may not have declined over time due to the importance of other sources of these ions (e.g., septic systems) and/or because legacy sources dominate changes due to reductions in input in road salt, atmospheric deposition and fertilizer.

Experimental section

Study sites BARN is a 420 hectare (ha) subwatershed (latitude 39°28′49.1″, longitude 76°41′15.0″) of the Gunpowder Falls watershed and is characterized by low density, large lot development on septic systems in the upper third of the watershed (Fig. 2). The remainder of the watershed is a forested park. POBR is a forested 40 ha subwatershed of BARN. The entire watershed is underlain by the medium- to coarse-grained micaceous schist of the Loch Raven Formation. Depth to saprolite is highest on ridges, thins (< 1 m) at steep midslope positions, and is 1–2 m in bottomland locations (Cleaves et al. 1970). Soils range from silt clay loam to silt loam in the riparian areas to sandy loam on steeper slopes. Forested areas are dominated

Table 1 Hydrologic data from the Baisman Run and Pond Branch watersheds

	Pond Branch (forested)				Baisman Run (exurban)			
	Highest discharge (m^3/d)	Lowest discharge (cm^3/d)	# grab samples	Average base flow ratio on sampling days	Highest discharge (cm^3/d)	Lowest discharge (m^3/d)	# grab samples	Average base flow ratio on sampling days
1999	2936	24	52	0.68	5627	2691	14	0.84
2000	1248	171	52	0.79	18594	1541	52	0.8
2001	489	73	55	0.76	5382	783	55	0.77
2002	245	2	55	0.66	3205	98	57	0.65
2003	1566	171	50	0.81	20135	2349	51	0.75
2004	2202	220	52	0.84	41592	1639	52	0.82
2005	1076	147	50	0.8	11597	979	53	0.79
2006	1028	98	53	0.78	16172	1248	55	0.79
2007	930	49	55	0.76	9297	367	54	0.74
2008	440	5	51	0.7	8245	269	51	0.76
2009	1688	122	47	0.75	17982	1884	48	0.79
2010	1101	122	49	0.76	11744	856	49	0.78
2011	979	73	51	0.73	13163	979	51	0.73
2012	1713	171	51	0.82	16001	1199	64	0.83
2013	1370	147	50	0.75	14508	1664	50	0.83
2014	8416	220	49	0.74	87098	2153	49	0.74
2015	1028	196	52	0.78	18790	1664	51	0.78
2016	1492	122	49	0.76	19157	1297	50	0.81
2017	3425	49	50	0.68	25689	1125	50	0.8
2018	294	73	13	0.68	17199	1395	53	0.8

by approximately 100 year old *Quercus spp*. (oaks) and *Carya spp.* (hickory).

Water Sampling and Analysis The BES has collected stream chemistry samples at POBR and BARN since 1998. Sites are continuously monitored for discharge by the USGS (BARN: https://waterdata.usgs.gov/usa/nwis/uv?0158358; Pond Branch: https://waterdata.usgs.gov/usa/nwis/uv?0158357) and weekly grab samples are taken for chemical analysis without regard to flow conditions. The weekly stream samples are filtered (0.45 µm) and analyzed for NO_3^- and Cl^- concentrations by ion chromatography (Groffman et al. 2018).

Hydrologic conditions at each sampling date were calculated using algorithms described by Nathan and McMahon (1990) that are incorporated into the EcoHydRology program (https://cran.r-project.org/web/packages/EcoHydRology/EcoHydRology.pdf). For each sample date, this program produces estimates of: (1) the total discharge (Q) in cubic meters per second (cms), (2) percentage of discharge attributable to base flow, (3) percentage of discharge attributable to stormflow and (4) base flow index, i.e., the ratio of base flow to stormflow (Table 1). The period of analysis for both sites was 1999 to 2018 (a 19-year range) because data on chloride and nitrate concentrations from 1998 were not available for BARN.

Flux calculations were made with Weighted Regressions on Time, Discharge, and Season (WRTDS), a USGS statistical tool (Hirsch et al. 2010), which calculates solute fluxes from stream flow, solute concentration, and time by fitting locally weighted regressions (Bettez et al. 2015; Reisinger et al. 2018). Yields were calculated by dividing flux by watershed area.

Road Salt Data Baltimore County publishes the mass of road salt applied annually (https://www.baltimorecountymd.gov/Agencies/publicworks/highways/stormrelatedcosts.html). Their data includes a table on Storm Related Costs, including the mass of salt used for each fiscal year (July 1 - June 30), the depth of snowfall, and the number of events requiring salt application, from 2001 to 2019. We assumed that BARN contains roads that are typical of Baltimore County and that county-wide trends were applicable to this watershed.

Fertilizer data Data on fertilizer usage in Baltimore County were derived from three sources: First, we used a national compilation of county-by-county fertilizer use, split into farm and non-farm use, compiled by the USGS: https://doi.org/10.5066/F7H41PKX.

However, these data are only available until 2012.

Second, data on fertilizer applied by county personnel on county owned and managed land are compiled by

Table 2 Fertilized area and amount of fertilizer applied in Baltimore County in 2015, 2017, 2018. Data compiled from Fertilizer Application Report produced by the Maryland Department of Agriculture as part of "lawn fertilizer law" that was passed in 2013. The data for 2016 are not included due to data quality concerns for that year

Year	Fertilized area (ha)	Nitrogen applied (kg)
2015	6241	402,099
2017	5412	507,955
2018	5308	515,797

Baltimore County for permit requirements: https://www.baltimorecountymd.gov/Agencies/environment/npdes/ and are presented in their annual report from 2018: http://resources.baltimorecountymd.gov/Documents/Environment/npdes/2018/fullnpdes2018.pdf There is almost no fertilized public land in the Baisman Run watershed. Rather, we are using these data as a "best case" indicator of the potential for fertilizer use reduction as Baltimore County is committed to reducing fertilizer use.

Third, Baltimore County implemented a "lawn fertilizer law" in 2013 (https://mda.maryland.gov/Pages/fertilizer.aspx) that mandates collection of data on fertilizer applied by professional lawn care services. Collection and organization of these data are incomplete and are only available for the years 2015, 2017 and 2018 (Table 2). We assumed trends in fertilizer use in BARN are consistent with the trends in Baltimore County as a whole.

Atmospheric Deposition Atmospheric nitrogen and chloride deposition are measured by the U.S. Environmental Protection Agency in Beltsville, MD, approximately 45 miles from BARN and data are available for nitrogen at https://www3.epa.gov/castnet/site_pages/BEL116.html and for chloride at http://nadp.slh.wisc.edu/data/ntn/ntnAllsites.aspx. Data available included wet NO_3^- and ammonium (NH_4^+) deposition as well as "dry deposition" of nitric acid vapor (HNO_3) and particulate NO_3^- and NH_4^+. Values for total annual deposition (wet plus dry) were used here and referenced as Total N Deposition.

Septic Systems Estimates of nitrate and chloride loading from septic systems were produced by assuming that each of the 120 houses in the BARN watershed has a septic system that produces 650 L/day of effluent that is discharged to groundwater (Rutledge et al. 1993) and that this effluent has a chloride concentration of 400 mg/L (Kochary et al. 2017) and a nitrate concentration of 70 mg N/L (Gold et al. 1990).

Climate Monthly precipitation and temperature data are available from the Baltimore Washington International airport site from the Climate and Hydrology Database Projects database (http://climhy.lternet.edu/).

Statistical analyses All analyses were done on annual values for all variables. Comparisons of the two watersheds were made using repeated measures analysis of variance to account for temporal autocorrelation among measurements at each site. To examine trends of nitrate, chloride, and atmospheric deposition through time (H1 and H3) we used linear (Pearson) and nonparametric (Spearman) correlations, and the highest values are reported. To explore if temporal trends were associated with climatic variables or atmospheric deposition (H2 and H4), relationships between nitrate and chloride concentrations and loads and predictor variables were explored with linear regression. Regression models were examined for temporal autocorrelation visually using scatterplots of residuals and autocorrelation function plots. Potential temporal autocorrelation was verified using the Durbin-Watson test. When temporal autocorrelation was detected, we utilized a first-order autoregressive model to examine relationships among variables. We selected a first-order autoregressive model as lags were not larger than one in these models. Relationships were considered statistically significant at $p < 0.05$. All analyses were done using SAS (version 9.4) and Stata (version 16.1).

Results

Hydrology and climate

At BARN, discharge ranged from 98 to 87,098 m^3/d (0.02 to 20.7 mm/d) over the 18 year data collection period (Table 1). POBR had stream discharge values ranging from 2 to 8416 m^3/d (0.02–21 mm/d). Average base flow index for all sample dates over the 19 year period was 0.78 ± 0.04 at BARN and 0.75 ± 0.05 at POBR (Table 1). There was no significant trend in discharge over time in either watershed.

Mean annual temperature showed a marginally significant increase ($r = 0.40$, $p < 0.10$) from 1998 to 2018 (data not shown) but there was no significant increase in winter temperature over this period. There was no trend in total annual or winter precipitation over the study period although Reisinger et al. (2018) reported a significant increase in winter precipitation between 1999 and 2016. There was also no trend in seasonal snowfall, the number of

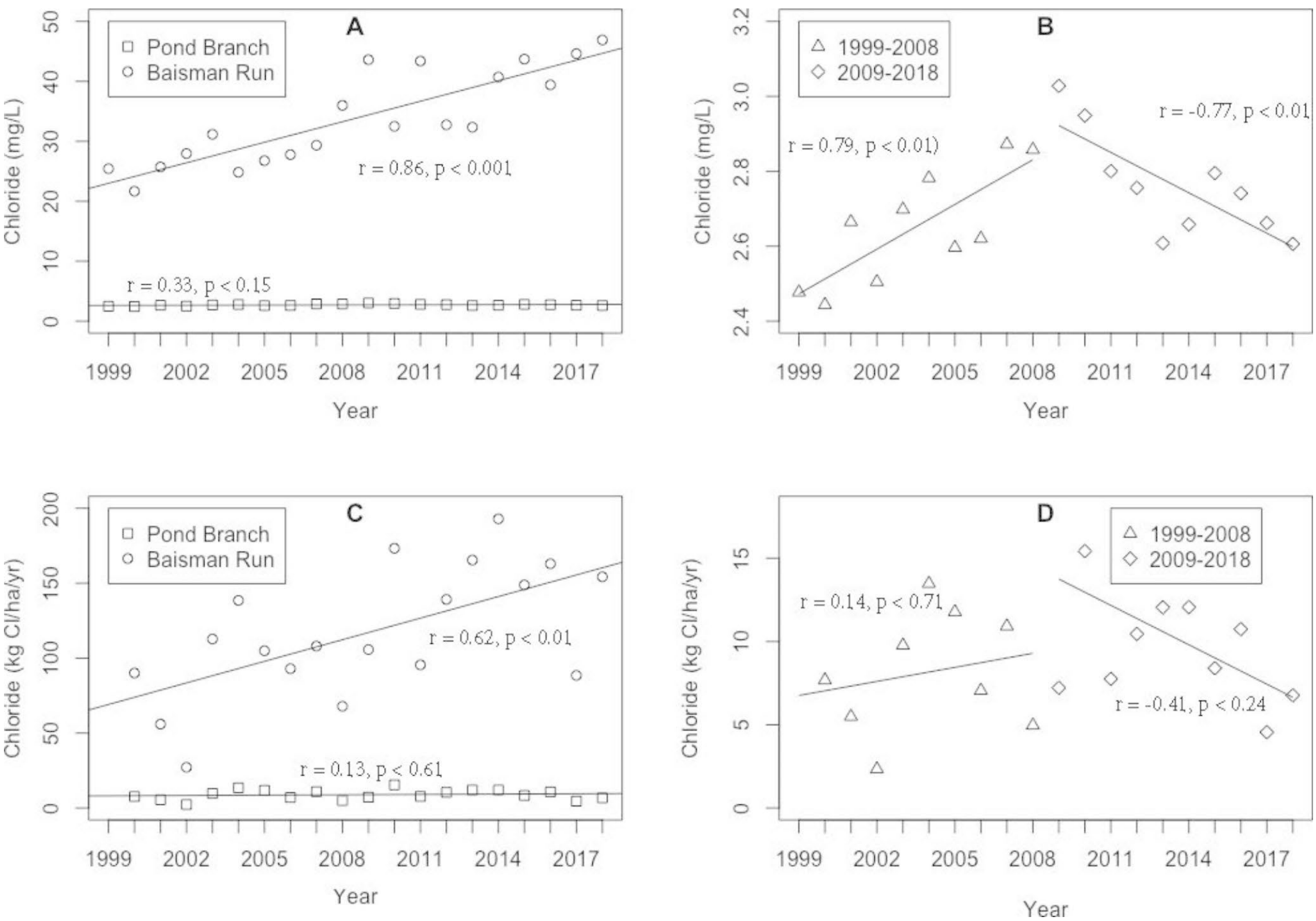


Fig. 3 A. Mean annual chloride concentrations in samples from Baisman Run (exurban) and Pond Branch (forested) streams from 1999–2018. B. Mean annual chloride concentrations in samples from Pond Branch from 1999–2018 showing differential patterns between 1999–2008 and 2008–2018. Note different scales on y axis between panels A and B. C. Annual chloride loads from Baisman Run (exurban) and Pond Branch (forested) watersheds from 1999–2018. D. Annual chloride loads from Pond Branch from 1999–2018 showing differential patterns between 1999–2008 and 2008–2018. Note different scales on y axis between panels C and D

snowstorms requiring application of road salt, or total salt use from 1999 to 2018.

Chloride

In an analysis over all years, chloride concentrations ($F_{(1,18)} = 314.0$, $p < 0.001$), Fig. 3a) and loads (Fig. 3c) were significantly higher ($F_{(1,18)} = 113.6$, $p < 0.001$) in the exurban stream, BARN (mean = 33.8, standard deviation = 7.9, range = 21.7 to 46.9 mg/L), than in the forested stream, POBR (mean = 2.7, standard deviation = 0.15, range = 2.4 to 3.0 mg/L). These differences increased over time. Concentrations ($r = 0.86$, $p < 0.001$) and loads ($r = 0.63$, $p < 0.01$) significantly increased from 1999 to 2018 in BARN (from ~25 to ~45 mg/L) and showed no significant change over the same period in POBR. Visual inspection of the data led us to determine that concentrations in POBR significantly ($r = 0.79$, $p < 0.01$) increased from 1999 to 2008 (from ~2.5 to ~3.0 mg/L) and significantly ($r = -0.78$, $p < 0.01$) decreased from 2008 to 2018 (Fig. 3b). These temporal trends in POBR were not significant for fluxes (Fig. 3d).

Models of mean annual chloride concentrations in BARN and POBR demonstrated temporal autocorrelation with all predictor variables and thus a first-order autoregressive model was used. We found mean annual chloride concentrations significantly increased with increased annual precipitation ($ß = 0.31$, $p < 0.001$, Table 3) in BARN. Chloride concentrations in POBR were not correlated with any climate variables. Chloride loads in BARN and POBR significantly increased with more winter precipitation ($ß = 8.98$, $p = 0.003$ in BARN and $ß = 0.65$, $p = 0.007$ in POBR, Table 4), snowfall ($ß = 1.14$, $p = 0.003$ in BARN and $ß = 0.08$, $p = 0.02$ in POBR, Table 4), and total salt mass applied ($ß = 0.0007$, $p = 0.04$ in BARN and $ß = 0.0005$, $p = 0.05$ in POBR, Table 4). Total salt mass applied significantly increased with lower mean annual temperatures ($ß = -14{,}117$, $p = 0.01$), and higher total annual precipitation ($ß = 1691$,

Table 3 Results from autoregressive model (AR1) for predictors of chloride concentrations. Bolded terms indicate significant predictor

Predictor	χ^2	P-value	Predictor coefficient	P-value	Lag 1 coefficient	P-value
BARN						
Annual precipitation	**47.63**	**< 0.001**	**0.31**	**< 0.001**	**0.77**	**< 0.001**
Winter precipitation	12.72	0.002	-0.36	0.20	0.76	0.001
Mean temperature	15.3	< 0.001	-1.27	0.29	0.81	< 0.001
Salt tons	8.36	0.02	0.00004	0.38	0.66	0.01
Snow	6.21	0.04	-0.02	0.58	0.67	0.01
Road salt applications	9.47	0.009	0.46	0.27	0.68	0.002
POBR						
Annual precipitation	5.62	0.06	-0.0006	0.87	0.57	0.02
Winter precipitation	5.36	0.07	0.002	0.86	0.56	0.02
Mean temperature	5.78	0.06	0.001	0.97	0.56	0.02
Salt tons	3.35	0.19	0.00	0.61	0.53	0.07
Snow	4.19	0.12	0.0004	0.85	0.52	0.04
Road salt applications	4.85	0.09	0.003	0.75	0.56	0.03

Table 4 Results from linear regression for predictors of chloride loads. Bolded terms indicate significant predictor

	BARN			POBR		
Predictor	Adj R^2	Predictor coefficient	P-value	Adj R^2	Predictor coefficient	P-value
Mean temperature	0.00	-1.13	0.89	0.00	-0.31	0.64
Annual precipitation	0.03	1.32	0.22	0.00	0.008	0.92
Winter precipitation	**0.38**	**8.98**	**0.003**	**0.32**	**0.65**	**0.007**
Snow	**0.39**	**1.14**	**0.003**	**0.27**	**0.08**	**0.02**
Road salt applications	0.02	2.29	0.25	0.00	-0.03	0.84
Salt mass	**0.19**	**0.0007**	**0.04**	**0.17**	**0.00005**	**0.05**

Table 5 Results from linear regression for predictors of salt mass. Bolded terms indicate significant predictor

Predictor	Adj R^2	Predictor coefficient	P-value
Mean temperature	**0.27**	**-14,117**	**0.01**
Annual precipitation	**0.25**	**1691**	**0.02**
Winter precipitation	**0.21**	**4884**	**0.03**
Snow fall	**0.66**	**1020**	**< 0.001**
Road salt applications	**0.35**	**3605**	**0.006**

$p = 0.02$), winter precipitation (ß = 4884, $p = 0.03$), total snowfall (ß = 1020, $p = 0.001$), and the number of storms requiring application of road salt (ß = 3605, $p = 0.006$) (Table 5). Atmospheric deposition of chloride ranged from 1.2 to 3.7 kg/ha/y, showed no trend with time, and was not correlated with stream concentrations or fluxes of chloride in either watershed.

Septic systems were estimated to add 11,388 kg of chloride to the BARN watershed, which is equivalent to ~21% of typical chloride exports from the watershed. The estimate of septic system chloride is based on literature values and is therefore approximate. The estimate of chloride exports is based on average flows and concentration over the study period.

Nitrate

Nitrate concentrations ($F_{(1,18)} = 139.1$, $p < 0.001$, Fig. 4a) and loads ($F_{(1,18)} = 263.2$, $p < 0.001$) Fig. 4c) were significantly higher in BARN (mean = 1.6, standard deviation = 0.15, range = 1.2 to 1.9 mg N/L than in POBR (mean = 0.04, standard deviation = 0.01, range = 0.01 to 0.07 mg N/L). These differences did not increase over time. Concentrations increased (from ~ 1.5 to ~ 1.7 mg N/L) significantly in BARN ($r = 0.52$, $p < 0.05$) and decreased (from ~ 0.06 to ~ 0.02 mg N/L) significantly in POBR ($r = -0.48$, $p < 0.05$) from 1999 to 2018 (Fig. 3b). There were no significant trends in loads with time in either BARN (Fig. 2c) or POBR (Fig. 3d).

In BARN, increased nitrate concentrations were associated with increased winter precipitation (ß = 0.39, $p = 0.001$; Table 6). However, in POBR, nitrate concentrations decreased with increased annual precipitation and a similar trend with winter precipitation was marginally significant (ß = -0.00009, $p = 0.01$; Table 6). Nitrate loads in BARN and POBR increased with increased winter precipitation (ß = 0.39, $p = 0.001$ in BARN and ß = 0.005, $p = 0.03$ in POBR) and snow (ß = 0.05, $p = 0.003$ in BARN and (ß = 0.0006, $p = 0.05$ in POBR) (Table 7).

Atmospheric deposition markedly decreased over time ($r = -0.93$, $p < 0.001$), but there were no significant regression relationships between nitrate concentrations or loads and

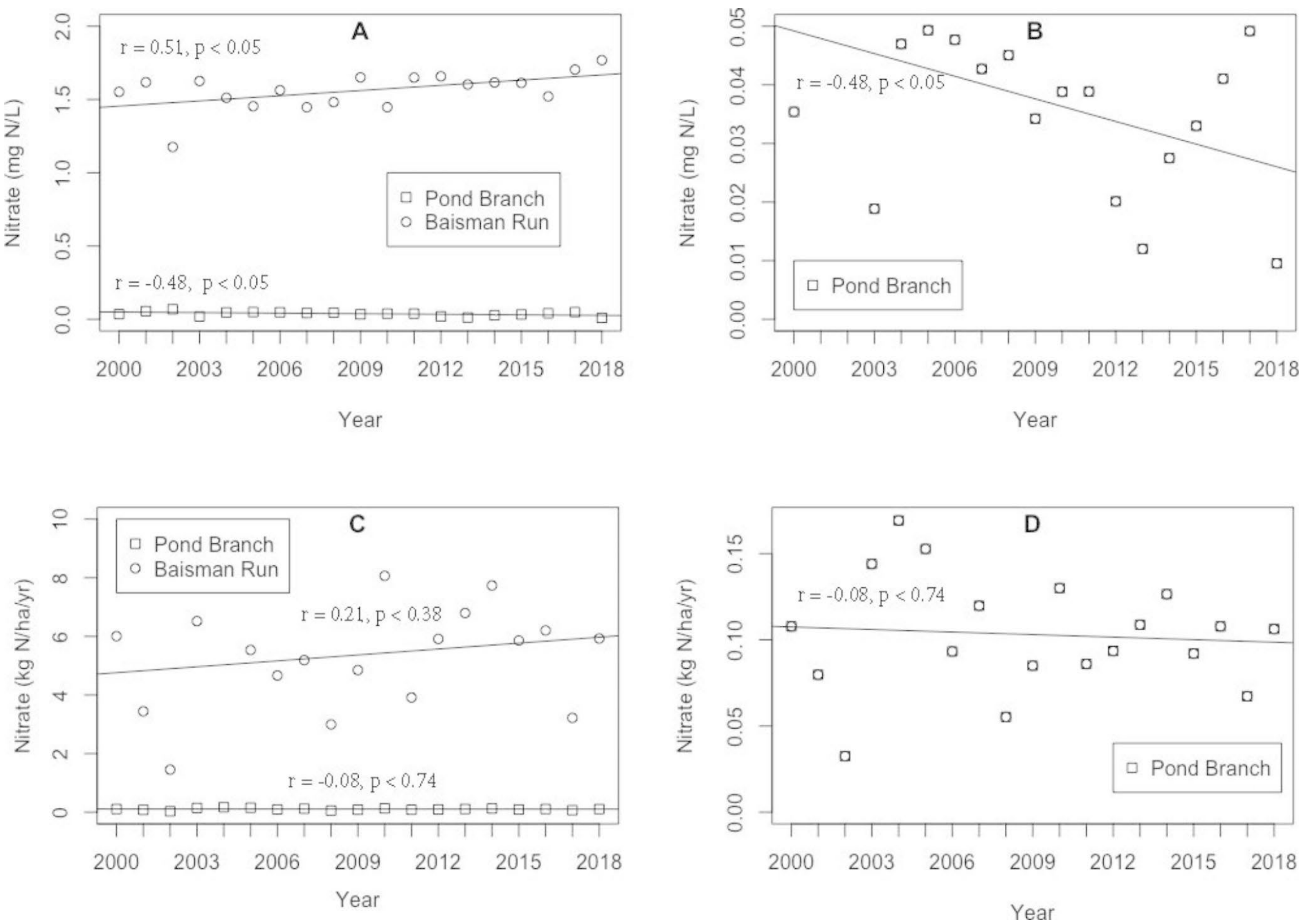


Fig. 4 A. Mean annual nitrate concentrations in samples from Baisman Run (exurban) and Pond Branch (forested) streams from 1999–2018. B. Mean annual nitrate concentrations in samples from Pond Branch Note different scales on y axis between panels A and B. C. Annual nitrate loads from Baisman Run (exurban) and Pond Branch (forested) watersheds from 1999–2018. D. Annual nitrate loads from Pond Branch from 1999–2018 showing differential patterns between 1999–2008 and 2008–2018. Note different scales on y axis between panels C and D

Table 6 Results from linear regression for predictors of nitrate concentrations. Bolded terms indicate significant predictor

	BARN			POBR		
Predictor	Adj R^2	Predictor coefficient	P-value	Adj R^2	Predictor coefficient	P-value
Mean temperature	0.02	-0.38	0.26	0.00	0.002	0.59
Annual precipitation	0.00	0.05	0.30	**0.27**	**-0.0009**	**0.01**
Winter precipitation	**0.44**	**0.39**	**0.001**	0.12	-0.002	0.08
Snow	0.00	0.0003	0.84	0.02	-0.0002	0.28
Atmospheric deposition	0.00	-0.10	0.57	0.07	0.002	0.15

Table 7 Results from linear regression for predictors of nitrate loads. Bolded terms indicate significant predictor

	BARN			POBR		
Predictor	Adj R^2	Predictor coefficient	P-value	Adj R^2	Predictor coefficient	P-value
Mean temperature	0.02	-0.38	0.26	0.07	-0.009	0.14
Annual precipitation	0.00	0.05	0.30	0.00	0.0009	0.30
Winter precipitation	**0.43**	**0.39**	**0.001**	**0.21**	**0.005**	**0.03**
Snow	**0.40**	**0.05**	**0.003**	**0.17**	**0.0006**	**0.05**
Atmospheric deposition	0.00	-0.10	0.57	0.00	0.003	0.43

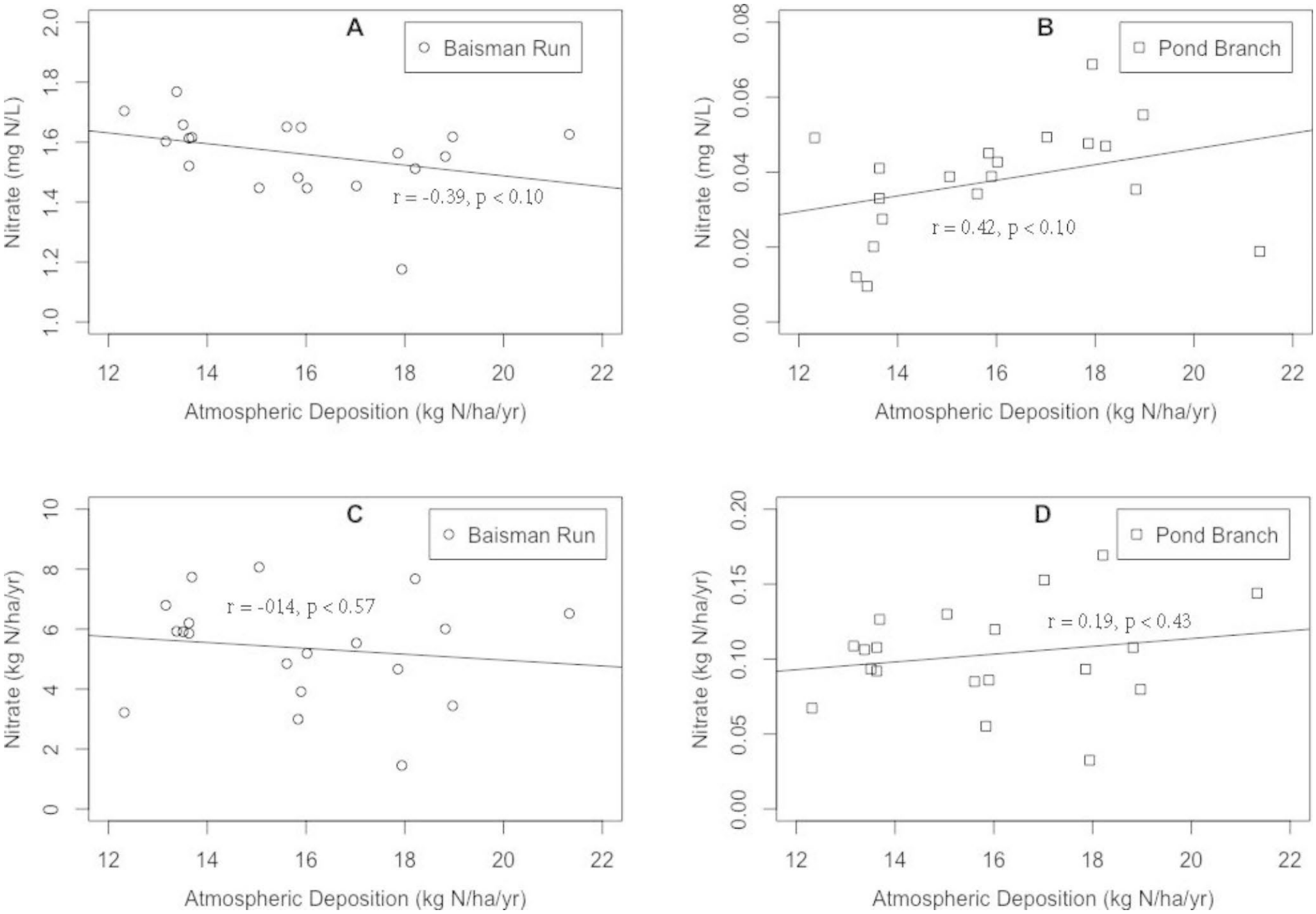


Fig. 5 Mean annual nitrate concentrations versus annual atmospheric nitrogen deposition in Baisman Run (exurban - A) and Pond Branch (forested –B) streams from 1999–2018. Note different scales on y axis between panels A and B. Annual nitrate loads versus annual atmospheric nitrogen deposition in Baisman Run (exurban - C) and Pond Branch (forested –D) streams from 1999–2018. Note different scales on y axis between panels C and D

atmospheric deposition in either BARN or POBR (Fig. 5c). However, there were marginally significant Spearman non-parametric correlations between atmospheric deposition and nitrate concentrations in POBR ($r = 0.43$, $p < 0.10$) (Fig. 5b) and significant negative correlations between atmospheric deposition and nitrate concentrations in BARN ($r = -0.39$, $p < 0.10$) (Fig. 5a). There were no correlations between nitrate loads and atmospheric deposition in either POBR or BARN (Fig. 5c and d).

There were no trends in non-farm fertilizer usage in Baltimore County from 1999 to 2012. Fertilizer applied by Baltimore county personnel on county owned and managed land showed no trend between 1999 and 2018. There were no relationships between fertilizer usage and nitrate concentrations or loads in BARN. Limited (but most relevant) data (2015, 2017, 2018) on fertilized area and amount of fertilizer applied in Baltimore County were compiled from the Fertilizer Application Report produced by the Maryland Department of Agriculture as part of the "lawn fertilizer law" that was passed in 2013. Fertilized area declined, but the total amount of fertilizer applied increased over this limited time period (Table 2).

Septic systems were estimated to add 1,993 kg of nitrate-N to the BARN watershed, which is equivalent to ~100% of typical nitrate-N exports from the watershed. The estimate of septic system nitrate is based on literature values and is therefore approximate. The estimate of nitrate exports is based on average flows and concentration over the study period.

Discussion

Long-term data on stream solute concentrations and loads are rare and valuable for understanding complex controls on water quality in both natural and human-dominated ecosystems (Frazar et al. 2019; Seybold et al. 2019). Nitrate and chloride have proven to be challenging to manage, in both urban and agricultural watersheds. The use of road salt and fertilizer is difficult to reduce, and interactions between management, climate change, and variability have reduced the effectiveness of management efforts (Bettez et al. 2015; Reisinger et al. 2018). The results here emphasize these challenges. In the exurban study watershed, stream chloride concentrations have risen markedly over a 20 year period even when snowfall and road salt use by Baltimore County has not increased. Fertilizer usage has not declined despite significant efforts to reduce its use, and marked declines in atmospheric deposition do not appear to have affected nitrate concentrations in this low density, exurban watershed.

Chloride

The consistently high chloride concentrations and loads in the exurban BARN stream compared to the forested POBR stream have been reported earlier (Kaushal et al. 2005). These results are consistent with many studies characterizing increases in salt concentrations in human-affected watersheds around the world (Kaushal et al. 2018). These studies have shown that watersheds with more human activity, especially roads treated with salt during winter, have high chloride concentrations in streams, throughout the year. Other important sources of chloride in exurban watersheds include septic systems, water softeners (discharged through septic systems), fertilizer, and atmospheric deposition (Oberhelman and Peterson 2020; Overbo et al. 2021). None of these sources has increased in BARN over the last 20 years, although there has been some new residential development with septic systems. We estimate that septic systems contribute an amount of chloride that is equivalent to ~21% of exports from the watershed. Septic effluents are added directly to the groundwater and may therefore be more readily transported to the stream than road salt under baseflow conditions. On the other hand, road salt is more readily transported to the stream by surface runoff.

There is much current research interest in and practical concern about the occurrence of high chloride concentrations in streams during seasons when chloride is not being applied to roads, and persistent increases in concentrations despite heightened awareness and efforts to reduce chloride contamination (Kelly et al. 2019). Our results may add to these concerns as chloride concentrations have increased markedly in BARN from 1999 to 2018, even though snowfall, road salt usage and urban land cover (Bird et al. 2018) have not increased over this time period. A new subdivision (~10 houses) was added to the watershed in 2007/2008, but we see no evidence of a change in the rate of increase in either chloride concentrations or loads after that time. The high concentrations in summer, and the persistent increase over the 20 year record are likely driven by storage of chloride in watershed groundwater which creates a lag between changes in road salt use and stream chloride concentrations (Gelhar and Wilson 1974). In an exurban watershed in New York, Kelly et al. (2019) estimated that it will take between 20 and 30 years for decreases in road salt use to be apparent in stream chloride concentrations.

Despite the importance of storage and lag effects, we did observe significant correlations between annual mean chloride concentrations and loads and total annual and winter precipitation, and with the number of snowfall events requiring the use of road salt. The correlations with precipitation are likely caused by increased precipitation flushing chloride across the landscape and into streams. We note that we did not do any specific storm event sampling, so the importance of storm events is underestimated in our study. The correlation with the number of snowfall events requiring the use of road salt is straightforward, i.e., we expect to see more salt in the stream in years with more salt application. Further, while snowfall depth did not change over the course of the study, there was a significant negative relationship between road salt usage and mean annual temperature (Table 5), and as expected a significant positive relationship between road salt usage and snowfall (Table 5). These results suggest that while annual variation in winter climate drivers and road salt usage is driving the year-to-year-variation in chloride concentrations and loads, the long-term trend is being driven by the constant accumulation of legacy chloride in groundwater. Still, the results suggest that continued climate warming and reductions in snowfall will ultimately lead to less road salt use. In combination with efforts to increase the efficiency of road salt use, these changes may ultimately result in decreases in chloride concentrations in streams (Kelly et al. 2019).

The complex changes in chloride concentrations in Pond Branch, the forested reference stream, illustrate how natural processes influence concentrations in complex and poorly understood ways. It is not clear why concentrations in this stream increased from 1999 to 2008 and then decreased from 2008 to 2018 and there were no correlations between these concentrations and any climatic variables, or with atmospheric deposition of chloride. The declining trend was not evident in earlier analyses of data from this stream (Reisinger et al. 2018) which shows the need for long-term data to elucidate complex trends in environmental data. Chloride concentrations in forested streams can be influenced by the source of precipitation, e.g., precipitation that originates over the ocean, or by evapotranspiration that removes water and concentrates chloride in the remaining soil solution (Lovett et al. 2005). Further research would likely help to isolate these mechanisms and to determine if they influence concentrations in more urbanized watersheds. It is interesting to note that while temporal patterns in chloride concentrations in POBR were strong and significant, there were no significant trends in loads. Trends in concentrations are likely more indicative of internal watershed processes as most of our samples were taken under base flow conditions (Table 1) and therefore are less affected by hydrologic conditions than load estimates (Wherry et al. 2021).

Nitrate

Along urban to exurban gradients, nitrate concentrations are often relatively high in exurban areas. There are multiple potential sources of nitrate in these areas, including atmospheric deposition, lawn and agricultural fertilizer, septic systems, and "legacy" nitrate in groundwater from past sources (Kaushal et al. 2011). Long-term data from POBR and BARN provide an opportunity to evaluate how these sources interact with climate variation and change. Of particular interest are marked declines in atmospheric deposition that have occurred over the past 20 years due to changes in the Clean Air Act (Sabo et al. 2016, 2019), and efforts to reduce fertilizer use as part of Watershed Implementation Plans to achieve Total Maximum Daily Load goals for reducing nitrogen delivery to the Chesapeake Bay (Birch et al. 2011; Wainger 2012).

While our results suggest that declining atmospheric deposition is driving declines in nitrate concentrations in POBR, it does not appear to be affecting concentrations in BARN. There was a positive correlation between deposition and nitrate concentration in POBR, i.e., concentrations declined along with deposition over the past 20 years. At the same time, there was a negative correlation between deposition and nitrate concentrations in BARN, i.e., concentrations increased as deposition declined over the past 20 years (Eshleman et al. 2013; Sabo et al. 2016). Interestingly, there was no correlation between deposition and nitrate loads in either stream. As with chloride, analysis of base flow nitrate concentrations may be more useful for assessing the effects of environmental change on internal watershed processes than analysis of loads, which are dominated by hydrologic factors (Wherry et al. 2021).

Clearly, other nitrogen sources, e.g., fertilizer, septic systems, overwhelm any declines in atmospheric deposition in BARN (Gold et al. 1990; Kaushal et al. 2011). Indeed, septic systems appear to be the overwhelmingly dominant source of anthropogenic N in BARN as our estimates of septic system nitrate-N additions are roughly equivalent to watershed exports. If distributed over the entire watershed, on an areal basis, septic inputs are lower than inputs from atmosphere (< 5.0 kg N/ha/y of septic versus ~ 10 kg N/ha/y from the atmosphere). Fertilizer inputs are similarly high, estimated at 9.5 kg N/ha/y in the BARN watershed (Law et al. 2004). But the septic N is added directly to the groundwater in a concentrated plume, facilitating transport to the stream in baseflow, while atmospheric deposition and fertilizer interact with surface soils and vegetation with high potential for uptake and retention (Raciti et al. 2008). The increase in nitrate concentrations in BARN over the past 20 years may be due to the addition of a new subdivision (~ 10 houses) to the watershed, or to storage of nitrate in groundwater similar to what occurs for chloride. The rate of increase in nitrate is much lower than the rate of increase of chloride, reflecting the high biological reactivity and diverse potential sinks for nitrate relative to chloride (Davidson et al. 2012; Byrnes et al. 2020). While the increase in nitrate over the last 20 years (~ 0.2 mg N/L) is small relative to the concentration (~ 1.5 mg N/L), it is still much higher than the concentrations in the forested reference watershed (< 0.05 mg N/L). And the increase is highly significant at a time when atmospheric deposition has been declining and efforts to reduce fertilizer use have been increasing.

As with chloride, the influence of annual climate was important for nitrate in both watersheds (Kaushal et al. 2008; Bettez et al. 2015; Loecke et al. 2017). There were significant negative correlations between annual and winter precipitation and stream nitrate concentrations in POBR, suggesting that increases in precipitation dilute nitrate concentrations in this watershed (Duncan et al. 2015). In contrast, there were positive relationships between nitrate loads and winter precipitation and snowfall in both POBR and BARN, suggesting that increased precipitation effectively flushes this ion out of these watersheds (Bird et al. 2018). Clearly, variation in discharge is a stronger regulator of nitrate export than variation in concentration in this watershed.

The high and stable nitrate concentrations in BARN suggest that efforts to reduce fertilizer usage in this watershed have yet to produce results. It is difficult to track changes in fertilizer usage, especially in specific locations. We see no evidence in national-scale assessments for declines in non-farm fertilizer usage in Baltimore County from 1999 to 2012, and there were no relationships between this usage and nitrate concentrations in BARN. We also see no trends in the amount of fertilizer used by county personnel between 1999 and 2018, but this usage is not particularly relevant or indicative of use in our specific study watershed. Baltimore County passed a new fertilizer law in 2013 and has started to collect more detailed data on fertilizer usage across the county. The limited data available from this collection show a small decline in the area fertilized, but a small increase in the total amount of fertilizer applied between 2015 and 2018. There is a clear need for further analysis of relationships between nitrate concentrations and fertilizer usage in BARN.

Given the importance of septic systems as the dominant source of nitrate to BARN, efforts to reduce nitrate exports may need to focus on installation of nitrate reducing septic systems (Withers et al. 2013). As with chloride, accumulation of nitrate in groundwater means that there will be a significant lag between any reductions in fertilizer or septic sources and nitrate concentrations in exurban streams (Wherry et al. 2021). Stream restoration, which has the capacity to increase biological uptake of nitrate, especially in base flow dominated watersheds such as BARN could also decrease nitrate export in this watershed (Craig et al. 2008; Reisinger et al. 2019).

Implications for management

Water quality in the exurban BARN watershed has clearly not improved over the past 20 years. Chloride concentrations have markedly increased and nitrate concentrations have remained stable, despite great concerns and efforts, including the mandated reductions of these loads in the Chesapeake Bay Watershed, to reduce the delivery of these solutes to receiving waters.

Reducing chloride concentrations will require significant reductions in salt usage, and patience as it may take decades for legacy chloride that has accumulated in groundwater to be flushed from the watershed. Some progress has already been made by the Baltimore Department of Public Works and Transportation Bureau of Highways to reduce the amount of salt applied to roads. At the start of each snow season, training and review of salt application procedures and best practices are provided to county crews. A goal for a quarter of the snow removal equipment to be equipped with computerized salt spreading systems by 2021was set, with the intention that all new pieces of snow removal equipment also be computerized. The storage of deicer salt is covered, on impervious surfaces, and surrounded by berms (Baltimore County Government 2021). More research on ways to reduce salt usage and the factors influencing retention and legacy dynamics would help develop solutions to persistent chloride problems.

Reducing nitrate will require significant reductions in fertilizer and/or septic system sources, coupled with practices to increase nitrate retention, and a better understanding of legacy effects. Detailed tracking of response to the new Baltimore County fertilizer law will likely be an important part of this assessment. At the state level, the Maryland Department of the Environment is actively encouraging the use of nitrogen-reducing technologies for septic systems (Maryland Department of the Environment 2022).

Improving water quality in exurban streams is not easy. Understanding the multiple factors affecting stream solute concentrations, and the slow and complex response to these factors is greatly aided by long-term data collection. Establishing and maintaining strong linkages between this data collection, models and management programs will be fundamentally important to this challenging endeavor.

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References

Baker LA, Hope D, Xu Y, Edmonds J, Lauver L (2001) Nitrogen balance for the central Arizona-Phoenix (CAP) ecosystem. Ecosystems 4:582–602

Baltimore County Government (2021) Baltimore County NPDES – 2021 Annual Report. https://www.baltimorecountymd.gov/departments/environment/npdes/

Bettez ND, Duncan JM, Groffman PM, Band LE, O'Neil-Dunne J, Kaushal SS, Belt KT, Law N (2015) Climate variation overwhelms efforts to reduce nitrogen delivery to coastal waters. Ecosystems 18:1319–1331

Birch MBL, Gramig BM, Moomaw WR, Doering IIIOC, Reeling CJ (2011) Why metrics matter: evaluating policy choices for reactive nitrogen in the Chesapeake Bay watershed. Environ Sci Technol 45:168–174

Bird DL, Groffman PM, Salice CJ, Moore J (2018) Steady-state land cover but non-steady-state major ion chemistry in urban streams. Environ Sci Technol 52:13015–13026

Blaszczak JR, Delesantro JM, Zhong Y, Urban DL, Bernhardt ES (2019) Watershed urban development controls on urban streamwater chemistry variability. Biogeochemistry 144:61–84

Boesch DF, Brinsfield RB, Magnien RE (2001) Chesapeake Bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. J Environ Qual 30:303–320

Byrnes DK, Van Meter KJ, Basu NB (2020) Long-term shifts in U.S. nitrogen sources and sinks revealed by the new TREND-nitrogen dataset (1930-2017). Global Biogeochemical Cycles

Cleaves ET, Godfrey AE, Bricker OP (1970) Geochemical balance of a small watershed and its geomorphic implications. GSA Bull 81:3015–3032

Craig LS, Palmer MA, Richardson DC, Filoso S, Bernhardt ES, Bledsoe BP, Doyle MW, Groffman PM, Hassett BA, Kaushal SS, Mayer PM, Smith SM, Wilcock PR (2008) Stream restoration strategies for reducing river nitrogen loads. Front Ecol Environ 6:529–538

Davidson EA, David MB, Galloway JN, Goodale CL, Haeuber R, Harrison JA, Howarth RW, Jaynes DB, Lowrance RR, Nolan BT, Peel JL, Pinder RW, Porter E, Snyder CS, Townsend AR, Ward MH (2012) Excess nitrogen in the U.S. environment: Trends, risks, and solutions. Issues in Ecology 15:1–16

Duncan JM, Band LE, Groffman PM, Bernhardt ES (2015) Mechanisms driving the seasonality of catchment scale nitrate

export: evidence for riparian ecohydrologic controls. Water Resour Res 51:3982–3997
Eshleman KN, Sabo RD (2016) Declining nitrate-N yields in the Upper Potomac River Basin: what is really driving progress under the Chesapeake Bay restoration? Atmos Environ 146:280–289
Eshleman KN, Sabo RD, Kline KM (2013) Surface water quality is improving due to declining atmospheric N deposition. Environ Sci Technol 47:12193–12200
Findlay SEG, Kelly VR (2011) Emerging indirect and long-term road salt effects on ecosystems. Ann N Y Acad Sci 1223:58–68
Frazar S, Gold AJ, Addy K, Moatar F, Birgand F, Schroth AW, Kellogg DQ, Pradhanang SM (2019) Contrasting behavior of nitrate and phosphate flux from high flow events on small agricultural and urban watersheds. Biogeochemistry 145:141–160
Gelhar LW, Wilson JL (1974) Ground-water quality modeling. Groundwater 12:399–408
Gold AJ, Deragon WR, Sullivan WM, Lemunyon JL (1990) Nitrate-nitrogen losses to groundwater from rural and suburban land uses. J Soil Water Conserv 45:305–310
Groffman PM, Band LE, Belt KT, Bettez ND, Bhaskar A, Doheny E, Duncan JM, Kaushal SS, Rosi EJ, Welty C (2019) Applying the watershed approach to urban ecosystems. In: Pickett STA, Cadenasso ML, Grove JM, Irwin EG, Rosi EJ, Swan CM (eds) Science for the Sustainable City. Yale University Press, pp 155–173
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, Rosi EJ, Martel L, Kaushal S (2018) Stream chemistry for core sites in Gwynns Falls: concentration of Cl, NO3, PO4, total N and P, SO4, dissolved oxygen, E. coli, plus temperature, pH, clarity, turbidity, isotopes, and pharmaceuticals ver 600. Environmental Data Initiative. https://doi.org/10.6073/pasta/9a7c95a4b7b12e7d97fc296b050ce8a5. Accessed 2020-05-13
Hale RL, Scoggins M, Smucker NJ, Suchy A (2016) Effects of climate on the expression of the urban stream syndrome. Freshw Sci 35:421–428
Hansen AJ, Knight RL, Marzluff JM, Powell S, Brown K, Gude PH, Jones K (2005) Effects of exurban development on biodiversity: patterns, mechanisms, and research needs. Ecol Appl 15:1893–1905
Hirsch RM, Moyer DL, Archfield SA (2010) Weighted regressions on Time, Discharge, and season (WRTDS), with an application to Chesapeake Bay River Inputs. JAWRA J Am Water Resour Association 46:857–880
Hobbie SE, Finlay JC, Janke BD, Nidzgorski DA, Millet DB, Baker LA (2017) Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. Proceedings of the National Academy of Sciences 114: 4177–4182
Kaushal SS, Groffman PM, Band LE, Elliott EM, Shields CA, Kendall C (2011) Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environ Sci Technol 45:8225–8232
Kaushal SS, Groffman PM, Band LE, Shields CA, Morgan RP, Palmer MA, Belt KT, Swan CM, Findlay SEG, Fisher GT (2008) Interaction between urbanization and climate variability amplifies watershed nitrate export in Maryland. Environ Sci Technol 42:5872–5878
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 USA 102:13517–13520
Kaushal SS, Likens GE, Pace ML, Utz RM, Haq S, Gorman J, Grese M (2018) Freshwater salinization syndrome on a continental scale. Proceedings of the National Academy of Sciences 115: E574-E583
Kelly VR, Findlay SE, Hamilton SK, Lovett GM, Weathers KC (2019) Seasonal and long-term dynamics in stream water sodium chloride concentrations and the effectiveness of road salt best management practices. Water, Air, & Soil Pollution 230
Kochary S, Byl T, Noori B (2017) Modeling the movement of septic water chloride through a soil profile. Sustainability 9:501
Law LN, Band EL, Grove JM (2004) Nitrogen input from residential lawn care practices in suburban watersheds in Baltimore County, MD. J Environ Planning Manage 47:737–755
Likens GE (2013) Biogeochemistry of a Forested Ecosystem, 3rd Edition. Springer-Verlag, New York
Loecke TD, Burgin AJ, Riveros-Iregui DA, Ward AS, Thomas SA, Davis CA, Clair MAS (2017) Weather whiplash in agricultural regions drives deterioration of water quality. Biogeochemistry 133:7–15
Lopez R (2014) Urban Sprawl in the United States: 1970–2010. Cities and the Environment (CATE) 7: Article 7. Available at: https://digitalcommons.lmu.edu/cate/vol7/iss1/7
Lovett GM, Likens GE, Buso DC, Driscoll CT, Bailey SW (2005) The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA. Biogeochemistry 72: 191–232
Maryland Department of the Environment (2022) Maryland's Nitrogen-Reducing Septic Upgrade Program. https://www.mdsg.umd.edu/wra/programs/nitrogen-reducing-septic-upgrade-program
Moore J, Bird DL, Dobbis SK, Woodward G (2017) Nonpoint source contributions drive elevated major ion and dissolved inorganic carbon concentrations in urban watersheds. Environ Sci Technol Lett 4:198–204
Nathan RJ, McMahon TA (1990) Evaluation of automated techniques for base flow and recession analyses. Water Resour Res 26:1465–1473
Newburn D, Berck P (2011) Exurban development. J Environ Econ Manag 62:323–336
Oberhelman A, Peterson EW (2020) Chloride source delineation in an urban-agricultural watershed: Deicing agents versus agricultural contributions. Hydrol Process 34:4017–4029
Overbo A, Heger S, Gulliver J (2021) Evaluation of chloride contributions from major point and nonpoint sources in a northern U.S. state. Sci Total Environ 764:144179
Raciti SM, Groffman PM, Fahey TJ (2008) Nitrogen retention in urban lawns and forests. Ecol Appl 18:1615–1626
Reisinger AJ, Doody TR, Groffman PM, Kaushal SS, Rosi EJ (2019) Seeing the light: urban stream restoration affects stream metabolism and nitrate uptake via changes in canopy cover. Ecol Appl 29:e01941
Reisinger AJ, Woytowitz E, Majcher E, Rosi EJ, Belt KT, Duncan JM, Kaushal SS, Groffman PM (2018) Changes in long-term water quality of Baltimore streams are associated with both gray and green-infrastructure. Limnol Oceanogr 17:1–17
Rossi ML, Kremer P, Cravotta CA, Scheirer KE, Goldsmith ST (2022) Long-term impacts of impervious surface cover change and roadway deicing agent application on chloride concentrations in exurban and suburban watersheds. Sci Total Environ 851:157933
Rutledge EM, Teppen BJ, Mote CR, Wolf DC (1993) Designing septic tank filter fields based on effluent storage during climatic stress. J Environ Qual 22:46–51
Sabo RD, Clark CM, Bash J, Sobota D, Cooter E, Dobrowolski JP, Houlton BZ, Rea A, Schwede D, Morford SL, Compton JE (2019) Decadal shift in nitrogen inputs and fluxes across the contiguous United States: 2002–2012. J Geophys Research: Biogeosciences 124:3104–3124
Sabo RD, Scanga SE, Lawrence GB, Nelson DM, Eshleman KN, Zabala GA, Alinea AA, Schirmer CD (2016) Watershed-scale changes in terrestrial nitrogen cycling during a period of decreased atmospheric nitrate and sulfur deposition. Atmos Environ 146:271–279

Seybold E, Gold AJ, Inamdar SP, Adair C, Bowden WB, Vaughan MCH, Pradhanang SM, Addy K, Shanley JB, Vermilyea A, Levia DF, Wemple BC, Schroth AW (2019) Influence of land use and hydrologic variability on seasonal dissolved organic carbon and nitrate export:. insights from a multi-year regional analysis for the northeastern USA. Biogeochemistry

Wainger LA (2012) Opportunities for reducing total maximum daily load (TMDL) compliance costs: Lessons from the Chesapeake Bay. Environ Sci Technol 46:9256–9265

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

Wherry SA, Tesoriero AJ, Terziotti S (2021) Factors affecting nitrate concentrations in stream base flow. Environ Sci Technol 55:902–911

Withers PJA, Jordan P, May L, Jarvie HP, Deal NE (2013) Do septic tank systems pose a hidden threat to water quality? Front Ecol Environ 12:123–130