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Key Points:

- Twenty-five-year time series of impervious cover linked to monthly stream conductivity at 12 long-term monitoring stations in a metropolitan area
- Conductivity did not rise monotonically with imperviousness but varied in space and time, ramping steeply at levels <5%
- Trends and seasonal patterns differed with impervious levels, as conductivity became increasing dominated by event-related signals

Supporting Information:

- Supporting Information S1
- Table S1

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Impacts of Expanding Impervious Surface on Specific Conductance in Urbanizing Streams

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Abstract Long-term analysis indicates that progressive salinization of freshwaters is widespread. Although increases are often associated with urbanization, knowledge of chemical dynamics during urbanization is limited and typically drawn from space-for-time studies. Thus, the potential role of stream chemistry in sharp biodiversity losses observed at low levels of urbanization is difficult to distinguish from other concurrent factors such as temperature, flow, or sediment. We used a 25-year annual time series of impervious cover for the Baltimore-Washington, DC, metropolitan area to interpret long-term records from 12 watershed-monitoring stations in the Mid-Atlantic Piedmont USA from 1986 to 2010 and explore stream conductivity under progressive urbanization. All 12 watersheds experienced variable but monotonic increases in impervious cover, which ranged from <1% to nearly 25% of contributing area. All monitoring stations exhibited elevated specific conductance relative to background concentrations. Proliferation of impervious cover led to seasonal shifts in monthly conductivity maxima, with progressive dominance of winter pulses and diminishing signal from evapotranspirative concentration in late summer. We found consistently steep increases in stream conductivity across years and seasons associated with incremental increases in low (0-4.5%) levels of watershed impervious cover; moderate to low rates of increase, but distinct seasonal concentrations from 4.5 to 13.8% impervious cover; and increasing predominance of pulses at high levels of impervious cover (>13.8%), particularly when conditioned on winter storm events. Observed patterns may suggest distinct sources and different degrees of hydrologic connection. Despite ubiquitous increases, variability in conductivity trends across space and time underscores the need for more intensive monitoring as urbanization progresses.

1. Introduction

Cities profoundly alter the biophysical properties of watersheds and stream ecosystems, leading to dramatic biological responses and a syndrome of physical and chemical changes (Dunne & Leopold, 1978; Paul & Meyer, 2001; Schueler et al. 2009; Walsh et al., 2005). The notion of a *syndrome* necessarily implies a set of intercorrelated, confounding effects that may operate differently in different geographies or at different levels of urbanization. Analysis of biotic response to gradients of urbanization, once thought to show degradation around 10% watershed impervious cover, has revealed dramatic changes to stream assemblages at levels much lower than previously described (Cuffney et al., 2010; King et al., 2011; King & Baker, 2010; Utz et al., 2009). Although hydrologic and geomorphic mechanisms are arguably important drivers, freshwater salinization has recently received renewed emphasis (Cañedo-Argüelles et al., 2016; Corsi et al., 2010; Griffith, 2017; Kefford et al., 2016). Given expansion of urban landscapes associated with global population patterns and the fact that biotic responses are often used to drive regulatory policy, understanding and disentangling potential drivers of biodiversity losses are essential for developing sustainable management paradigms.

Urban areas may present many diverse sources of specific conductance due to increasing population density (Tu et al., 2007), transportation and other infrastructure (Daley et al., 2009), and sewage treatment (Andersen et al., 2004). Although increases in ionic fluxes have long been a focus of urbanization study (e.g., Prowse, 1987), investigation has increasingly highlighted dissolved solids and conductivity as key urbanization signals, whether from organic waste, inorganic solutes, or synthetic compounds (Kaushal et al., 2018; Rosi-Marshall & Royer, 2012; Walsh et al., 2005). Apart from water contact with weathered soils and bedrock or evapotranspirative concentration, anthropogenic sources of dissolved ions include weathering of infrastructure (e.g., concrete; Davies et al., 2010; Rose, 2007; Wright et al., 2011), sewage, wastewater from fossil fuel production, industrial effluent, rock salt deicers, and agricultural runoff (Griffith, 2014; Kaushal et al., 2014, 2018).

Even though the predominant ions responsible vary regionally, increases in dissolved ions are characteristic of urban landscapes (Griffith, 2014; Walsh et al., 2005) even in regions without regular snowfall and the associated application of deicers (Corsi et al., 2015; Hatt et al., 2004; Roy et al., 2003; Sprague et al., 2007). Studies have demonstrated long-term salinization of freshwaters in the northeastern United States (Daley et al., 2009; Jackson & Jabbogy, 2005; Kaushal et al., 2005; Kelly et al., 2008), and further work suggests that this pattern is much more widespread (Cañedo-Argüelles et al., 2016; Corsi et al., 2010, 2015). Such trends are alarming and a renewed source of concern for the sustainability of freshwater ecosystems given the threat that ionic extremes pose for aquatic life (Clements & Kotalik, 2016; Corsi et al., 2010; Cormier et al., 2013; Griffith, 2017; Johnson et al., 2015; Mount et al. 1997; Paul & Meyer, 2001; Weber-Scannell & Duffey, 2007).

Despite the breadth of potential sources and their inherent temporal variability, dissolved solutes contributing to specific conductance are often characterized as increasing monotonically with urbanization through time (Corsi et al., 2015; Kaushal et al., 2005; Kaushal et al., 2018; Sprague et al., 2007). Many studies rely on either “space-for-time substitution” (Pickett, 1989) or long-term observations at a limited number of locations; yet tracking chemical dynamics of landscape change through both space and time remains elusive (Morse & Wolheim, 2014). Spatial data can be used to infer general trends (e.g., Aichele, 2005; Conway, 2007; Corsi et al., 2015; Interlandi & Crockett, 2003; Morse et al., 2003; Williams et al., 2005), but they do not distinguish episodic events from progressive storage and accumulation, increases in source area, or the accumulation of different types of impervious surfaces (e.g., roads and rooftops,; Smith et al., 2010) concurrent with urban expansion. Conversely, temporal studies have successfully documented trends and episodic events but have not explicitly linked dynamics to the urbanization process (Corsi et al., 2010, 2015; Daley et al., 2009; Kaushal et al., 2005). Despite long-term water monitoring records, geographic datasets characterizing patterns of urbanization through time are often either too coarse in their temporal resolution (e.g., 5- to 10-year frequency; e.g., Homer et al., 2004, 2007) or too limited in spatial extent to capture broader, regional patterns (e.g., Kaushal et al., 2005).

Regional assessments of dynamic changes in conductivity and stream chemistry during urbanization are needed to understand variation among watersheds to distinguish the cumulative versus incremental effects of land development and to understand differences associated with underlying physical drivers (e.g., Utz et al., 2016). Using a satellite-based, 25-year time series of annual impervious cover maps for the Baltimore-Washington, DC, metropolitan area (Sexton et al., 2013), we explored the complex relationship between regional urban expansion and stream ion concentrations. Specifically, we asked whether the spatial proliferation of impervious cover provides sufficient insight to explain patterns and sources of elevated conductivity within the study area. We were especially interested in these dynamics as a potential driver of observed changes to stream biota at exceptionally low levels of satellite-derived impervious cover (i.e., ~4%; King et al., 2011) as well as at higher levels, where biological change is commonly observed using community level indices (e.g., 10-12%; Cuffney et al., 2010; King et al., 2005; King & Baker, 2010; Schueler, 1994); thus, our analysis sought to document when, and by how much, patterns of conductivity exceeded regional background concentrations in ways that might inform analysis of biotic responses.

2. Materials and Methods

2.1. Study Area

The study watersheds comprise 12 of the Maryland Department of Natural Resources (MDNR) nontidal, long-term assessment stations surrounding the urban cores of Baltimore, Maryland, and Washington, DC, and encompassing much of Maryland's Upper Piedmont (Figure 1 and Table 1). The Upper Piedmont spans a broad ridge west of the Baltimore-Washington corridor and largely consists of resistant Precambrian schist, quartzite, gneiss, and small patches of marble or Paleozoic granitic quartz. Study watersheds in this region drain to the south toward the Potomac River or east and southeast towards the Piedmont/Coastal Plain fall line and the Chesapeake Bay. For the purposes of this study, a background conductivity of ~100 μS/cm was defined empirically by the lower quartile of a large distribution of water samples from randomized stream surveys within the Piedmont ecoregion (Griffith, 2014). These estimates correspond closely to conservative interpretation of values modeled by an independent geographic approach (Olson & Hawkins, 2012) for

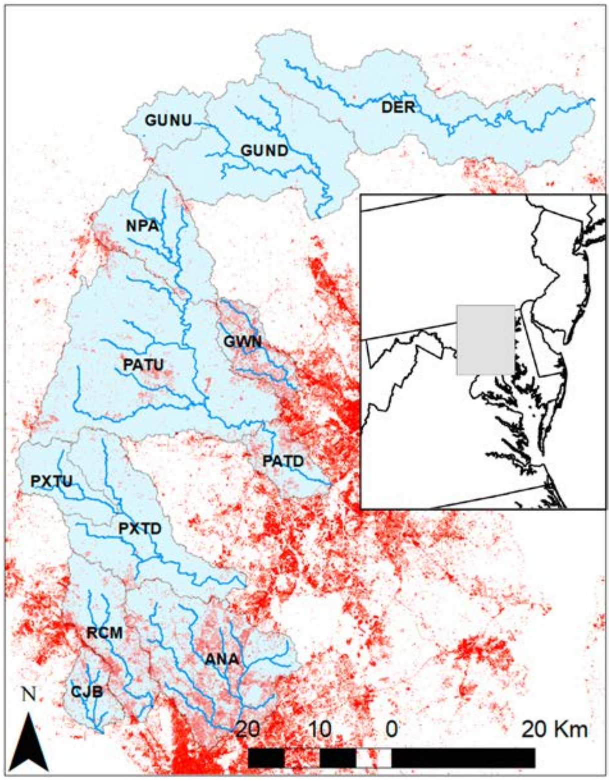

Figure 1. Map of watershed boundaries and river networks showing Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious cover (red shading) in the Baltimore-Washington, DC, metropolitan area (inset). Study watersheds include Deer Creek (DER), Gunpowder Falls (GUNU, GUND), North Branch Patapsco River (NPA), Patapsco River (PATU, PATD), Gwynns Falls (GWN), Patuxent River (PXTU, PXTD), Anacostia River (ANA), Rock Creek (RCM), and Cabin John Branch (CJB).

nonlimestone based bedrock within the region (i.e., ~80-100 μS/cm; Olson & Cormier 2019). Of the 20 watersheds monitored within the Piedmont physiographic context, eight were excluded from further consideration due to substantial dolomite, marble, or shale formations, which were likely to confound the land use signal (see Utz et al., 2016).

2.2. Data Sources

2.2.1. Impervious Cover

Impervious cover was estimated from a time series of Landsat satellite imagery using the Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS; Sexton et al., 2013). DISCORS uses high-resolution, municipal planimetric data collected over time to train a nonparametric regression tree, which is then applied to estimate impervious cover at annual, 30-m resolution across the study area from 1985 to 2010. Only 1 year in the series, 2009, was interpolated from 2008 and 2010 due to insufficient cloud-free satellite measurements. DISCORS produced a 25-year time series of annual impervious cover for the Baltimore-Washington, DC, metropolitan area with misclassification error (i.e., ~6% per pixel RMSE) comparable to the impervious cover layer of the National Land Cover Database (NLCD; Homer et al., 2007).

Because interannual differences in reflectance could produce small anomalies in predicted impervious cover, we distinguished substantive change from noise by ignoring annual per-pixel differences <12% (i.e., RMSE*2). Comparison of adjusted DISCORS estimates to those of the 2006 NLCD product across 20 watersheds showed strong agreement, yet areal estimates from DISCORS were slightly higher than the national dataset at low levels of urbanization (NLCD=-1.6 + 0.9946*DISCORS, F=925, df=18, p<2e-16; Figure S1 in the supporting information). Both products have been validated and vetted (Homer et al., 2004, 2007; Jones & Jarnagin, 2009; Nowak & Greenfield, 2010); yet the NLCD does not exist as an annual product and has been criticized for underrepresenting impervious cover in rural areas (Claggett et al., 2013). Our comparison thus suggested that DISCORS was of comparable overall quality to the NLCD for ranking impervious areas, yet more likely to detect low levels of impervious cover. Therefore, we summarized DISCORS proportions for each contributing area across all years (i.e., 1985-2010).

2.2.2. Water Chemistry

The MDNR nontidal assessment program began in 1985, but annual data collection did not occur in all study watersheds until January 1986. Water chemistry samples have been collected monthly for the past 30 years and analyzed for a variety of chemical constituents according to federal standards (USEPA 2002). Because measurements are collected by a single sample at low flow, they do not capture event-flow concentrations but may include effects of postevent recession in addition to baseflow conditions. Coordinates for each monitoring station were used to locate watershed outlets along a 1:24000 stream map (U.S. Geological Survey [USGS] National Hydrography Data), and contributing drainages were delineated using a 10-m digital elevation model (USGS National Elevation Data; Gesch et al., 2009) modified to enforce agreement with the stream map (Baker et al., 2006).

2.2.3. Weather Records

Monthly temperature means and minima as well as precipitation totals from 1985 to 2010 were obtained from the National Climate Data Center (https://www.ncdc.noaa.gov). These values were summarized by season and year for the study period. In addition, a history of Maryland's winters was obtained from regional National Weather Service stations (http://www.weather.gov/lwx/winter_storm-pr#TopDaySnowfall) and used as reference in interpreting NCDC data.

Analysis of historical weather records suggested that lower-than-normal mean temperatures occurred during the winters of 1988, 1993, 1994, 1996, and 2003, whereas higher-than-normal precipitation totals

Table 1
Characteristics of Maryland DNR Core/Trend Watersheds Selected for Analysis, in Order of Maximum Percent Imperviousness

Name	Code	Size (km^2)	Dom. geology	Imperviousness (%)
Patuxent	PXT0972 (PXTU)	88.7	PreCamb. Schist; Phyllite	1.2-2.1
Deer Creek	DER0015 (DER)	436.3	PreCamb. Schist	0.8-2.1
Gunpowder Falls	GUN0258 (GUND)	413.5	PreCamb. Schist	0.9-2.1
Gunpowder Falls	GUN0476 (GUNU)	70.6	PreCamb. Schist	1.6-3.5
Patuxent	PXT0809 (PXTD)	341.2	PreCamb. Schist	1.8-3.9
Patapsco	PAT0285 (PATU)	736	PreCamb. Schist	2.6-5.3
N Branch Patapsco	NPA0165 (NPA)	173.7	PreCamb. Schist; Phyllite	3.0-6.6
Patapsco	PAT0176 (PATD)	815.4	PreCamb. Schist; Gabbro	7.0-13.1
Cabin John Branch	CJB0005 (CJB)	63.7	PreCamb. Schist	12.3-19.3
Rock Creek	RCM0111 (RCM)	151.6	PreCamb. Schist,Diorite	13.1-19.6
Anacostia	ANA0082 (ANA)	330.6	PreCamb. Schist; Sand & Gravel	14.2-21.5
Gwynns Falls	GWN0115 (GWN)	85.8	PreCamb. Schist; Gabbro	12.6-24.1

occurred during the winters of 1993, 1994, 1996, and 2003. Nonetheless, winters between 1986 and 2010 produced 8 of the 20 largest snowstorms on record, and both 1994 and 1999 recorded substantial ice storms. Therefore, we used this set of 10 years (i.e., 1987, 1993, 1994, 1996, 1999, 2000, 2003, 2006, 2009, and 2010) to evaluate the effect of major winter storm events on the conductivity-impervious relationship.

2.3. Data Analysis

We assessed the distribution of impervious cover across all site-by-year combinations to understand how effectively and continuously our sample represented the range of watershed development. Next, we characterized conductivity regimes for each study watershed in several ways. First, annual mean and median conductivity values were assessed for trends through time with a nonparametric Mann-Kendall Tau test using Holm's correction for multiple comparisons. Second, we compared the levels of conductivity relative to watershed percent impervious cover with a Kendall test, also using Holm's correction. Third, we compared monthly mean and median values throughout the time series to understand seasonal (i.e., winter: January-March; spring: April-June; summer: July-September; and fall: October-December) patterns of conductivity across sites using measures of central tendency with different responses to extreme values. Finally, we assessed patterns of signal in conductivity time series using wavelet power spectra of monthly conductivity data using the R package *WaveletComp* (Roesch & Schmidbauer 2018). Wavelet analysis is similar to Fourier transforms but employs a series of wavelet (i.e., instead of sinusoidal) functions to analyze and distinguish signals at multiple temporal scales (Cazelles et al., 2008; Torrence & Compo, 1998; White et al., 2005).

We took advantage of the temporal and spatial integration of our dataset by assessing the overall relationship between annual values of watershed impervious cover and annual, or seasonal, means of conductivity. We assessed annual relationships using linear regression, piecewise regression (R package “segmented”; Muggeo 2008), and generalized additive models (GAMs). Segmented regression uses an efficient iterative search algorithm to identify breakpoints for piecewise linear regression, whereas GAMs (R package “mgcv”; Wood, 2017) estimate the value of a response variable using additive smoothing functions (e.g., splines or cubic regressions) of independent variables (Wood 2017; Zuur et al., 2009). All modeling approaches were assessed using Akaike information criteria (AIC). Seasonal patterns of conductivity were subsequently fit to annual impervious cover using GAMs for all years and those distingusihed by major storm events.

Frequency distributions across sites were assessed with exceedance curves developed from the cumulative distribution of 25 years of monthly conductivity across watershed groups. Watersheds were grouped for this analysis on the basis of breakpoints established in annual and seasonal impervious conductivity relationships across all years and watersheds. Next, we characterized trends of annual and seasonal mean conductivity with impervious cover across all sites for each individual year (i.e., what would typically be analyzed via synoptic sampling of many sites within a single year) using linear regression, where comparisons or the results from year to year allowed us to examine variation in those trends. The slopes and intercepts of all significant regressions were retained and examined for temporal and spatial consistency; slopes were

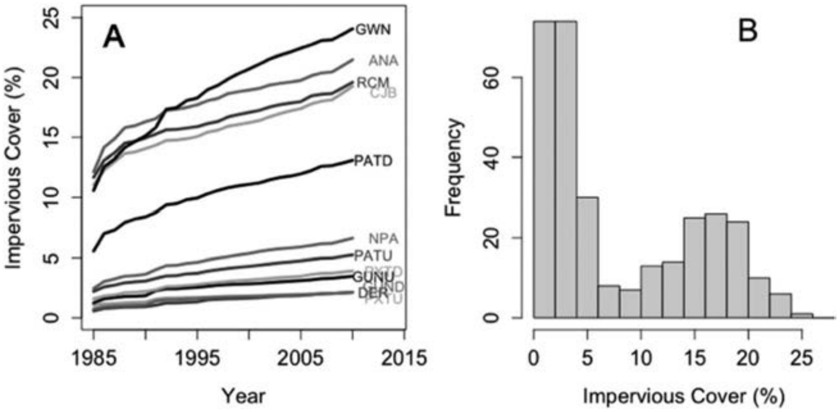

Figure 2. Distribution of (A) DISCORS time series of impervious cover estimates from 1985 to 2010 for 12 study watersheds in the Baltimore-Washington, DC, metropolitan area and (B) collective frequency of site by year observations in increments of 2% of impervious cover.

evaluated relative to climatic data and historical records, grouped by years with and without a major event, and their distributions compared with a t-test.

3. Results

3.1. Patterns of Urbanization Through Time

Impervious cover increased across all watersheds from 1985 to 2010, though the time of greatest change differed among watersheds (Figure 2a). In general, the mid 1990s and the late 2000s were periods of the greatest annual increases in impervious area across watersheds. Sharp increases occurred during the early 1990s in the Gwynn's Falls (GWN), the North Branch of the Patapsco (NPA), Patuxent (PXTU; label underneath DER), and upper Gunpowder Falls (GUNU) drainages. Baltimore experienced a dramatic local acceleration of growth with the completion of the I-795 spur northwest of the city in 1987 as well as the expansion of US-29 southwest of the city around the same time. Rapid suburban expansion apparent in GWN (and echoed in NPA and GUNU) along the I-795 corridor represented the largest cumulative change detected in our time series.

Similar increases appeared earlier in the mid 1980s following the widening of I-270 a few years earlier within more suburban watersheds outside of Washington, DC, such as the Anacostia (ANA), Cabin John Branch (CJB), and Rock Creek (RCM). Several watersheds showed a decrease in the annual impervious increment during economic downturns of 2008 but appeared to recover in 2009 and 2010.

Analysis of the distribution of impervious cover across all watersheds and all years suggested the combined dataset contained at least seven observations for every increment of 2% impervious cover from 0 to 18% imperviousness (Figure 2b). The relative dearth of observations apparent in Figure 2b at moderate levels of impervious cover was somewhat mitigated by initial levels in the more developed watersheds and latter levels in less developed watersheds. Between 6 and 14% there was only one increment with fewer than 10 observations. Several increments between 8 and 12% consisted entirely of observations from the lower Patapsco (PATD). We therefore evaluated PATD samples in subsequent analyses for any indication that they were anything other than intermediate between observations at lower and higher levels of impervious cover.

3.2. Patterns of Conductivity Through Time Across Watersheds

Significant trends in conductivity occurred in all watersheds (Holm-corrected Mann-Kendall *Tau* $p<0.05$; Figure 3). Trends were ubiquitous across all watersheds, yet they appeared consistently stronger for watersheds with lower levels of urbanization (top row in Figure 3: $\tau>0.74$ for medians and $\tau>0.68$ for means). At higher levels of impervious cover (middle and bottom rows, Figure 3), significant trends were still apparent through time, yet medians often showed stronger trends than means, and this largely appeared to result from more variable mean values across years at higher levels of imperviousness.

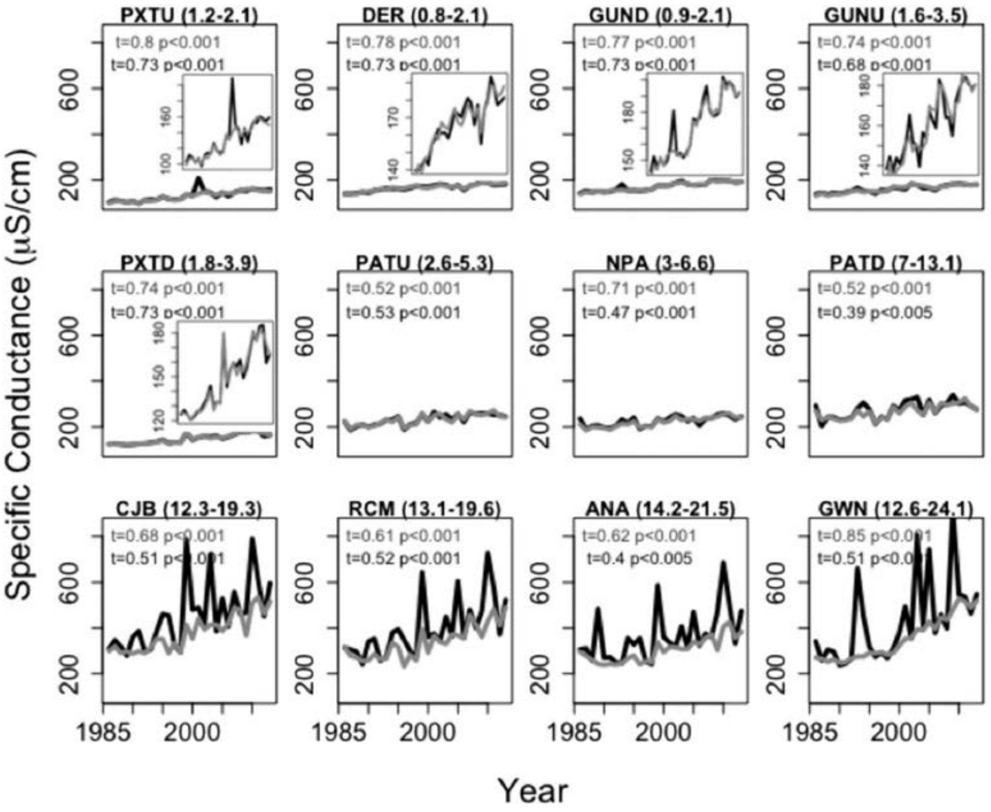

Figure 3. Time series of annual median (grey) and mean (black) specific conductance for 12 study watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. The range of impervious cover within each watershed is shown parenthetically next to each watershed code and panels are organized according to rank 2010 percent imperviousness. Conductivity axes are standardized to facilitate cross-panel comparison, whereas the first five panels are inset with unstandardized plots. Holm-corrected Mann-Kendall *Tau* and associated *p*-values indicating the strength of trends in the mean (black) and median (grey) are shown in each panel.

Temporal trends in conductivity in each watershed were distinguished from higher magnitudes and greater interannual variability across spatial gradients of watershed impervious cover (Figure 3). Throughout the time series, spikes in mean and median conductivity often cooccurred among some, but not all, watersheds, whereas annual means departed from annual medians to reveal periodic extremes. This was most apparent within the more urban watersheds, where mean conductivity was more variable and less associated with medians, especially after 1999. PATD showed a similar pattern of variation that was intermediate between watersheds at both lower and higher levels of development. Specifically, early levels of conductivity (~250 μS/cm) in PATD matched the latter levels of sparsely developed NPA and PATU, whereas latter levels of PATD at ~300 μS/cm corresponded with initial levels of greater development in CJB, RCM, ANA, and GWN.

Specific conductance was also strongly seasonal in many watersheds (Figure 4; see also Figure S2). Among the first four panels (top row; PXTU-GUNU), conductivity levels generally peaked during the winter (January-March), declined during the late winter and spring (April-June), then typically increased throughout summer (July-September) and fall (October-December) samples. This pattern was consistent with concentration and dilution from seasonal cycles of evapotranspiration and precipitation, as well as increased recharge during leaf-off periods. However, the magnitude of this subtle seasonal variation was difficult to discern in standardized plots relative to extremes in more developed watersheds. Across watersheds with lower levels of impervious cover, monthly means tracked medians fairly closely (i.e., within 10-20 μS/cm, with the exception of PXTU; see Figure 5 below), suggesting a relatively normal distribution across time series within each month. Beginning with PATU (middle row), an increase in overall conductivity levels was apparent as impervious cover surpassed ~4-5% and winter means were consistently elevated relative to medians. Similarly, wintertime conductivity became noticeably greater than other seasons for PATD, yet once

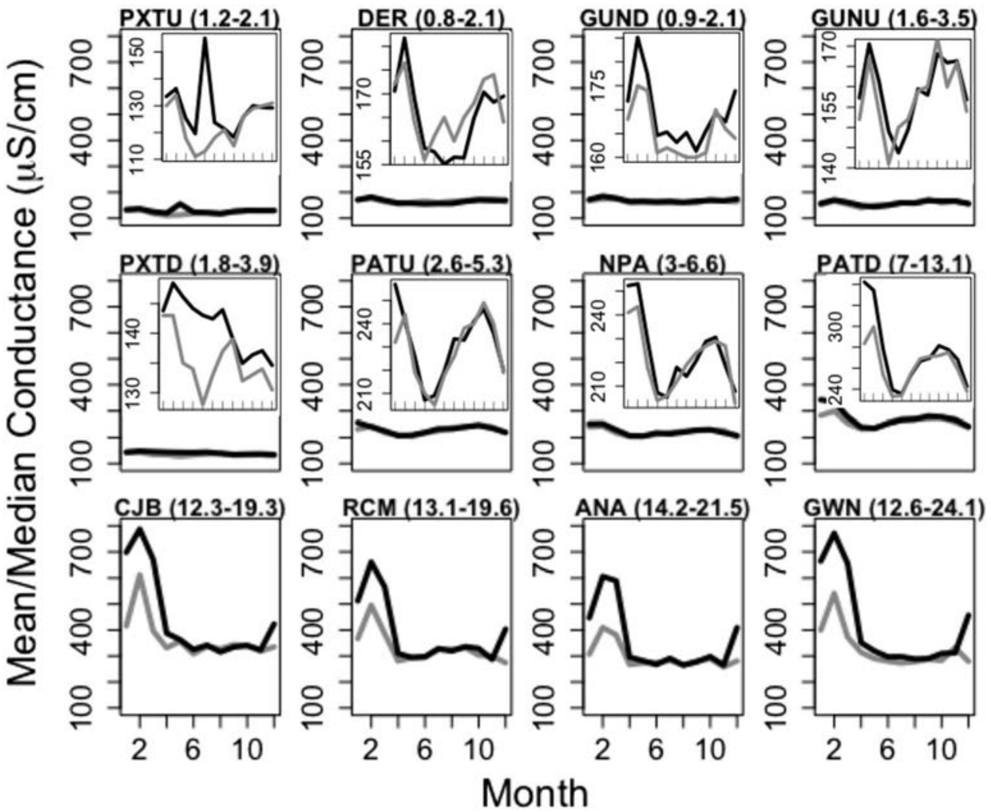

Figure 4. Monthly (January-December) median (grey) and mean (black) specific conductance for 12 study watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. The range of impervious cover is shown parenthetically next to each watershed code and panels are organized according to rank 2010 percent imperviousness. Conductivity axes are standardized to facilitate cross-panel comparison, whereas the first eight panels are inset with unstandardized plots to better illustrate seasonal variation.

again its variation appeared intermediate relative to watersheds with lower and higher levels of urbanization. At higher levels of impervious cover (bottom row), overall conductivity increased, winter conductivity increased relative to other seasons, and both fall and winter means deviated strongly from medians, indicating an increased frequency of extreme values.

Temporal analysis revealed increases in dissolved ions across all watersheds. Trends (quantified in Figure 3) appeared consistently stronger at low levels of development. In more urban watersheds, trends showed greater variability with more extreme values and seasonal shifts toward the predominance of extremes during winter. However, the magnitude of conductivity in each watershed did not entirely correspond to the rank order of impervious cover. GUND had higher levels of conductivity than GUNU even though the latter maintained greater impervious cover throughout the study period. A similar pattern was observed for CJB relative to both RCM and ANA. Further, extremes apparent in the time series of one watershed did not always appear in others, suggesting that mechanisms for generating extreme values occasionally could be relatively local (i.e., watershed-specific).

Analysis of wavelet power spectra revealed further variation in monthly patterns of specific conductance throughout the study period (Figures 5 and S3). Two types of patterns emerged among watersheds with limited development (i.e., <4% impervious cover), where most watersheds exhibited signal associated with seasonal fluctuations from year to year (Figure S3). Anomalously high conductivity levels and significant signal were observed in PXTU during a 2002 drought (Figure S4), yet without the anomalous observations, no significant signal was detected over any temporal period, as annual conductivity remained <160 μS/cm (Figure 3). Like other low-impervious watersheds, DER showed strong signal associated with annual (~12 month) or seasonal (<6 month) time periods, but not both (Figures 3 and 5).

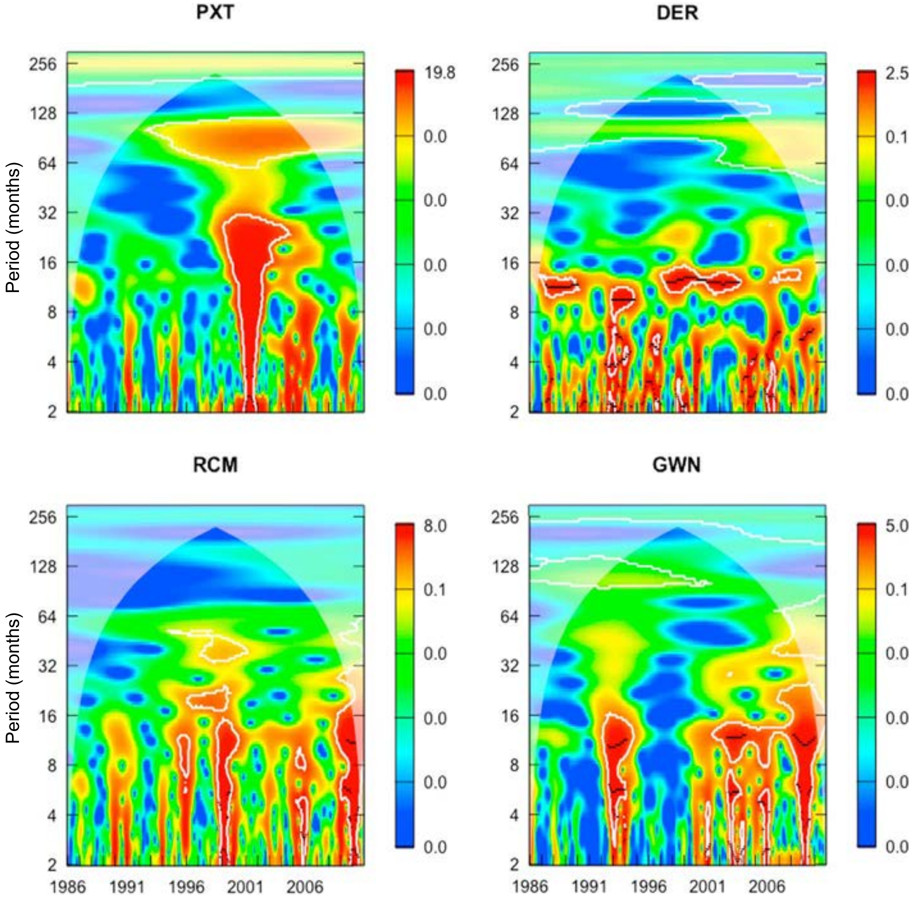

Figure 5. Wavelet power spectra showing intensity of monthly specific conductance across various temporal periods in selected low impervious (top row spanning 0.8-2.1%) and high Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious (bottom row spanning 12.6-24.1%) watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. Colors correspond to relative signal strength, the white lines delineate zones of significant signal ($p<0.01$), and the black lines represent signal maxima in the frequency domain.

By contrast, conductivity patterns in watersheds at moderate levels showed a patchy pattern of discontinuous intra-annual signals (Figure S3), whereas higher levels of development (RCM and GWN) showed *continuous* signal from months to annual intervals, but in different years (without drought) from those with the signal in less developed watersheds (Figure 5). Such patterns may indicate substantial responses to pulsed events rather than annual or seasonal fluctuations (e.g., Figures 3 and 4) and are perhaps indicative of a shift in watershed function. Therefore, we pursued further exploration of impervious-conductivity relationships.

3.3. Relationships Between Impervious Cover and Conductivity

Analysis of the relationship between all years of impervious cover and annual means of conductivity across all watersheds was helpful in reducing confounding effects of other potential covariates across time or space in the study. The resulting set of 336 observations revealed relatively consistent increases across watersheds despite differing patterns of land-use, year of development, or historical legacies, particularly at lower levels of impervious cover (Figure 6). Annual mean conductivity increased across the range of impervious cover, but not at a consistent rate (Figure 6a). Model comparison of linear regression (intercept=131.63, slope=15.45, $p<0.001$), segmented regression (est.breaks= 4.46 se=1.49, 13.77 se=1.74; intercept=108.8; slopes=26.3, 8.8, 24.1; $p<0.001$), and GAM (intercept=268.0, edf=5.36, $p<0.001$) fits suggested that the GAM was superior to the linear model (δAIC>7, $p<0.008$), but only marginally better than the piecewise regression fit (δAIC>2.5, $p=0.0073$). Although the slope of the linear regression was just over 15 μS/cm per unit % impervious cover, slopes of identical units for the piecewise regression and the GAM were noticeably steeper (i.e., ~26), before declining substantially (i.e., ~9) above 4.5% impervious cover, and steepening

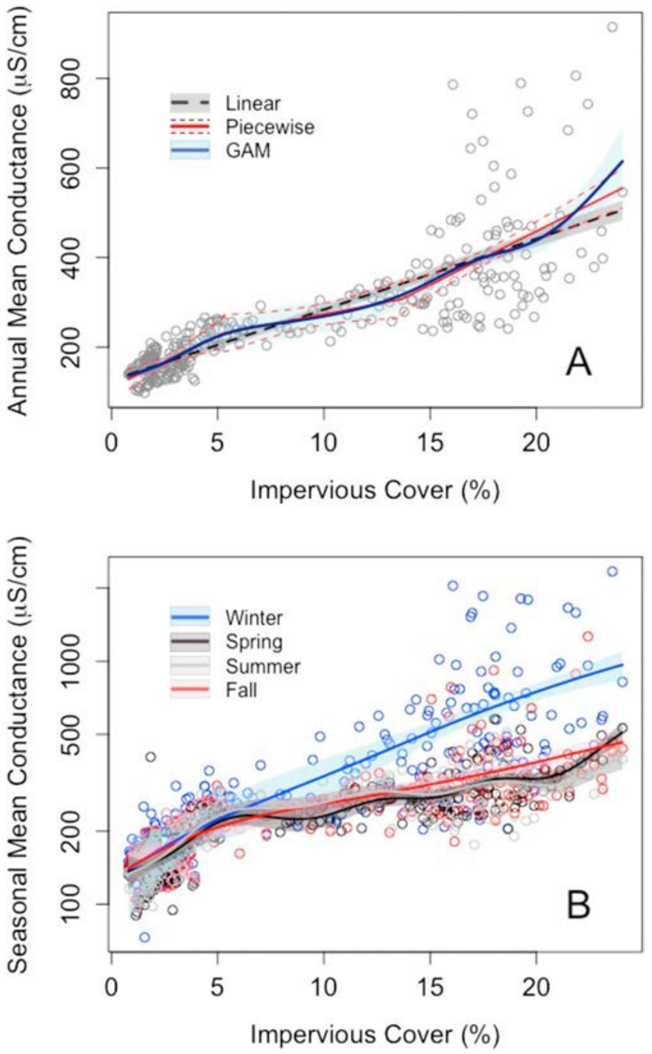

Figure 6. Scatterplots of (a) annual and (b) seasonal mean specific conductance relative to Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious cover across 11 study watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. In A, annual mean conductivity is predicted by three models: linear regression, segmented regression, and a generalized additive model (GAM). Confidence intervals (95%) for the GAM, segmented, and linear model are shown in light blue shading, red dashes, and grey shading, respectively. All three models were significant, but the GAM was the superior predictor (δAIC>6, p<0.008). In panel b, GAMs (±CI) of seasonal mean conductivity show overlapping increases in conductivity until ~5% impervious cover, whereupon increases in winter conductivity levels exceed those of other seasons. Above ~14% impervious cover, extremes in fall conductivity lead to separation between fall and spring/summer levels.

again (i.e., ~24) above 13.8% imperviousness (Figure 6a). Both piecewise and GAM slopes differed significantly (p<0.05) from the simple linear regression, and confidence intervals around the fitted GAM suggested an overall pattern very similar to the piecewise fit.

Decomposition of conductivity into seasonal components (Figure 6b) revealed patterns consistent with nonlinear models of annual means. All seasons showed similarly strong increases in conductivity up to ~5% impervious cover. By 6.5% impervious cover, winter conductivity was elevated relative to spring conductivity, and by 7.5% impervious cover winter conductivity was elevated relative to summer and fall as well. Differences appeared to result largely from declines in the slope of spring, summer, and fall conductivity at moderate levels of impervious cover. Above ~14% impervious cover, the GAM for fall conductivity showed elevated values relative to spring and summer conductivity. Thus, patterns of seasonal conductivity appeared to support break points detected with annual means.

Integrated analysis of impervious-conductivity relationships revealed distinct nonlinear patterns of increase across space and time. Several additional patterns support this nonlinear interpretation. Annual and seasonal analysis revealed correspondence in conductivity ranges among watersheds between 0 and 5% impervious cover. Above 14% impervious cover, there were substantial increases in the variability of annual mean conductivity in Figure 6a. However, from ~5% up until ~20% impervious cover, all watersheds exhibited at least some annual mean values that hovered between 200 and 300 µS/cm. This pattern was corroborated by Figure 6b, where it was clear that lower quantiles of conductivity above 4.5% imperviousness included representative observations from all seasons. Despite fewer observations between 6 and 12% impervious cover, there was ample evidence at higher levels that mean conductivity did not continue to increase the way it did below 4.5%. Further, seasonal analysis demonstrated that the high annual means above 14% impervious cover were likely due to extremes expressed most distinctly in the winter and fall rather than an increase in seasonal minima. Such winter extremes did occur in PATD between 6 and 12%, but they were apparently not large or frequent enough to substantively alter annual means.

3.4. Frequency of Monthly Conductivity

Based on differences observed in impervious-conductivity relationships through time in Figure 3, across seasons in Figure 4, and across both annual and seasonal patterns in Figure 6, we placed monthly observations across all watersheds into three groups to compare and contrast distinct patterns in the relative frequency of conductivity levels. Because impervious cover time series in some watersheds spanned breakpoints used to group monthly observations, some watersheds contributed observations to two groups (Table S1 in the supporting information). In addition, exceedance curves for each individual watershed are provided in Figure S5.

Among watersheds with low (<4.5%) impervious cover (n=1620 individual samples, or 135 site-by-year combinations of 12 months), 95% of observations exceeded background conductivity of 100 µS/cm, but only 5% exceeded 200 µS/cm (Figure 7a). Across seasons, distributions were remarkably similar, with only slightly dilute springtime values in contrast with slightly elevated values in the fall and winter (Figure 7b). Lack of variation among seasonal exceedance curves indicated that either all seasons were equally variable or each season showed consistent trends through time.

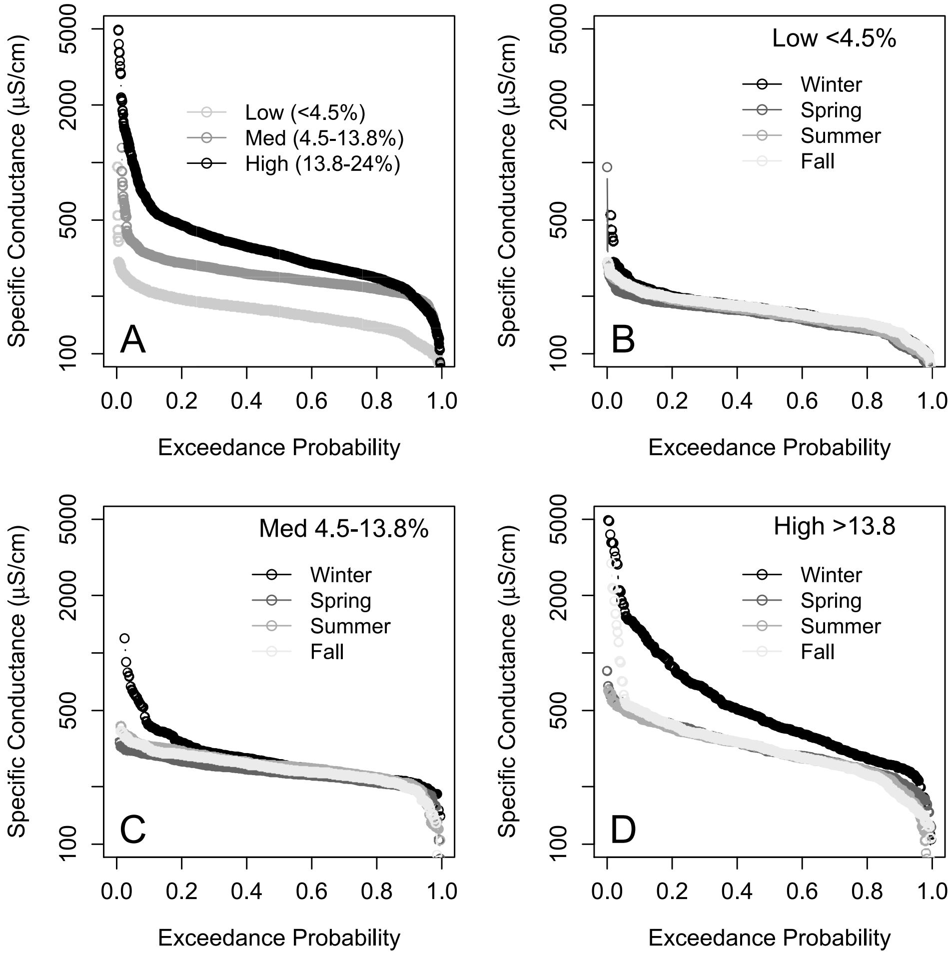

Figure 7. Exceedance curves for (a) cumulative and seasonal specific conductance in (b) low, (c) medium, and (d) high levels of Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious cover from 12 study watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010.

As impervious cover increased from low to moderate (4.5-13.8%) levels (*n*=828, or 69 site-by-year combinations), conductivity quantiles nearly doubled and 95% of observations equaled or exceeded what had previously been an infrequent value (e.g., 200 µS/cm). Although conductivity approached 300 µS/cm for 10% of monthly observations, 5% surpassed 500 µS/cm. Overall, the conductivity increase from low to moderate imperviousness was a near-uniform doubling of the distribution. Across seasons, again, the samples tracked closely, with springtime showing slightly lower levels across all probabilities, yet approximating extremes at lower impervious levels (Figure 7c). However, among 20% of the monthly observations, winter conductivity appeared to increase sharply, so that 10% of wintertime means exceeded 500 µS/cm and extremes surpassed 1000 µS/cm.

The jump from moderate to high (13.8-24%) impervious cover (*n*=1248, or 104 site-by-years) led to distinct changes in the distribution of conductivity (Figure 7a). Instead of rather uniform increases across all exceedance probabilities observed between low and medium impervious levels, differences between medium and high impervious observations were much smaller for common (e.g., >80% exceedance probability) than less frequent values (e.g., <40% exceedance; note that Figure 7 *y* axes are log transformed). Once again, levels of conductivity (e.g., 300 µS/cm) that were rarely exceeded in medium impervious watersheds were equaled or exceeded in 70% of observations from high impervious watersheds. Across seasons, winter conductivity values almost never overlapped with those of other seasons, and this distinction increased with less frequent exceedance probabilities (Figure 7d). Winter overlap with other seasons appeared limited to rare (<2%) but

Table 2

Summary Across All Years (1986-2010) of Regressions Relating Percent Impervious Cover to Annual and Seasonal Characterizations of Monthly Specific Conductivity per Year From 12 Watersheds in the Baltimore-Washington, DC, Metropolitan Area

Parameter	Slope					Intercept				
Metric	Mean	*SD*	CV	Min	Max	Mean	SD	CV	Min	Max
Annual median	10.5	2.2	0.20	7.3	15.4	143.5	8.8	0.06	128.9	164.5
Annual mean	14.8	5.5	0.37	6.9	26.0	131.1	16.8	0.13	99.7	165.0
Winter mean	28.7	17.6	0.61	6.7	67.1	96.0	54.0	0.56	-55.9	149.4
Spring mean	9.8	2.8	0.28	6.1	16.5	139.2	17.7	0.13	116.7	193.8
Summer mean	9.3	2.6	0.28	3.5	14.3	148.0	13.6	0.09	109.6	175.0
Fall mean	11.5	7.9	0.68	5.1	41.0	141.4	29.5	0.21	33.9	183.5

extreme (>2,000 μS/cm) values occurring during the fall index period. On the other hand, winter conductivity at moderate levels approximated distributions from other seasons at higher impervious levels.

Analysis of exceedance probabilities thus supported the distributions of conductivity grouped by breakpoints depicted in Figure 6 and revealed by distinct patterns in Figures 3 and 4. The results underscore the stability of conductivity across watersheds and seasons at low levels of imperviousness, while emphasizing markedly high variability of conductivity at high levels of impervious cover, particularly during the winter. Therefore, we sought to further disentangle responses of wintertime conductivity at high levels of impervious cover.

3.5. Temporal Variability in the Impervious Cover and Conductivity Relationship

Because of the degree of variation observed across annual mean, seasonal mean, and monthly values of conductivity in highly developed watersheds, we explored potential contributions to that variability arising from interannual patterns. First, we compared year-to-year changes in the slope and intercept of regressions relating impervious cover to conductivity across watersheds within a single year (Figure S6). As expected, regression slopes of annual means were typically larger (and intercepts lower) and more variable from year to year than medians, reflecting their sensitivity to extreme values (Table 2). Seasonal averages also followed patterns consistent with previous observations (e.g., Figure 4 and 6b), with the largest regression slopes observed in winter, followed by fall, spring, and summer, respectively (Table 2). Slopes were equally variable across years using mean conductivity in the winter or fall, but the magnitude of wintertime coefficients was more than twice as large as those in fall. Intercept magnitude generally followed a pattern inverse to slopes, with values averaging <150 μS/cm and variability greatest within the winter season. These patterns were further evaluated based on winter weather extremes.

Comparison of significant regression slopes relating annual mean conductivity and impervious surface across watersheds (Figure S6) were significantly greater (p=0.019) when conditioned on a major winter storm event, but seasonal decomposition of slope distributions indicated that annual differences were driven entirely by even more substantial differences (p=0.005) in wintertime relationships (Figure 8). In winters experiencing a substantial snow or ice storm, the average effect of a unit increase in percent imperviousness was 43.6 μS/cm (39.6 μS/cm for medians), whereas the average unit effect of imperviousness in winters without a major storm event was less than half as large, or 18.8 μS/cm (17.9 μS/cm for medians). Among event years, the strongest effect of unit percent impervious cover (64.8 and 66.2 μS/cm) was observed during the winters of 1999 and 2010, whereas the weakest effect was observed during 1987 and 2006. During years without an event, the strongest effects (i.e., the only years with slopes >25 μS/cm)

occurred during the winters of 2001 and 2005. Therefore, we sought to understand whether winter storm events could explain variation in wintertime conductivity.

Across a collective wintertime site-by-year gradient, a GAM with a single smoother explained 45% of model variance. However, a GAM that allowed different intercepts for event years explained 49.8%, whereas a GAM that allowed distinct smoothers for event and nonevent years explained 60%. Model comparison suggested that the GAM with distinct smoothers was superior relative to either of the simpler models (δAIC>50, p<0.001). Comparison from the fitted GAM (Figure 9) indicated that predicted conductivity became distinct for years with and without a major storm event by 14.5% impervious cover, consistent with earlier results.

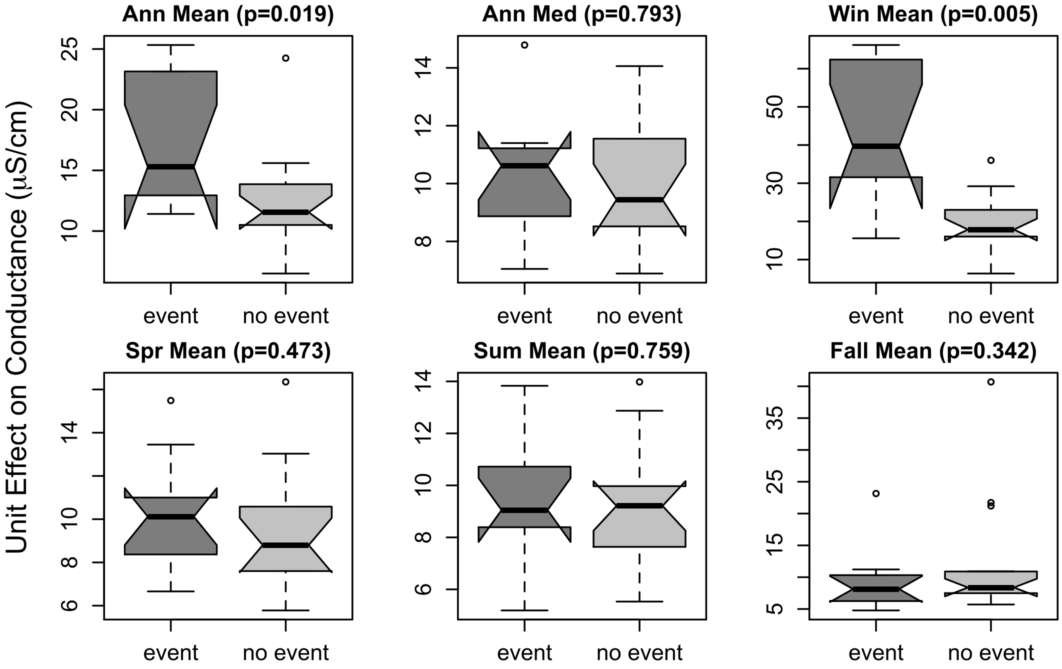

Figure 8. Boxplots of significant ($p<0.05$) unstandardized regression coefficients relating percent Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious cover to increases in annual or seasonal specific conductance with and without a major winter storm event in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. Comparison of distributions within each panel was accomplished with a *t* test (*p* values shown in panel heading).

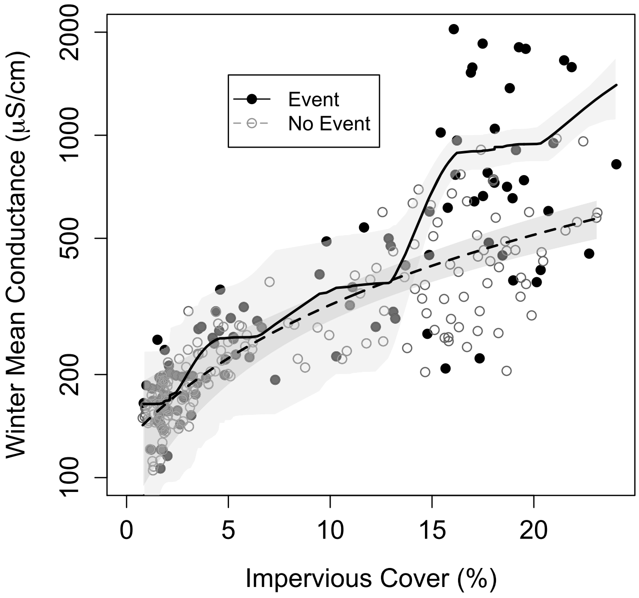

Figure 9. Scatterplot of winter mean monthly conductivity values relative to Dynamic Impervious Surface Cover Observation and Retrieval System (DISCORS) impervious cover across 12 study watersheds in the Baltimore-Washington, DC, metropolitan area from 1986 to 2010. Wintertime means are shaded to contrast years (black) with a major winter storm and nonevent years (grey). A generalized additive model tracks differences in overall trends associated with winter storm events. The event year smoother exceeds the 95% CI of the nonevent year smoother at 4.5% and 13.7% impervious cover, whereas overlap of 95% CIs ends at14.5% impervious cover.

4. Discussion

4.1. Patterns of Urbanization Through Time

Areal impervious cover increased monotonically in all watersheds and included both expansion of development into rural areas and “infill” development of already populated watersheds. Rapid expansion of impervious cover in the late 1980s and 1990s was associated with the construction of major transportation arteries. The GWN watershed along the I-795 corridor experienced a near doubling of its impervious cover in our study time series. Although not surprising given the population growth in the region, patterns of urban expansion meant that there were many opportunities to compare conductivity in watersheds with similar levels of impervious cover in different years.

With the possible exception of the 8-10% impervious cover increment, our data provided a relatively robust representation of patterns of specific conductance relative to impervious cover within the study area. Because of the limited number of watersheds and observations within this moderate range, we considered additional evidence that the PATD observations were consistent with other watersheds in our sample. The pattern of conductivity relative to impervious cover within PATD was entirely intermediate to those watersheds with lower and higher levels of urbanization. Early in the time series, conductivity in PATD was frequently just over 230 μS/cm and matched well with those watersheds at slightly lower levels of impervious cover, whereas its later conductivity levels commonly exceeded 300 μS/cm, approaching early values among watersheds that experienced more intense development throughout the time series. When compared to overall model fits, PATD samples showed uniformly negative residuals below all three fitted models in the 8-10% impervious range, suggesting these observations might contribute to the flattening of nonlinear predictions. However, the distribution of PATD values from 6 to 8% and 10 to 14% showed even distributions of positive and negative residuals around the nonlinear fits and residuals around the linear model, consistent with those of other watersheds. When patterns of conductivity were regressed on impervious cover between 6 and 14%, the slope of the model (10.7, se=2.2, $p<0.001$) was no different than the slope when the PATD samples were excluded (9.8, se=2.3, $p<0.01$), and neither was significantly different from the slope of the piecewise regression in that range. Because our additional analysis revealed no anomalous patterns in the PATD samples, we concluded that they were representative of watersheds in the region and consistent with our broader sample.

4.2. Patterns of Conductivity Through Time

The time series of monthly conductivity across all study watersheds increased with trends in impervious cover. Corsi et al. (2010, 2015) described a pattern of increasing dissolved material across the conterminous United States, even in cases with low levels of urbanization or where areal impervious cover had not increased. In our study, increasing conductivity was thus expected due to ubiquitous, monotonic increases in impervious cover. Yet despite patterns of incremental imperviousness, observed increases in conductivity were neither monotonic through time nor across space. In nearly all cases, areal estimates of impervious area alone were insufficient for ranking single measures of conductivity across the range of urbanization in our study in given year, in direct contrast to general expectations derived from spatial patterns. Anomalies associated with both the year or season of observation were apparent in nearly every time series. Similar long-term variability has been observed in many trends of specific conductance and chloride concentration throughout the northeast as well as in the Mid-Atlantic U.S. (Corsi et al., 2015; Findlay & Kelly, 2011; Kaushal et al., 2005; Kelly et al., 2008; Tu et al., 2007).

Annual or seasonal levels of specific conductance did increase with impervious cover across watersheds regardless of period or the measure of central tendency, just not at the same rate in all watersheds. Increasing conductivity is generally consistent with previous studies relating urban development to concentrations of dissolved ions (Aichele, 2005; Conway, 2007; Interlandi & Crockett, 2003; Morse et al., 2003; Williams et al., 2005). Median values in our study generally showed stronger trends than those using means even if mean values often exceeded medians; likewise relationships between urbanization and conductivity within winter and fall were stronger than spring or summer and driven by extremes at high levels of imperviousness.

A key signal that emerged from our contemporaneous study of conductivity time series at both low and high levels of watershed impervious cover was a marked increase in variation. Whether in deviation of means from medians across years or seasons, distinct patterns of exceedance, or dispersion across space and time at high levels of watershed impervious cover, urban streams clearly experience massive swings in conductivity. Such variation implies that simple grab samples are inadequate for characterizing the range of dissolved ion concentrations (Griffith, 2014; Olson & Cormier 2019) and the osmotic stress subsequently experienced by aquatic organisms (Corsi et al., 2010; Griffith, 2017; Utz et al., 2016). Again, these patterns are generally consistent with what has been observed elsewhere (e.g., Cañedo-Argüelles et al., 2016; Corsi et al., 2015; Sprague et al., 2007). However, without direct comparison of watersheds spanning similar ranges of impervious cover within similar regional contexts over the same years, such patterns would be difficult to detect.

Seasonal patterns consistent with increased wintertime recharge and decreased late summer flows were apparent in watersheds with low levels of urban expansion. However, as urban expansion progressed, wintertime conductivity levels eclipsed those of other seasons, and this was most apparent as impervious levels approached and surpassed 14% watershed area. Similar seasonal patterns associated with concentration or dilution were indicated by Sprague et al. (2007) and Corsi et al. (2015), although high chloride concentrations in summer base flow have also been observed in smaller urban streams in both Baltimore and the northern U.S. (Casey et al., 2013; Daley et al., 2009).

4.3. Relationships Between Impervious Cover and Conductivity

Analysis of the overall pattern of relationship between impervious cover and conductivity through both time and space revealed remarkable consistency across watersheds despite different physical settings, land-use arrangement, or year of development. Even when watersheds achieved a particular level of imperviousness in different years, they often exhibited similar subsequent levels of annual mean conductivity and interannual variation. This concordance among watersheds made changes along the impervious gradient all the more apparent.

Unit increases in conductivity were not monotonic across different levels of urbanization, showing steeper increments of conductivity below 4.5% impervious cover that flattened out at higher levels. Conway (2007) also described greater rates of change in specific conductance at low (i.e., <5%) impervious cover than higher levels in the New Jersey coastal plain. In our study, increases in conductivity at low levels of impervious cover were also relatively insensitive to season; rather, they appeared systemic and ubiquitous. Rather than road-salt deicers associated with increasing chloride concentrations, such patterns may well indicate the effects of prior land disturbance, septic or sewage treatment, concrete piping, or the these effects combined with road crossings (Bain et al., 2012; Corsi et al., 2015; Daley et al., 2009; Kaushal et al., 2014; Prowse, 1987). Indeed, Kaushal et al. (2018) emphasized the potential for weathering of urban infrastructure and increases in septic density as important sources of dissolved material. This pattern was sharply contrasted by annual, seasonal, and spatial variability at higher levels of imperviousness.

Once levels exceeded 4.5% impervious cover, annual conductivity did not increase as rapidly between 4.5% and 13.8%. However, site-by-year combinations highlighted greater variation for sites at similar levels of impervious cover than lower on the gradient. Such patterns were also similar to those found from 5 to 13% in a space-for-time study in New Jersey (Conway, 2007). Overlap of both the piecewise regression and the GAM confirmed this pattern, which appeared to emerge from uniform minima punctuated by occasional extremes. Further, extremes in the 5-13% range appeared to result from patterns of winter conductivity, which were elevated relative to other seasons. At levels of impervious cover >13.8%, trends steepened once again, largely driven by extreme winter or fall conductivity levels eclipsing intraannual variability. Although some increase was observed across all seasons, the greatest values of mean conductivity registered in punctuated winter samples, consistent with national patterns (Corsi et al., 2010, 2015). The overall pattern of results may indicate several interacting processes, including progressive storage and accumulation of ions (Casey et al., 2013; Findlay & Kelly, 2011; Kaushal et al., 2005; Kaushal et al., 2018), increases in source area with urban expansion (Corsi et al., 2015; Daley et al., 2009; Kaushal et al., 2014; Smith et al., 2010), and pulse signals from episodic events (Cooper et al., 2014). However, we believe that the results we report here are among the first to link differential rates of increase among seasons at different levels of urbanization.

At the highest levels of impervious cover in our sample (i.e., 14-24%), annual conductivity and seasonal conductivity were highly sensitive to episodic events such as winter storms, even as annual and seasonal minima remained consistent with nonevent years. Although interannual wintertime variability at lower levels of imperviousness routinely exceed 200 μS/cm, or twice background, we found no increases in monthly observations specifically associated with winter storms. Sensitivity to storm events appeared only at higher levels of watershed impervious cover, where signal from a single event could last for months, and where watersheds nonetheless contained rather moderate impervious proportions (<25%) compared to other, more highly urbanized systems (e.g., Cuffney et al., 2010; Smith et al., 2010). Heightened response to storm events may be indicative of shifts in the nature of impervious cover (i.e., roads versus rooftops; Smith et al., 2010) or greater hydrologic connectivity long posited as watershed impervious cover exceeds ~10% (Schueler, 1994; King et al., 2005; Utz et al. 2011). However, even steepened trend lines typically underpredicted extremes such as those noted by Cooper et al. (2014) and Corsi et al. (2015). Because such extremes require application of deicers in response to specific stimuli, our results emphasize the important role of human response to meteorological events and/or forecasts in exacerbating the effect of impervious cover on ionic concentrations and the salinization of streams.

5. Conclusion

Long-term serial land cover maps enabled annual views of land use change and revealed sharp increases in impervious cover that may otherwise have been indistinct across longer intervals. Serial maps also allowed us to test, and reject, the idea that urban expansion alone was sufficient for explaining patterns of downstream ionic content. By contrast, we observed very broad ranges (i.e., >1,000 μS/cm) of monthly conductivity associated with moderate to high levels of imperviousness. In addition, the quarter-century record was important for capturing periods of expansion in regional infrastructure, especially when coupled with monthly water quality measurements to distinguish impacts of urban growth from extreme weather events or within-region variation.

Although increases in dissolved ions from urbanization were generally expected, distinct rates of increase persisted across both watersheds and years depending on the level of urbanization, and this pattern may be diagnostic of important processes. We detected strong increases in conductivity associated with incremental increases of very low levels (<4.5%) of watershed impervious cover. The consistency of the increases across watersheds, years, and seasons points to sources other than road salt and suggests a ramp disturbance (Lake, 2000) that may only emerge gradually after years of repeated seasonal sampling. Because this signal corresponds closely to sharp biological changes observed at lower levels of imperviousness (e.g., <4%; King et al., 2011), further understanding of mechanisms of biodiversity loss at low levels of development is warranted.

We also found that seasonal responses diverged dramatically at higher levels of development across watersheds and, regardless of what year such levels were achieved, the predominant pattern of increase shifted from ramping to episodic pulses. Strong seasonality in extremes indicated that water samples collected by bioassessment surveys during spring or summer are likely insensitive to pulse events in other seasons (i.e., winter or fall) and may provide a misleading indication of water quality impacts on stream biota at moderate to high levels of urbanization. Multiple samples across seasons in these systems should show higher levels of conductivity and greater variability only after winter events. At moderate impervious levels, pulse responses during winter events may return within weeks or months to preevent levels. As impervious levels increased beyond 14%, there was ample evidence that watersheds were no longer able to flush event-related ions, so extremes from individual pulses could become chronic, press disturbances (Lake, 2000). Multiple conductivity samples from these systems should produce enormously variable levels and may exhibit massive peaks following winter storms.

Winter storms had an overwhelming effect on observed patterns of conductivity in urban watersheds, and our results confirm a substantial role of deicers influencing stream chemistry for long periods following an application event. Although the effect of such deicing is detectable at lower levels of impervious cover, changes become dramatic when impervious levels exceeded ~14%. When road salt was applied across watersheds with high levels of impervious cover, the effect of wintertime stimuli (e.g., major winter storms) tended to subsume other conductivity patterns (e.g., Wallace & Biastoch 2016). Because such inputs accumulate within the system, the consequences of their application appear to extend well beyond the winter season, leading to subsequent accrual of dissolved ions and disturbing patterns of sustained salinization.

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