Title. Physicochemical Factors and Urban Land-Use Characteristics Associated with Resistance to Precipitation in Estuaries Vary Across Scales

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Abstract

Urban estuaries are subject to frequent stressors, including nutrient loading and hydrological flashiness, which worsen water quality and disrupt ecosystem function. Land use changes associated with urbanization, as well as atypical precipitation conditions can exacerbate stress on estuarine health. However, generalizable patterns and parameters involved in estuarine responses to urbanization and extreme precipitation events remain unknown. We investigated physicochemical factors and urban land-use characteristics that associate with estuarine resistance to precipitation within and across estuaries ranging in urbanization, salinity, and precipitation. Using population and land use/land cover data combined with long-term meteorological, nutrient, and water quality data from the National Estuarine Research Reserve System, we focused on five estuaries distributed across the continental United States. We hypothesized that estuaries with higher urban impact exhibit lower resistance to precipitation events. We investigate this through relationships between the resistance index – a proxy for ecosystem stability calculated using dissolved oxygen – and various physicochemical factors and urban land-use characteristics on local and continental scales. Contrary to our hypothesis, we found that estuaries with higher urban influences were more resistant to precipitation events, and that water temperature, water column depth, nitrogen, and chlorophyll-a were related to estuarine resistance on a continental scale. However, these trends interacted with estuarine salinity and varied across individual estuaries; where we found additional relationships of resistance with salinity, turbidity, phosphate concentrations, N:P ratio, and tree cover. Considering emerging stressors from new climatic scenarios and urbanization-driven changes, these results are important for informing decisions for determining the appropriate estuarine water-quality standards.
Introduction

Estuaries are highly dynamic environments that often connect freshwater and saltwater systems, cycle organic matter and nutrients from land to oceans, and provide essential ecosystem services (Bianchi, 2007; He & Silliman, 2019). Estuarine ecosystem function, which relies on stability of a predictable range of dynamic processes like temperature fluctuations, hydrology and nutrient mixing, is threatened by anthropogenic activities and extreme climatic events like storms (Kemp et al., 2009; Zhang et al., 2010). Yet, generalizable factors involved in resistance of ecosystem function to precipitation in freshwater and saltwater estuaries impacted by urbanization are not fully understood. Predicted increases in urban population size and in frequency and intensity of precipitation events (Kyzar et al., 2021; Li et al., 2019; Martínez et al., 2007; Pickett et al., 2011) highlight the urgency to understand the response of estuaries to new urban and climatic scenarios.

When combined with intense precipitation, watershed urbanization and associated changes in land use/land cover (LULC) (Grimm et al., 2008) often result in increases in stream hydrological flashiness (Gannon et al., 2022; Reisinger et al., 2017). Triggered by extreme precipitation, hydrological flashing induces increased flow rates that cause changes in channel morphology (Booth & Jackson, 1997; Gregory, 2011; Leopold, 1968; Vietz et al., 2016), habitat destruction (Walsh et al., 2005), and disruption of microbial metabolic processes (Reisinger et al., 2017; Uehlinger, 2000). Flashiness can also drastically affect in-stream primary production (e.g., phytoplankton) – a critical component of dissolved oxygen (DO) delivery to aquatic environments – through increases in flow velocity, transport of phytoplankton, and light limitation (Bernot et al., 2010; Fisher et al., 1982; Reisinger et al., 2017; Uehlinger, 2000).

Additionally, extreme precipitation events are often associated with excess nitrogen (N) delivery, particularly for streams adjacent to urban-type LULC (Walsh et al., 2005). Nitrogen is central to mediating ecosystem functions across systems and urbanization gradients (Mulholland et al., 2008; Schindler, 1977; S. V. Smith, 1984; Vitousek & Howarth, 1991). It is particularly important for primary production because many phytoplankton species are N-limited (Evans & Seemann, 1989; Howarth, 1988; Vitousek & Howarth, 1991). This means that N directly affects DO production in aquatic environments. Therefore, N delivery associated with precipitation could temporarily have a positive effect on phytoplankton community rebound, DO
concentrations, and functional stability in estuaries impacted by urbanization. Also, extreme precipitation events are often associated with influx of freshwater and/or saltwater into estuaries, which changes salinity and impacts ecosystem metabolic functions. However, depending on the temporal and spatial scales of evaluation, the reported trends of system responses to precipitation and salinity changes can be conflicting.

Trends for stream responses to disturbances identified on continental-scale (i.e., regardless of system specifics) can help in projecting long-term ecosystem function under changing climatic and urban conditions, but they have been difficult to decipher due to variation across local scales. While Ombadi & Varadharajan (2022) report contrasting effects of urbanization on salinity during flood events when regional climatic conditions were considered, a continental-scale study by Kaushal et al. (2018) suggests that anthropogenic activity is associated with increasing salinity in streams over time. However, the later study recognizes that regional, climatic, LULC, and geologic variabilities also influence stream salinization patterns. Similarly, continental-scale evaluations showed that streams within small watersheds appear consistently less flashy than streams in large watersheds; while there was a substantial amount of variability in these relationships at regional scale (Baker et al., 2004; Gannon et al., 2022; Hopkins et al., 2015; Poff et al., 2006). Such variation in relationships across scales may be particularly prevalent in ecosystems influenced by anthropogenic activities (Hopkins et al., 2015; Poff et al., 2006). This demonstrates the importance of considering multiple spatial scales in understanding ecosystem responses to changes in precipitation patterns and watershed land use.

We aim to uncover generalizable patterns of responses to precipitation events across estuaries in the continental U.S. across gradients of urbanization and physicochemical properties. Using DO as a response variable and a proxy for ecosystem function, we evaluate estuary resistance to precipitation in the context of physicochemical factors and land-use characteristics at: 1) the continental-scale (i.e., across all estuaries); 2) across estuaries grouped by average annual salinity; and 3) within each estuary. We hypothesize that urbanization decreases estuarine resistance to precipitation. Also, we expect that relationships between resistance and physicochemical factors and land-use characteristics will diverge with spatial scale. Moreover, we expect that salinity impacts estuarine resistance to precipitation because of its effects on DO solubility and phytoplankton biomass. This study is essential for understanding how ongoing changes in climate and urbanization conditions influence estuarine ecosystem health.
Methods

Study sites.

We used long-term water quality monitoring data from five estuaries in the National Estuarine Research Reserve System (NERRS, https://coast.noaa.gov/nerrs/) to understand factors associated with ecosystem resistance to precipitation events. Lake Superior (LKS), WI; Chesapeake Bay Maryland (CBM), MD (Jug Bay only); Guana Tolomato Matanzas (GTM), FL; Weeks Bay (WKB), AL; and San Francisco Bay (SFB), CA span climatic zones, land uses, and salinity (range: 0.1 - 35 ppt) (Fig. 1, Table 1). Across all estuaries, there were a total of 19 monitoring locations (3 at CBM, and 4 at LKS, GTM, WKB, and SFB). Dissolved oxygen, water temperature, conductivity, pH, turbidity, salinity, water column depth, and meteorological conditions are measured at 15-min intervals. PO$_4^{3-}$, NO$_3^-$, NH$_4^+$, NO$_2^-$ and chlorophyll-a (Chl-a) were measured monthly (NERRS, 2023). Water column depth was calculated as the sum of measured water depth and depth of the monitoring probe to the sediment bed. The sum of NO$_3^-$, NO$_2^-$, and NH$_4^+$ was used to assess dissolved inorganic nitrogen (DIN) concentrations, and DIN to PO$_4^{3-}$ was used to calculate N:P mass ratio. Also, we used data from two years at each estuary between 2016 to 2020; one relatively wet year and one relatively dry year to span different baseline hydrologic and chemical conditions (see below). We removed all data flagged as ‘suspect’ or ‘out of range’.
Fig. 1. Selected National Estuarine Research Reserve (NERR) stations. a) Map of monitoring locations and land use/land cover within associated watersheds at Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. b) Salinity from 2012 to 2022 for each monitoring location at each NERR (all n > 150,000). Boxes indicate interquartile range. Means are shown in black-and-white circles. Black lines indicate medians.

Watershed characteristics.

To assess the relationships between resistance and urbanization, we used NERR watershed boundaries from https://cdmo.baruch.sc.edu (NERRS, 2023), LULC data at 10-meter resolution from Esri (https://livingatlas.arcgis.com/landcover/), and U.S. (2020) constrained population density data at 100-meter resolution from World Population Hub (https://www.worldpop.org/) (Bondarenko et al., 2020). We used LULC data from 2020 (LKS), 2018 (CBM, SFB), and 2017 (GTM, WKB) to keep the LULC within the range of wet and dry years selected for each estuary (see below). Analyses of LULC and population density were performed in QGIS 3.30.3 (QGIS Development Team, 2023) equipped with a semi-automatic classification plug-in.
Further, because the resistance index was calculated for precipitation events across short
time-scales (i.e., days), which underrepresents the draining time of some watersheds, we
considered LULC and population density from a 10-km proximity zone to the monitoring
locations (Table 1). For SFB NERR, we used 10-km proximity zones from San Pablo and Suisun
embayments to quantify LULC and population density, because the embayments separate China
Camp and Gallinas Creek from First Mallard and Second Mallard monitoring locations,
respectively.

**Table 1**: Land use/land cover (LULC) and population density in each estuary.

<table>
<thead>
<tr>
<th>LULC class</th>
<th>Estuary and % area by LULC class</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Top number: watershed scale</td>
<td>Bottom number: local scale (within 10 km of the monitoring locations)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LKS</td>
<td>CBM (Jug Bay)</td>
<td>GTM</td>
<td>WKB</td>
</tr>
<tr>
<td>Water</td>
<td>3.62</td>
<td>0.97</td>
<td>6.78</td>
<td>2.19</td>
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<tr>
<td></td>
<td>10.43</td>
<td>2.30</td>
<td>8.58</td>
<td>4.85</td>
</tr>
<tr>
<td>Tree cover</td>
<td>73.1</td>
<td>38.34</td>
<td>45.67</td>
<td>39.58</td>
</tr>
<tr>
<td></td>
<td>58.78</td>
<td>53.72</td>
<td>45.11</td>
<td>38.52</td>
</tr>
<tr>
<td>Flooded vegetation</td>
<td>0.2</td>
<td>0.22</td>
<td>9.48</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>1.37</td>
<td>13.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Crops</td>
<td>0.9</td>
<td>8.14</td>
<td>0.19</td>
<td>27.35</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>4.63</td>
<td>0.19</td>
<td>30.36</td>
</tr>
<tr>
<td>Built area</td>
<td>2.75</td>
<td>44.41</td>
<td>28.43</td>
<td>23.8</td>
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<tr>
<td></td>
<td>18.84</td>
<td>27.19</td>
<td>23.99</td>
<td>19.33</td>
</tr>
<tr>
<td>LULC Definitions</td>
<td>Watershed Scale</td>
<td>Local Scale</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bare ground</strong></td>
<td>0.20</td>
<td>0.06</td>
<td>0.16</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Surface area and population estimates**

Top number: watershed scale  
Bottom number: local scale (within 10 km of the monitoring sites)

<table>
<thead>
<tr>
<th>Area (km²)</th>
<th>11,703.6</th>
<th>1,392.8</th>
<th>921</th>
<th>523.8</th>
<th>114.05</th>
<th>378.16</th>
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<tr>
<td></td>
<td>488.7</td>
<td>218.2</td>
<td>645.6</td>
<td>213.0</td>
<td>105.01</td>
<td>205.86</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Estimated population within the area (ppl)</th>
<th>167,164</th>
<th>670,180</th>
<th>288,031</th>
<th>58,937</th>
<th>49,622</th>
<th>134,972</th>
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<tr>
<td></td>
<td>71,111</td>
<td>49,291</td>
<td>148,557</td>
<td>17,404</td>
<td>48,161</td>
<td>100,582</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Population density (ppl km⁻²)</th>
<th>14</th>
<th>481</th>
<th>312</th>
<th>112</th>
<th>435</th>
<th>356</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>145</td>
<td>225</td>
<td>230</td>
<td>81</td>
<td>458</td>
<td>488</td>
</tr>
</tbody>
</table>

LULC definitions per Esri (see [https://livingatlas.arcgis.com/landcover/](https://livingatlas.arcgis.com/landcover/))

**Water** – areas where water was present throughout the year. Excludes man-made structures like docks.

**Tree cover** – vegetation with closed/dense canopy ≥ 15 meters.

**Flooded vegetation** – areas with intermixing of water and vegetation flooded seasonally or predominantly throughout the year.

**Crops** – human planted vegetation (cereals, grasses, and corps) that are not at tree height.

**Built area** – human made structures like roads, rail road networks, parking spaces, industrial and residential buildings.
**Bare ground** – areas dominated by rocks, soil, sand (i.e. desert) with sparse to no vegetation throughout the year.

**Rangeland** – homogeneous grasses, mixes of vegetation below tree-height with rocks and soil, clearings in the forests.

**Major precipitation events.**

To capture responses to precipitation events from years with contrasting annual precipitation patterns, we selected comparatively wet and dry years for each estuary. Using precipitation records from nearby airports we calculated a long-term interquartile range (IQR, 1990-2020) of total monthly precipitation for each estuary following Murrell et al. (2018). Relatively wet/dry years were selected based on the number of months plotting above/below IQR and total annual precipitation, while considering completeness of water quality, nutrient, and meteorological data of each monitoring location (Fig. S1). Long-term precipitation records included: Duluth International, Washington Reagan International, Jacksonville International, Birmingham Airport, and San Francisco International airports (all available at: https://www.ncei.noaa.gov/cdo-web/datasets). Further, we selected major precipitation events within each wet and dry year by plotting daily precipitation using data from NERR meteorological stations, which revealed clear outlier events for each estuary (Fig. S2). Individual events were down-selected based on data availability at each monitoring location (event details in Table S1).

**The resistance index.**

To understand and compare physicochemical factors and urban land-use characteristics involved in estuarine responses to precipitation events, we calculated the resistance index described in Orwin & Wardle (2004). Briefly, the index (range: +1 to -1) uses concentrations of a response variable measured pre- and post-disturbance to represent system shift from an initial condition (equation 1).

\[
Resistance = 1 - \frac{2|D_0|}{C_0 + |D_0|} \quad (eq. 1)
\]
where, $C_0 = \text{concentration of the response variable pre-disturbance}$, and $D_0 = \text{difference between the concentration of the response variable pre- and post-disturbance (P_0)}$. An index value of +1 indicates maximum resistance. Index values between 0 and 1 show that $|D_0| \leq C_0$ (i.e., $P_0$ is between 0 and $2C_0$). Resistance index of 0 indicates 100% decrease or increase in $P_0$ (i.e., $|D_0| = C_0$), whereas index values between < 0 and -1 show that $|D_0| > C_0$ (i.e., $P_0 > 2C_0$). Overall, index values below +1 indicate stronger effects of the disturbance and less resistant systems (Orwin & Wardle, 2004).

Because DO measurements are widely available, and are often used as a proxy for water quality, trophic state, and ecosystem metabolism (Caffrey, 2004; Mulholland et al., 2001; Murrell et al., 2018; Odum, 1956), we used DO as the response variable in resistance calculations. Because DO is impacted by temperature, salinity, and tidally induced advection, we calculated $C_0$ as an average concentration within a timespan ≥ 24 hours that was not affected by precipitation (Fig. S3, Table S1). Also, because the response time for DO concentration following precipitation is not uniform across monitoring locations, the timespan for estimating $P_0$ was selected in the context of the precipitation record for each event as maximum displacement from $C_0$ within and past the event (Fig. S3, Table S1).

Statistical analysis.

**Linear Regression Analysis.** To test associations of specific physicochemical factors and land-use characteristics with estuarine resistance to precipitation, we used linear regressions at continental and local scales independently (i.e., all estuaries combined vs. within each individual estuary) and within salinity-based groups (i.e., average annual salinity less than or above 10 ppt). The ‘low salinity’ group included all monitoring locations at LKS and CBM, Fish River and Middle Bay monitoring locations at WKB, and First Mallard and Second Mallard monitoring locations at SFB. The ‘high salinity’ group included all monitoring locations at GTM, China Camp and Gallinas Creek at SFB, and Weeks Bay at WKB during the dry year only. For continental-scale and salinity-based regressions, the response variable was annual mean resistance, regressed against mean annual physicochemical factors (i.e., water temperature, water column depth, salinity, turbidity, DIN, PO$_4^{3-}$, and Chl-$a$) for wet and dry years, respectively, and LULC and population density as individual predictors. Annual means were used because of lack of nutrient and Chl-$a$ measurements surrounding selected precipitation events. Because of that,
regressions at each individual estuary (i.e. local-scale) also used annual mean resistance and
annual mean nutrient and Chl-a concentrations. However, local-scale regression analysis
involving water temperature, water column depth, salinity, and turbidity as individual predictors
of resistance used mean values calculated in the context of each precipitation event (see extent of
the event in Table S1), and the corresponding resistance values as response variables.

We did not include LULC and population density as predictors of resistance at individual
estuaries because of the close proximity of some monitoring locations to one another (< 800 m).
Comparative statistics within and between estuaries were conducted using Shapiro-Wilk
normality test followed by ANOVA with post-hoc Tukey HSD or Kruskal-Wallis test as
appropriate. Statistical analyses were performed in Python 3.10.11 using scipy.stats,
statsmodels.stats.multicomp.pairwise_tukeyhsd, and seaborn.regplot packages.

Results
Land use/land cover and nutrient concentrations across estuaries.
Using LULC and population density adjoining monitoring locations at each estuary, we
found that SFB was surrounded by predominantly urban-type land characteristics (e.g., built
area, population density) and that LKS had the lowest degree of urbanization (i.e., lowest
population density and highest percent tree cover) (Table 1). SFB San Pablo Bay (i.e., China
Camp and Gallinas Creek locations) had the largest percent built area (31.65 %), while SFB-
Suisun Bay (i.e., First Mallard and Second Mallard locations) had the highest population density
(448 ppl km\(^{-1}\)). Adjoining LULC at LKS was dominated by tree cover (58.78\%). LULC
surrounding monitoring locations at CBM also had high percentages of tree cover (53.72\%) and
built area (27.19\%), with high population density (225 ppl km\(^{-2}\)). Agricultural land was prevalent
at WKB (30.36\%). Overall, SFB and CBM estuaries were characteristically more urbanized
compared to GTM and LKS estuaries. LULC breakdown and population density for all estuaries
on watershed level and adjacent to monitoring locations are shown in Table 1.

SFB and CBM had high DIN concentrations across both wet and dry years compared to
LKS and GTM (mean > 0.504 mg-N L\(^{-1}\) versus mean < 0.16 mg-N L\(^{-1}\), all \(p < 0.01\), Fig. S4).
Phosphate concentrations were the highest at SFB (mean = 0.135 mg-P L\(^{-1}\), all other means <
0.03 mg-P L\(^{-1}\), \(p < 0.001\), Fig. S4). Overall, mean N:P ratios across LKS, CBM, GTM, WKB,
and SFB estuaries were 28.04, 26.56, 2.84, 83.82, and 5.10, respectively (Fig. S5), with GTM and SFB indicating N limiting conditions based on a 16N:1P Redfield ratio (Redfield, 1934).

Resistance to precipitation and changes in dissolved oxygen across estuaries and monitoring locations.

Resistance varied across all estuaries (F = 21.6, p < 0.0001, Fig. 2). SFB showed the highest resistance (range of means: 0.56 - 0.81) while at LKS resistance reached some of the lowest values (range of means: 0.30 - 0.64). Within individual estuaries (Fig. 2), resistance was most variable at LKS (F = 13.9, p < 0.0001, the resistance index range: -0.26 - 0.89). At CBM, resistance also varied across monitoring locations (F = 7.9, p < 0.01, range: 0.18 - 0.76). Resistance values across GTM monitoring locations did not show significant differences (F = 3.5, p = 0.32, range: 0.01 - 0.81). Compared with other estuaries, resistance to precipitation across WKB was most uniform, with no significant differences across WKB monitoring locations (F = 0.9, p = 0.81, range: 0 - 0.73). Lastly, at SFB resistance values varied across the estuary (F = 10.2, p < 0.001, range: 0.43 - 0.87).

DO concentrations pre- and post-precipitation varied across all estuaries (C₀: F = 45.6, p < 0.0001, P₀: F = 17.1, p < 0.0001, Fig. 2). At SFB and CBM (i.e., more urban estuaries), DO declined following precipitation (both p < 0.01). At LKS, precipitation events significantly increased DO concentration (F = 5.1, p = 0.027). At WKB – an agriculture-dominated watershed – DO decreased following precipitation as compared to its baseline concentration (F = 86.9, p < 0.0001). There was no significant difference between pre- and post-precipitation DO concentrations at GTM (F = 0.5, p = 0.48).
Variation in resistance within individual estuaries with pre- and post-disturbance distribution of dissolved oxygen. Boxes show the quartiles of the dataset and the whiskers show the rest of the distribution. Means are shown in white circles, and medians are shown in black solid lines. P-values are at the top of each panel. a) Lake Superior (LKS) NERR (all n = 7). b) Chesapeake Bay (CBM) NERR (all n = 10). c) Guana Tolomato-Matanzas (GTM) NERR (all n = 7). d) Weeks Bay (WKB) NERR (all n = 15). e) San Francisco Bay (SFB) NERR (n = 8 except Second Mallard (SM) n = 7). f-j) Distribution of dissolved oxygen concentrations prior to (C₀, darker shades) and post (P₀, lighter shades) precipitation.

Cross-scale relationships of resistance with physicochemical factors, land use/land cover characteristics, and population density.

When data from the five estuaries were considered together (i.e., continental-scale), we found significant positive relationships of annual mean resistance to water column depth, DIN, percent built area, and population density; and significant negative relationships to water temperature and Chl-α (all: p < 0.027; R² > 0.12) (Fig. 3).

When grouped by salinity, estuarine resistance to precipitation was more tightly correlated to physicochemical factors and land-use characteristics (i.e., higher R²) compared to continental-scale relationships (Fig. 3). Within ‘low-salinity’ estuaries, annual mean resistance was positively related to depth of the water column, which is consistent with the trend observed on continental-scale; and negatively related to annual mean salinity – a relationship not found on continental-scale (both: p < 0.03, R² > 0.19). Within ‘high-salinity’ estuaries – annual mean
resistance showed positive relationships to annual mean log(DIN) and to percent built area (both: $p < 0.005$, $R^2 > 0.54$), which also was consistent with continental-scale results. Observations present in ‘high-salinity’ estuaries but absent from continental-scale evaluations included negative relationships of annual mean resistance to tree cover, and negative relationships to N:P ratio and turbidity (all: $p < 0.012$, $R^2 > 0.45$). Additionally, annual mean resistance in both low- and high-salinity groups was positively related to population density, and negatively related to water temperature and Chl-α (all: $p < 0.0511$, $R^2 > 0.15$). The latter trends were consistent with continental-scale observations. Generally, ‘low-salinity’ estuaries showed fewer relationships of annual mean resistance to annual mean physicochemical factors, LULC, and population density compared to ‘high-salinity’ estuaries.

**Fig. 3.** Relationships of continental-scale and salinity-based resistance to physicochemical factors, land use/land cover, and population density. Continental-scale regressions considered all monitoring locations across all estuaries. Significant relationships ($p < 0.05$) are shown in
black, red, and blue for continental-scale, high-salinity estuaries, and low-salinity estuaries, respectively. Standard errors of the mean are shown in vertical and horizontal lines.

On local scales (i.e., within each estuary), resistance was related to some physicochemical factors that were not observed in continental-scale relationships. Moreover, the number, strength, and trends of relationships between local-scale resistance and physicochemical factors varied substantially across estuaries (Fig. 4, Figs. S7, S8). Resistance at GTM had the most relationships to physicochemical factors. It was negatively related to water temperature, PO$_4$$^-$, and Chl-$\alpha$ concentrations; and positively related to salinity and N:P (all: $p < 0.014$, $R^2 > 0.23$). In contrast, at CBM, the resistance was related only to water column depth (positive, $p = 0.013$, $R^2 = 0.21$). At LKS, resistance was positively related to water column depth, and negatively related to turbidity (both: $p < 0.002$, $R^2 > 0.32$). At WKB, relationships of resistance to water temperature, salinity, and Chl-$\alpha$ concentrations were all negative (all: $p < 0.015$, $R^2 > 0.16$). At SFB, resistance was negatively related to water column depth, which opposed the general trend, and positively related to salinity (both: $p < 0.0004$, $R^2 > 0.40$).
Fig. 4. Relationships between resistance and physicochemical factors for each estuary. National Estuarine Reserve System (NERR) estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. Significant correlations ($p < 0.05$) are shown with black lines. Standard errors of the mean are shown in vertical and horizontal lines for relationships using annual means for predictor and response variables. For additional results see Figs. S7 and S8.

Overall, we found that some relationships of resistance with physicochemical factors and urban land-use characteristics appeared to be universal while others varied across scales (Fig. 5). This included the uniquely identified relationships between resistance and PO$_4^{3-}$ at GTM, and resistance to tree cover found within ‘high-salinity’ estuaries. Cross-scale relationships of resistance included: 1) positive relationships to N:P ratio, salinity (positive and negative), and turbidity (positive), which were identified in both local-scale and salinity-based evaluations; 2) relationships to log(DIN), percent built area, and population density (all positive), which were identified in continental-scale and salinity-based evaluations; and 3) relationships to water temperature (negative), water column depth (positive and negative), and Chl-$a$ (negative) identified across continental- and local-scales, and within salinity-based estuary groups.

Fig. 5. Cross-scale relationships of estuarine resistance to physicochemical factors and land-use characteristics. a) Venn diagram of resistance relationships to physicochemical factors and land-
use characteristics in high- vs. low-salinity estuaries. Positive or negative relationships are indicated with ‘+’ and ‘−’ respectively. b) Venn diagram of resistance relationships with physicochemical factors and land-use characteristics in continental, local, and salinity-based groups. Estuarine resistance to land use/land cover and population density marked with asterisks (*) were not evaluated at local-scale due to overlap in the spatial domains of some monitoring locations.

Discussion

Understanding patterns in estuarine responses to precipitation at continental-to-global scale is important for predicting impacts of urbanization and climate change on estuarine environments as a whole. However, the patterns identified at such large scales may not be applicable when it comes to predicting estuarine behavior at local scales. As shown by previous studies that focused on anthropogenic influences on streams and estuaries, contrasting relationships between drivers and responses to disturbances are common for systems with different climatic conditions, regional geology, and other ecosystem factors (Baker et al., 2004; Gannon et al., 2022; Hopkins et al., 2015; Kaushal et al., 2018; Ombadi & Varadharajan, 2022; Poff et al., 2006). Our results underscore the importance of cross-scale evaluations. We show that while relationships between estuarine resistance, urbanization, and DIN may be overarching dynamics at the continental-scale they may not relate to resistance on the estuary level. Local resistance can be impacted by myriad factors that are different from factors identified at larger scales. Also, in contrast to our overarching hypothesis, we find that urbanized estuaries tend to have higher resistance than more pristine estuaries. These results suggest that the effects of watershed urbanization could positively impact estuarine ecosystem stability by providing a mechanism that allows estuaries responding to major precipitation events to withstand large shifts in DO concentrations or quickly restore DO back to its baseline.

Baseline and post-precipitation dissolved oxygen concentration vary across estuaries.

Estuaries with urban (i.e., built area, population density) and agriculture-dominated LULC, showed an overall decrease in DO concentrations after precipitation events (SFB, CBM, and WKB: $p < 0.0001$, Fig. 2). This suggests that precipitation generally has a predominantly negative effect on DO concentration in urbanized estuaries (i.e., SFB and CBM), and estuaries
surrounded by agricultural land (i.e., WKB). Simultaneously, at LKS – a less urbanized estuary, post-precipitation DO concentrations increased ($F = 5.1, p = 0.027$, Fig. 2). No differences between pre- and post-precipitation DO concentrations were found at GTM.

There are vast differences in geometry, circulation, and hydrologic conditions among SFB, CBM, and WKS and yet, they exhibit similar DO concentration patterns. At the local-scale, a wide range of physical factors can impact DO concentrations in estuaries including channel geometry and river discharge (Kemp & Boynton, 1980; Raymond et al., 2012; Raymond & Cole, 2001), wind (Scully, 2010; Zheng et al., 2024), and circulation (Raimonet & Cloern, 2017). Urban estuaries often serve as basins for wastewater treatment outflows which can supply continued freshwater discharge and nutrients when river discharge is low. Both urban and agriculturally influenced estuaries are prone to increased nutrient loading during and shortly after precipitation events (Bernhardt et al., 2008; Walsh et al., 2005), which impacts primary production and microbial metabolism and may lead to declines in DO concentrations.

Also, local controls on DO dynamics are likely different among SFB, CBM, and WKS estuaries. In addition to being the most urban estuaries in our study, SFB and CBM are also the largest and deepest. Therefore, at SFB and CBM, DO may be governed more heavily by physical controls like circulation (Raimonet & Cloern, 2017) and wind (Zheng et al., 2024) in addition to anthropogenic factors like wastewater discharge. In contrast, WKS is a small, shallow, and highly productive estuary. Therefore, at WKB, DO may be more heavily governed by nutrient loading that fosters primary production, and by rapid flushing during storm events (Novoveská, 2019). Differences in primary DO controls may help explain why estuaries with similar DO concentration patterns have different resistance to precipitation.

**Urbanization and inorganic nitrogen correspond with elevated resistance to precipitation at the continental-scale.**

The overall higher resistance values of the most urbanized estuaries and the overarching relationships of urban LULC with resistance suggest that estuaries within urban watersheds may be able to withstand and/or recover faster from major precipitation events (Fig. 3). This result contradicts our overarching hypothesis that urban estuaries should show low resistance to precipitation because of frequent physical and chemical disturbances, like flashiness, streambed scouring, and N loading, which alter hydrology, turbidity, and interfere with stream metabolism.
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(Bernhardt et al., 2008; Groffman et al., 2004; Hession et al., 2003; Walsh et al., 2005).

However, anthropogenically induced physicochemical alterations may also increase estuarine resistance to precipitation events. As such, it is possible that watershed urbanization could equip estuaries with a set of controls that allow mitigation of processes that drive DO to extreme concentrations, like algal blooms, which can induce large DO fluctuations in water by overproducing DO during the day above saturation levels and severely depleting DO at night (Chapin et al., 2004; Ni et al., 2020). For instance, an increase in flashiness would increase flow velocity and reaeration of the water column (Raymond et al., 2012; Raymond & Cole, 2001), and contribute to phytoplankton removal via transport or turbidity-driven light attenuation, which limits phytoplankton growth (Caffrey, 2004; Pennock & Sharp, 1986). Turbidity-driven control on phytoplankton was previously reported for SFB estuary (Cloern, 1987), despite N abundance. Such control for overgrowth of phytoplankton would help maintain DO near baseline. We found positive relationships of turbidity with percent built area and population density ($p < 0.00051, R^2 > 0.28$), and negative relationships of Chl-a with percent built area and population density ($p < 0.02, R^2 > 0.14$) (Fig. S6).

Also, watershed urbanization is often related to high N export to freshwater, marine environments, and estuaries (Bettez et al., 2015; Reisinger et al., 2016). We found that in addition to urbanization, estuary N content was also a major predictor of resistance at the continental-scale. While excess nutrients is a significant problem for urban aquatic environments (Beman et al., 2005; Bernot et al., 2010; Black et al., 2011; Mulholland et al., 2008), appropriate levels of N support basic metabolic functions across a wide range of systems and environmental conditions (Camenzind et al., 2018; Howarth, 1988; Schimel & Bennett, 2004; Sullivan et al., 2014; Q. Zhang et al., 2021). N plays a major role in phytoplankton growth in streams and estuaries across urbanization gradient (Foldager Pedersen & Borum, 1996; Gobler et al., 2006; Howarth & Marino, 2006; Larsen & Harvey, 2017; Moore & Hunt, 2013; Vitousek & Howarth, 1991; Woodland et al., 2015). This link between N availability and phytoplankton is important because phytoplankton is a part of the DO delivery mechanism to aquatic systems, traditionally incorporated in models for net ecosystem respiration as a gross primary production term (Odum, 1956). We found DIN concentrations to positively correlate with urban land characteristics (e.g., percent crops and population density; $p < 0.025, R^2 > 0.12$, Fig. S6) and with resistance at the continental-scale ($p = 0.031, R^2 = 0.12$; Fig. 3).
Moreover, relationships of resistance with N and urbanization were particularly evident in high-salinity estuaries. We found positive relationships of resistance with built area and N:P in high-salinity estuaries and negative relationships between resistance and percent tree cover \( (p < 0.012, R^2 > 0.45; \text{Fig. 3}) \). Nitrogen limitation occurs across a wide range of aquatic environments and is particularly prevalent in marine systems (Elser et al., 2007; Guildford & Hecky, 2000; Paerl, 2018; Paerl & Piehler, 2008). Additionally, a recent study suggests that riparian zones have a high capacity to retain N concentrations in surface runoff and groundwater (Lyu et al., 2021). In concert with N limitation that prevails in marine environments, N retention by riparian zones can exacerbate N-limiting growth conditions in estuaries with high salinity, and particularly for phytoplankton.

**Water column depth, temperature, and Chl-a relate to resistance across all scales.**

Across all scales, we found a generalizable pattern where resistance was often related to water column depth (overall positive relationship), water temperature (negative relationship), and concentration of phytoplankton (negative relationship) (Figs. 3-5). Urbanization-driven changes to watershed LULC from forested to agriculture and infrastructure dominated landscapes, can deepen the channel through processes like increased runoff and sediment transport, hydrological flashiness, channel dredging, and/or other anthropogenic activities (O’Driscoll et al., 2010; Simon & Rinaldi, 2006; Walsh et al., 2005). Generally, to induce similar shifts in ecosystem resistance in relatively deep versus shallow streams or estuaries, the magnitude of the disturbance should be proportional to the system’s volume. Through dilution, deeper streams have greater capacity to resist changes associated with precipitation that affect DO availability like influx of oxygen-saturated rain water, nutrient loading, and turbulence and water-atmosphere gas exchange. Also, channels can have an increased seasonal gross production rate of DO compared to shoal sites (Murrell et al., 2018). Similarly, deeper streams have longer equilibration time with environmental conditions and less diel variability in parameters like temperature (Caissie, 2006; Macan, 1958), which affects diel and seasonal DO dynamics, likely resulting in a tighter range in baseline DO.

Moreover, because temperature is a major control for various chemical and biological processes known to impact DO availability in aquatic systems (e.g., microbial metabolic and growth rates, oxygen solubility), many studies have focused on the impact of rising temperature...
on DO dynamics in streams and estuaries (Apple et al., 2006; Caffrey, 2003; Caffrey et al., 2014). Highlighted results link climate change and urbanization to thermal pollution of urban streams following rain events (Zahn et al., 2021), and show connections of elevated global temperatures with decreased primary production (Song et al., 2018) and increased planktonic N demand (Toseland et al., 2013). Therefore, the combined effects of watershed urbanization and global temperature increase on phytoplankton could exacerbate DO dynamics in estuaries and significantly shift the range of DO baseline. We found a negative relationship between resistance and water temperature across all analyses (Figs. 3, 4).

Finally, our results suggest that negative relationships between estuarine resistance to precipitation and concentration of Chl-a may be generalizable features of estuaries (Figs. 3, 4). This supports previous reports of DO deviations from baseline induced by excess phytoplankton (Beman et al., 2005; Paerl, 2018; Wang & Zhang, 2020).

**Predictors of resistance on local scales vary across estuaries and differ from continental-scale predictors.**

The contrasting relationships between physicochemical factors and resistance across individual estuaries highlight substantial local scale variation (Fig. 4). For example, resistance at CBM is related to one factor, water column depth, while at GTM, resistance is related to five factors. This suggests that while water temperature, water column depth, and Chl-a may be generalizable predictors for estuarine resistance at the continental scale, individual estuaries may need to consider additional factors in water-quality management and conservation strategies. For example, Chl-a and dissolved inorganic phosphorus have been shown to respond to storms in some systems more than in others (Chen et al., 2015; N. G. Dix et al., 2008; Liao et al., 2021; M. Zhang et al., 2022). This is because variability in controls on phytoplankton biomass on local scales (i.e., light limitation, benthic and pelagic grazing, nutrient conditions, precipitation extent) can influence Chl-a concentrations and its responses to storms (Cloern, 2001; Cloern & Jassby, 2010; N. Dix et al., 2013). Likewise, water temperature and salinity also vary in response to storms in estuaries (Buelo et al., 2023; Chen et al., 2015; N. G. Dix et al., 2008), and were previously identified as primary drivers of variability of biological processes and phytoplankton activity across NERR estuaries (Apple et al., 2008). Moreover, seasonality and long-term
climatic conditions are known to change resistance to disturbances in aquatic systems (Beaulieu et al., 2013; Reisinger et al., 2017; Van Meerbeek et al., 2021).

While there are myriad potential system-specific interactions that may result in different responses to stressors, our results highlight that system-variability is important when identifying parameters involved in ecosystem resistance to precipitation, which may or may not be reflected in relationships and trends evaluated at the continental scale. We also acknowledge that other scales of investigation (e.g., regional) could introduce additional insight into predictors of estuarine resistance.

**Could N play a central role in increased resistance to precipitation in urban estuaries?**

Based on our findings that urban estuaries may be more resistant to precipitation than more natural estuaries, we suggest that watershed urbanization may be accompanied by adaptation mechanisms that help estuaries offset the effects of precipitation. In particular, we hypothesize that hydrological flashiness and N delivery associated with precipitation can influence phytoplankton and DO concentrations to have an overall positive effect on functional stability in estuaries impacted by urbanization.

Dissolved oxygen availability in aquatic environments, including estuaries, is tightly linked to phytoplankton, which in turn relies on adequate N availability (Evans & Seemann, 1989; Howarth, 1988; Vitousek & Howarth, 1991). This is particularly true for high-salinity estuaries, which are often N-limited (Howarth & Marino, 2006; Pael, 2018), and are comparatively more restrictive for phytoplankton development because of growth-limiting salt concentrations (Flameling & Kromkamp, 1994; Mo et al., 2021; Russell et al., 2023). However, excess phytoplankton growth, often referred to as algal blooms, still occurs, even in high-salinity estuaries (Anderson et al., 2021). Also, because watershed urbanization is often accompanied by increased flashiness during rain events (B. K. Smith & Smith, 2015), it follows that precipitation may rapidly remove phytoplankton through increased flow velocity. Storm runoff may also simultaneously deliver necessary N concentrations that help phytoplankton biomass recover and restore baseline DO concentrations in urban estuaries, where N loadings tend to be higher (Bettez et al., 2015; Reisinger et al., 2016). Collectively, these processes could lead to higher resistance to precipitation in urban estuaries that may be more responsive to N inputs. However, we note that high-resolution measurements surrounding precipitation events, as well as careful
evaluations of phytoplankton, salinity, and N surrounding the events are needed to distinguish effects on DO concentrations pre- and post-precipitation. We also highlight the importance of evaluating N as species, because of known inhibitory effects of excess ammonium on nitrate uptake by phytoplankton, which reduces the likelihood of algal blooms (Dugdale et al., 2007; Parker et al., 2012).

Conclusions
In light of emerging climatic and urban scenarios, cross-scale evaluations of parameters involved in system responses to perturbations are important when considering management strategies for water quality suitable for continental and local scales. We found that (1) urban estuaries are more resistant to precipitation; and (2) depth of the water column, water temperature, and Chl-a are generalizable cross-scale predictors for estuarine resistance. However, across different scales, we found that system-variability, including salinity, can interfere with the generalizable patterns and result in additional relationships between resistance and physicochemical factors and land-use characteristics. We also propose a hypothesis that urban estuaries may have adaptation mechanisms that help DO resist the combined effects of watershed urbanization and major precipitation events. However, high-resolution water quality and nutrient data surrounding precipitation events, as well as models for system responses to precipitation, are needed to help elucidate the underlying mechanisms for high resistance of urban estuaries.

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References


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Data Availability Statement:
This study used publicly available datasets, which included: 1) Long-term estuarine water quality, nutrients and meteorological conditions and watershed boundaries for Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR stations from [https://cdmo.baruch.sc.edu](https://cdmo.baruch.sc.edu); 2) Long-term precipitation data from U.S. airports from [https://www.ncei.noaa.gov/cdo-web/datasets](https://www.ncei.noaa.gov/cdo-web/datasets); 3) Land use/land cover maps from [https://livingatlas.arcgis.com/landcover/](https://livingatlas.arcgis.com/landcover/); 4) U.S. population data from [https://www.worldpop.org/](https://www.worldpop.org/).

Author Contribution Statement
E.B.G. and A.B.T. developed the study and interpreted the results. A.B.T. performed data analysis and drafted the manuscript. All authors contributed to manuscript editing.
Supplementary Material for:

Title. Physicochemical Factors and Urban Land-Use Characteristics Associated with Resistance to Precipitation in Estuaries Vary Across Scales

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**Supplementary Tables.**

**Table S1.** Threshold value for major precipitation events and breakdown of the number of events during wet and dry years at each National Estuarine Research Reserve (NERR) station.

<table>
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<th>NERR Station</th>
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<th>Wet/Dry Year</th>
<th>Precip. Threshold (mm/day)</th>
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** San Francisco Bay, CA (SFB) **

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* For GTM 2016 the selected events were: Colin, Julia, Hermine, and Matthew. For 2017 the events were Irma and two Nor’easters.

** This resistance calculation does not include dissolved oxygen measurements during the actual rain event from 2019/04/25 only dissolved oxygen after the event, because data during the event is missing from MB monitoring location.

*** Dissolved oxygen data for the SM site is missing. No resistance was calculated for SM during that time.
Fig. S1. Long-term (30-year) interquartile range and monthly precipitation during relatively wet and dry years. Long term precipitation data obtained from airports located in the vicinity of each selected estuarine station. a) Precipitation records from Duluth International airport were used to infer wet/dry years at Lake Superior (LKS) station. b) Washington Reagan International Airport precipitation records were used for Chesapeake Bay (CBM) station. c) Jacksonville International Airport precipitation record was used for Guana Tolomato Matanzas (GTM) station. d) Birmingham Airport precipitation records were used for Weeks Bay (WKS) station. e) San FranciscoInternational Airport precipitation records were used for San Francisco Bay (SFB) station.
Fig. S2. Major precipitation events for each estuary during wet and dry years. The major precipitation events (red circles) were identified by plotting National Estuarine Research Reserve (NERR) precipitation data collected at each estuary. The events were down-selected based on water quality data availability for each estuary. Estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. For details about events used for resistance index calculations, please see Table S1.
Fig. S3. Example for visualizing the selection of variables for resistance index calculations. Yellow shaded box indicates the time used to calculate average pre-disturbance dissolved oxygen concentration (average $C_0$). Red shaded box indicated the time used to identify dissolved oxygen concentration post-disturbance ($P_0$). $P_0$ was identified as the maximum displacement from average $C_0$. a) Dissolved oxygen and precipitation at Guana Tolomato Matanzas (GTM) National Estuarine Research Reserve (NERR) during hurricane Matthew. b) Dissolved oxygen and precipitation at Lake Superior (LKS) NERR during a precipitation event on 06-28-2017.
Fig. S4. Dissolved inorganic nutrient concentrations at each estuary. Dissolved inorganic nitrogen (DIN) (i.e., NO$_3^-$ + NO$_2^-$ + NH$_4^+$). Estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. For LKS estuary, the NH$_4^+$ measurements for dry-year (2020) were missing at all monitoring locations. For WKB, the PO$_4^{3-}$ measurements for wet-year (2018) were missing at WB, MB, and MR monitoring locations.
Fig. S5. Variation in resistance within individual estuaries. Estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. Means are shown in white circles, and medians are shown in black solid lines. Boxes show the quartiles of the dataset and the whiskers show the rest of the distribution. The stoichiometric N:P ratio was calculated using dissolved inorganic nitrogen species (i.e., NO$_3^-$ + NO$_2^-$ + NH$_4^+$) and phosphate. We note that because of missing measurements for PO$_4^{3-}$ during the wet year at WKB- WB, MB, and MR – the N:P ratios at these locations were calculated only for the dry year.
**Fig. S6.** Relationships of dissolved inorganic nitrogen (DIN), chlorophyll-\(a\) (Chl-\(a\)), and turbidity to land use/land cover and population density. Estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. Regressions for significant relationships (p-value < 0.05) are shown in black lines. All relationships use annual means for physicochemical factors calculated for wet and dry years separately and land use/land cover characteristics adjoined to monitoring locations at each estuary.
Fig. S7. Relationships of resistance to water temperature, water column depth, turbidity, and salinity at each estuary. Estuary abbreviations: Lake Superior (LKS) NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. Significant correlations ($p < 0.05$) are shown in black lines. Relationships consider mean values of physicochemical factors in context of precipitation events used in resistance index calculations (see dates for $P_0$ in Table S1).
Fig. S8. Relationships of resistance to dissolved inorganic nitrogen (DIN), phosphate (PO$_4^{3-}$), N:P ratio, and chlorophyll-$a$ (Chl-$a$) at each estuary. Estuary abbreviations: Lake Superior (LKS), NERR, Chesapeake Bay, Maryland (CBM) NERR, Guana Tolomato Matanzas (GTM) NERR, Weeks Bay (WKB) NERR, and San Francisco Bay (SFB) NERR. Significant correlations ($p < 0.05$) are shown in black. Standard errors of the mean are shown in horizontal and vertical black lines. Relationships consider annual mean values of resistance and annual mean values for nutrients, N:P, and Chl-$a$ calculated for wet and dry years separately.