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Particulate and Dissolved Organic Matter in Stormwater Runoff Influences Oxygen Demand in Urbanized Headwater Catchments

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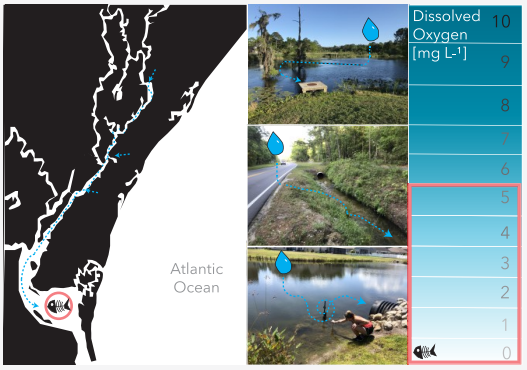
ABSTRACT: Increasing inputs of organic matter (OM) are driving declining dissolved oxygen (DO) concentrations in coastal ecosystems worldwide. The quantity, source, and composition of OM transported to coastal ecosystems via stormwater runoff have been altered by land use changes associated with urbanization and subsequent hydrologic flows that accompany urban stormwater management. To elucidate the role of stormwater in the decline of coastal DO, rain event sampling of biochemical oxygen demand (BOD) in samples collected from the outfall of stormwater ponds and wetlands, as well as samples of largely untreated runoff carried by stormwater ditches, was conducted across a range of urban and suburban development densities. Sampling also included measurements of particulate and dissolved carbon and nitrogen, carbon and nitrogen stable isotopes, and chlorophyll-*a*. Results suggest stormwater may be a significant source of labile OM to receiving waters, especially during the first flush of runoff, even though BOD concentrations vary both among and within sites in response to rain events. BOD variability was best predicted by particulate OM (POM) and chlorophyll-*a*, rather than the larger pool of dissolved OM. These findings demonstrate the importance of managing episodic stormwater discharge, especially POM, from urbanized areas to mitigate DO impairment in larger downstream systems.



INTRODUCTION

Urbanization is a leading cause of water quality degradation[1] in coastal riverine and marine ecosystems, including occurrences of low dissolved oxygen (DO). The level of DO in coastal waters is controlled by a variety of natural processes as well as by anthropogenic point and nonpoint source discharge of allochthonous organic matter (OM) and autochthonous OM production enhanced by nutrient pollution. The quantity and composition of the supplied OM determine the amount and rate of oxygen removal by microbial aerobic respiration.[2] Organic matter is comprised of a diverse array of particulate and dissolved organic matter (POM and DOM, respectively), with compounds ranging from simple bioavailable forms (e.g., sugars, proteins, and amino acids) to more complex structures that are not readily catabolized (e.g., humic substances).[2−5] When the respiration of supplied OM drives daily average DO concentrations below 5 mg L^{-1} (≤4 mg L^{-1} for blackwater systems), the threshold often used to define DO impairment,[6,7] aquatic life becomes stressed. Once DO concentrations reach hypoxic levels (<2 mg L^{-1}), major mortality events occur.[8,9]

Consistent with urban and agriculture expansion throughout the 20th and 21st centuries, coastal water DO has declined, leading to an increase in the number, size, duration, and severity of hypoxic zones globally.[9−11] In the United States, the rise in impaired and hypoxic waters led to the 1972 implementation of the National Pollution Discharge Elimination System (NPDES) permitting program and total maximum daily load (TMDL) plans, which set limits on pollutants either discharged from a given source or concentrations that enter a receiving water body, to ensure sufficient DO levels for sustaining aquatic life.[13,14] These regulations rely on biochemical oxygen demand (BOD) to establish effective limits. BOD is defined as the concentration of oxygen consumed by OM microbial decomposition and the conversion of nitrogen compounds to the stable forms of nitrite and nitrate over a specified incubation period at 20 °C.[12] Thus, BOD defines the amount of biodegradable OM in a water sample over a specified time period, based on a fixed concentration of DO. While much is known about point source BOD, less is known about nonpoint source BOD,

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especially from urban areas, which hinders the effectiveness of NPDES permits and TMDL plans.[13,14]

Water runoff from storm events is a primary transport mechanism delivering nonpoint source OM from land to receiving waters. The replacement of once permeable natural landscapes with impervious surfaces, such as roads, parking lots, and buildings, alter natural hydrologic regimes by increasing the volume and velocity of stormwater flow across land surfaces.[1,15,16] This runoff mobilizes large quantities of OM and nutrients from land into aquatic systems, especially during peak water discharge termed the first flush and intense storms.[1,17,18] In order to reduce the transport of OM via urban stormwater runoff and comply with water quality regulations, best management practices (BMPs; e.g., retention ponds and constructed wetlands) have been integrated into the complex networks of more traditional engineered stormwater conveyances (e.g., pipes, culverts, and ditches) during development. BMPs are designed to reduce first flush effects. This BMP design assumes that reducing peak water discharge will effectively treat stormwater by trapping OM that drives BOD within the BMP and improve water quality downstream.[19] Reducing first flush effects, however, may not be enough to reduce the overall volume nor OM contents of stormwater runoff that travels downstream to receiving waters. Even with the implementation of BMPs, research shows that, due to the coverage of impervious surfaces, the density and connectivity of modern stormwater flow paths, and climatic change, urban areas continue to release greater volumes of runoff than forested areas.[19−24] Indeed, the source, magnitude, and biodegradability of OM carried in runoff from various urban stormwater catchments remain relatively ambiguous.

Dissimilar landscapes produce different organic compounds that are transported to aquatic systems and drive low DO.[25−28] A growing body of literature suggests that urban landscapes may export OM that is more bioavailable compared to natural landscapes, causing an outsized impact on DO in aquatic systems.[24,27,29−33] However, the underlying causes that drive changes in OM source and lability associated with increasing urbanization and their subsequent effects on BOD remain uncertain. Some of this ambiguity stems from the complex transport pathways within the coastal environment, including the networks of modern stormwater infrastructure that may transform, trap, or contribute additional OM export from watersheds.[27] Stormwater BMPs treat stormwater by effectively retaining suspended sediments and, in some cases, nutrient inputs from land.[22,34] However, processes within BMPs, including POM/DOM tranformations,[35−37] microbial and photochemical degradation,[36,38−40] and autochthonous production,[41,42] may also make BMPs significant sources of labile OM. Thus, effective stormwater management requires an understanding of how both land cover alterations and the type of stormwater control measure used influence OM composition and BOD of nonpoint source discharge.

The goal of this study was to quantify stormwater BOD concentrations and identify the quantity, composition, and lability of OM, using a combination of elemental analyses and stable isotopes, to better understand drivers of BOD concentrations in samples collected from BMP ponds, BMP wetlands, and ditches that drain a range of development densities. This knowledge is critical for understanding the contribution of stormwater to coastal DO impairment and supporting effective management of coastal waters. Here, the focus is in the coastal plain of South Carolina (SC). Like many coastal regions, the SC coast is experiencing rapid urbanization. Despite the construction of various stormwater infrastructures, including a rise in BMP detention ponds,[33] SC now identifies low DO as the primary water quality issue impacting aquatic life within coastal riverine and marine waters in all counties along the 301 km of coastline.[6,43] For example, the Waccamaw River, a coastal plain blackwater system that flows south from southeast North Carolina (NC) to the Atlantic Ocean at Winyah Bay, SC, has experienced persistent low DO during summers despite the establishment of a TMDL two decades ago in 1999.[44]

METHODS

Study Sites. Stormwater runoff was collected from 16 urban stormwater catchments within the coastal plain of the lower Pee Dee watershed in SC. This basin encompasses the Myrtle Beach metropolitan area and the southern Grand Strand (see Supporting Information, Figure S1). Urban sites included conventional stormwater ditches (sites D1−D10), which provide minimal direct treatment of stormwater runoff, and BMP ponds (sites P1−P3) and BMP wetlands (sites W1−W3), which both provide some degree of stormwater treatment, as discussed previously. ArcGIS was used to delineate individual site microwatersheds (see Supporting Information) that spanned low to high density urban and suburban developments with high percentages of impervious surface cover (%IC, ∼4.5 to ∼43%; Supporting Information, Figure S1 and Table S1). Runoff from four blackwater streams that drain natural forests and wetlands (sites F1−F4) was also collected to determine BOD concentrations from undeveloped areas in the region.

Sample Collection and Processing. In 2018 and 2019, sampling occurred in the late spring and summer (May−August), a period of high precipitation[45] that coincides with the onset of the seasonal DO decline in the Waccamaw River.[44] Samples were collected along the rising and falling limb of 17 rain event hydrographs as captured by HOBO Water Level data loggers (Onset Corp, USA). Prior to rain events, Nalgene Stormwater Samplers (Thermo Scientific, USA) were placed inside a rain proof casing mounted at the outlet of individual stormwater catchments with the sampler intake positioned just above the base flow water level.[46,47] The sampler began filling upon a rise in the hydrograph and collected a fixed 1 L sample that was sealed by the sampler's floating ball valve.[46,47] Retrieval times varied based on the timing, duration, and intensity of a given rain event but were always <16 h after the start of precipitation. Additional 1 L manually collected samples were retrieved after rain events if water levels in the catchments were still receding (termed falling limb) as confirmed by event hydrographs.

Samples were kept cool until returned to the laboratory (<3 h), where they were equilibrated to 20 °C in a water bath (∼1 h). The pH and percent DO saturation at 20 °C were recorded; and samples with a percent DO saturation below 90% were bubbled to saturation (90−100%). Temperature and oxygen equilibrated samples were then transferred to borosilicate glass BOD bottles (300 mL nominal volume) for the determination of both 5 day BOD (BOD5) and 28 day BOD (UBOD). Remaining sample water was filtered through precombusted, glass fiber filters (GF/Fs; 0.7 μm mesh size) under low vacuum to collect particulates (POM) and filtrate (DOM). Filters were kept frozen (−80 °C) until further analyses of particulate C (PC) and nitrogen (PN) and POM

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isotopic composition (δ^{13}C and δ^{15}N). An additional filter was stored at −20 °C for 24 h for chlorophyll-*a* (Chl) analysis. The filtrate was stored frozen (−80 °C) in acid-washed HDPE bottles until further analysis of dissolved organic C (DOC) and N (DON) and δ^{13}C-DOC.

BOD Incubations. BOD5 was determined according to Standard Method 5210 B.[48] No artificial bacterial seed population additions nor sample dilutions were made per Standard Method 5210 C.[48] Nutrient buffer additions were added in 2018 but not in 2019 (see Supporting Information, Appendix 2). Samples were kept in borosilicate glass bottles with a DO sensor membrane affixed to the inside of the bottle. The sample bottles were placed on shaker tables within thermostatically controlled air incubators kept dark at 20 ± 1 °C.[48] DO was monitored over five days using a Wiltrox chemiluminescent sensor spot system (Loligo Systems, Denmark). The chemiluminescent system has a DO precision of ±0.05 mg L^{-1}.[49] Because no seed culture was added and no dilutions were made, BOD5 was calculated using eq 1:

$$BOD_5 = (D_1 - D_2) \quad (1)$$

where D_1 is the initial DO concentration in mg L^{-1}, and D_2 is the final DO concentration after five days of incubation in mg L^{-1}.[48]

To observe extended degradation of OM and to evaluate BOD degradation kinetics, incubations without nutrient buffer additions were continued for a total of 28 days (see Supporting Information and Figure S2). This 28 day incubation is operationally defined as UBOD; and the amount of DO ultimately consumed by respiratory and nitrification processes (see Supporting Information, Figure S3).[50] Following Standard Methods 5210 C,[48] with repeated DO measurements made possible by the Wiltrox system, UBOD kinetics were measured. Incubation bottles were only opened for reaeration, on those occasions when the DO concentrations dropped below 1.5 mg L^{-1}.[49] Conventional BOD degradation is estimated by a first-order decay equation (eq 2) to define individual sample BOD decay kinetics:

$$BOD_t = UBOD(1 - e^{-kt}) \quad (2)$$

where BOD_t is the measured BOD at time t, UBOD is the ultimate BOD consumed, k is the exponential decay coefficient, and t is the time since the start of the incubation.[48] Eq 2 was applied to the BOD time course measurements to calculate an UBOD value.

Particulate Carbon and Nitrogen Analyses. Particulate C and N filters were analyzed using a Costech ECS 4010 elemental analyzer using the methods of Hedges and Stern[51] without digestion with 10% hydrochloric acid (HCl) to remove inorganic C (see Supporting Information, Appendix 4). Because SC stormwater catchments contain a negligible amount of inorganic C,[34] total PC was assumed equal to particulate organic C (POC; see Supporting Information). The analytical error is reported in the Supporting Information, Table S2.

Particulate OM was further characterized by measurements of the Chl concentration and bulk POC and PN isotopic composition. Chl concentrations were determined following the U.S. EPA method 445.0[52] and measured (7% in duplicate; error reported in Table S4) using a Turner Trilogy laboratory fluorometer with a chlorophyll acidified/nonacidified application module (model #7200−046). The isotope compositions of δ^{13}C-POC and δ^{15}N-PN were analyzed using an elemental combustion analyzer attached to an isotopic ratio mass spectrometer (IRMS).[53] Only a limited number of samples were analyzed for δ^{15}N-PN (Supporting Information, Table S3) due to detection limits as described in the Supporting Information, Appendix 6.

Dissolved Carbon and Nitrogen Analyses. Total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN; nitrate + nitrite and ammonium) concentrations were measured using an autoanalyzer (AA3 HR, SEAL Analytical Inc., Mequon, WI) according to Standard Methods[48] and EPA method 350.1.[54] For TDN, samples were oxidized with alkaline potassium persulfate using a 2:1 sample/reagent ratio and autoclaved at 120 °C for 1 h prior to analysis described above.[48] DON was mathematically calculated as the difference between TDN and DIN. Quality control checks and spikes accompanied each run including certified external nitrate and ammonium standards (HACH Company, Loveland, CO).

DOC samples were acidified to a pH of 2 with 10% HCl prior to concentration analysis via high-temperature combustion using a TOC-VCPN Shimadzu analyzer.[55] Samples were run alongside a Consensus Reference Material (Miami, FL USA), and a subset of samples were run in duplicate with an average analytical error of <1% coefficient of variation. The DOC fraction was further characterized using stable isotopes. The δ^{13}C-DOC was determined by wet chemical oxidation as described in detail in the Supporting Information, Appendix 6.[56]

Data Analysis. Linear correlations were used to determine the relationships between BOD5 and measured and calculated UBOD as well as Chl. Due to the nonparametric nature of much of the data, log−log transformations and power functions described the relationships between particulate and dissolved organic C and N and BOD. Two sample t tests and analysis of variance (ANOVA) tests were conducted to compare the difference in BOD and OM concentrations among infrastructure types and watershed %IC. A matched paired t test was used to describe the difference between both measured and calculated UBOD values and the difference in BOD and OM concentrations between paired samples collected along the rising and falling limbs of rain event hydrographs.

RESULTS AND DISCUSSION

Urban Stormwater BOD Concentrations. BOD concentrations measured in stormwater discharged from BMP ponds, BMP wetlands and untreated stormwater runoff carried by conventional ditches, varied among and within sites in response to rain events. Collectively (n = 108), urban runoff from the three stormwater infrastructure types had BOD5 concentrations ranging from 0.67 to 10.74 mg L^{-1} (mean = 2.92 mg L^{-1}; Figure 1) and UBOD concentrations ranging from 2.24 to 26.52 mg L^{-1} (mean = 8.45 mg L^{-1}; Supporting Information, Table S4). Urban stormwater BOD concentrations are presented collectively because BOD statistical midpoints and distributions were similar across the three stormwater infrastructure types. This suggests BMP ponds and wetlands are not effectively treating stormwater in order to reduce BOD concentrations. However, BOD concentrations alone do not explain whether BMPs are simply not removing allochthonous OM or whether this removal is masked by simultaneous production of autochthonous OM within the BMP (see Stormwater OM Source and Composition section).

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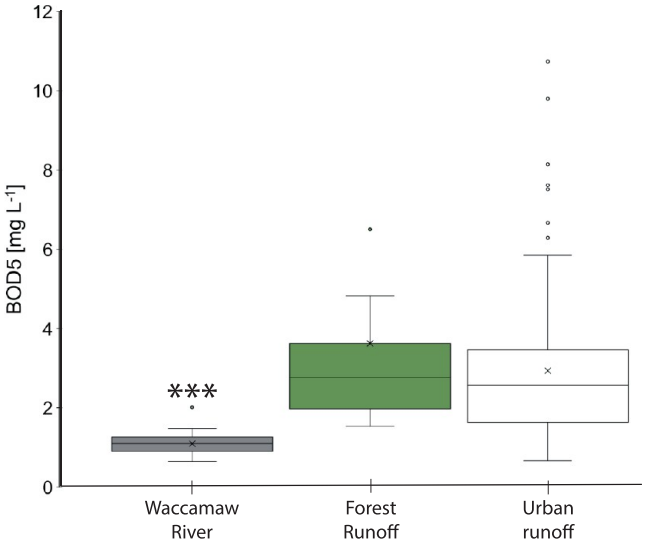

Figure 1. Stormwater BOD5 loads from pristine forested streams (one outlier not on scale) and urban catchments with BOD5 of ambient Waccamaw River water (left box; http://bccmws.coastal.edu/river_gauge/) measured in the summers of 2018 and 2019. Circles above the whiskers represent outliers, and asterisks mark significant differences between ambient river and stormwater BOD.

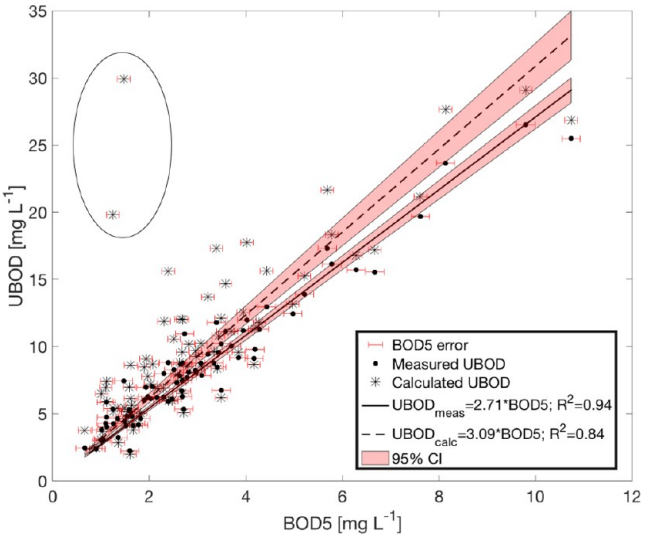

Figure 2. All 2018 and 2019 measured urban UBOD (black circles) and calculated UBOD concentrations (gray asterisks) vs BOD5 loads. A strong linear relationship (R^2 > 0.94; p < 0.001) exists between measured UBOD and BOD5 and calculated UBOD and BOD5 (R^2 > 0.84; p < 0.001).

Urban stormwater BOD concentrations measured here are comparable to that measured in urban lotic and lentic systems of coastal NC,[57,58] although our range is larger. This is likely the result of our targeted rain event sampling. The two NC studies did not specifically target storm events, but noted elevated BOD concentrations in samples retrieved immediately after rain events. When compared to point source BOD concentrations in this region, urban stormwater BOD concentrations were much lower.[44] They were, however, substantially greater than ambient BOD concentrations in receiving waters (Figure 1; $p \leq 0.001$). In fact, BOD in stormwater runoff was ~3 times higher than average ambient BOD in the Waccamaw River. Combined with elevated stormflow associated with increased %IC[19,20,22,59] and the close proximity of the stormwater outfalls to these receiving waters (<6 km), which limits processing of OM within the stormwater network,[33] our results suggest stormwater runoff is an important contributor of BOD that results in observed declines in receiving water DO.

Results suggest stormwater BOD must be effectively integrated into regulatory models in order to manage downstream coastal DO. Regulatory agencies often rely on BOD5-to-UBOD conversion factors in order to develop TMDL plans.[14] Measured UBOD concentrations were ~3 times greater than BOD5 concentrations and are highly correlated (Figure 2). Time-course measurements over the 28 day incubation show that the consumption of OM in stormwater primarily follows first-order decay (eq 2, R^2 > 0.9), despite contributions to BOD from nitrification (NBOD) at 20−28 days (~20% of UBOD; Supporting Information, Figure S2). A few UBOD values for rising limb samples could either not be calculated using first-order decay kinetics (ditches 8 and 10; not graphed) or were poorly described by a first-order decay model ($R^2 \leq 0.9$; $k \sim 0.01$) (circled points in Figure 2; sites P1 and D7). The other 72 fitted decay curves produced k coefficients that ranged from 0.03 to 0.89 and UBOD ranging from 2.00 to 29.10 mg L^{-1} (Supporting Information, Table S4). Calculated UBOD was significantly higher than measured UBOD (p < 0.001), which suggests that degradation continues to occur beyond the 28 day incubation length. Nonetheless, BOD5 is scalable to UBOD using a conversion factor of 3.09 (Figure 2). This conversion factor falls at the high end of BOD5-to-UBOD ratios summarized for point source effluent (1.2 to 3.2) in TMDL guidelines[14] but is similar to the $BOD5\text{-to-}UBOD_{measured}$ conversion factor reported here (2.71; Figure 2) and estimated from urban aquatic BOD data in NC (~2.9).[57]

Landscape Influences. Runoff collected from forested areas had BOD concentrations that varied both among and within sites in response to rain events. BOD5 concentrations ranged from 1.53 to 6.5 mg L^{-1} (n = 16; mean = 2.98 mg L^{-1}), and UBOD concentrations ranged from 4.56 to 15.01 mg L^{-1} (n = 13; mean = 8.75 mg L^{-1}), excluding one outlier with a large contribution of nitrogenous BOD (Figure 1). Previous work suggests that runoff from developed landscapes increases BOD concentrations relative to undeveloped landscapes, but this was not evident here. Average BOD concentrations in forest runoff were equivalent to average urban stormwater BOD concentrations (Figure 1; Supporting Information, Table S4). Statistical midpoints and distributions for BOD concentration were similar regardless of watershed development. Surprisingly, this result suggests that in the coastal SC system, unlike other systems previously studied,[57,58] stormwater runoff has high BOD concentrations regardless of land cover and land use. This is likely a reflection of the naturally high organic content of SC forested wetlands[59] that are the predominate type of predeveloped land cover in the SC coastal plain.

The observed similarity in BOD concentrations between undeveloped and developed sites does little to explain the continued decline in DO levels in the Waccamaw River over the past several decades.[43,60] Differences in BOD fluxes, however, could explain declining DO. Although direct stormflow volume measurements were outside the scope of this study, dramatic increases in stormwater runoff volume

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associated with urbanization are well documented[15,16,19,24,59] and likely result in subsequently higher fluxes of OM and BOD (also termed BOD loads) in the urbanized catchments sampled here. For example, a previous work in the same region of SC found that an urban stream that drained 18% IC, released an annual volume of water ~1.7 times greater than a stream that drained an undeveloped watershed[59] and is similar to the volume increases reported in other studies. The 16 urban sites monitored here drained watersheds with ~5 to 48% IC, which would likely result in annual volume changes that scale above and below 1.7 times background volumes. Without measuring BOD fluxes, we can only speculate that the urban stormwater runoff BOD concentrations reported herein scale to larger BOD fluxes relative to the background loads and contribute to worsening downstream DO impairment, although this is entirely consistent with other recent studies in this region.[24,33]

Hydrologic Influences. Hydrologic influences such as flushing effects strongly impact our stormwater OM concentrations. In order to differentiate temporal processes in flushing events, paired BOD samples were collected during rising and falling limbs at 14 individual sites (n = 29). Rising limb BOD was significantly higher than falling limb BOD ($p \leq 0.01$; Figure 3). These rising limb BOD concentrations were

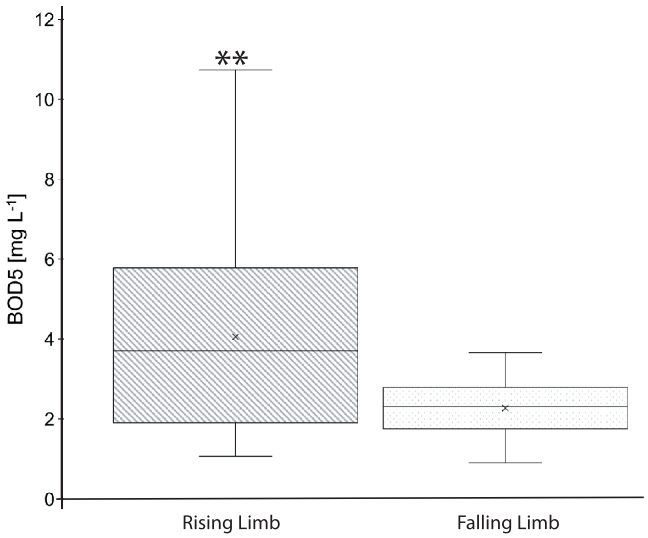

Figure 3. Stormwater BOD5 values measured on paired samples collected along the rising and falling limb of rain event hydrographs in 16 urbanized catchments. Asterisks denote a significant difference (p < 0.01).

accompanied by the highest POC and PN concentrations, sometimes surpassing DOC and DON concentrations. These findings support the hypothesis of a first flush effect where the mobilization of larger quantities of OM, specifically POM, occur with the initial rise in the hydrograph or initial pulse of stormwater runoff.[1,17,61] As the hydrograph falls and the rate of flow slows to baseflow, less OM is carried downstream.[1] Flushing effects thus explained some of the within site BOD variability, although the range in both rising and falling limb BOD values at a single site were still quite large.

BMPs are designed to mitigate first flush effects by attenuating flood pulses.[15,61] Peak hydrograph height declined at BMP sites, as evident in water level logger data (data not shown), but BOD, DOM, and POM, particularly Chl concentrations, were not reduced (Supporting Information, Tables S4 and S5). High Chl (mean = 26.4 mg L^{-1}) was even observed downstream in the ditches draining retention ponds. Other studies have also documented high levels of OM in BMP outflow,[41,42] and stormwater ponds were shown to be ineffective at sequestering autochthonous POM.[34] These results argue that hydrological alterations must be considered in the context of catchment biogeochemistry to ensure water quality improvement.

OM Concentrations Driving BOD. Stormwater pulses create high flow regimes capable of mobilizing large quantities of POM, especially during first flush.[1] Concentrations of POM measured in stormwater runoff were variable (Supporting Information, Table S5) but tended to exceed the range of POC and PN concentrations previously reported in the Waccamaw River and Winyah Bay.[54] Stormwater POC and PN concentrations did not differ significantly among sites. Instead, high variability at individual locations was driven primarily by flushing effects. Stormwater rising limb samples exhibited higher POC and PN concentrations when compared to paired falling limb samples (p < 0.01 and p < 0.05, respectively). Suspended POM has historically been considered to comprise a small fraction of largely refractory OM in aquatic systems with average turnover times on the order of weeks to years.[62−64] However, UBOD was positively correlated to POC and PN concentrations (R^2 = 0.30 for both; p < 0.001; Figure 4a), suggesting that POM is an important driver of BOD. These findings contribute to a growing body of evidence reassessing the importance of POM to aquatic microbial respiration, especially in urban catchments.[24,57,65−67]

While POM was shown to be a significant predictor of BOD, it only explained 30% of UBOD variability (Figure 4a). Some amount of DOM, the primary substrate for microbial respiration, must therefore also contribute to UBOD. Indeed, DOM tended to be the larger pool of OM in runoff regardless of the site (Supporting Information, Table S5), although stormwater from developed catchments consistently had lower DOC and DON concentrations compared to forested runoff (p < 0.001; Supporting Information, Table S5). The difference in DOM concentrations decreased the average ratio of DOC to POC from 9.7 (2.7 for N) in waters draining forested areas to 3.1 (1.4 for N) in waters draining urban areas, highlighting the importance of POM to BOD in urban aquatic ecosystems. Others have also reported decreases in lotic DOC and DON concentrations associated with urbanization in the SC and NC coastal plains, but noted these urban DON, and in some cases, DOC concentrations scale with increased stormwater runoff volume to levels that are comparable to the annual DOM export of forests.[24,59,68] Bulk DOM is often degraded and recalcitrant[69] with only a small labile fraction of DOM cycling rapidly.[17] Thus, it is difficult to detect trends in the respiration of DOM with bulk measurements, and it is not surprising that no significant correlations (R^2 < 0.2 and p > 0.05) were observed between UBOD and DOC or DON (Figure 4b).

Driven by the difference in DOC concentrations, total organic carbon (TOC = POC + DOC) in urban stormwater runoff (median = 10.8 mg L^{-1}) was approximately half the concentration measured in runoff from forested streams (median = 25.4 mg L^{-1}), yet BOD concentrations were similar. As such, while stormwater from forested streams had higher concentrations of TOC, a smaller fraction of TOC was ultimately consumed. Assuming a conversion factor of 1.2,[70] the percentage of TOC consumed from UBOD in urban runoff

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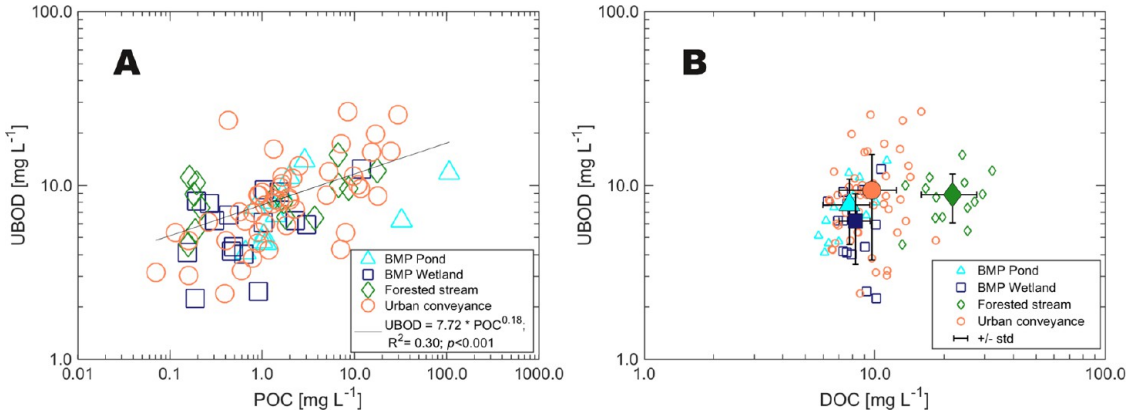

Figure 4. Measured UBOD vs the concentrations of (A) POC and (B) DOC. Data are displayed by catchment type: forested streams, BMP wetlands, BMP ponds, and urban ditches. Panel (B) depicts the average DOC and UBOD concentrations for each stormwater site type as the larger filled symbols and error bars represent the standard deviation. Individual sample error is smaller than the individual sample symbols.

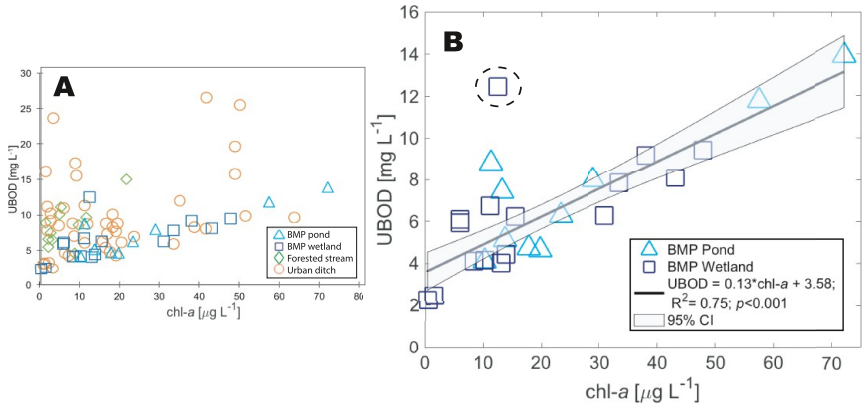

Figure 5. UBOD vs Chl. There is no significant relationship across the full dataset (A). A strong relationship emerges between UBOD and Chl when considering just the BMP sites (B; R^2 = 0.75; p < 0.001).

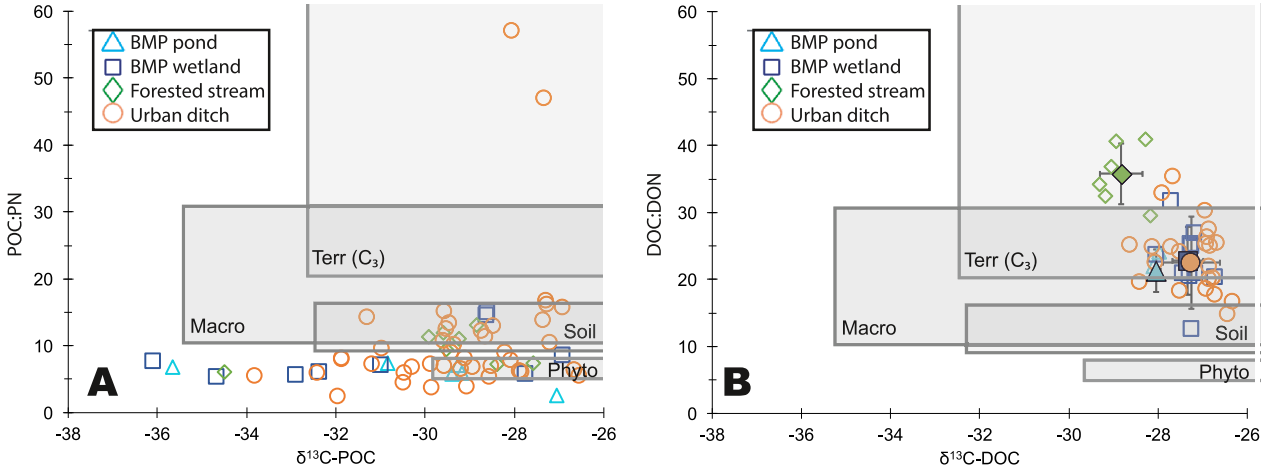

Figure 6. Stable isotopic fractions of (A) POC and (B) DOC vs molar ratios of C:N for forested streams, BMP wetlands, BMP ponds, and urban ditches. Boxes illustrate compositional ranges derived from previously published studies,[53,78,79] including: Terr (C_3), terrestrial C_3 vascular plants; Phyto, freshwater algal material; Soil, soil OM; and Macro, aquatic macrophytes. Larger filled symbols in panel (B) represent average values with their standard deviations.

(20 ± 9%, including BMP ponds, BMP wetlands, and ditches) was significantly higher than in forested runoff (12 ± 4%; p < 0.001; see Supporting Information, Figure S4). Therefore, more of the OM released in urban runoff was labile relative to OM discharged from forested streams, consistent with similar recent findings.[24,33]

Stormwater OM Source and Composition. Relationships between BOD and OM stable isotope values and C:N ratios, as well as Chl concentrations, were used to assess the degree to which BOD variability was driven by differences in OM source and composition. Concentrations of Chl were used as a proxy for phytoplankton biomass, and therefore the role of

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autochthonous production in fueling oxygen demand, directly or indirectly. Urban stormwater collected from BMP ponds and ditches that drain BMP ponds had significantly higher Chl versus ditches with no pond drainage and forested streams (all $p < 0.05$; Supporting Information, Table S5). Such high Chl has been previously reported in other SC stormwater ponds[71−74] and supports recent work that suggests BMPs, especially ponds, are significant sources of autochthonous material.[41,42,57] When considering all BOD measured, no significant relationship with Chl was observed. However, when BMP ponds and wetlands were examined separately, Chl explained 75% of the BOD variability, with the exclusion of one outlier from a wetland site (12; Figure 5; $p < 0.001$). Similarly, high correlations (R^2 ~0.61 to 0.76) between Chl and BOD have been reported in urban NC lakes.[57] While a portion of oxygen consumption in BOD measurements performed on samples high in Chl is undoubtedly due to respiration of living phytoplankton, these findings add further support to the hypothesis that lentic BMPs introduce a significant source of autochthonous OM that exacerbates low DO conditions in receiving waters.

The lability of POM in urban stormwater is further supported by the isotopic composition and C:N ratios. Across stormwater infrastructure type and watershed %IC, POM was largely a heterogeneous mixture of N-rich allochthonous and autochthonous plant materials, especially compared to DOM (Figure 6). Low C:N ratios in BMP sites and ditches draining BMP ponds may be indicative of a greater contribution of freshwater phytoplankton or of microbial alterations of terrestrial OM[48,54,64] because those samples also exhibit high Chl concentrations and near zero δ^{15}N-PN values (i.e., δ^{15}N of N-fixing algal biomass is ~0‰;[75] Supporting Information, Table S3). Fecal matter, typically from pets and wildlife, is often present in urban stormwater of this region,[43] and thus a potential source of OM that may contribute to BOD. However, fecal matter tends to be isotopically enriched in C and especially N,[76] and bulk POM characterization showed no clear indication of fecal matter sources or uptake, as C and N tended to be isotopically depleted (Figure 6; Supporting Information, Table S3). A few samples, largely collected from wetland sites (W1 and W2), a sample from a stream, a BMP pond, and a ditch that drained multiple ponds (F2, P1, and D10), had bulk δ^{13}C-POC <−32‰ (Figure 6a) and were enriched in N (C:N ~ 5 to 8; Figure 6a). These signatures, especially those from BMPs, again are likely indicative of autochthonous sources such as a mixture of aquatic macrophytes and algal material.[53,77] Emergent wetland species that often have depleted C isotopic signatures (as low as −36‰) relative to submerged vegetation and floating leaf plants,[77] were present in large quantities at all wetland sites. Overall, these proxies for lability further support that POM in urban runoff is comprised of a significant autochthonous fraction that fuels BOD.

Unlike POM, DOM stoichiometric ratios and isotopic compositions in urban runoff suggest a more refractory pool of terrestrial C.[48] Forest runoff contained more N-poor DOM (C:N > 25) and depleted bulk δ^{13}C-DOC (−28.8‰) relative to urban runoff (Figure 6b). The DOM in urban runoff also indicated some enrichment in DON and bulk δ^{13}C-DOC (Figure 6b). Further, the DOM in urban runoff had characteristics unique to stormwater site type, but not watershed %IC, as indicated by the data clusters (Figure 6b). On average, the DOM released from BMP catchments was more N-rich and δ^{13}C depleted compared to stormwater ditches; however, the difference is not statistically significant (Figure 6b). The slight enrichment in δ^{13}C-DOC and low C:N reported in urban stormwater runoff compared to forested runoff, especially from BMPs and ditches draining BMPs, suggests a contribution of labile autochthonous material,[53] consistent with the POM observations.[3,4] Combined, these results support the growing body of literature that suggest urbanization and the accompanying alterations to headwaters are enhancing the bioavailability of OM in aquatic systems.[18,80−82]

Management Recommendations. BOD concentrations in stormwater runoff are significantly higher than ambient river concentrations, and should thus be considered as factors when managing coastal DO impairment in downstream systems. Land use characteristics were not significant predictors of stormwater BOD concentrations in this region, although land use was clearly an important factor altering the hydrology of stormwater flow, and thus may significantly scale BOD and OM exports. No significant differences in BOD concentrations were observed in stormwater sampled from conventional ditch conveyances, compared to stormwater BMPs (ponds and wetlands). Results suggest retention ponds and wetlands may act as significant sources of labile OM by supporting increased algal production.[42] As such, urbanization and the associated headwater alterations are changing the source and composition of POM and increasing the fraction of labile DOM available to fuel microbial respiration within receiving waters. Mitigating DO impairment of coastal waters must therefore include stormwater BOD as a contributing source. In particular, stormwater managers should focus on reducing stormwater POM exports from stormwater infrastructures that promote increased BOD. Efforts that reduce the so-called first flush effects may be particularly effective in this regard.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04502.

Sampling locations and land cover analysis and characteristics (Figure S1 and Table S1); nutrient additions and nitrogenous oxygen demand effects on BOD concentrations (Figures S2 and S3); analytical error calculations (Table S2); expanded organic carbon and nitrogen methods and stable nitrogen isotope results (Table S3); BOD concentrations (Table S4); POM and DOM concentrations (Table S5); and total carbon consumption results (Figure S4) (PDF)

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Notes

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