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Nutrient removal using biosorption activated media: Preliminary biogeochemical assessment of an innovative stormwater infiltration basin

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ABSTRACT

Soil beneath a stormwater infiltration basin receiving runoff from a 23 ha predominantly residential watershed in north-central Florida, USA, was amended using biosorption activated media (BAM) to study the effectiveness of this technology in reducing inputs of nitrogen and phosphorus to groundwater. The functionalized soil amendment BAM consists of a 1.0:1.9:4.1 mixture (by volume) of tire crumb (to increase sorption capacity), silt and clay (to increase soil moisture retention), and sand (to promote sufficient infiltration), which was applied to develop an innovative stormwater infiltration basin utilizing nutrient reduction and flood control sub-basins. Comparison of nitrate/chloride (NO_3^-/Cl^-) ratios for the shallow groundwater indicates that prior to using BAM, NO_3^- concentrations were substantially influenced by nitrification or variations in NO_3^- input. In contrast, for the new basin utilizing BAM, NO_3^-/Cl^- ratios indicate minor nitrification and NO_3^- losses with the exception of one summer sample that indicated a 45% loss. Biogeochemical indicators (denitrifier activity derived from real-time polymerase chain reaction and variations in major ions, nutrients, dissolved and soil gases, and stable isotopes) suggest that NO_3^- losses are primarily attributable to denitrification, whereas dissimilatory nitrate reduction to ammonium is a minor process. Denitrification was likely occurring intermittently in anoxic microsites in the unsaturated zone, which was enhanced by the increased soil moisture within the BAM layer and resultant reductions in surface/subsurface oxygen exchange that produced conditions conducive to increased denitrifier activity. Concentrations of total dissolved phosphorus and orthophosphate (PO_4^{3-}) were reduced by more than 70% in unsaturated zone soil water, with the largest decreases in the BAM layer where sorption was the most likely mechanism for removal. Post-BAM PO_4^{3-}/Cl^- ratios for shallow groundwater indicate predominantly minor increases and decreases in PO_4^{3-} with the exception of one summer sample that indicated a 50% loss. Differences in nutrient variations between the unsaturated zone and shallow groundwater may be the result of the intensity and duration of nutrient removal processes and mixing ratios with water that had undergone little biogeochemical transformation. Observed nitrogen and phosphorus losses demonstrate the potential, as well as the future research needs to improve performance, of the innovative stormwater infiltration basin using BAM for providing passive, economical, stormwater nutrient-treatment technology to support green infrastructure.

1. Introduction

Capturing stormwater runoff for infiltration or harvesting is a valuable resource management practice for addressing the growing demand for fresh water worldwide, yet potential adverse effects on groundwater due to nutrient impacts, in particular nitrogen (N) and phosphorus (P) species, must be recognized (Clark and Pitt, 2007; Göbel et al., 2007; Page et al., 2010). Additionally, as competition increases for natural resources within society as well as between man and the environment, the importance of promoting green infrastructure in stormwater management is growing (Pataki et al., 2011). When using a stormwater infiltration basin, a balance must be maintained between augmenting the quantity while protecting the

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Abbreviations: BAM, biosorption activated media; CEC, cation exchange capacity; DNRA, dissimilatory nitrate reduction to ammonium; DO, dissolved oxygen; DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; IC, inorganic carbon; IN, inorganic nitrogen; OC, organic carbon; ON, organic nitrogen; SMRC, soil moisture retention curve; TDR, time domain reflectometry; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; TIC, total inorganic carbon; TN, total nitrogen; TP, total phosphorus.

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quality of groundwater. Assessment of basin performance, and urban infrastructure in general, from a biogeochemical cycling perspective is essential to gleaning a process-based understanding of nutrient dynamics in urban soils (Lorenz and Lal, 2009) and a more holistic determination of positive and negative feedbacks between the natural and built environments (Pataki et al., 2011). Borch et al. (2010) describe the importance of biogeochemical cycling on contaminant dynamics and the potential such understanding provides for the development of engineered remediation strategies.

Stormwater infiltration basins can contribute to elevated nutrient concentrations in groundwater in urban environments (O'Reilly et al., 2011; Taylor et al., 2005). For example, nitrate-nitrogen (NO_3^-–N) concentrations have increased in many Upper Floridan aquifer springs in central and north Florida since the 1950s, exceeding 1 mg L^{-1} in recent years at some springs (Katz, 2004; Knowles et al., 2010; Phelps, 2004; Phelps et al., 2006). A NO_3^-–N (plus nitrite) concentration of 0.35 mg L^{-1} was recently proposed as a protective criterion for aquatic life in Florida's springs and clear streams (US Environmental Protection Agency, 2011), thus reduction of nutrient contributions from urban stormwater can be part of the mitigation strategy for meeting such goals.

The existing design criteria for a typical stormwater infiltration basin involves excavation of a basin above the water table, leaving the natural soil profile unmodified except by possible incidental compaction during the construction process and the addition of vegetation on the sides and bottom such as sod. Stormwater runoff is directed to the infiltration basin for surface water pollution reduction and flood control purposes, where stormwater exits the basin by only infiltration or evaporation. Therefore, impacts to groundwater can be substantial.

Alternative design criteria focus on different media (natural soil and amendment mixtures) that can facilitate nutrient removal. Success of this technology, in terms of both physicochemical and biological processes, recently has been documented. For example, Bhatnagara and Sillanpää (2011) and Gupta et al. (2009) presented extensive overviews of materials with potential application as sorbents for pollutant removal, focusing on low cost and waste materials and nitrate (NO_3^-) sorbents. Chang et al. (2010a; 2010b) also presented extensive discussions of sorption media, focusing on the removal of N and P species and engineering applications in natural and built environments. Shaddox (2004) reported substantial reductions in NO_3^-, ammonium (NH_4^+), and orthophosphate (PO_4^{3-}) leaching with the use of surfactant-modified amendments in golf course putting greens. Tire crumb has proven to be an effective nutrient reduction media for total nitrogen (TN), NO_3^-, total phosphorus (TP), or PO_4^{3-} in a variety of applications including golf course putting greens (Lisi et al., 2004), green roof installations (Wanielista and Hardin, 2006), constructed wetlands (Xuan et al., 2009), stormwater treatment facilities (Hossain et al., 2010; Ryan et al., 2010; Wanielista and Chang, 2008), and septic tank drainfields (Chang et al., 2010c). Hossain et al. (2010) and Wanielista and Chang (2008) investigated nutrient removal by media comprising 50% sand, 20% limestone, 15% sawdust, and 15% tire crumb and reported removal efficiencies exceeding 75% for total dissolved phosphorus (TDP) and PO_4^{3-} and exceeding 60% for NO_3^- and NH_4^+, which they partly attributed to the tire crumb by a combination of adsorption, absorption, and ion exchange processes. Biosorbents—amendment material composed of non-growing or non-living microbial biomass—have proven very effective for removal of metals and organic compounds (Aksu, 2005; Vieira and Volesky, 2000), although applications to nutrient removal are not well documented. Successful applications utilizing biological processes to promote denitrification in a saturated groundwater setting are reported by Schipper and Vojvodic-Vukovic (2000, 2001). Smith (2008) described a media of expanded clay and elemental sulfur with NO_3^- removal up to 98%. Removal efficiencies depended on input concentrations and hydraulic retention time and were hypothesized to be due to combined ion exchange and biological activity. However, large field-scale testing of such “bioreactor” technology is limited and previous studies have generally not distinguished the specific pathways for NO_3^- removal (Seitzinger et al., 2006). Chang et al. (2010a) noted that scale-up of laboratory tested nutrient reduction technologies and assessment of the cost effectiveness of field-scale applications are important research needs. Taylor et al. (2005) suggested an important area for future stormwater research is improved treatment designs to enhance dissolved N removal by denitrification and plant uptake. Stormwater treatment application of soil amendments commonly has been implemented in relatively small-scale applications (<1 ha drainage area), such as low-impact development bioretention cells and rain gardens (Davis et al., 2009; Hunt et al., 2006). O'Reilly et al. (2012b) showed that soil textural and hydraulic properties, as critical determinants of soil moisture retention capacity, are important controls on the natural biogeochemical processes that affect N fate beneath stormwater infiltration basins.

To better understand the processes integrating stormwater infiltration impacts on groundwater resources in a field-scale setting, O'Reilly et al. (2011) conducted a study from 2007 through 2010 to identify both the hydrologic conditions and the biogeochemical processes beneath two stormwater infiltration basins. The objective of this paper is to describe the development of an innovative design for stormwater infiltration basins using biosorption activated media (BAM)—an amended soil designed to mimic natural physicochemical and biogeochemical processes—and demonstrate its potential for nutrient (N and P) removal by assessing its performance during a preliminary monitoring period. BAM was designed to function by combined sorption and biodegradation processes and is “activated” by microorganisms under wet conditions. The desired properties of BAM are:

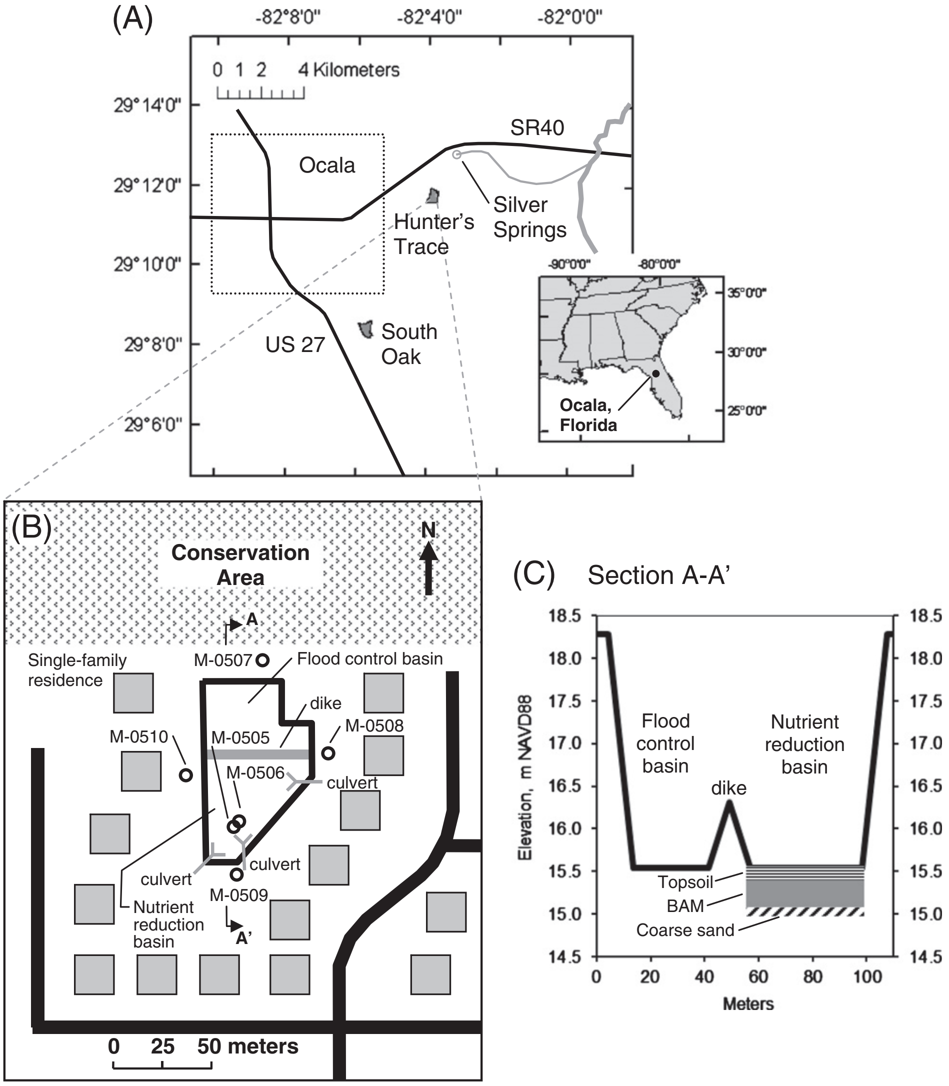
- sorption properties that retard movement of N and P;
- physical and textural properties that provide a large proportion of saturated pore space and provide surfaces for biofilm formation and denitrifier growth;
- passive, requiring no changes in operation and maintenance practices from a typical stormwater infiltration basin, and potentially “self sustaining” with respect to N removal; and
- promote green infrastructure by utilizing recycled or naturally available materials.

A field implementation of BAM was constructed at one of the basins previously studied by O'Reilly et al. (2012b), and is the first full-scale implementation of this technology known to the authors for regional stormwater infiltration basins serving watersheds >20 ha. A combination of hydrologic, soil and water chemistry, dissolved and soil gas, isotopic, and microbial data was used to provide a better understanding of the factors controlling groundwater quality both before and after construction of the new basin. By providing a preliminary assessment of BAM performance from a biogeochemical cycling perspective, results can lead to an improved basin design to mitigate nutrient impacts to groundwater while supporting green infrastructure development.

2. Material and methods

2.1. Description of study site

A stormwater infiltration basin located 2 km southwest of Silver Springs in north-central Florida, USA, was monitored during 2007–2010 (Fig. 1a). The Silver Springs springshed is characterized by karst topography consisting of predominantly internal drainage into closed depressions or diffuse seepage into the highly permeable surficial sediments (Phelps, 2004). Climate of the area is humid subtropical, with hot, rainy summers and cool, relatively dry winters (Phelps, 2004). Long-term (1901–2010) annual averages indicate rainfall of about 1360 mm yr^{-1} and mean daily air temperature of about 22 °C at the National Oceanic and Atmospheric Administration (NOAA) Ocala station (COOP ID 086414) approximately 13 km south of the stormwater basin (National Climate Data Center, 2011).



Note: Rain gage located at well M-0505.
Lysimeters, soil moisture probes, and soil temperature probes located at wellM-0506.

Fig. 1. Diagrams showing (A) locations of the Hunter's Trace and South Oak watersheds; (B) the Hunter's Trace stormwater infiltration basin, adjacent residences, and monitoring sites; and (C) cross-sectional view of nutrient reduction basin showing placement of engineered soil layers and biosorption activated media (BAM).

North-central Florida is underlain by three principal hydrogeologic units in order from shallowest to deepest: (1) surficial aquifer system, consisting of varying amounts of sand, silt, and clay; (2) intermediate confining unit, which is predominantly clay; and (3) Floridan aquifer system, which is a thick sequence of carbonate formations. The top of the limestone at the study site was found at a depth of 11.5 m at well M-0506 (Fig. 1b) (O'Reilly et al., 2012b), indicating the top of the Floridan aquifer system. The Floridan aquifer system comprises the Upper and Lower Floridan aquifers; the Upper Floridan aquifer is generally 90 m thick in north-central Florida and serves as the primary source of fresh water for numerous springs as well as for drinking water and irrigation purposes (Phelps, 2004).

The stormwater infiltration basin is located in a watershed that has transitioned from rural to residential land use during 1973–1990 and has remained predominantly residential during the study period. The basin is 2800 m^2 in bottom area with a watershed of 22.7 ha encompassing the Hunter's Trace residential community (Fig. 1a,b). The watershed consists of 14.1 ha of medium-density residential lots, 7.2 ha of undeveloped conservation area (pine forest), and 1.4 ha of curb-and-gutter roadway. The basin was originally constructed in 1985 utilizing a typical stormwater infiltration basin design that involves excavation of a basin above the water table, without modification of the underlying soil, where stormwater runoff is directed for surface water pollution reduction and flood control purposes. The basin was excavated to a depth of about 2.8 m in a relatively flat terrain.

2.2. Innovative stormwater infiltration basin

During 3–6 November 2009, the existing Hunter's Trace stormwater infiltration basin was modified utilizing a new integrated design technology. The innovative design was thus developed not only to satisfy the flood-control performance of the original basin but also to incorporate improved nutrient control utilizing BAM.

2.2.1. Integrated nutrient reduction and flood control design

Three design goals guided the development of the new integrated design technology: (1) maintain the flood control capacity of the original stormwater infiltration basin; (2) reduce the nutrient loading to groundwater by implementing a passive technology that promotes potentially self-sustaining natural biogeochemical processes; and (3) maximize economic feasibility by minimizing design and construction costs and keeping operation and maintenance costs comparable to existing stormwater infiltration basin designs. The new design consists of dividing the original stormwater infiltration basin into two approximately equal sub-basins—the south basin functions as the nutrient reduction basin and the north basin functions as the flood control basin—thus integrating stormwater quality and quantity control into a single design (Fig. 1b). The nutrient reduction basin was formed by excavating the 0.15-m thick topsoil layer and 0.40 m of underlying parent soil and stockpiling separately onsite. The excavation was filled with three engineered sub-layers (from bottom to top): 0.10-m thick coarse sand filter layer, 0.30-m thick amended soil (BAM) layer, and 0.15-m thick layer of the native topsoil (Fig. 1c). The remaining excavated parent soil was used to create a 0.76-m high dike separating the nutrient reduction and flood control basins. To minimize erosion, the dike side slope was constructed at 10:1 (H:V) slope and an erosion control blanket installed along the entire downstream (north) side. In order to ensure that the hydraulic operation of the innovative stormwater infiltration basin achieves the intended enhanced nutrient removal while maintaining the flood control requirements, a runoff/water-balance model was developed and is described in the Supplemental Information.

2.2.2. Biosorption activated media (BAM) design

The three soil sub-layer structure engineered beneath the nutrient reduction basin was designed to increase soil moisture, reduce oxygen diffusion into the subsurface, and increase adsorption/absorption capacity while still maintaining an infiltration capacity near that of the original basin (Fig. 1c). The intended result is to increase biological activity, specifically denitrifying bacteria, within and below the modified soil layers. The coarse sand layer is included to encourage rapid drainage to maintain low moisture content (0.67 mm median grain size; Supplemental Fig. S3). Because unsaturated soil hydraulic conductivity is directly and nonlinearly related to moisture content (Koorevaar et al., 1983), such a well-drained layer will have a low unsaturated hydraulic conductivity during dry periods and will cause substantially increased retention of water in an overlying finer-textured layer (Gardner, 1979), (the amended soil layer is this application). The amended soil layer consists of BAM, which is a 1.0:1.9:4.1 mixture (by volume) of tire crumb, silt + clay (<0.075 mm grain size), and sand (>0.075 mm grain size). Tire crumb increases sorption capacity primarily through adsorption/absorption processes (Hossain et al., 2010), the silt and clay increase soil moisture retention, and the sand limits the reduction in permeability (and infiltration capacity) that would result from higher silt + clay contents. The BAM layer has the effect of increasing the moisture retention capacity of the soil beneath the nutrient reduction basin because of its relatively fine-grained texture (0.19 mm median grain size; Supplemental Fig. S3). Lastly, the top sub-layer of native topsoil, because of its organic matter content developed by the growth of natural herbaceous vegetation, is intended to provide a source of organic carbon to serve as an electron donor during denitrification or other biogeochemical processes.

2.3. Hydrological monitoring

Hydrological monitoring consisted of measurements of rainfall, basin stage (stored stormwater level in the original infiltration basin and in the nutrient reduction basin), groundwater level, subsurface temperature, and volumetric soil moisture content as described by O'Reilly et al. (2012b). Matric head (soil moisture pressure head) was measured using tensiometers equipped with pressure transducers. Data were recorded at 5-minute intervals from December 2007 through October 2010.

Monitor wells were installed by hollow-stem auger in March 2007. The wells consisted of a 5.1-cm-diameter PVC casing with a 1.5-m-length screen. One 4.6 m deep well (M-0506) and one 9.4 m deep well (M-0505) were installed inside the basin (in an area which would later become the nutrient reduction basin), and four wells (9.2–9.6 m deep, 6.0–6.4 m below the bottom of the basin) were installed around the basin perimeter (Fig. 1b). As described by O'Reilly et al. (2012b), suction lysimeters with a 20-cm long porous cup were installed at depths of 0.5, 0.9, and 1.3 m and time domain reflectometry (TDR) and thermistor probes were installed at depths of 0.3, 0.6, and 0.9 m adjacent to well M-0506 in June 2008. During construction of the nutrient reduction basin, TDR and thermistor probes were reinstalled at the midpoint of the BAM layer (0.3 m depth) and at the midpoint of the coarse sand layer (0.5 m depth). The deepest set of probes remained in the native soil at a depth of 0.9 m. Tensiometers (field tensiometer SW-03, Soil Measurement Systems, Tucson, AZ[1]) with a 2.2-cm long porous cup were installed July 2008 adjacent to the lysimeters in a single borehole at depths of 0.3, 0.6, and 0.9 m; porous cups were embedded in silica flour slurry and bentonite chips were used to isolate monitoring zones.

2.4. Soil assessment

A combination of soil physical, mineralogical, and chemical properties was measured on samples collected before and after construction of the nutrient reduction basin. An outline of the data collected is provided below, and the reader is referred to O'Reilly et al. (2012b) for further details on the relevant analytical methods. Soil samples were collected by hand auger, double-cylinder hammer-driven core sampler (Grossman and Reinsch, 2002), or split-barrel sampler (ASTM D 1586-84, American Society for Testing Materials, 1994) at depths ranging from 0.1 to 9.7 m in unconsolidated sediments overlying the Upper Floridan aquifer. Soil physical property measurements included particle size gradation and soil moisture retention curve (SMRC). Soil mineralogical and chemical analyses were performed at the University of Florida Soil Core Laboratory in Gainesville, FL. Samples were analyzed for silt and clay mineralogy by X-ray diffraction, cation-exchange capacity (CEC), soil solids N and C contents, and extractable N and C contents. Soil solids were analyzed for organic carbon (OC), total carbon (TC), and total N (TN). Both potassium chloride (KCl) and water extractions were performed and analyzed for NH_4^+, NO_3^- plus NO_2^- (denoted NO_x), and NO_3^-; water extractions were analyzed for OC, TC, and TN.

2.5. Geochemical assessment

Water samples for major ion, trace metal, nutrient, and OC analysis were collected June 2007 to August 2010; water samples for dissolved gas and stable isotopes were collected March 2008 to August 2010; and soil gas samples were collected only after construction of the nutrient reduction basin from November 2009 to August 2010.

2.5.1. Water chemistry

Precipitation, stormwater, soil water, and groundwater samples were collected to determine their chemical characteristics. Water samples were collected following standard U.S. Geological Survey (USGS) protocol (US Geological Survey, 1998) as described by O'Reilly et al. (2012b). Field properties (temperature, specific conductance, pH, dissolved oxygen, and redox potential) were measured for water samples using a YSI 556MPS multiparameter sonde (prior to May 2008) and YSI 6920V2 multiparameter sonde (May 2008 and later) (YSI Incorporated, Yellow Springs, OH); a flow-through chamber was used for groundwater samples. Stormwater samples were collected from water at five locations within each basin and composited by stirring. Soil–water samples were collected by first purging the lysimeter and then applying a pressure of −60 kPa and allowing the lysimeter to fill for 6 − 48 h, depending on ambient soil moisture content. Atmospheric air was used to apply a pressure to force the water into a 1 L amber glass bottle from which water was withdrawn by peristaltic pump for filtration and

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[1] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

bottle filling. Precipitation (bulk deposition) samples were obtained by collection in an 8 L plastic bucket from which water was withdrawn by peristaltic pump for filtration and bottle filling. Alkalinity was determined for all samples by incremental titration with 0.16 N or 1.6 N sulfuric acid. Samples collected for precipitation, soil water, and groundwater were filtered through 0.45-μm pore-size disposable encapsulated filters for all analytes; unfiltered samples for TN and TP were also collected for groundwater samples; and both filtered and unfiltered samples for all analytes were collected for stormwater. All major ion, trace element, nutrient, and OC samples were analyzed by the USGS National Water Quality Laboratory in Denver, CO. Further details on specific analytes and laboratory analytical methods are provided by O'Reilly et al. (2012b). Water samples for total inorganic carbon (TIC) analysis were analyzed at the USGS laboratory in Boulder, CO (R.L. Smith, personal communication, 2010), using the method described for dissolved inorganic carbon (DIC) by Antweiler et al. (2005).

2.5.2. Dissolved and soil gases

Water and soil gas samples were collected. For major dissolved gases (Ar, N_2, O_2, CO_2, and CH_4), groundwater samples were collected as described by O'Reilly et al. (2012a) and were analyzed by gas chromatograph according to the methods of Busenberg et al. (2001) by the USGS Chlorofluorocarbon Laboratory in Reston, VA. Additionally, N_2O and CH_4 analyses for groundwater and soil gas and Ar, N_2, and O_2 analyses for soil gas were analyzed at the USGS laboratory in Boulder, CO (R.L. Smith, personal communication, 2010), based on the methods outlined by Antweiler et al. (2005), Smith et al. (2004), and Smith et al. (2005). Soil gas samples were collected using a diffusion monitor device (Rolston, 2002) as described in the Supplemental Information. Soil gas monitors were installed by hand excavation adjacent to the lysimeters during construction of the nutrient reduction basin at depths of 0.3, 0.5, 0.9, 1.3, and 1.8 m.

2.5.3. Stable isotopes

Isotopic values are reported using standard delta (δ) notation (Clark and Fritz, 1997) as follows: $R_{sample} = [(R_{sample}/R_{standard})-1] \times 1000$; for $\delta^{15}N$, R = $^{15}N/^{14}N$; for $\delta^{18}O$, R = $^{18}O/^{16}O$; and for $\delta^{13}C$, R = $^{13}C/^{12}C$. Results are reported in parts per thousand (per mil, ‰). N isotopes are reported relative to N_2 in air (Mariotti, 1983); O isotopes are reported relative to Vienna Standard Mean Ocean Water (Coplen, 1988; Coplen, 1994); and C isotopes are reported relative to Vienna Peedee belemnite and normalized (Coplen et al., 2006). $\delta^{15}N$ values of NO_3^- and dissolved N_2, $\delta^{18}O$ values for NO_3^- and H_2O, and $\delta^{13}C$ values of DIC and dissolved organic carbon (DOC) were determined. Isotopic analyses of NO_3^-, H_2O, DIC, and DOC samples were performed by the USGS Reston Stable Isotope Laboratory in Reston, VA. NO_3^- samples were analyzed by bacterial conversion of NO_3^- to N_2O and subsequent measurement on a continuous flow isotope ratio mass spectrometer (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004; Révész and Casciotti, 2007). $\delta^{18}O$ of H_2O was determined using the CO_2 equilibration technique (Epstein and Mayeda, 1953; Révész and Coplen, 2008). DIC and DOC samples were analyzed on a carbon dioxide (CO_2) dual inlet isotope ratio mass spectrometer (Coplen, 1973; Singleton et al., in press). Isotopic analysis of N_2 samples was performed (after gas concentration analysis [Section 2.5.2]) at the USGS laboratory in Reston, VA (J.K. Böhlke, personal communication, 2010) on an isotope ratio mass spectrometer based on the method described by Tobias et al. (2007).

2.6. Microbiological assessment

Since Braker et al. (1998) first developed a primer system to amplify the *nirK* and *nirS* genes that encode the copper and cytochrome cd1 NO_2^- reductases, respectively, the key enzymes in the denitrification process, polymerase chain reaction technology has been widely used to quantify denitrifying bacteria in soil. Quantification of bacteria by gene copy number is important for a better understanding of denitrifying activity in the environment (Henry et al., 2004). In this work, quantitative real-time polymerase chain reaction (qPCR) was applied to gain insight into denitrifier activity by measuring *nirK* gene density (gene copy number normalized to soil mass) in extracted DNA according to the method described by Xuan et al. (2009). Interpretation of the qPCR results is based on the assumption that the presence of the *nirK* gene in bacterial DNA also indicates that the bacteria are actively producing the Nir enzyme required for this denitrification step. Soil samples for qPCR analysis were collected at depths ranging from 0.08 to 1.9 m in the same manner and in the same boreholes used to collect other soil samples described in Section 2.4.

3. Results and discussion

3.1. Hydrological conditions

Hydrological monitoring indicates frequent stormwater storage in the nutrient reduction basin (Fig. 2b). Because the nutrient reduction basin is approximately half the area of the original stormwater infiltration basin, stormwater accumulates deeper for any given rainfall event. Therefore, the nutrient reduction basin stays flooded longer (flooded 15% of the post-BAM period) than the original basin (flooded 7% of the pre-BAM period), although there was a greater number of large storm events during the post-BAM period (Fig. 2a). The more frequent water storage in the nutrient reduction basin combined with the fine-grained texture of the BAM layer causes higher soil moisture contents (0.3-m probe, Fig. 2c), leading to conditions more favorable for anaerobic processes such as denitrification. Analysis of basin stage recession curves both before and after construction of the new basin indicates similar infiltration rates, averaging about 9.1 mm h^{-1} in the original basin and 8.6 mm h^{1} in the nutrient reduction basin (Table 1). Therefore, about 90 h is required for a full nutrient reduction basin (0.76 m deep) to drain completely. Simulation of the hydraulic performance of the new integrated design indicates that an 88% treatment volume (percentage of total runoff that infiltrates through the BAM layer) can be expected for the nutrient reduction basin under typical rainfall conditions for north-central Florida (see Supplemental Information).

3.2. Nutrient concentrations in stormwater, soil water, and groundwater

Total dissolved nitrogen (TDN) in soil water and shallow groundwater beneath the basin was almost exclusively in the NO_3^- form throughout the entire monitoring period June 2007–August 2010 (Fig. 3a–c,e). In stormwater, TDN was predominantly in the organic form; particulate and colloidal N (greater than 0.45 μm computed from unfiltered and filtered samples) was at times an important constituent of the TN in stormwater (Fig. 3d). Stormwater samples were collected during groundwater sampling events when water was stored in the basin. Flow-weighted concentrations for individual runoff events would be different.

Total dissolved phosphorus (TDP) in soil water, groundwater, and stormwater was generally in the orthophosphate (PO_4^{3-}) form (Fig. 4). Particulate and colloidal P (greater than 0.45 μm computed from unfiltered and filtered samples) was at times an important constituent of the TP in stormwater (Fig. 4d; particulate and colloidal P fraction not shown). High TDP concentrations in deeper groundwater (well M-0505, 9.4 m deep) ranging from 0.46 to 0.90 mg L^{-1} (median = 0.60 mg L^{-1}, n = 20; data not shown) are due to the prevalence of phosphate minerals confirmed by X-ray diffraction analyses of the sediments at this depth.

Temporal variations in nutrient concentrations in soil water and groundwater were influenced by changing hydroclimatic conditions and variable N and P concentrations in runoff. The transport and fate of N and P in the subsurface are governed by a combination of conservative

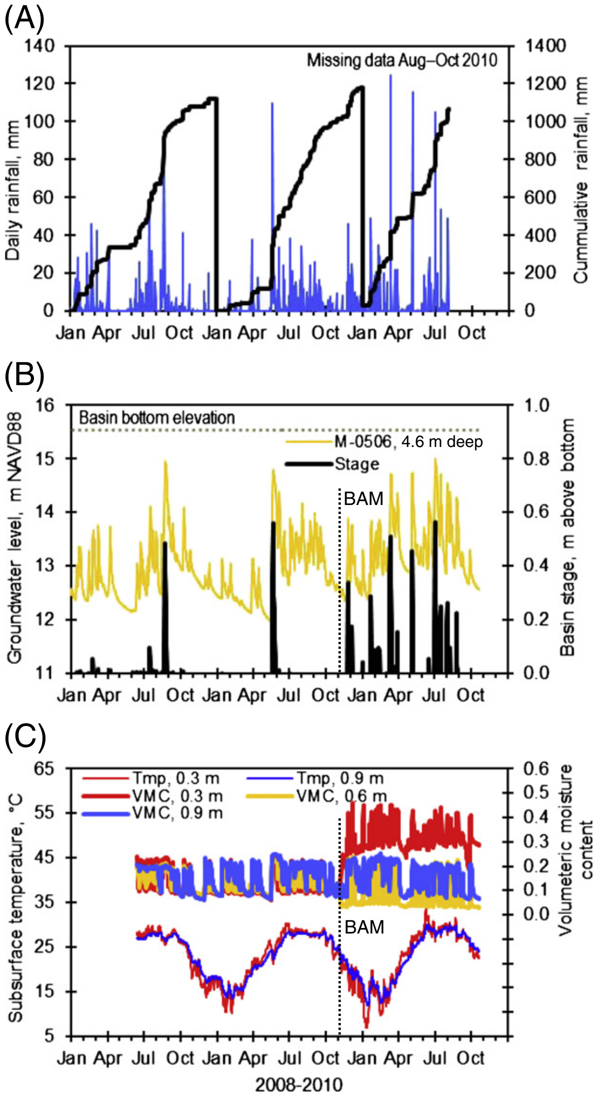

Fig. 2. Hydrologic monitoring at the stormwater infiltration basin 2008–2010: (A) rainfall, (B) basin stage and groundwater level, and (C) soil moisture content (VMC) and subsurface temperature (Tmp). The innovative stormwater infiltration basin incorporating biosorption activated media (BAM) was constructed 3–6 November 2009, and measurements made after this date represent conditions in or beneath the nutrient reduction basin. The soil moisture probe at 0.6-m depth was relocated to 0.5-m depth after construction.

mixing and physical, chemical, and biological reactions. Understanding these varied mechanisms, as described below in Sections 3.3 and 3.4, is important to understanding the effectiveness of BAM.

Table 1
Infiltration rates at the stormwater infiltration basin before and after construction of the nutrient reduction basin incorporating biosorption activated media (BAM).

Date	Rain (mm)	Duration (h)	Infiltration (mm h^{-1})
Before biosorption activated media			
23-Jan-08	20.3	4.75	8.6
23-Feb-08	46.2	5.33	8.9
7-Mar-08	36.3	7.75	10.2
15-Jul-08	50.0	1.33	10.7
22-Aug-08	155.4	33.08	7.3
After biosorption activated media			
25-Nov-09	42.9	1.33	9.4
17-Jan-10	17.0	2.64	10.4
21-Jan-10	48.5	5.83	8.9
11-Mar-10	122.7	6.25	6.6
21-Mar-10	21.8	6.17	7.6

3.3. Nitrogen transport and fate before and after BAM application

3.3.1. Conservative transport of nitrate

NO$_3^-$ concentrations can be affected by physical processes as well as a variety of chemical reactions that generally are biologically mediated (nitrification, denitrification, dissimilatory reduction to ammonium (DNRA), microbial assimilation, or plant uptake). In contrast, chloride (Cl$^-$) and bromide (Br$^-$) generally are considered to be affected by only physical processes and thus are transported conservatively in the subsurface (Panno et al., 2006). Therefore, examination of these data in combination can give insight into NO$_3^-$ variations due to processes other than conservative transport, that is, the net effects of reaction-based processes and source inputs. During 2007–2010, a decline in Cl$^-$ concentration is apparent (Fig. 5a). The cause of this long-term decline is uncertain, but based on specific conductance measurements made during well development, a significant increase in Cl$^-$ occurred prior to collection of the first sample on 22 June 2007. A linear regression between specific conductance and Cl$^-$ ($R^2 = 0.96$) indicates that Cl$^-$ was 41 and 48 mg L^{-1} on 28 March and 31 May 2007, respectively, whereas measured Cl$^-$ was 78 mg L^{-1} on 22 June. Similar Cl$^-$ trends are apparent in well M-0505 (data not shown), which is 4.8 m deeper than M-0506, indicating water chemistry trends existed in shallow groundwater prior to well installation. Thus the decline probably reflects mixing of more mineralized groundwater with relatively dilute infiltrated stormwater. Similar downward trends in Br$^-$ concentration existed before and after construction of the new basin (Fig. 5a). However, a substantial increase in Br$^-$ occurred November 2009 through January 2010 following construction, suggesting a possible source of Br$^-$ in the BAM layer to which the groundwater chemistry was equilibrating. The increase in Cl$^-$ relative to Br$^-$ in August 2010 is likely caused by the infiltration of fertilizer-impacted stormwater because Cl$^-$ is more prevalent in fertilizer than Br$^-$ (Panno et al. (2006) reported a Cl$^-$/Br$^-$ ratio of 510 for a commercial KCl fertilizer).

Because Cl$^-$ is present and generally acts as a conservative tracer in fertilizer-impacted stormwater runoff, NO$_3^-$/Cl$^-$ ratios were analyzed; whereas, Br$^-$ was not present in stormwater runoff in measureable concentrations (laboratory reporting limit for Br$^-$ is 0.02 mg L^{-1}). In order to quantify the difference in NO$_3^-$ concentration associated with the NO$_3^-$/Cl$^-$ ratio changes (Fig. 5a), a "reconstructed" NO$_3^-$ time series was computed based on the fractional change in Cl$^-$ concentration between consecutive sampling events. This reconstructed concentration represents the NO$_3^-$ concentration that would have occurred if only conservative transport and NO$_3^-$/Cl$^-$ mass input variations were affecting concentrations during the time period from collection of one sample to the next. Further details on the assumptions and interpretation of NO$_3^-$/Cl$^-$ ratios and reconstructed NO$_3^-$ concentrations are provided in the Supplemental Information.

For each sample event, a reconstructed NO$_3^-$ concentration was computed as follows:

$$\mathrm{NO}^{i}_{3,R} = \mathrm{NO}^{i-1}_{3,M}\Delta \mathrm{Cl} + \mathrm{NO}^{i-1}_{3,M} \qquad (1)$$

$$\Delta \mathrm{Cl} = \left(\mathrm{Cl}^{i} - \mathrm{Cl}^{i-1}\right) \Big/ \mathrm{Cl}^{i-1} \qquad (2)$$

where, NO$^{i}_{3,R}$ is the reconstructed NO$_3^-$ concentration for the current sampling event; NO$^{i-1}_{3,M}$ is measured NO$_3^-$ concentration for the preceding sampling event; ΔCl is the fractional change in Cl$^-$ concentration; Cl^{i} is Cl$^-$ concentration for the current sampling event; and Cl^{i-1} is Cl$^-$ concentration for the preceding sampling event. This yields an incrementally reconstructed NO$_3^-$ time series showing what NO$_3^-$ concentrations would have been due to dilution or NO$_3^-$/Cl$^-$ mass input variations for only the time period between current and preceding sampling events. The percent difference in NO$_3^-$ concentration between

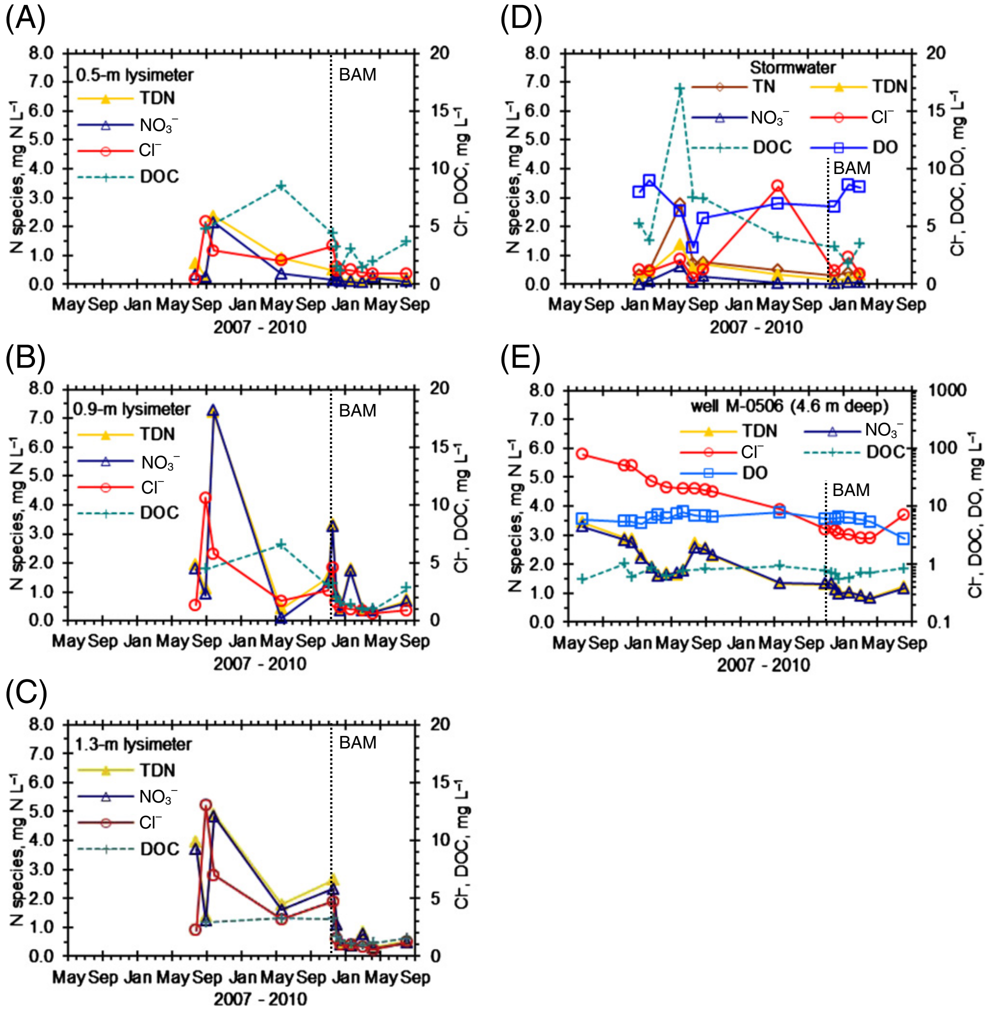

Fig. 3. Temporal variations in nitrogen species, dissolved organic carbon (DOC), chloride, and dissolved oxygen (DO) (not available for lysimeters) concentrations before and after placement of biosorption activated media (BAM) in (A) soil water (0.5-m deep lysimeter); (B) soil water (0.9-m deep lysimeter); (C) soil water (1.3-m deep lysimeter); (D) stormwater; and (E) groundwater (well M-0506, 4.6 m deep).

measured and reconstructed values ($\%\Delta NO_{3,M-R}$) is computed as follows:

$$\%\Delta NO_{3,M-R} = 100\left(NO_{3,M} - NO_{3,R}\right)\Big/ NO_{3,M} \tag{3}$$

where, $\%\Delta NO_{3,M-R}$ represents a percentage measure of the net effects of NO_3^- reaction and changes in NO_3^-/Cl^- inputs. If additionally it is assumed that Cl^- input is relatively consistent, then $\%\Delta NO_{3,M-R}$ represents the net effects of NO_3^- reaction and NO_3^- input variations only. This assumption is supported by the consistent exponential decline in Cl^- experienced throughout the study period, with the exception of the relatively large increase that occurred in August 2010 (Fig. 5a). Therefore, positive values of $\%\Delta NO_{3,M-R}$ represent a reaction gain or input increase in NO_3^- and negative values of $\%\Delta NO_{3,M-R}$ represent a reaction loss or input decrease in NO_3^-. Values of $\%\Delta NO_{3,M-R}$ near zero indicate that NO_3^- was being transported conservatively, thus any observed changes in NO_3^- are attributable to dilution effects.

Prior to construction of the new basin, NO_3^- fate was dominated by nitrification or NO_3^- input increases with isolated periods of conservative movement possibly influenced by ephemeral reaction losses, as indicated by the percentage differences between measured and reconstructed NO_3^- concentrations ranging from −3 to 120% (Fig. 5b). In contrast, from November 2009 to April 2010 after the addition of BAM, NO_3^- was controlled by intermittent periods of slight reaction losses and nitrification as indicated by the percentage differences between measured and reconstructed NO_3^- concentrations ranging from −8 to 4% (Fig. 5b). However, the August 2010 sample indicated an increase in NO_3^- considerably less than that expected based on the Cl^- increase, yielding a percentage difference between measured and reconstructed NO_3^- concentrations of −45% (Fig. 5b). This indicates that in the absence of any NO_3^- reaction or input decrease, the NO_3^--N concentration would have been 2.12 mg L^{-1} rather than 1.18 mg L^{-1}, suggesting nearly half (0.94 mg L^{-1}) was lost. An increase in NO_3^- input is expected in late spring to early summer as suggested by the samples collected in 2007–2009, coinciding with the start of the summer growing season and fertilizer application in residential landscapes. Therefore, the large percentage difference is reaction based. Another important difference attributable to the new integrated design is the prevalence of pre-BAM increases in NO_3^- percentage differences and the absence of post-BAM increases (Fig. 5b). This is suggestive of reduced nitrification after construction of the nutrient reduction basin and was concurrent with increased soil moisture (Fig. 2c) and lower DO concentrations (Fig. 3e), both of which are conditions less favorable for nitrification.

3.3.2. Biogeochemical assessment of nitrogen fate

To provide further insight into reaction based reductions in NO_3^-, such as denitrification or DNRA, occurring after the addition of BAM, several additional types of biogeochemical data were examined:

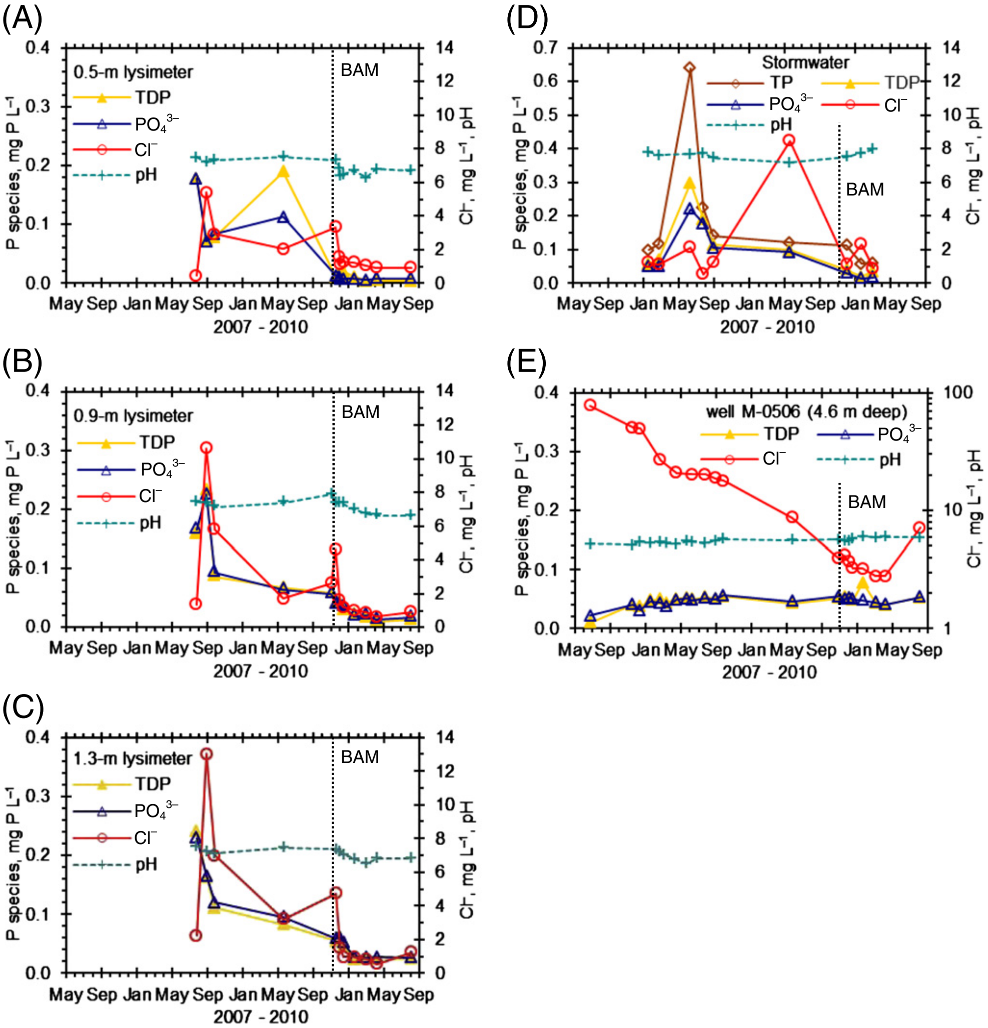

Fig. 4. Temporal variations in phosphorus species and chloride concentrations and pH before and after placement of biosorption activated media (BAM) in (A) soil water (0.5-m deep lysimeter); (B) soil water (0.9-m deep lysimeter); (C) soil water (1.3-m deep lysimeter); (D) stormwater; and (E) groundwater (well M-0506, 4.6 m deep).

dissolved gases, soil gases, soil chemistry, stable isotopes, and denitrifier activity. Analysis of these data provides independent evidence of NO_3^- reactions to support the inferences derived from examination of NO_3^-/Cl^- ratios, as well as providing insight on C cycle coupling with other biogeochemical processes. The evidence for reaction based reductions in NO_3^- provided by any of these datasets individually is limited. However, the following discussion shows that all of these lines of evidence taken in combination provide a consistent indication that NO_3^- losses are primarily attributable to denitrification in the BAM layer, whereas other processes such as DNRA and plant uptake are less important.

3.3.2.1. Biogenic gases and effects of soil moisture. Analysis of dissolved N_2 and Ar in groundwater (well M-0506) for estimation of excess N_2 is difficult given the dynamic nature of the shallow groundwater system beneath the stormwater infiltration basin. A method described by O'Reilly et al. (2012a) was applied to derive estimates of excess N_2 concentrations by computing minimum (excess $N_2 = 0$) and maximum (excess air = 0) values of excess N_2. Corresponding recharge temperatures, which were estimated iteratively to meet each criterion, fell within the range of measured subsurface temperatures (Fig. 2c). Because recharge temperatures could not be constrained by measured subsurface temperatures, final estimates of excess N_2 were computed using the average of the estimated minimum (for excess air = 0 criterion) and maximum (for excess $N_2 = 0$ criterion) recharge temperatures. Only two samples were collected during the pre-BAM period, with estimated excess N_2 concentrations of 0.11 and 0.37 mg L^{-1} (Fig. 6a). The lower value occurred in March 2008 when the basin had remained dry for 4.7 days prior to sampling, thus the soil was well aerated. In contrast, the higher excess N_2 concentration occurred in May 2009 during a major rainfall event when the basin had been continuously flooded 2.1 days prior to sampling (up to 0.7 m deep), potentially allowing for anoxic conditions to develop within the saturated soil profile. Estimated excess N_2 concentrations during the post-BAM period were modest as well, ranging from 0.16 to 0.34 mg L^{-1} (Fig. 6a). Given the uncertainty of the estimation procedure, excess N_2 estimates could range from zero to about double these values. However, NO_3^-/Cl^- ratio analyses described in Section 3.3.1 indicate NO_3^--N losses ranging 0.012 to 0.94 mg L^{-1} during the post-BAM period, which is equivalent to 0.006 to 0.47 mg L^{-1} of excess N_2. These excess N_2 concentrations inferred from NO_3^-/Cl^- ratio analyses encompass and are reasonably comparable to the range of excess N_2 concentrations estimated from the dissolved gas analyses. Even though DO was decreasing during much of the post-BAM period (Fig. 3e), it still was above the maximum DO level of about 2 mg L^{-1} (or about 60 µmol L^{-1}) commonly reported for aquifers experiencing documented denitrification (McMahon and Chapelle, 2007; Tesoriero and Puckett, 2011). Therefore, it is postulated that denitrification was occurring in the unsaturated zone, in particular within the BAM layer.

Concentrations of the biogenic gases N_2O, CH_4, O_2, and N_2 derived from the soil gas samples (collected after construction of the nutrient reduction basin) indicate significant biogeochemical activity within the shallow unsaturated zone. Subsurface generation of N_2O and CH_4

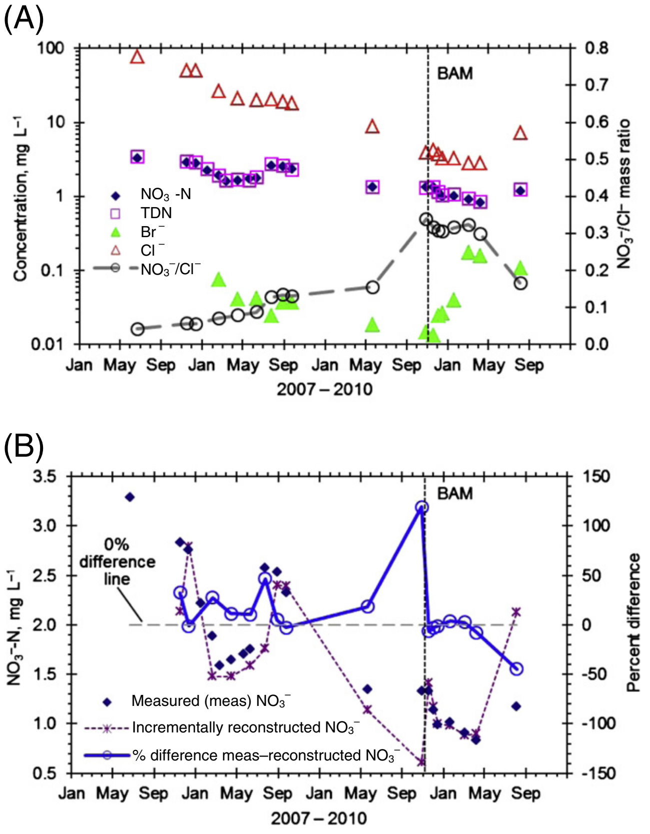

Fig. 5. NO_3^-–N variations in groundwater beneath the stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM): (A) comparison of NO_3^-–N, total nitrogen (TN), Cl^-, and Br^- concentrations; and (B) incrementally reconstructed NO_3^-–N and the incremental percentage differences assumed to be attributable to NO_3^- reactions or NO_3^- input variations.

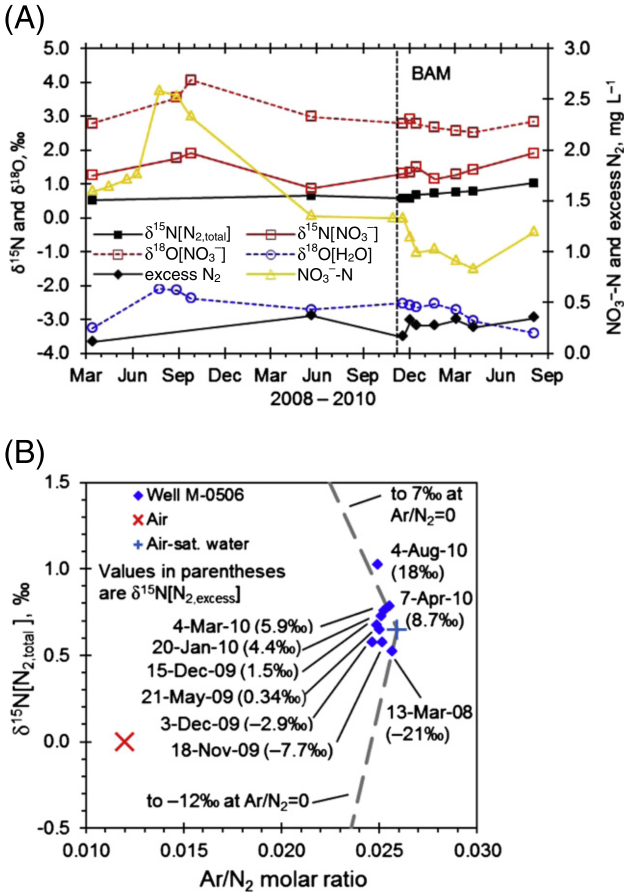

Fig. 6. Dissolved gas concentrations and isotope ratios for groundwater beneath the stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM) for (A) temporal variations $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-, excess N_2, $\delta^{15}N$ of N_2, and $\delta^{18}O$ of H_2O; and (B) $\delta^{15}N$ of N_2 compared to Ar/N_2 ratios.

is indicated by concentrations exceeding ambient atmospheric levels (approximately 0.3 and 1.7 ppmv, respectively [US Environmental Protection Agency, 2006]) (Fig. 7a,b); whereas subsurface consumption of O_2 is indicated by concentrations below ambient atmospheric levels (approximately 21%v) and generally downward concentration gradients (Fig. 7c). Given the high ambient atmospheric levels of N_2 and the relatively slight contribution by excess N_2, Ar/N_2 ratios were computed. Ar/N_2 ratios that are consistently less than the ratio for ambient atmospheric concentrations (0.012) are consistent with the presence of excess N_2 in the unsaturated zone (Fig. 7d). Soil moisture content is an important control on both the generation and transport of gases in the unsaturated zone by affecting the amount of gas-filled pore space and inhibiting surface/subsurface O_2 exchange leading to the development of anoxic conditions (Bateman and Baggs, 2005; Christensen et al., 1990a; Jin and Jury, 1996). Accordingly, significant correlations with the degree of soil saturation were found for N_2O, Ar/N_2 ratio, and CH_4 (Table 2). The largest statistically significant correlations correspond to the BAM layer where much of the variability in soil gas concentrations can be explained by soil saturation (fraction of water-filled pore space): N_2O is negatively correlated ($R^2=0.81$, $p=0.005$) with the 7-day average soil saturation, Ar/N_2 ratio is negatively correlated ($R^2=0.81$, $p=0.006$) with the same-day soil saturation, and CH_4 is positively correlated ($R^2=0.71$, $p=0.017$) with the 14-day average soil saturation. No correlations for O_2 are significant at the 0.1 level, however there is a weak negative correlation ($R^2=0.43$, $p=0.16$) with the 28-day average soil saturation. Because all of these gases are actively consumed or produced by biological activity, these results underscore the importance of elevated soil moisture content on biogeochemical cycling by inhibiting gas transport and promoting anoxic conditions that would tend to promote the reduction of O_2 and the accumulation of N_2O and CH_4.

N_2O can be produced in soil environments by both nitrification and denitrification and generally is reported to increase with increasing moisture content, with substantial increases at saturations above 60% (Abbasi and Adams, 2000; Bateman and Baggs, 2005; Dobbie et al., 1999). Based on laboratory incubations of an agricultural silt loam soil, Bateman and Baggs (2005) attributed N_2O production at 35–60% saturations to primarily nitrification with denitrification as a minor component, whereas denitrification was the sole source of N_2O at saturations exceeding 70%. The median moisture content of the BAM layer was 0.30, indicating a saturation of 61%, thus the observed N_2O profiles are the product of both nitrification and denitrification (Fig. 7a). Soil saturation varied among the seven soil gas sampling events, for example, 7-day average soil saturation ranged from 48 to 71%. The significant negative correlations between soil saturation and both N_2O concentration and Ar/N_2 ratio in the BAM layer suggest N_2O consumption by denitrification to N_2 (Table 2). Progression of denitrification to N_2 is favored for soil pH values exceeding 6 (Van den Heuvel et al., 2011) and when O_2 levels are very low (Rivett et al., 2008). Pore water pH varied 6.3–7.4 after the addition of BAM (Fig. 4a–c), and low O_2 levels in soil microsites are implied by the presence of CH_4.

Methanogenesis probably was occurring in the BAM layer causing the elevated CH_4 levels (Fig. 7b). The significant positive correlation with a longer period of wetter soil conditions (14-day average soil saturation, Table 2) is consistent with a longer time required for highly reducing conditions to develop. Since methanogenesis as well as

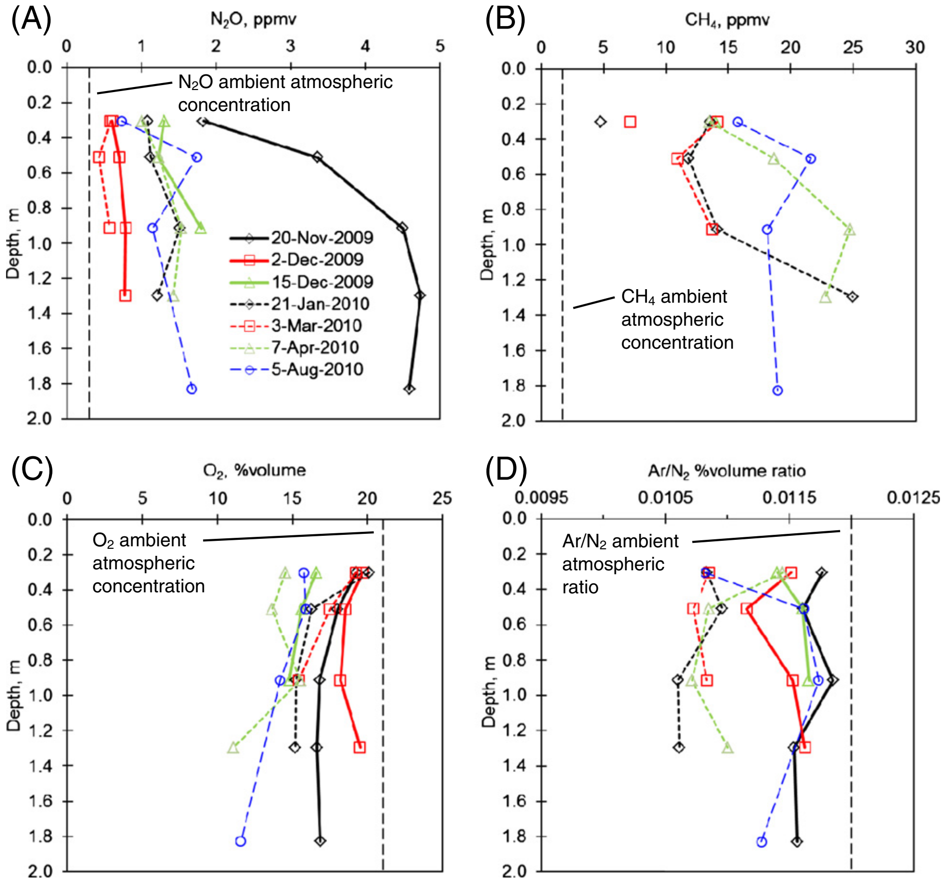

Fig. 7. Soil gas profiles beneath the stormwater infiltration basin after placement of biosorption activated media (BAM) for (A) N_2O, (B) CH_4, and (C) O_2, and (D) Ar/N_2.

denitrification requires low O_2 conditions yet the unsaturated zone was aerobic (Fig. 7c), these processes were occurring in anoxic microsites or cyclically during periods when the soil was wet or saturated and O_2 levels were low (Christensen et al., 1990a,b; Koba et al., 1997; O'Reilly et al., 2012a; Parkin, 1987; Raciti et al., 2011). The generation of CH_4 provides indirect evidence that the observed N_2O concentrations are at least partly attributable to denitrification, because NO_3^- is a more thermodynamically favorable electron acceptor than CO_2 (McMahon and Chapelle, 2007) indicating that denitrification would have preceded methanogenesis. Additionally, soil chemistry results are consistent with NO_3^- reduction, where water extractable NO_x–N concentrations were not detectable for samples collected in the BAM layer or below yet were elevated prior to construction, frequently exceeding 0.5 mg kg^{-1} (volumetric concentrations frequently exceeding 10 mg L^{-1}) (Supplemental Fig. S5, Supplemental Table S2). NO_3^- in soil water derived from the three lysimeters also showed decreases from pre- to post-BAM periods (Fig. 3a–c), with the lowest concentrations in the BAM layer where NO_3^--N ranged from 0.056 to 0.23 mg L^{-1} (average 0.14 mg L^{-1}, n = 8) (Fig. 3a). These results suggest that NO_3^- was depleted in the BAM layer, where anoxic microsites would have been most likely to develop due to elevated moisture contents (Fig. 2c), consistent with denitrification and methanogenesis.

Table 2
Linear correlation between soil saturation (percentage of water-filled pore space) and soil gas concentrations for O_2, N_2O, CH_4, and Ar/N_2 after construction of the nutrient reduction basin incorporating biosorption activated media (BAM). Average soil saturation computed for the number of stated days preceding sampling (inclusive of day of sampling) based on volumetric moisture content at the same depths as soil gas monitors.

Depth	Gas	Pearson R for average saturation of periods				
		1 d	3 d	7 d	14 d	28 d
All	O_2	0.11	0.00	0.07	−0.06	−0.10
	N_2O	-0.51^{**}	-0.42^{*}	-0.50^{**}	-0.51^{**}	−0.09
	CH_4	−0.43	−0.14	−0.07	0.01	0.03
	Ar/N_2	−0.23	−0.09	−0.09	−0.17	−0.18
0.3 m (BAM layer)	O_2	0.11	−0.18	−0.22	−0.59	−0.65
	N_2O	-0.81^{**}	-0.75^{*}	-0.90^{**}	-0.70^{*}	0.02
	CH_4	0.67	0.75^{*}	0.71^{*}	0.84^{**}	0.71
	Ar/N_2	-0.90^{**}	-0.88^{**}	-0.79^{**}	−0.52	−0.24
0.5 m	O_2	0.36	0.08	0.24	−0.39	−0.44
	N_2O	−0.62	−0.30	−0.44	−0.67	−0.19
	CH_4	−0.83	0.13	0.31	0.41	0.07
	Ar/N_2	-0.69^{*}	−0.07	0.15	−0.07	−0.22
0.9 m	O_2	−0.36	−0.30	−0.14	−0.12	−0.27
	N_2O	-0.71^{*}	-0.72^{*}	-0.83^{**}	−0.65	0.04
	CH_4	−0.82	−0.90	−0.79	0.22	0.21
	Ar/N_2	−0.03	0.00	−0.16	−0.28	−0.35

** Indicates $p \leq 0.05$.
* Indicates $0.05 < p \leq 0.1$.

Substantial reductions in soil gas O_2 occur in the two shallowest soil monitors, which respectively correspond to the midpoints of the BAM and coarse sand layers (Fig. 1c), relative to ambient atmospheric concentration. O_2 is being depleted by serving as the electron acceptor for DOC oxidation, consistent with decreasing DOC concentrations with depth in the unsaturated zone (Fig. 3a–c) and even lower DOC concentrations in shallow groundwater (Fig. 3e). These relatively steep downward gradients and the negative correlation with soil saturation (Table 2) suggest that the elevated soil moisture contents in the BAM layer (Fig. 2c) are inhibiting surface/subsurface O_2 exchange. Decreasing DO concentrations in the underlying groundwater since December 2009 is further indication of reduced O_2 transport into the subsurface or increased O_2 consumption compared to the pre-BAM period (Fig. 3e).

3.3.2.2. Stable isotopes and denitrification. Isotope data collected after construction of the nutrient reduction basin provide evidence of denitrification when considered in combination with other data. The slight but consistent upward trends in $\delta^{15}N[NO_3^-]$ and $\delta^{15}N[N_2]$ are consistent with modest excess N_2 concentrations (Fig. 6a), indicating enrichment in the heavy ^{15}N isotope that would occur if denitrifiers were preferentially metabolizing ^{14}N of NO_3^-. It is important to note that variations in the isotopic composition of the NO_3^- source will affect the isotopic composition of the residual NO_3^- and N_2. Therefore, deviations of $\delta^{15}N[N_2]$ on both the low side and the high side of air-saturated-water values could be a result of denitrification (Fig. 6b), depending on the progress of the reaction (it starts out producing light N_2, then evolves to higher values as the reaction proceeds). Computation of $\delta^{15}N[N_{2,excess}]$ for the fraction of total N_2 attributable to denitrification, based on linear mixing using $\delta^{15}N$ of air-saturated water of 0.7‰ (Böhlke et al., 2002; Green et al., 2008), indicates substantial enrichment over time (Fig. 6b). This enrichment trend persists despite large uncertainty in excess N_2 estimates, which significantly affect $\delta^{15}N[N_{2,excess}]$ values such that a doubling of excess N_2 results in a 50% decreases of $\delta^{15}N[N_{2,excess}]$. The single relatively high value of $\delta^{15}N[N_2]$ in August 2010 may be the result of an isotopically heavy NO_3^- source, a denitrification reaction that proceeded to completion (NO_3^- source depleted), or some combination of these factors. Highly enriched $\delta^{15}N[NO_3^-]$ yielding elevated $\delta^{15}N[N_2]$ could have resulted from a depleted NO_3^- source even though NO_3^--N was 1.2 mg L^{-1} in August 2010, if a pool of NO_3^-, perhaps in anoxic microsites, had been depleted. The August 2010 sample is reflective of denitrification considering NO_3^-/Cl^- ratios indicated a 45% NO_3^- loss. Given the aerobic conditions in groundwater and the biogenic gas trends noted in the unsaturated zone, these trends in groundwater isotopic composition and N_2 concentrations reflect biogeochemical processes occurring in the BAM layer.

3.3.2.3. Stable isotopes and carbon cycling. The C cycle is generally closely linked with the N cycle because denitrification is commonly mediated by heterotrophic bacteria. Thus stable C isotopes were examined to better understand how BAM influenced these linked biogeochemical cycles. The $\delta^{13}C[DOC]$ data indicate that DOC is derived from the decomposition of vegetation at land surface and in the shallow soil zone. Typical $\delta^{13}C$ values for vegetation using the Calvin (C_3) photosynthetic pathway to fix atmospheric CO_2 into OC (plant biomass) are −24 to −30‰ (Clark and Fritz, 1997). The C_3 pathway dominates in most terrestrial ecosystems. The $\delta^{13}C[DOC]$ values for all stormwater, soil water, and groundwater samples (only post-BAM samples collected) fall within this range, varying from −25.0 to −27.9‰ (data not shown). These results are consistent with the overland runoff in a residential area where the predominant OC source is a vegetative material from which DOC leaches during contact with stormwater. Additionally, DOC likely is acquired by contact with herbaceous vegetation (both living and dead) in the stormwater basin and during percolation through the topsoil layer and root zone, resulting in DOC concentrations of 1.2–4.4 mg L^{-1} in stormwater and soil water after construction of the nutrient reduction basin (Fig. 3a,d). Substantial solid-phase organic matter in the topsoil layer is indicated by soil solid OC contents exceeding 20,000 mg kg^{-1} (Supplemental Fig. S4, Supplemental Table S1), which is consistent with water extractable TC contents in the topsoil layer substantially higher than underlying layers (Supplemental Fig. S5, Supplemental Table S2). Oxidation of this plant derived OC, comprising DOC and soil organic matter, is suggested by $\delta^{13}C[DIC]$ results (Fig. 8). DIC comprises dissolved CO_2 and alkalinity, which for the pH values of shallow groundwater (Fig. 4e) is predominantly HCO_3^-. In March 2010, alkalinity began increasing steadily and $\delta^{13}C[DIC]$ began decreasing (Fig. 8). This is consistent with microbially mediated oxidation of OC to DIC (CO_2 and HCO_3^-), because DIC of biogenic origin will be depleted in ^{13}C resulting in more negative values of $\delta^{13}C[DIC]$ (Li et al., 2005). This oxidation of OC is coupled with O_2 reduction given the aerobic conditions in the unsaturated zone, but in anoxic microsites OC oxidation is coupled with NO_3^- reduction by denitrification as suggested by soil gas data. These results suggest that the BAM layer was receiving DOC from the surface and topsoil layer, where cycling of N (denitrification) and C (associated with O_2 reduction and heterotrophic denitrification) was occurring.

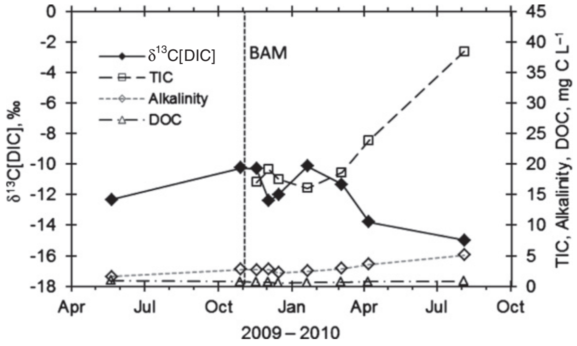

Fig. 8. Temporal variations in groundwater beneath the stormwater infiltration basin (well M-0506) of $\delta^{13}C$ of dissolved inorganic carbon (DIC), total inorganic carbon (TIC), alkalinity, and dissolved organic carbon (DOC) before and after placement of biosorption activated media (BAM).

3.3.2.4. Denitrifier activity. Results of the qPCR analyses indicate the presence of denitrifying bacteria inferred from *nirK* gene density, confirming the "activated" nature of BAM. Two sets of soil samples for qPCR analysis were collected prior to construction of the nutrient reduction basin in 2009; after construction, three sets were collected in 2010 and two sets were collected in 2011 for further confirmation (Supplemental Table S3). Denitrifier activity was somewhat lower after construction at similar soil depths (Fig. 9), but this is expected due to the disruption of construction and the time required for microbial acclimation and growth as well as possible natural spatial and temporal variations. Because of the markedly different soil environments before and after construction and the limited number of samples, it is more appropriate to note the change in denitrifier activity only after BAM was added. Denitrifiers were concentrated in the BAM layer, indicating the innovative basin design incorporating BAM can produce conditions conducive to the growth of denitrifiers that possess the *nirK* gene. Furthermore, denitrifier density has increased, starting at 3.6×10^4 gene copies g^{-1} in the BAM mixed and

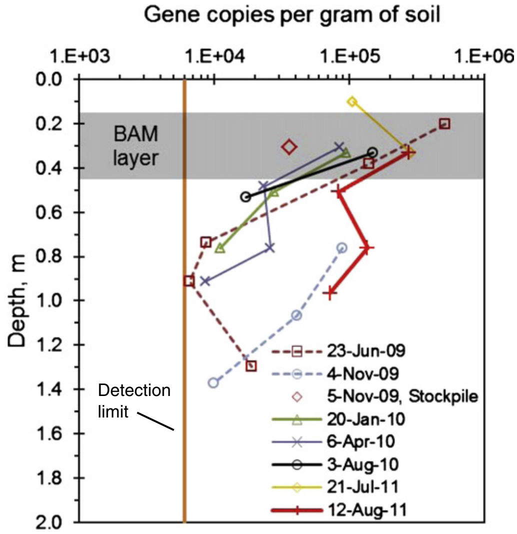

Fig. 9. Denitrifier activity inferred from copper containing nitrite reductase (*nirK*) gene density measured by qPCR before and after placement of biosorption activated media (BAM). See Supplemental Table S3 for data values.

stockpiled onsite (4 November 2009 sample) before placement in the ground to 1.5×10^5 gene copies g^{-1} in August 2010 (Fig. 9; average of replicates for 3 August 2010 sample in Supplemental Table S3), suggesting denitrifiers were acclimating to the new environment. This increase in denitrifier activity occurred during the post-BAM period and is consistent with previously discussed chemical evidence for denitrification. Samples collected in the summer of 2011 indicate further increases in denitrifier abundance, suggesting continued functioning of the BAM layer to provide conditions conducive for denitrifier growth (Fig. 9).

3.3.2.5. Other nitrogen transformation processes. Observed decreases in NO_3^- beneath the nutrient reduction basin, exclusive of those attributable to conservative processes inferred from NO_3^-/Cl^- ratios (Fig. 5), could be caused not only by denitrification, but also by microbial assimilation, plant uptake, DNRA, or some combinations of these processes. Both microbial assimilation and vascular plant uptake can impart N fractionations, averaging −0.52‰ and −0.25‰, respectively (Kendall and Aravena, 2000). These fractionations are similar to the slight enrichments over time observed in $\delta^{15}N[NO_3^-]$ in the groundwater beneath the basin (Fig. 6a). However, post-BAM lysimeter samples analyzed for $\delta^{15}N[NO_3^-]$ indicate much larger enrichments with depth, with values ranging from −3.7‰ to 8.9‰, averaging −2.2‰ at 0.5-m depth, 0.37‰ at 0.9-m depth, and 4.8‰ at 1.3-m depth. These results indicate that microbial assimilation and plant uptake are relatively minor and denitrification in the unsaturated zone is the more important cause of nonconservative NO_3^- variations, which is consistent with other water chemistry and soil gas data. Additionally, Rivett et al. (2008) report that microbial assimilation generally is not a major sink for NO_3^- relative to denitrification in the subsurface, and visual observation of vegetation growth within the stormwater infiltration basin throughout the study suggests that plant uptake was not substantially different before than after construction of the nutrient reduction basin even though NO_3^-/Cl^- ratios indicate a substantial change in nonconservative NO_3^- variations. However, possible DNRA is indicated by soil samples collected from the BAM layer with KCl extractable NH_4^+ of 5.9 mg kg^{-1} in August 2010, which is approximately four times greater than BAM samples collected in January and March 2010 (Supplemental Fig. S5, Supplemental Table S2). Under such dynamic conditions of rapid infiltration beneath the stormwater basin, observed NO_3^- concentrations in the shallow groundwater are related to the intensity and duration of denitrification and DNRA and mixing ratios with water that has undergone little biogeochemical transformation.

3.4. Phosphorus transport and fate before and after BAM application

In soil water, P concentrations (both TDP and PO_4^{3-}) indicate generally downward trends throughout the entire monitoring period, although notable decreases occur shortly after construction of the nutrient reduction basin (Fig. 4a–c). Comparison of median concentrations in soil water indicates 70–90% reductions in TDP from pre-BAM to post-BAM periods. Decreases in P concentrations are due to conservative mixing, sorption, precipitation, microbial assimilation, or some combination of these processes. However, the lowest P concentrations consistently occurred in the 0.5 m deep lysimeter, which spans the lower portion of the BAM layer and the entire coarse sand layer, suggesting reaction-based P losses in the BAM layer where NO_3^- reduction also was identified. The reductions in TDP and PO_4^{3-} not only are consistent with P sorption attributable to tire crumb (Hossain et al., 2010) and clay (Chang et al., 2010a; Harris et al., 1996), which are components of BAM, but also may be partly caused by lower P concentrations in the stormwater during this period (Fig. 4d).

In groundwater, P concentration trends are less apparent, but were slightly upward prior to BAM and slightly downward after BAM. TDP and PO_4^{3-} were consistently lower in well M-0506 (Fig. 4e) than in lysimeters (Fig. 4a–c) during the pre-BAM period, suggesting that some P was removed naturally by the native sediments that become substantially finer in texture (from <5% to >40% silt + clay contents) at a depth of approximately 1.6 m. However, during the post-BAM period, TDP and PO_4^{3-} were generally higher in well M-0506 than in lysimeters, consistent with inferred P losses in the BAM layer. PO_4^{3-}/Cl^- ratios were examined to elucidate PO_4^{3-} variations attributable to the net effects of reaction-based processes and source inputs using the methodology applied for NO_3^- described in Section 3.3.1 and Eqs. (1–3). PO_4^{3-}/Cl^- ratios (Fig. 10a) show similar trends to NO_3^-/Cl^- ratios (Fig. 5a). Reconstructed concentrations indicate larger PO_4^{3-} increases (1–180%) and only one sample indicating a PO_4^{3-} loss prior to the addition of BAM, and after the addition of BAM smaller increases (6–18%) occurred with four samples indicating PO_4^{3-} losses (Fig. 10b). The August 2010 sample indicated an increase in PO_4^{3-} considerably less than that expected based on the Cl^- increase, yielding a change of −50% (Fig. 10b), which is comparable to the NO_3^- loss during the same period (Fig. 5b). This indicates that in the absence of any PO_4^{3-} reaction or input decrease, the PO_4^{3-}–P concentration would have been 0.11 mg L^{-1} rather than 0.054 mg L^{-1}, suggesting half was lost. An increase in PO_4^{3-} input is expected due to the fertilizer application in residential landscapes commonly conducted at the start of the growing season in late spring to early summer, coinciding with NO_3^- increases (Fig. 5b), and thus the large decrease is reaction based. Difference in P concentrations between the unsaturated zone and shallow groundwater may be the result of the intensity and duration of reaction processes and mixing ratios with water that had not undergone significant chemical changes.

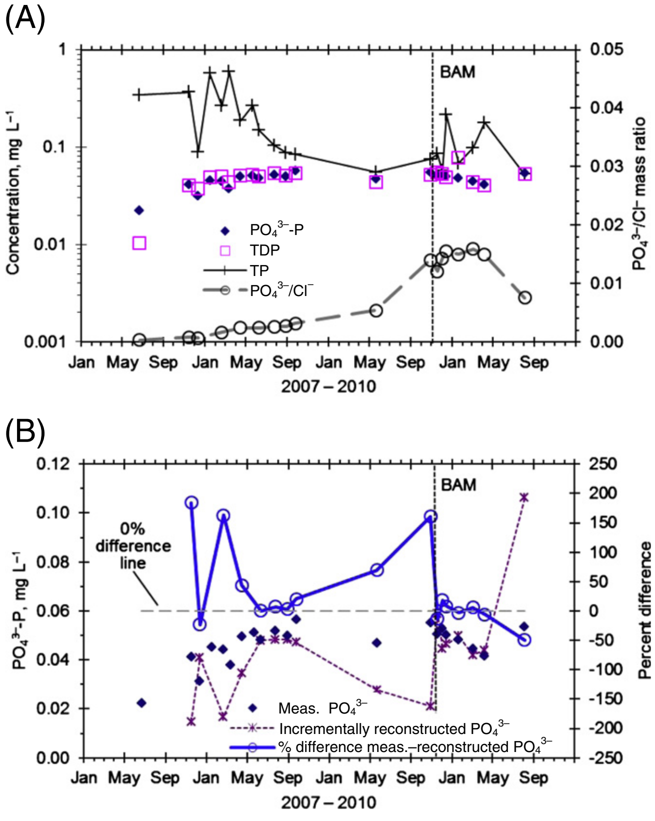

Fig. 10. PO_4^{3-} P variations in groundwater beneath the stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM): (A) comparison of PO_4^{3-} P, total phosphorus (TP), total dissolved phosphorus (TDP), and Cl^- concentrations; and (B) incrementally reconstructed PO_4^{3-} P and the incremental percentage differences assumed to be attributable to PO_4^{3-} reactions or PO_4^{3-} input variations.

3.5. Nutrient reduction strategies using BAM

In a functionalized soil amendment each component of the amendment mixture possesses particular functional characteristics to improve attenuation of a pollutant of concern in a specific environmental setting (Wanielista and Chang, 2008). For BAM, the functional characteristics and related markers are abiotic nutrient retention (fostered by tire crumb and clay content) and biological nutrient removal (fostered by soil texture). Given that the initial full-scale field application described herein constitutes a prototype application of BAM, detailed identification of nutrient reduction processes and rates as quantitatively related to BAM composition is limited.

Other applications of BAM might yield different results depending on site-specific nutrient concentrations. Relative to other sources such as septic tanks, secondary treated wastewater, or agricultural drainage, urban stormwater runoff typically is relatively dilute with respect to nutrient concentrations. Median concentrations reported for stormwater runoff in urban areas include TN and TDN of 1.80 and 1.15 mg L^{-1}, respectively (Taylor et al., 2005); NO_x–N of 0.35–1.1 mg L^{-1} (Clark and Pitt, 2007; Göbel et al., 2007; Taylor et al., 2005); and TP of 0.09–0.29 mg L^{-1} (Clark and Pitt, 2007; Göbel et al., 2007), and TDP of 0.13 mg L^{-1} (Clark and Pitt, 2007). These concentrations are comparable to values measured in this study (Figs. 3d and 4d), indicating good potential for transferability of results for other stormwater treatment applications. Several general guidelines for BAM design and implementation, based on the physicochemical and biogeochemical effects described below, can be derived.

3.5.1. Physicochemical effects of tire crumb and clay in BAM

The nutrient retention potential of tire crumb (Hossain et al., 2010) and clay (Chang et al., 2010a) contributes to the sorption properties of BAM. Sorption of nutrient species controls biogeochemical processes by retarding or immobilizing ions, such as NO_3^-, NH_4^+, and PO_4^{3-}, providing additional time for biological processes to facilitate removal. For an amendment mixture containing 15% tire crumb and an assumed stormwater filtration application, Hossain et al. (2010) reported that abiotic processes yield a life expectancy of about 16 years for TDP and PO_4^{3-}removal, whereas life expectancy for NO_3^- removal was 2.1 years and only 0.24 years for NH_4^+ removal. Thus, for BAM, physicochemical processes are expected to be more effective for P removal and biological processes for N removal. The silt and clay contents of BAM are provided by incorporation of clayey sand (72% sand, 4% silt, and 24% clay by weight). Mineralogical identification of the silt and clay fractions by X-ray diffraction indicated that the silt fraction is predominantly quartz and wavellite with smaller quantities of kaolinite and crandallite, and the clay fraction is predominantly smectite and kaolinite with smaller quantities of quartz, mica, and crandallite. Harris et al. (1996) noted the importance of clay mineralogy for P sorption when occurring as coatings on quartz grains (soils ranging from 0.6% to 7.3% silt + clay). Kaolinite may be the clay mineral in BAM most likely to contribute to P retention (Parfitt, 1979), although noncrystalline metal oxides, such as those of Al or Fe, are particularly effective anion sorbents (Pachepsky et al., 1994). Extractions for Al or Fe oxides were not performed, but analyses for the total Al and Fe contents of BAM indicate 29,200 and 10,000 mg kg^{-1}, respectively (see Supplemental Information). These large values suggest that some fraction may be composed of noncrystalline Al and Fe oxides. Smectite, although having relatively little affinity for P, contributed substantially to the measured CEC of 10 $cmol_c$ kg^{-1} for the bulk clayey sand sample. CEC of a tire crumb sample was only 1 $cmol_c$ kg^{-1}; for BAM samples collected from three locations, CEC varied 0.8–4 $cmol_c$ kg^{-1} probably due to natural heterogeneity. Soil chemistry data indicate NH_4^+ sorption in the BAM layer, especially for the August 2010 sample (5.9 mg N kg^{-1}, Supplemental Fig. S5, Supplemental Table S2), and even a modest CEC of 1 $cmol_c$ kg^{-1} represents a sorption potential for NH_4^+ of 140 mg N L^{-1}. It is important to note that the CEC complex is readily exchangeable by other hydrated cations. This complex is maintained by relatively weak electrostatic forces and would not include cations sorbed hysteretically or irreversibly as by surface complexation reactions. These physicochemical effects noted in previous studies and observed in the field study described herein indicate that BAM should include a tire crumb component of about 15% (by volume) and a clay mineral component possessing high Al and Fe oxide contents and CEC to promote physicochemical nutrient attenuation. The clay percentage of BAM significantly affects its textural properties, and a recommended percentage is best derived from an assessment of the effects of BAM texture on biogeochemical cycling.

3.5.2. Biogeochemical effects of BAM texture

During a comparative study of biogeochemical processes beneath the Hunter's Trace stormwater infiltration basin (prior to construction of the nutrient reduction basin) and a stormwater infiltration basin in the nearby South Oak watershed (Fig. 1a), O'Reilly et al. (2012b) demonstrated that soil texture controls moisture retention capacity, which in turn controls subsurface O_2 transport, which in turn controls denitrification and other biogeochemical processes. Therefore, moisture content as controlled by texture may be the single most important functional characteristic of BAM, and the SMRC can be used to assess

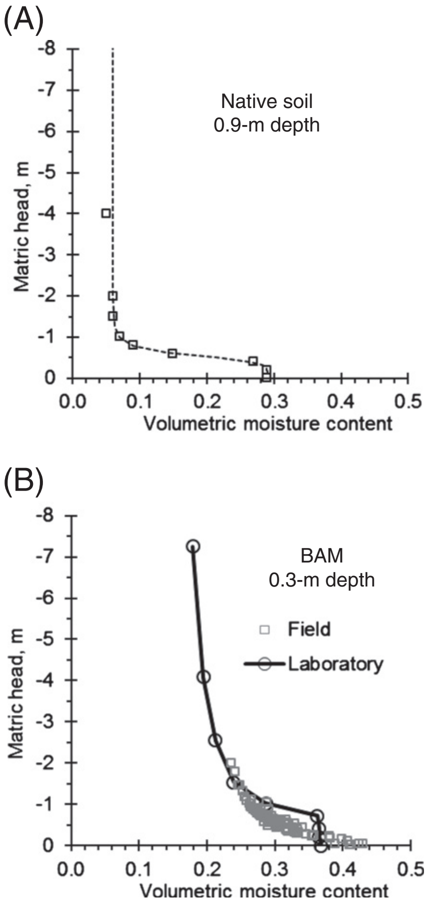

Fig. 11. Soil moisture retention curves for (A) native soil 0.9 m beneath the stormwater infiltration basin (data for 0.3- and 0.6-m depths were nearly identical), and (B) biosorption activated media. Laboratory derived soil moisture retention curves were measured for the main drying curve on undisturbed soil cores using the pressure cell method (Dane and Hopmans, 2002; Naujock, 2008). For the native soil samples, undisturbed cores were used. For the BAM sample, a laboratory packed sample was used consisting of a slightly different mixture (1.1:2.2:3.7 mixture (by volume) of tire crumb, silt + clay, and sand) than that used for the innovative stormwater infiltration basin. Field measurements were obtained by continuous monitoring beneath the nutrient reduction basin using time domain reflectometry and tensiometers.

this characteristic. A laboratory derived SMRC for a BAM mixture similar to that used at the nutrient reduction basin (consisting of a 1.1:2.2:3.7 mixture (by volume) of tire crumb, silt + clay, and sand) (Fig. 11b) demonstrates the greater moisture retention capacity of BAM over the native soil at the basin (Fig. 11a), which is directly attributable to the silt + clay content of BAM. A field-estimated SMRC (Fig. 11b) was derived using matric head computed from tensiometer measurements and volumetric moisture content measured by TDR probes at 0.3 m depth (within the BAM layer), showing behavior under typical hydroclimatic conditions. The BAM layer retains substantially more water than the native sandy soil after gravity drainage effectively ceases. For the BAM layer, field capacity (approximated as the volumetric moisture content at a matric head of −2 m) was 0.24 (Fig. 11b) indicating a saturation of 49%; whereas for the native sandy soil in the original basin, field capacity was 0.07 (Fig. 11a) indicating a saturation of 24%. Compared to the laboratory derived SMRC, higher field measured moisture contents at low matric heads (0 to −0.25 m) and lower field measured moisture contents at higher matric heads (−0.25 to −1.25 m) are likely caused by macropore structure. The macropore structure of BAM is attributable to the presence of natural silt and clay aggregates in the clayey sand component of BAM, which were resistant to disaggregation during mixing onsite (with the tire crumb and sand components) and during placement in the ground (compacted by repeated passes with a bulldozer). Macropores were evident by visual observation of undisturbed soil cores collected from the BAM layer, whereas macropores were not present in laboratory samples of BAM that were dried and aggregates broken by mortar and pestle prior to mixing and packing. Macropores form preferential flow paths (Arora et al., 2011) that enable infiltrating water to bypass biogeochemically active areas (Baram et al., 2012; O'Reilly et al., 2012a); this phenomenon negatively impacted BAM nutrient removal performance.

Denitrification will terminate in the release of N_2 rather than N_2O at soil saturations exceeding 70% (Bateman and Baggs, 2005) to 90% (Smith et al., 1998). De Klein and van Logtestijn (1996) and Sexstone et al. (1988) confirm the importance of soil texture, reporting a strong effect of soil moisture on increasing denitrification in fine-textured soil where small increases in moisture content can fill narrow pore spaces and saturate soil aggregates. The BAM layer saturations ranged from 38% to 95%, with 50th and 90th percentiles of 61% and 84%, respectively, and were nearly always greater than the 49% field capacity saturation (5th percentile). These results suggest that denitrification in the BAM layer usually did not progress to N_2, which is consistent with the limited excess N_2 detected. Higher saturations likely would have promoted N_2O reduction to N_2 in the unsaturated zone, mitigating potential greenhouse gas concerns and permanently removing reactive N from the subsurface. Therefore, the silt + clay content of about 25% (by volume) in the BAM mixture used in the nutrient reduction basin probably represents the minimum value that is adequate for increasing the fraction of saturated pore space to promote anoxic microsites that may serve as hotspots for denitrification.

The fine-grained texture of BAM also provides a large surface area per volume of soil for biofilm development. Although, due to the physical size of bacteria (typically 1 μm), pore size limitation of very fine grained sediments can inhibit biofilm development (Rivett et al., 2008). The incorporation of sand (>0.075 mm diameter) and tire crumb (~1 mm diameter) in BAM yields an amendment mixture where 80% of the particles have effective diameters greater than 75 μm (Supplemental Fig. S3). As a result, BAM likely contains a large proportion of pore sizes greater than 50 μm, a pore size that Seiler and Vomberg (2005) report to be large enough for biofilm formation in a carbonate rock matrix suspected to be the location of denitrification microsites. O'Reilly et al. (2012b) report high denitrifier activity and other corroborating evidence indicating active denitrification for soils having median silt + clay contents of 41%. Therefore, for the conditions reported in this work, a BAM mixture containing a maximum 50% (by volume) silt + clay content probably is most amenable to denitrifier growth.

3.5.3. Carbon cycling effects on denitrification in BAM

The C cycle affects O_2 levels in the subsurface, because DOC oxidation is coupled with O_2 reduction. As a result, the C cycle affects heterotrophic denitrification directly by potentially limiting substrate availability and indirectly by promoting anoxic conditions required to switch the facultative metabolism of denitrifiers from O_2 to NO_3^- respiration. Assuming CH_2O as a simplified representation of DOC, stoichiometry indicates that 1 mg L^{-1} DOC is oxidized to reduce 2.7 mg L^{-1} O_2 (O'Reilly et al., 2012a). Average DOC concentrations in stormwater and groundwater (well M-0506) were 8.3 and 0.74 mg L^{-1}, respectively; whereas average DO concentrations in stormwater and groundwater were 7.0 and 6.1 mg L^{-1}, respectively (Fig. 3d,e). These results suggest that surface/subsurface O_2 exchange was supporting the oxidation of DOC in the unsaturated zone, thus demonstrating the importance of maintaining high soil moisture contents to mitigate this gas exchange. Reduced surface/subsurface O_2 exchange not only promotes the development of anoxic conditions but also prevents the complete aerobic oxidation of DOC, preserving it for use during heterotrophic denitrification. According to denitrification stoichiometry, 1 mg L^{-1} DOC is oxidized to reduce 0.93 mg L^{-1} NO_3^-–N to N_2 (O'Reilly et al., 2012a). For the highest NO_3^-–N recorded (7.23 mg L^{-1} in the 0.9-m lysimeter, Fig. 3b), a minimum of 7.77 mg L^{-1} DOC would be required for complete denitrification, which is more than the measured DOC concentrations in stormwater (Fig. 3d). Therefore, an additional source of OC is needed. The OC content of BAM (18,000 mg kg^{-1}; see Supplemental Information) is higher than other soil layers, except the topsoil layer. The OC in BAM is primarily attributable to the tire crumb, but the bioavailability of the OC content of tire crumb is unknown. DOC supplied to the BAM layer by infiltrating stormwater likely is supplemented by leaching from root growth and C cycling in the overlying topsoil layer, where soil solid OC contents are high (exceeding 20,000 mg kg^{-1}; Supplemental Table S1). Organic matter present in stormwater and in the topsoil layer and natural C cycling indicated by stable C isotopes (Fig. 8) suggests that the innovative basin design promotes a passive, low maintenance, self-sustaining treatment system. This too supports a green infrastructure as DOC is at least partly provided by photosynthetic fixing of CO_2 by herbaceous vegetation in the stormwater basin.

4. Conclusions

A stormwater infiltration basin that under its current design was leaching N and P into the subsurface was modified using an innovative design integrating sub-basins for nutrient reduction and flood control. In the nutrient reduction basin, the functionalized soil amendment BAM was incorporated to mitigate nutrient impacts on groundwater resources. A full-scale application of this technology for regional stormwater infiltration basins serving watersheds >20 ha, such as described in this work, has received little or no attention. The new integrated design preserves the needed flood control capacity of the basin by providing sufficient storage and infiltration of runoff to contain at least the 100-year rain event based on the runoff/water-balance model and field monitored infiltration rates. Under normal rainfall conditions, an 88% treatment volume is achieved in the nutrient reduction basin.

Biogeochemical assessment of this full-scale field application of BAM in an innovative stormwater infiltration basin demonstrated increased removal of NO_3^-, TDP, and PO_4^{3-} before infiltrating stormwater entered the groundwater. Examination of previous studies and physicochemical and biogeochemical effects observed during the present study indicate that key BAM properties are a 15% by volume component of tire crumb and a 25–50% by volume component of fine-textured (silt + clay) soil, with the balance consisting of sand. Both the high moisture retention capacity of BAM and the new integrated design incorporating a nutrient reduction basin with a greater frequency of stormwater storage contribute to conditions more favorable for formation of anoxic conditions within microsites in the BAM layer that enable the progression of biogeochemical processes toward denitrification. BAM can also be applied in an off-line retention treatment system. BAM can be easily adapted to any retention system including underground retention, exfiltration systems, or swales.

Other benefits of BAM are support of green infrastructure and economical implementation. BAM incorporates naturally occurring soils, blending them with recycled materials (tire crumb). The process is also deemed economical as the materials and labor costs (in 2009) were only about $US 65 m^{-2} of basin bottom to construct the new integrated design incorporating BAM in the existing stormwater infiltration basin (Wanielista et al., 2011). This cost did not include profit or permit fees. There is minimal to no additional operation and maintenance cost, and operation, maintenance, and repairs are similar to those expected with existing stormwater infiltration basins.

While this preliminary assessment demonstrates that nutrient reduction is achieved using BAM for a relatively low cost, several areas exist where further research would be beneficial. Further hydrologic and water quality monitoring is needed to ascertain the long-term sustainability of the nutrient removal capabilities. Further research of BAM by both bench-scale laboratory testing and full-scale field testing—for example, application of conservative and isotopic tracers such as Br^- and ^{15}N labeled NO_3^-—is needed to elucidate the individual physical, chemical, and biological processes controlling the environmental effectiveness of BAM under various moisture retention conditions. Improved technology is needed to economically increase nutrient retention time in the BAM layer, while maintaining substantial treatment volume and flood control, and mitigate potential greenhouse gas emissions. Improvements to BAM may include reducing preferential flow macropores, increasing the sorption capacity, and reducing O_2 concentrations. Such additional research would promote future development and refinement of design guidelines for functionalized soil amendments, enabling applications under a wide range of environmental conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.05.083.

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