

THE EFFECTIVENESS OF BIOSORPTION ACTIVATED MEDIA (BAM) TO REDUCE NITRATE AND ORTHOPHOSPHATE IN STORMWATER RUNOFF

PART 2: Science, Engineering and Application

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A summary of published data primarily from O'Reilly, A.



OVERVIEW

- 3 ½ years of field data collection
- Analysis of biogeochemical cycling beneath two stormwater basins
- Design and construction using BAM
- Biogeochemical assessment of pre/post data at a retention basin using Biosorption Activated Media (BAM)
- Quantitative analysis of N budget and flux beneath a BMP retention basin using BAM

PARTNERS

- Marion County, Florida
- Florida Department of Environmental Protection
- Southwest Florida Water Management District
- St. Johns River Water Management District
- University of Central Florida
- U.S. Geological Survey
- University of Florida Soil and Water Science Department

HYPOTHESES

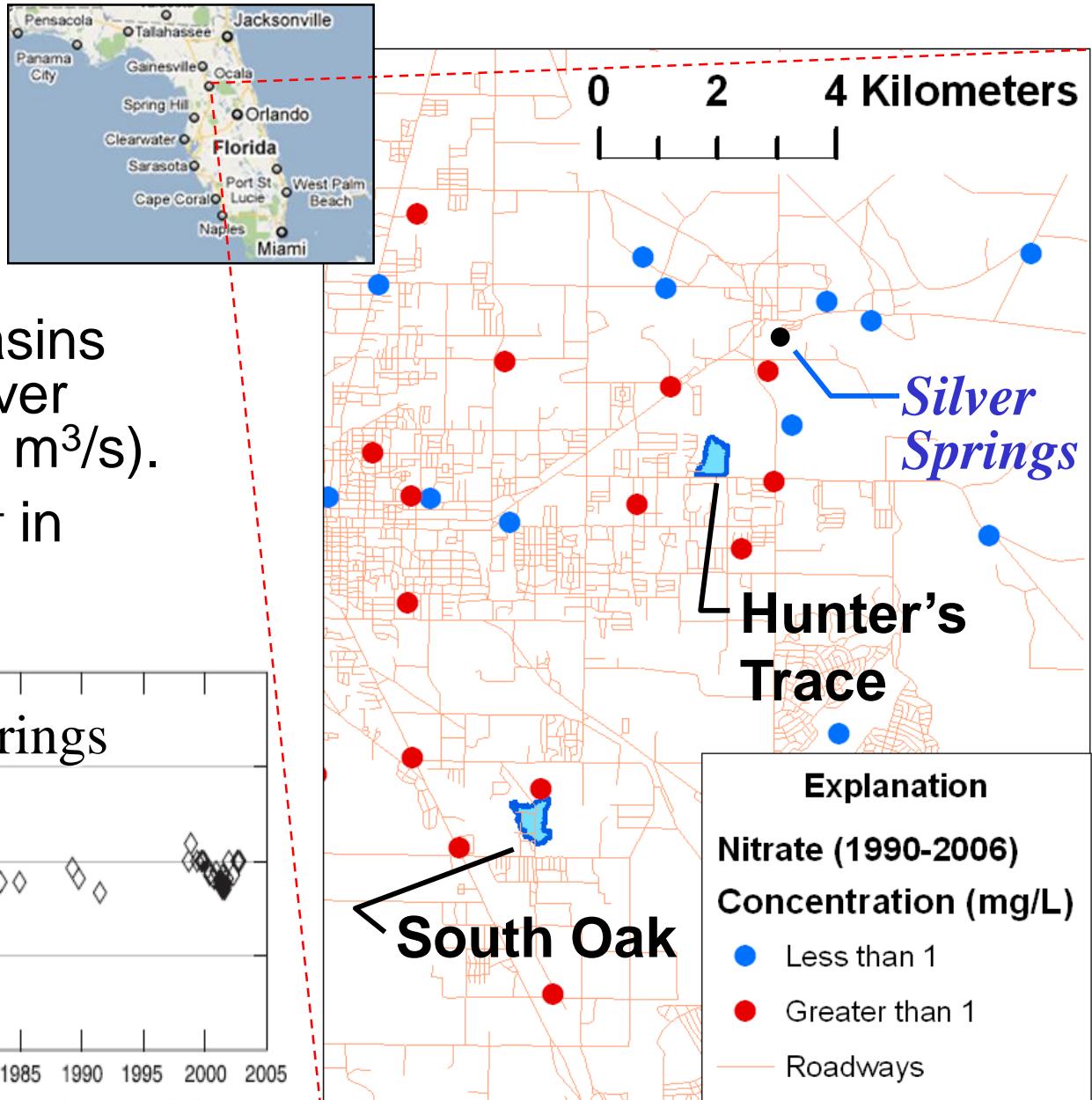
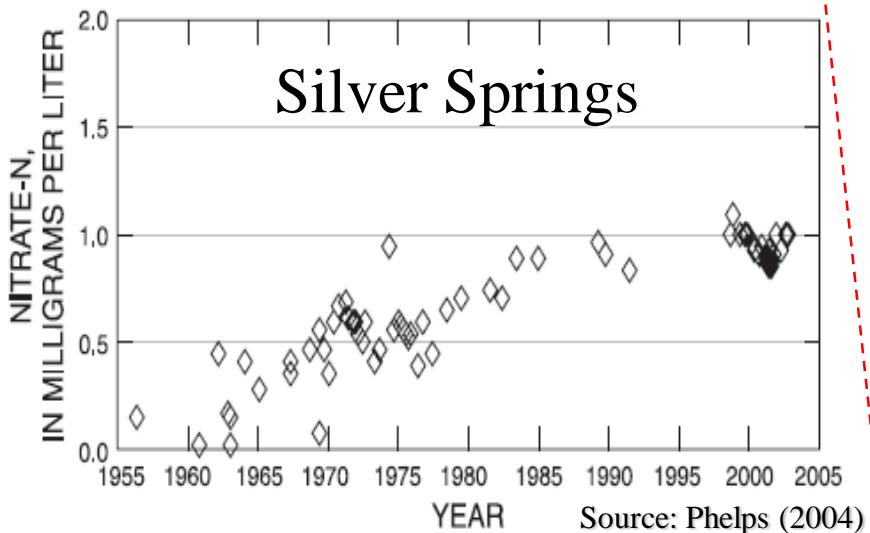
1. Soil texture controls surface/subsurface oxygen exchange, thereby controlling biogeochemical processes and N and C cycling.
2. Variations in hydrologic conditions result in cyclic biogeochemical processes, switching N fate from NO_3^- leaching to reduction and gas production.
3. Nutrient input into groundwater from stormwater basins can be reduced by implementing an infiltration BMP using biosorption activated media (BAM) that replicates natural biogeochemical processes.
4. N budget and fluxes beneath stormwater basins can be quantified using a system dynamics modeling approach.

PROBLEM

- Elevated NO_3^- concentrations are common in Florida groundwater, especially in sensitive karst areas.
- NO_3^- concentrations have increased in many Florida springs since the 1950s.
- Stormwater runoff is one source of N into the ground.
- Little research is available on *biogeochemical cycling* beneath stormwater infiltration basins on which to base new management strategies.

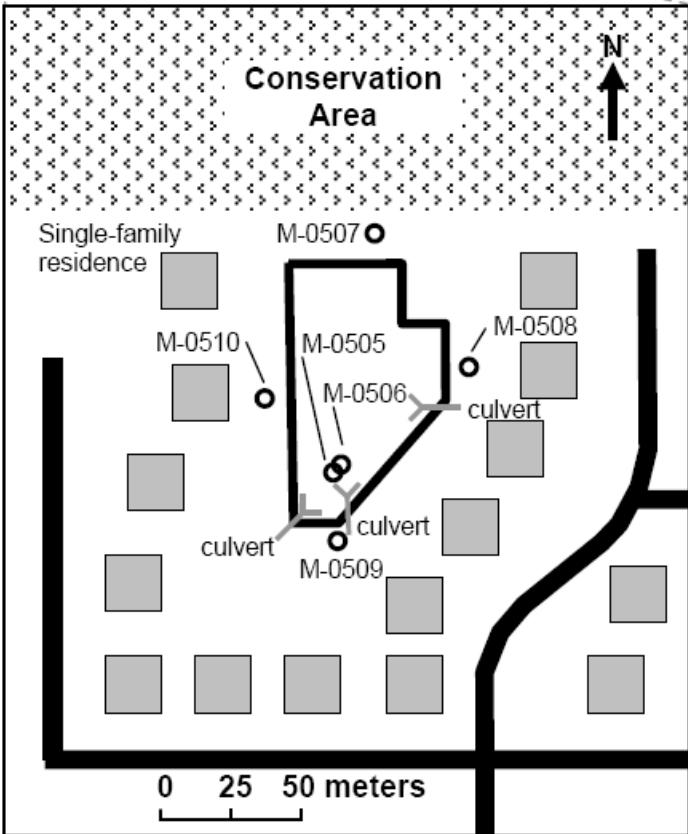
STUDY AREA

- 2 stormwater basins studied near Silver Springs ($Q = 22 \text{ m}^3/\text{s}$).
- Increasing NO_3^- in Silver Springs.



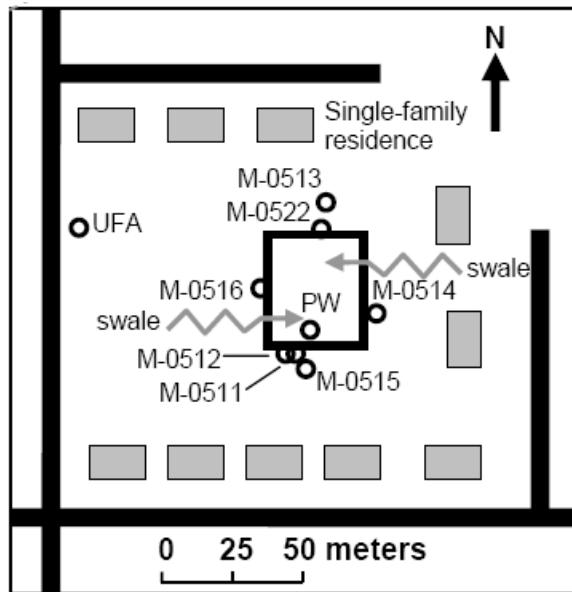
HUNTER'S TRACE BASIN

- 2800 m² basin
- 23 ha watershed
- Water table < 3 m below basin bottom
- Residential land use



SOUTH OAK BASIN

- 1600 m² basin
- 29 ha watershed
- Water table < 1 m below basin bottom
- Residential land use



WATER QUALITY MONITORING

- Major elements
- Nutrients (nitrogen and phosphorus)
- Organic carbon
- Trace metals
- Dissolved and soil gases
- Stable oxygen and hydrogen isotopes of water; and oxygen and nitrogen isotopes of nitrate and nitrogen gas
- Soil mineralogy and chemistry
- Nitrite reductase gene density by real-time polymerase chain reaction (RT-PCR)



HYDROLOGIC MONITORING

- Rainfall
- Basin (stored stormwater) stage
- Groundwater level
- Soil moisture content
- Soil temperature
- Soil matric potential (tensiometers)
- Soil moisture retention curves



HYPOTHESIS #1

- Soil texture controls surface/subsurface oxygen exchange, thereby controlling biogeochemical processes and N and C cycling.

SOILS and Moisture

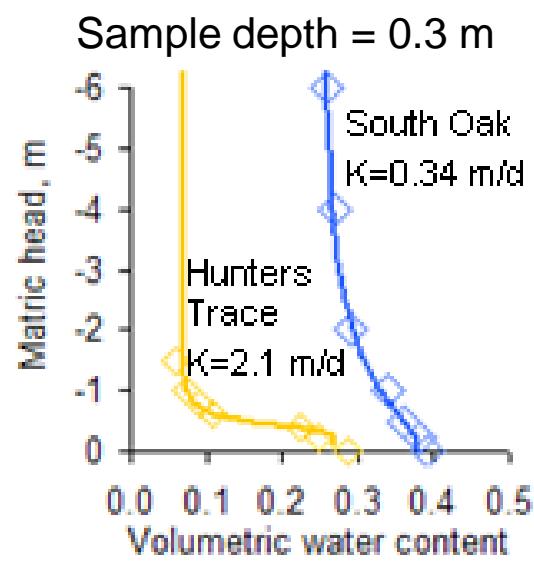
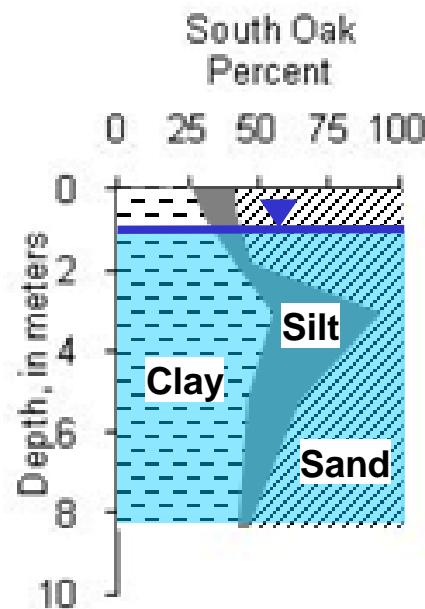
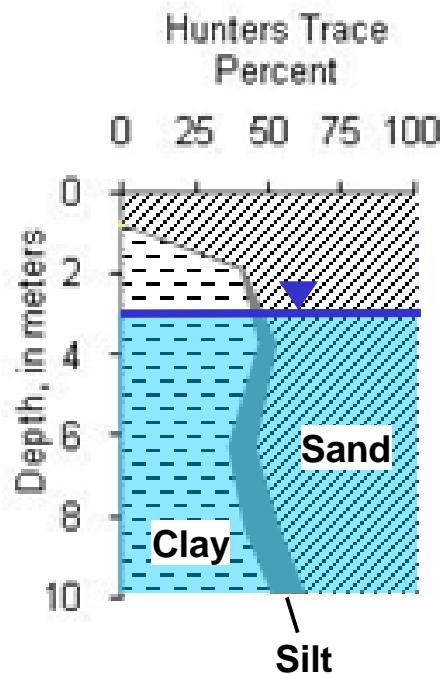
- At the SO basin, fine-textured soil causes higher soil moisture content, inhibiting O₂ diffusion into the subsurface.
- At the HT basin, coarse-textured soil causes lower soil moisture content, allowing O₂ diffusion into the subsurface.
- O₂ availability is a critical control for denitrification and other biogeochemical processes.

SITE COMPARISONS

Hunter's Trace (HT)	Parameter	South Oak (SO)
Deeper	Water Table	Shallower
Less	Silty/Clayey Soils	More
Lower	Cation Exchange Capacity	Higher
Higher	Infiltration Rate	Lower
Higher	Dissolved Oxygen	Lower
Lower	Alkalinity	Higher
Lower	Organic Carbon	Higher
Higher (median=2.2 mg/L)	Groundwater Nitrate	Lower (median=0.03 mg/L)
No	Nitrate Decline with Time	Yes

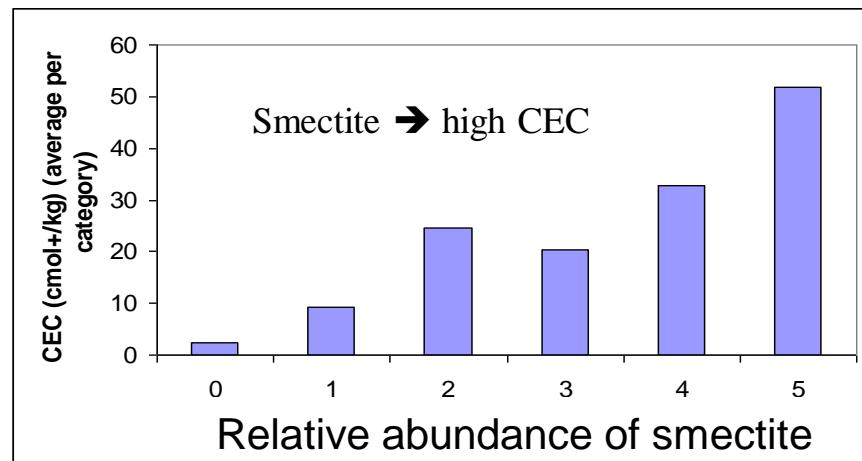
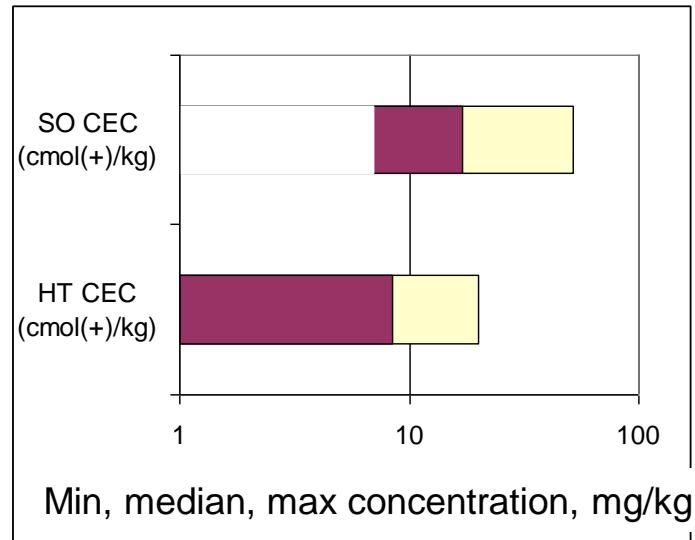
SOIL CHARACTERISTICS

- Textural differences contributed to large differences in the soil moisture retention curves.



SOIL ANALYSIS – Chemistry

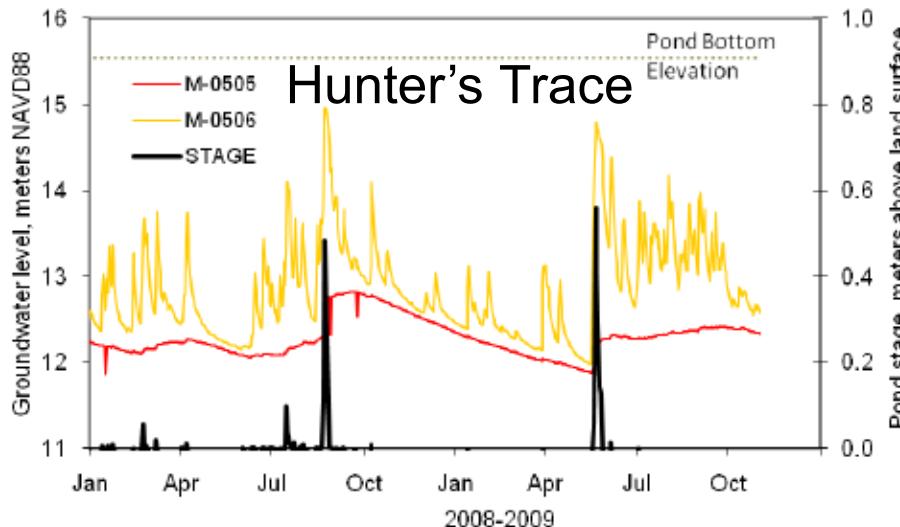
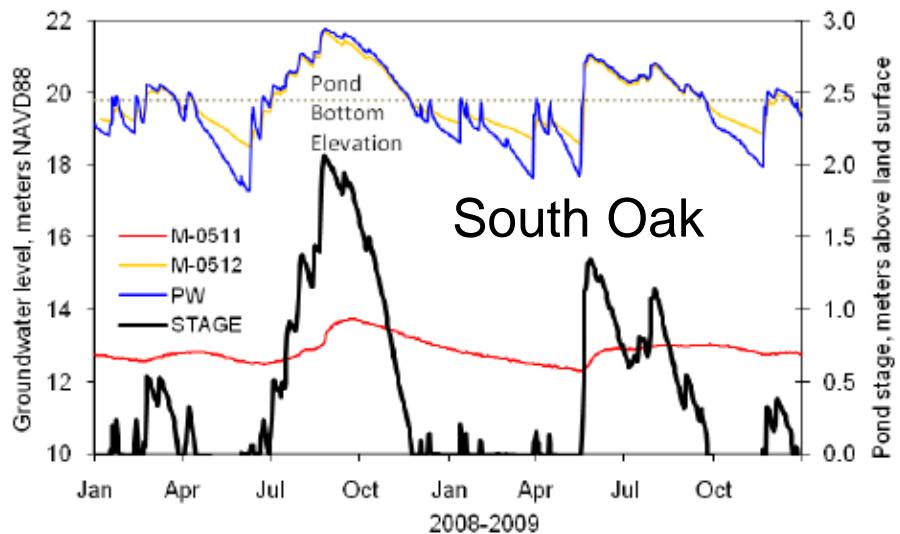
- CEC higher at South Oak
- Higher CEC than typical Florida soils, likely due to prevalence of clay mineral smectite



HYDROLOGIC CONDITIONS

Runoff & Infiltration

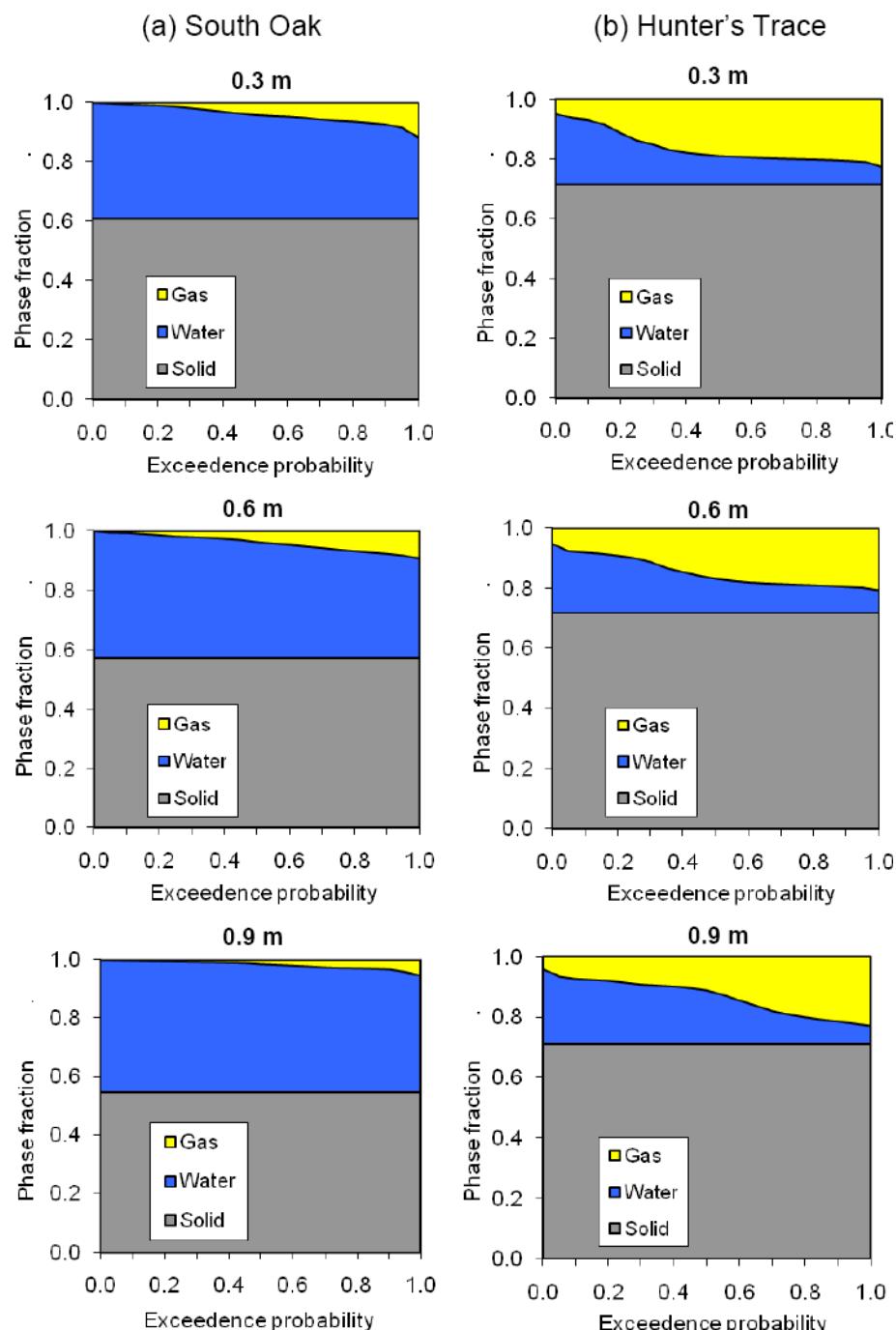
- Prolonged flooding of SO basin – infiltration rate 14–29 mm/d
- Intermittent flooding of HT basin – infiltration rate 170–260 mm/d
- Comparison of CN-estimated runoff, basin volume, and stage changes indicates 17% (SO basin) and 32% (HT basin) of runoff volume reaches infiltration basin for 155 mm storm (Tropical Storm Fay)



HYDROLOGIC CONDITIONS

Soil Moisture

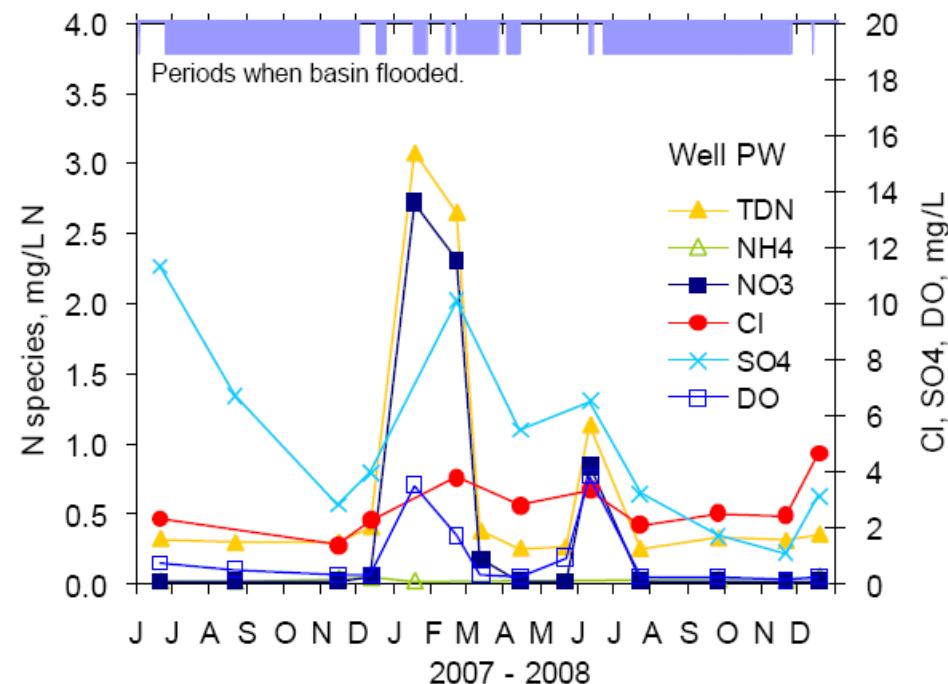
- Soil moisture data indicate soil stays wetter longer at the SO site compared to the HT site
- A substantial gas phase fraction is more conducive to O₂ diffusion and aerobic groundwater



GROUNDWATER QUALITY

South Oak basin

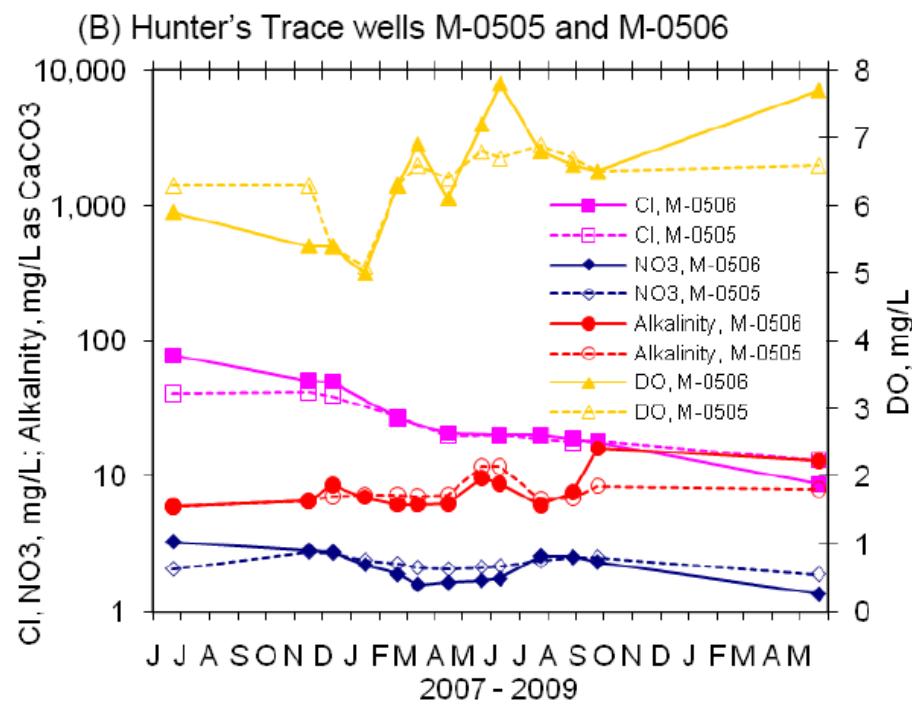
- N primarily in organic form when O_2 low and NO_3^- form when aerobic
- Typically low O_2 or anoxic
- GW DOC $\sim\frac{1}{2}$ of SW DOC
- Cl and NO_3^- variations dissimilar ($r^2 = 0.21$ for well PW) suggests ***reaction***-dominated N fate



GROUNDWATER QUALITY

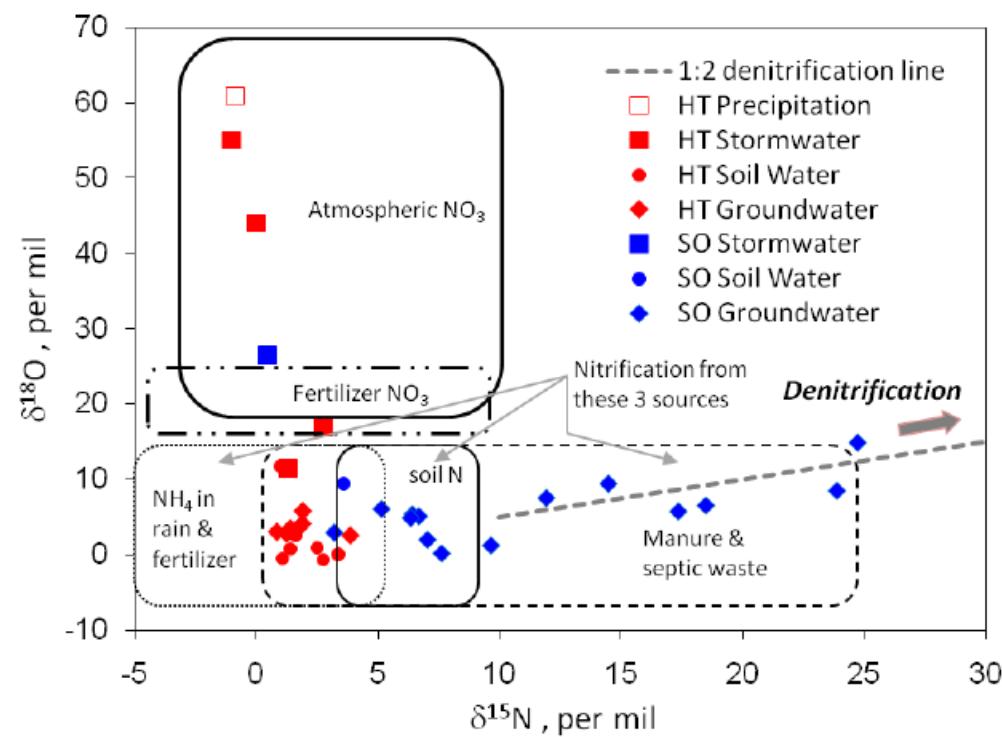
Hunter's Trace Basin

- N nearly exclusively in NO_3^- form
- Aerobic, DO 5–8 mg/L
- Low DOC 0.5–1.0 mg/l
- Cl and NO_3^- variations very similar ($r^2 = 0.64$ for M-0506) suggests **advection**-dominated N fate



NITRATE SOURCES, TRANSPORT, & FATE

- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- indicate various sources: atmospheric, fertilizer, and nitrification of soil N and rain/fertilizer NH_4^+
- At the SO basin, isotopic enrichment and excess N_2 .
- At the HT basin, no isotopic enrichment and no excess N_2 .



Outlines of typical nitrate source ranges
from Kendall and Aravena (2000)

DENITRIFICATION SUMMARY

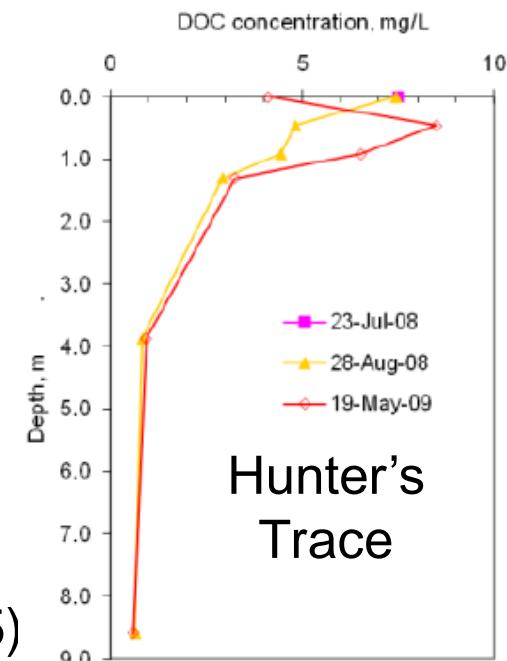
The four conditions required for denitrification are:

- (1) Nitrate present (electron acceptor);
- (2) Oxygen very low or absent;
- (3) Electron donor present (typically an organic carbon compound); and
- (4) Denitrifying bacteria present.

- Conditions 2, 3, and 4 exist at the SO basin, therefore when nitrate is present denitrification occurs rapidly.
- At the HT basin, data indicate condition 2 is the critical missing condition.
- Differing oxygen levels between the two basins likely are due to soil textural characteristics. The fine-textured soil at the SO basin retains moisture, thereby substantially *reducing oxygen transport* into the subsurface.

SURFACE/SUBSURFACE O₂ EXCHANGE

- Photosynthesis does not occur in the subsurface, O₂ can only be replenished by diffusion of atmospheric O₂ into the subsurface or by advective transport dissolved in infiltrating water.
- Soil moisture is important because O₂ diffusion through water is 10,000 times less than through air.
- Anoxic conditions will develop in the subsurface if (1) O₂ respiring micro/macro organisms are present, (2) sufficient organic matter is present, (3) water infiltrates more slowly, and (4) the soil stays wet.
- Differences in mean soil solid OC contents between the two basins are not statistically significant ($p > 0.5$)
- At the HT basin, sharp decreases in soil water DOC in the upper 1.3 m of soil with further decreases to less than 1 mg/L in groundwater suggest that O₂ is replenished more quickly than it can be reduced by organic matter oxidation

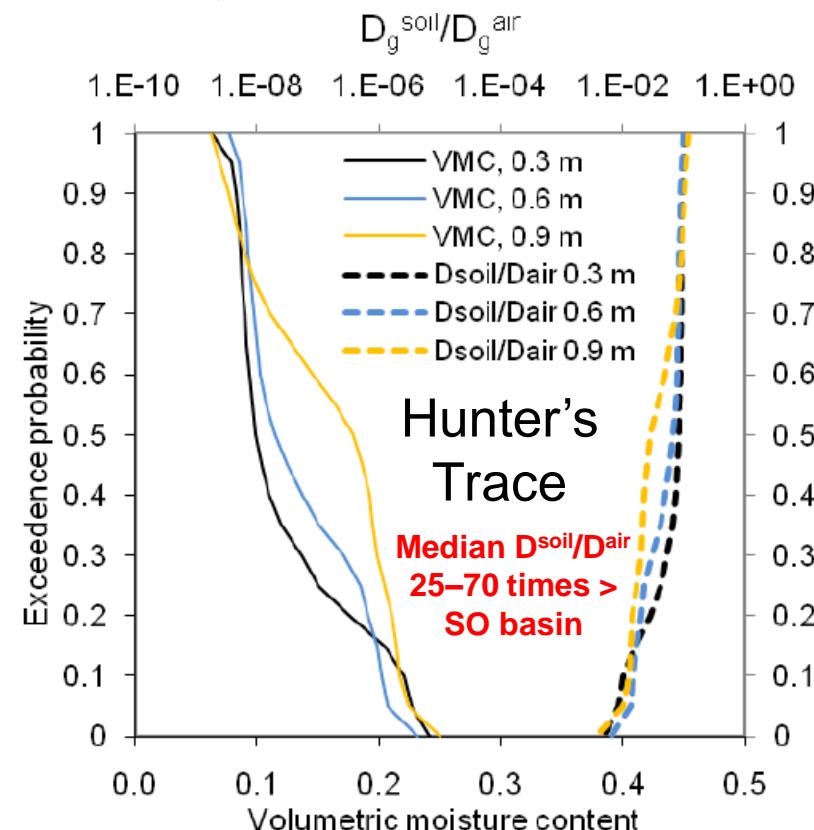
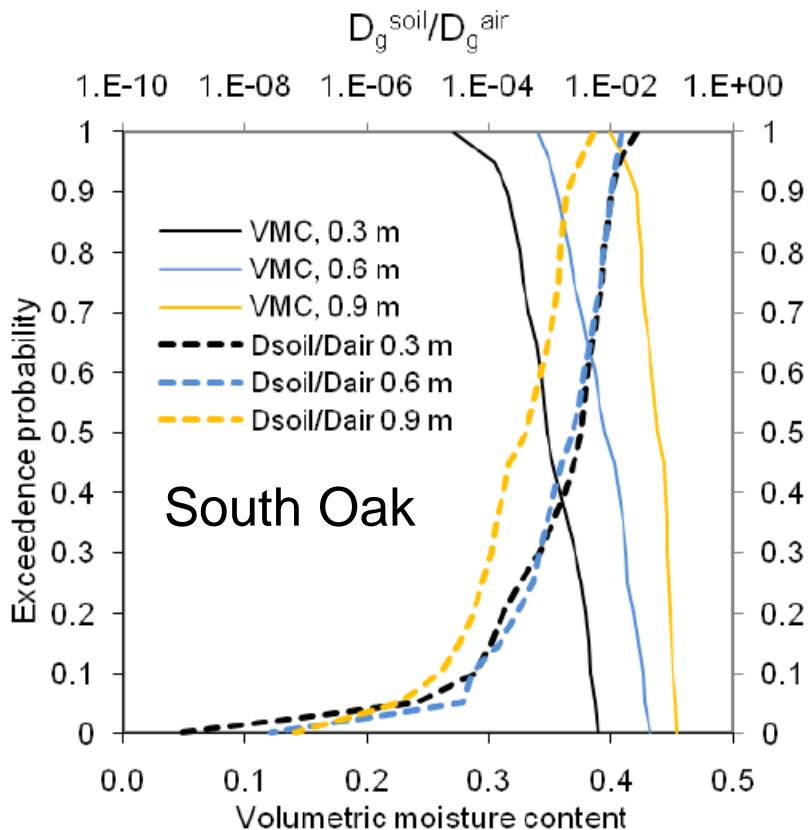


SURFACE/SUBSURFACE O₂ EXCHANGE

- O₂ diffusion in soil depends on porosity and moisture content

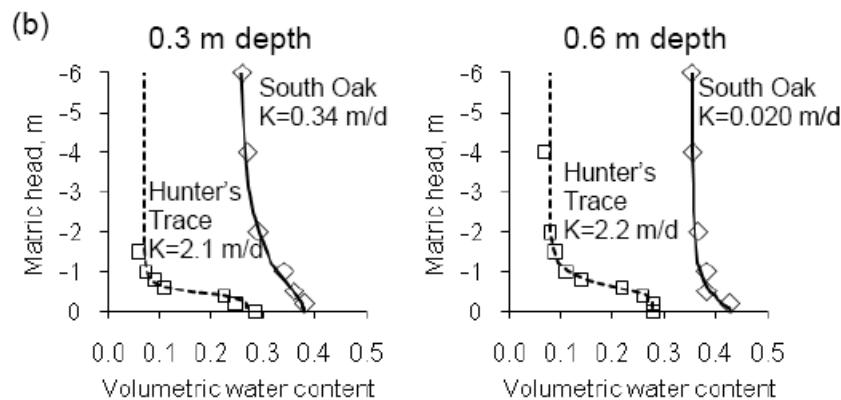
$$D_{g,i}^{soil} = \frac{\phi_g^2}{\phi^{2/3}} D_{g,i}^{air}$$

$D_{g,i}^{soil}$ is the diffusion coefficient of gas i through soil ($\text{cm}^2 \text{ d}^{-1}$), $D_{g,i}^{air}$ is the diffusion coefficient of gas i through air ($\text{cm}^2 \text{ d}^{-1}$), ϕ_g is the total volumetric gas-phase content (cm cm^{-1}), and ϕ is the volume fraction of soil pores (porosity) (cm cm^{-1}). Because $\phi_g = \phi - \phi_w$, where ϕ_w is the volumetric moisture content (cm cm^{-1}), the gas transport abilities of a soil decrease considerably as the soil becomes wetter and ϕ_w increases.



SOIL TEXTURE & O₂ EXCHANGE

- Median silt+clay content in upper 1.6 m of soil is 41% at the SO basin and 2% at HT basin
- Textural differences contributed to large differences in the soil moisture retention curves
- Median volumetric gas-phase contents were 0.04 beneath the SO basin and 0.19 beneath the HT basin at a 0.3-m depth
- The narrow pores of a fine-texture soil (1) increase frictional resistance to water flow causing lower saturated hydraulic conductivity values; and (2) remain wet for extended periods because of capillary wicking and adhesion of soil water in the narrow pores
- O₂ exchange inhibited at SO basin but not at HT basin → different redox conditions
- Anoxic conditions led to denitrification and DOC serving as electron donor for progression of biogeochemical processes at the SO basin. Aerobic conditions led to NO₃⁻ leaching and DOC depletion at HT basin.



HYPOTHESIS #2

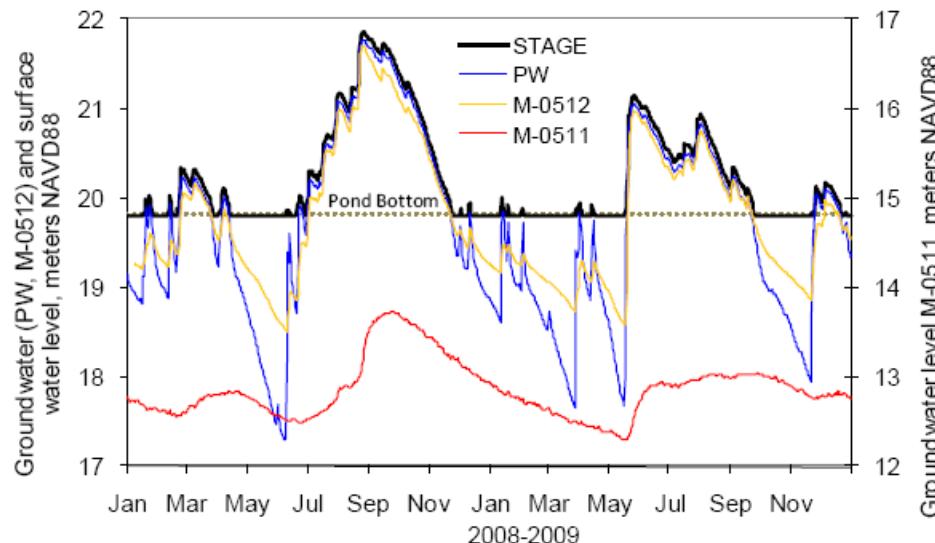
- Variations in hydrologic conditions result in cyclic biogeochemical processes, switching N fate from NO_3^- leaching to reduction.

Bio Geochemical Information

- A temporal succession of biogeochemical processes was identified in shallow groundwater beneath the SO basin according to the following thermodynamically governed and microbially mediated succession of terminal electron accepting processes (TEAPs):



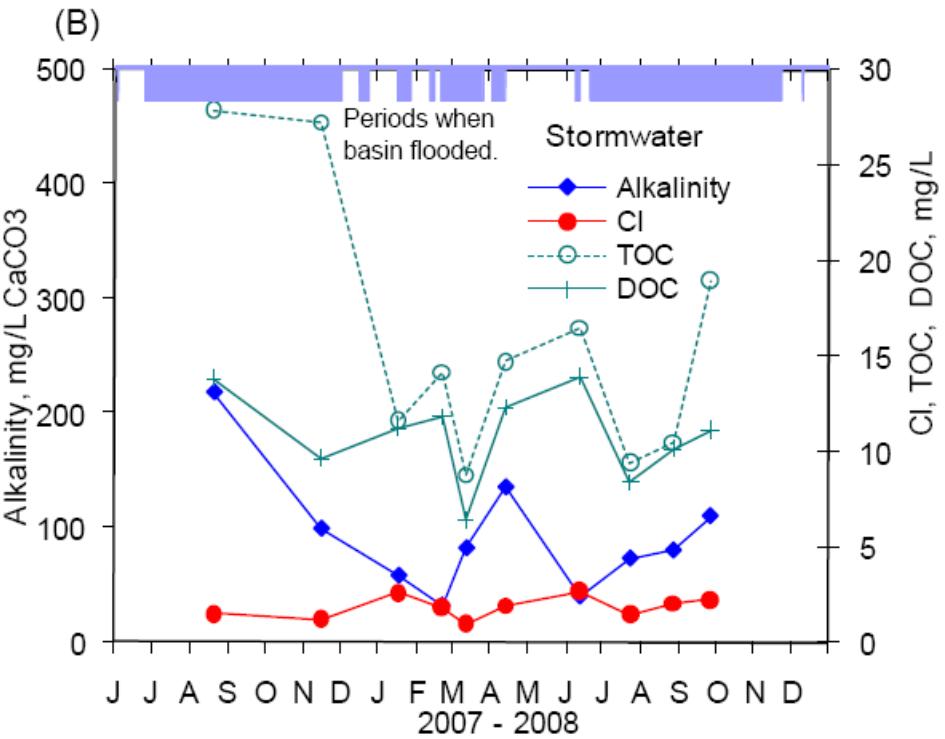
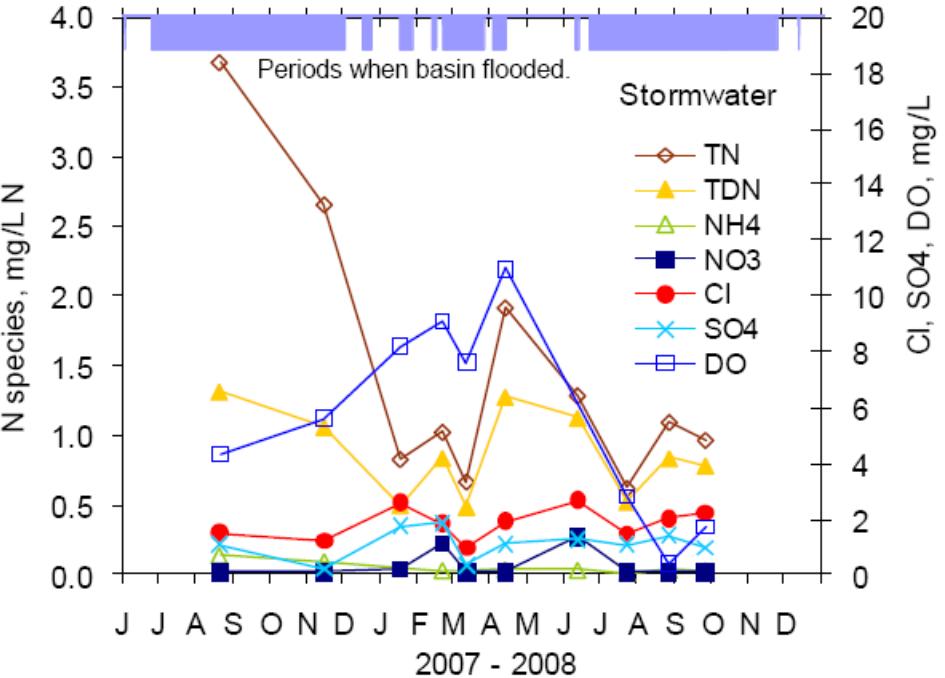
- Hydroclimatic conditions (rainfall and basin flooding) affected timing of biogeochemical processes.
- Cyclic denitrification resulted



STORMWATER QUALITY

South Oak basin

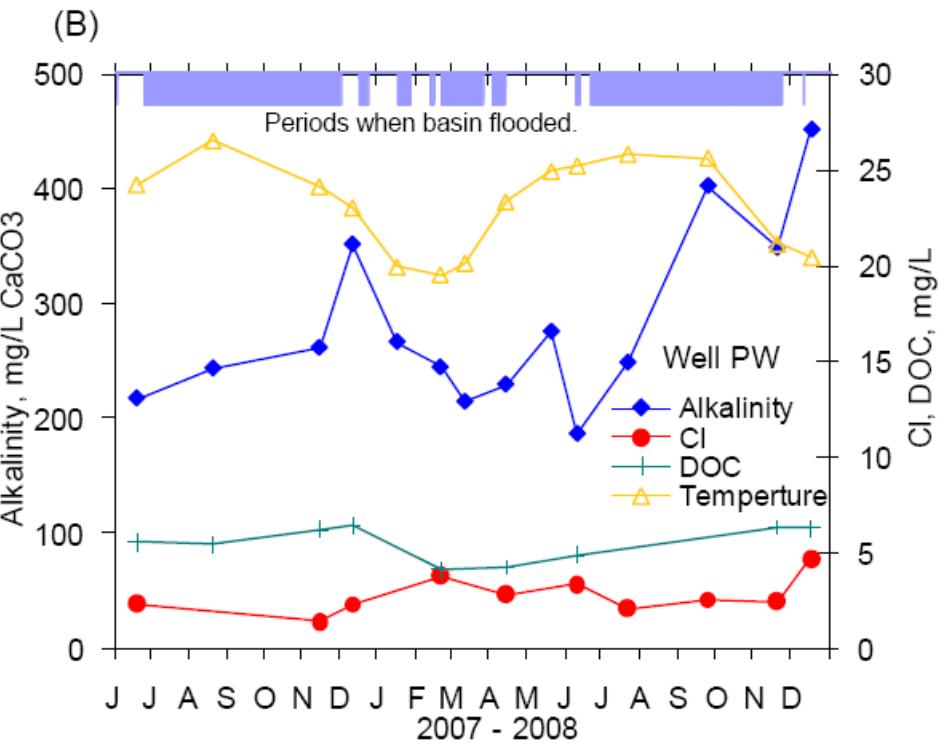
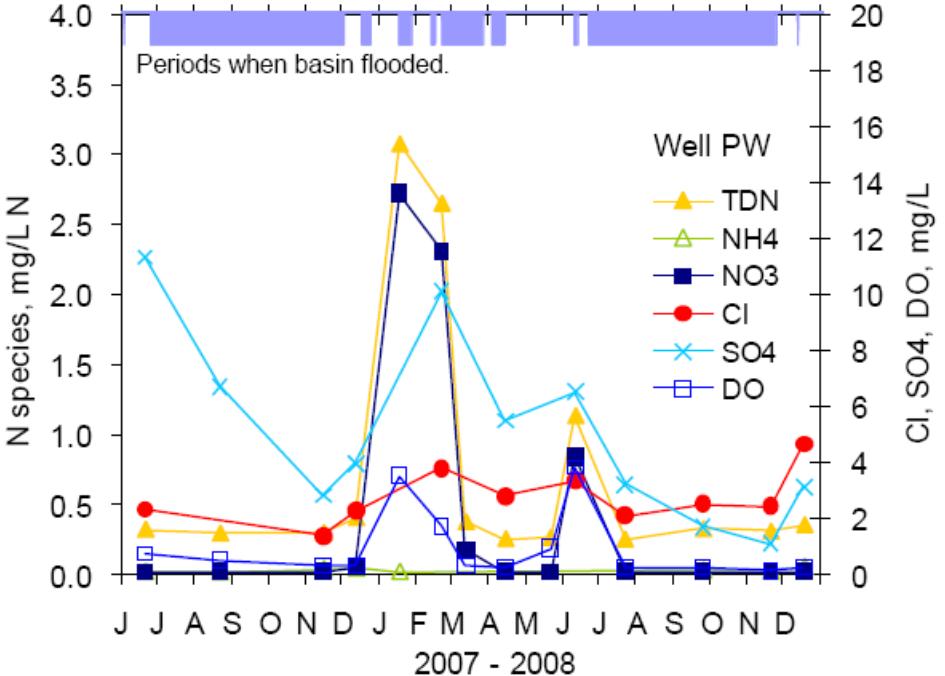
- N primarily in organic form
- Typically aerobic
- Substantial amount of organic C
- Particulate/colloidal fractions significant at times



GROUNDWATER QUALITY

South Oak basin

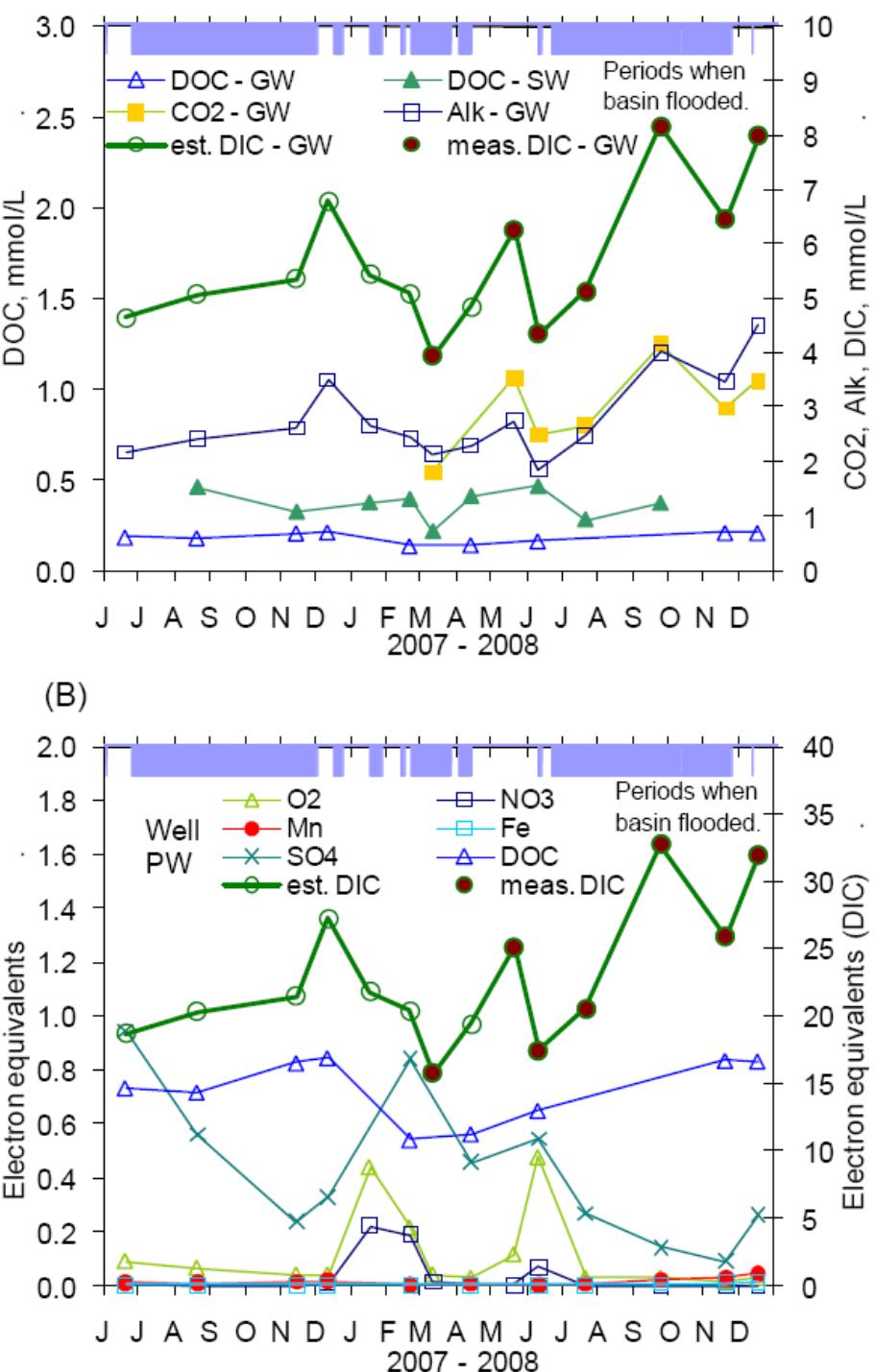
- N primarily in organic form when O₂ low and NO₃⁻ form when aerobic
- Typically low O₂ or anoxic
- GW DOC ~½ of SW DOC
- Particulate/colloidal fractions insignificant
- Cyclic variations in redox sensitive constituents: O₂, NO₃⁻, Mn²⁺ & Fe²⁺ (not shown), SO₄²⁻, CH₄ (not shown), & alkalinity
- GW Cl similar to SW Cl suggests reaction-dominated transport of N



BIOGEOCHEMICAL PROCESSES

South Oak basin

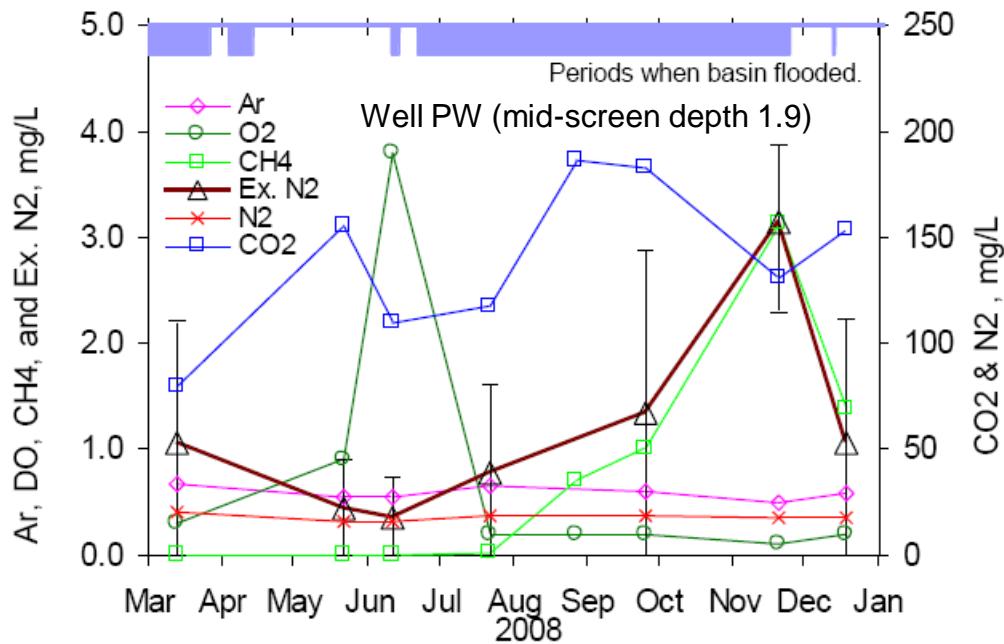
- For each TEAP, reduction half-reaction transfers electrons: O_2 (4), NO_3^- (5), Mn^{4+} (2), Fe^{3+} (1), SO_4^{2-} (8), & DIC (4)
- Compute electron acceptor (EA) electron (e-) equivalents = $(\#e-) * (mM)$
- DIC e- gains \gg e- losses indicates carbonate interaction
- DOC e- losses $>$ EA e- gains indicates plenty of DOC likely available to support heterotrophic processes



BIOGEOCHEMICAL PROCESSES

South Oak basin

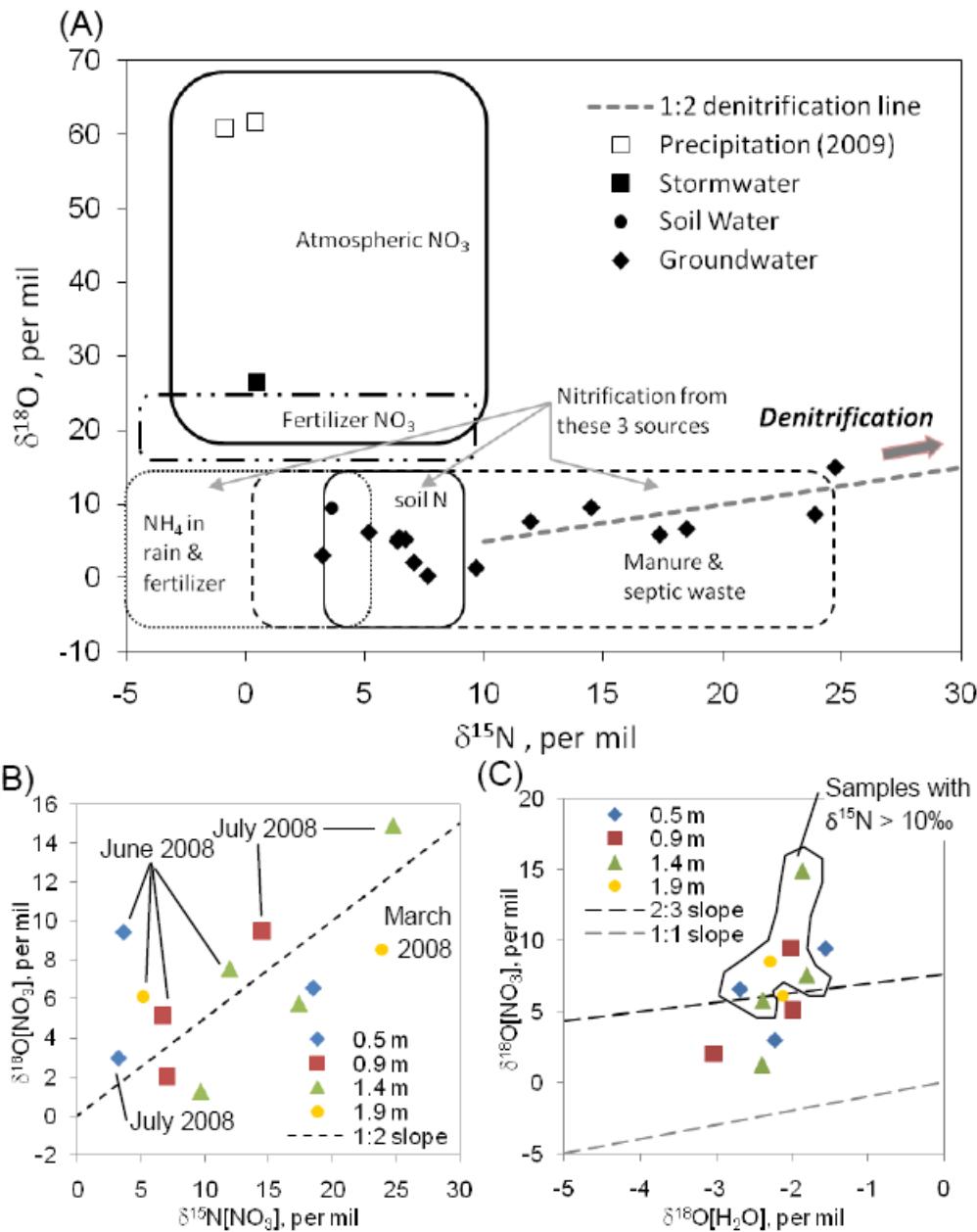
- CH_4 increases during prolonged flooding indicates highly reducing conditions and methanogenesis
- N_2 produced by denitrification (excess N_2) present during flooded periods
- CO_2 produced by organic C oxidation; organic C likely the predominant electron donor



DENITRIFICATION

South Oak basin

- Excess N_2 concentrations as high as 3 mg/L
- Isotopically heavy $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate (up to 25 and 15‰, respectively)
- June 2008 samples collected 2 days after infiltration suggests little denitrification at 0.5 m, but possibly some at 0.9 and 1.4 m
- July 2008 samples indicate greater isotopic enrichment 29 days after flooding – more time for denitrification



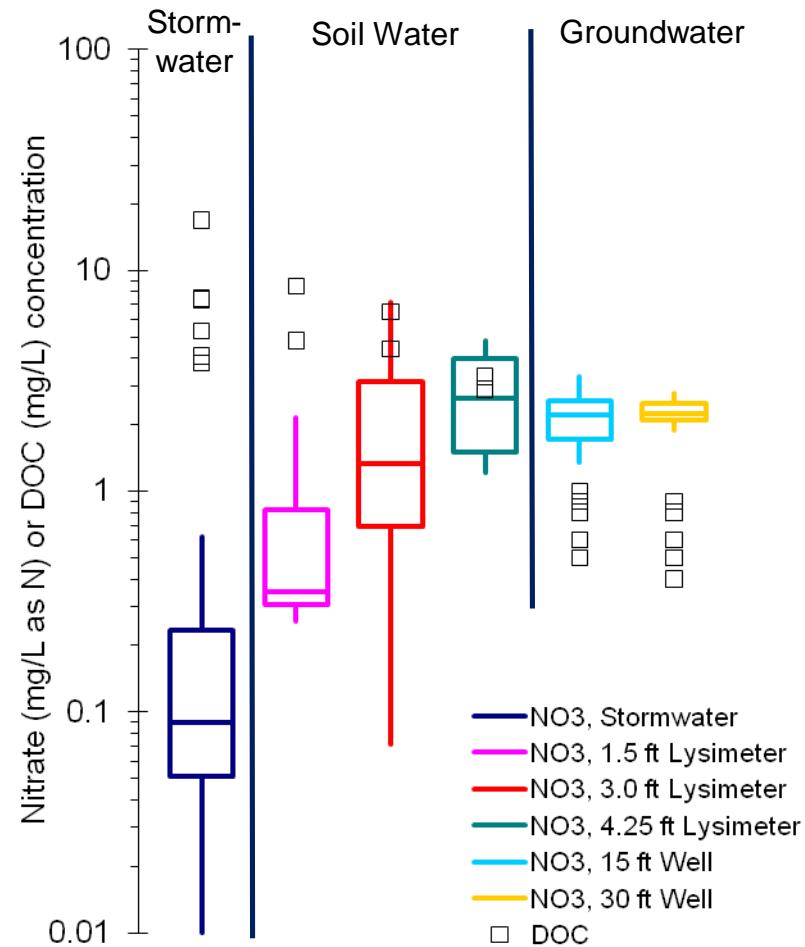
BIOGEOCHEMICAL CYCLING AND NITROGEN FATE

- Cyclic biogeochemical processes occur at different time scales: O_2 & NO_3^- (≤ 1 month), Mn & Fe (seasonal), SO_4^{2-} (2–5 months), CH_4 (seasonal)
- The progression of biogeochemical conditions to Mn reduction and to more highly reductive processes provides strong evidence that NO_3^- , when present, would be reduced by denitrification.
- Therefore, the periodic introduction of additional NO_3^- electrons from infiltration of oxygenated stormwater redirected the flow of electrons from the more highly reductive processes to denitrification.
- The substantial transfer of electrons supported by these more highly reductive processes, particularly SO_4^{2-} reduction, implies sufficient electron flow capacity is available to ensure denitrification would deplete NO_3^- .

BIOGEOCHEMICAL PROCESSES

Hunter's Trace

- Aerobic conditions (dissolved oxygen 5-8 mg/L) persisted beneath the HT basin, resulting in depletion of dissolved organic carbon (DOC) and NO_3^- leaching.
- Aerobic conditions precluded the reduction of other electron acceptors.
- *Can we replicate the conditions at the SO basin at the HT basin?*



HYPOTHESIS #3

- Nutrient input into groundwater from stormwater basins can be reduced by retrofitting an infiltration basin with BAM that replicates natural biogeochemical processes.

Can Use BAM

- Integrated design effectively promotes nutrient reduction while maintaining stormwater volume control.
- Nutrient losses occurred in biosorption activated media (BAM) that produced conditions conducive to denitrification and phosphorus sorption.
- Denitrification was likely occurring intermittently in anoxic microsites in the unsaturated zone, which was enhanced by increased soil moisture within the BAM layer.

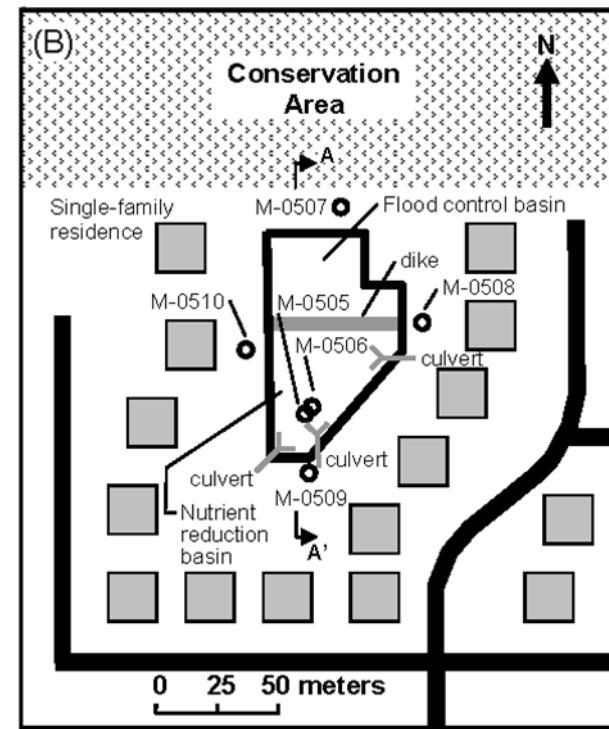
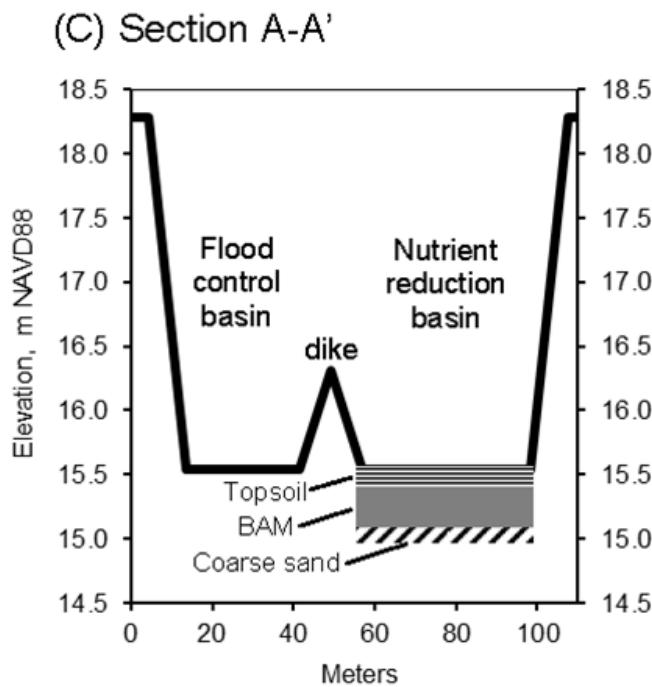
INFILTRATION Basin with BAM

A retrofit to an existing basin was developed based on the natural biogeochemical processes identified at the existing stormwater basins using a “sub-basin” design:

1. Excavation of native soil in the bottom of a portion of an existing pond;
2. Emplacement of a 0.3 m thick amended soil layer (“Biosorption Activated Media” mix): 1.0:1.9:4.1 mixture (by volume) of tire crumb (to increase sorption capacity), silt+clay (to increase soil moisture retention), and sand (to promote sufficient infiltration); and
3. Construction of a berm forming separate nutrient reduction and flood control basins.

HUNTER'S TRACE – Basin retrofit with BAM

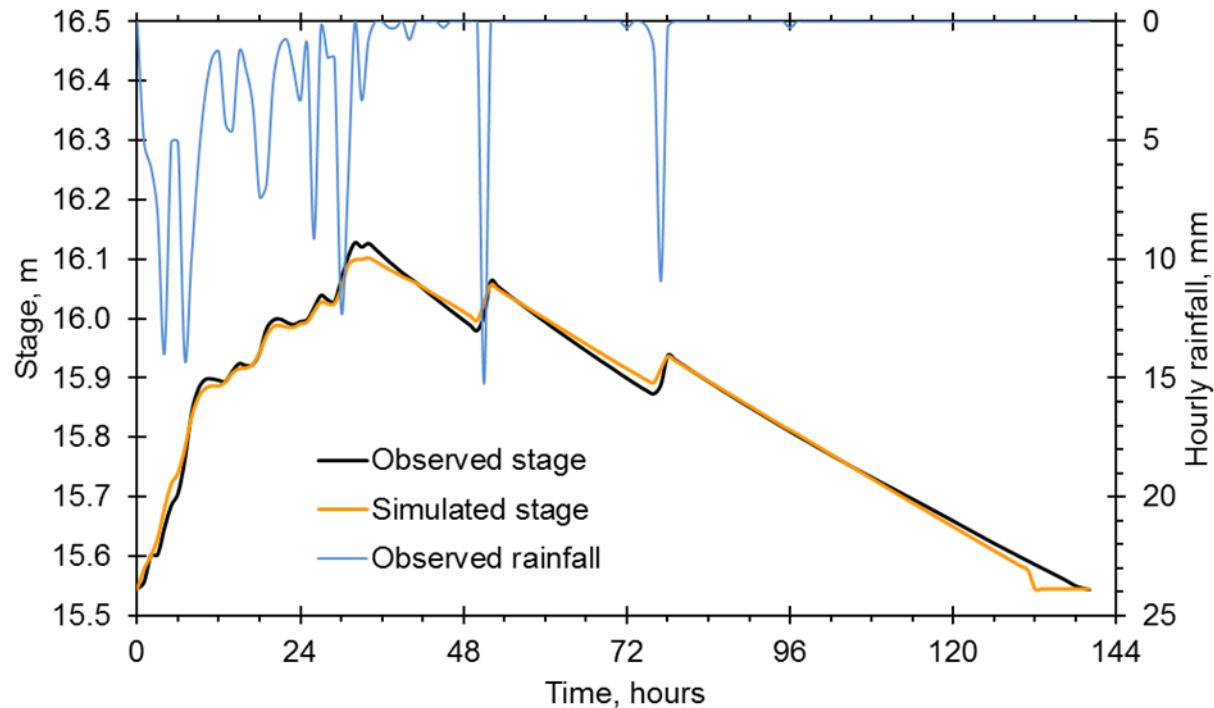
- Reproduce soil conditions that exist at the SO basin by using an amended soil layer (BAM):
 - Increase soil moisture
 - Reduce oxygen transport
 - Increase sorption capacity
 - encourage denitifier growth



Basin with BAM – Model Calibration

EIA (hectares)	1.67
Rainfall (mm)	185
Infiltration (mm/h)	7.3

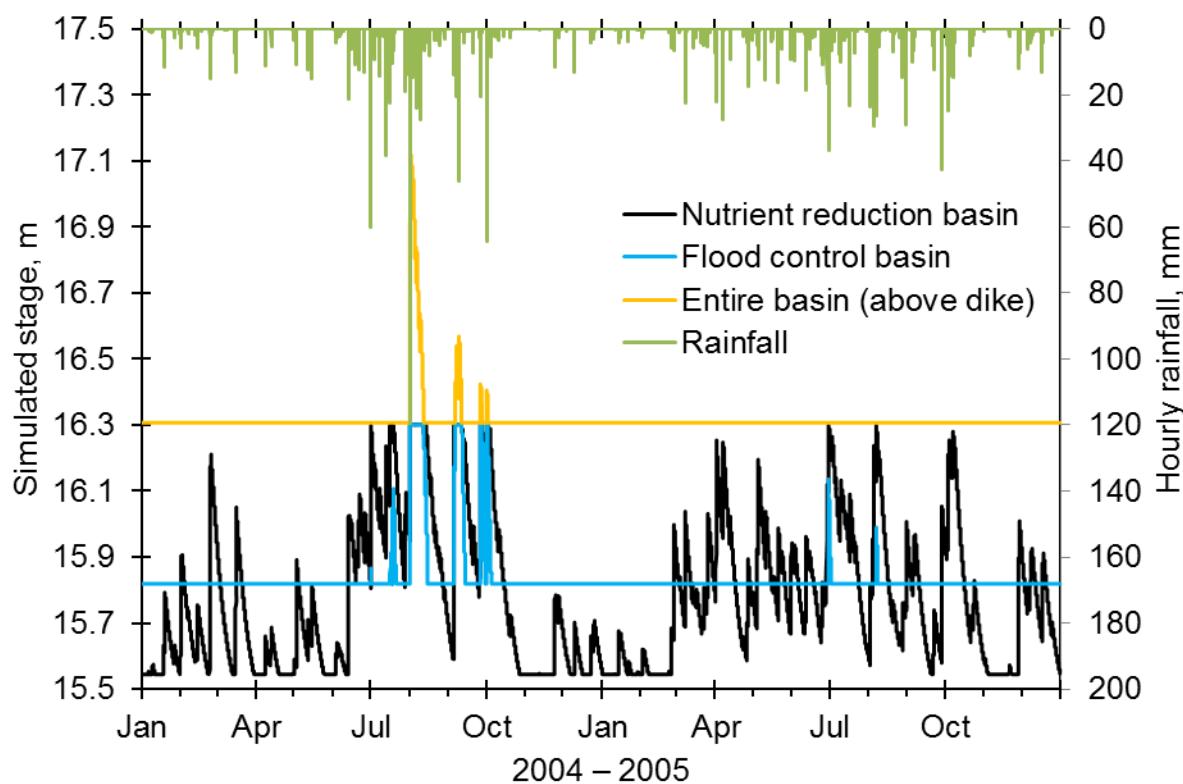
- Runoff/water-balance model:
 $R \times EIA - \text{Infil.} = \Delta \text{Storage}$
- Simulate August 2008 Tropical Storm Fay event.
- Good match to field data using realistic model parameters indicates model is suitable for design purposes.



Basin with BAM – Design Simulation

- Embed 100-yr (280 mm) 24-hr storm event in 2 years of actual rainfall (2004-2005)
- Conservative nutrient reduction basin infiltration rate = 0.73 mm/h
- For more realistic 7.3 mm/h infiltration + no 100-yr storm treatment volume = 88%, peak stage = 16.3 m.

NR basin Infiltration = 0.73 mm/h
Peak stage = 17.1 m
Treatment volume = 30%



Basin with BAM Construction

After placement of erosion control blanket on berm
and 3.7 inch storm

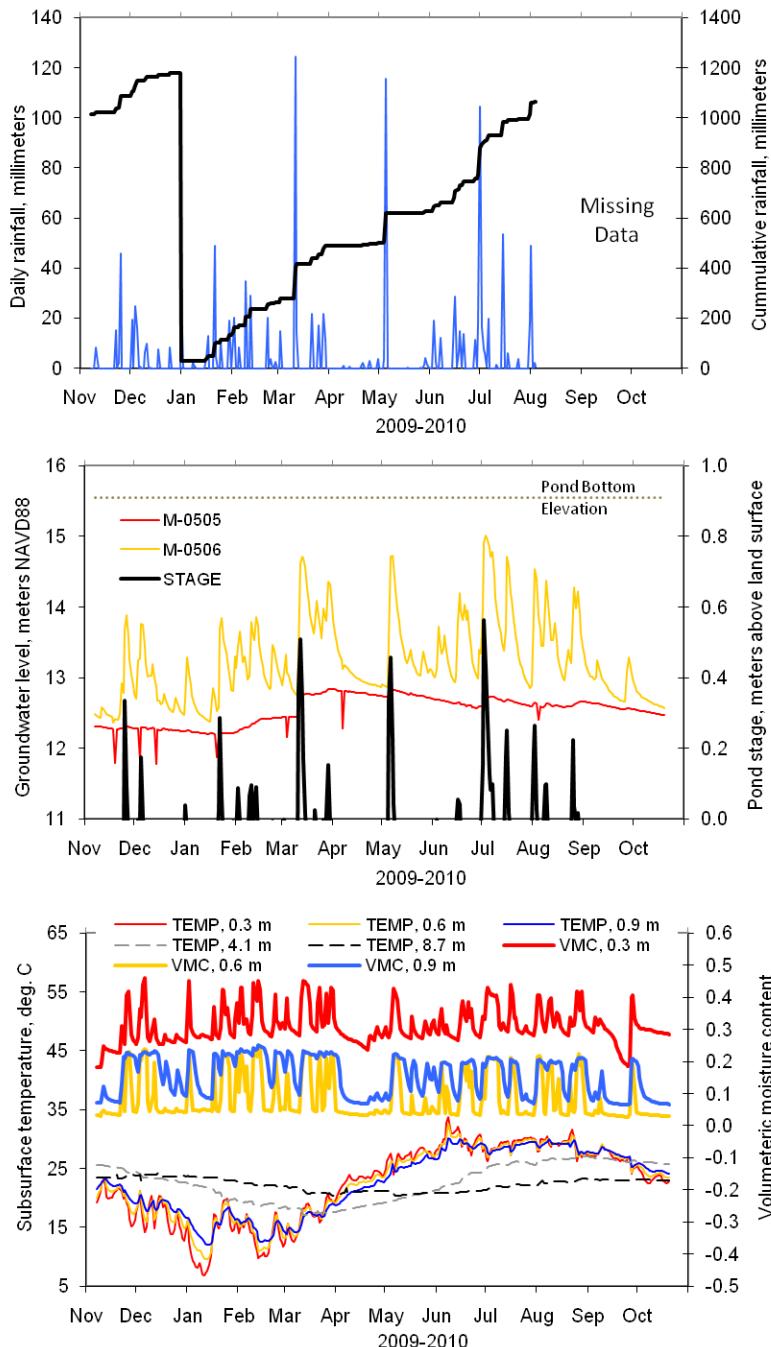


On-Site ~ Mixing Operation~



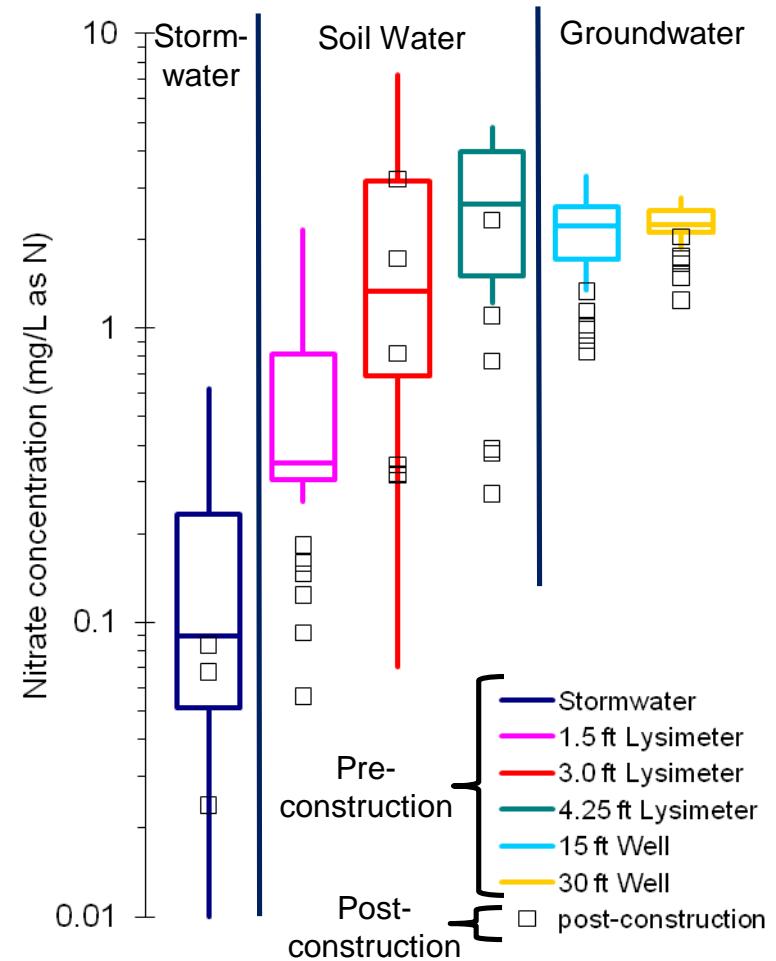
Basin with BAM HYDROLOGIC MONITORING

- Nutrient reduction basin (NR) basin has overflowed berm during 123,116, and 105 mm storms.
- NR basin holds ~80 mm storm.
- Infiltration rate ~8.6 mm/h → ~90 hours to drain full NR basin.
- Higher soil moisture content due to BAM and more frequent ponding in NR basin.



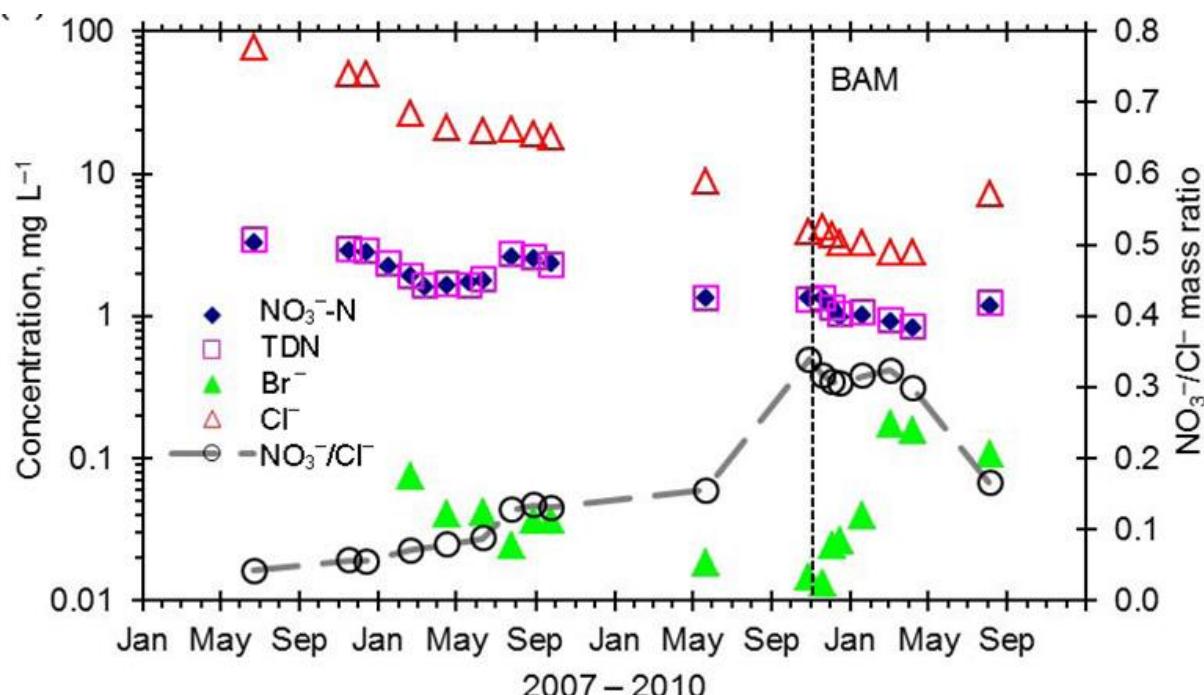
Basin with BAM – NITRATE

- ~ 70% reductions in nitrate from pre-construction (2007–2009) to post-construction (2009–2010) median concentrations in soil water and at the water table.
- Nitrate decreases may be due to dilution, sorption, reduced nitrification, denitrification, or some combination of these processes



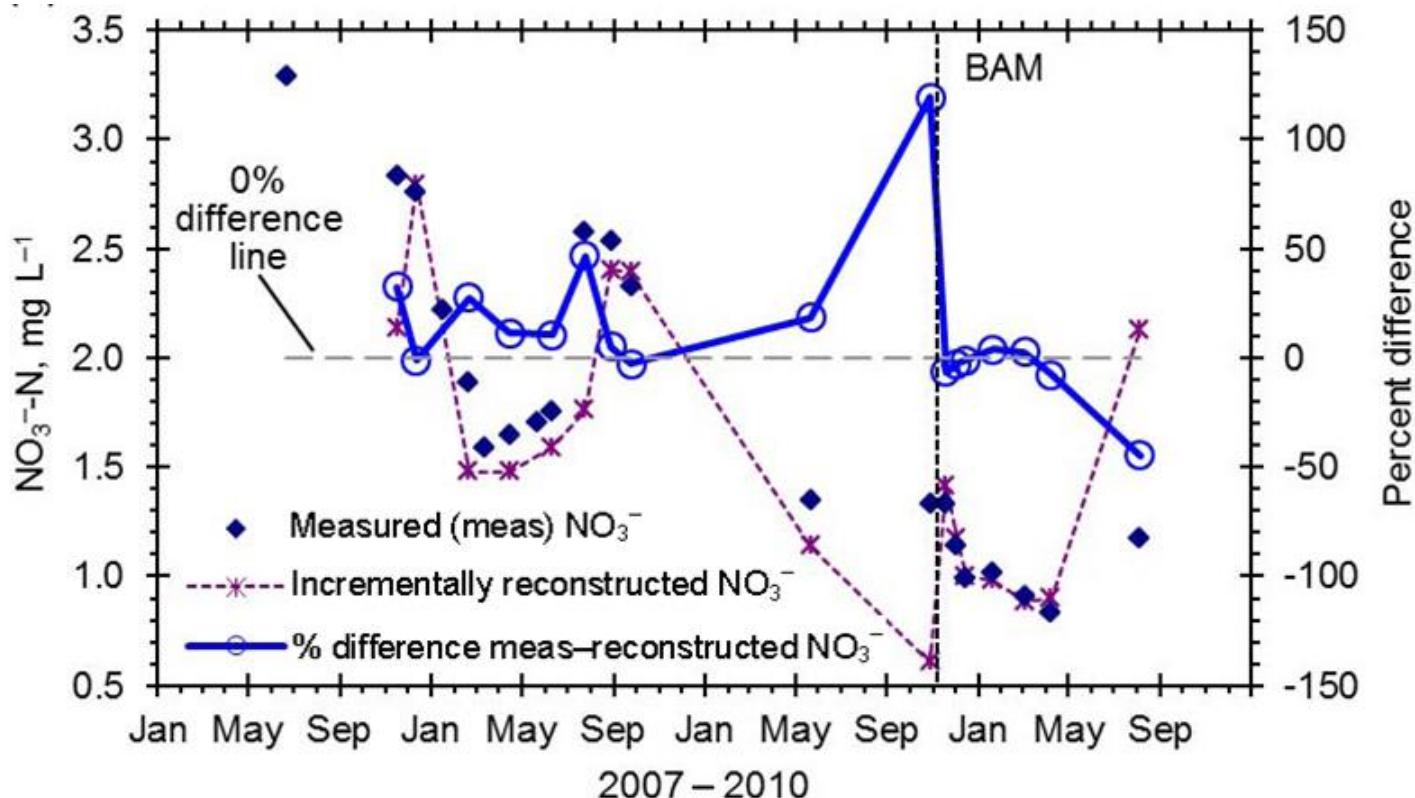
Basin with BAM– $\text{NO}_3^-/\text{Cl}^-$ Ratios

- Compare NO_3^- and Cl^- to determine dilution effects
- A positive $\text{NO}_3^-/\text{Cl}^-$ ratio slope indicates NO_3^- is decreasing slower or increasing faster than Cl^- due to nitrification, NO_3^- input increased relative to Cl^- , or Cl^- input decreased relative to NO_3^-
- A negative $\text{NO}_3^-/\text{Cl}^-$ ratio slope indicates NO_3^- is increasing slower or decreasing faster than Cl^- , possibly due to reaction (for example, denitrification), NO_3^- input decreased relative to Cl^- , or Cl^- input increased relative to NO_3^-
- A zero $\text{NO}_3^-/\text{Cl}^-$ slope indicates NO_3^- and Cl^- are changing at the same rate due to dilution.



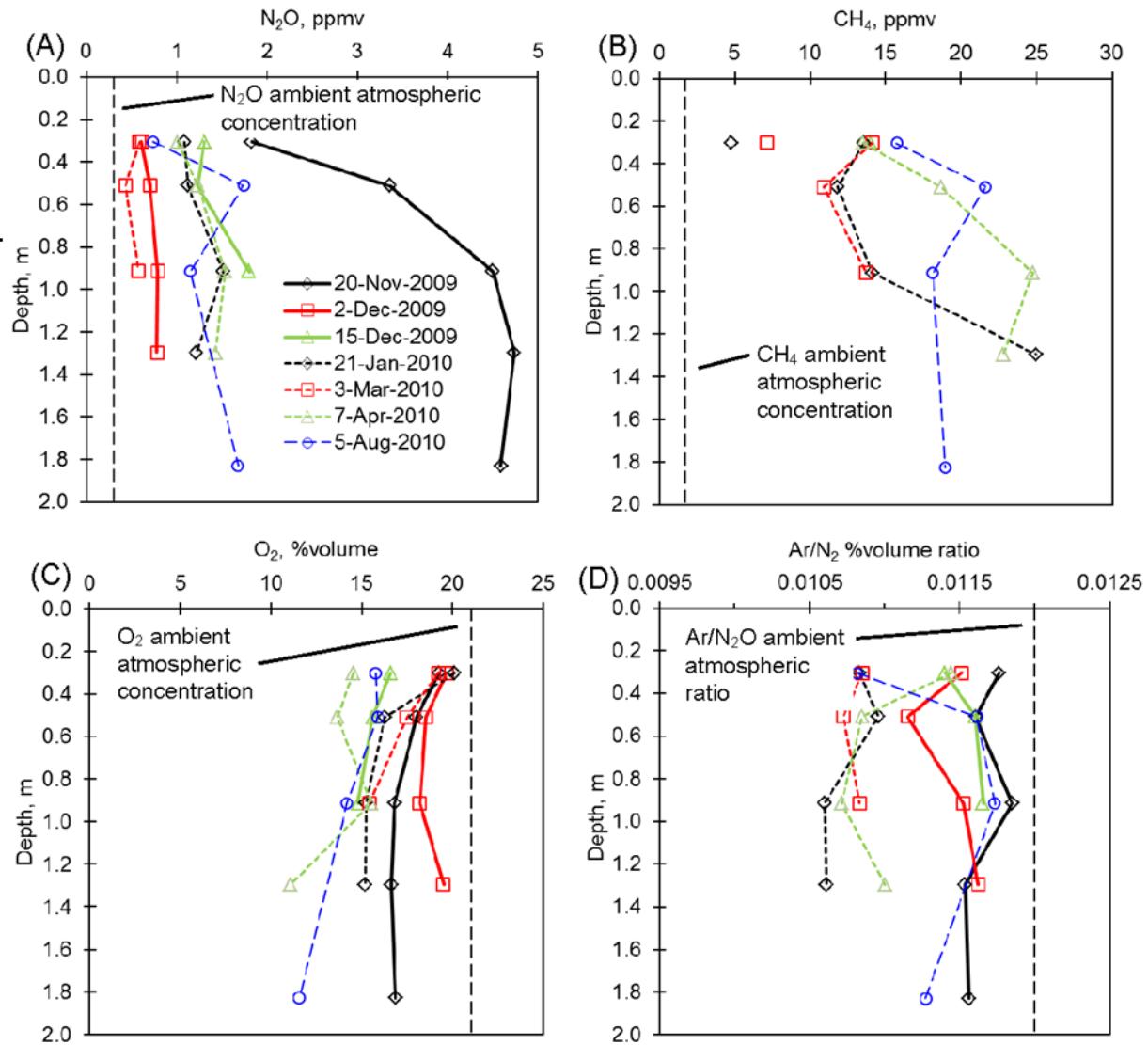
Basin with BAM– $\text{NO}_3^-/\text{Cl}^-$ Ratios

- Deviations suggest reaction losses of NO_3^- or variations in NO_3^- input
- Positive percentages indicate NO_3^- gains and negative percentages indicate NO_3^- losses.



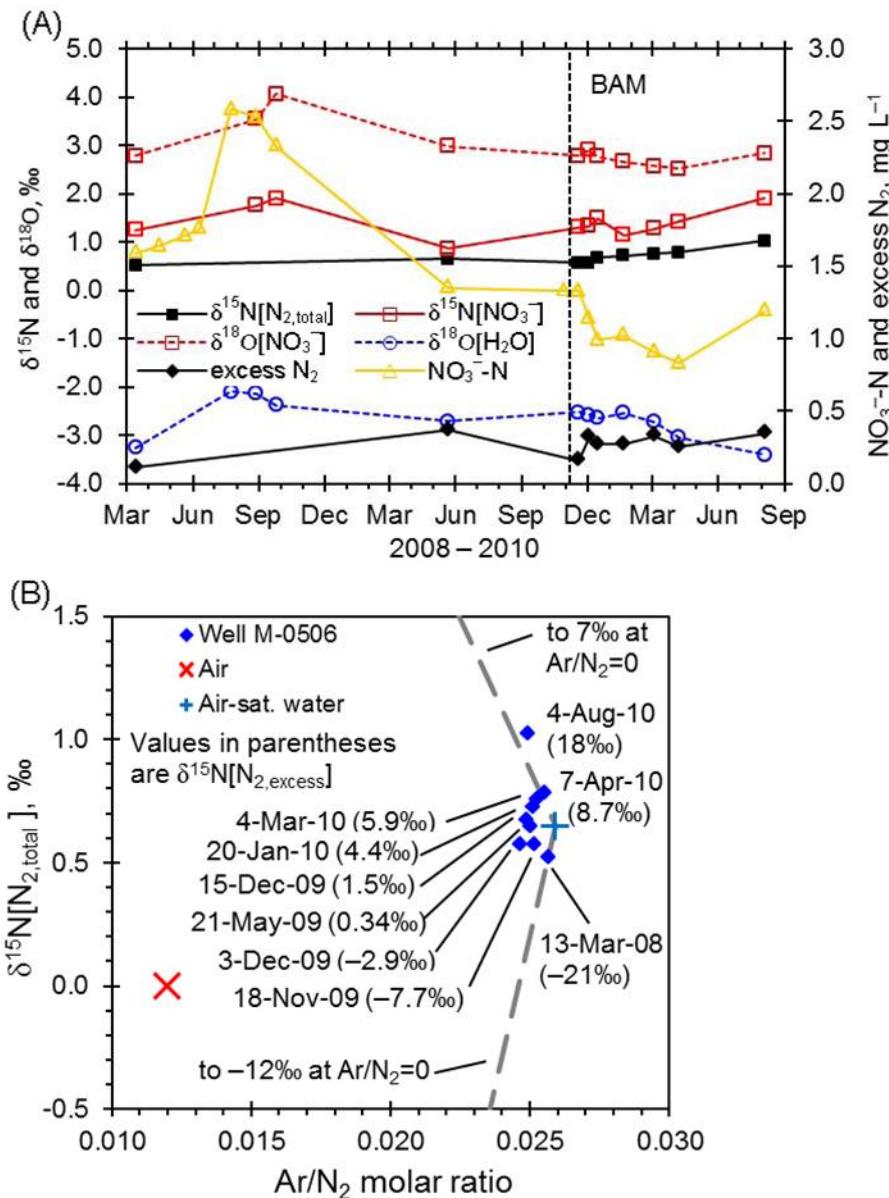
Basin with BAM– SOIL GAS

- Soil gas sampling conducted during post-BAM period (N_2 , O_2 , Ar , N_2O , CH_4)
- $\text{N}_2\text{O} >$ ambient atmospheric levels (~0.3 ppmv) suggest denitrification.
- $\text{CH}_4 >$ ambient atmospheric levels (~1.7 ppmv) suggest methanogenesis.
- Anoxic microsites likely exist in the aerobic vadose zone



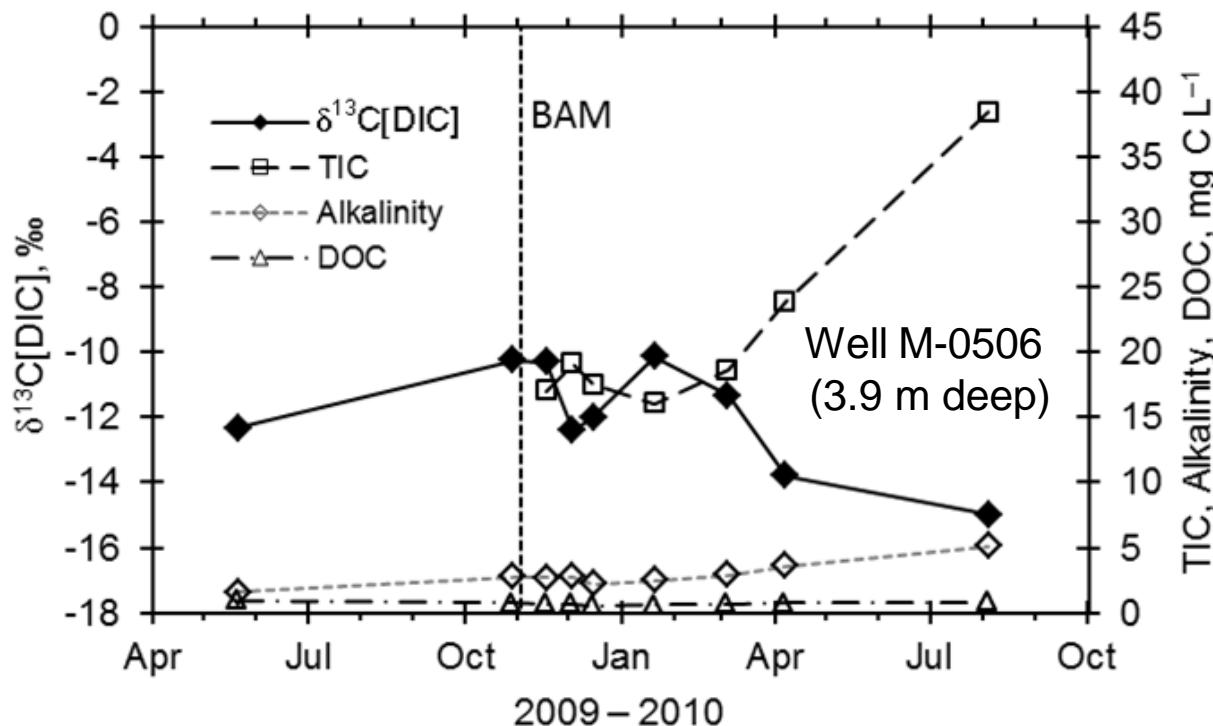
Basin with BAM— DENITRIFICATION

- Slight isotopic enrichments for NO_3^- and N_2 after BMP in well M-0506 (3.9 m deep)



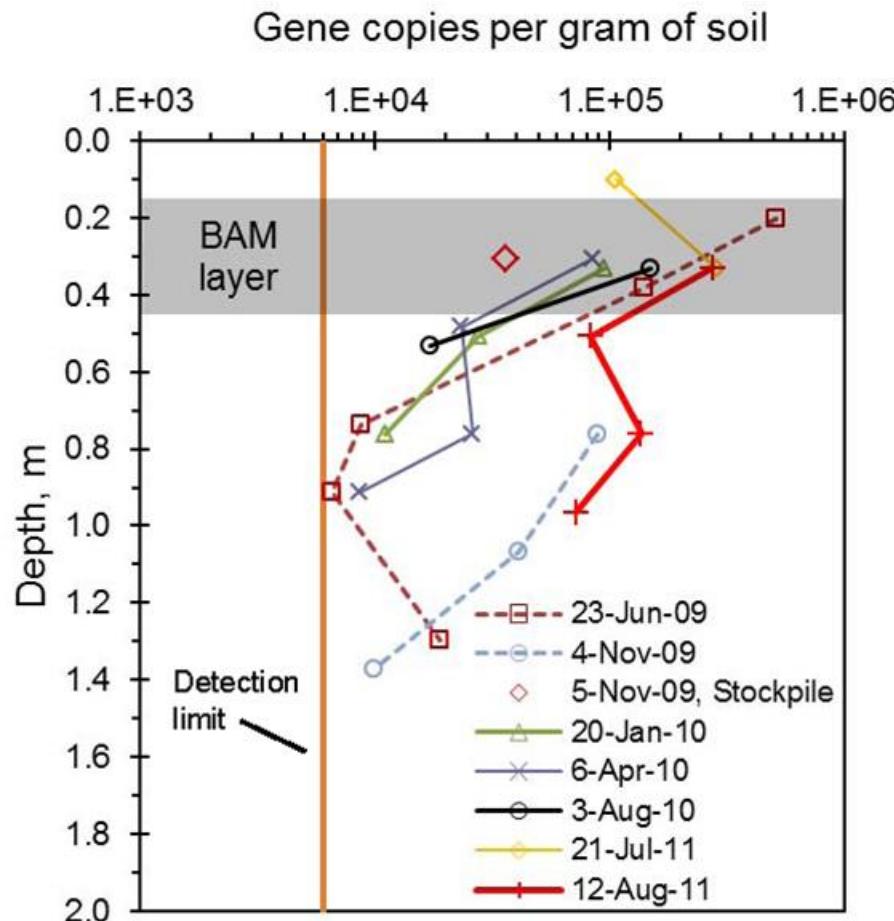
Basin with BAM– C Cycling

- Increasing alkalinity and decreasing $\delta^{13}\text{C}$ of DIC suggests oxidation of organic matter to DIC.



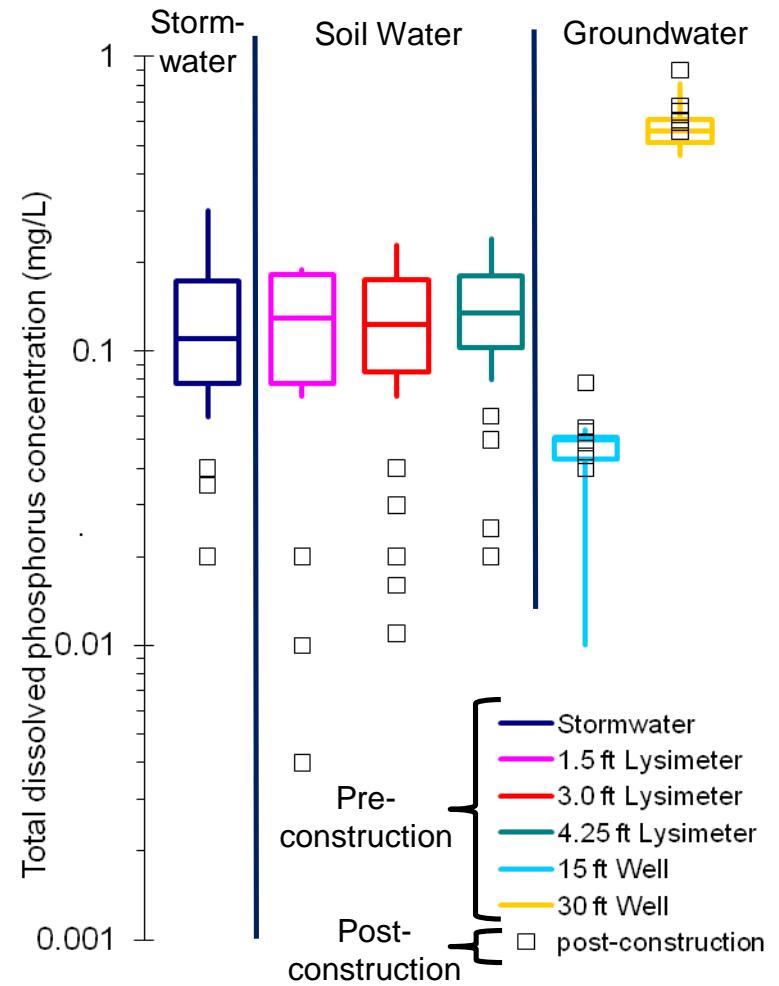
Basin with BMP – Denitrifiers

- Real-time PCR data suggests BAM layer is conducive to the growth of denitrifiers that possess the nirK gene



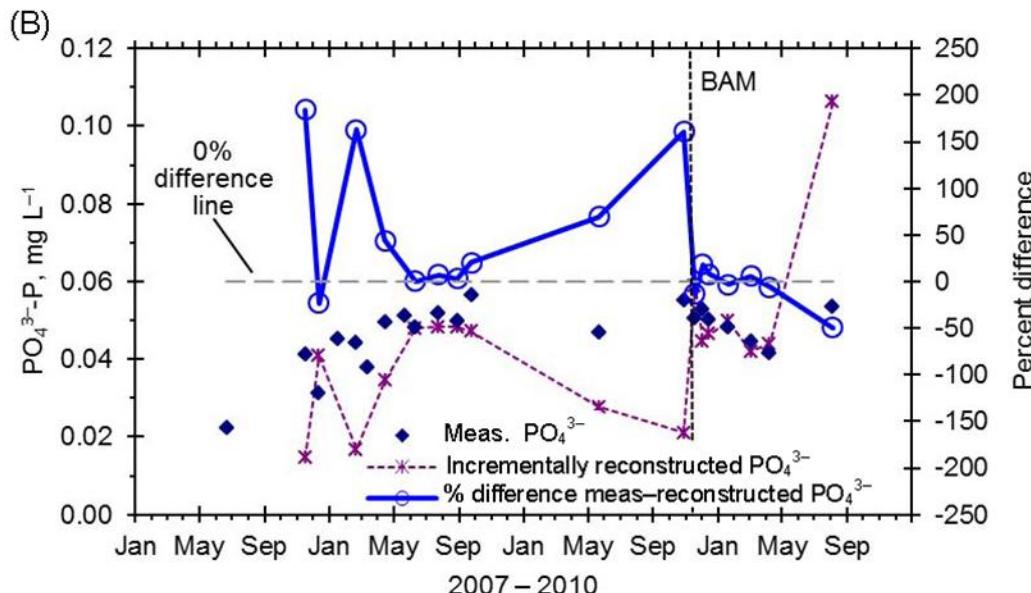
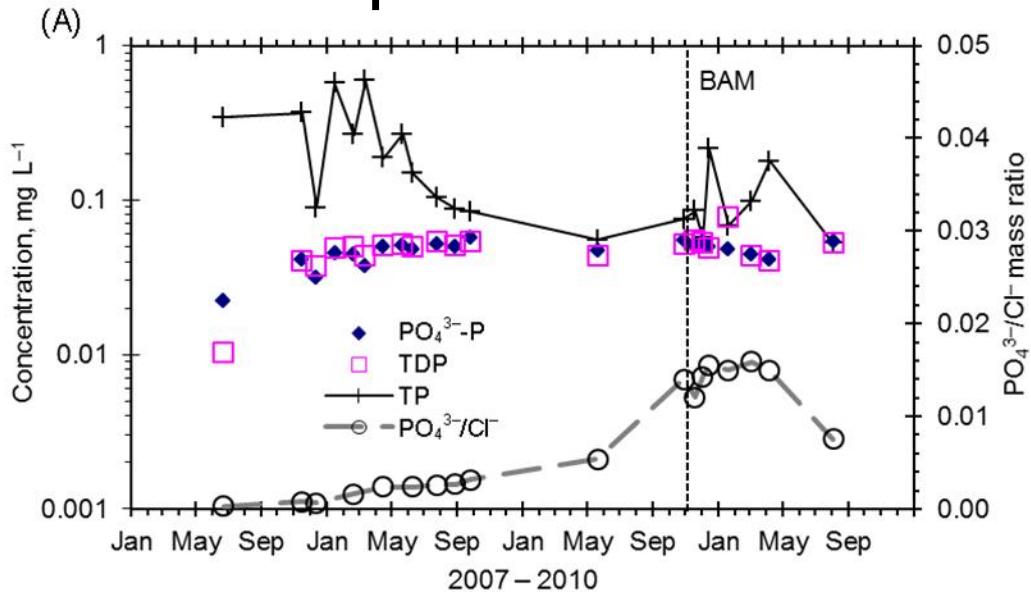
Basin with BAM – PHOSPHORUS

- ~ 80% reductions in total dissolved phosphorus (TDP) from pre-construction (2007–2009) to post-construction (2009–2010) median concentrations in soil water
- No change in TDP at water table.
- TDP decreases may be due to dilution, sorption, precipitation, microbial assimilation, or some combination of these processes
- ortho-P > 80% TDP, total P (unfiltered) is ~1–10x TDP



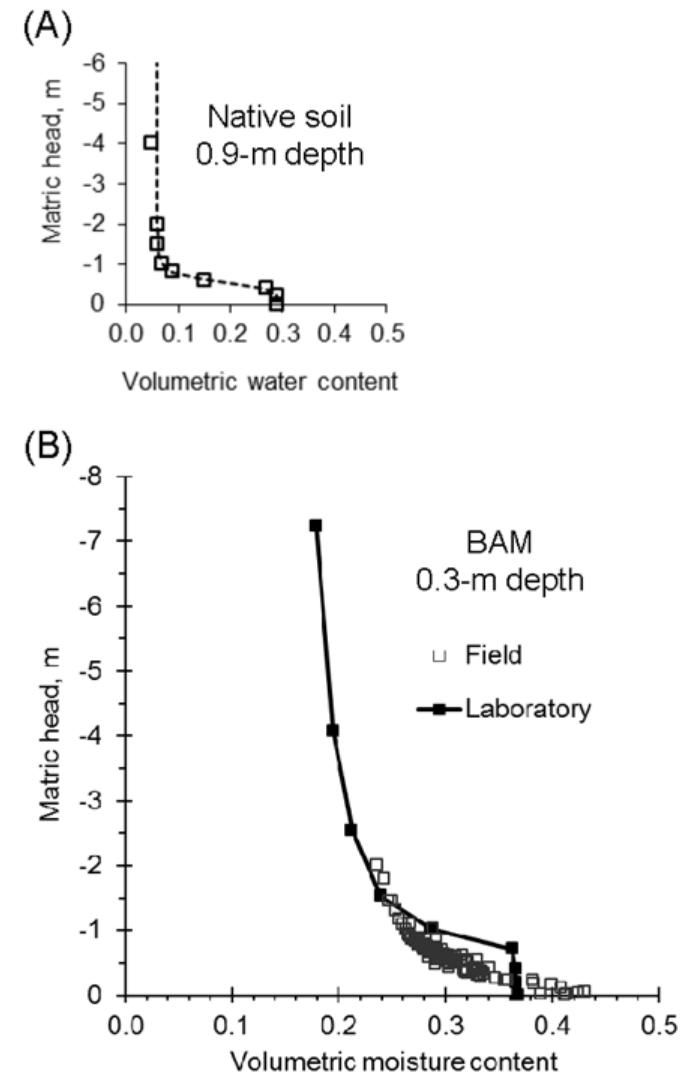
Basin with BAM— $\text{PO}_4^{3-}/\text{Cl}^-$ Ratios

- Deviations suggest reaction losses of PO_4^{3-} or variations in PO_4^{3-} input
- Positive percentages indicate PO_4^{3-} gains and negative percentages indicate PO_4^{3-} losses.



SOIL MOISTURE RETENTION

- Moisture content as controlled by texture may be the single most important functional characteristic of BAM, and the SMRC can be used to assess this characteristic.
- A silt+clay content of ~25% (by volume) in BAM 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.



HYPOTHESIS #4

- N budget and fluxes beneath stormwater basins can be quantified using a system dynamics modeling approach.

What Happened?

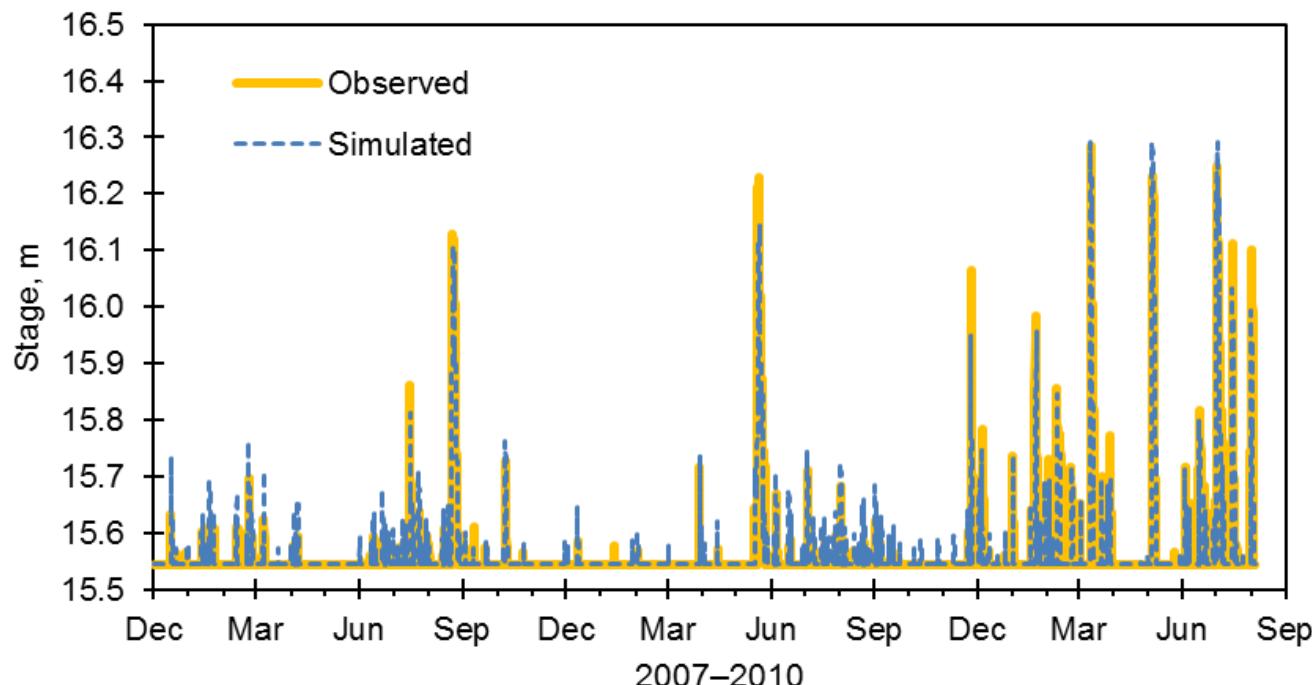
- System dynamics modeling is an effective tool for modeling the N cycle.
- BAM contributed to removal of about one-third of the N mass inflow.
- The new integrated design using the functionalized soil amendment BAM is a promising passive, economical, stormwater nutrient-treatment technology.

APPROACH

- Use hydrologic data to compute water budget and fluxes and N loading
 - compute surface infiltration rate
 - compute surface infiltration N loading
 - compute subsurface rates
- Use water chemistry and system dynamics model to compute N budget and fluxes
 - calibrate and validate using field data
 - simulate N budget and fluxes

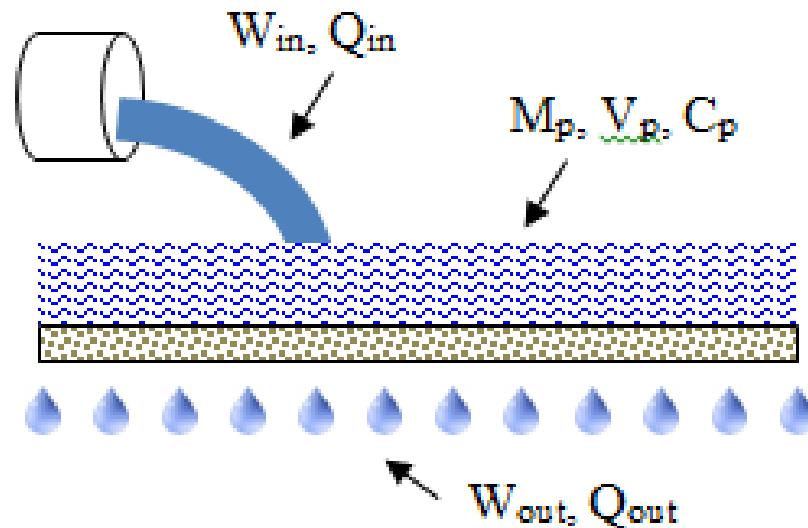
SURFACE INFILTRATION

- Use the runoff/water-balance model and calibrate to observed field conditions 2007–2010
- Matched observed stage well
- Use simulated infiltration volumes



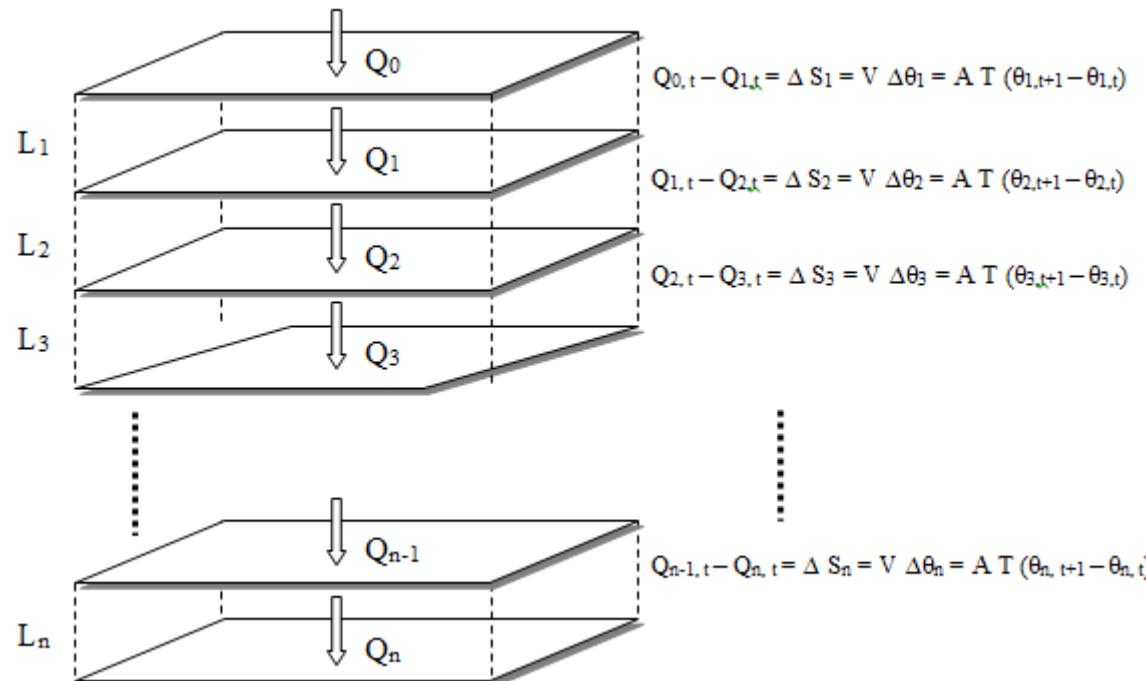
SURFACE NITROGEN LOADING

- Use water-volume and N-mass balances to compute N concentration in ponded water (C_p) and N mass loading in surface infiltration (W_{out})



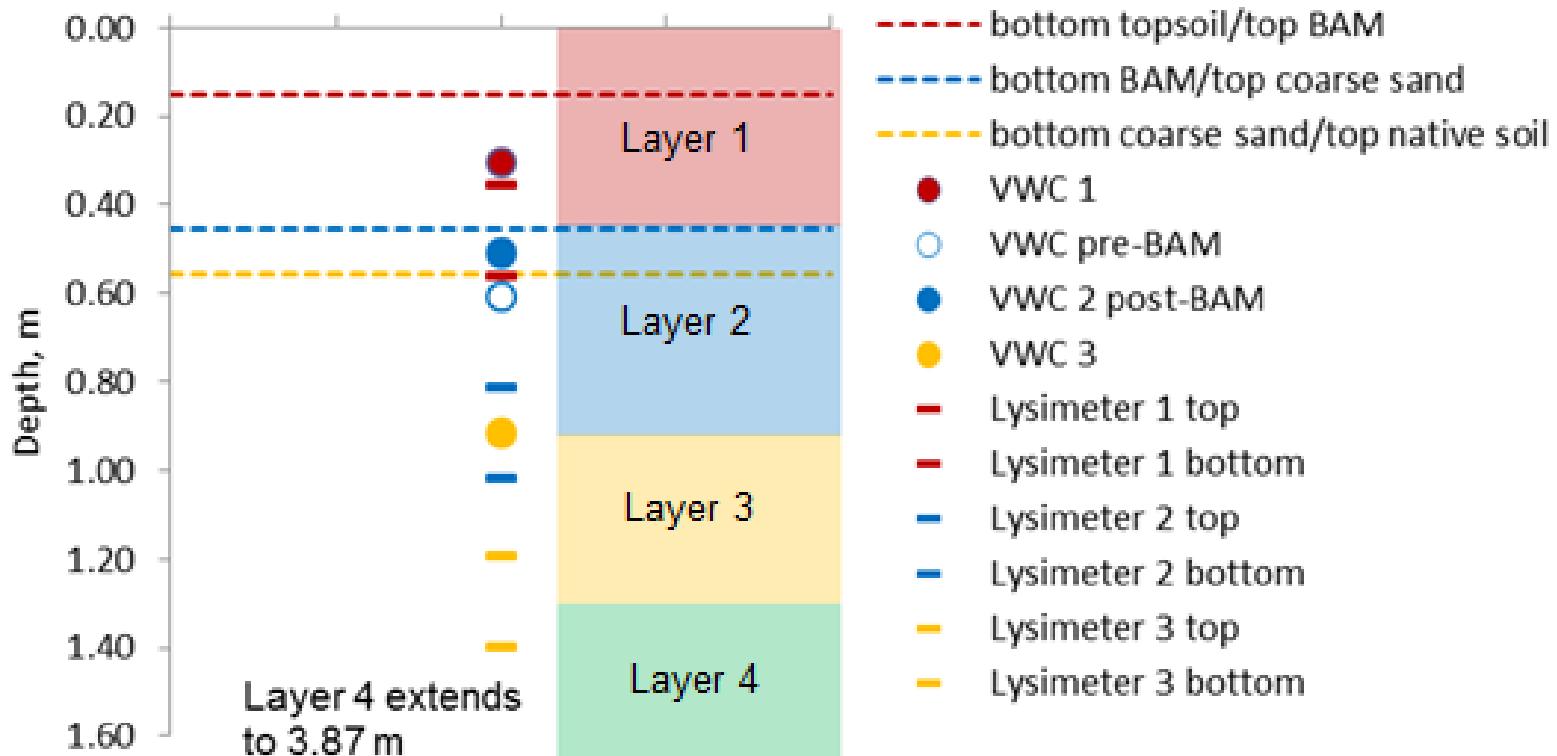
SUBSURFACE FLUXES

- Compute subsurface fluxes using 1-D continuity equation and field-measured volumetric water contents



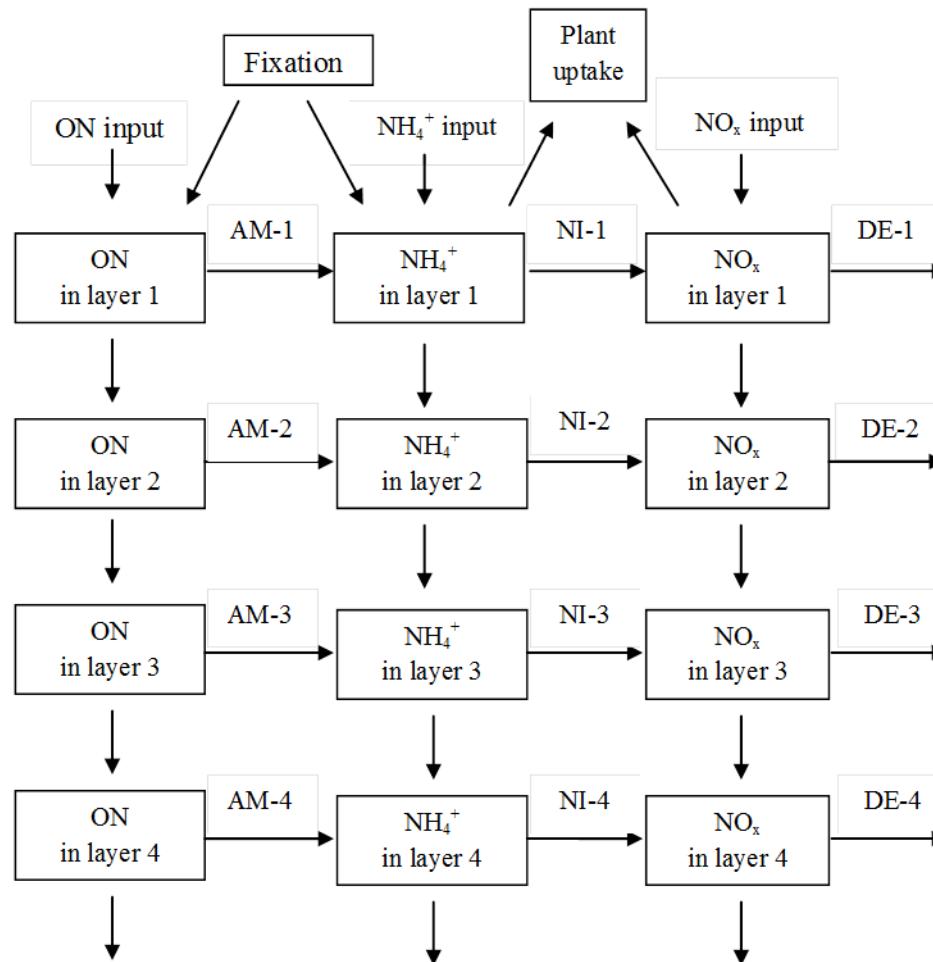
SYSTEM DYNAMICS MODEL

- 1-D vertical, 4 layers
- Only water phase (gas and solid phases not modeled)
- Model layers approximate field conditions, e.g. BAM layer and locations of instrumentation



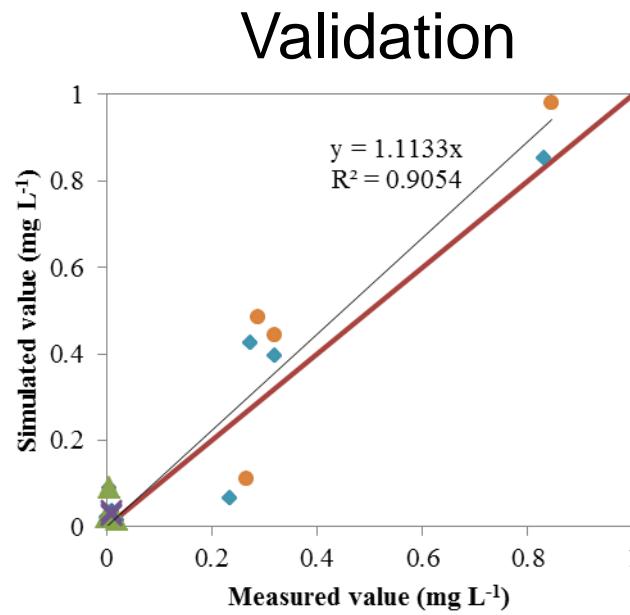
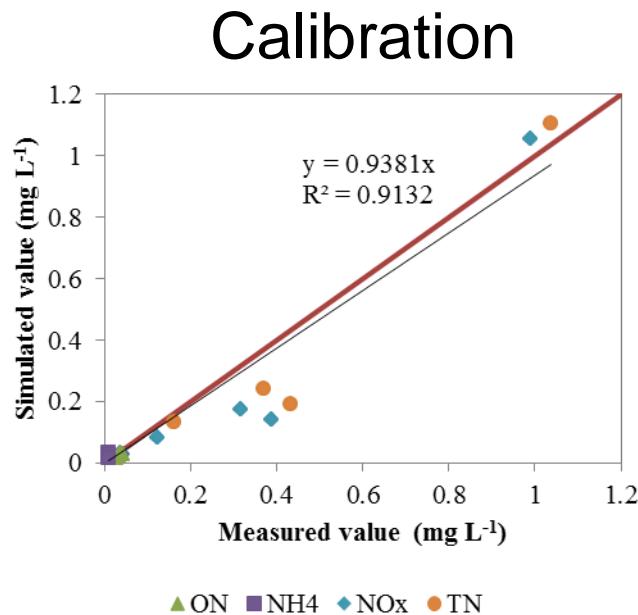
CONCEPTUAL MODEL

- Simulate advective inflow/outflow, fixation, ammonification, nitrification, denitrification, and plant uptake



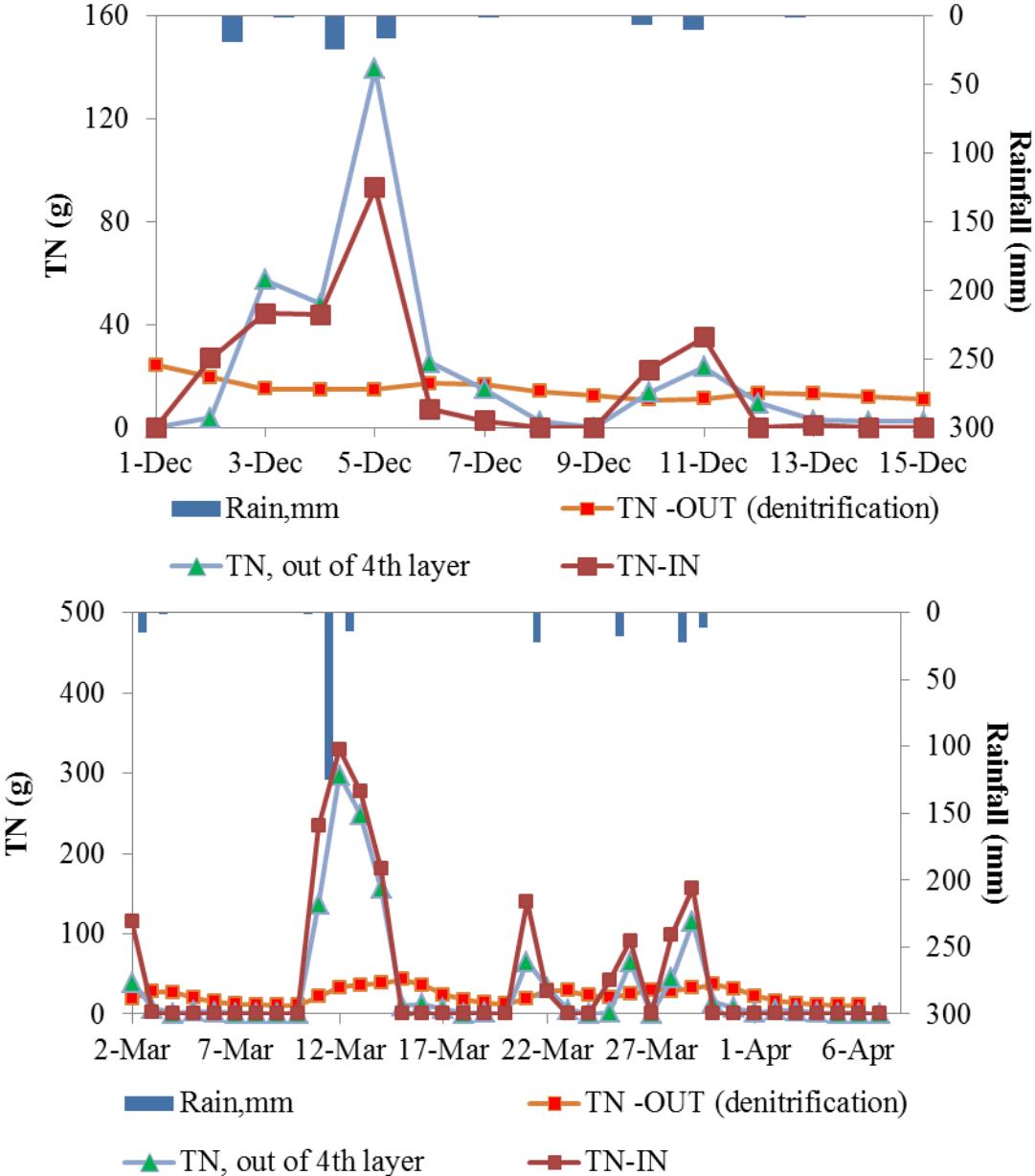
CALIBRATION & VALIDATION

- Calibrate model for period 1–15 December 2009
- Validate model for period 2 March – 7 April 2010



NITROGEN FLUXES

- Temporal variability in N removal by denitrification was slight
- But denitrification consistently increased during the periods following large storm events
- Denitrification coincides with increased soil moisture.



NITROGEN Model BUDGET

- Leaching (advective outflow from layer 4) was the primary mechanism for N mass loss
- Denitrification losses are about one-third of the total N inflow

Component	Budget		Total nitrogen, g	
	Calibration	Validation	Calibration	Validation
Storage, initial			1,016	839
Runoff (infiltration)			277	1,696
Fixation			167	412
Uptake			23	57
Denitrification			221	837
Leaching (out layer 4)			346	1,296
Storage, final			836	679
In – Out – Δ Storage			34	78

CONCLUSIONS

1. Fine-textured soil controls surface/subsurface oxygen exchange by maintaining elevated moisture content, thereby controlling biogeochemical processes and N and C cycling.
2. Variations in hydroclimatic conditions result in cyclic biogeochemical processes leading to cyclic denitrification.
3. Retrofitting of an infiltration basin using BAM resulted in decreased nitrate concentrations, which is partly due to intermittent denitrification, and decreased phosphorus, which is likely due to sorption.
4. A BAM mixture can be used to remove nutrients. Soil moisture content is important to maintain.
5. About 70 % reduction in nitrate, and about 80% reduction in phosphorus was obtained at the Hunter's Trace Retrofit stormwater basin.
6. System dynamics modeling can provide quantitative estimates of N budget and fluxes, which indicated that in the stormwater basin with BAM, denitrification accounted for a loss of about one-third of the total nitrogen mass inflow and was occurring predominantly in the BAM layer..

PUBLICATIONS Used

1. O'Reilly, et.al. 2011. "Soil Property Control of Biogeochemical Processes beneath Two Subtropical Stormwater Infiltration Basins, 2012." *Journal of Environmental Quality* 41(2), 564–581—
2. O'Reilly, et. al. 2011. "Cyclic Biogeochemical Processes and Nitrogen Fate beneath a Subtropical Stormwater Infiltration Basin," *Journal of Contaminant Hydrology* —
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5. Wanielista, et.al. 2011. Nitrogen Transformation beneath Stormwater Retention Basins in Karst Areas. FDEP S0316, Tallahassee.
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THE EFFECTIVENESS OF BIOSORPTION ACTIVATED MEDIA (BAM) TO REDUCE NITRATE AND ORTHOPHOSPHATE IN STORMWATER RUNOFF

PART 2: Science, Engineering and Application

Questions and Comments

www.stormwater.ucf.edu

Marty Wanielista, 2013

