Nitrogen Biogeochemistry

Summary: Year 2

UF/IFAS Soil and Water Sciences:

Patrick Inglett, Xiaolin Liao, Katelyn Foster

St Johns River Water Management District:

Dean Dobberfuhl, Andy Canion

Karst Environmental

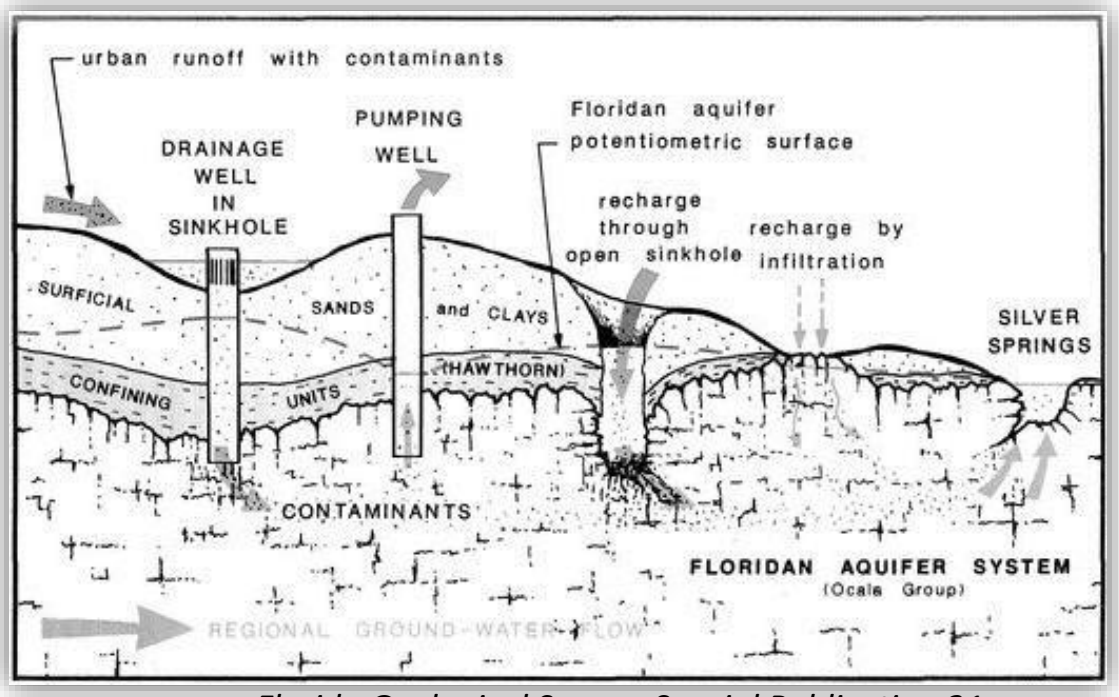
Pete Butt, et al.

Objectives

1. Characterize sources of N and potential denitrification loss in soils of major land uses

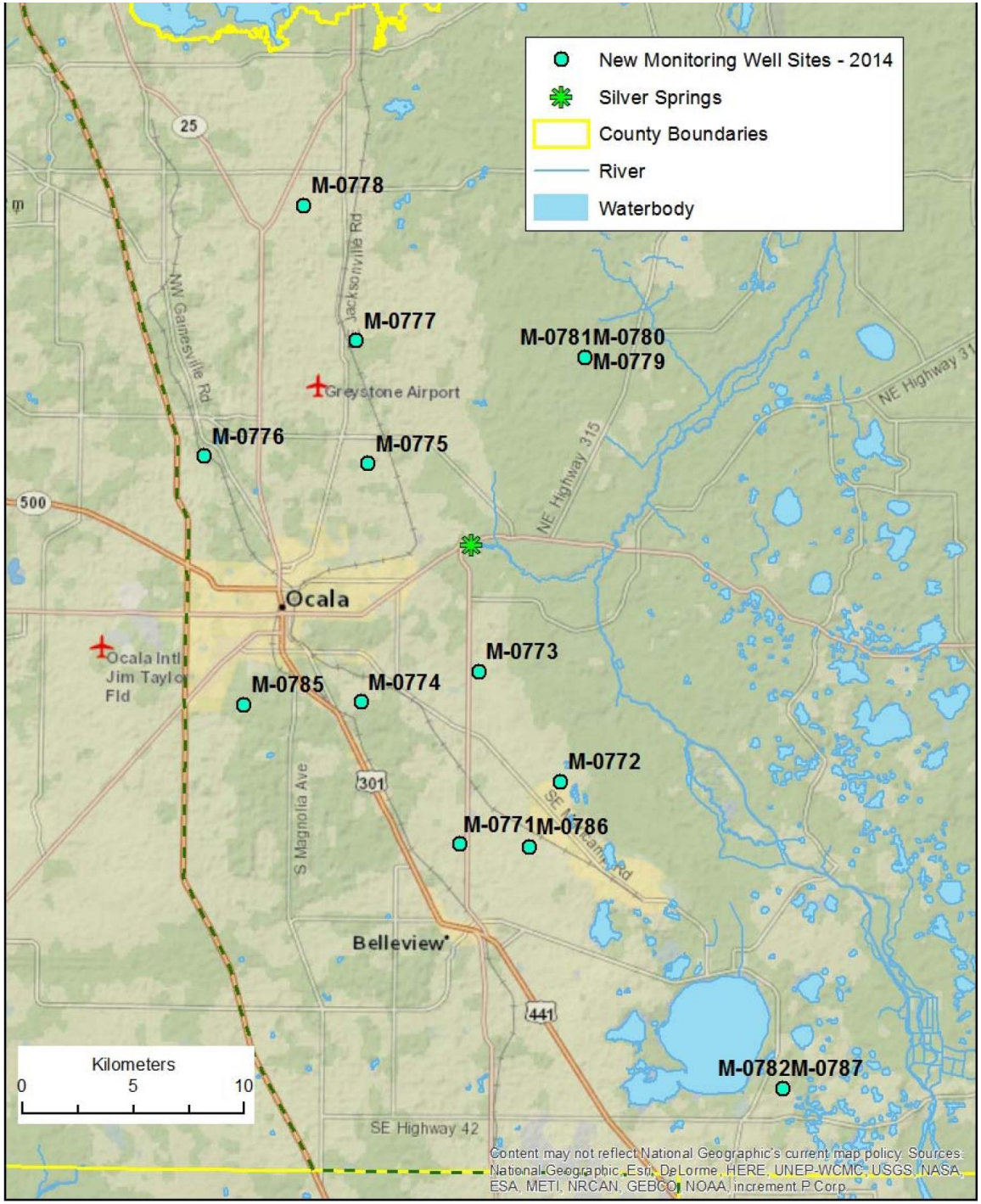
2. Determine the impact of denitrification within the Surficial/Floridan Aquifer Systems on N loading to Silver Springs

3. Identify hot spots and hot moments of N delivery and attenuation within the Silver Springs springshed

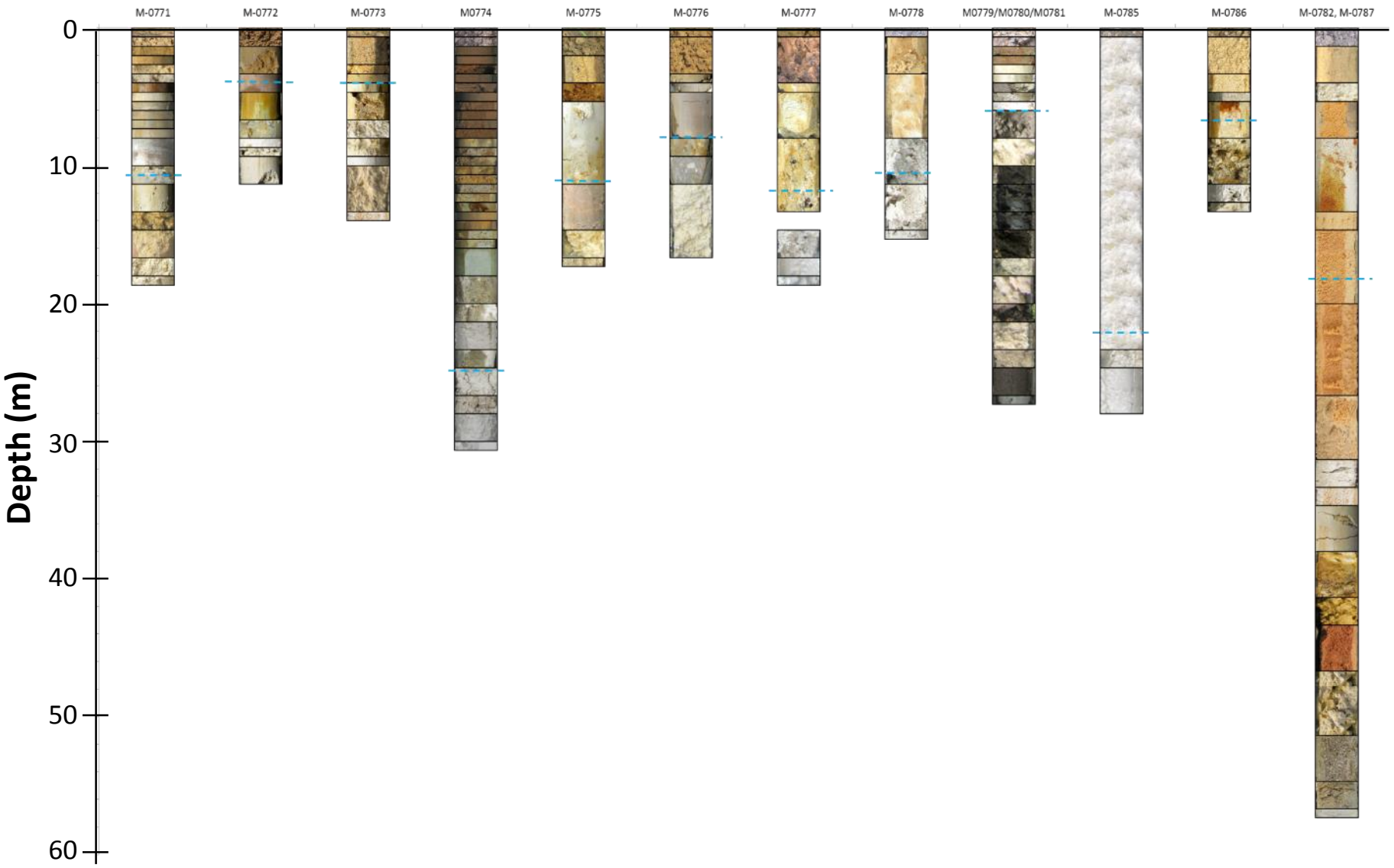


Florida Geological Survey Special Publication 31

$N \rightarrow NO_3^- \rightarrow N_2 \quad ?$

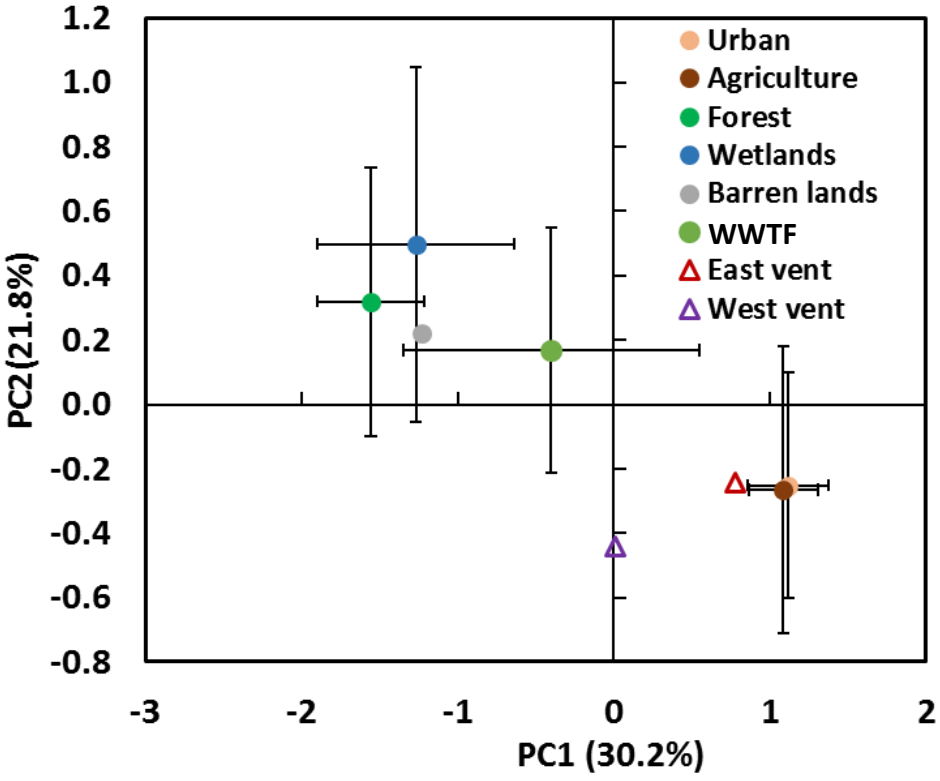

New Monitoring Well Sites - 2014
Silver Springs
County Boundaries
River
Waterbody
M-0778
M-0777
M-0781
M-0780
M-0779
M-0776
M-0775
M-0773
M-0785
M-0774
M-0772
M-0771
M-0786
M-0782
M-0787
Greystone Airport
Ocala
Ocala Intl
Jim Taylor
Fld
Belleview
NW Gainesville Rd
Jacksonville Rd
NE Highway 315
NE Highway 31
S Magnolia Ave
SE Maricamp Rd
SE Highway 42
25
500
301
441
Kilometers
0
5
10
Content may not reflect National Geographic's current map policy. Sources: National Geographic, Esri, DeLorme, HERE, UNEP-WCMC, USGS, NASA, ESA, METI, NRCAN, GEBCO, NOAA, increment P Corp.

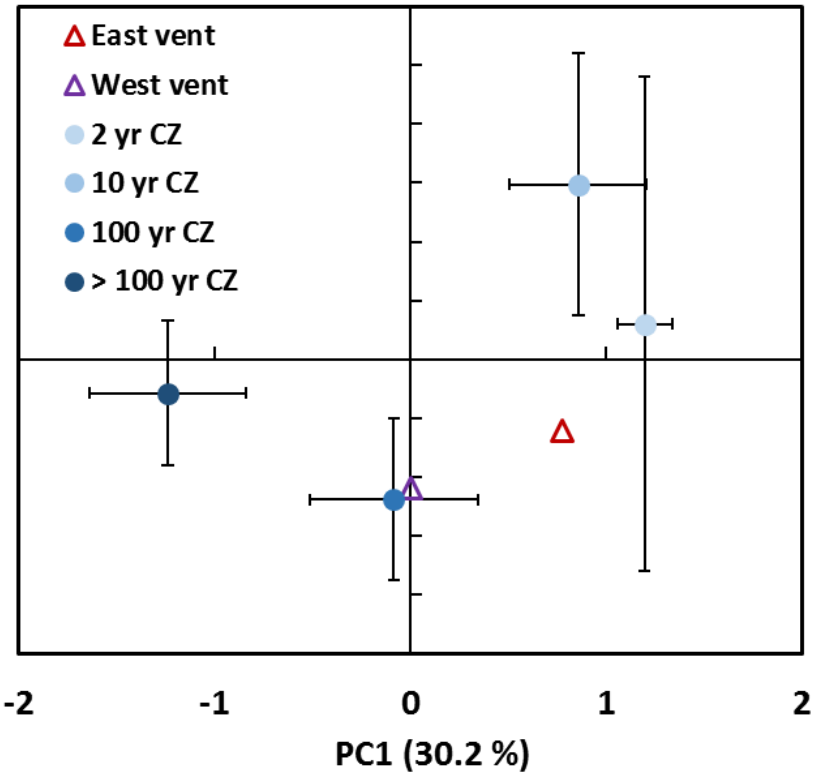
Subsurface Profiles

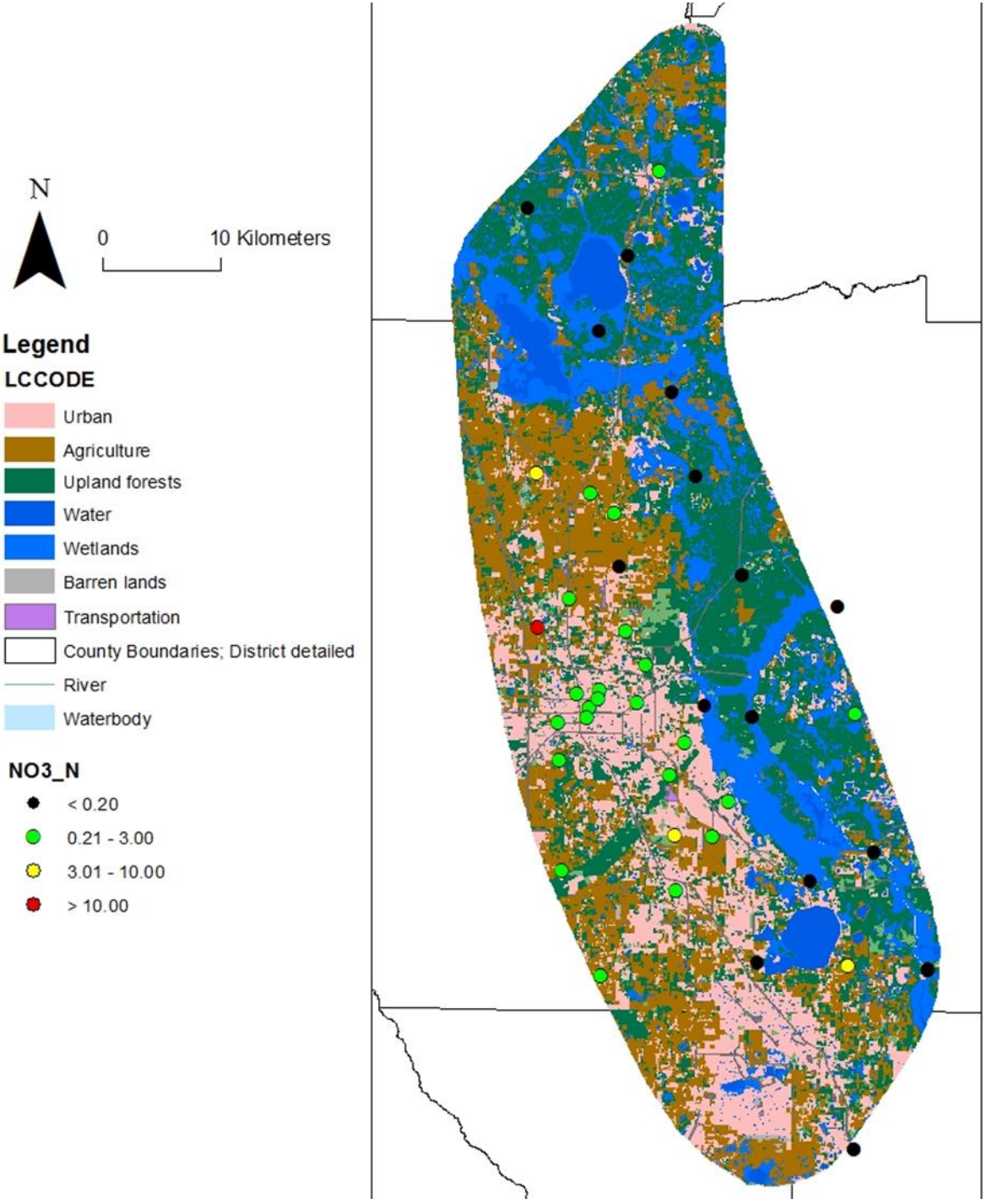


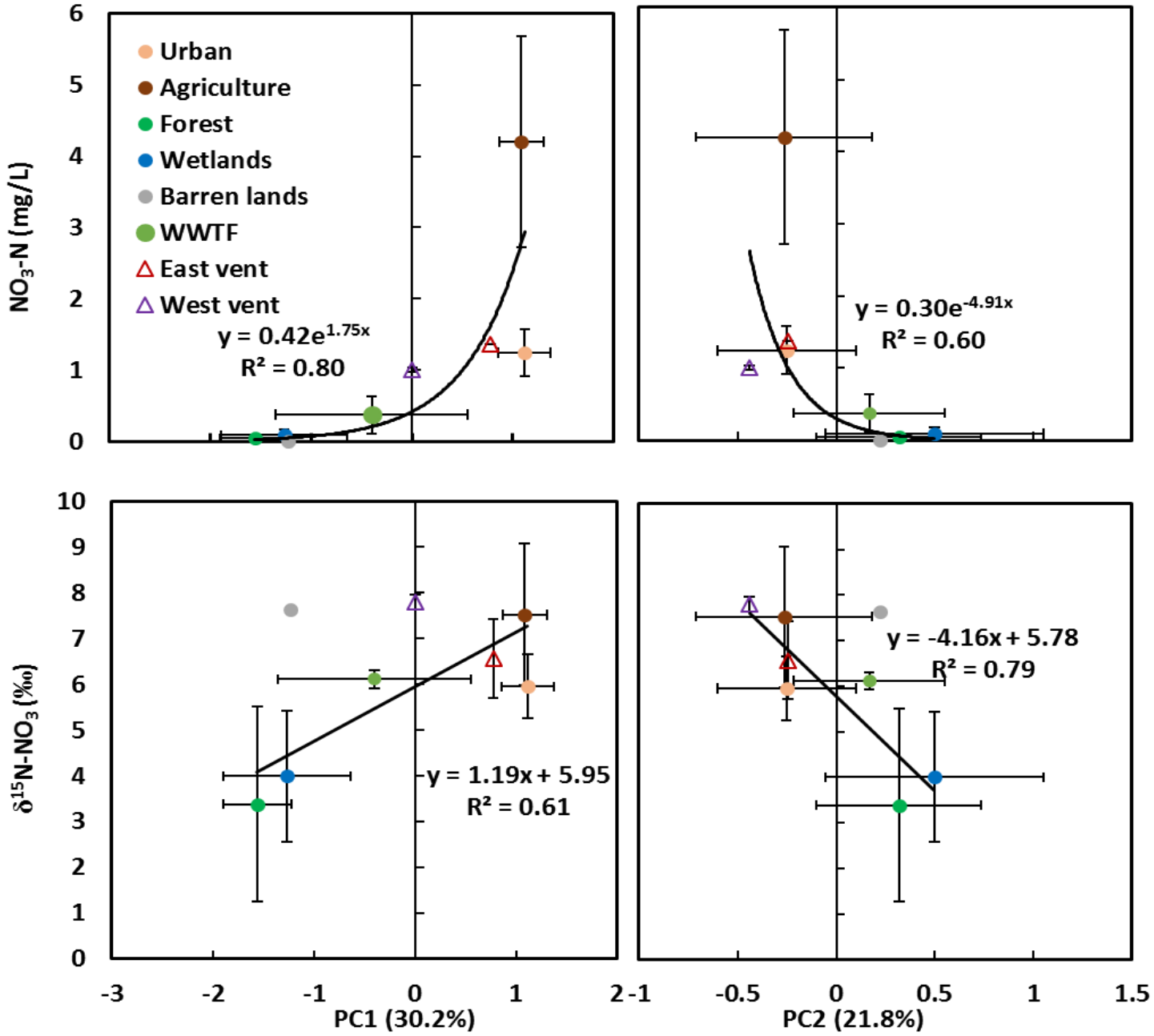
Aquifers

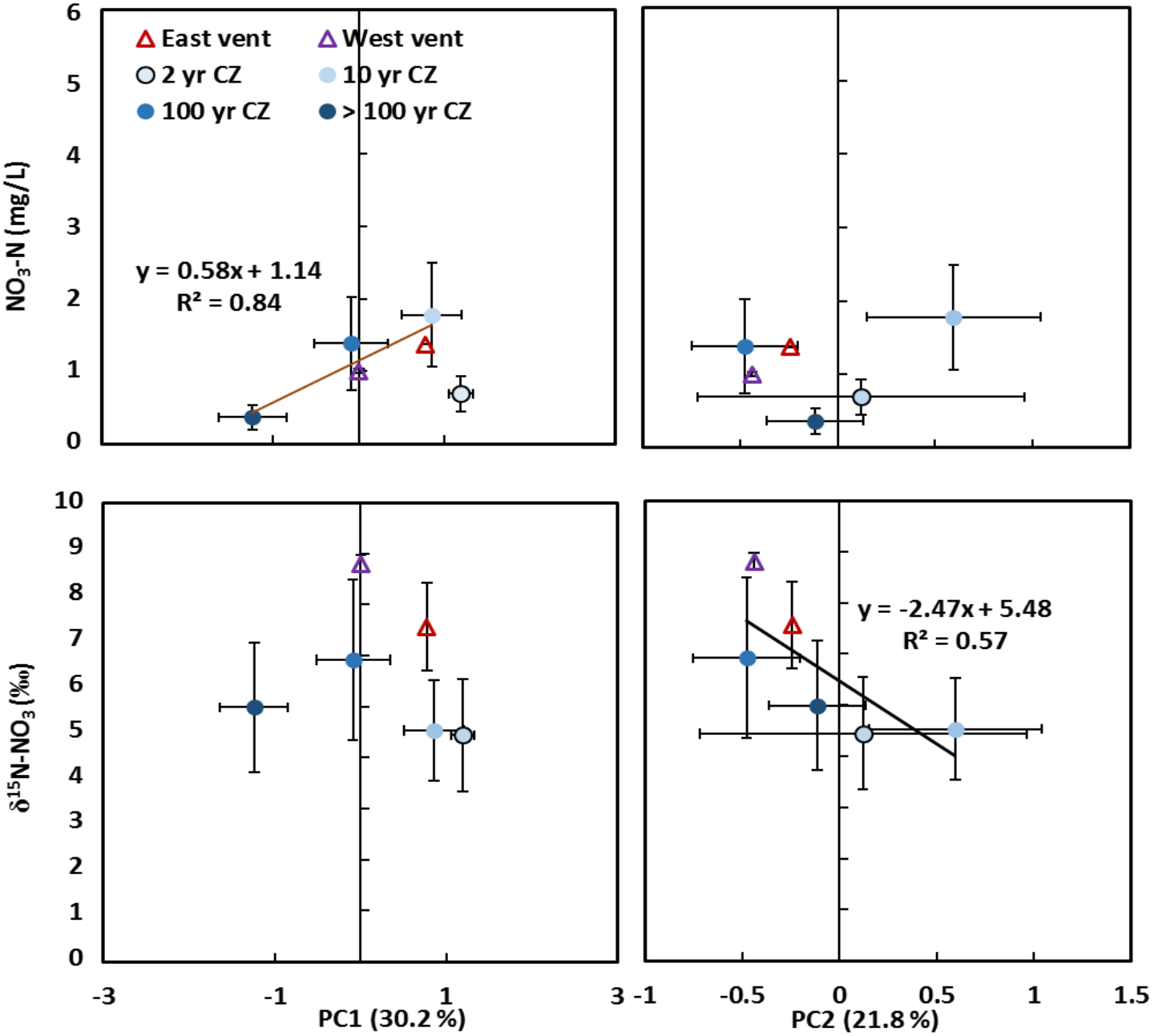
Parameter	PC1	PC2
Dissolved CH_4	-0.42	0.04
(DO)	0.36	-0.32
Water Temperature	0.39	-0.06
Ca-T	0.12	0.38
Cu-T	0.35	0.34
Fe-T	-0.10	0.45
Cl	0.10	0.46
SO_4-T	0.30	0.40
NH_4-T	-0.42	0.20
TOC	-0.35	0.15





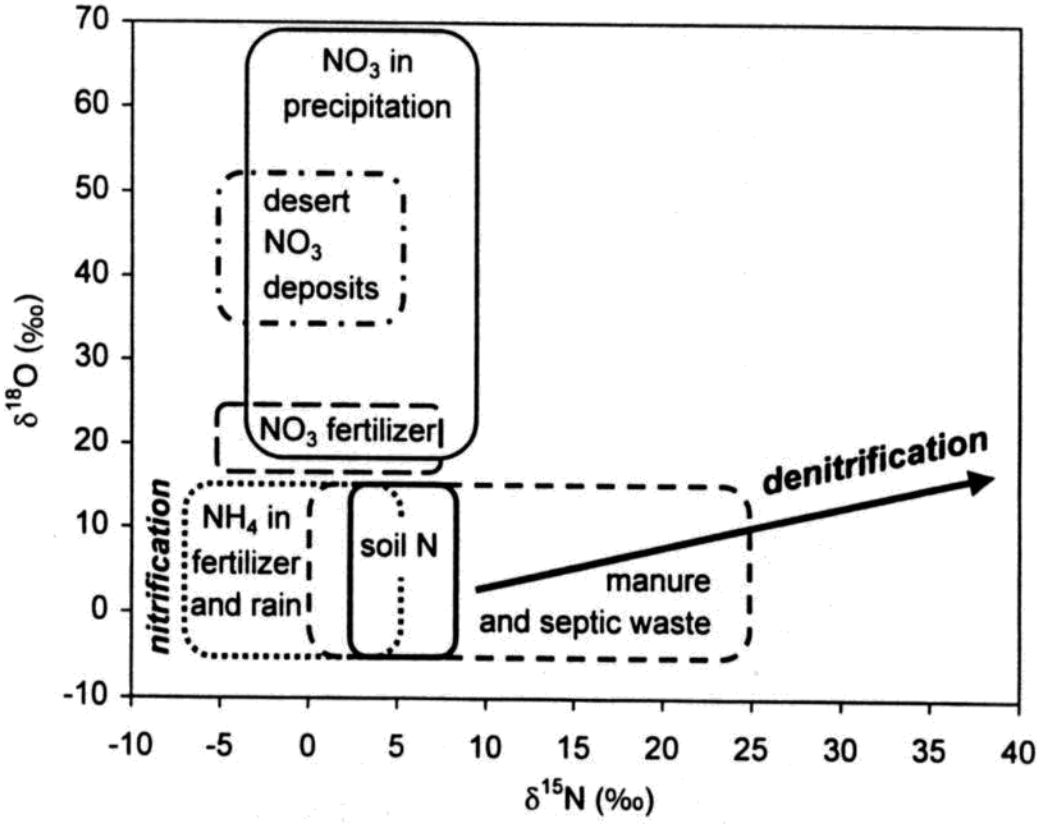

N
0
10 Kilometers
Legend
LCCODE
Urban
Agriculture
Upland forests
Water
Wetlands
Barren lands
Transportation
County Boundaries; District detailed
River
Waterbody
NO3_N
< 0.20
0.21 - 3.00
3.01 - 10.00
> 10.00


Urban
Agriculture
Forest
Wetlands
Barren lands
WWTF
East vent
West vent
y = 0.42e1.75x
R² = 0.80
y = 0.30e-4.91x
R² = 0.60
y = 1.19x + 5.95
R² = 0.61
y = -4.16x + 5.78
R² = 0.79
NO3-N (mg/L)
δ15N-NO3 (‰)
PC1 (30.2%)
PC2 (21.8%)


East vent
West vent
2 yr CZ
10 yr CZ
100 yr CZ
> 100 yr CZ
y = 0.58x + 1.14
R² = 0.84
y = -2.47x + 5.48
R² = 0.57
NO3-N (mg/L)
δ15N-NO3 (‰)
PC1 (30.2 %)
PC2 (21.8 %)
0
1
2
3
4
5
6
7
8
9
10
-3
-1
1
3
-1
-0.5
0
0.5
1
1.5

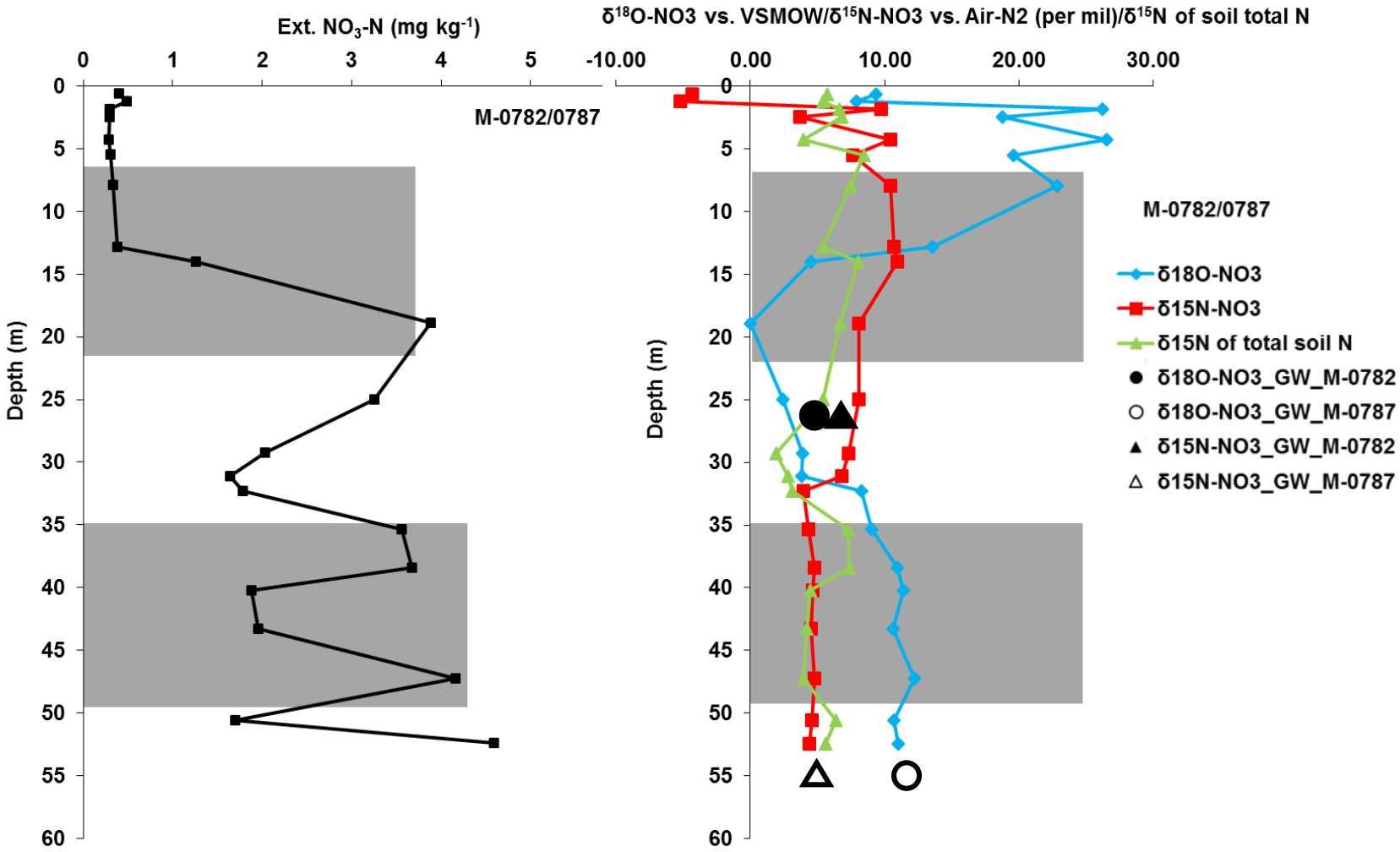
NO_3^- Stable isotopes ($\delta^{18}O$ and $\delta^{15}N$)

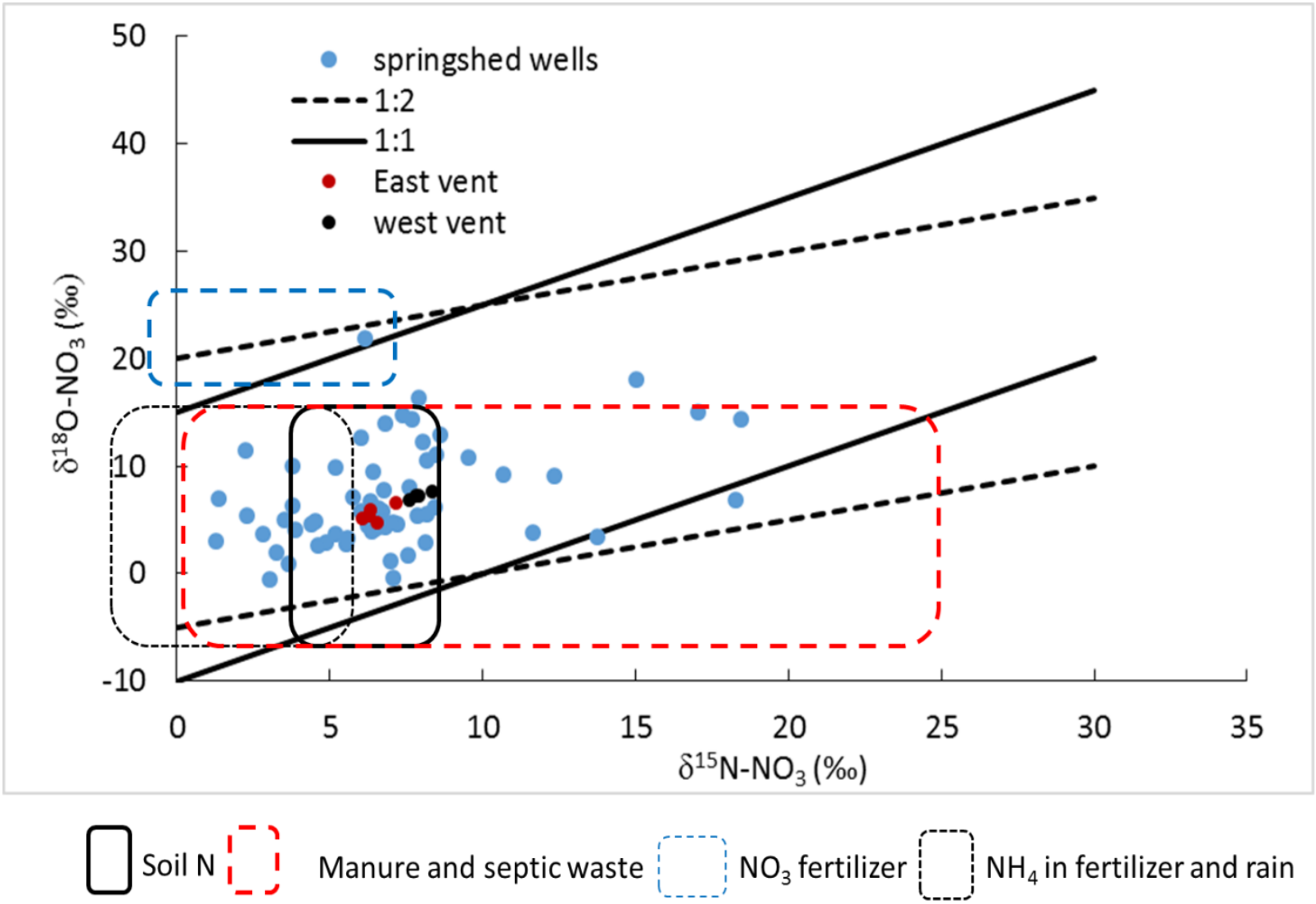
- Water extractable solution



Schematic of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ of nitrate from various sources as well as the isotopic effect of denitrification. (Adapted from http://wwwrcamnl.wr.usgs.gov/isoig/isopubs/Fig16-9.jpg)

Mixed nursery/pasture (L. Weir)

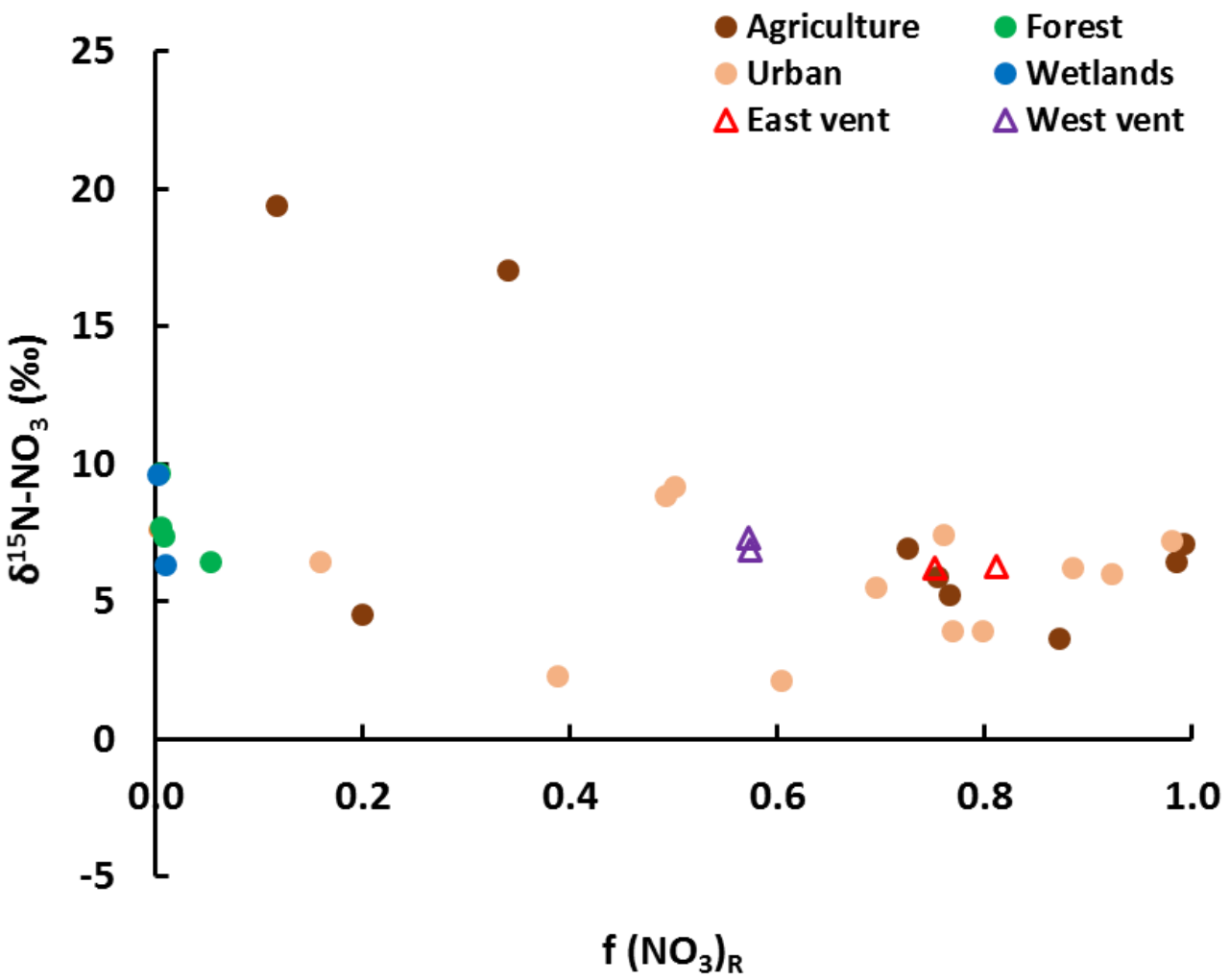



springshed wells
1:2
1:1
East vent
west vent
50
40
30
20
10
0
-10
0
5
10
15
20
25
30
35
δ18O-NO3 (‰)
δ15N-NO3 (‰)
Soil N
Manure and septic waste
NO3 fertilizer
NH4 in fertilizer and rain

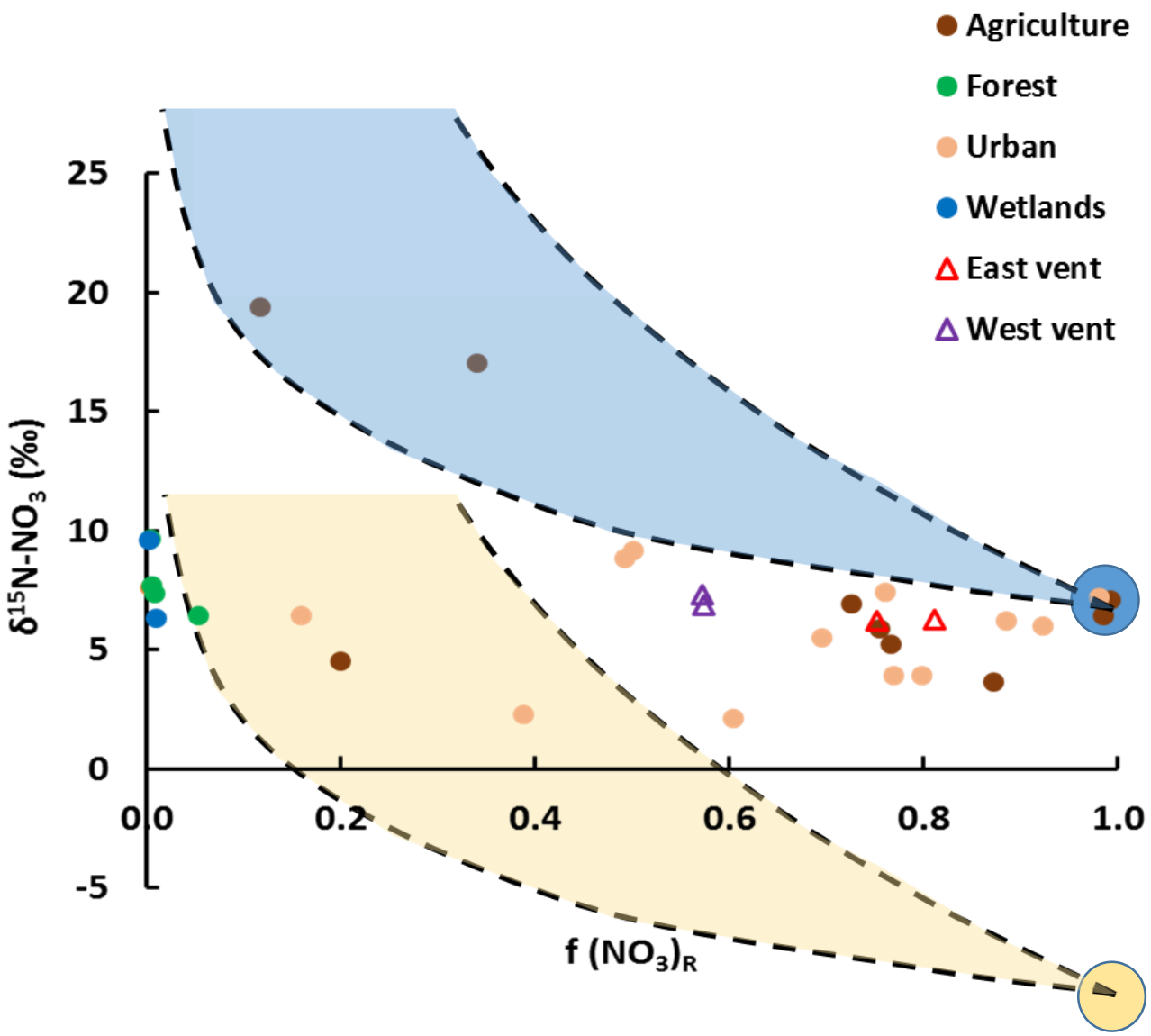
Dissolved gases

- Dissolved N_2
  - Soluble (P_{N2})
  - Produced by denitrification
- Dissolved noble gases (Ar, Ne, …)
  - Recharge temperature
  - Excess air

Denitrification Progression



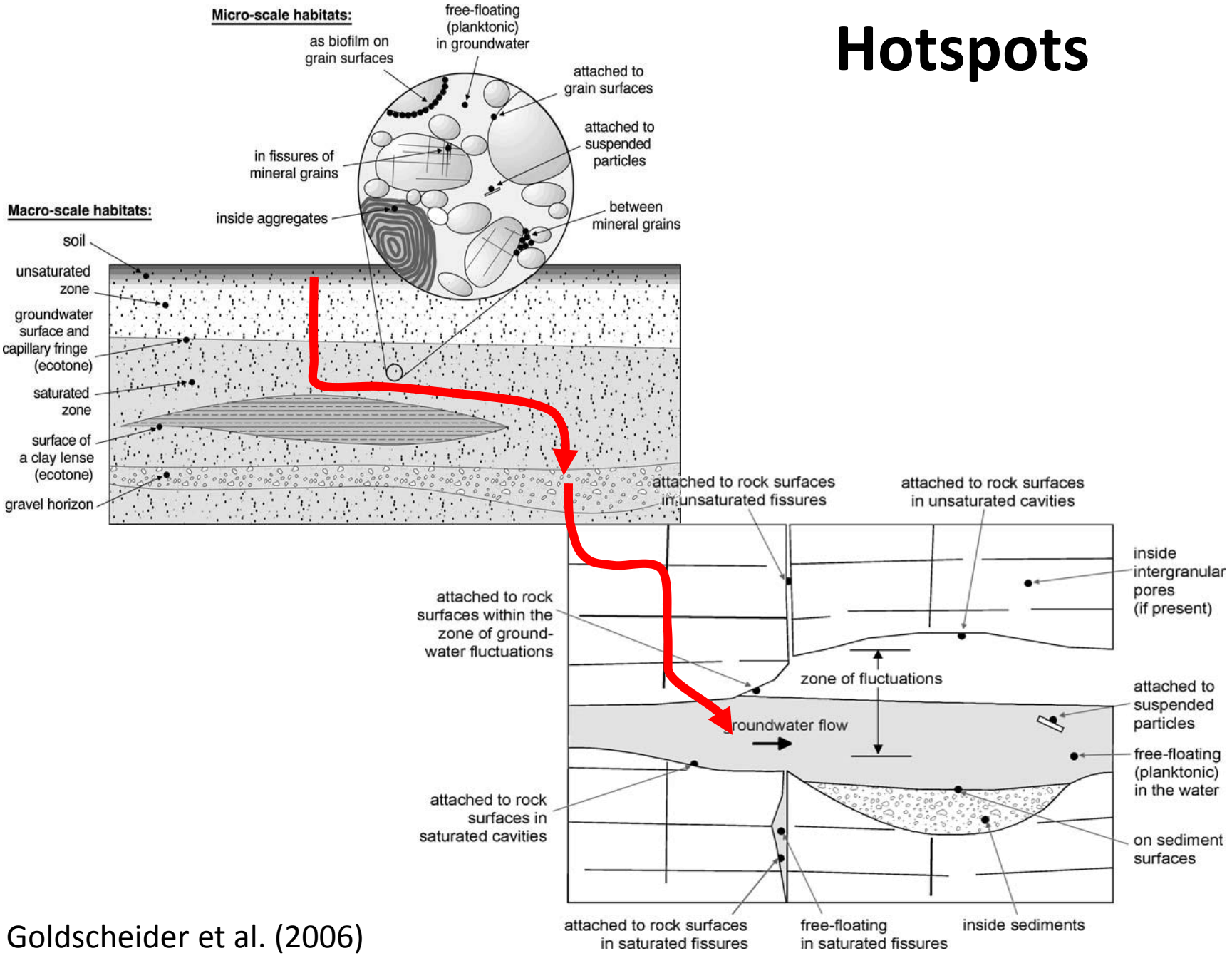
Source ID


Agriculture
Forest
Urban
Wetlands
East vent
West vent
25
20
15
10
5
0
-5
0.0
0.2
0.4
0.6
0.8
1.0
δ15N-NO3 (‰)
f (NO3)R

Sources: Conclusions/Next steps

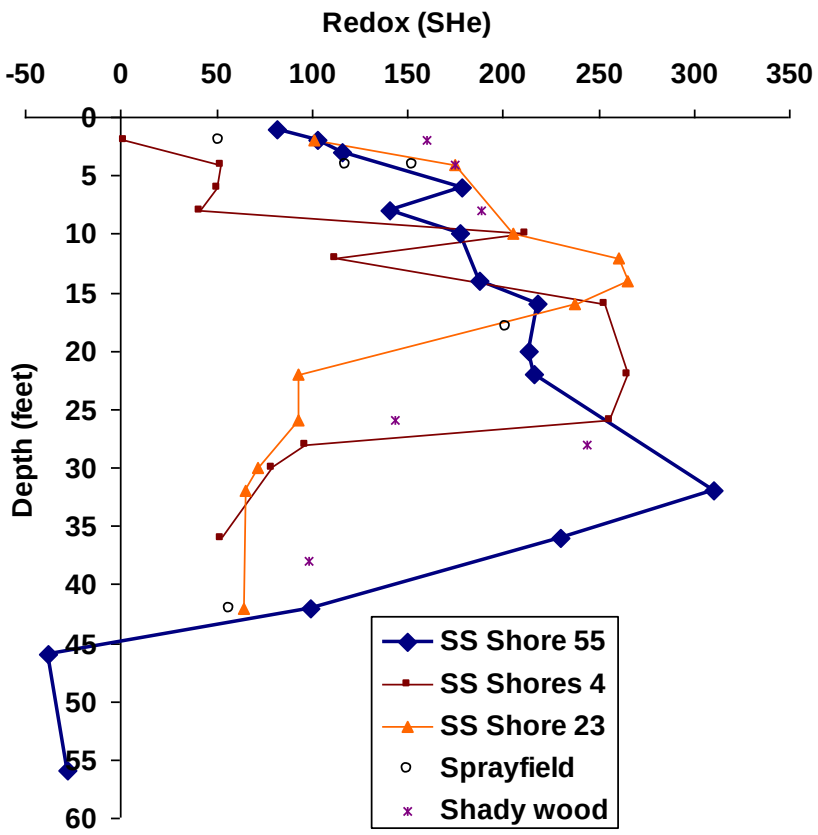
- Springshed sources
  - Ag and Urban, West (mostly-unconfined)
  - Highest in 10yr capture zone
- Source ID
  - Most wells/vents, $\delta^{15}N$=7‰, $\delta^{18}O$=5‰
  - Evidence for both organic (Ag) and inorganic sources (Urban)
- Additional vents
  - Source, denitrification, chemical composition
- Boron and B isotopes to separate soil N and manure/urban?

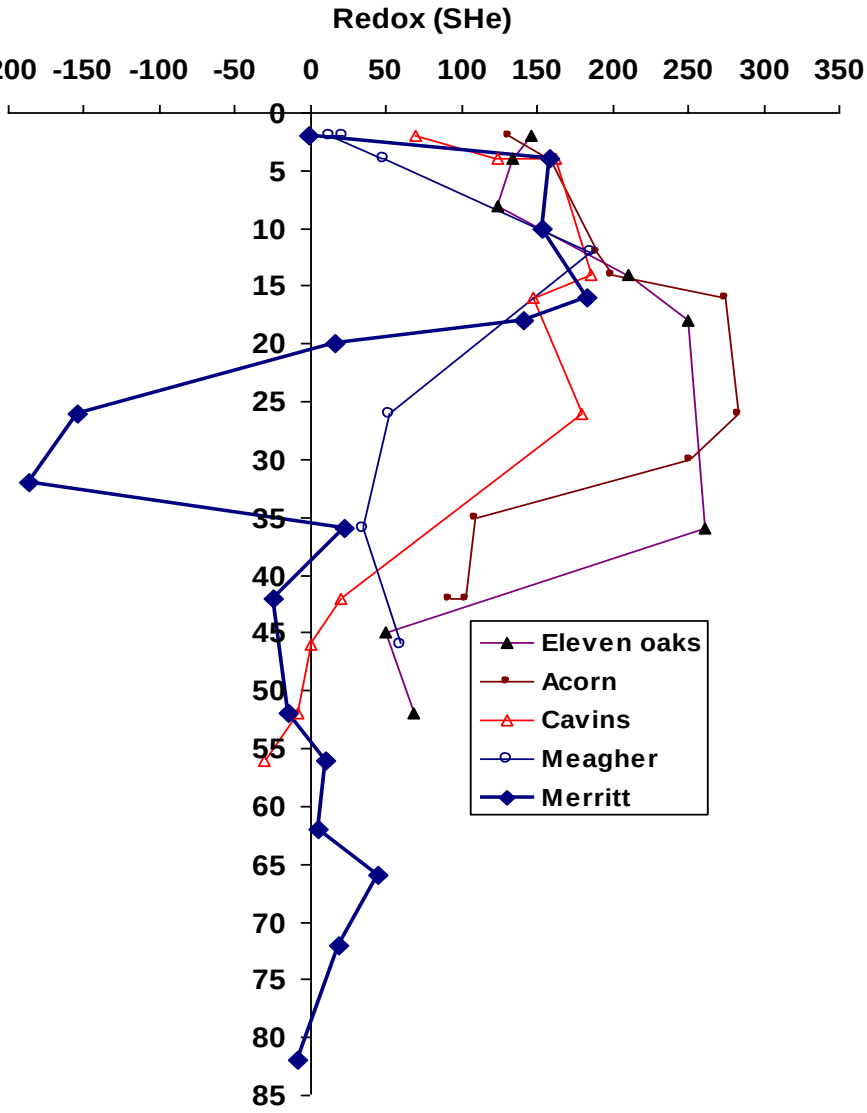
Hotspots



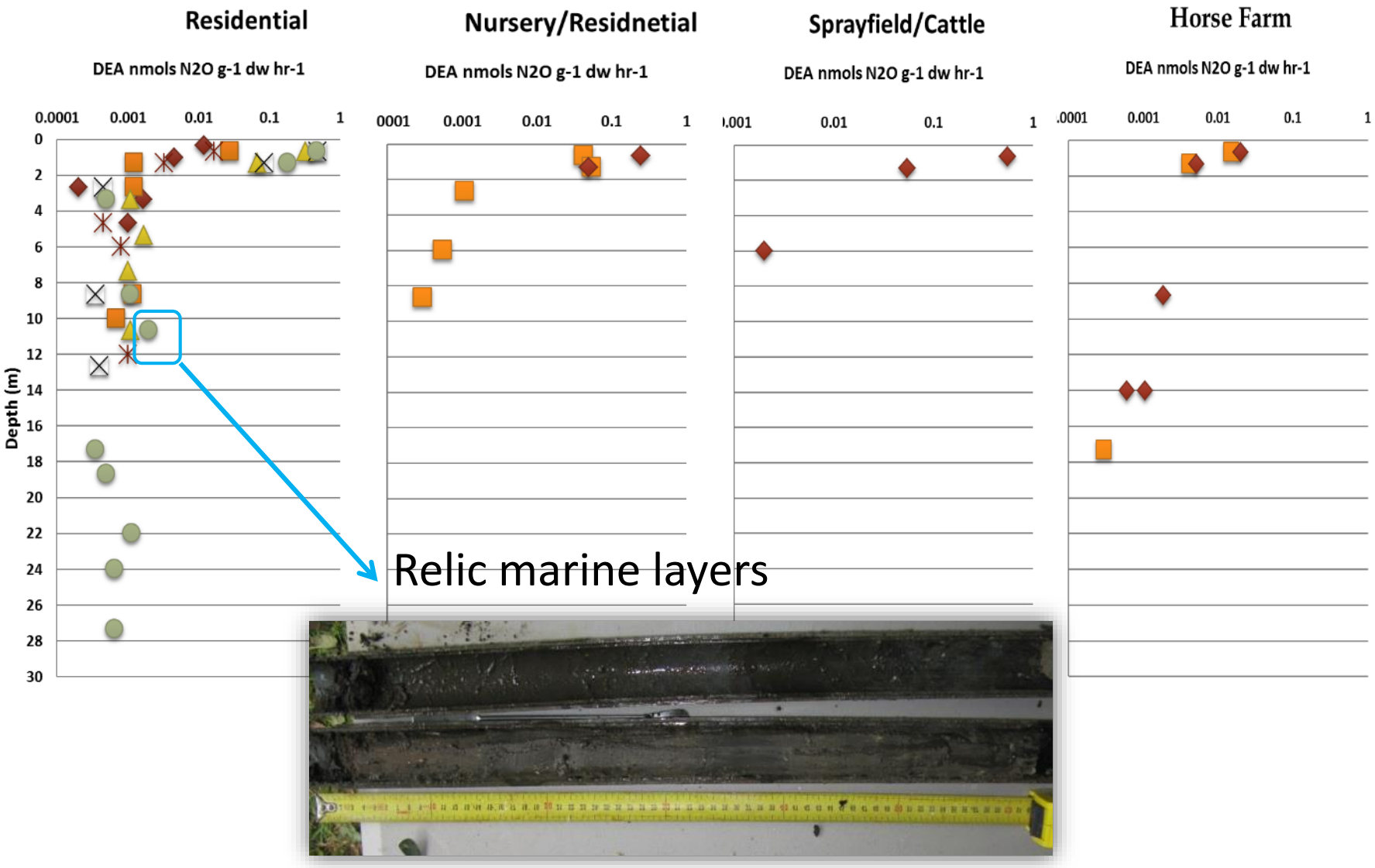
Goldscheider et al. (2006)

Denitrification - Hotspots

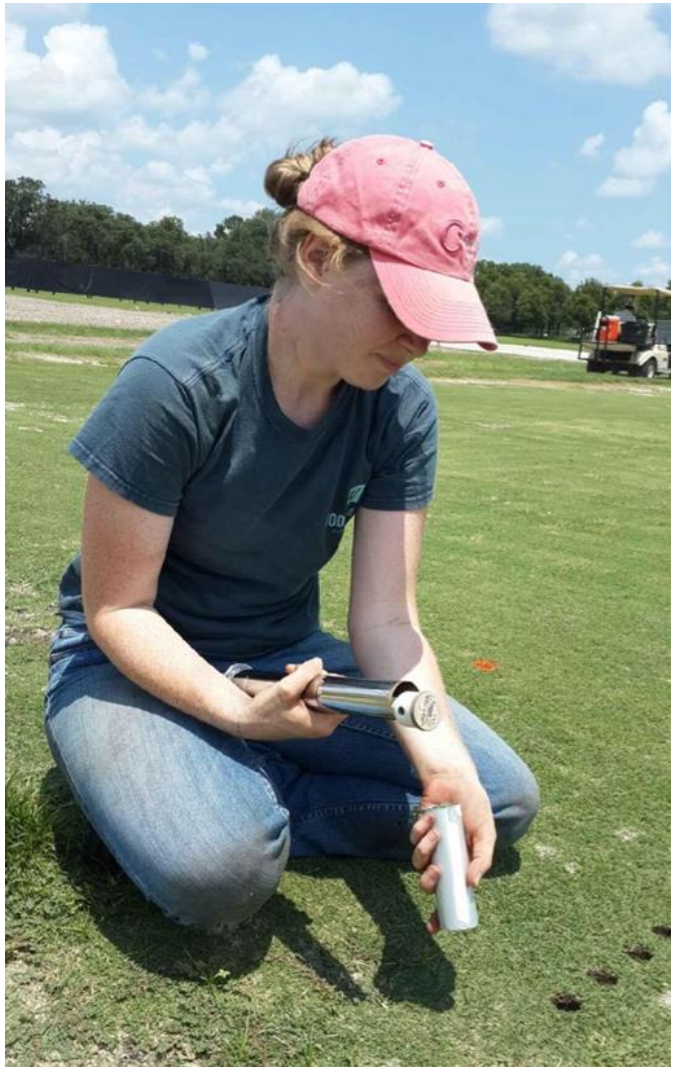




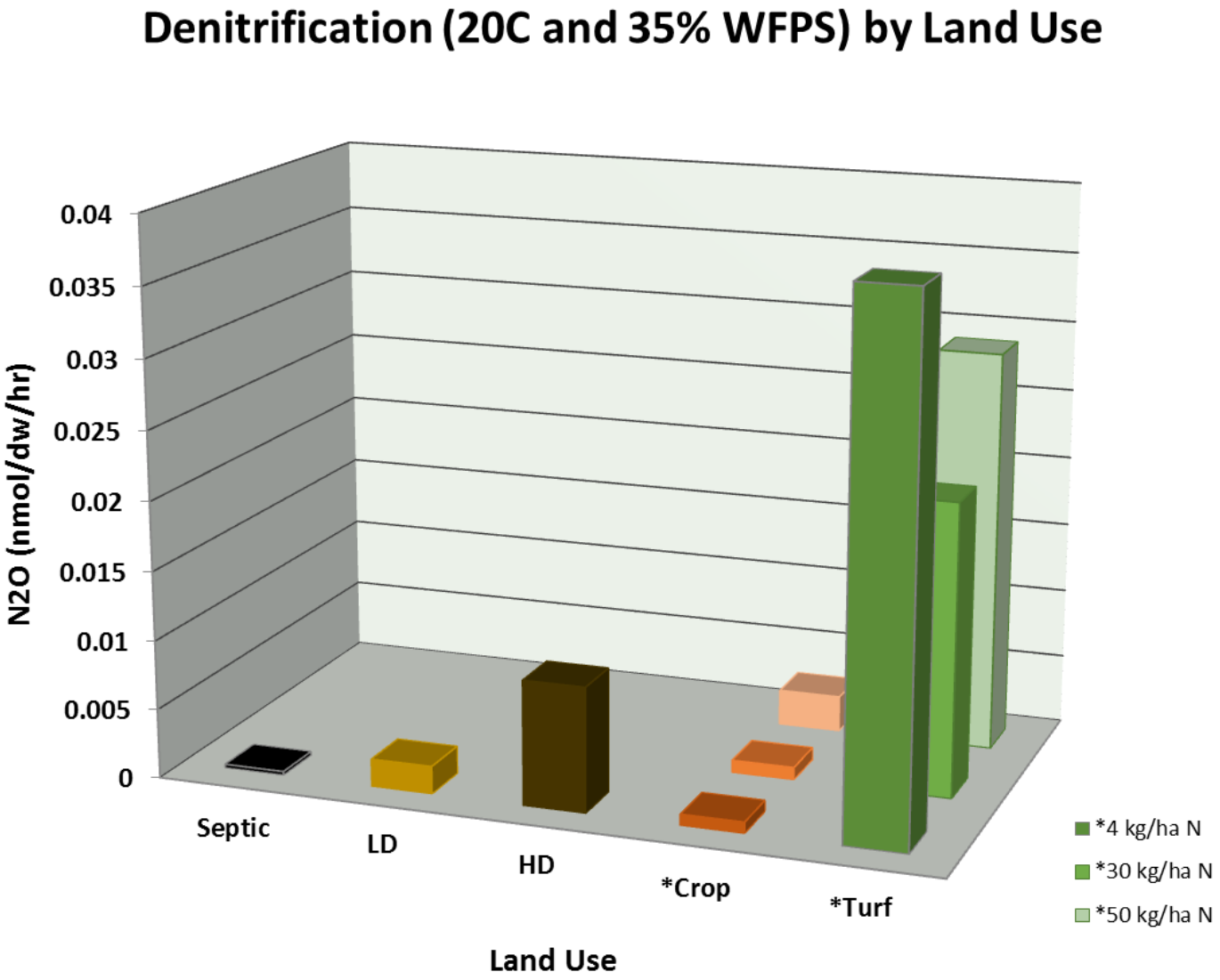
Denitrification



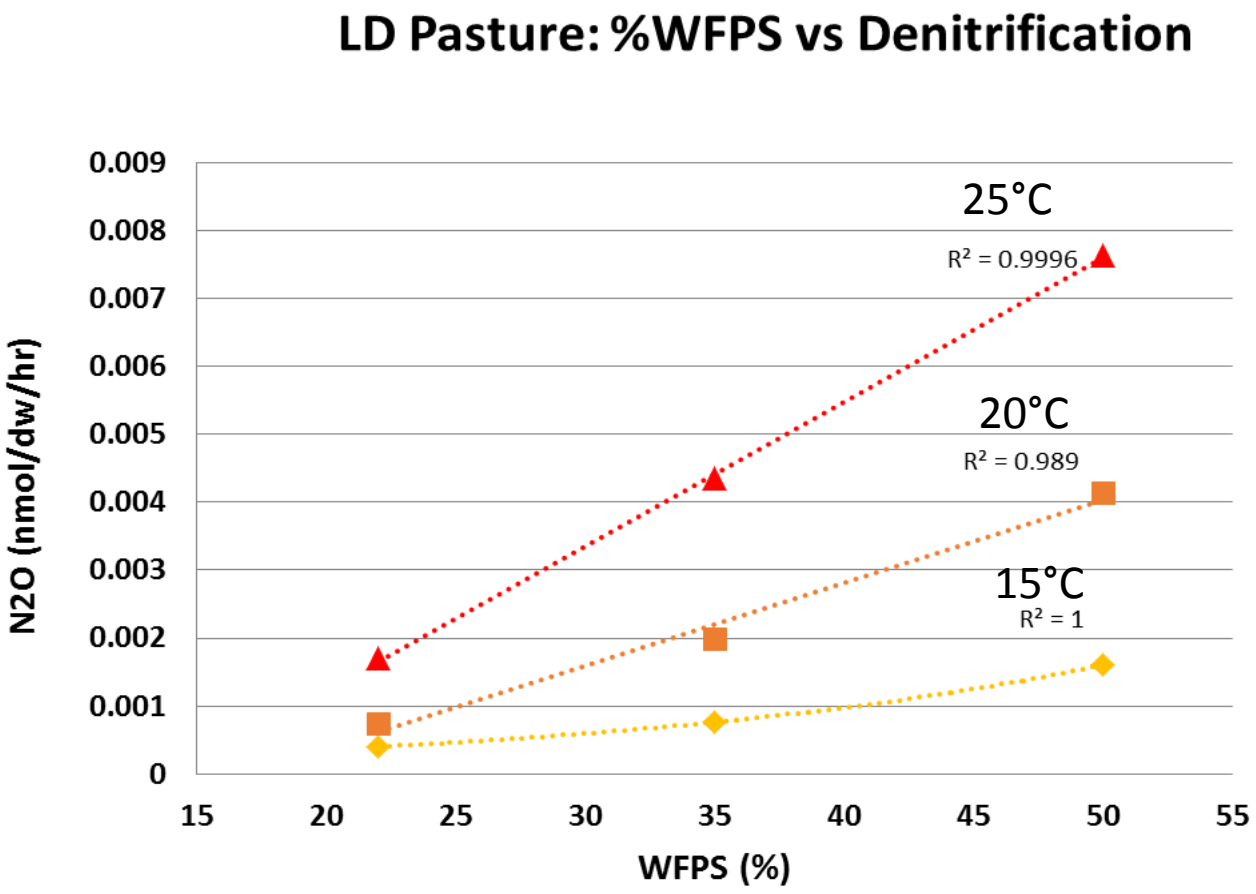
Soil Denitrification



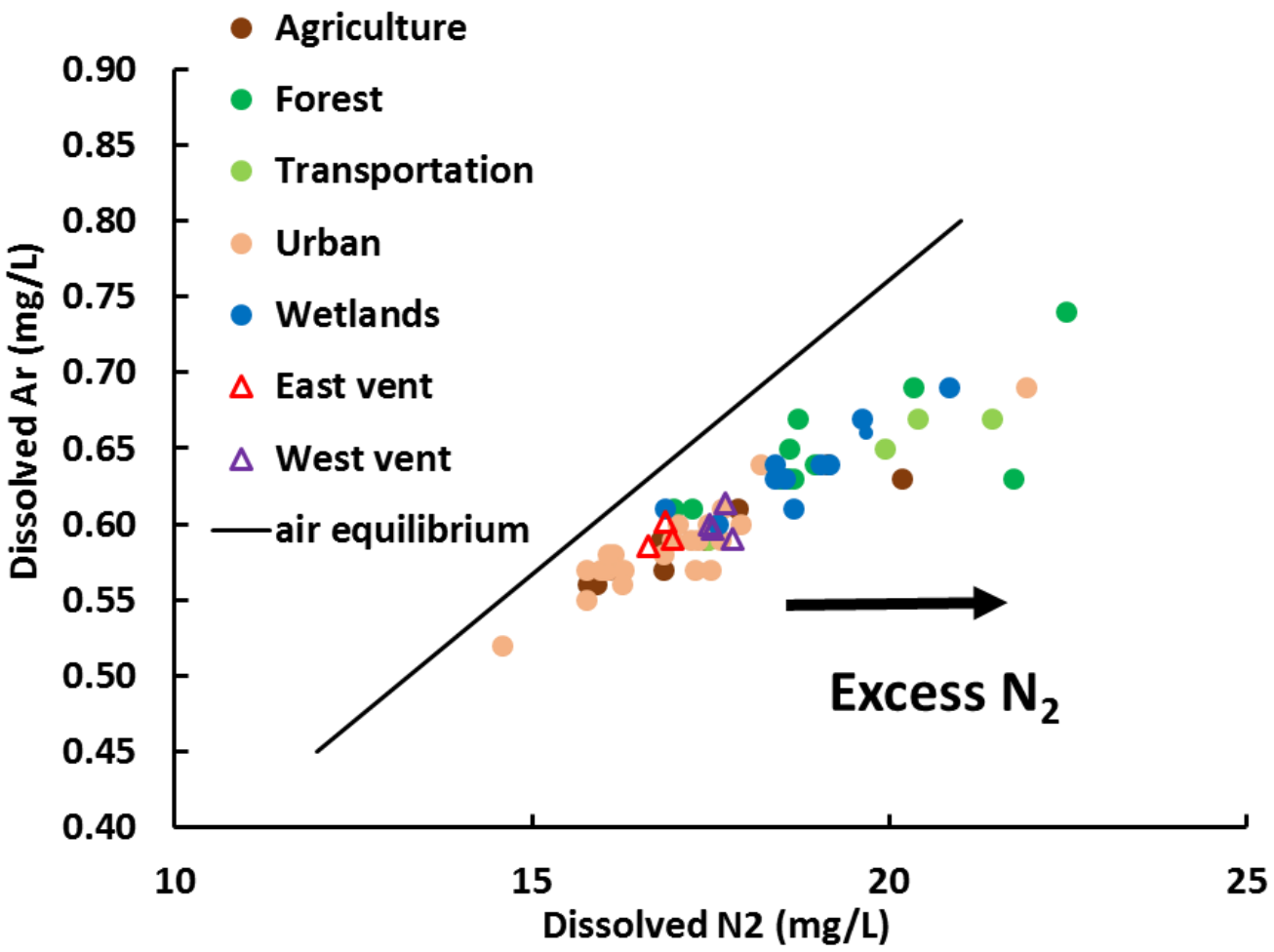
Soil Denitrification

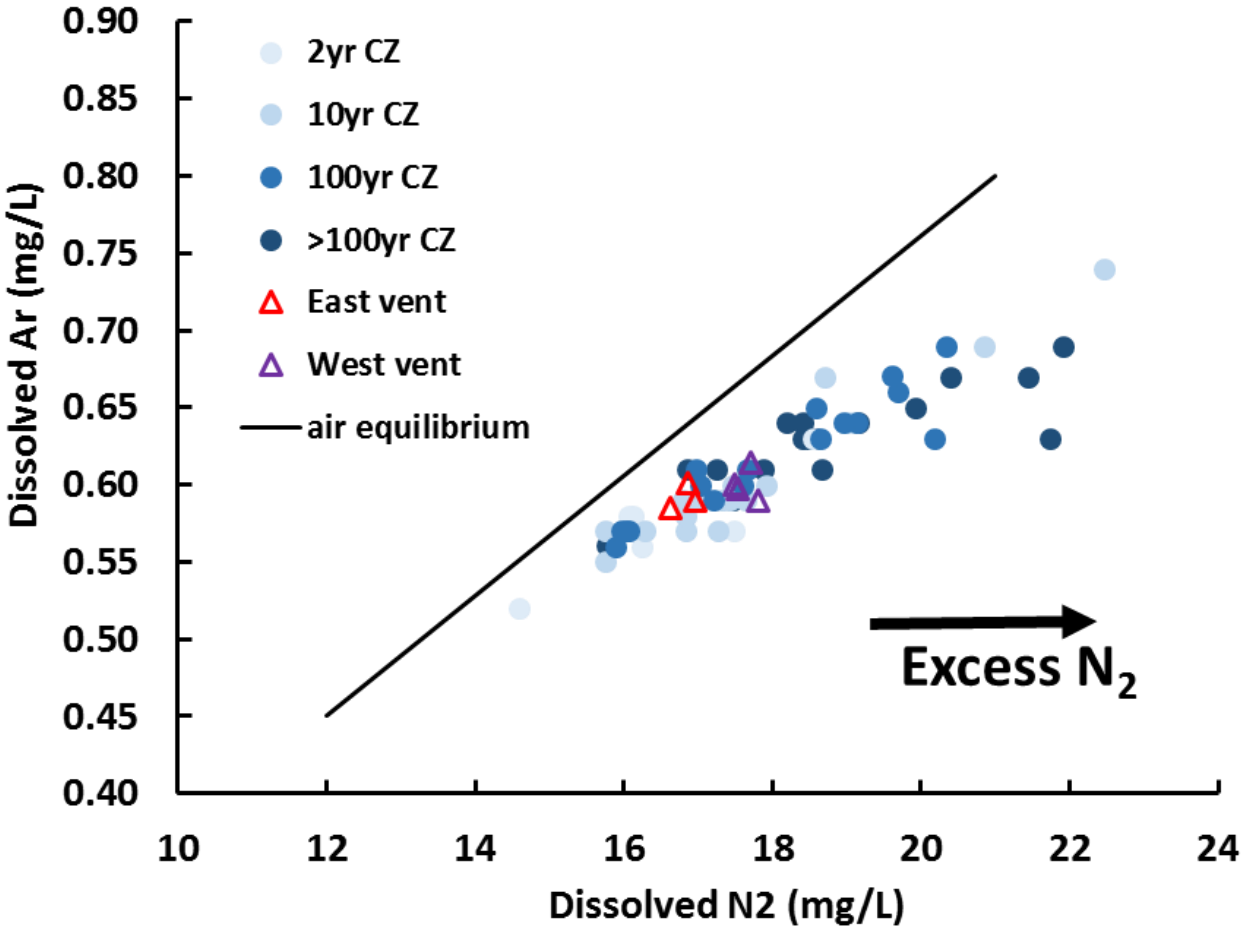


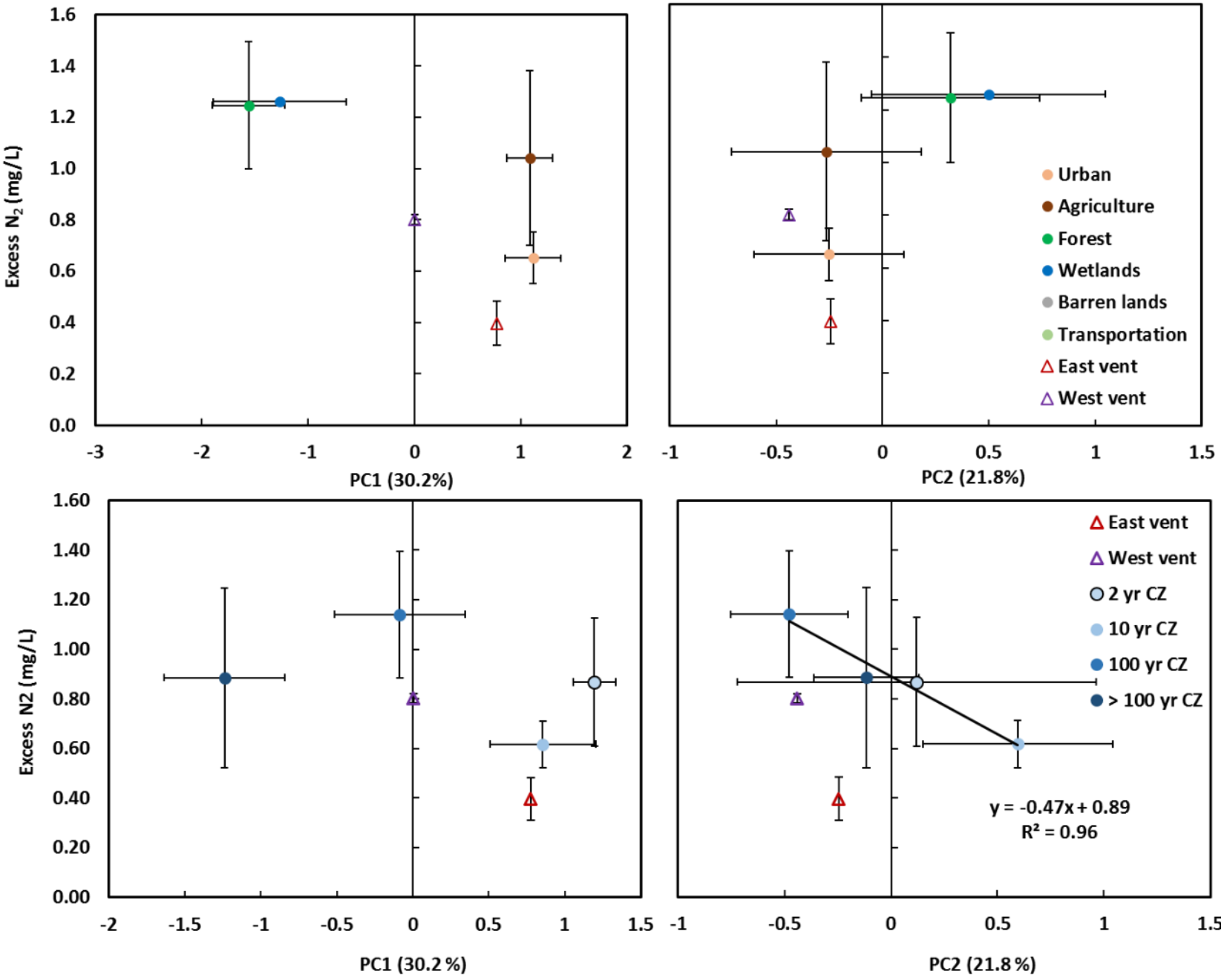
Soil Denitrification



Aquifer denitrification

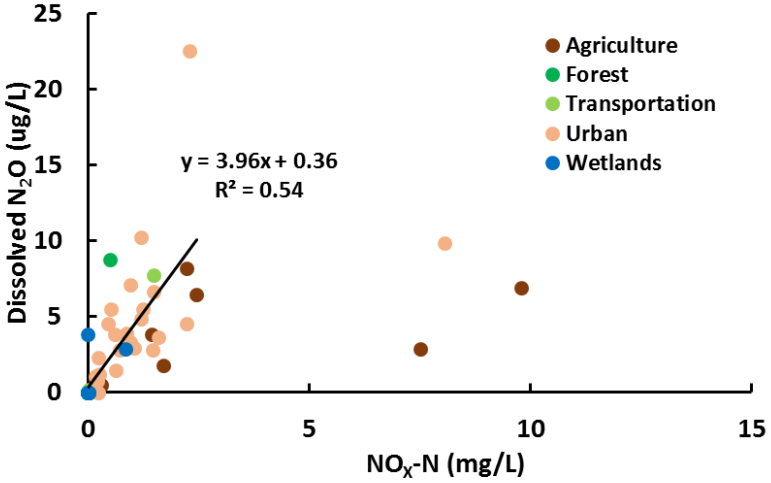


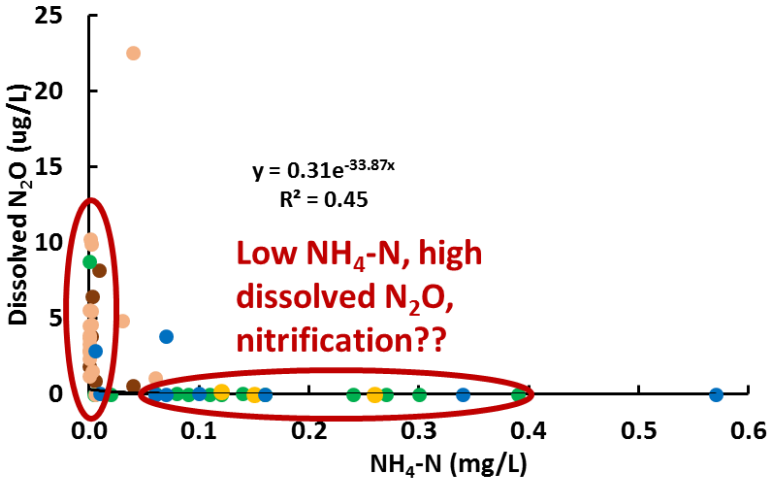

0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
Dissolved Ar (mg/L)
10
12
14
16
18
20
22
24
Dissolved N2 (mg/L)
2yr CZ
10yr CZ
100yr CZ
>100yr CZ
East vent
West vent
air equilibrium
Excess N2

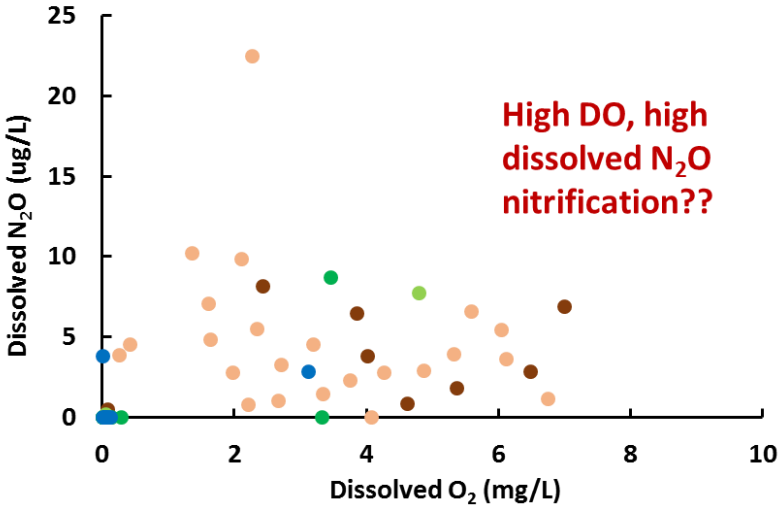

Excess N_2 (mg/L)
PC1 (30.2%)
PC2 (21.8%)
Urban
Agriculture
Forest
Wetlands
Barren lands
Transportation
East vent
West vent
Excess N2 (mg/L)
PC1 (30.2 %)
PC2 (21.8 %)
2 yr CZ
10 yr CZ
100 yr CZ
> 100 yr CZ
y = -0.47x + 0.89
R² = 0.96

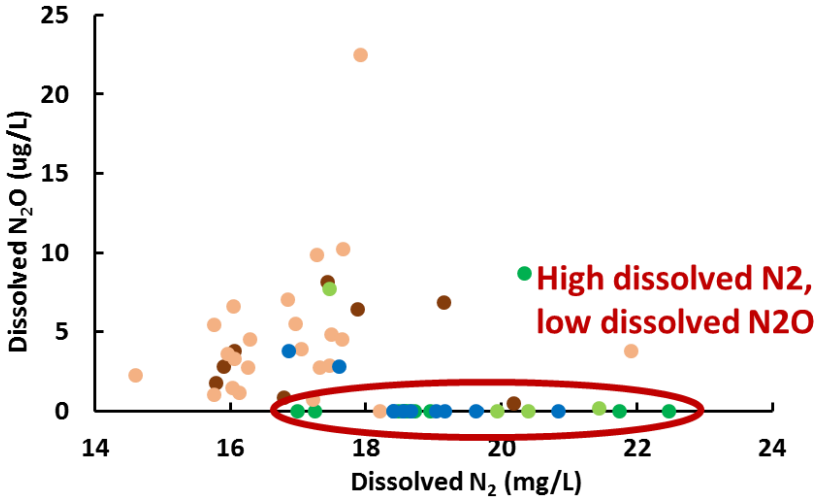
N Processes, Controls

$$CH_4 + 4NO_3^- \rightarrow CO_2 + 4NO_2^- + 2H_2O$$
$$3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O$$
$$CH_4 + NO_3^- + 2H^+ \rightarrow CO_2 + NH_4^+ + H_2O$$



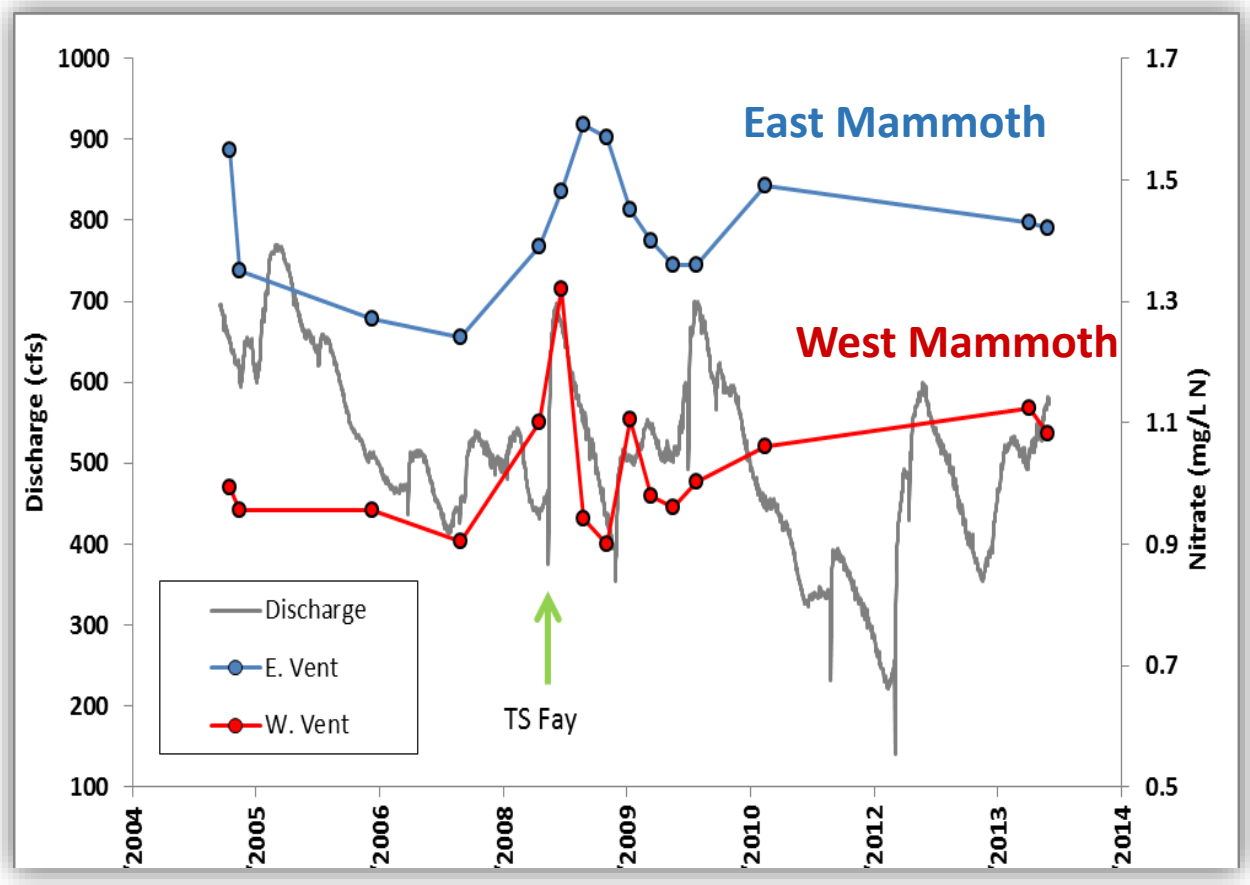




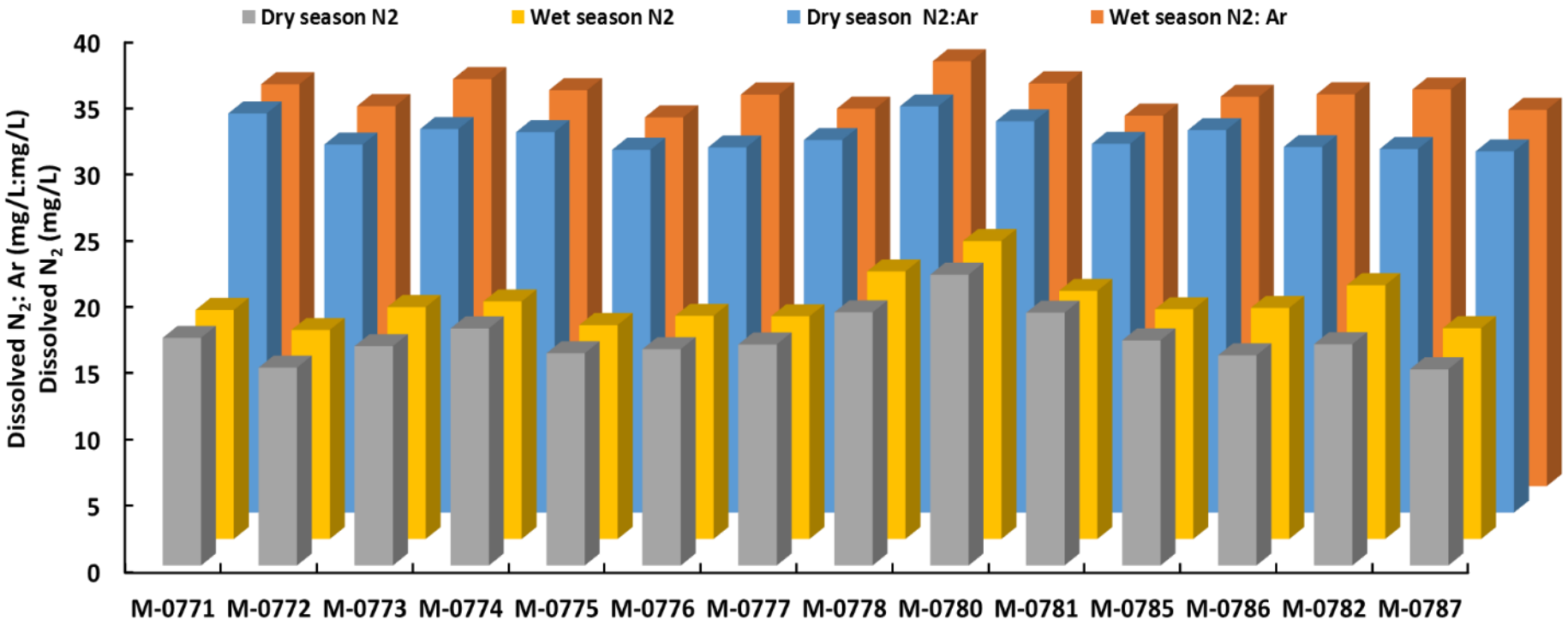


Hot Moments?

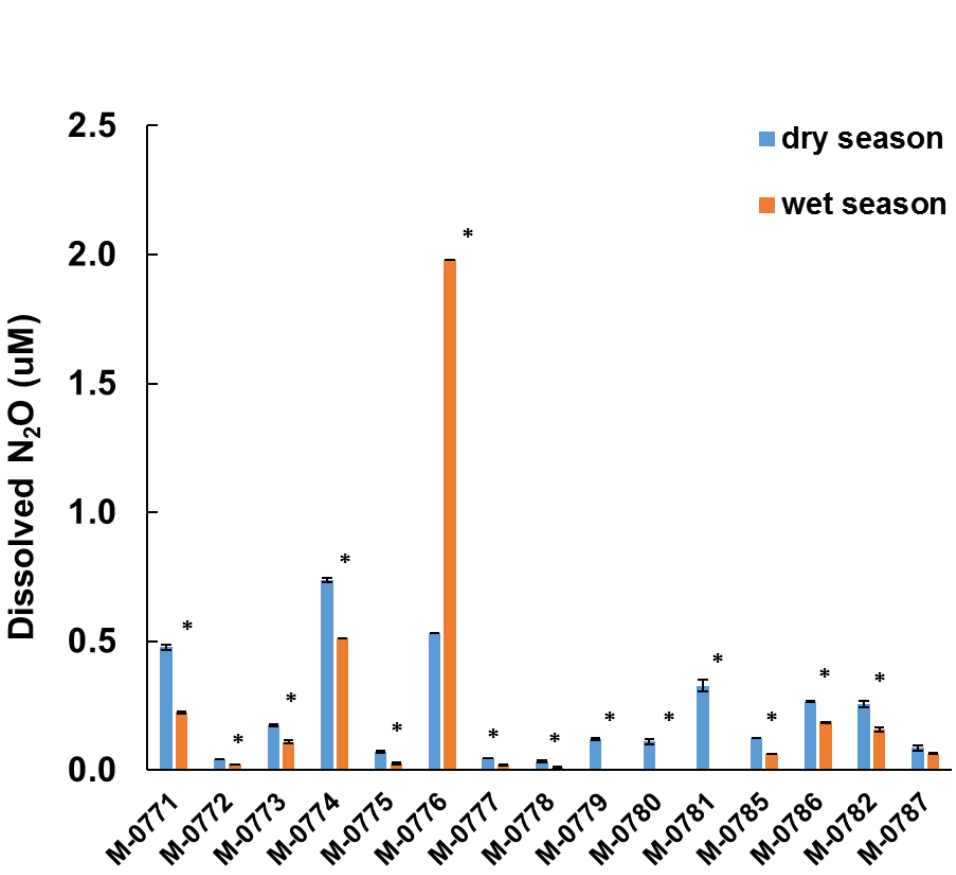
- Seasonal
  - Wet/Dry season changes
  - Growth cycles, Land use activities
- Events
  - Storm events, stormwater discharges

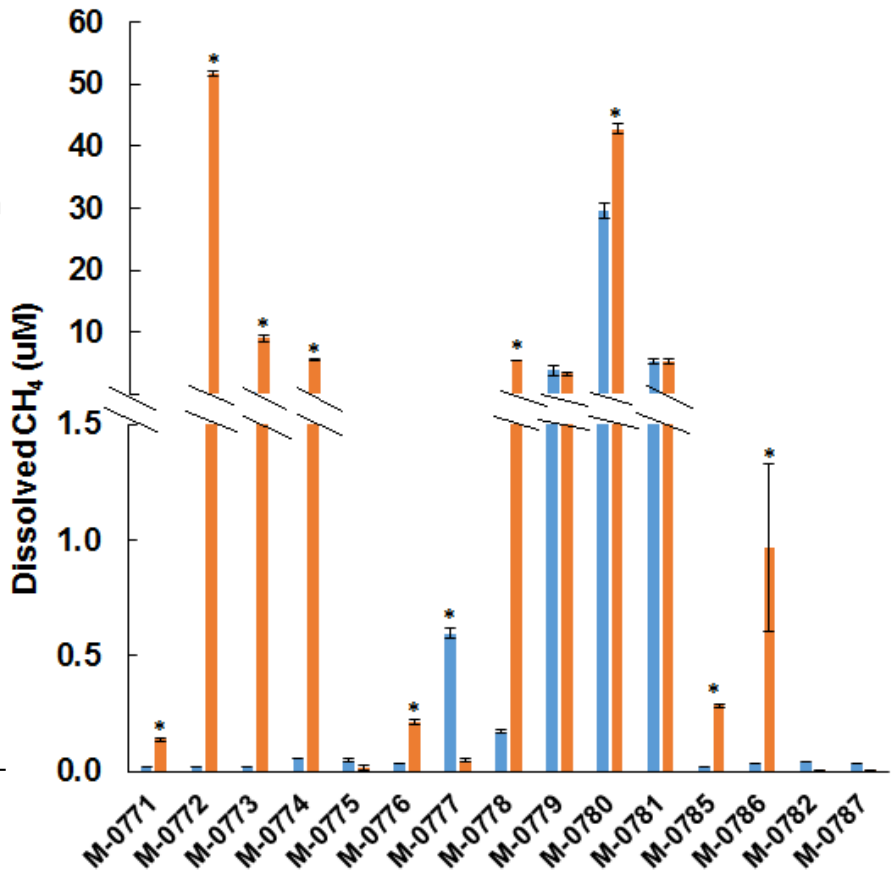


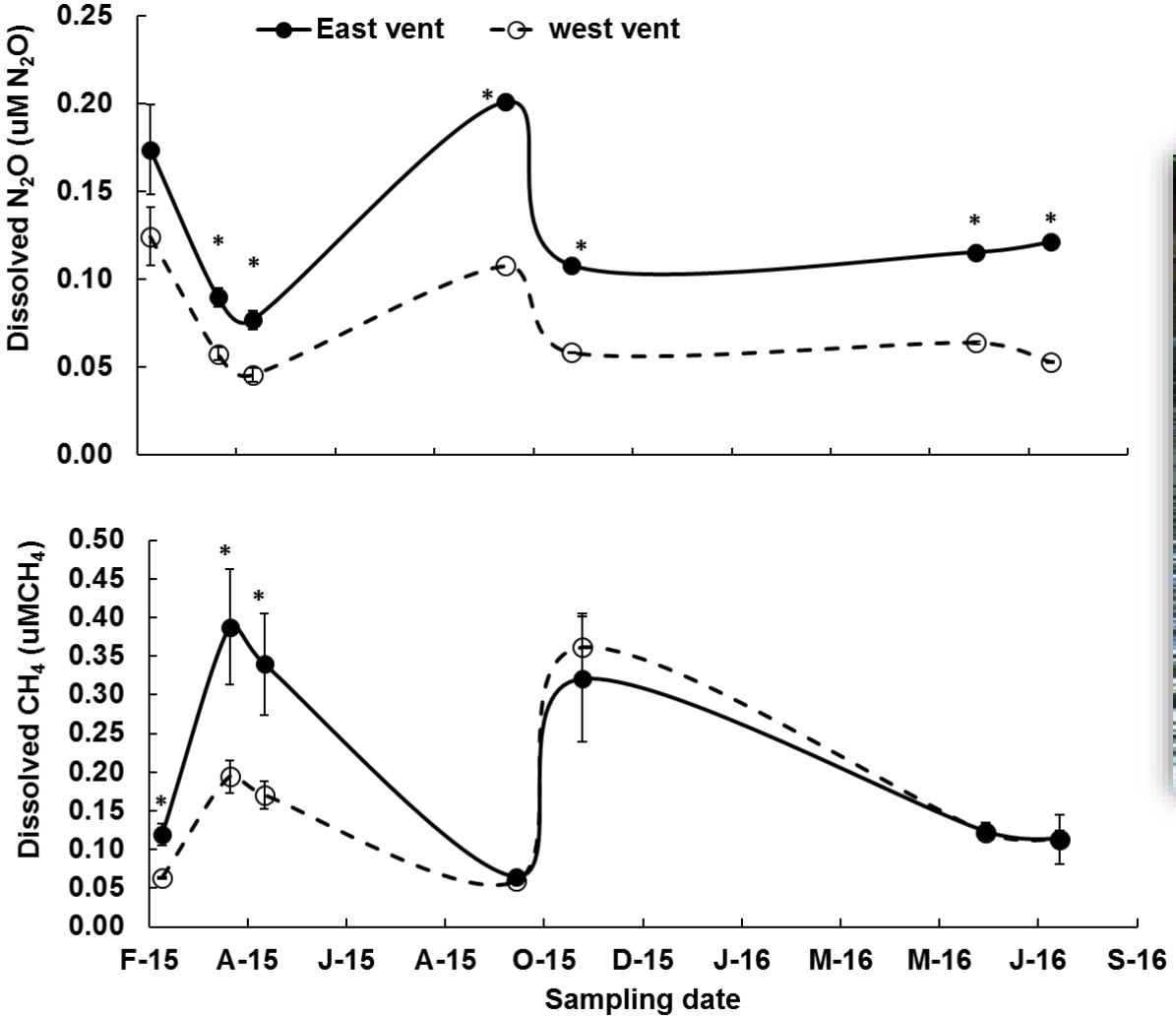
Dry/Wet Sesonality

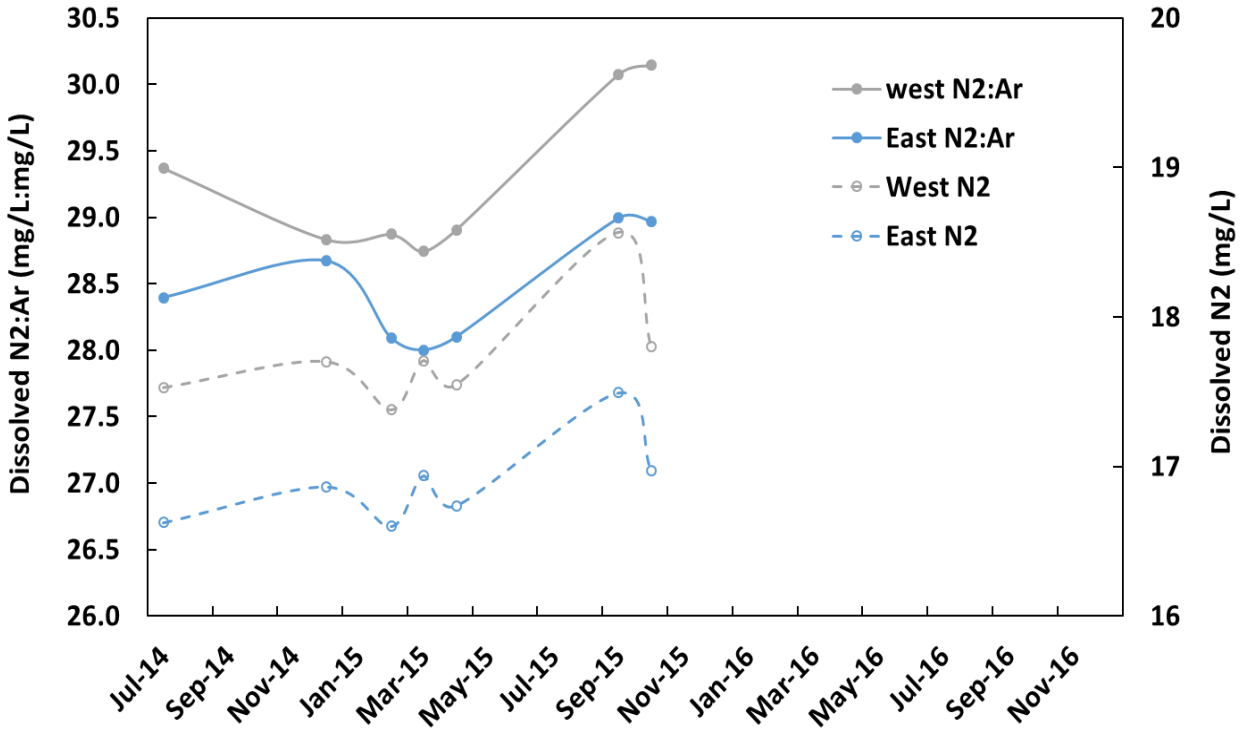


- N_2O highest in dry season
- CH_4 highest in wet season






East vent
west vent
Dissolved N_2O (uM N_2O)
0.25
0.20
0.15
0.10
0.05
0.00
Dissolved CH_4 (uMCH_4)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
F-15
A-15
J-15
A-15
O-15
D-15
J-16
M-16
M-16
J-16
S-16
Sampling date


30.5
30.0
29.5
29.0
28.5
28.0
27.5
27.0
26.5
26.0
Dissolved N2:Ar (mg/L:mg/L)
20
19
18
17
16
Dissolved N2 (mg/L)
west N2:Ar
East N2:Ar
West N2
East N2
Jul-14
Sep-14
Nov-14
Jan-15
Mar-15
May-15
Jul-15
Sep-15
Nov-15
Jan-16
Mar-16
May-16
Jul-16
Sep-16
Nov-16

Conclusions/Next steps

- Improved soil model:
  - N loading/level, moisture (rainfall), temperature
- Significant N loss (soils and aquifer)
  - Highest rates in Forest/Wetland/Ag
  - Highest levels in >100yr CZ (also 2yr CZ)
  - Highest rates from Estimate ~35% NO_3 in Silver Spring
- Seasonality/variability
  - Denitrification (CH_4/DO)
  - Sources (N_2O/NO_3)
- Potential for non-C-based nitrate attenuation pathways
  - N_2O-source indicator?
  - CH_4-hotspots?
- Age dating to estimate rates?