The role of redox surfaces in explaining catchment nitrogen export across multiple scales

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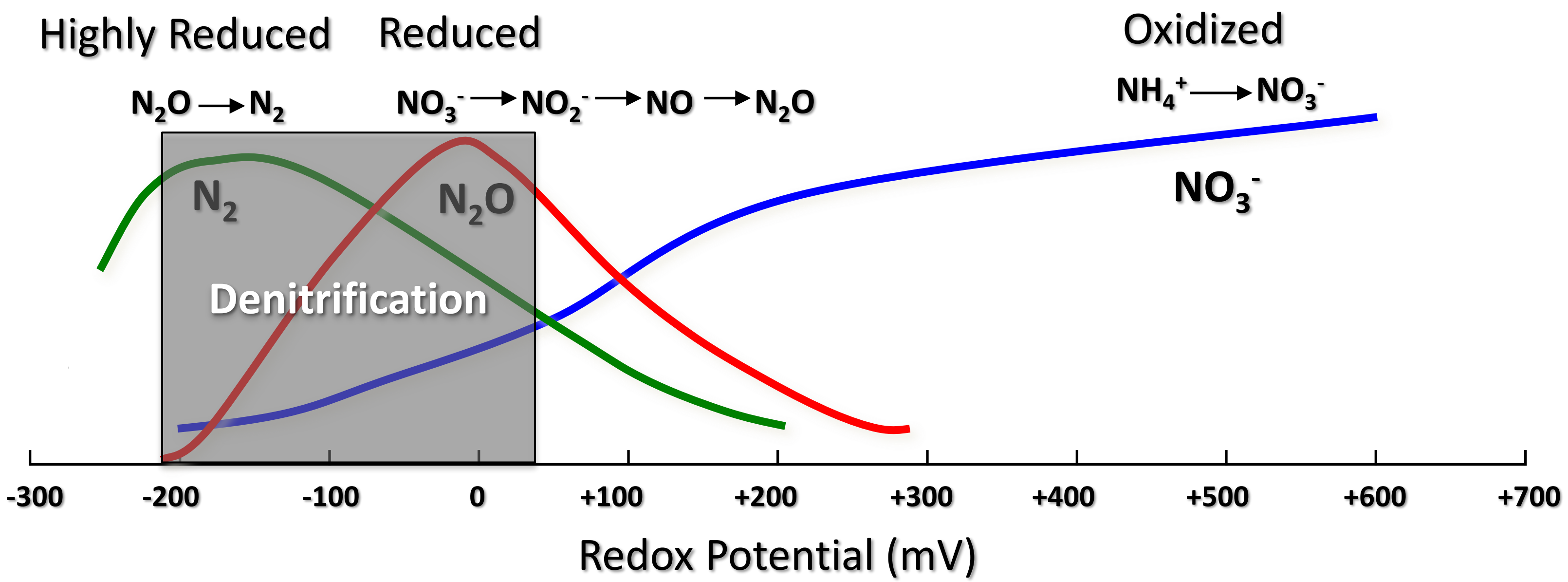
The problem

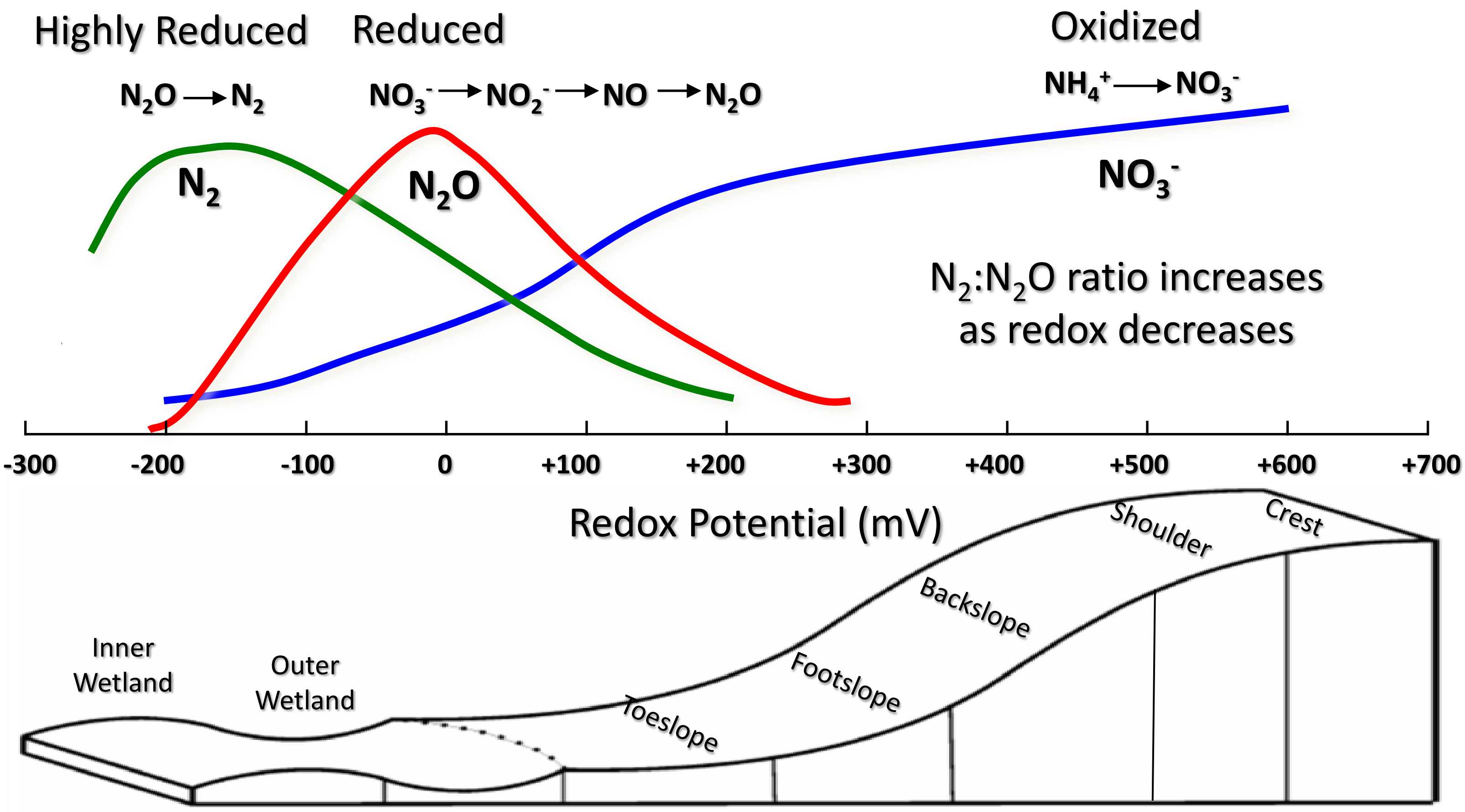
N mass budgets of forests reveal a missing N "sink".

We **hypothesize** that this sink is the conversion of NO_3^- to gaseous forms, which is strongly influenced by the redox condition of surface soils.



Hypothesis

Topography controls fate of N, by regulating the **delivery of precursors of gaseous forms** (DOC, NO_3^-) and the **formation of redox conditions** needed for denitrification reactions to occur.



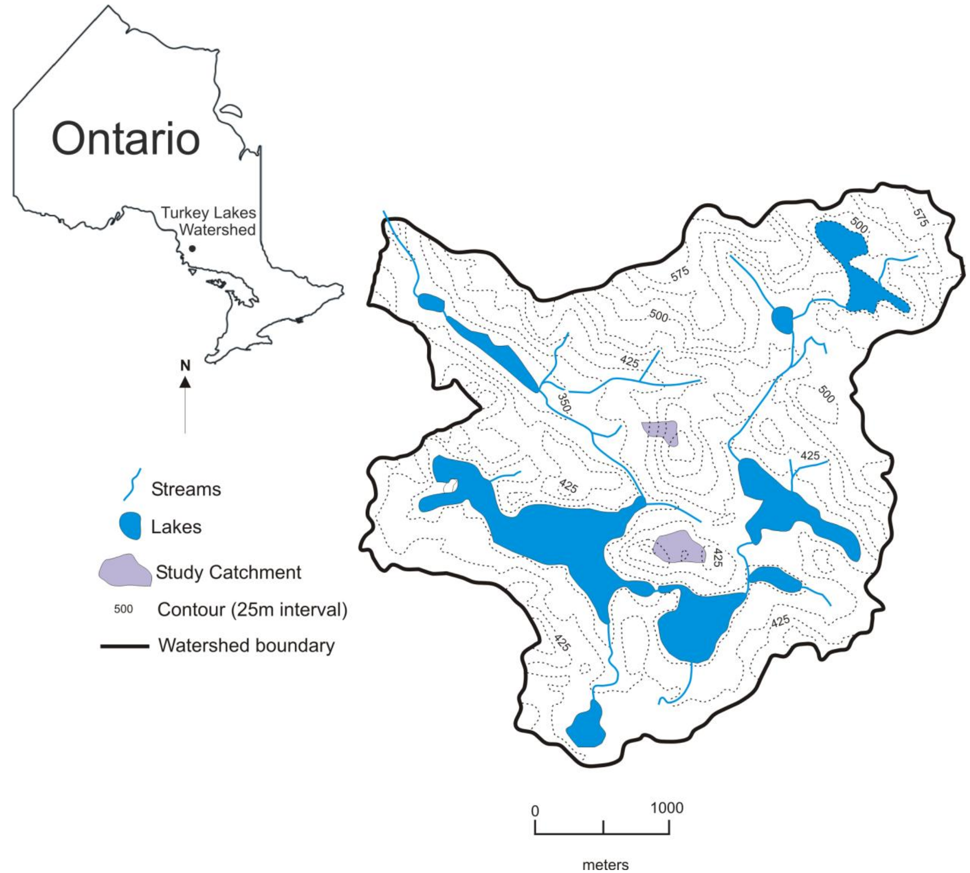
Study Site

Algoma Highlands
Ontario, Canada

Canadian Forestry Service long-term experimental catchment

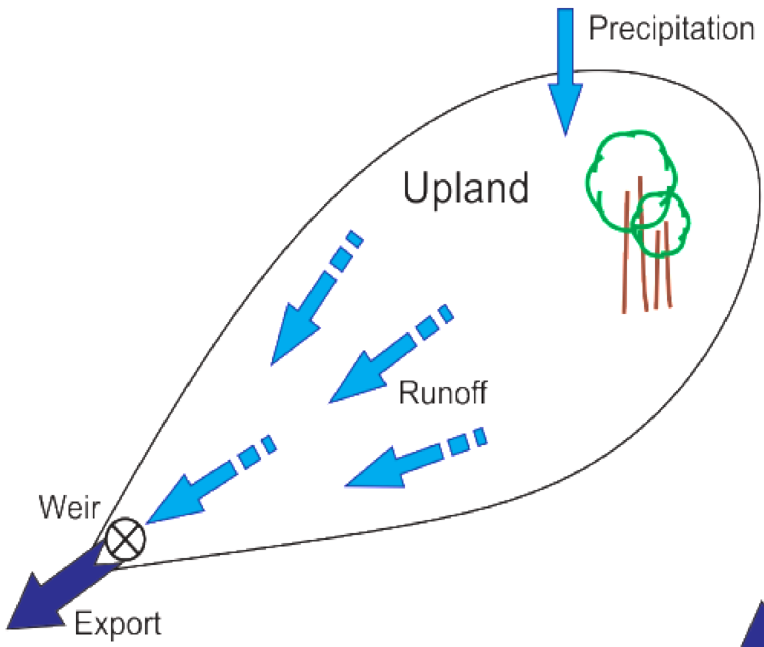
30 years of N export data

c35 and c38 (25% wetland)

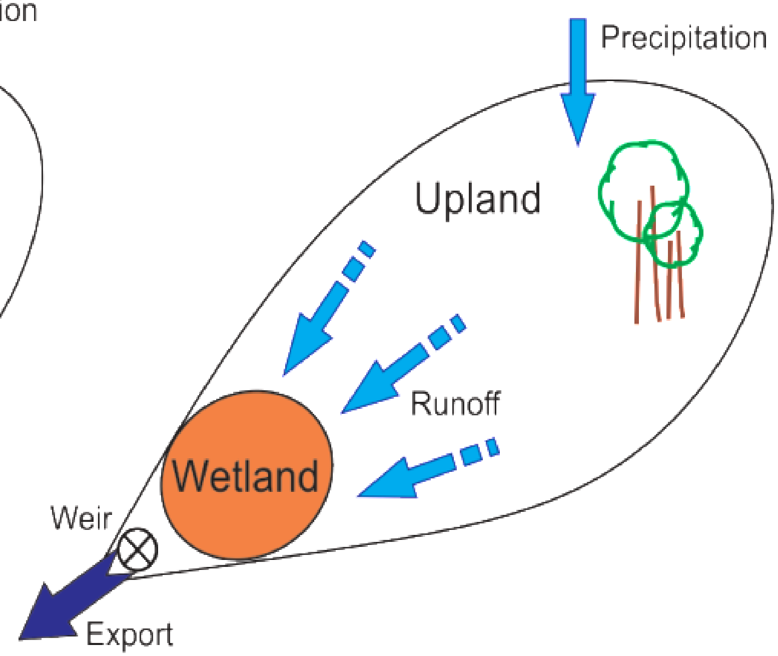


Experimental Approach

Paired catchment approach



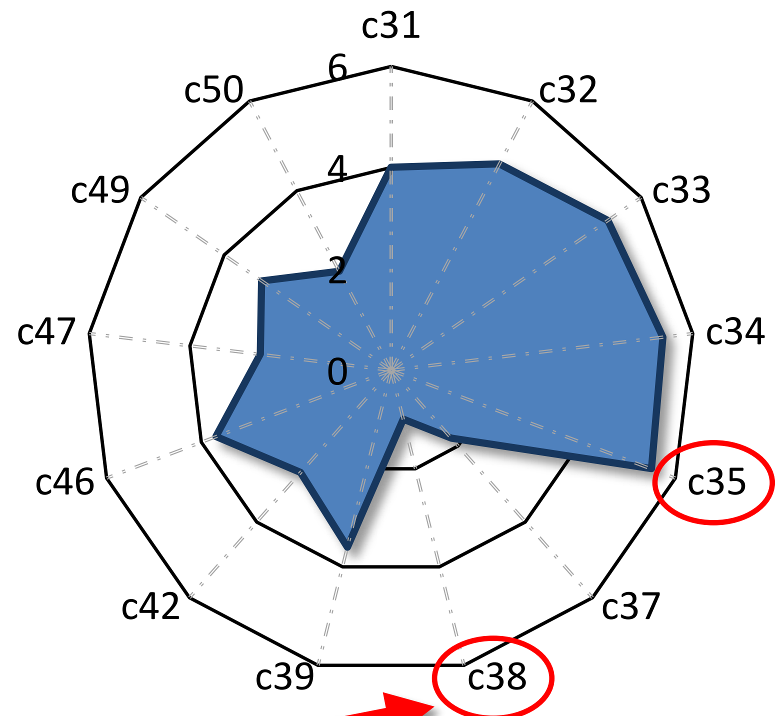
c35



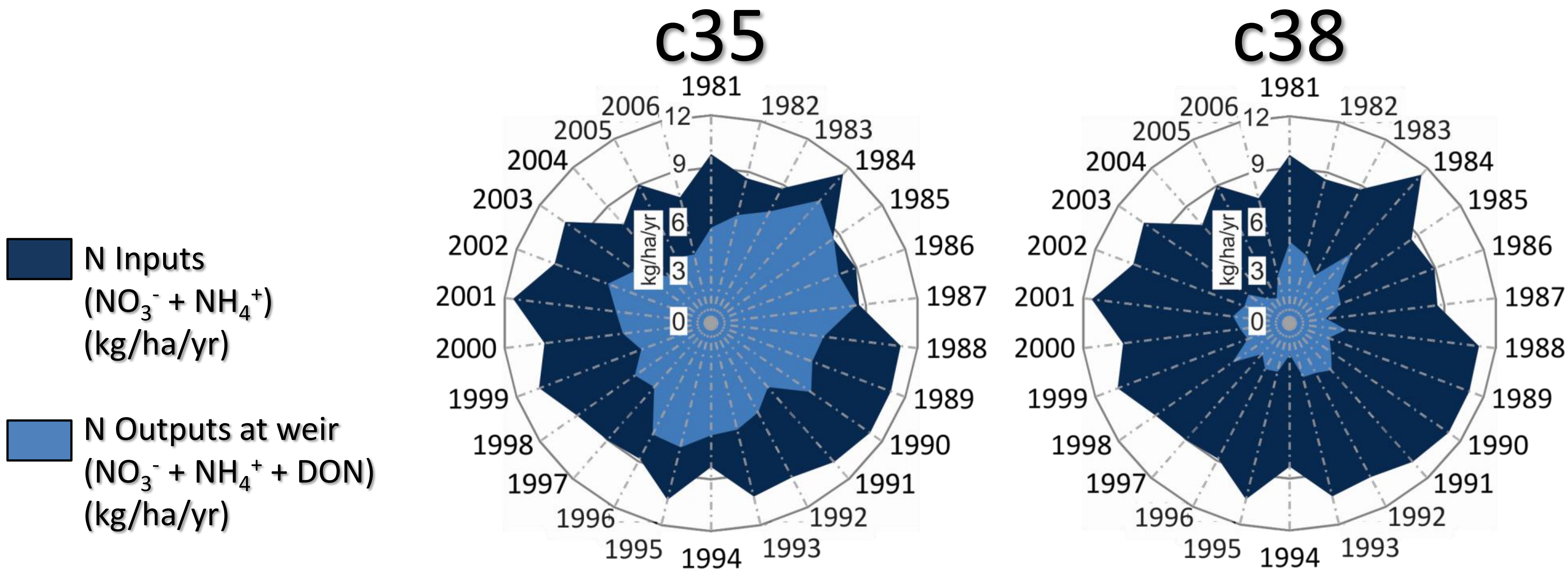
c38 (25% wetland)

Let's first look at NO_3^--N export patterns

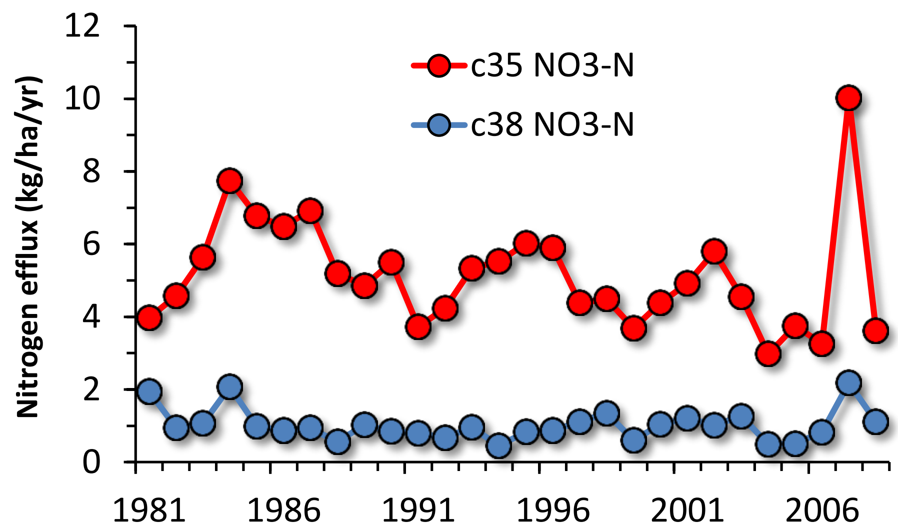
Catchment	Area (ha)	NO_3^-–N (kg/ha/yr)	DON (kg/ha/yr)
c31	4.9	4.0	1.1
c32	6.5	4.6	1.0
c33	23.4	5.2	1.0
c34	68.6	5.4	1.3
c35	4.0	5.5	1.3
c37	15.4	1.8	1.7
c38	6.5	1.0	2.2
c39	17.3	3.6	1.0
c42	18.5	2.[illegible]	1.1
c46	43.2	3.7	1.4
c47	3.4	2.6	1.0
c49	14.8	3.1	1.3
c50	9.5	2.2	1.9
Average	18.1	3.5	1.3



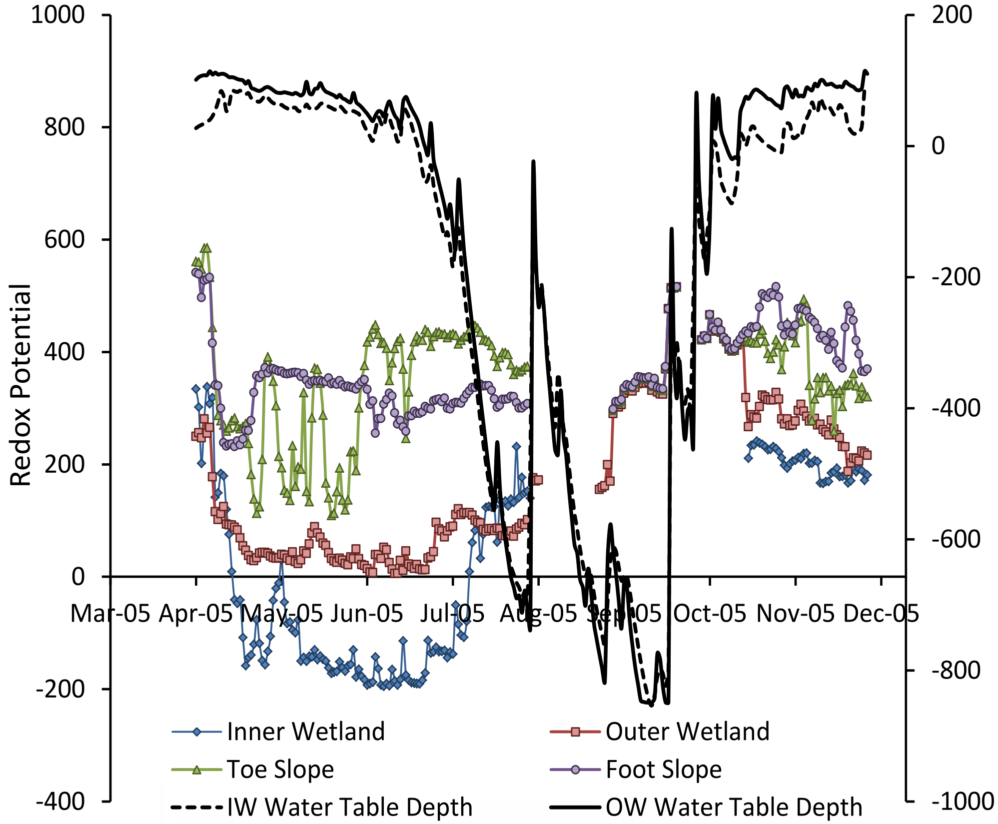
Let's look at the extremes



Can we close the gap in c35 vs. c38 N export?

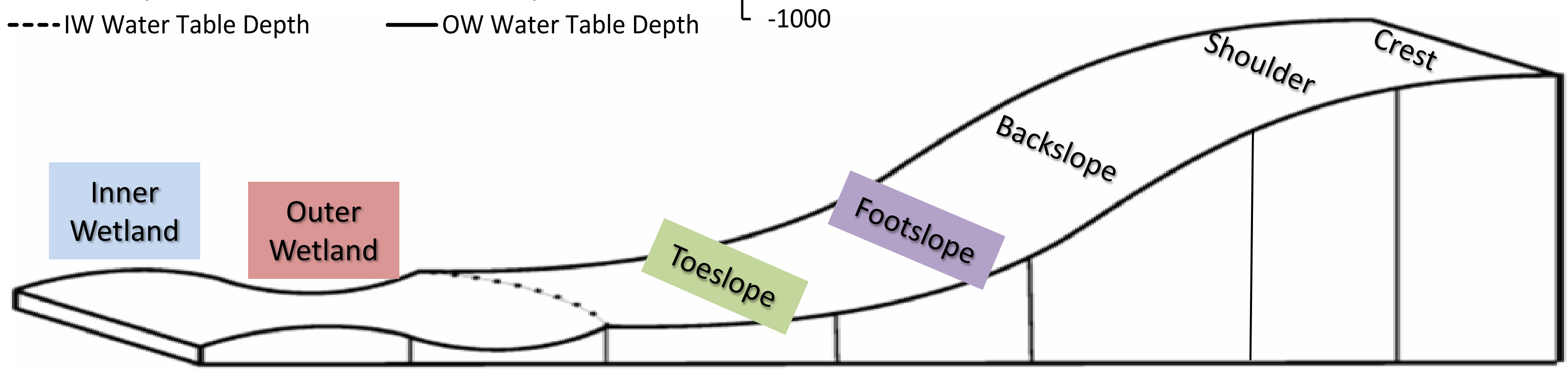


2005 redox patterns



Outer wetland defined as areas with peat depths < 0.5 m.

Beyond 0.5 m, the peat depth increases rapidly.



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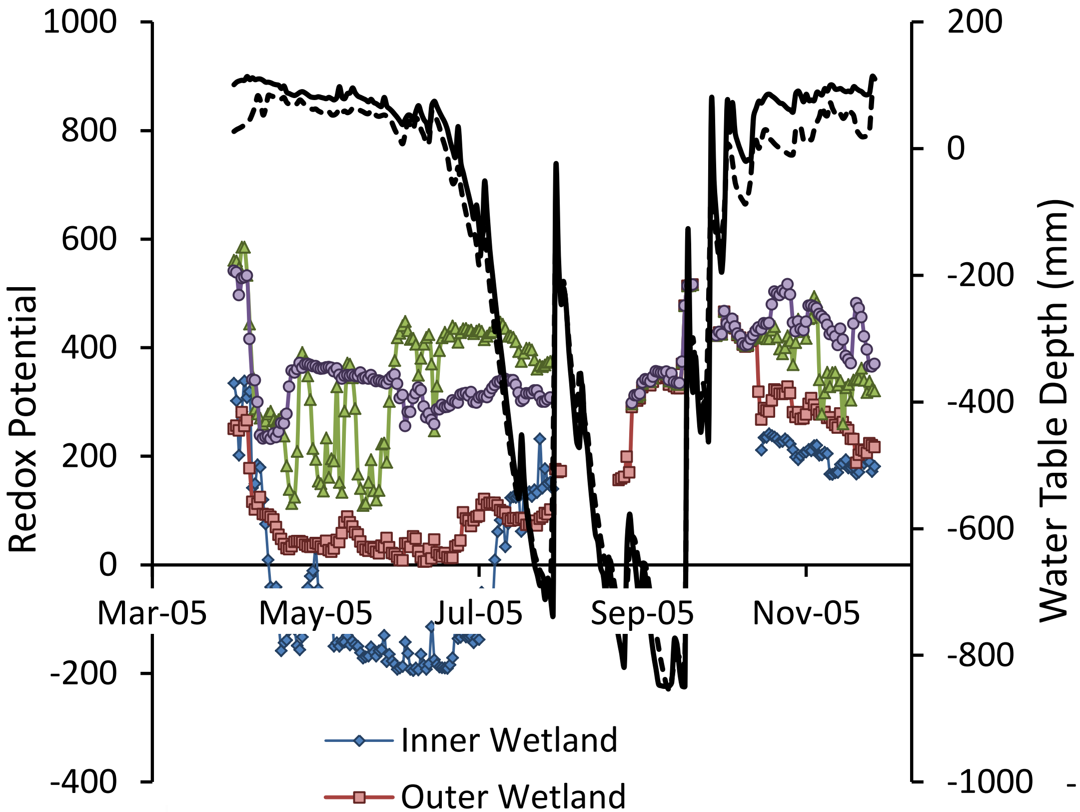
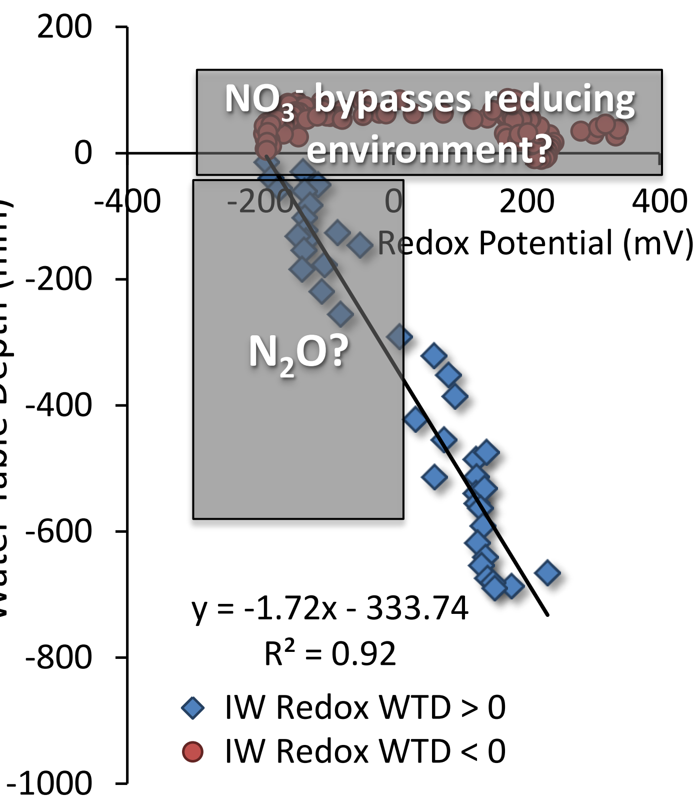
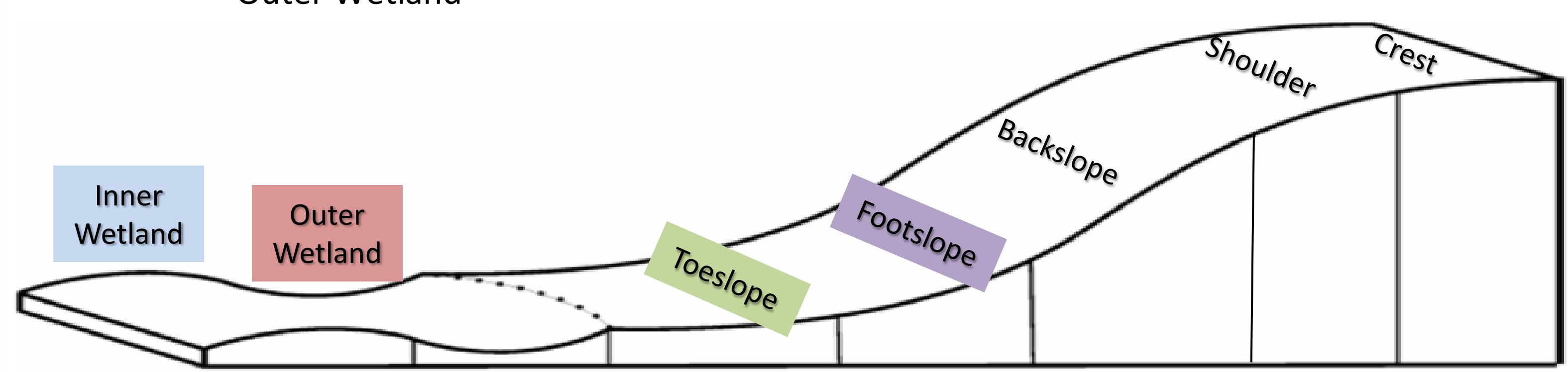
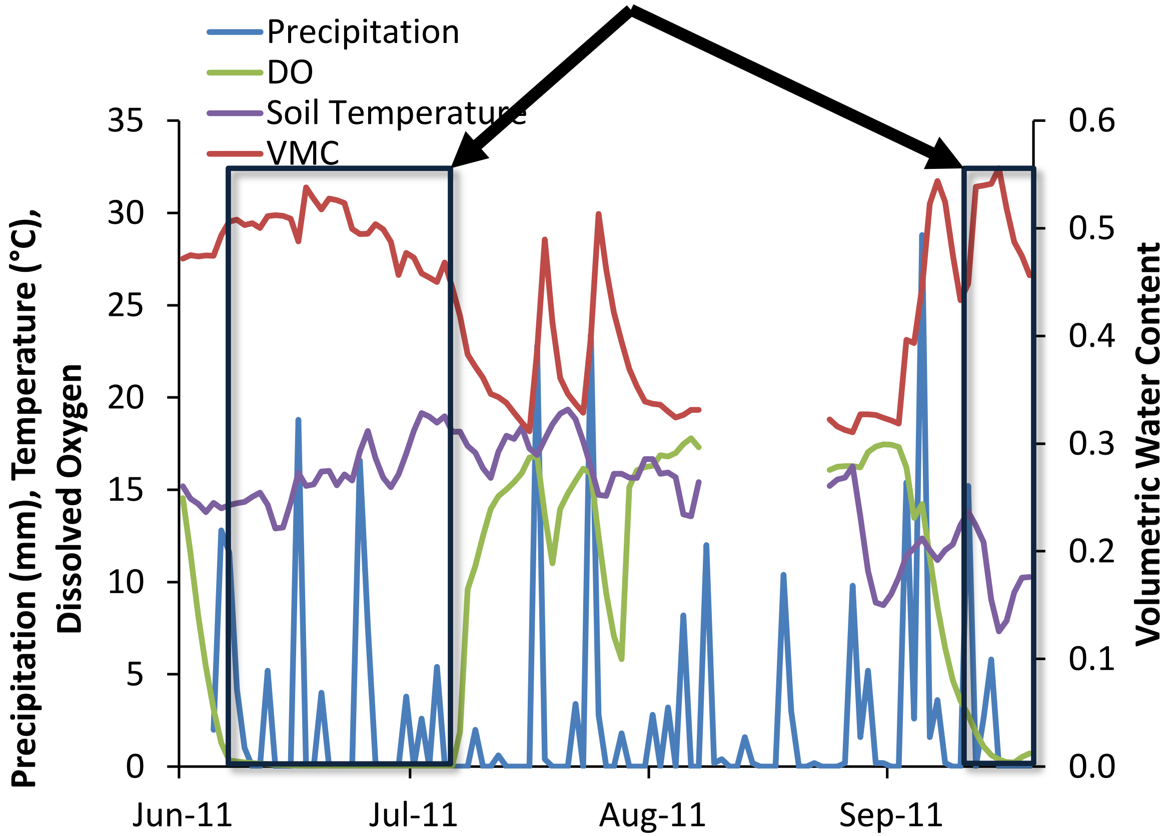






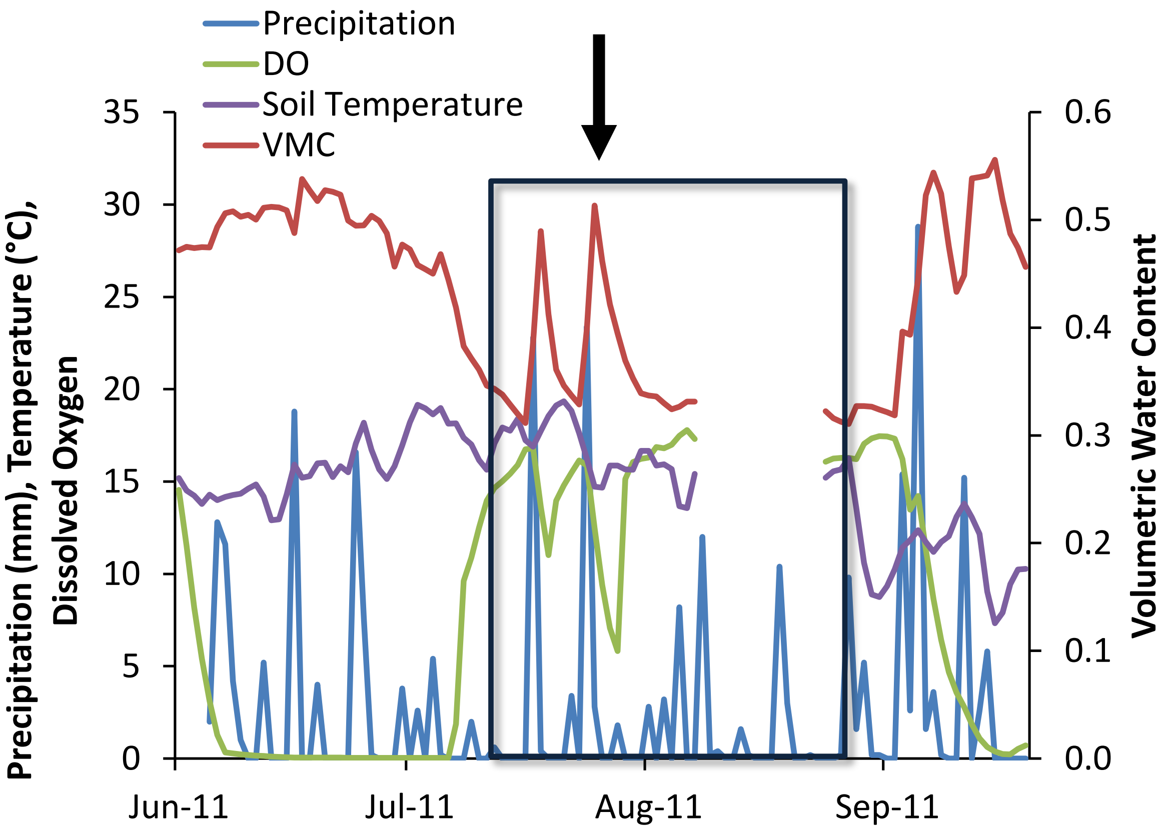
Relationship between hydrologic dynamics, redox and dissolved oxygen conditions

Highly reducing conditions occur below just soil surface during these hydrologically *connected* periods

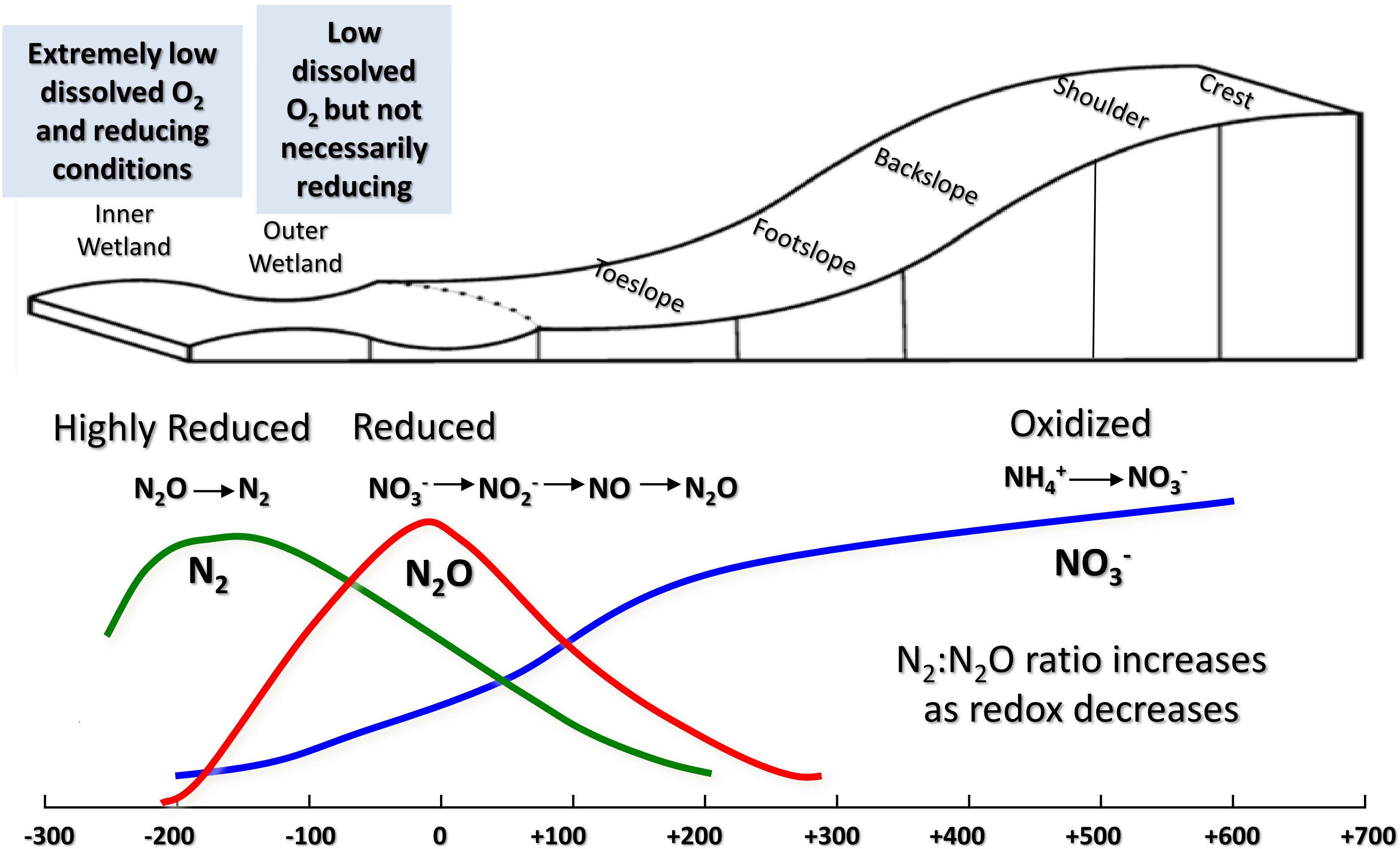


Relationship between hydrologic dynamics, redox and dissolved oxygen conditions

Rain trigged drops in dissolved oxygen occur just below soil surface during these hydrologically *disconnected* periods



Redox control on N speciation



Measuring N_2:
Acetylene inhibition technique

Acetylene inhibits N_2O reductase,
the enzyme that mediates reduction of N_2O to N_2.

N_2 is estimated by subtracting the difference between
N_2O from control collars (untreated) and
N_2O from acetylene treated collars.

Measuring N_2: Acetylene inhibition technique

25 collars, 5 controls and 20 treatments.

Saturated the soil with simulated rain equivalent to 10 mm using MilliQ.

Pumped in acetylene after scrubbing it of impurities.

Let the acetylene set for 1 hr before lifting up the chamber, airing it out and replacing it on the collar.

Collected samples at 15 min intervals for 1 hr.

Following methods of Groffman et al. 2006. Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecological applications* 16: 2091-2112.

Measuring N_2: Acetylene inhibition technique

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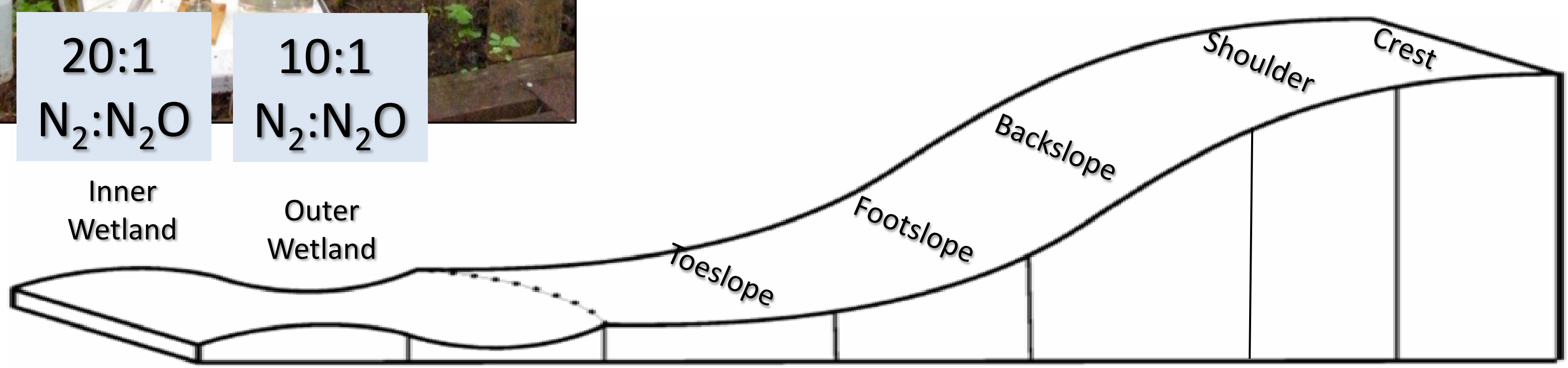
20:1 N_2:N_2O

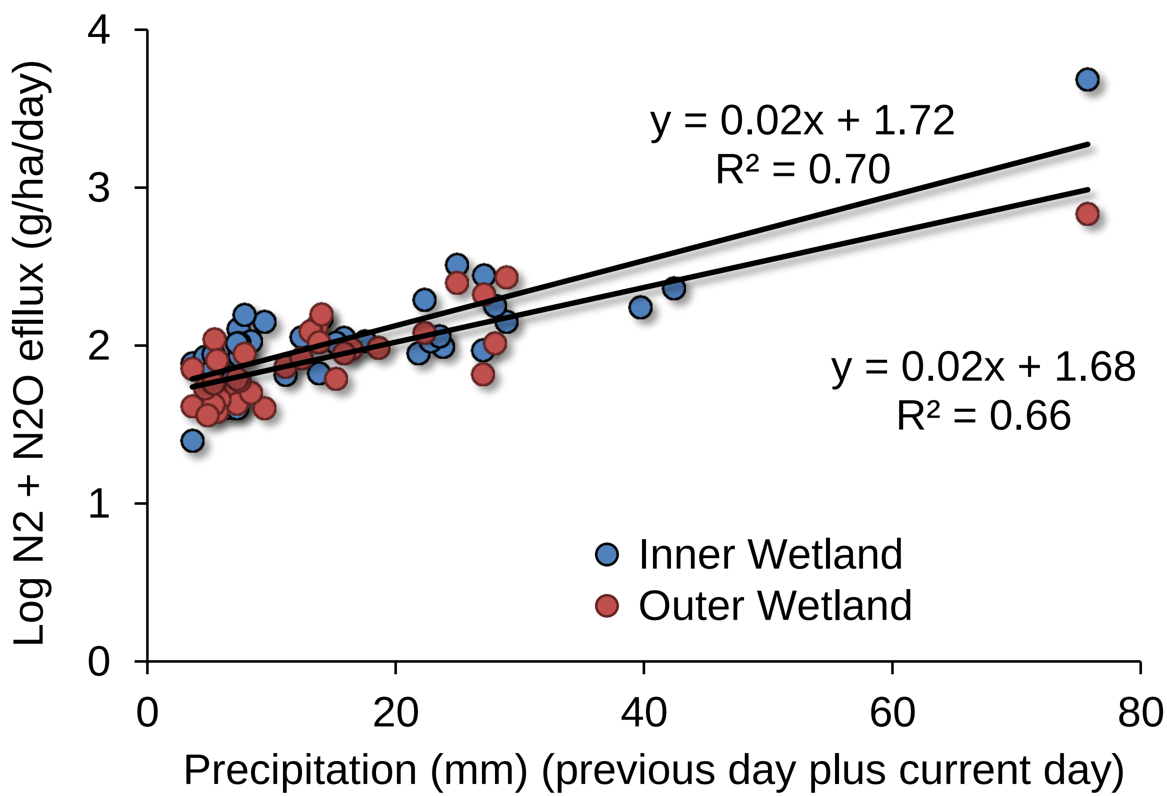
Inner Wetland

10:1 N_2:N_2O

Outer Wetland

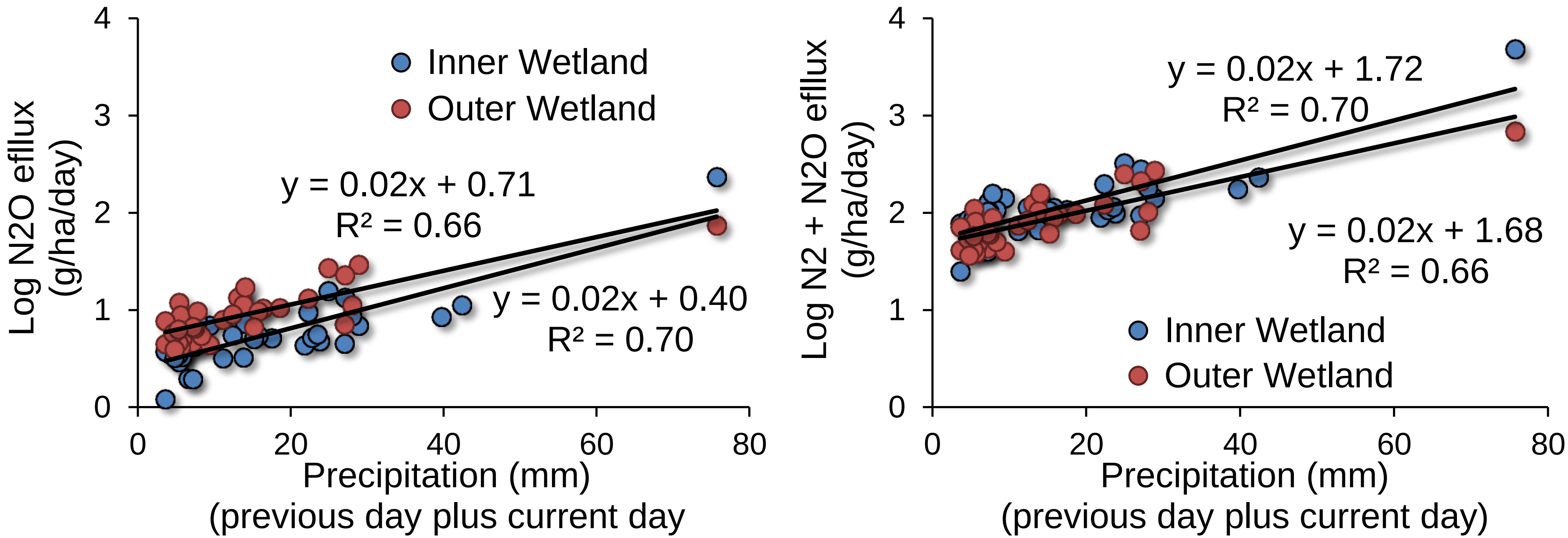


Five years of chasing storms …
Rain triggered denitrification (N_2O)



Enanga, Casson, Fairweather and Creed. In Prep. Rain triggered gaseous N export: finding the missing N in N mass balances.

Five years of chasing storms …
Rain triggered denitrification (N_2+N_2O)

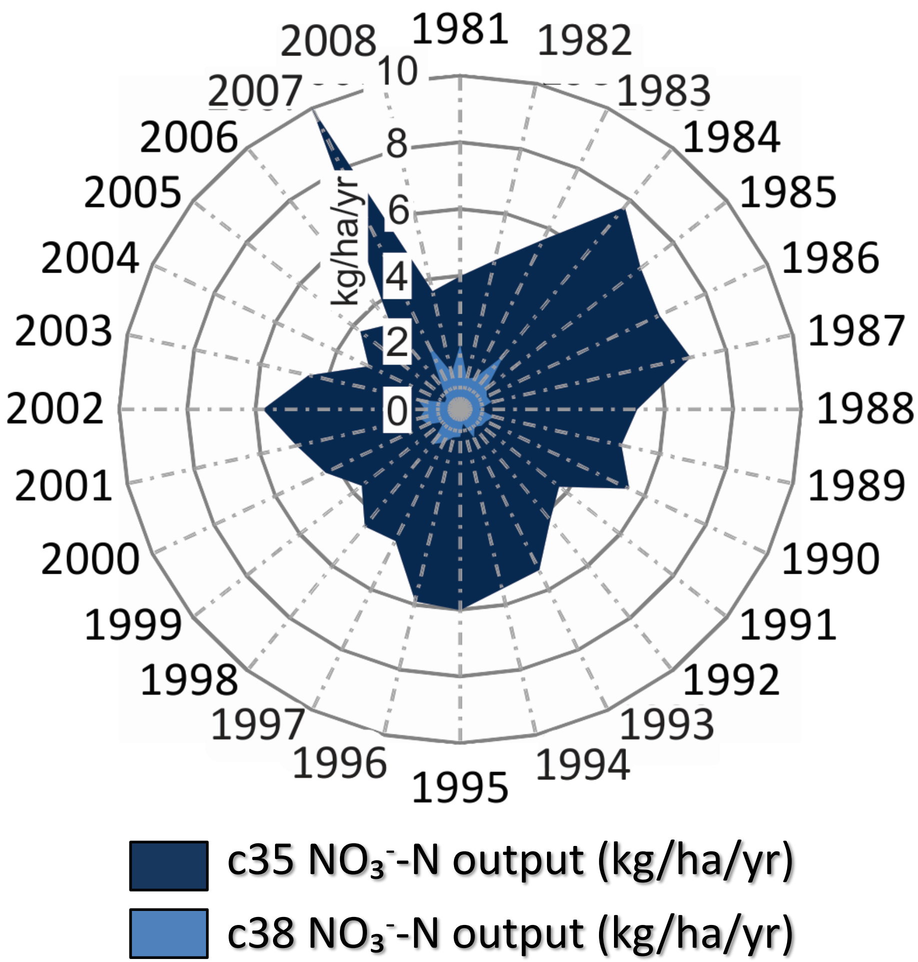


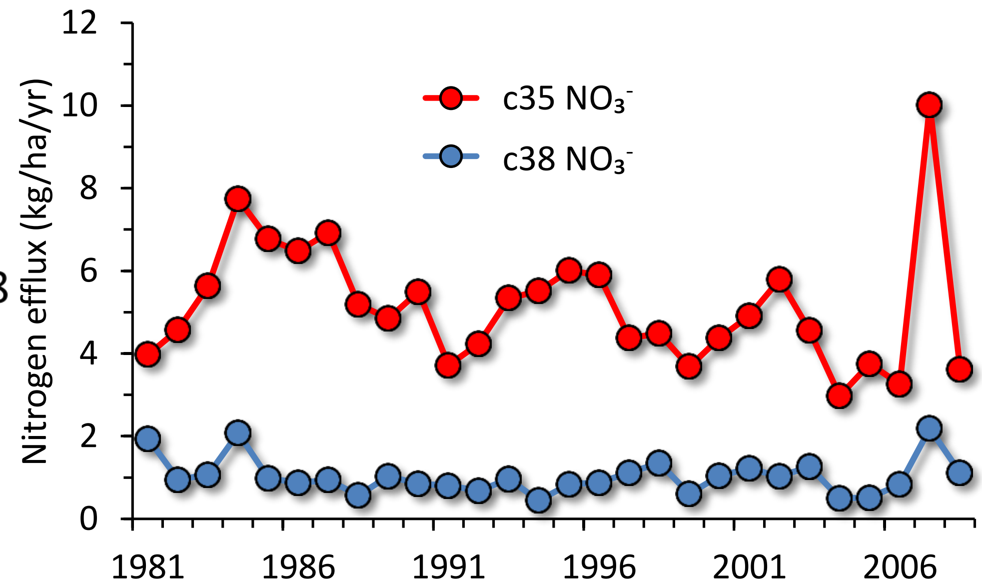
If we account for **redox-dependent denitrification pathways**, we see significantly higher denitrification rates

Enanga, Casson, Fairweather and Creed. In Prep. Rain induced bursts of denitrification and abiotic immobilization account for differences in dissolved nitrogen export from forested catchments

Can we close the gap in N export?

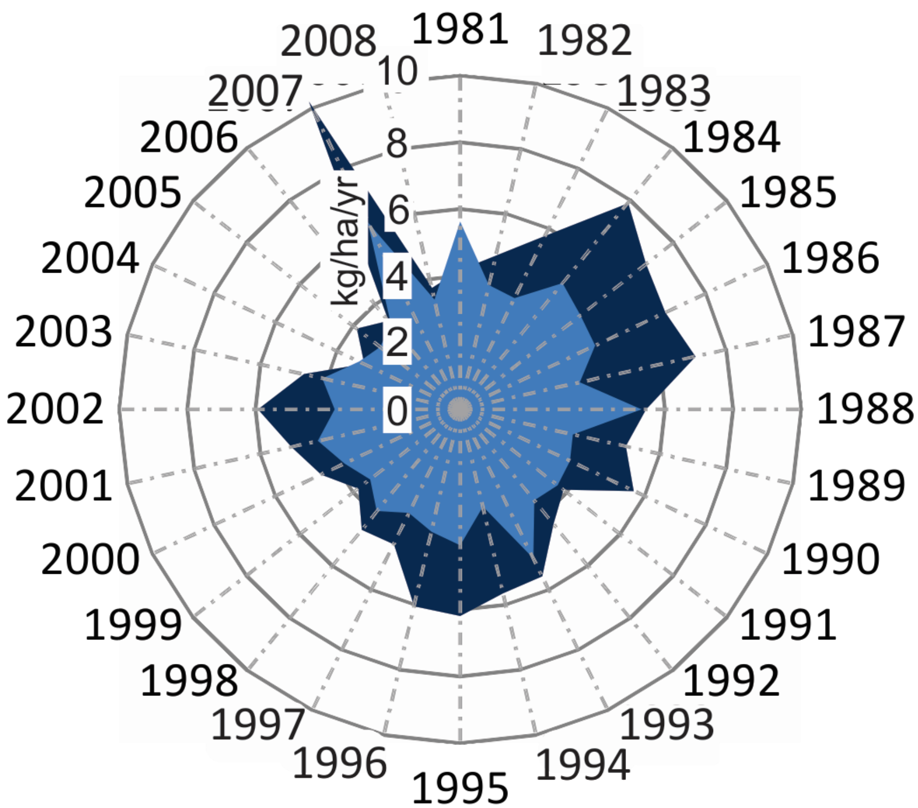
Recall that N export from c38 is significantly lower than c35





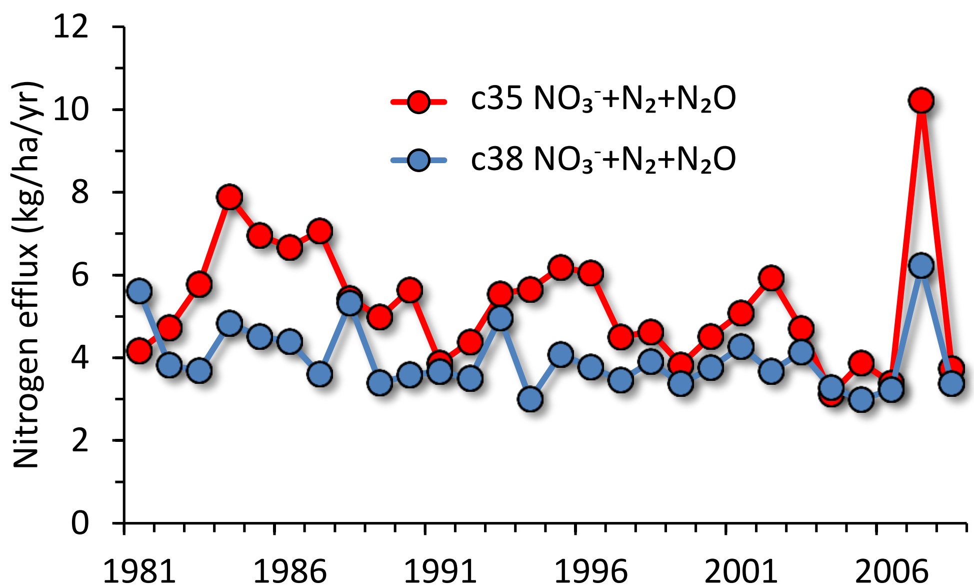
Can we close the N output gap?

If we include gaseous N outputs (N_2+N_20), c38 N export is much closer to that of c35.



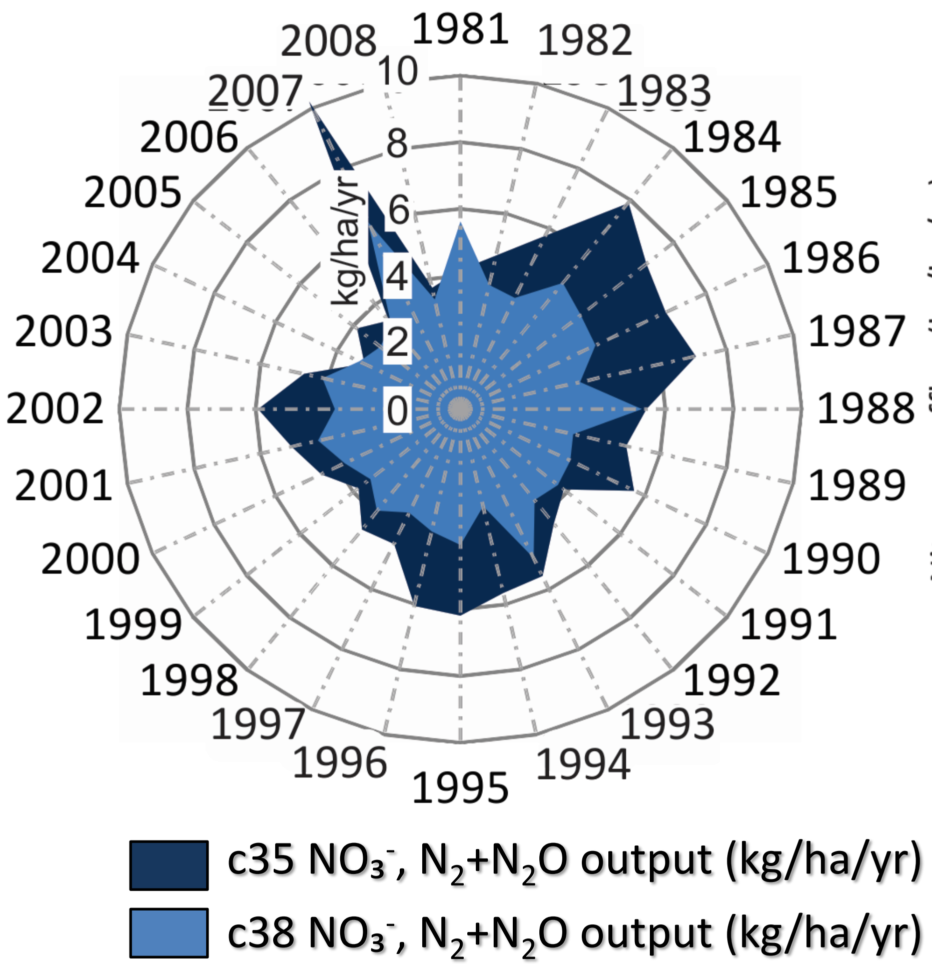
c35 NO_3^-, N_2+N_2O output (kg/ha/yr)

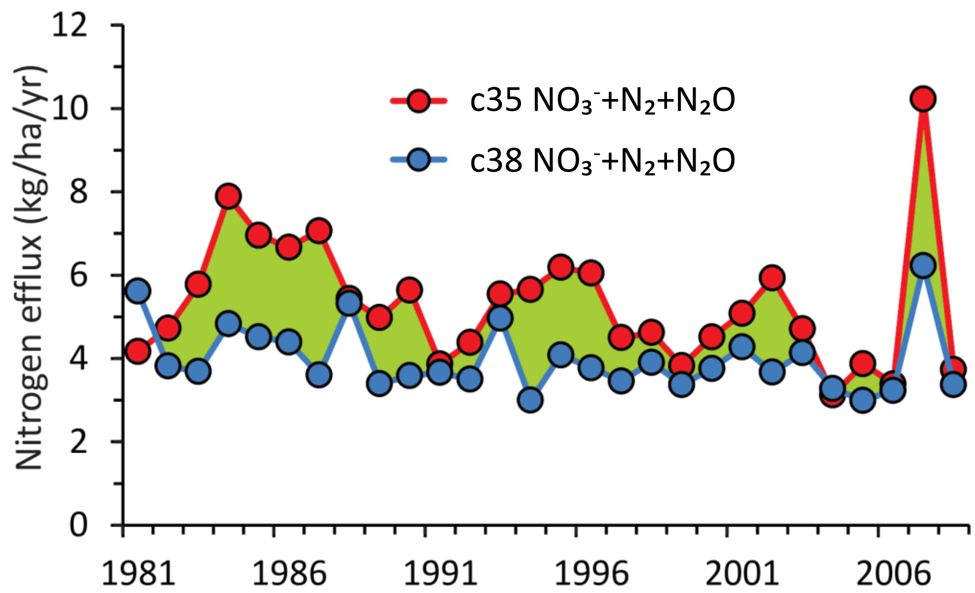
c38 NO_3^-, N_2+N_2O output (kg/ha/yr)



Can we close the N output gap?

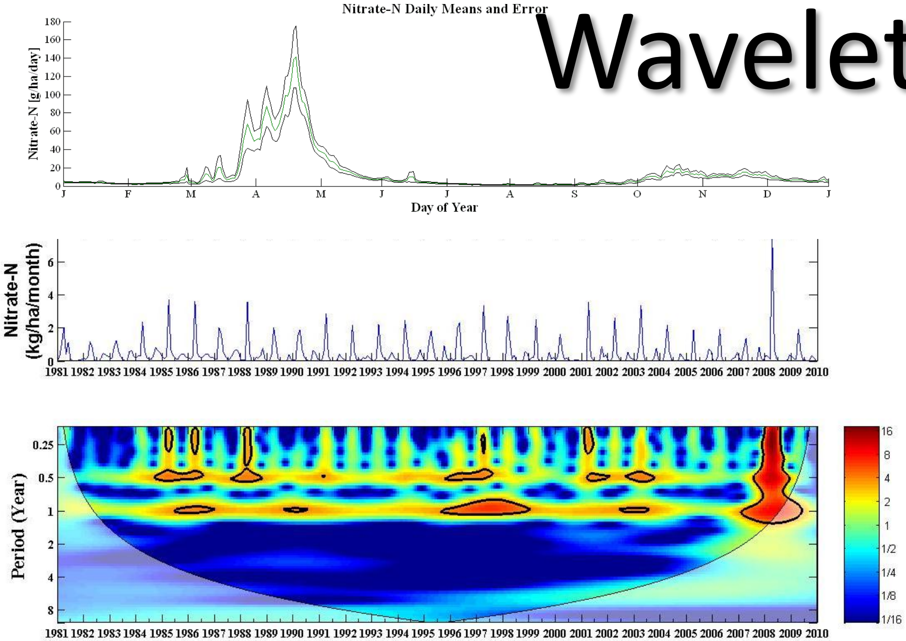
But a N gap still remains.



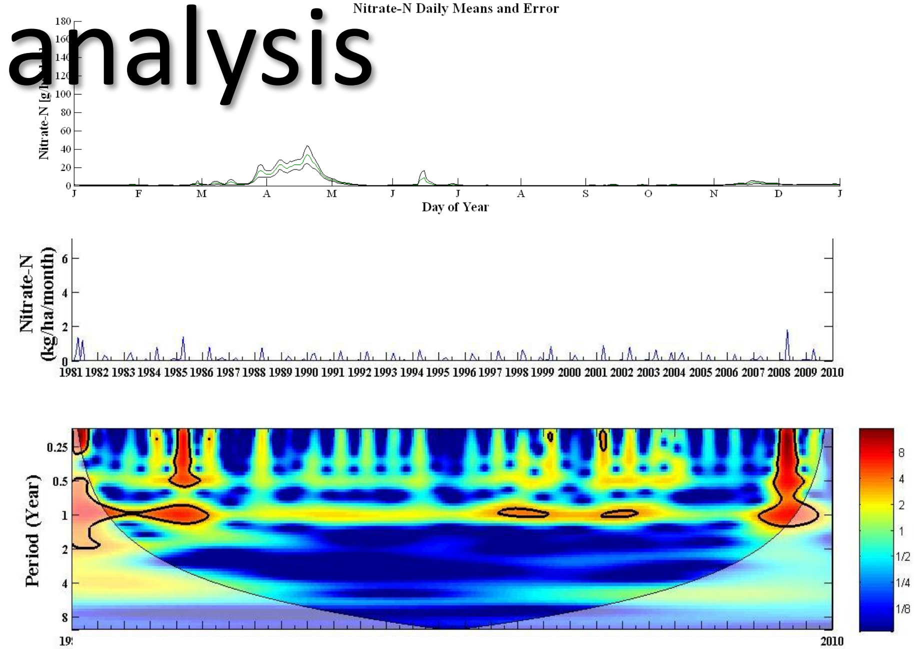


Wavelet analysis

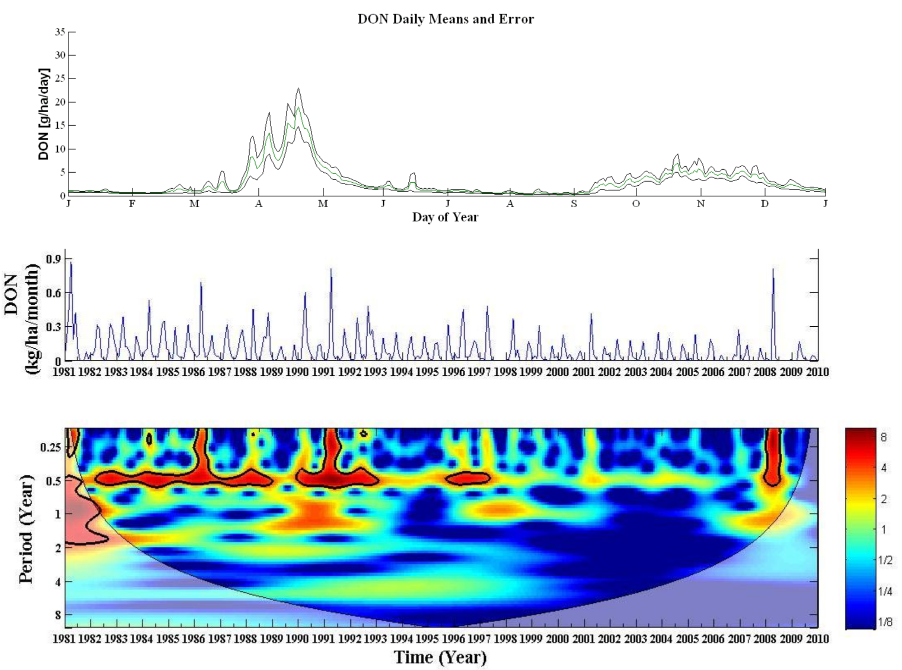
c35 NO_3^-



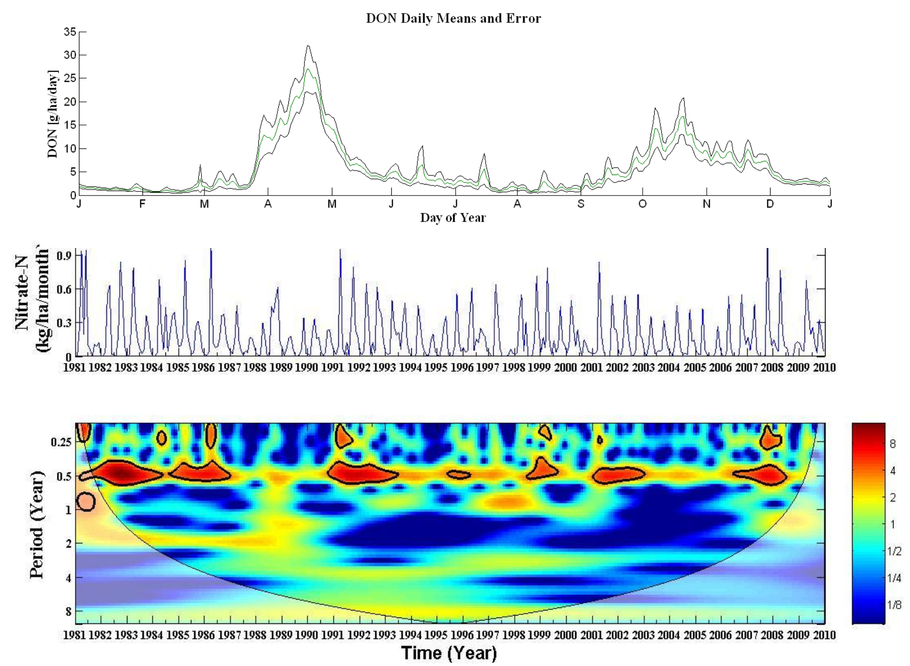
c38 (25% wetland) NO_3^-



c35 DON

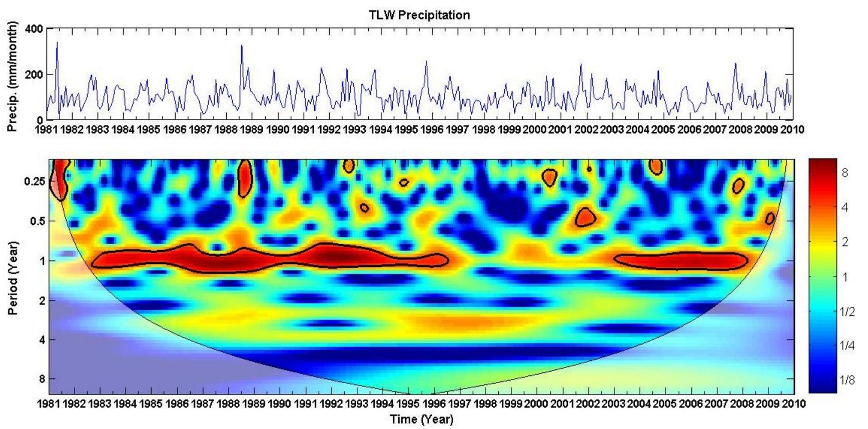


c38 (25% wetland) DON



Wavelet coherence

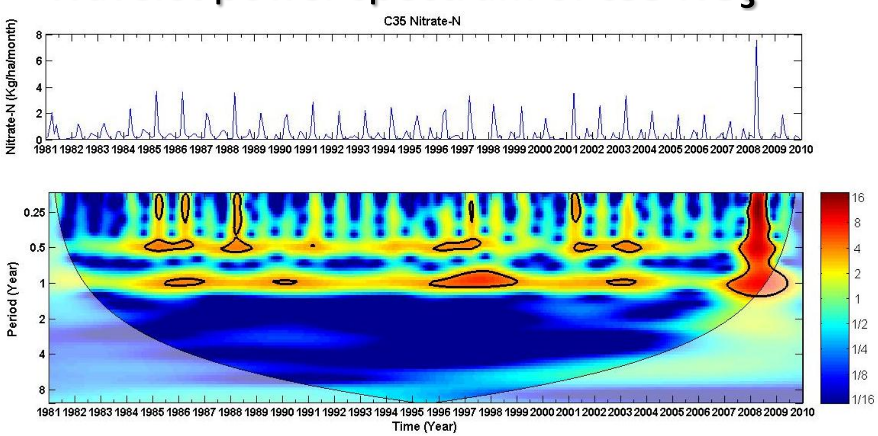
Wavelet power spectrum of **precipitation**



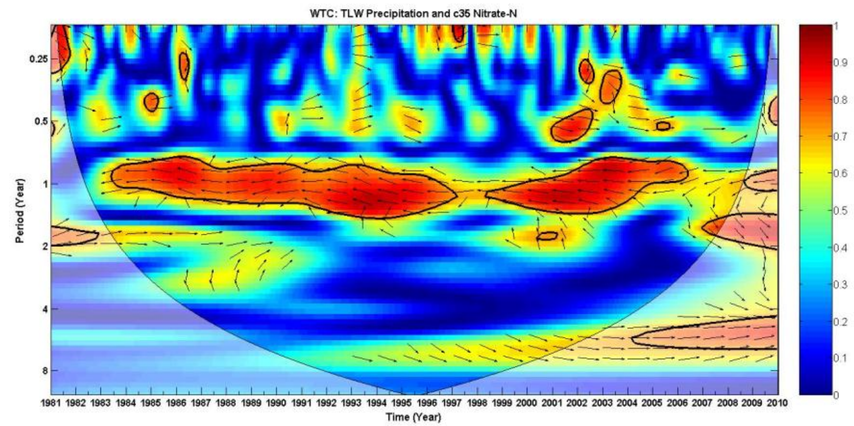
Versus

=

Wavelet power spectrum of **c35 NO_3^-**

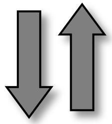


The **thin solid line (**cone of influence), delimits region not influenced by edge effect. The **thick solid lines** show the 95% confidence level.



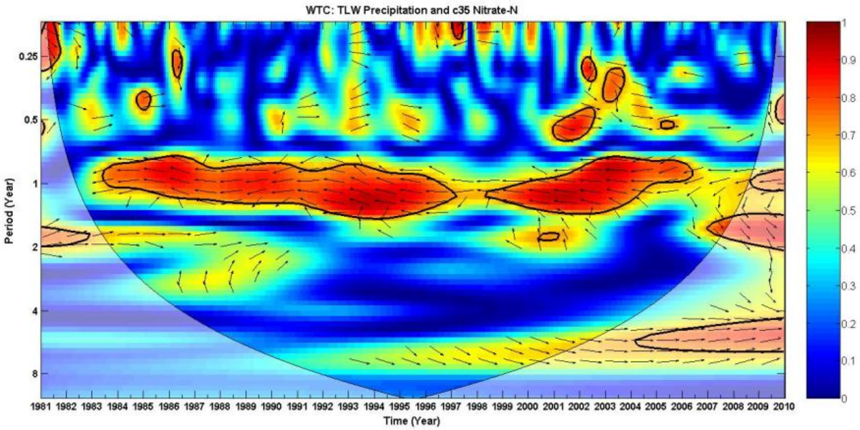
Negative correlation

Positive correlation

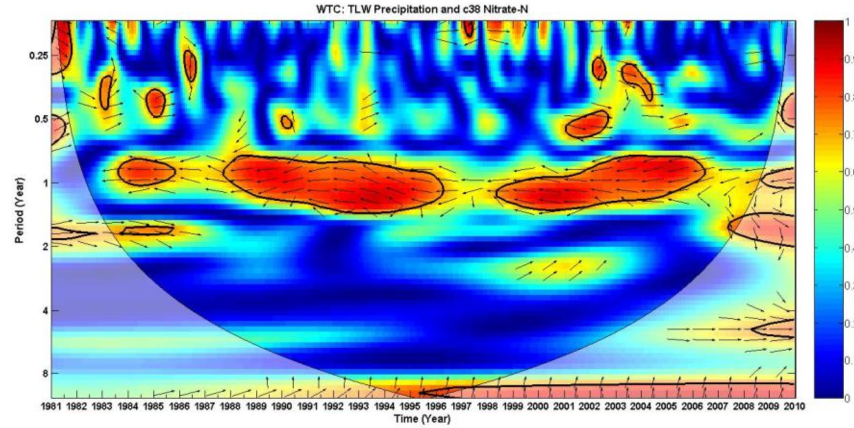


Lead or lag relationship

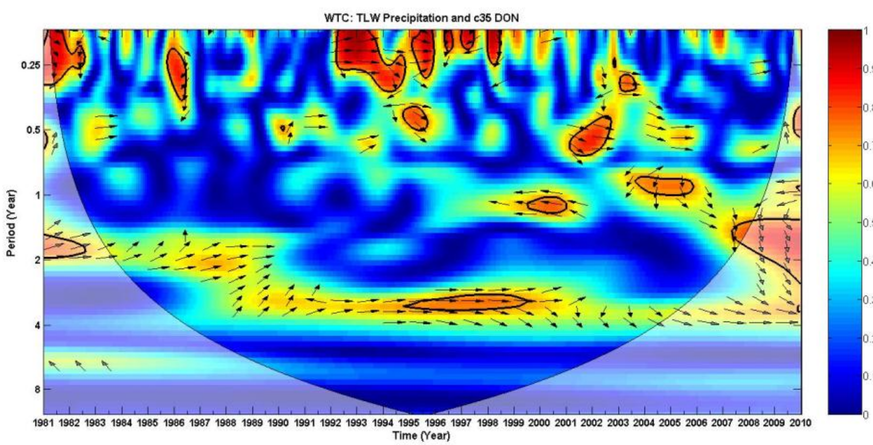
Precipitation vs. c35 NO_3^-



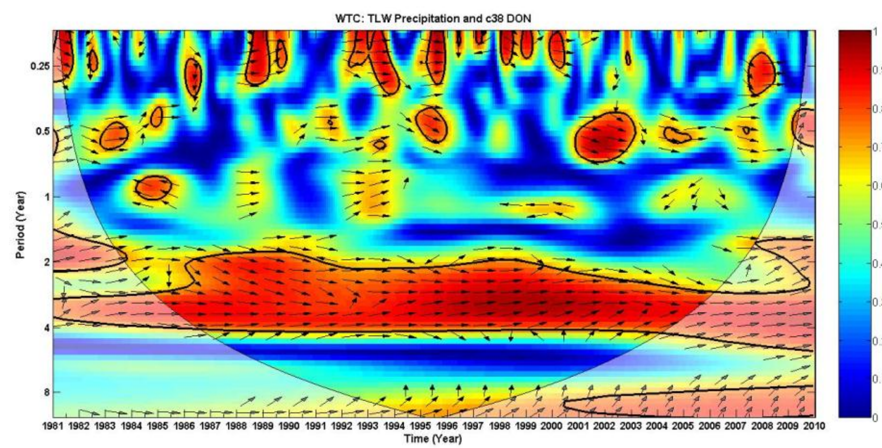
Precipitation vs. c38 NO_3^-



Precipitation vs. c35 DON

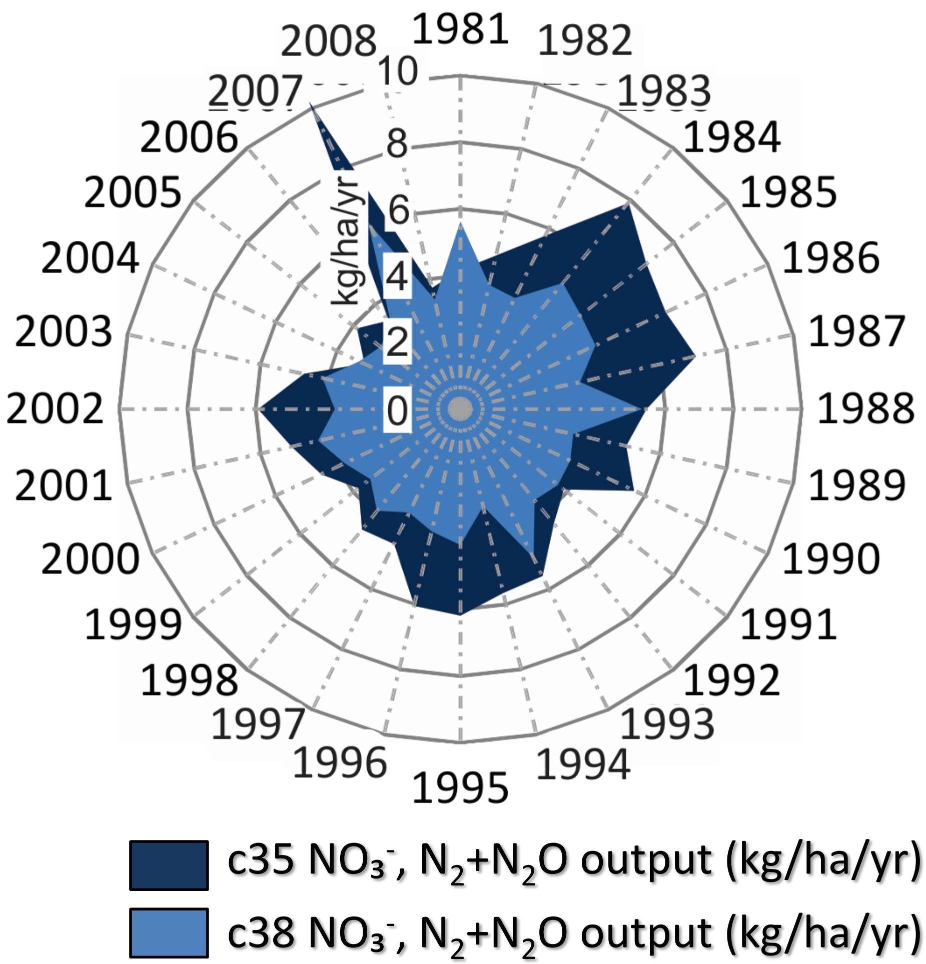


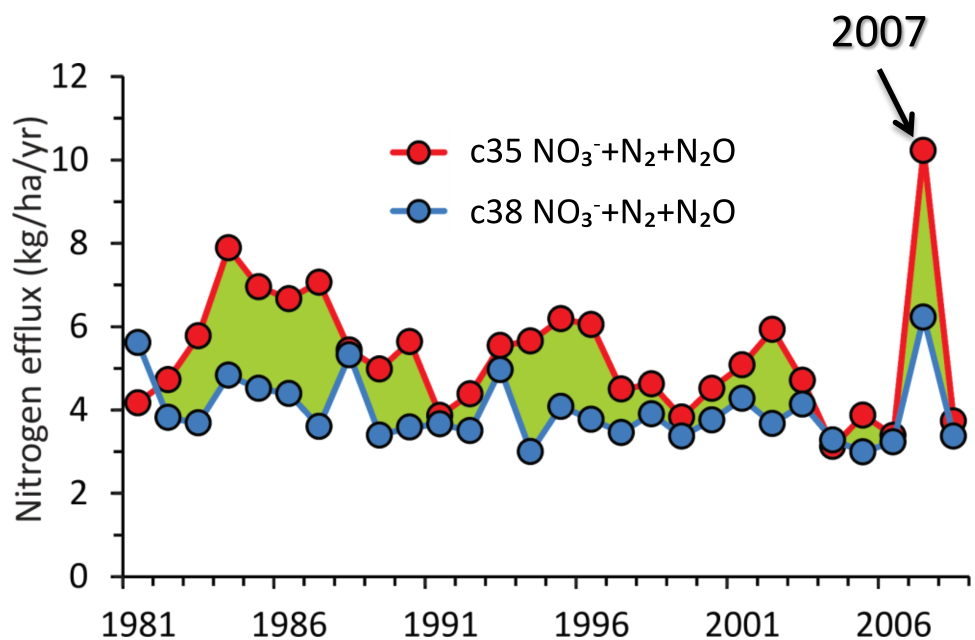
Precipitation vs. c38 DON



Samson and Creed. In Prep. Wavelet analysis of N export – insights into N cycling mechanisms in forested catchments.

What could be causing enhanced DON export on a period of every 2-4 years?





Now let's look at DON export patterns

Catchment	Area (ha)	NO_3^-N (kg/ha/yr)	DON (kg/ha/yr)
c31	4.9	4.0	1.1
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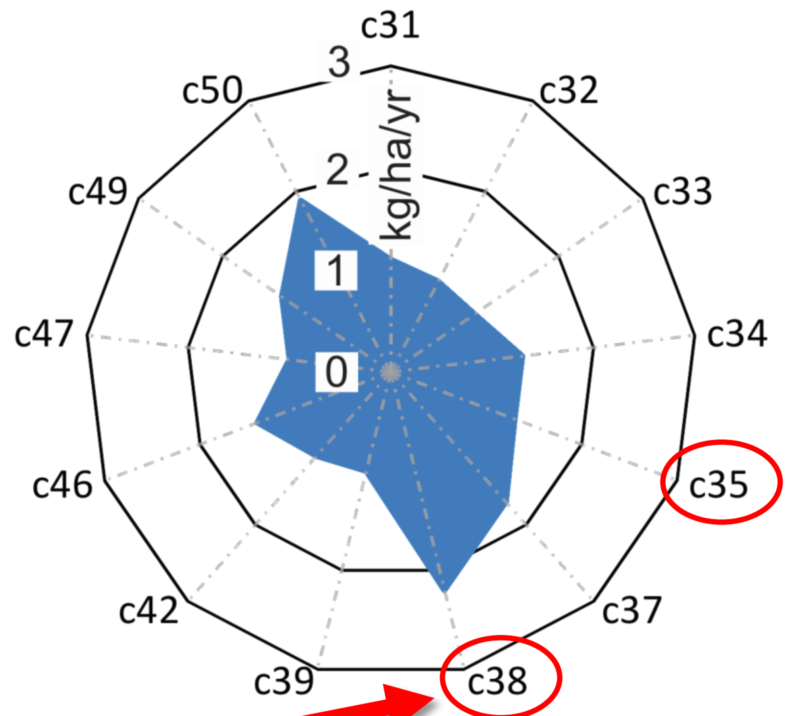
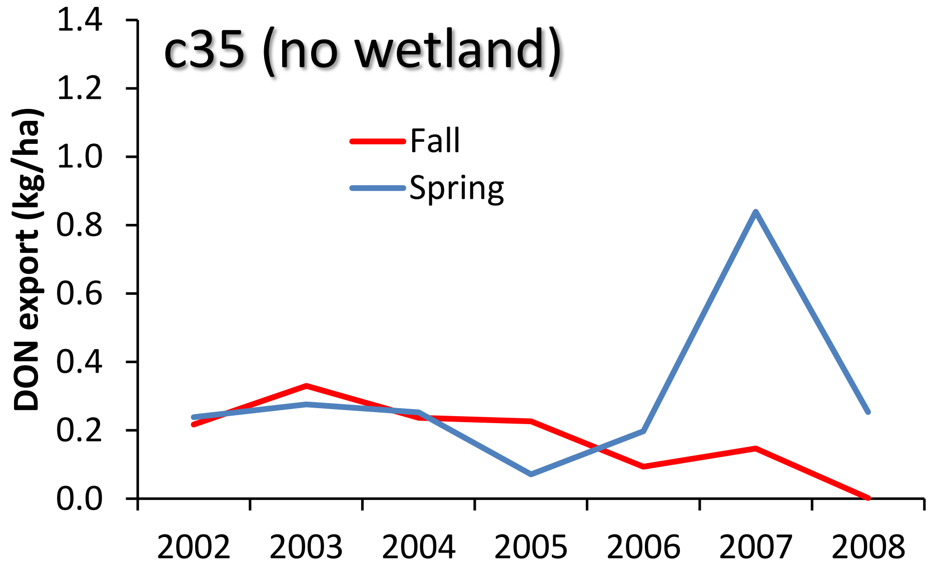
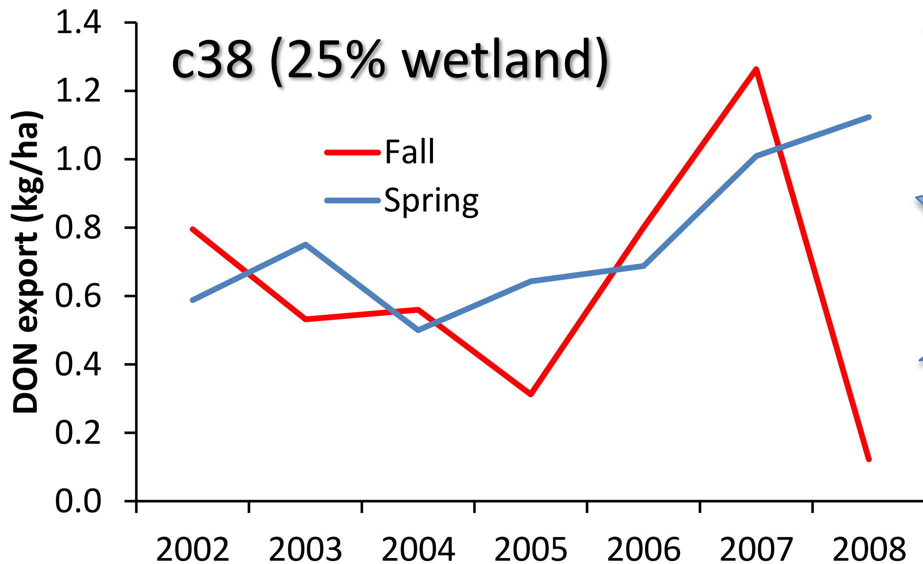


Almost the extremes

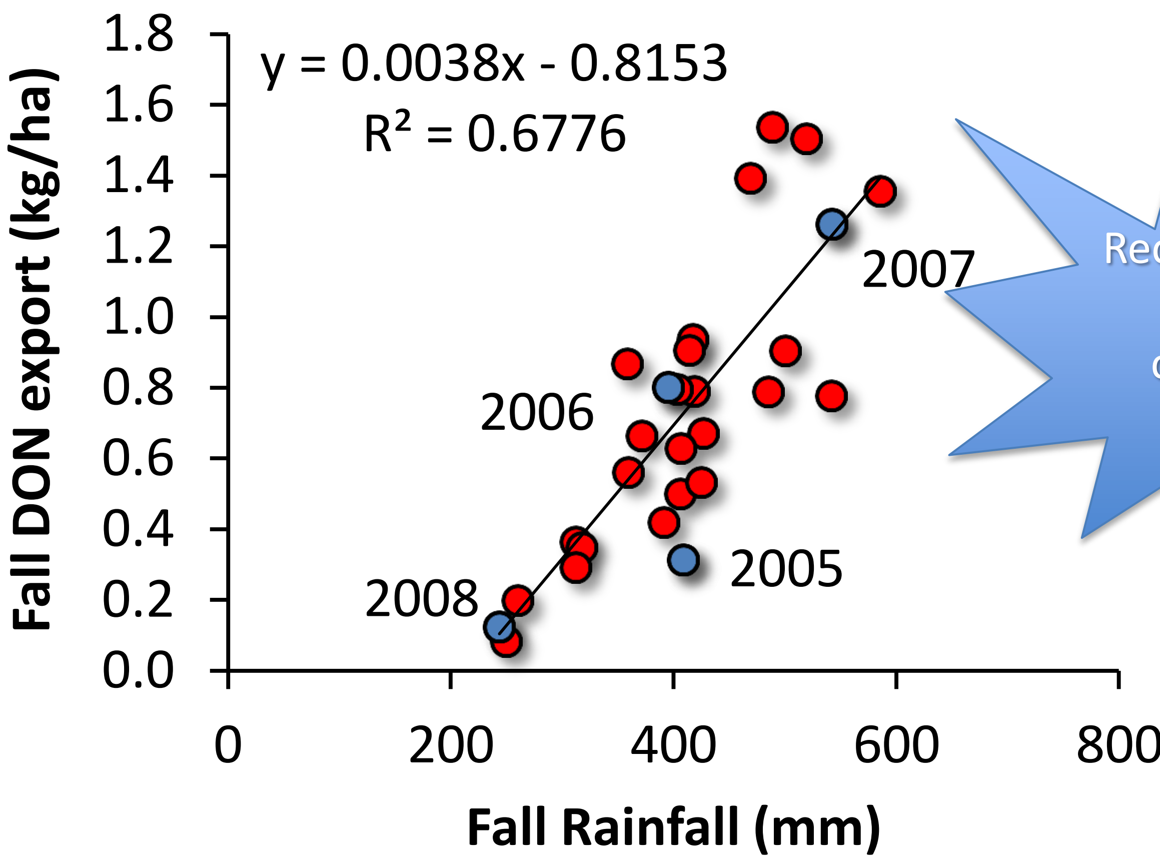
Spring *versus* fall DON export





How is DON being formed during fall storms?

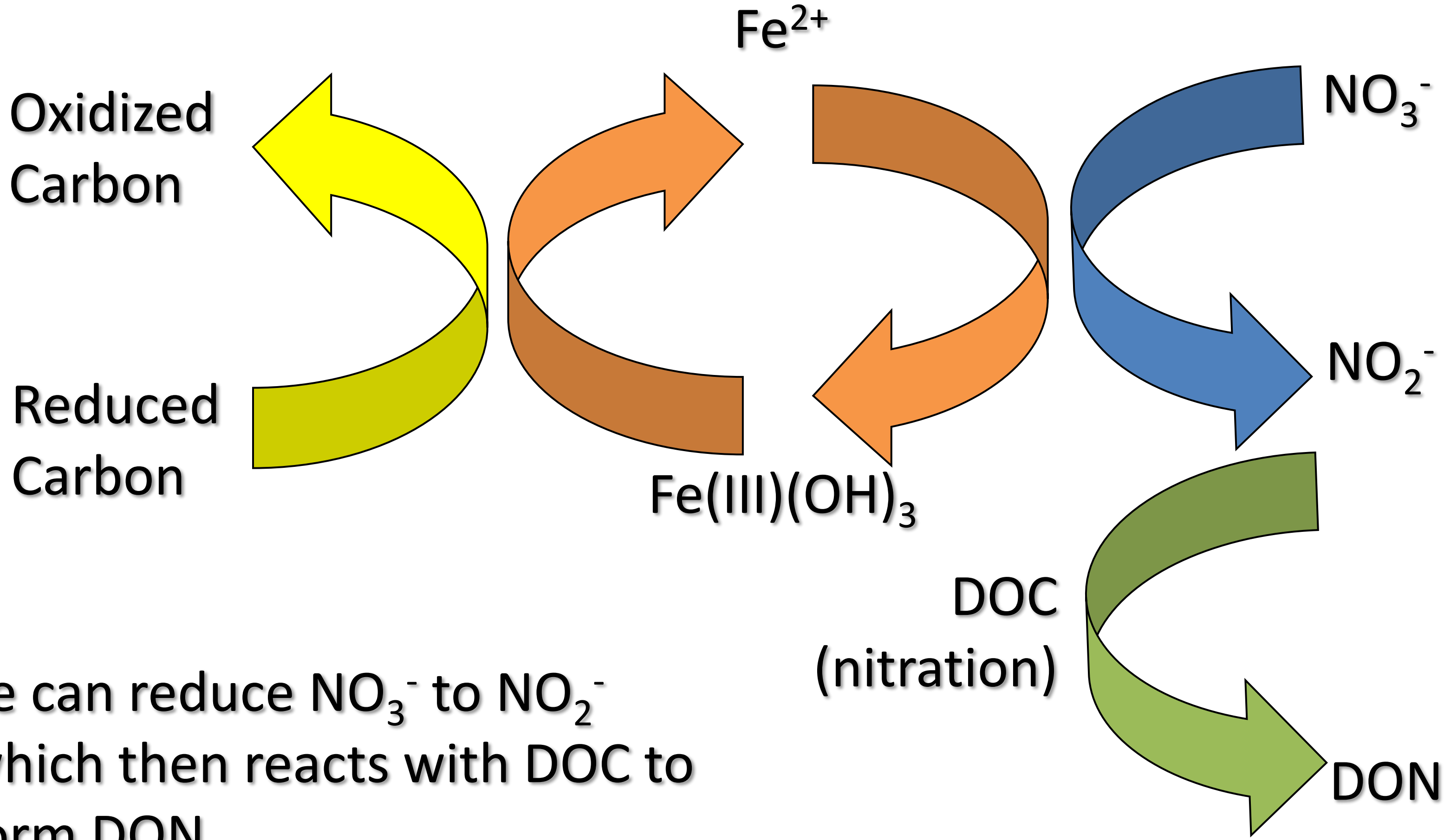
Rain triggered DON export?



Recall the large N gap in c35 vs. c38 in 2007?

Rain triggered DON export?

The ferrous wheel hypothesis

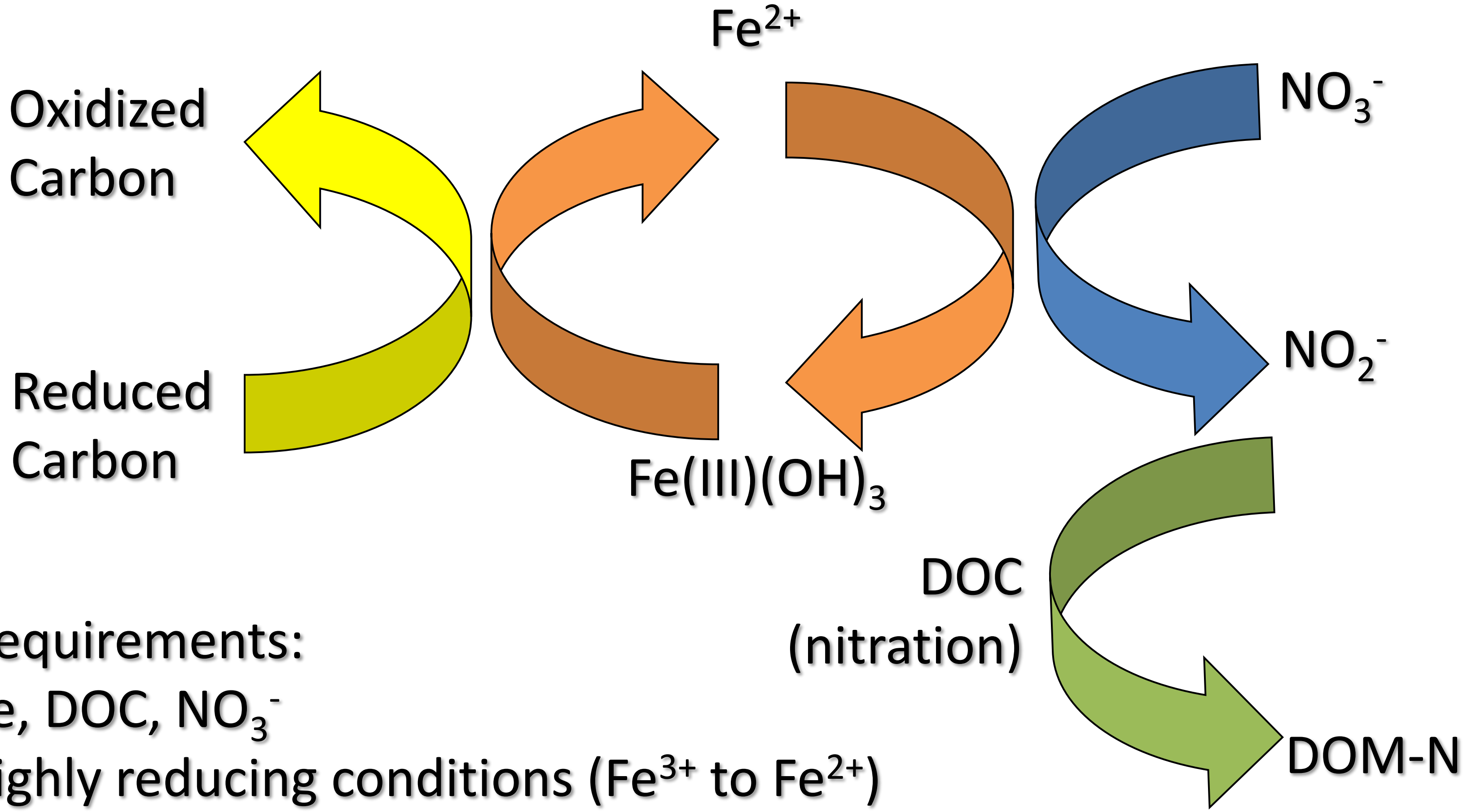


Fe can reduce NO_3^- to NO_2^- which then reacts with DOC to form DON

Davidson, Chorover, Dail. 2003 A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. *Global Change Biology* 9:228-236.

Rain triggered DON export?

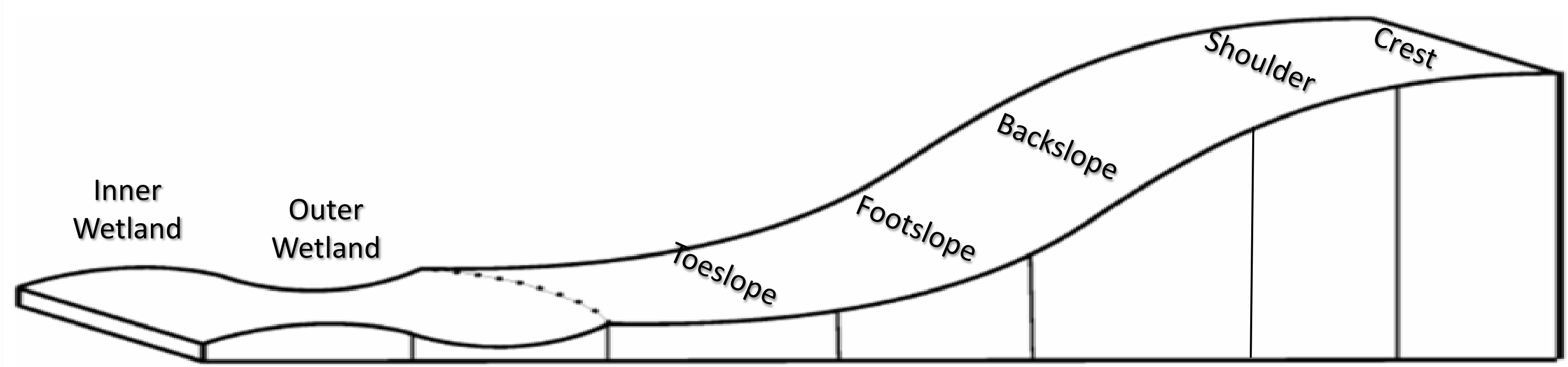
The ferrous wheel hypothesis



Requirements:
Fe, DOC, NO_3^-
highly reducing conditions (Fe^{3+} to Fe^{2+})

Where and when do these conditions occur?

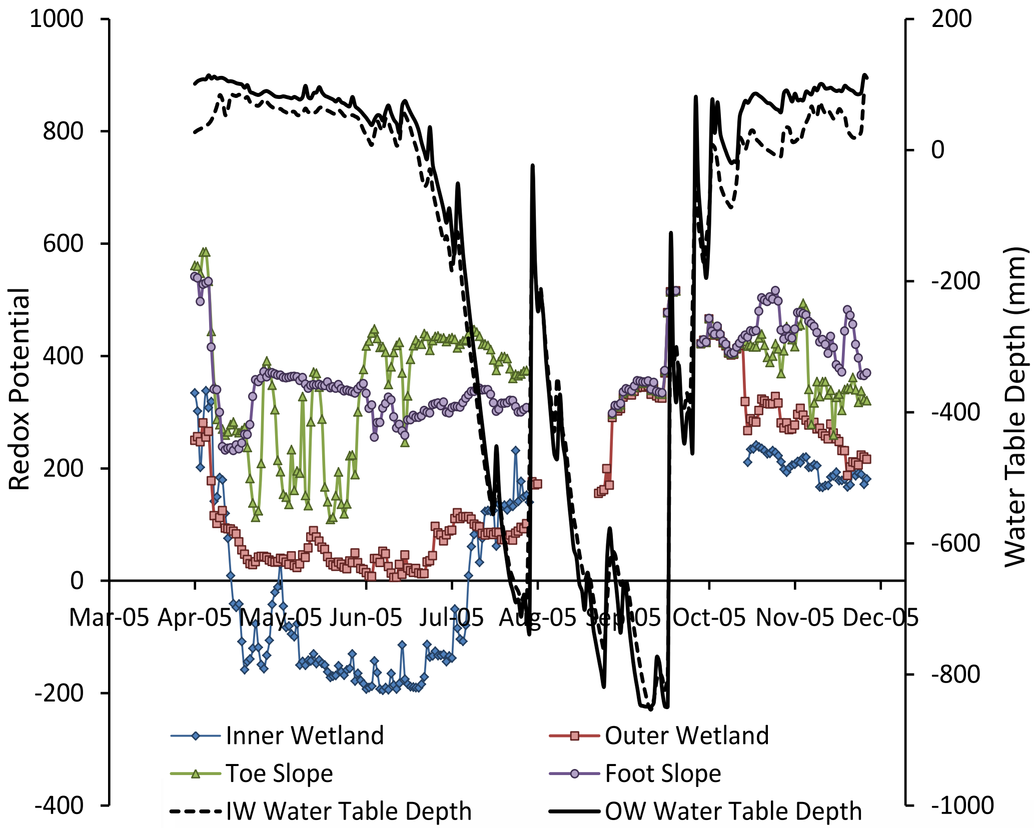
Distribution of precursors for DON formation *via* ferrous wheel hypothesis

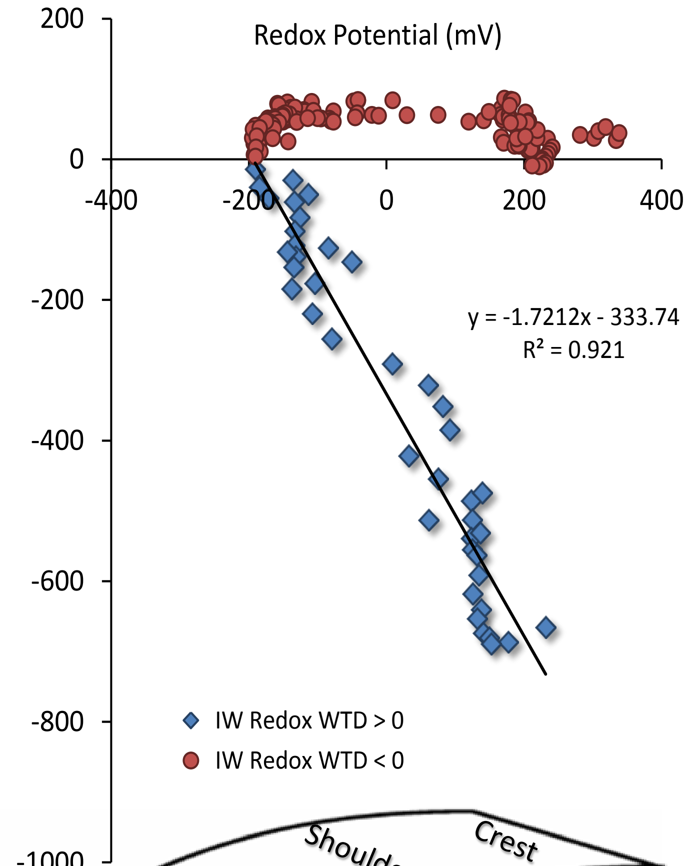


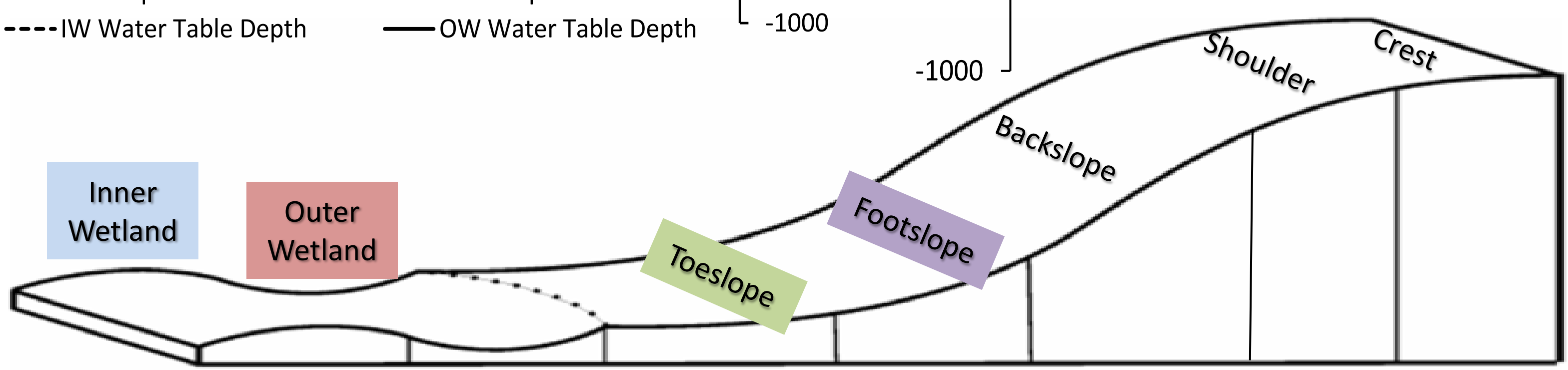
	Inner Wetland	Outer Wetland	Toeslope	Footslope	Backslope	Shoulder	Crest
Fe and Al oxyhydroxides	1.7 mol m^{-2}	3.2 mol m^{-2}	23.3 mol m^{-2}	14.0 mol m^{-2}	7.9 mol m^{-2}	11.6 mol m^{-2}	9.6 mol m^{-2}
DOC	8.4 mg L^{-1}	9.8 mg L^{-1}	21.1 mg L^{-1}	38.9 mg L^{-1}	39.7 mg L^{-1}	31.9 mg L^{-1}	32.5 mg L^{-1}
NO_3^-	1.1 mg L^{-1}	1.3 mg L^{-1}	1.4 mg L^{-1}	0.6 mg L^{-1}	1.5 mg L^{-1}	2.0 mg L^{-1}	1.9 mg L^{-1}

Creed, Webster, Braun, Bourbonnière, Beall. Topographically regulated traps of dissolved organic carbon create hotspots of soil carbon dioxide efflux in forests. Revised and Submitted to Biogeochemistry. December 1, 2011.

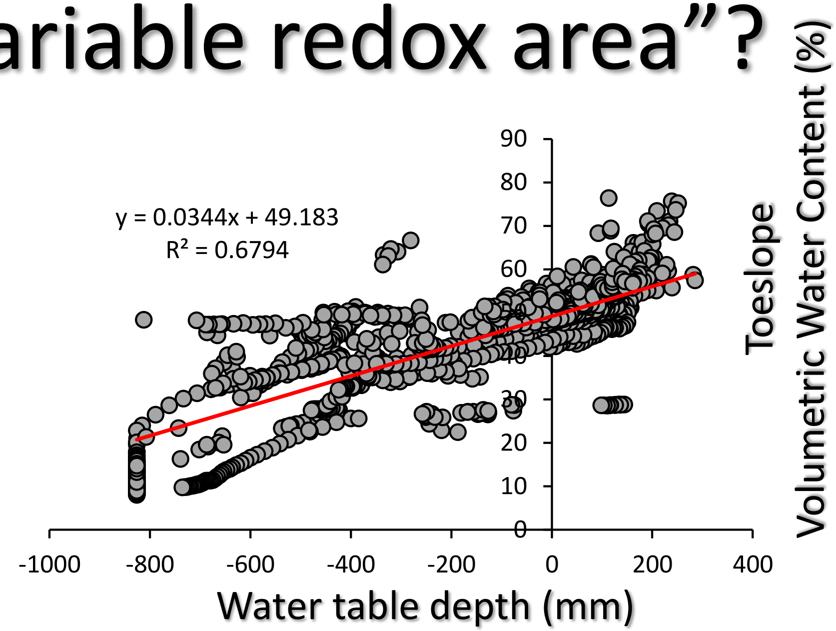
In 2005 reducing conditions restricted to the inner wetland (drought year)

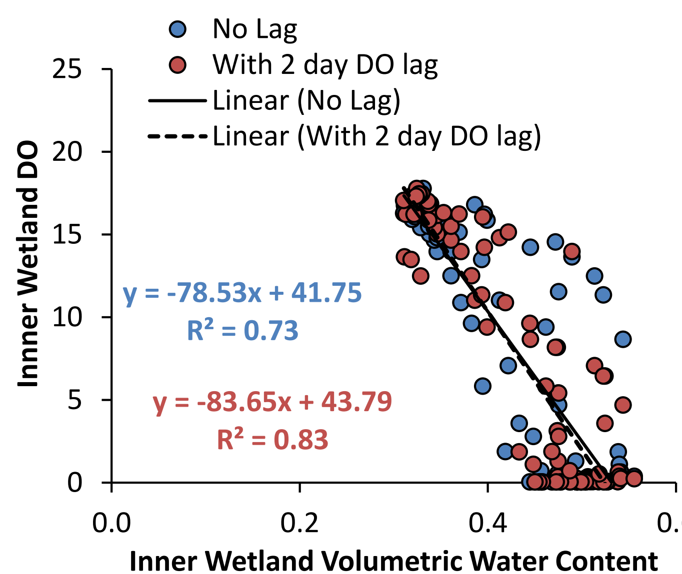






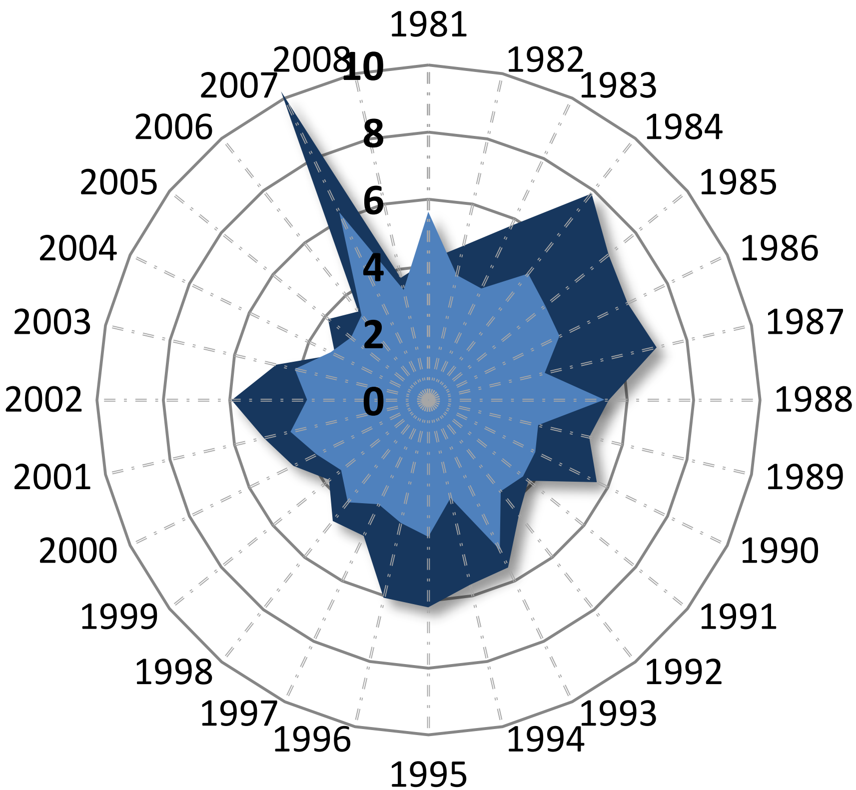
Does a shift to wetter conditions result in an expansion of the “variable redox area”?





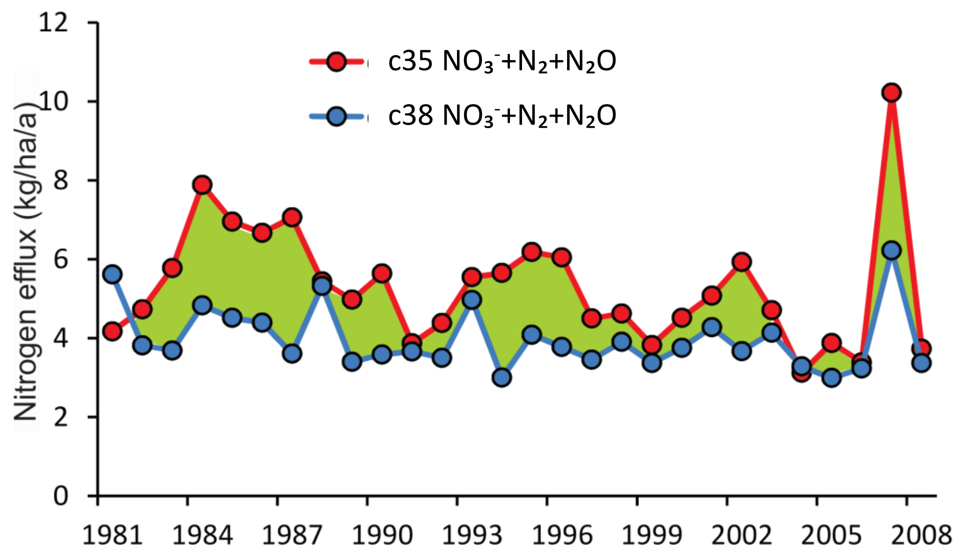
Rising water table
from 2005 to 2010 leads to saturated
and anoxic soils in toeslope

Does DON close the gap in c35 vs. c38 N export?

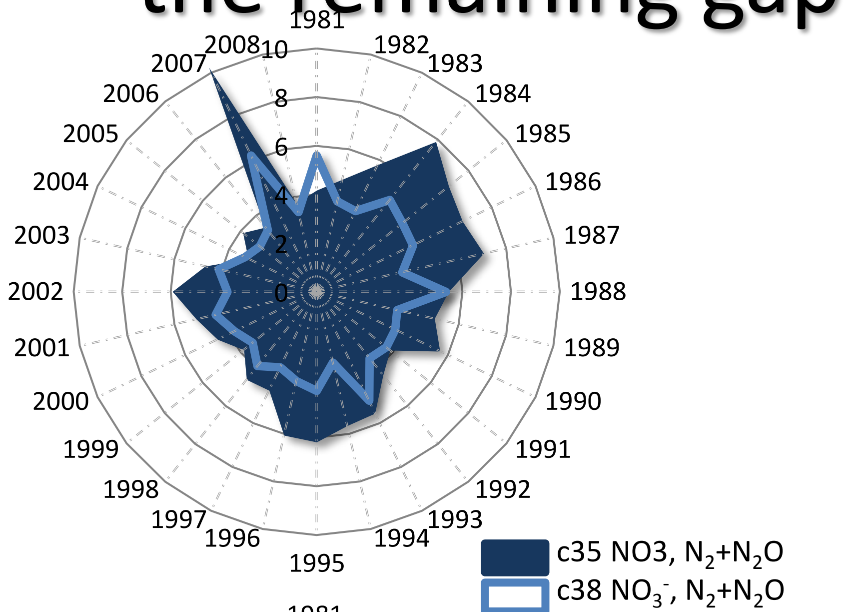


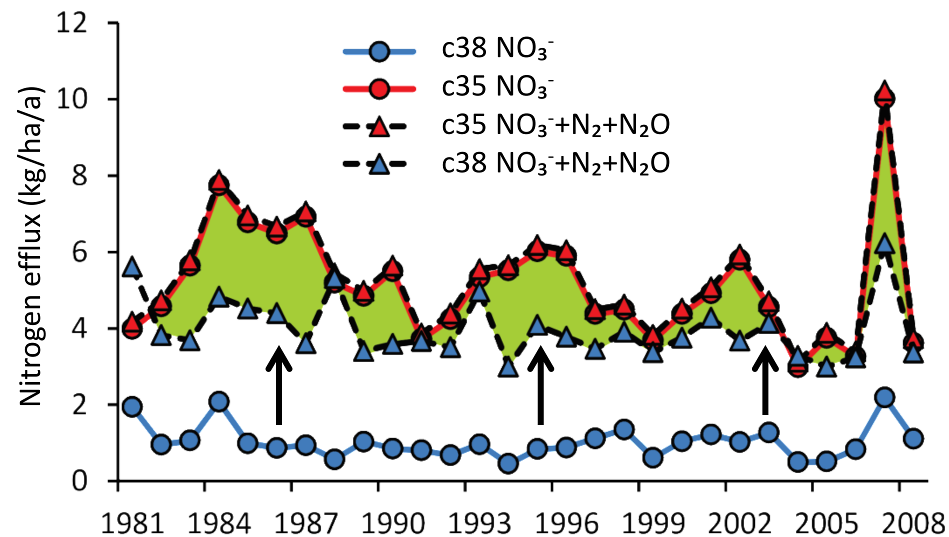
c35 NO_3^-, N_2+N_2O output (kg/ha/yr)

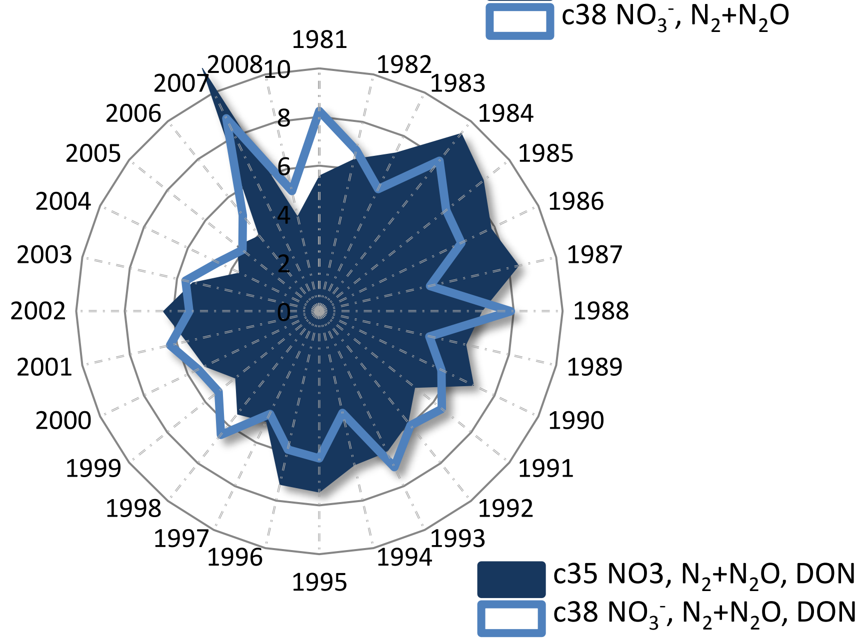
c38 NO_3^-, N_2+N_2O output (kg/ha/yr)

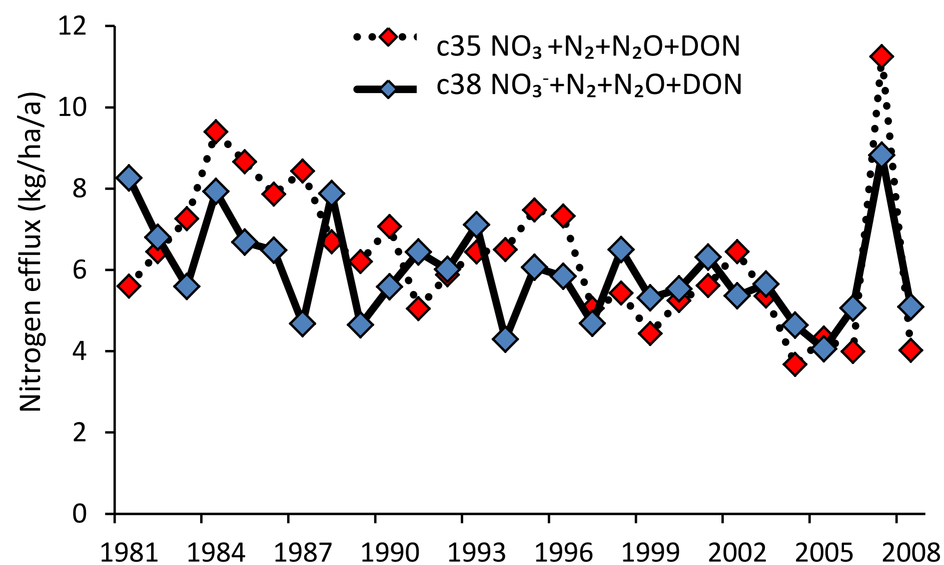


YES! Accounting for DON eliminates the remaining gap in c35 *vs.* c38 N export









Conclusions

- Topography creates a spatially and temporally dynamic redox surface that influences N speciation and N fate
- During periods of spring hydrological connection to weir (melt),
  - NO_3^- is the dominate species of N export; it may "bypass" the reducing environments of riparian areas *via* surface flow
- During periods of hydrological disconnection from weir (summer storms),
  - NO_3^- entering reducing environments is transformed into N_2O and/or N_2 and lost via gaseous N export
- During periods of fall hydrological connection to weir (storms),
  - NO_3^- infiltrating Fe^{2+}-rich soils may be transformed into DON and lost via dissolved N export (need further evidence in support of this "ferrous wheel" mechanism)
- Failure to account for N cycling processes across multiple space/time scales may result in incomplete accounting of N in N mass balances of catchments