Soil, groundwater and surface water chemistry of nitrogen

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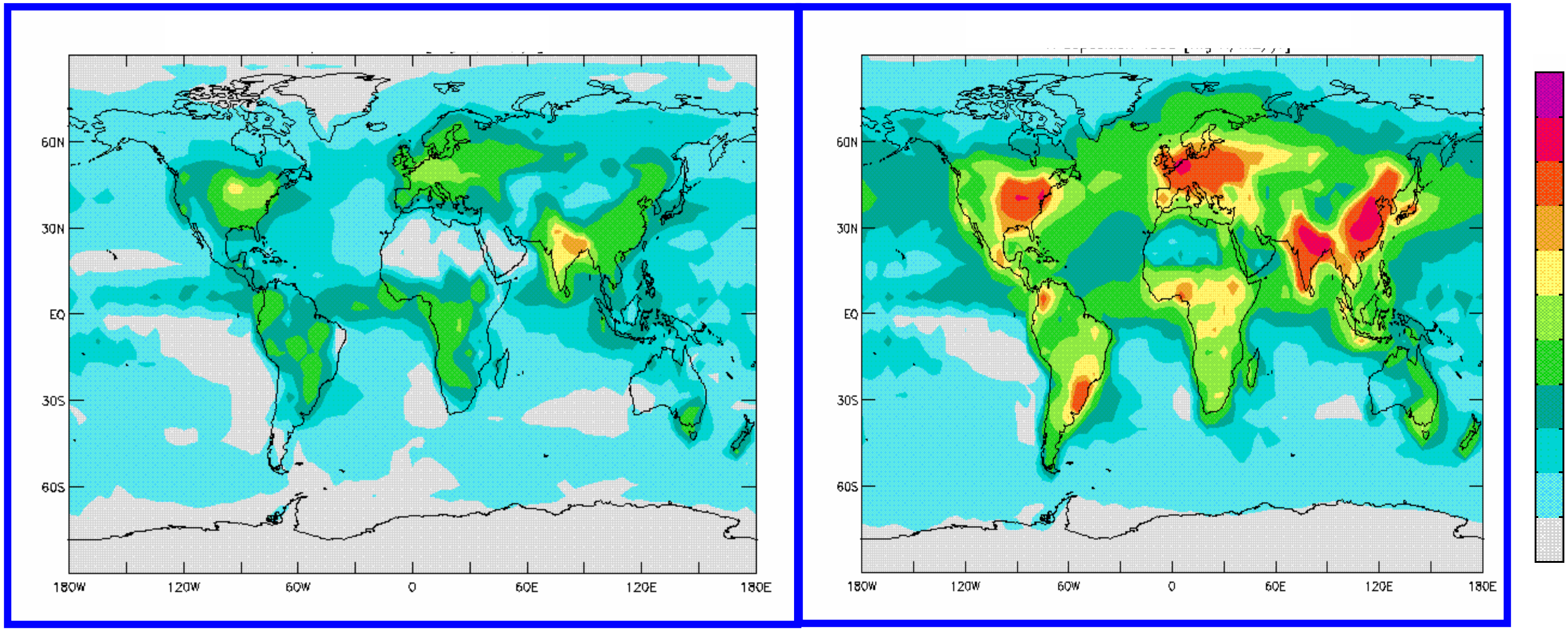
Nitrogen Deposition

Past and Present

mg N/m²/yr



1860

1993

Galloway and Cowling, 2002; Galloway et al., 2002b

Some basic information on nitrogen:

- ***Forms and functions of N in plants***
  - N required by plants in large amounts
    - Usually the limiting nutrient in unfertilized systems
  - Amino acids, amides, amines
    - Building blocks, intermediary compounds
  - Proteins, chlorophyll, nucleic acids
    - Proteins/enzymes regulate biochemical reactions
    - N is an integral part of chlorophyll structure
      - Pale green/yellow color of N deficient plants
    - Nitrogenous bases of DNA, RNA

- ***N mobility***
  - Translocated from older leaves to younger leaves
  - Deficiencies occur first on lower, older leaves

Ammonium and nitrate dominate:

- ***Ammonium* (NH_4^+)**
  - Does not have to be reduced
    - Conserves energy
  - Rhizosphere pH
    - Roots release H^+

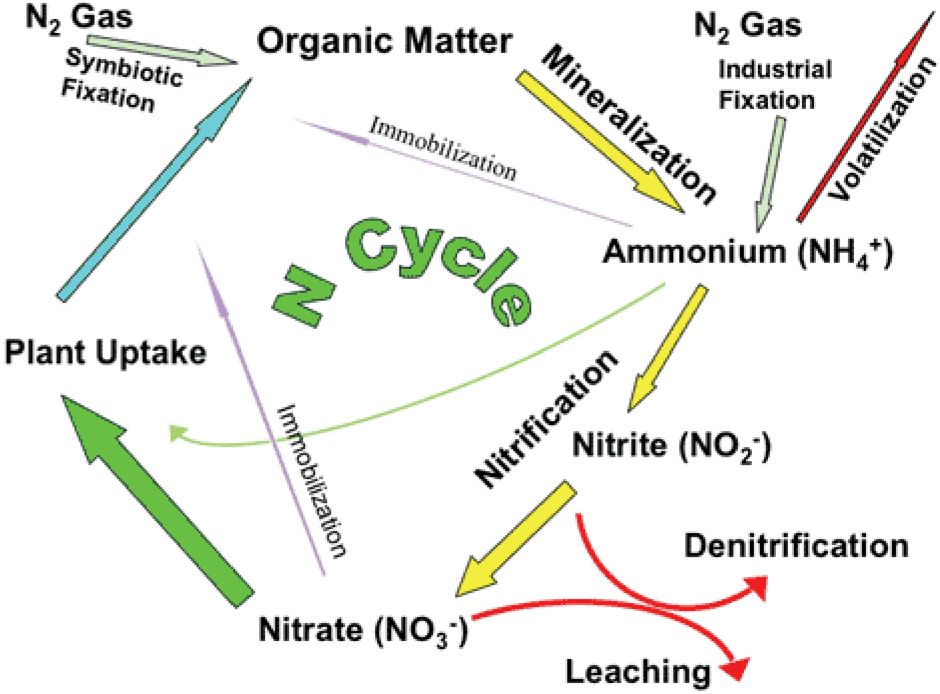
- ***Nitrate* (NO_3^-)**
  - Must be reduced before synthesis of amino acids, etc.
  - Rhizosphere pH
    - Roots release HCO_3^- (OH^-)

Nitrogen dynamics are complex:

The Nitrogen Cycle

N transformations:

- Mineralization
- Immobilization
- Nitrification
- Denitrification
- Volatilization
- N Fixation



- ***Mineralization***

1. Release of organic N as plant available inorganic NH_4 -N
2. Heterotrophic bacteria and fungi
3. Soil OM ~5% N (*considerable variation*)
4. ~1 to 4% of organic N mineralized each year (*considerable variation*)

• *Immobilization (assimilation)*

1. Reverse of mineralization
2. Uptake of inorganic N from the soil and incorporation into organic N forms by microbes

   Can be NH_4^+ or NO_3^-
3. *<u>Mass balance studies often show vast majority of N is retained in soils</u>*

- ***Nitrification***

1. Conversion of NH_4^+ to NO_3^-
2. Two-step process
3. Primarily performed by two types of autotrophic bacteria

    Obtain energy from N oxidation

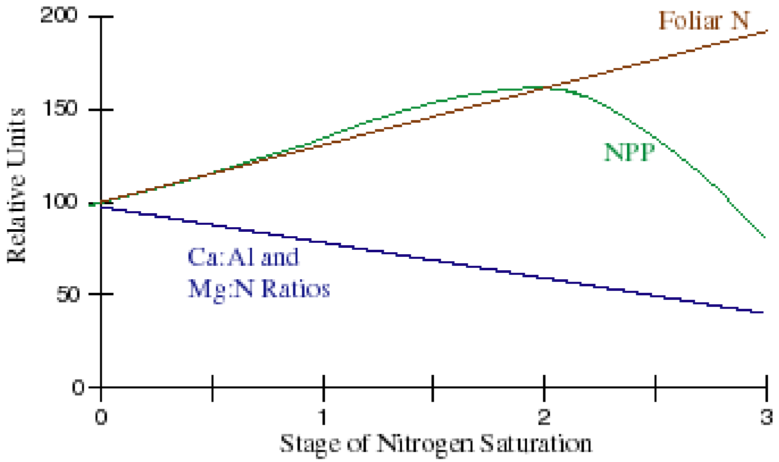
- ***Denitrification***

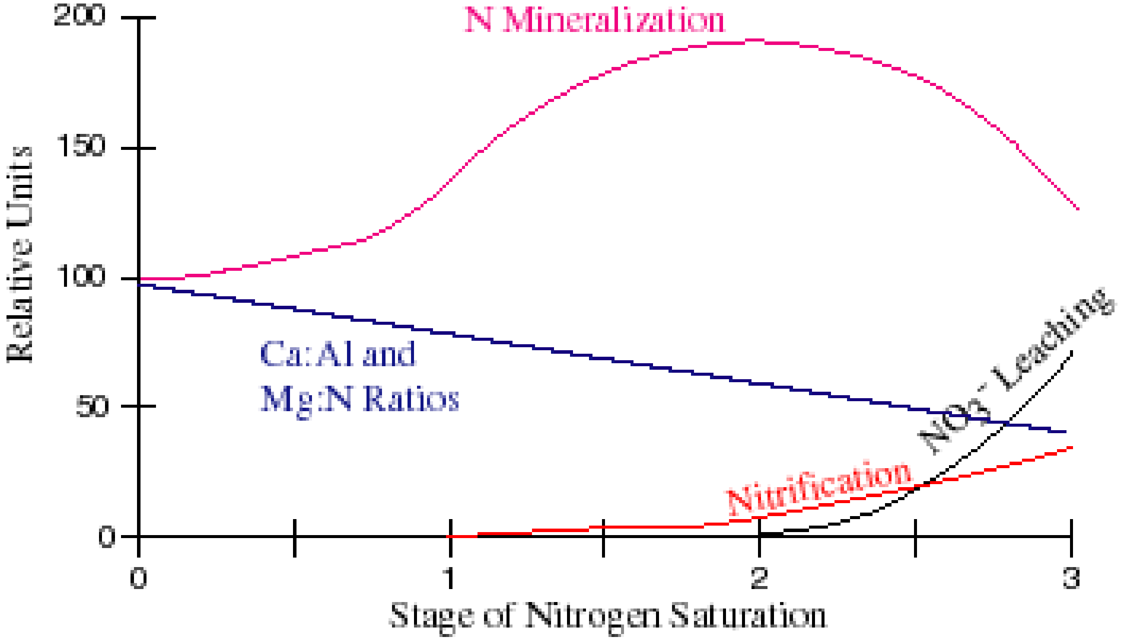
1. Gaseous loss of N
    Conversion of NO_3^- to N_2 and N_2O
2. Anaerobic bacteria
    Pseudomonas, *Bacillus*, and other species
        Facultative anaerobes
    Use oxidized N as their O_2 source for respiration

– Waterlogged soils or low O_2 microsites in soil
    e.g. around roots or decomposing residues

- ***Volatilization***
  - Gaseous loss of NH_3
  - Primarily from surface-applied N fertilizers
    - NH_3 loss favored by high pH
    - Solution pH >7 or 7.5

Nitrogen Saturation





Hypothesized biogeochemical response of temperate forest ecosystems to long-term nitrogen additions (modified from Aber *et al* 1998).

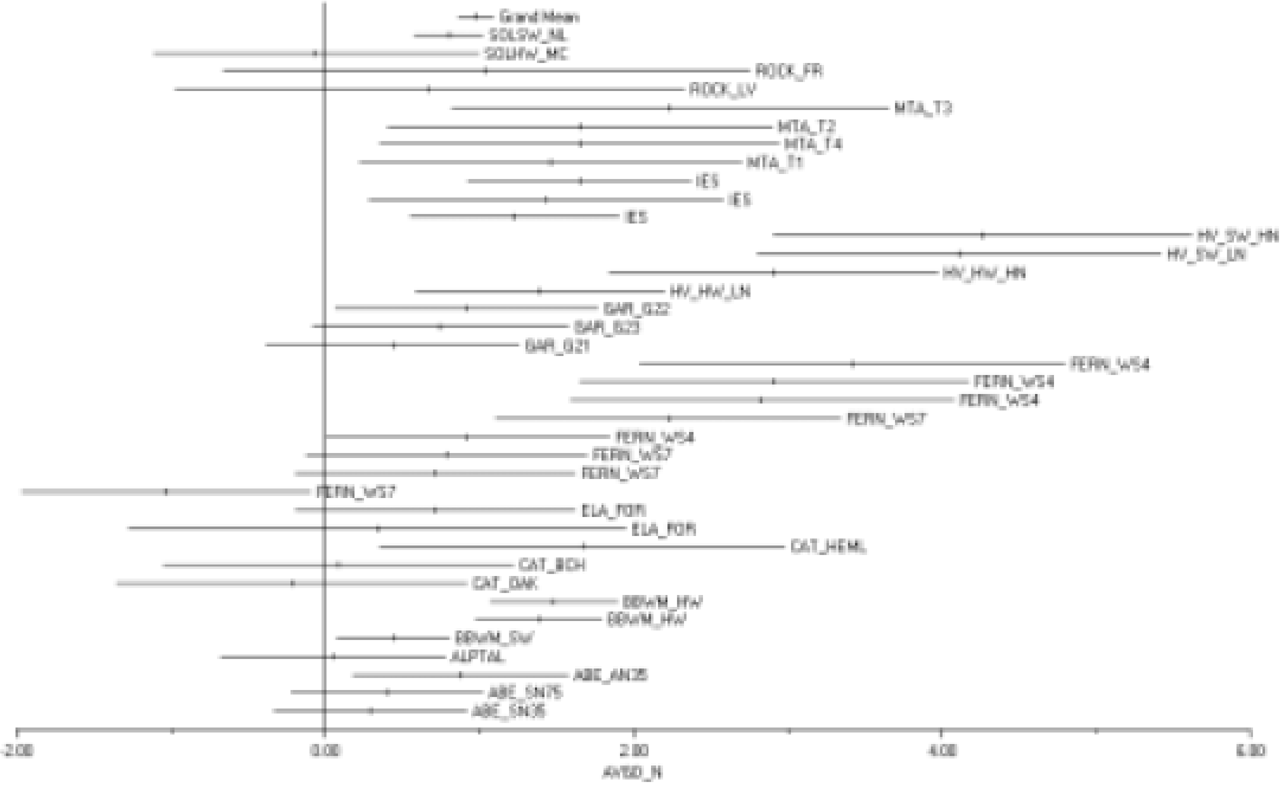
'N in excess of biotic demands'

Experimental Studies

- Many experimental studies have demonstrated the potential negative impacts of N deposition.
- Common for N to be applied at a level far greater than current observed values
- Many studies show expected response to elevated N application.

N fertilization plot at Harvard Forest

Rustad et al. are working on a meta-analysis of experimental N addition studies (www.ecostudies.org/nerc)



Summary of the response of Foliar N to N additions (56 manipulations in 8 countries)

Other Processes

- Regina et al (1998) demonstrated that net N mineralization, N_2O and NO fluxes from a drained forested peatland may be affected by N additions (100 kg N ha^{-1}), although response varies depending upon form of N application.

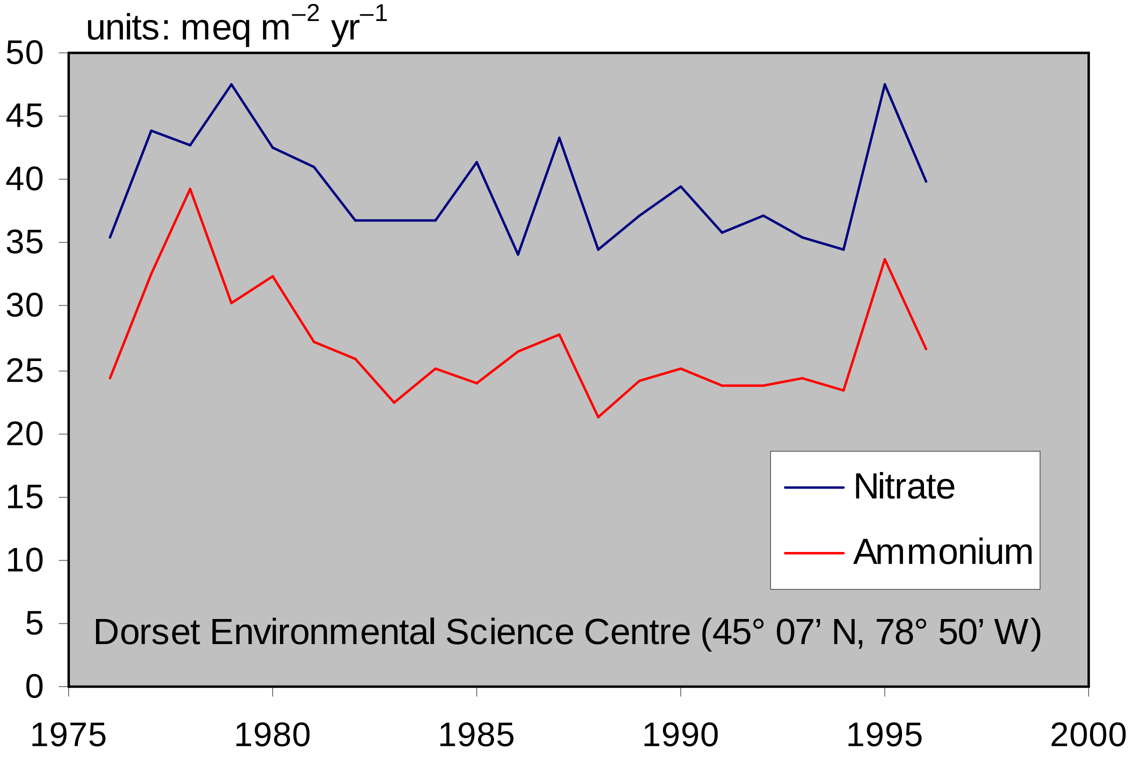
Results from experimental studies:

- Some things (commonly measured) to look for with respect to ‘N-saturation’.
  - Increased mineralization
  - Increased nitrification
  - Increased foliar N (uptake)
  - Decreasing soil C:N ratio (N-immobilized)

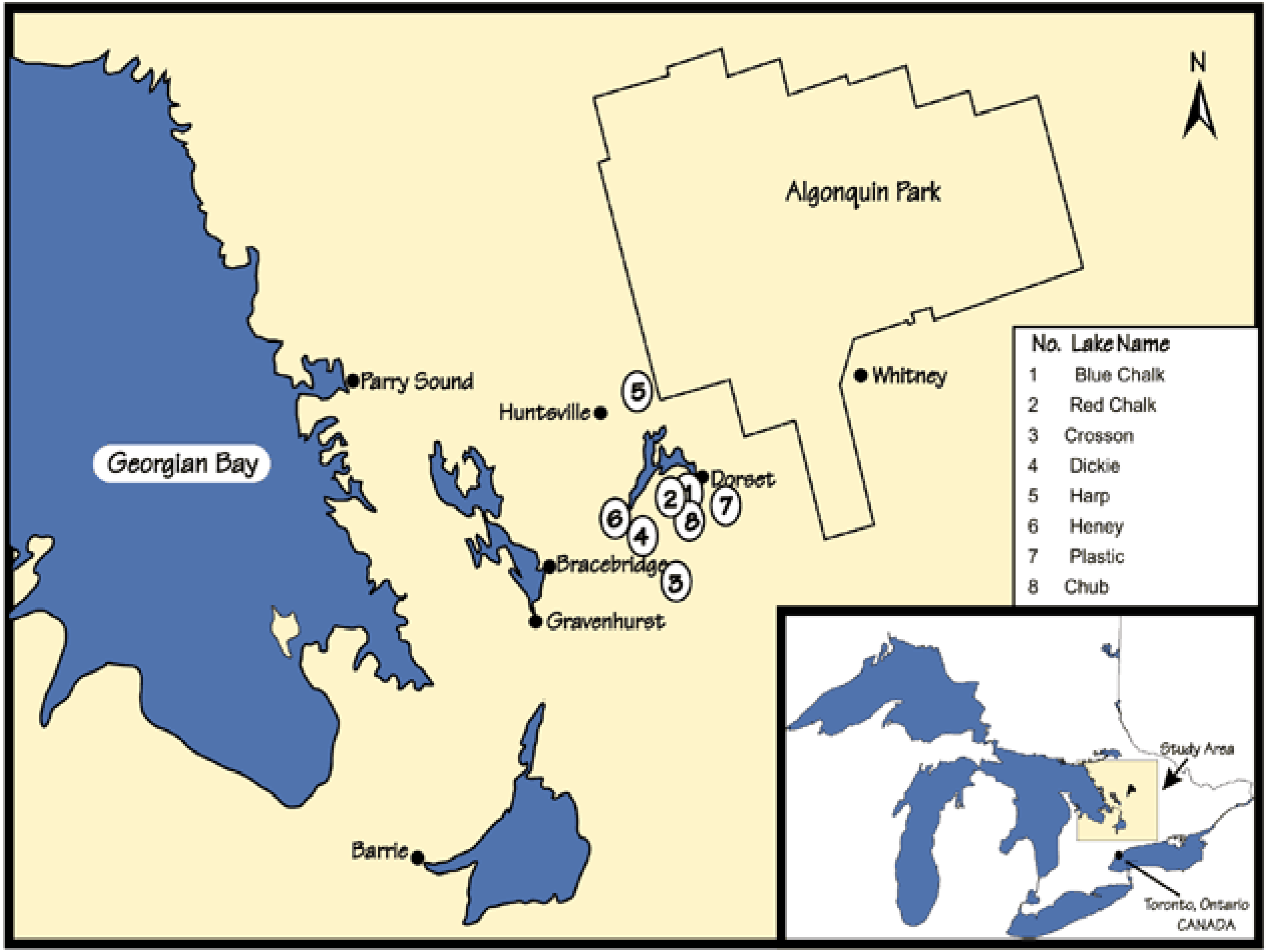
Monitoring and Gradient Studies

- Nitrogen budgets in central Ontario Forests
  - Catchment scale
  - Role of climate
  - Forest plots
- Nitrogen budgets in eastern North America and European catchments

Nitrogen Budgets in Central Ontario



Nitrogen bulk deposition is around 70 meq m^{-2} yr^{-1} (~10 kg N ha^{-1} yr^{-1})

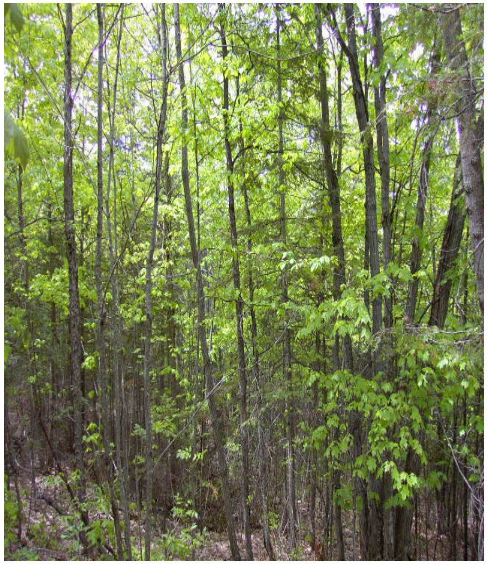

N
Algonquin Park
Georgian Bay
Parry Sound
Huntsville
Whitney
Dorset
Bracebridge
Gravenhurst
Barrie
5
2
1
7
6
8
4
3
No. Lake Name
1 Blue Chalk
2 Red Chalk
3 Crosson
4 Dickie
5 Harp
6 Heney
7 Plastic
8 Chub
Study Area
Toronto, Ontario
CANADA

The region in summer

and in winter

Deposition

Net forest uptake



Soil nitrogen pool

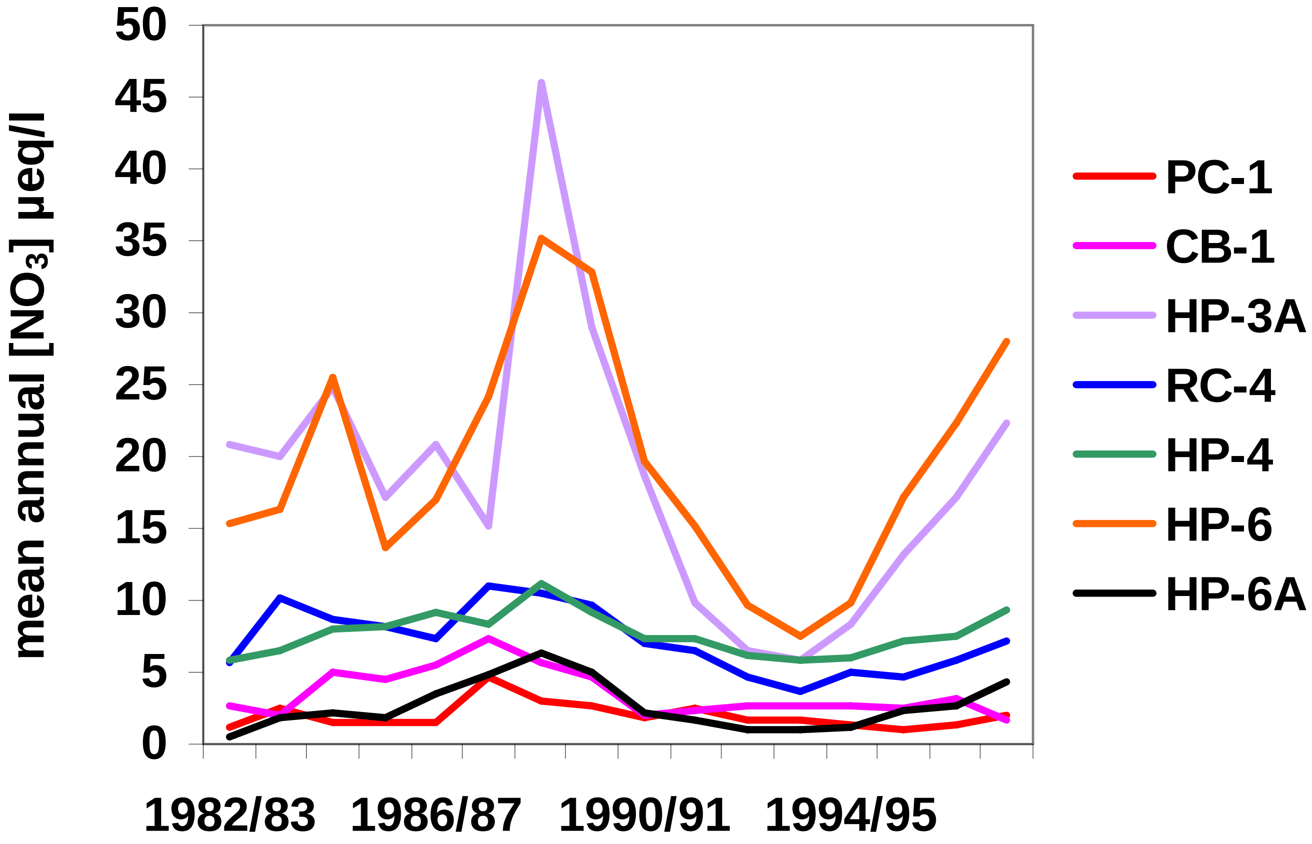
Soil leaching losses

Most nitrogen is retained

	% N retention	% N exported as organic N	Cumulative N accumulation
PC1	81.3	90.6	120
CB1	87.0	82.6	128
RC4	69.8	78.3	102
HP3A	71.4	45.6	105
HP4	76.0	73.6	112
HP6	62.9	53.9	93
HP6A	84.0	87.9	124
Average	76.1	73.2	112

And, most of N exported is organic and the catchments accumulated between 93 and 128 kg ha^{-1} over a 17-yr period (1982-1999)

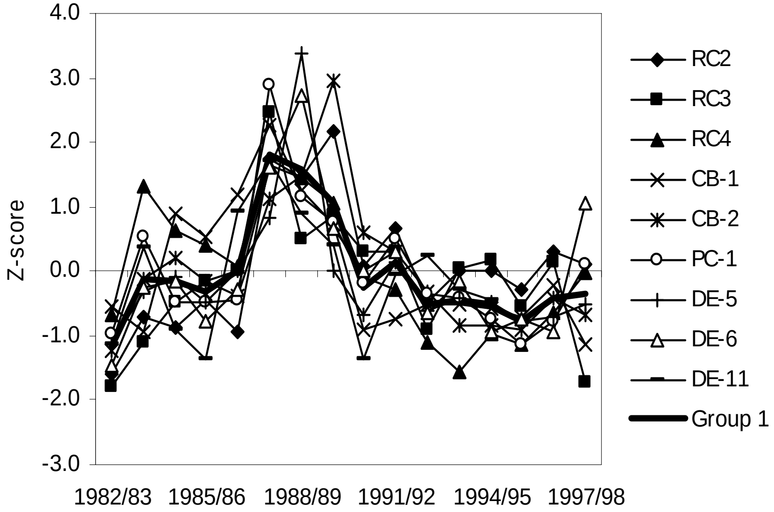
Nitrate leaching varies considerably among catchments – no increasing trend

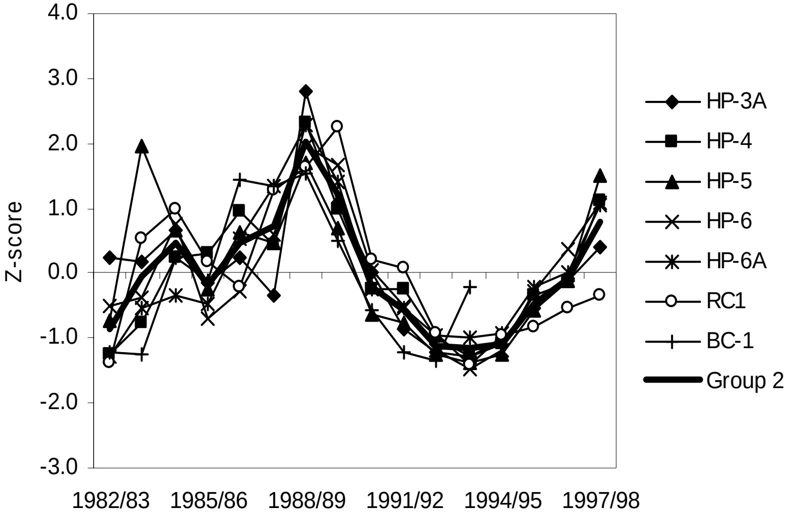


So what is responsible for the spatial and temporal variability?

Expanded to 17 catchments

- Two ‘groups’ identified with respect to NO_3 leaching.





The first group are seemingly more wetland influenced

	% Peat	Grade (%)	% deep till (>1 m)	Upland Forest	Annual NO_3^--N (mg/l)	% N retention	% NO_3 (of total stream N)	Trend slope (mg/l)
RC2	10.5	1.5	0	SM, YB, HE	0.04	72.6	8.7	+0.007*
RC3	9.9	3.5	81.7	SM, YB, RO	0.12	67.1	25.8	n.s.
RC4	2.9	2.5	76.3	SM, RO, RM	0.10	69.8	21.7	n.s..
CB1	2.8	3.0	24.2	RM, RO, SM	0.05	87.0	17.4	n.s.
CB2	8.0	2.0	16.7	SM, RM, RO	0.05	71.5	10.2	n.s
PC1	7.0	5.9	9.6	WP, HE, RO	0.03	81.3	9.4	n.s.
DE5	25.4	1.0	0.0	RM,SM, YB	0.10	72.5	2.4	n.s.
DE6	22.0	1.6	0.0	RM, SM, YB	0.02	67.1	3.9	n.s
DE11	20.9	1.0	0.0	RM, SM, YB	0.03	72.4	5.6	n.s.
mean	12.2	2.4	23.2		0.06	73.5	11.6	

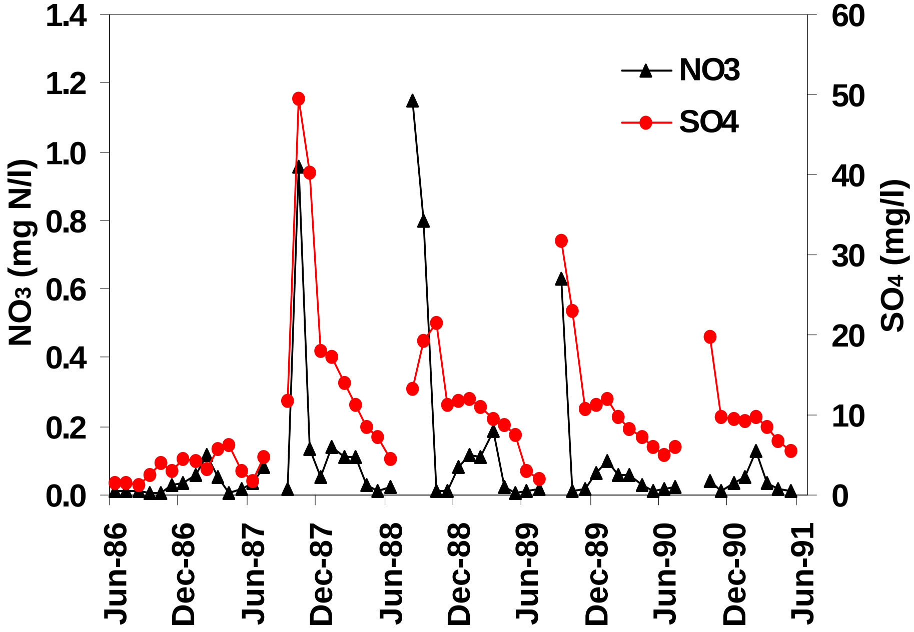
The second group is less influenced by wetlands

	% Peat	Grade (%)	% deep till (>1 m)	Upland Forest	Annual NO_3^- N (mg/l)	% N retention	% NO_3 (of total stream N)	Trend slope (mg/l)
HP3A	2.9	8.0	97.1	SM, YB, RM	0.29	71.4	54.3	n.s.
HP4	0.0	5.0	56.1	SM, RM, YB	0.11	75.9	26.4	n.s.
HP5	13.3	3.0	34.5	SM, YB, RM	0.14	63.9	24.8	n.s.
HP6	0.0	8.0	45.2	SM, HE, YB	0.27	62.9	46.1	n.s.
HP6A	10.0	8.5	6.6	SM, HE, YB	0.04	84.0	12.1	n.s.
RC1	0.0	1.0	53.2	SM, YB, HE	0.10	78.8	26.4	n.s.
BC1	0.0	7.0	94.0	SM, YB, BE	0.08	89.5	35.1	n.s.
mean	3.7	5.8	55.2		0.15	75.2	32.2	

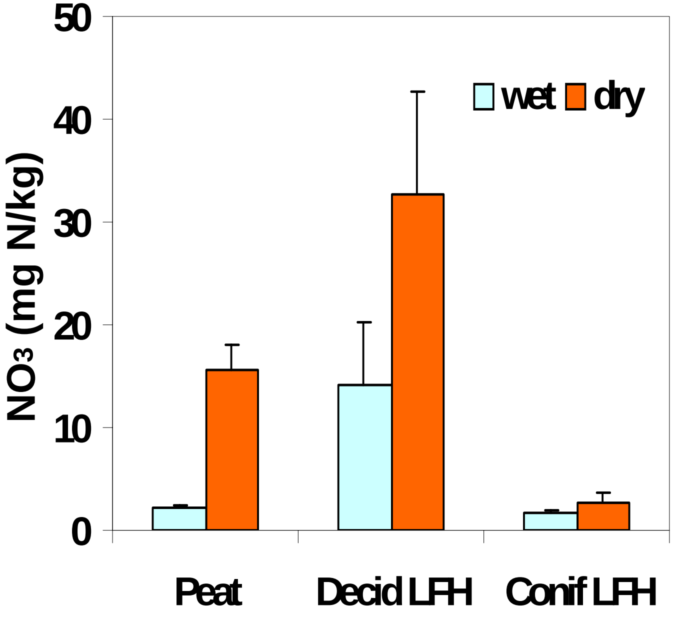
Explanations

- Likely a number of climate-related factors.
- Stepwise multiple regression indicated that summer drought (both groups) and cumulative frost depth (sum of daily frost depths – group 1) could explain around 50% of the variability in annual NO_3 concentrations.

Net NO_3 production also sensitive to changes in soil moisture:

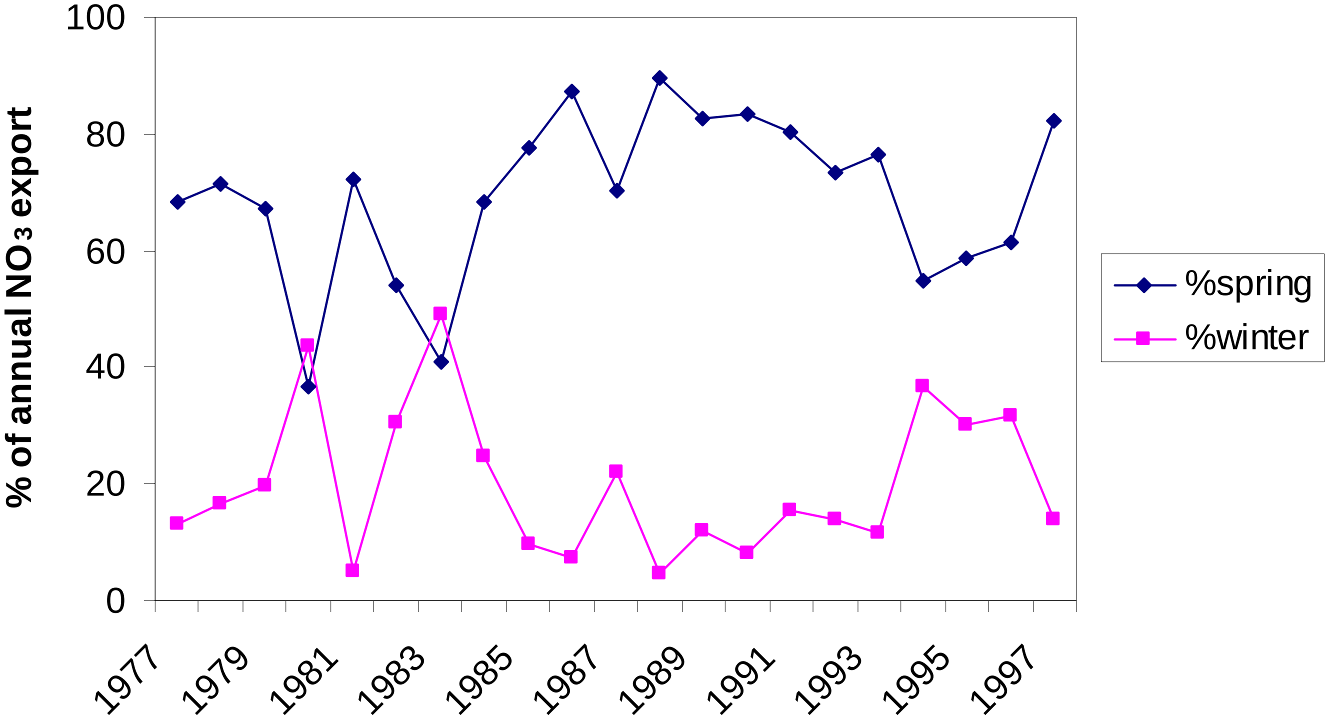


NO_3 concentrations increase following summer drought



Drying and rewetting results in increase NO_3 availability in lab studies

Seasonal pattern of NO_3^- export in upland catchments indicates that changes in winter temperature and precipitation could have implications for NO_3^- leaching

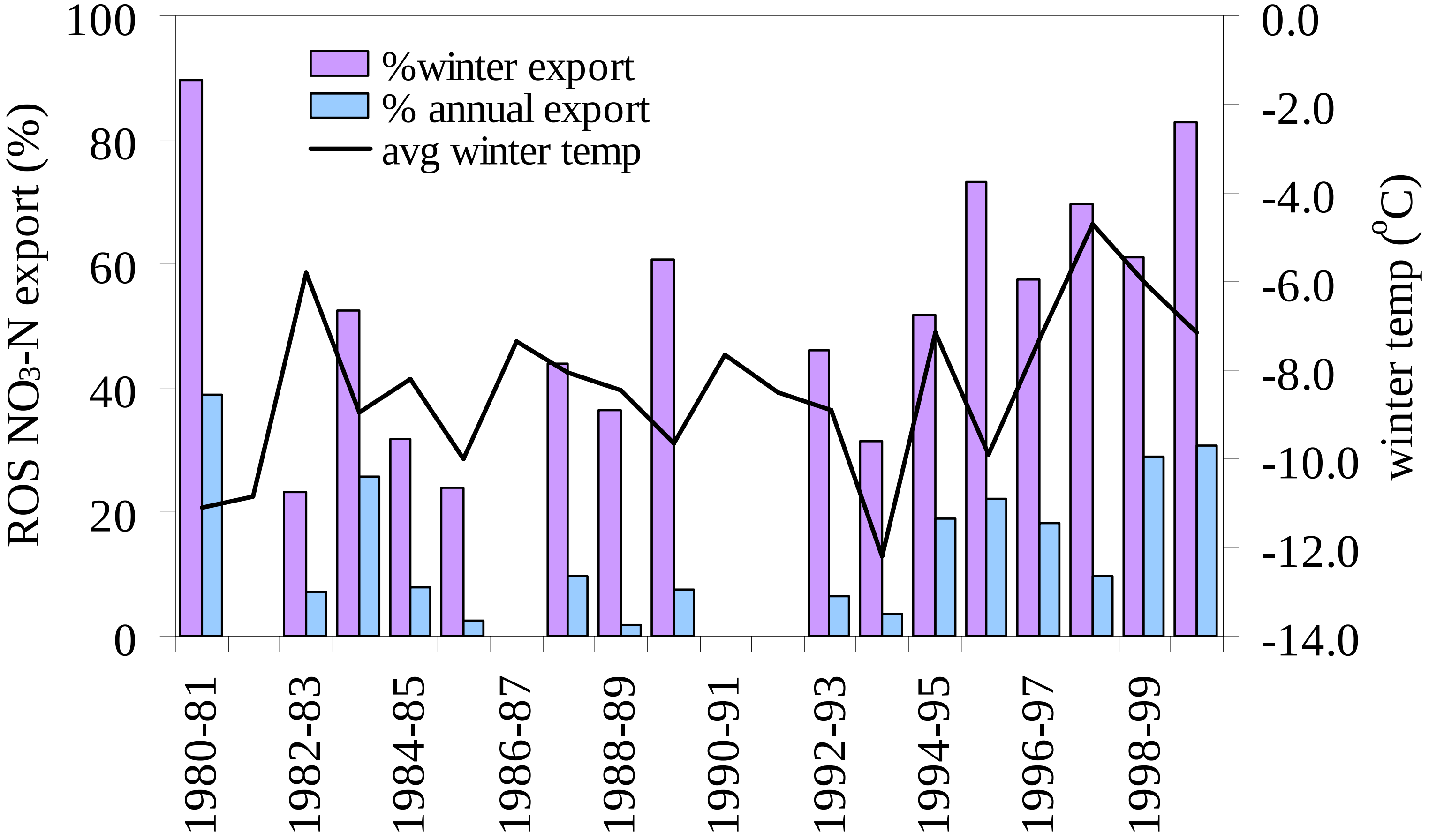


Rain-on-snow events

- Three factors indicate that much of the NO_3-N and acidity associated with ROS events is transported relatively conservatively to drainage streams

1. High [NO_3-N] in precipitation (also snow pack)
    - Bulk dep: 280 to 2000 μg/L (annual avg streams: 28 -280 μg/L; max ROS event = 1480 μg/L)
    - Snow: 300-700 μg/L
2. Limited interaction with soil beneath snow pack
3. Relatively low potential for biological retention during ‘dormant’ season

Contribution of ROS events to NO_3-N export at an upland forested catchment:

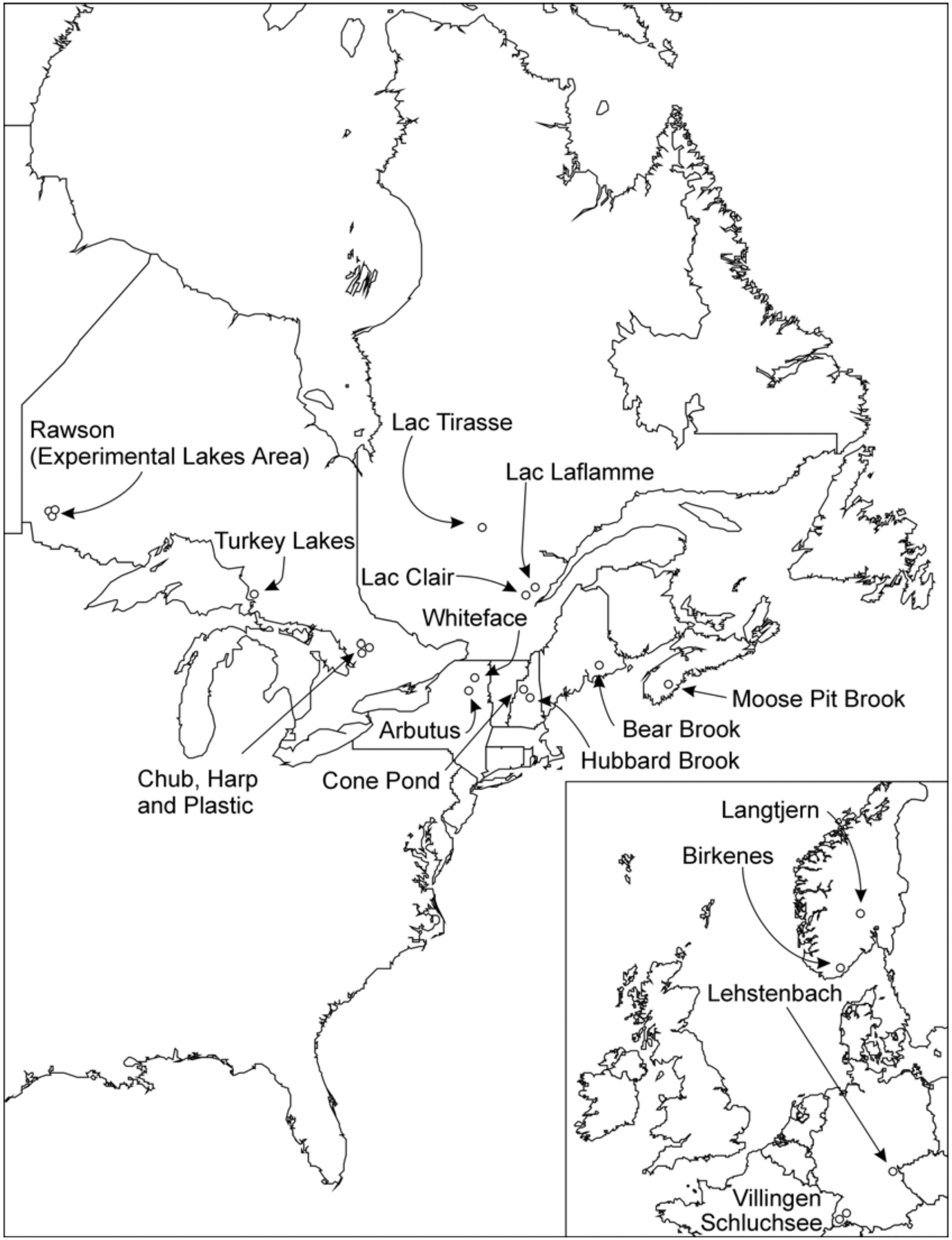


N budgets in Eastern North America and European Catchments

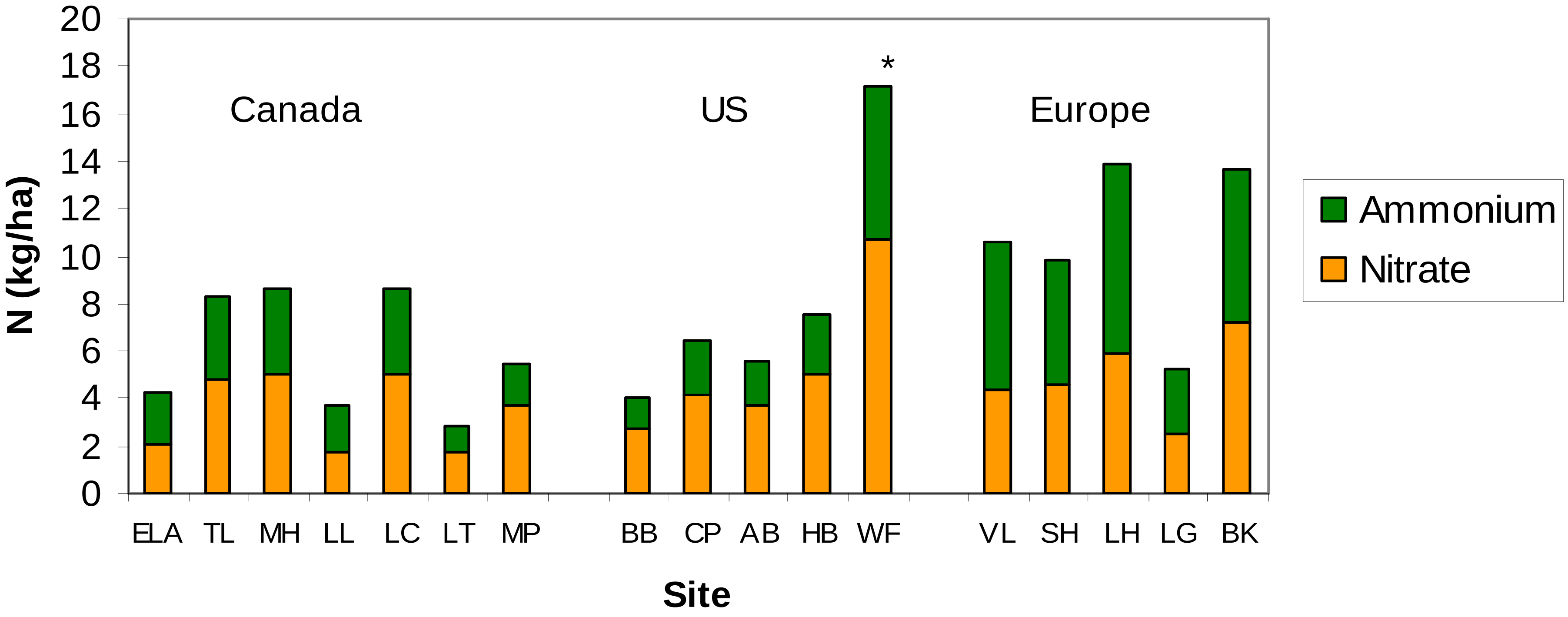
- N budgets (1990s average) calculated for 21 sites that span a deposition gradient.

- Trend analysis was conducted on monthly NO_3 and NH_4 concentrations when there were more than 9 years of data (14 regions; 17 sites).

The Sites


Rawson
(Experimental Lakes Area)
Lac Tirasse
Lac Laflamme
Turkey Lakes
Lac Clair
Whiteface
Moose Pit Brook
Bear Brook
Arbutus
Hubbard Brook
Chub, Harp
and Plastic
Cone Pond
Langtjern
Birkenes
Lehstenbach
Villingen
Schluchsee

Nitrogen Deposition:

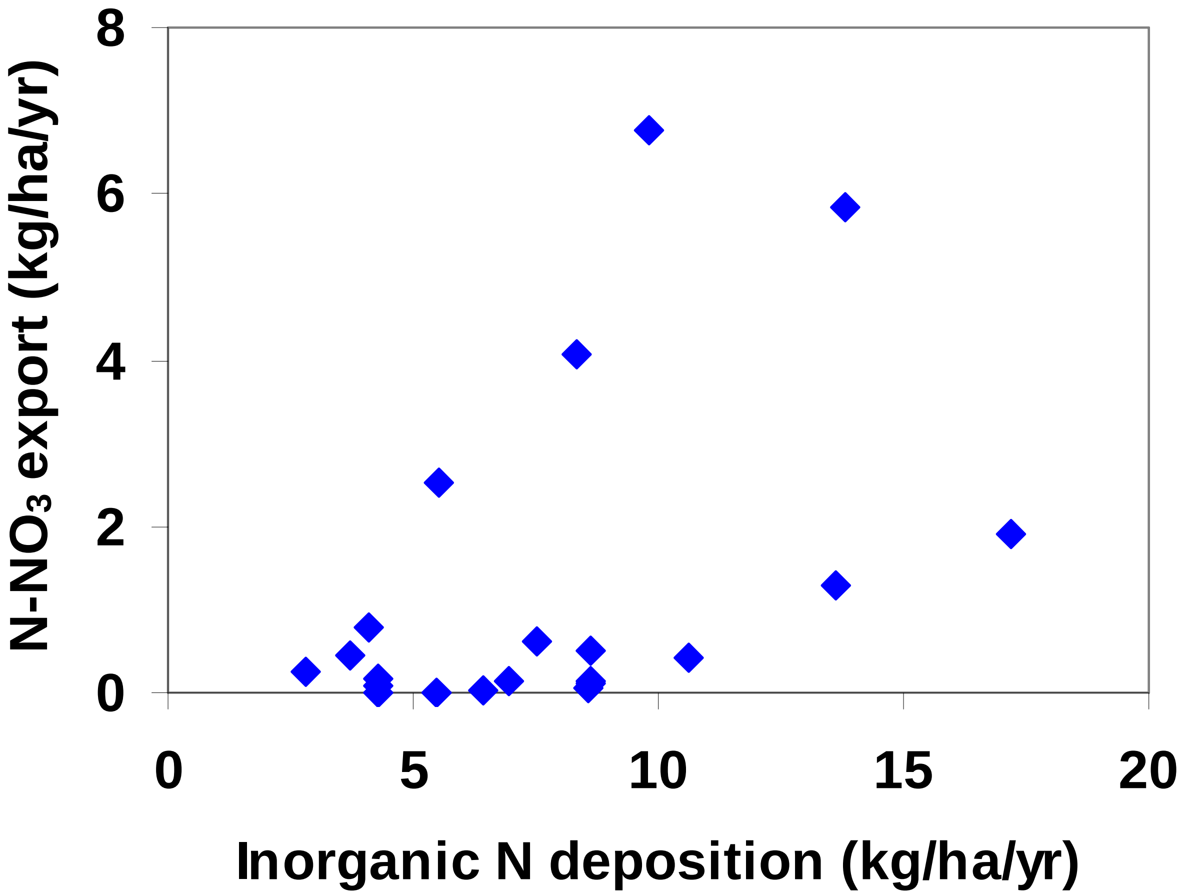


Annual N deposition (1990s) was between 2.8 kg/ha and 13.7 kg/ha (excluding WF). Nitrogen deposition was generally higher at the European sites where a greater proportion of the annual N deposition was as NH_4.

Trends in deposition/runoff

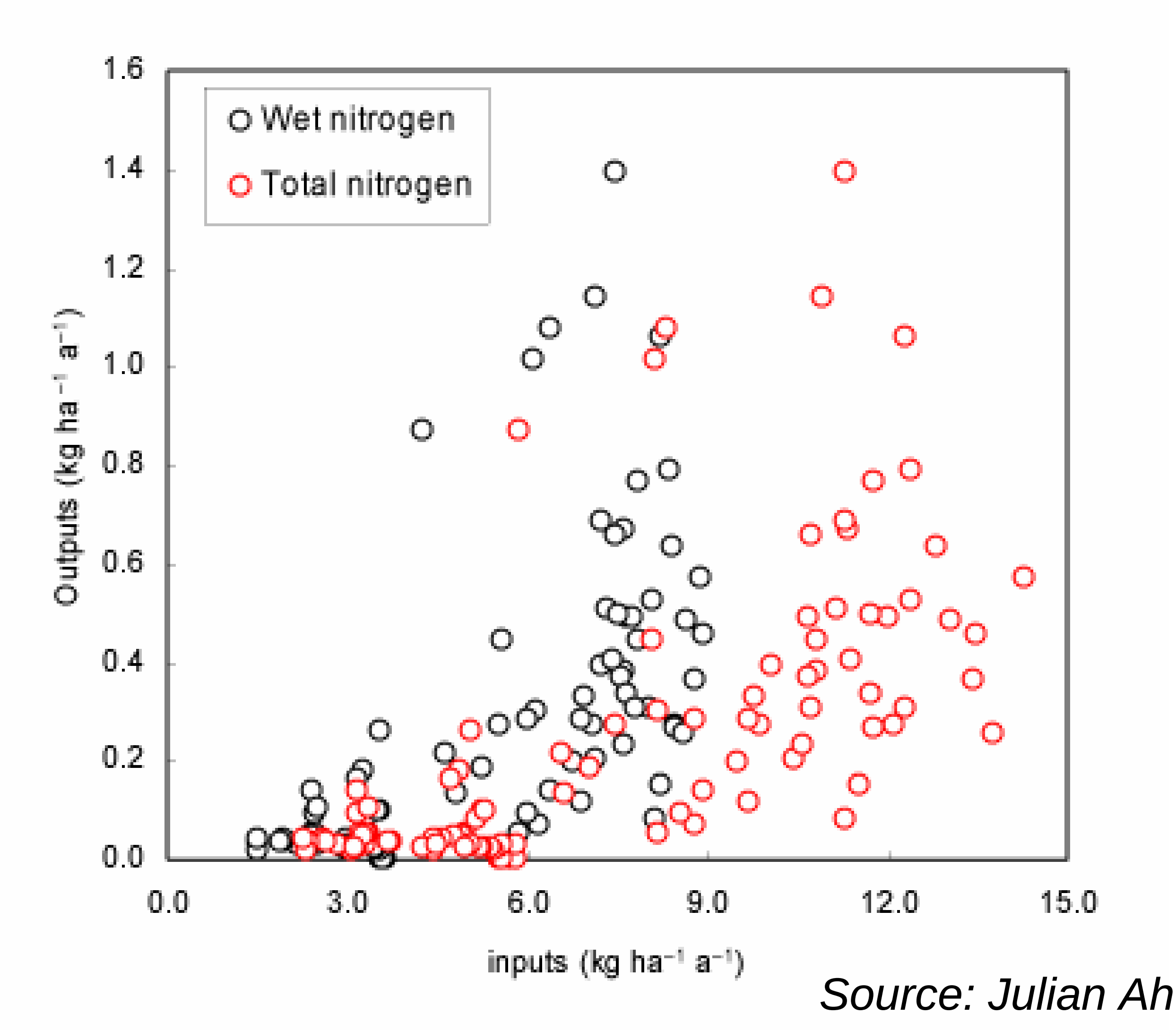
- Only a significant decline in NO_3 deposition in 1 region.
- NH_4 deposition response was varied – increasing in 3 regions and decreasing in 2.
- NO_3 concentrations in runoff decreased at 4 sites and increased at 1 site.
- NH_4 concentrations increased in runoff at 5 sites (mineralization/climate?)

Currently - the majority of N is retained:



Between 31 and 100% of inorganic N input in deposition was retained across the study sites; median retention of 94%

Similar pattern found in eastern Canadian lakes



Source: Julian Aherne, Trent University

NO_3-N decrease down the soil profile:

LFH; NO_3-N; 117 µg L^{-1}

A; NO_3-N; 142 µg L^{-1}

B; NO_3-N; 87 µg L^{-1}

Stream; NO_3-N; 37 µg L^{-1}

A quick word on Critical Loads (Acidification)

$$CL\ (S+N) = BC_{dep} - Cl_{dep} + BC_w - BC_u + N_u + N_{de} + N_i + ALK_{le(crit)}$$

$$\Big\downarrow$$

$$CL\ (S+N) = CL\ (S) + N_u + N_{de} + \boxed{N_i}$$

- Nitrogen represents between **44 and 67%** (median value **58%)** of the bulk S and N deposition.
- But, NO_3 leaching only represents between **0 and 32 %** (median value **5 %)** of the total SO_4 and NO_3 export.

Current vs. long-term N behaviour

- Given the increasing relative importance of N deposition (with respect to S), exceedance of the critical load of acidity is greatly influenced by assumptions about the long-term N behaviour.
- Which NO_3 values are important - soils vs. streams vs. lakes

N in Ontario hardwood forest plots

- A number of sugar maple dominated plots are currently being monitored by the Ontario Ministry of Environment.

- These sites span a considerable range of N deposition.

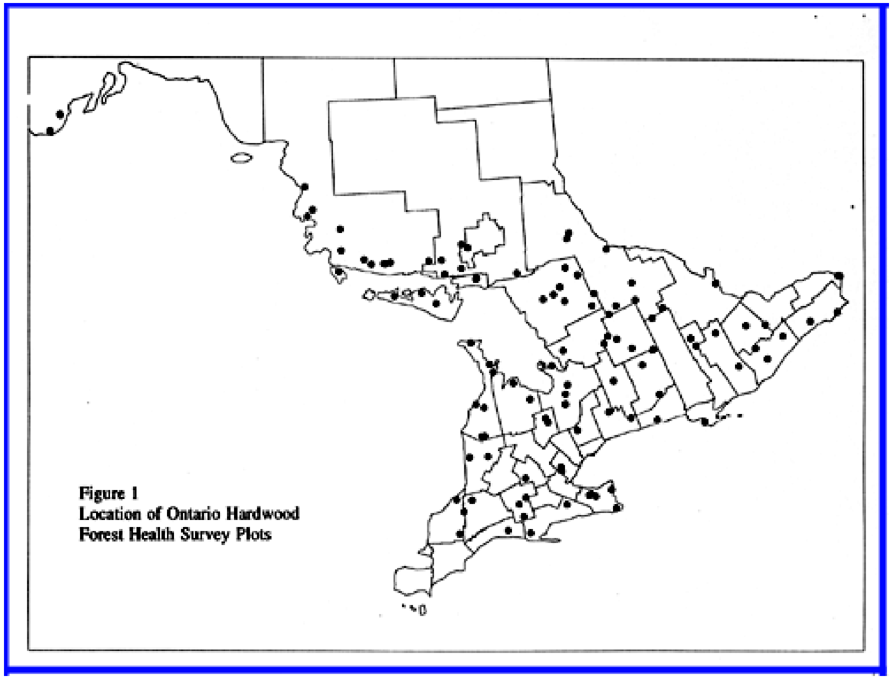
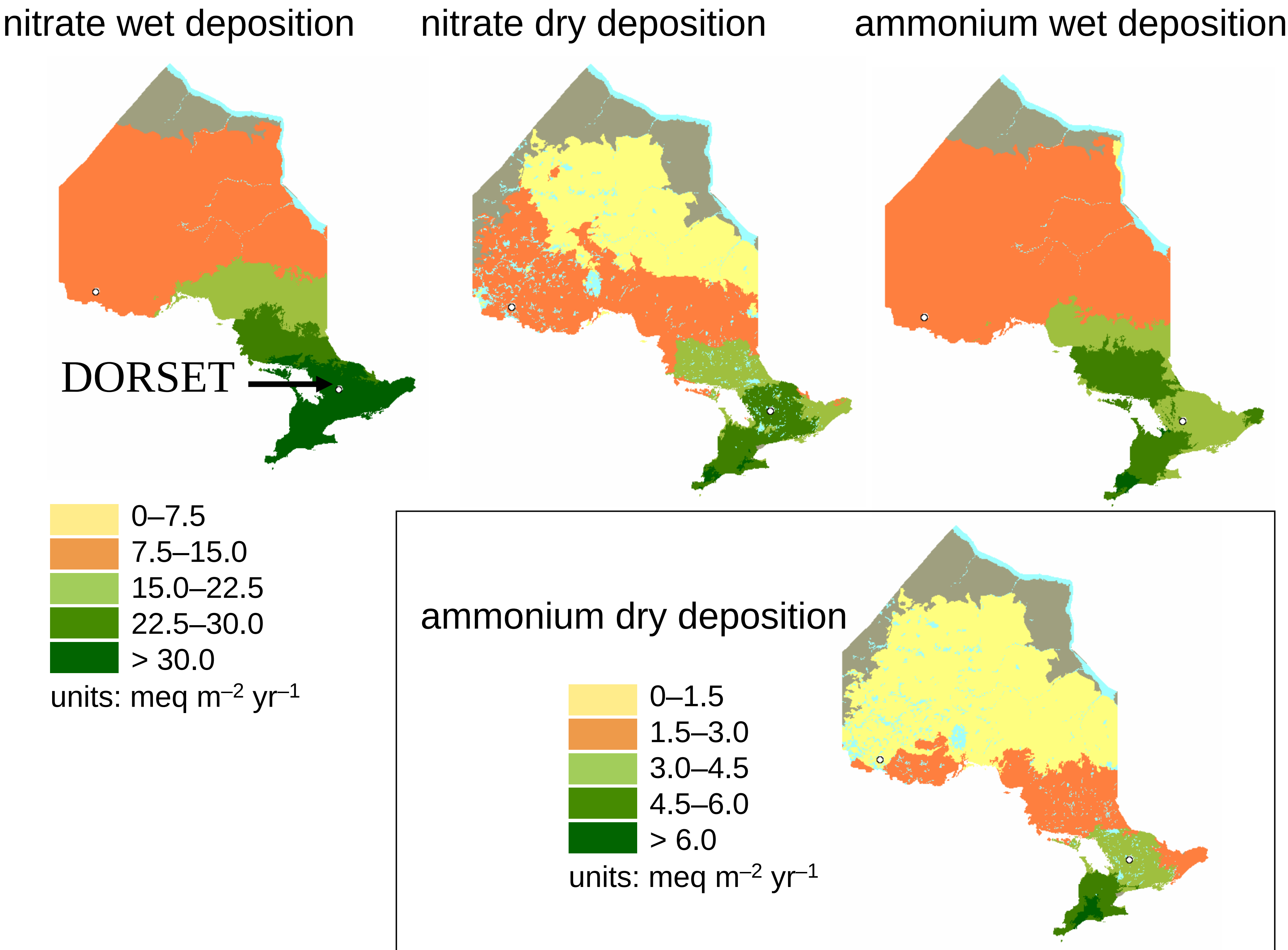
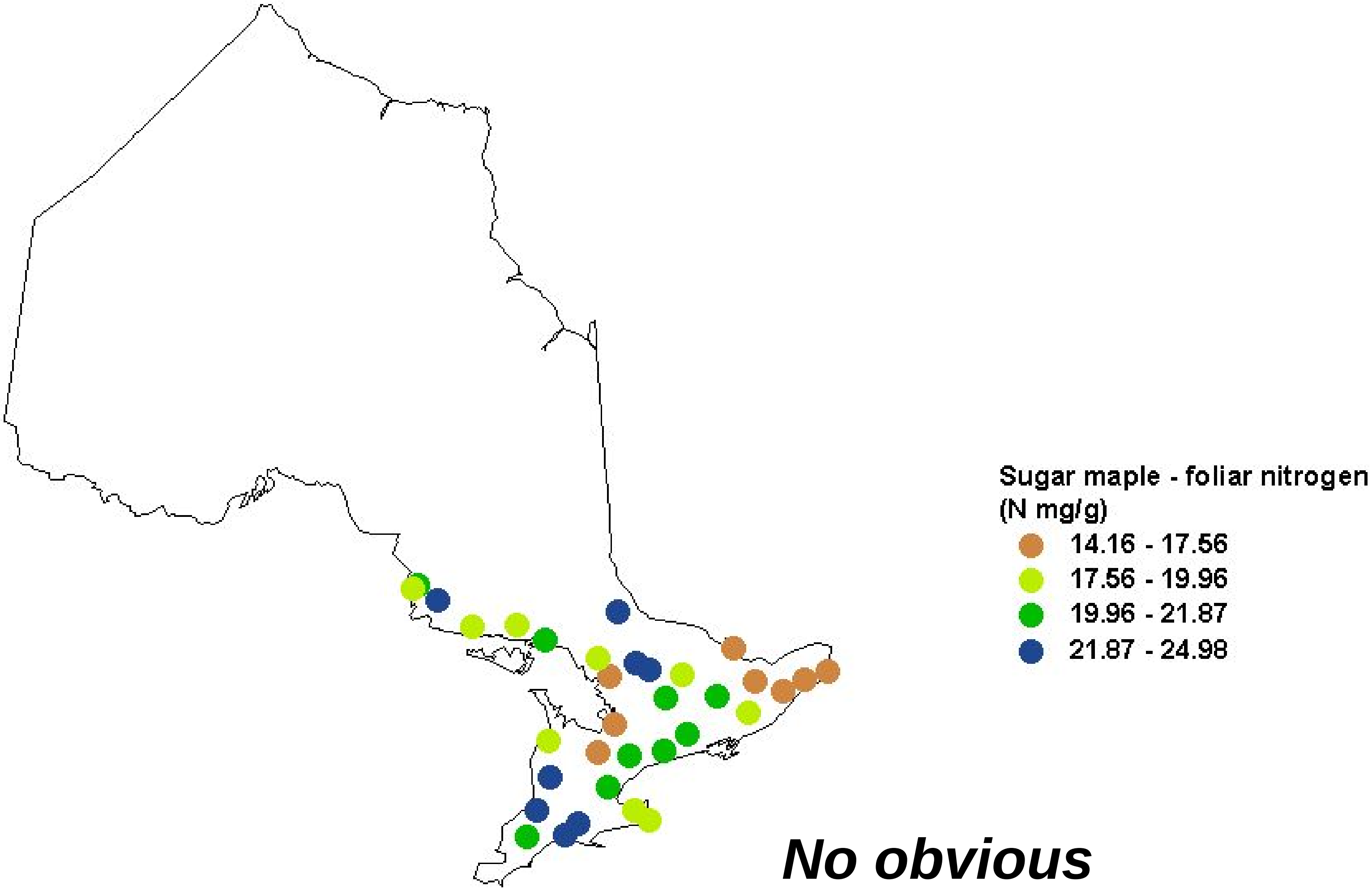


Figure 1
Location of Ontario Hardwood
Forest Health Survey Plots

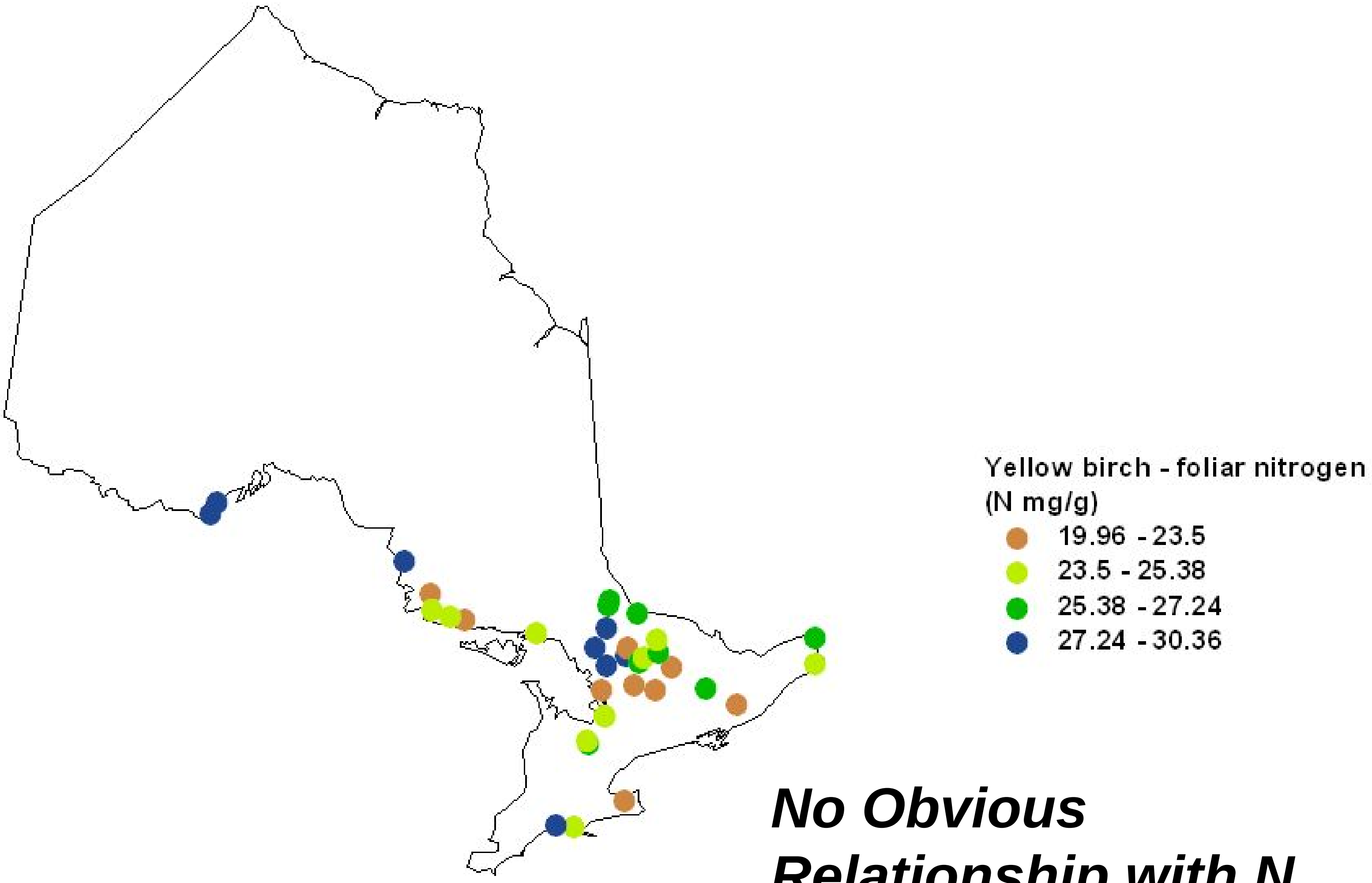

nitrate wet deposition
nitrate dry deposition
ammonium wet deposition
DORSET
0–7.5
7.5–15.0
15.0–22.5
22.5–30.0
> 30.0
units: meq m⁻² yr⁻¹
ammonium dry deposition
0–1.5
1.5–3.0
3.0–4.5
4.5–6.0
> 6.0
units: meq m⁻² yr⁻¹

Sugar maple - foliar nitrogen



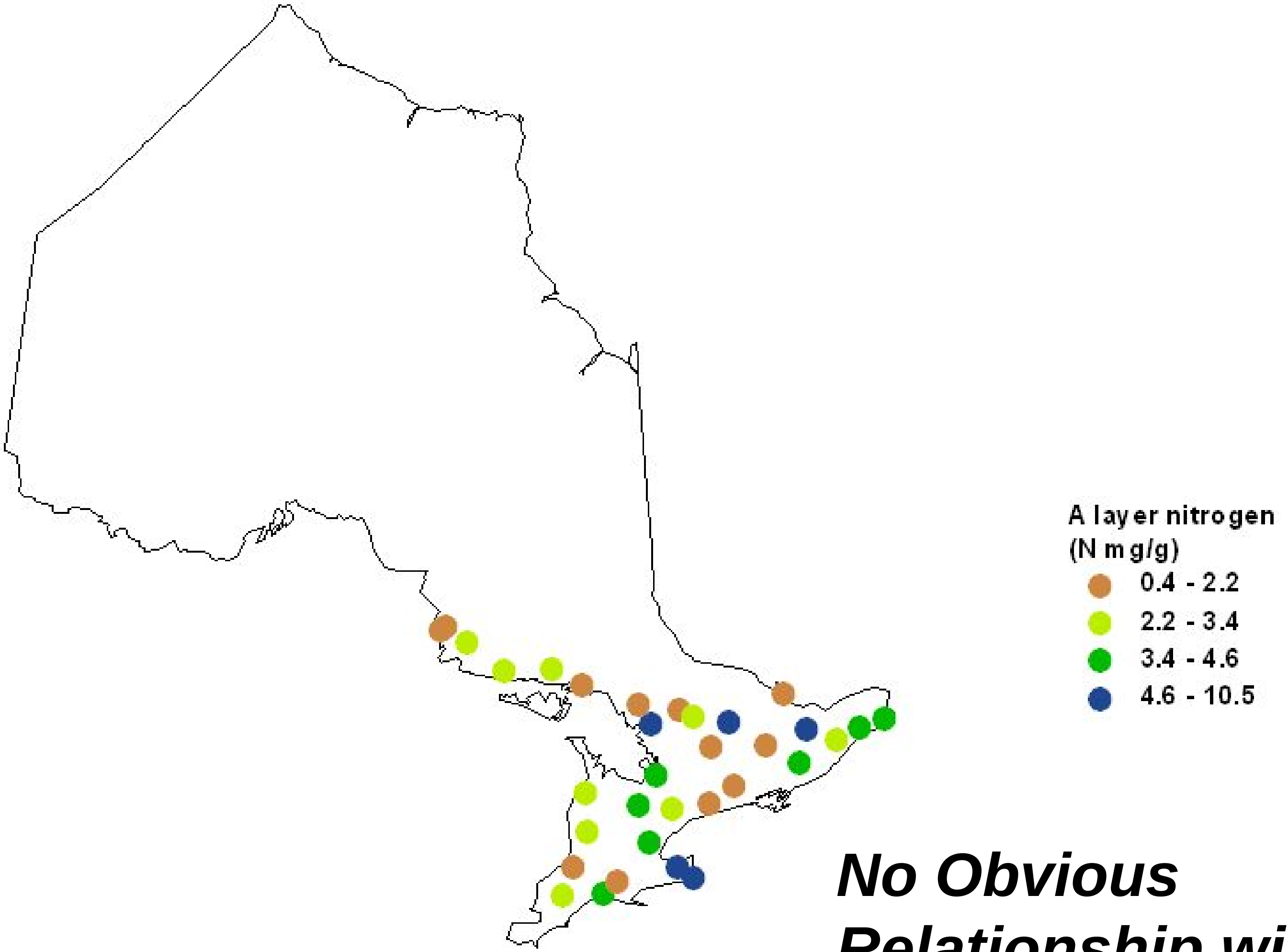
No obvious relationship with N deposition

Yellow birch - foliar nitrogen



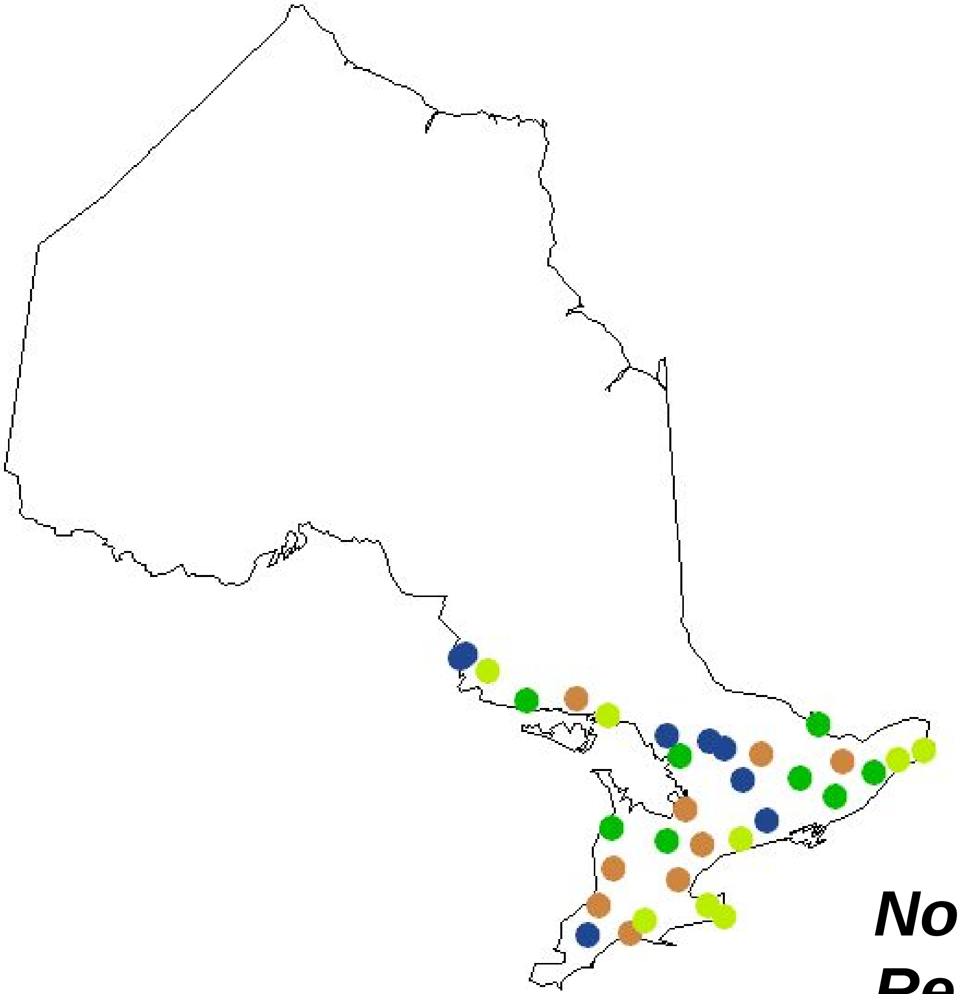
No Obvious Relationship with N deposition

A layer - nitrogen



No Obvious Relationship with N deposition

A layer - C/N ratio



No Obvious Relationship with N deposition

Summary

- Basic processes affecting N cycling are understood.
- Much less certainty in how these process vary with respect to:
  - *biotic and abiotic factors (climate, forest type etc.)*
  - *Changes in N deposition/time*

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