

Long term trends in atmospheric deposition and their significance to the nitrification of Lake Superior

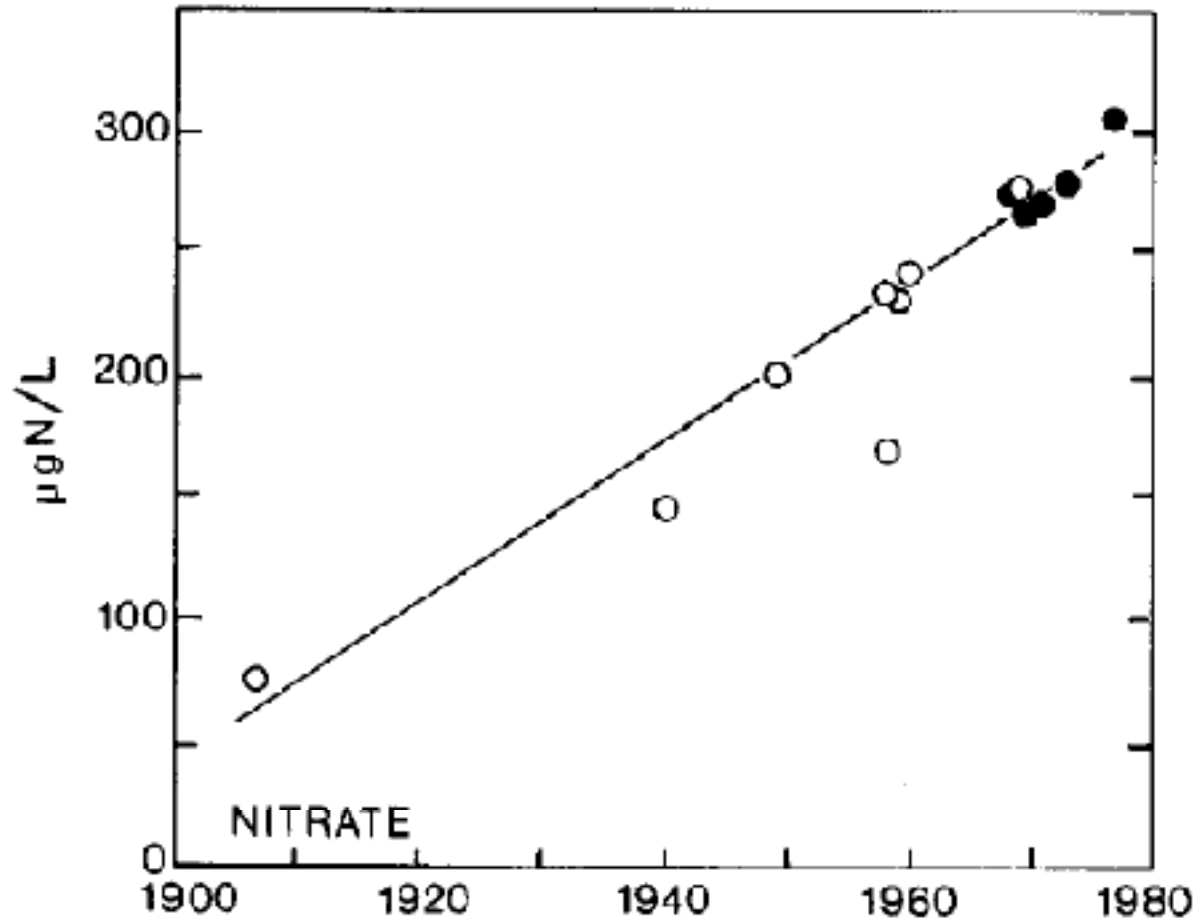
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A Century of Nitrification in Lake Superior



Weiler (1978) *J. Great Lakes Research*

Bennett (1986) *Ambio* "nitrification"

Superior catchment is sparsely populated, but the lake's long water residence time and large surface area makes it sensitive to atmospherically-transported pollutants such as organochlorines and other semi-volatile compounds in particular NO_x , NH_3 and org N

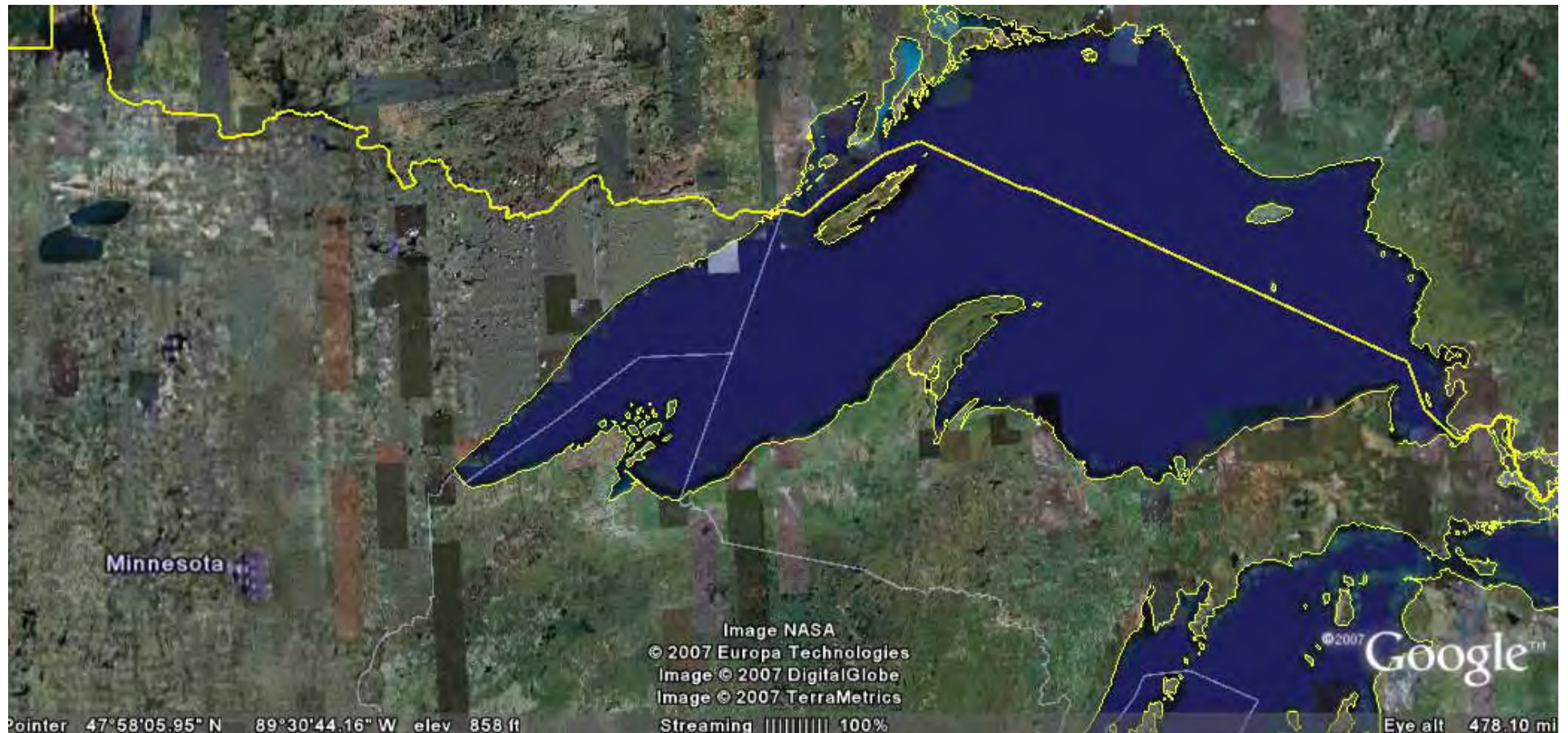
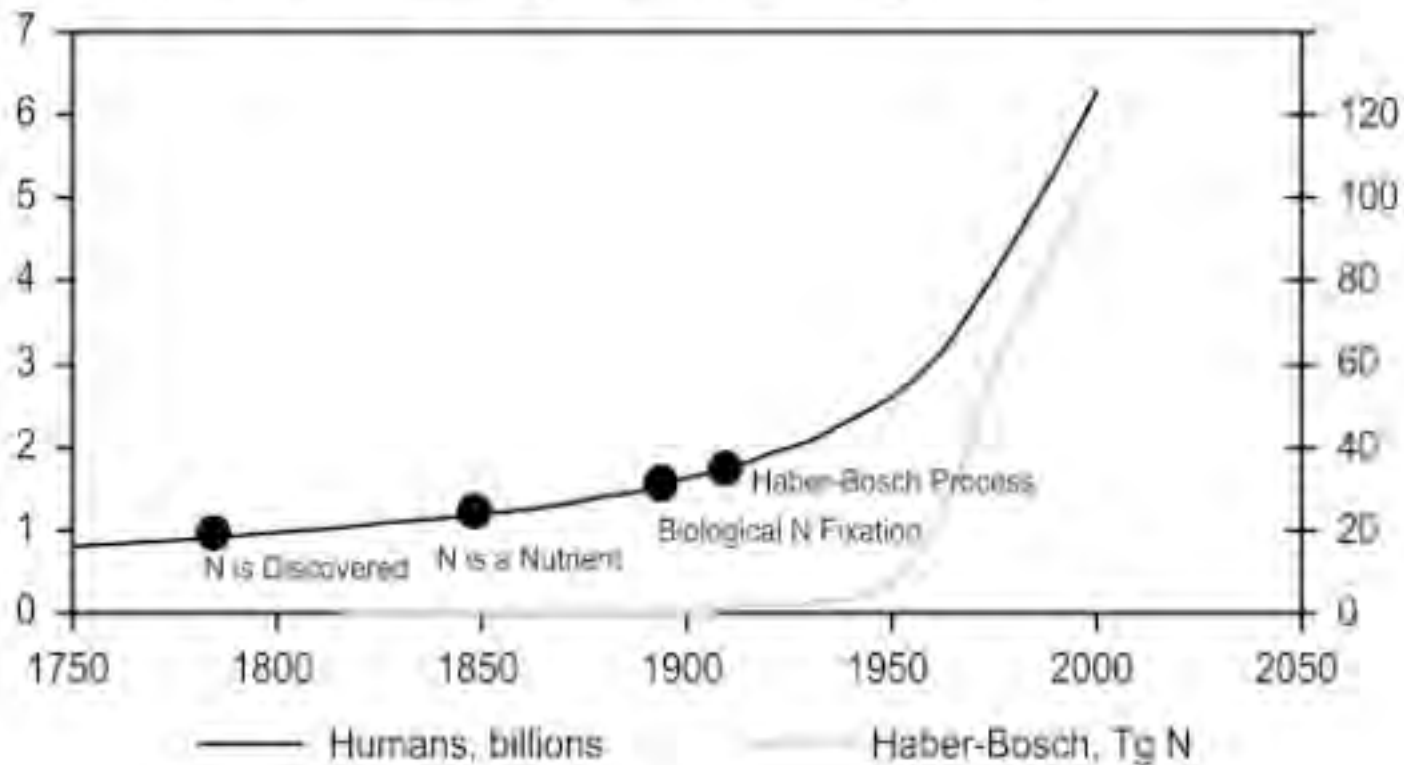
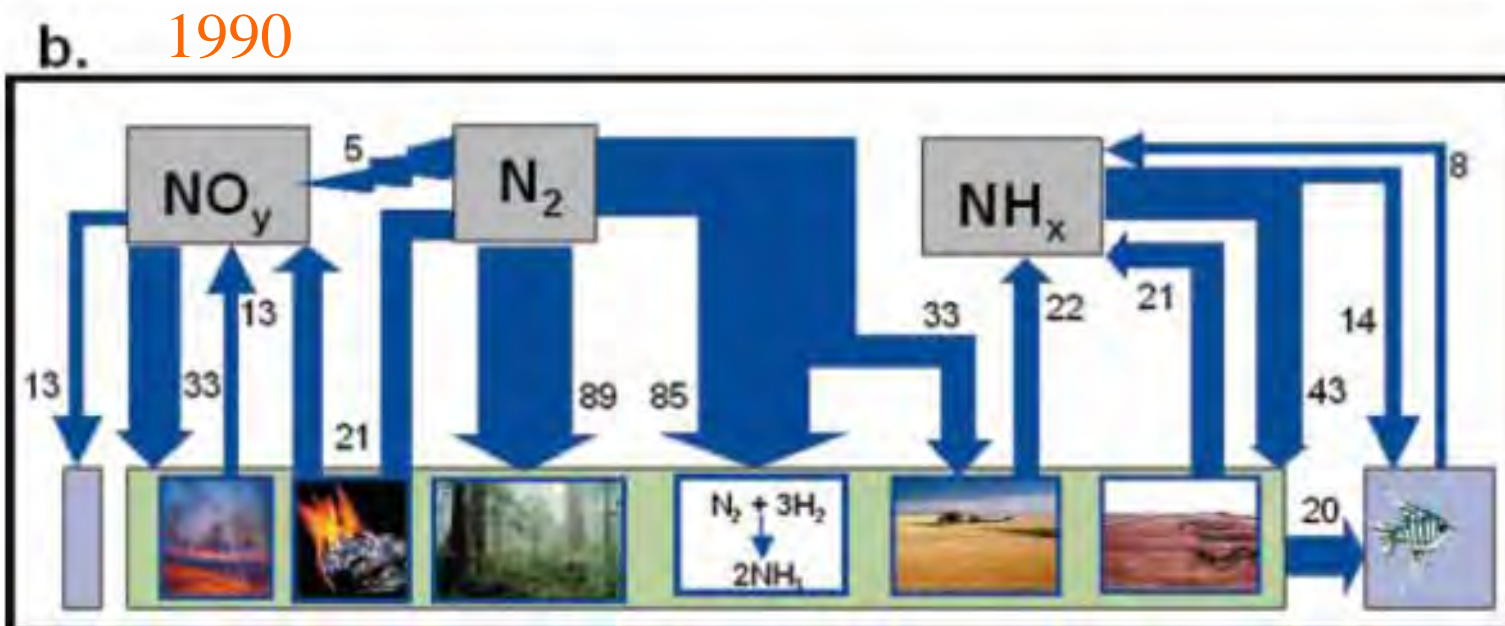
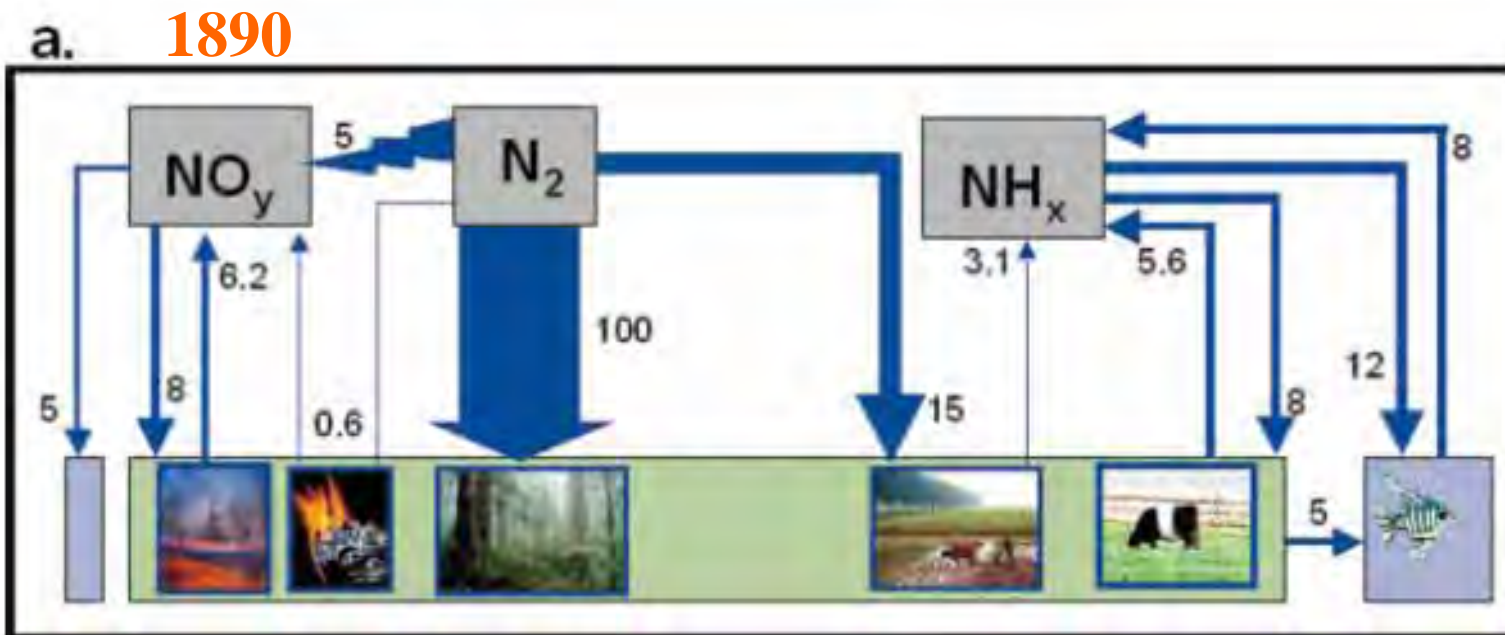


Figure 1. Global population trends (36, 53) with key dates for the discovery of N as an element in the periodic table and its role in various biogeochemical processes. Also shown is an estimate of the annual production of Nr by the Haber-Bosch process.

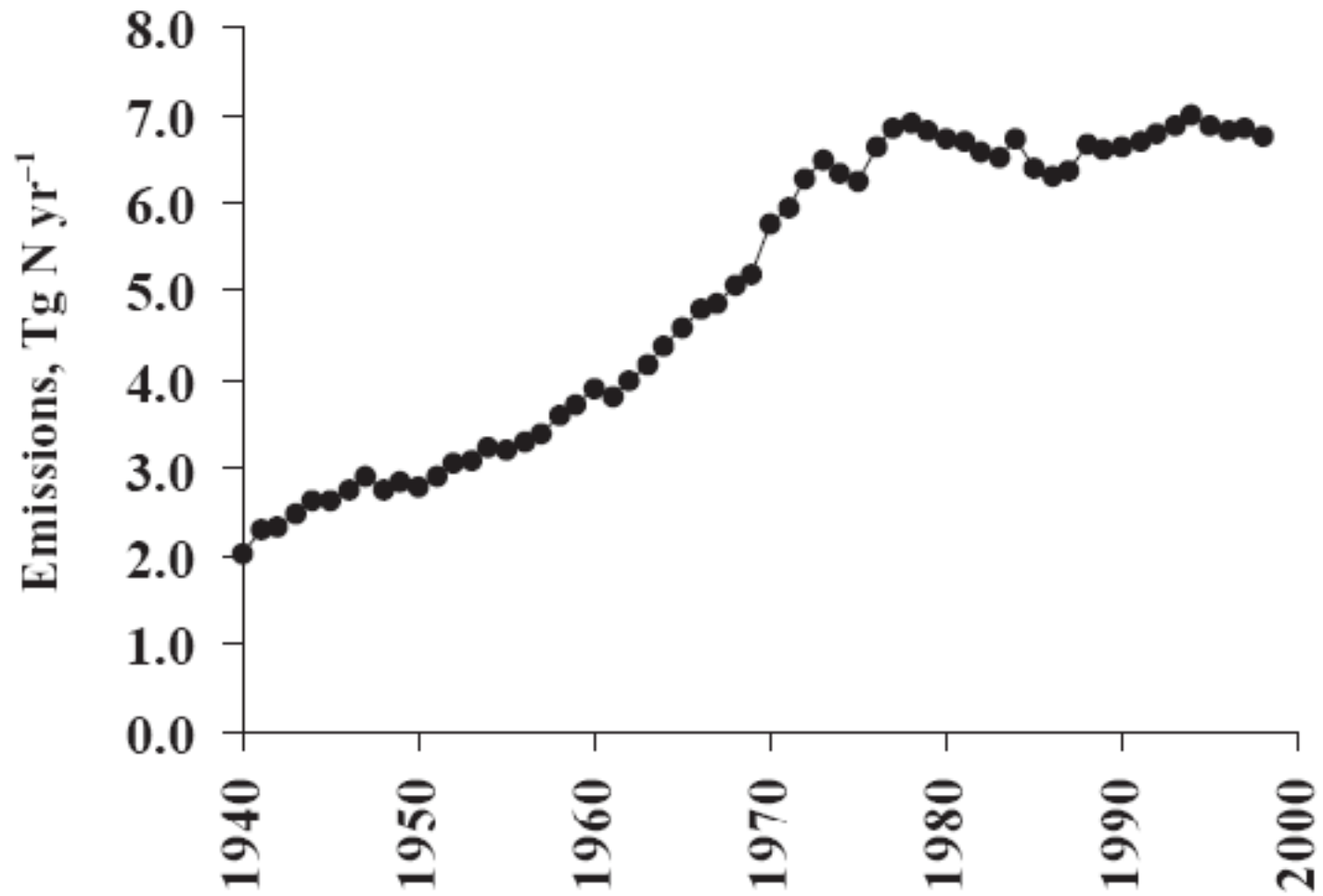


Galloway and Cowling 2002 *Ambio*



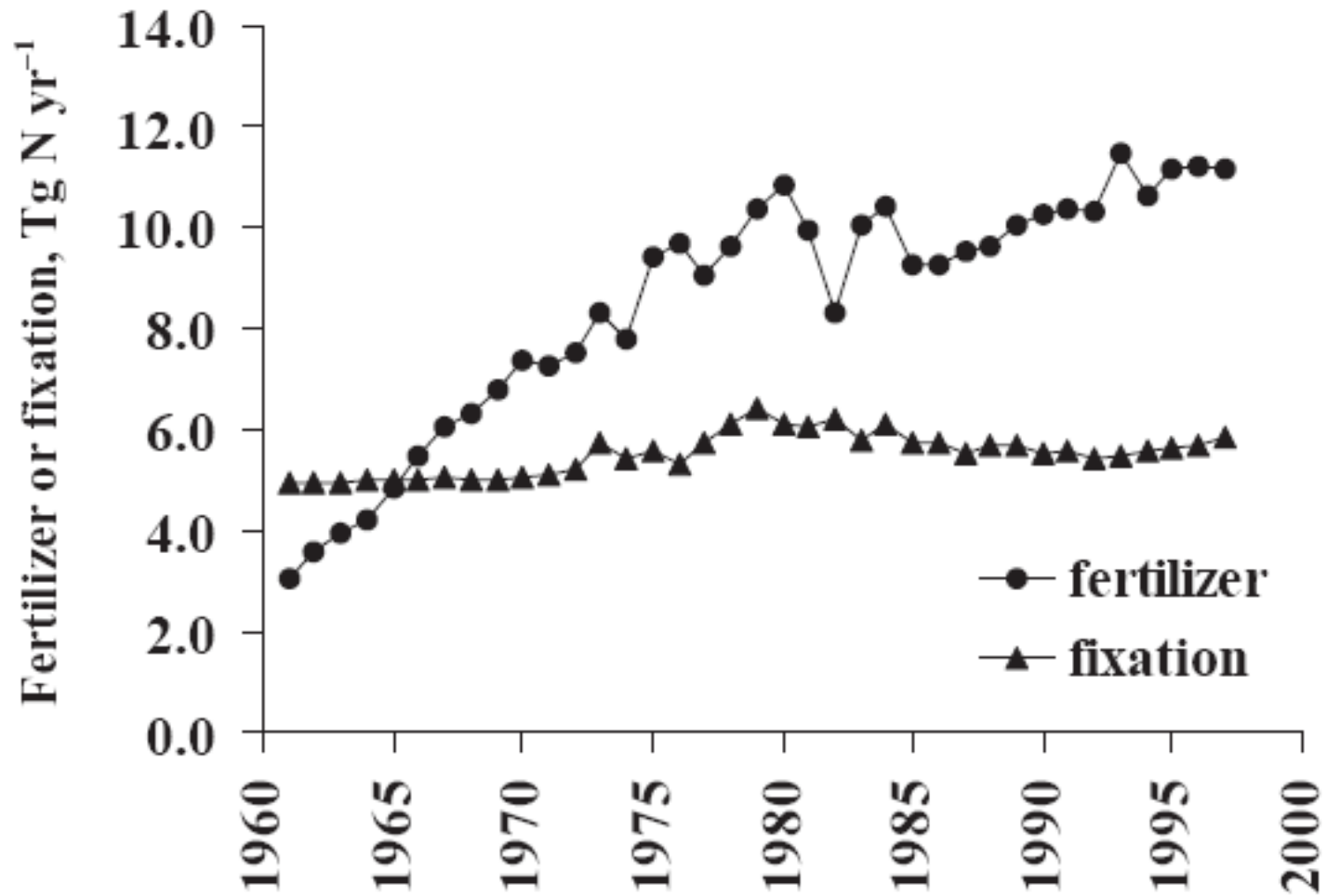
Global N cycle: Past and Present (from Galloway and Cowling 2002 *Ambio*)

Figure 1. Atmospheric NO_x emissions in the USA from 1940–2000.
Data from US EPA (18).

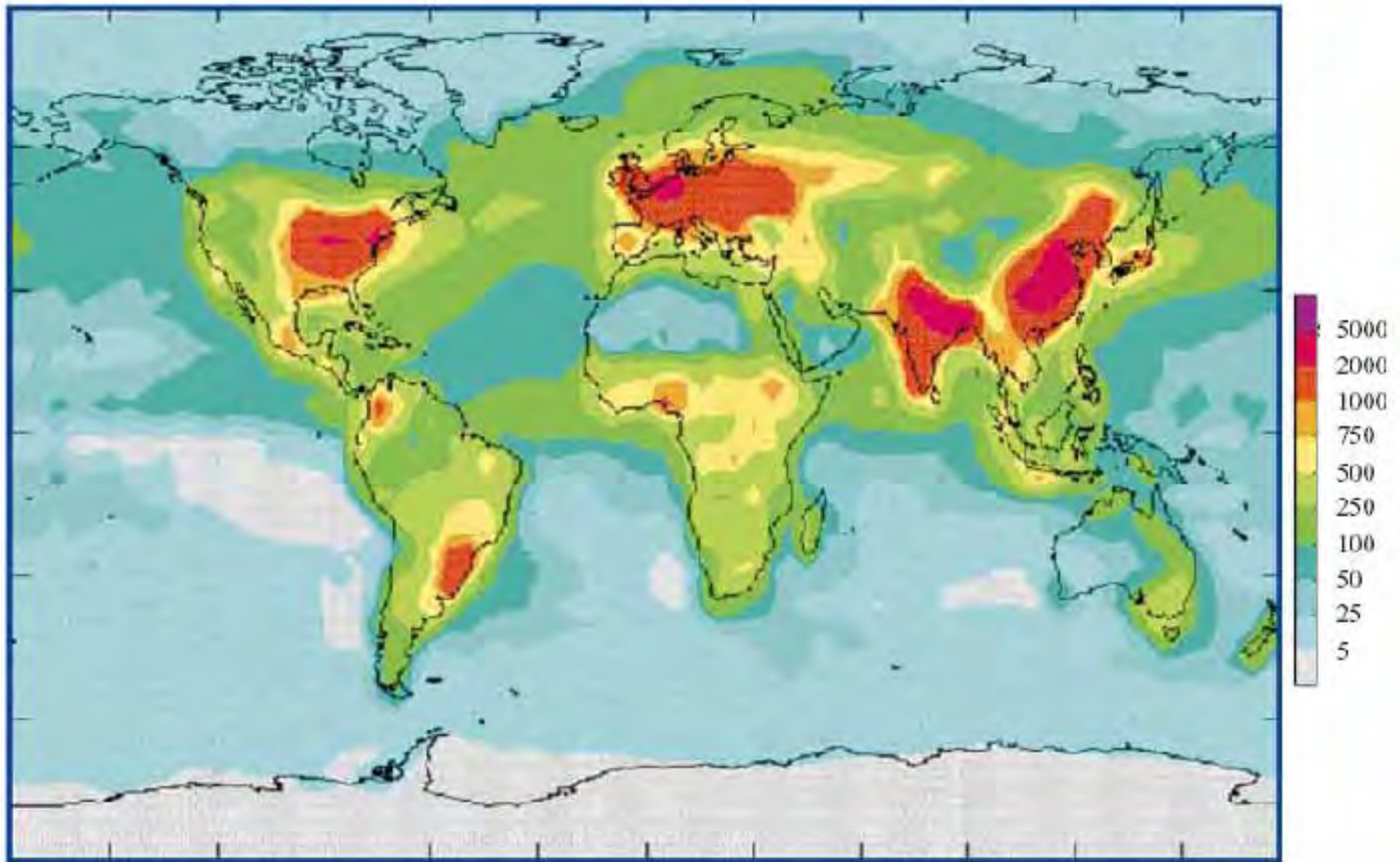


Howarth et al 2002 *Ambio*

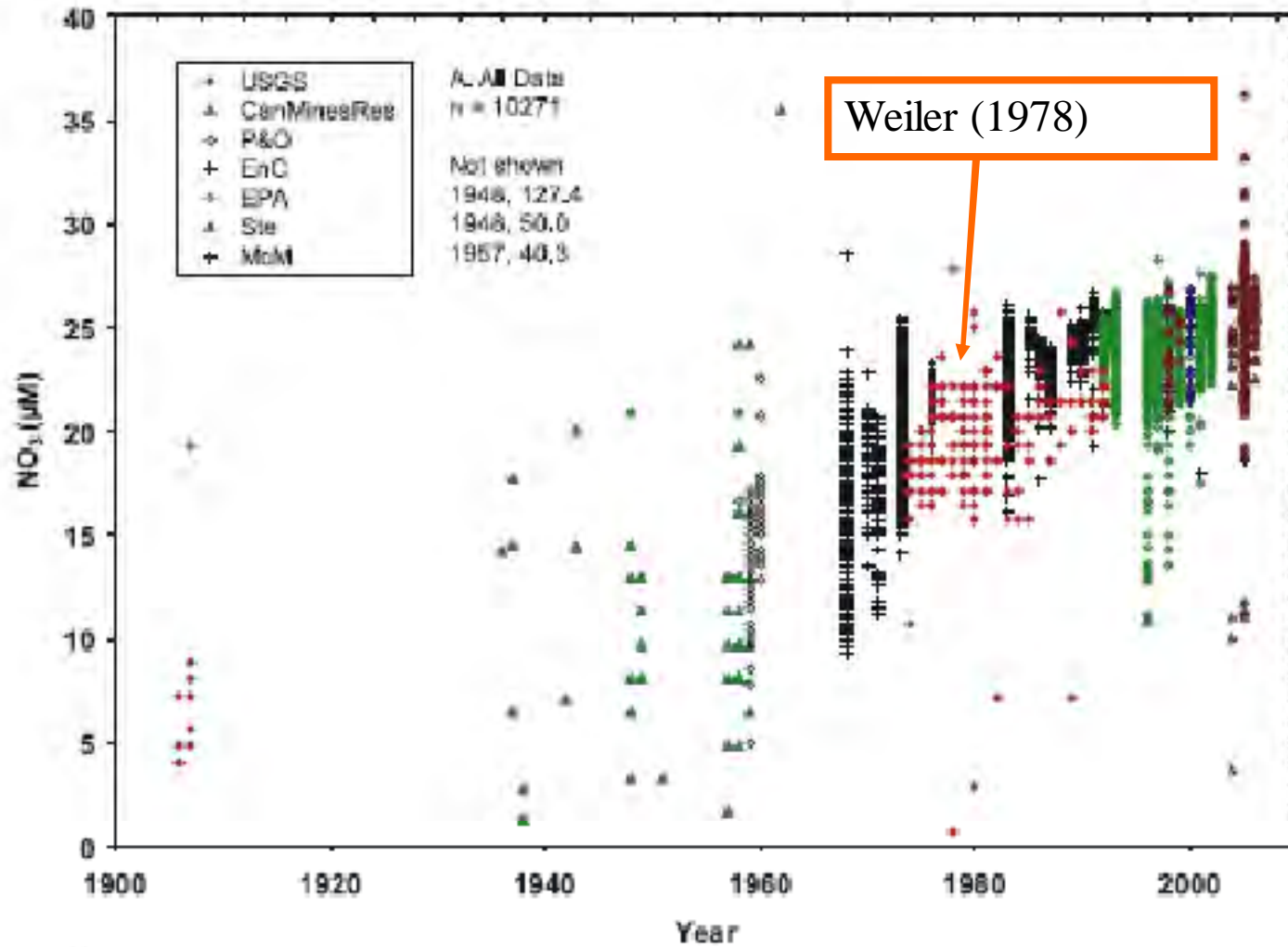
Figure 2. Nr inputs to the USA from 1961–2000 from use of inorganic N fertilizer and from N fixation in agricultural systems. See text for sources and derivation of estimates.



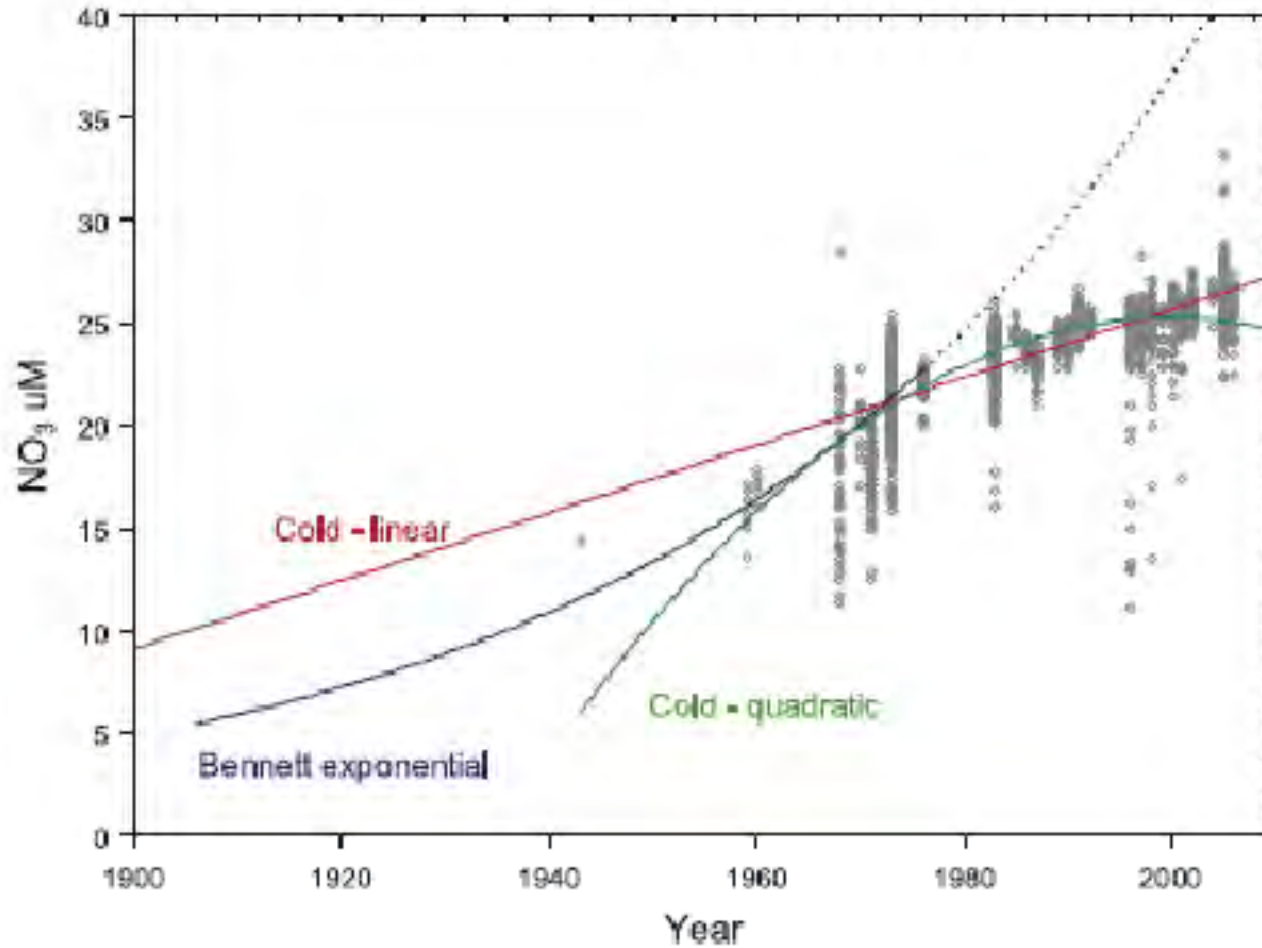
Howarth et al 2002 *Ambio*



Annual deposition of N in mg/m²/y (Galloway and Cowling. 2002. *Ambio*)



From Sterner et al. 2007.
Geophysical Research Letters



From Sterner et al. (2007) GRL

The range of values in any year was reduced if only deep, cold waters were included; best fit to data is a quadratic equation suggesting rate of increase might be declining since 1980

Nitrogen Mass Budget to determine if possible recent decrease is a result of rising outputs or falling inputs:

Inputs:

- 1) rivers,
- 2) atmospheric direct deposition (**add in organic N**),
- 3) ground water (negligible)
- 4) biological N fixation within the lake (negligible)

Outputs:

- 1) St. Mary's River
- 2) **Sedimentation (poorly known, discontinuous in space and time)**
- 3) **Denitrification (microbial production of gaseous nitrogen compounds, poorly known)**

Lake Superior Nitrogen Budget

(Sternner et al. 2007 *Geophysical Research Letters*; amendments in red)

INPUTS	Precipitation	mmol/m ² /y
	ammonium	12.9
	nitrate	17.2
	organic N	7.5 ELA average
	Watershed	
	ammonium	3.3
	nitrate	5.9
	organic N	22.6
	Total Inputs	69.4
OUTFLOW		
	ammonium	0.2
	nitrate	22.4
	organic N	5.7
SEDIMENTATION		
	organic N	15 Kemp et al (1978) J. Great Lakes Res.
DENITRIFICATION		
	nitrate removal	22 Carlton et al (1989) J. Great Lakes Res.
BUILDUP (Storage in the lake)		
	nitrate	23.4
	Total Output	88.7

Difference between inputs and outputs is indication of **ERROR**

IF the rate of nitrification of the lake is decreasing what are possible explanations:

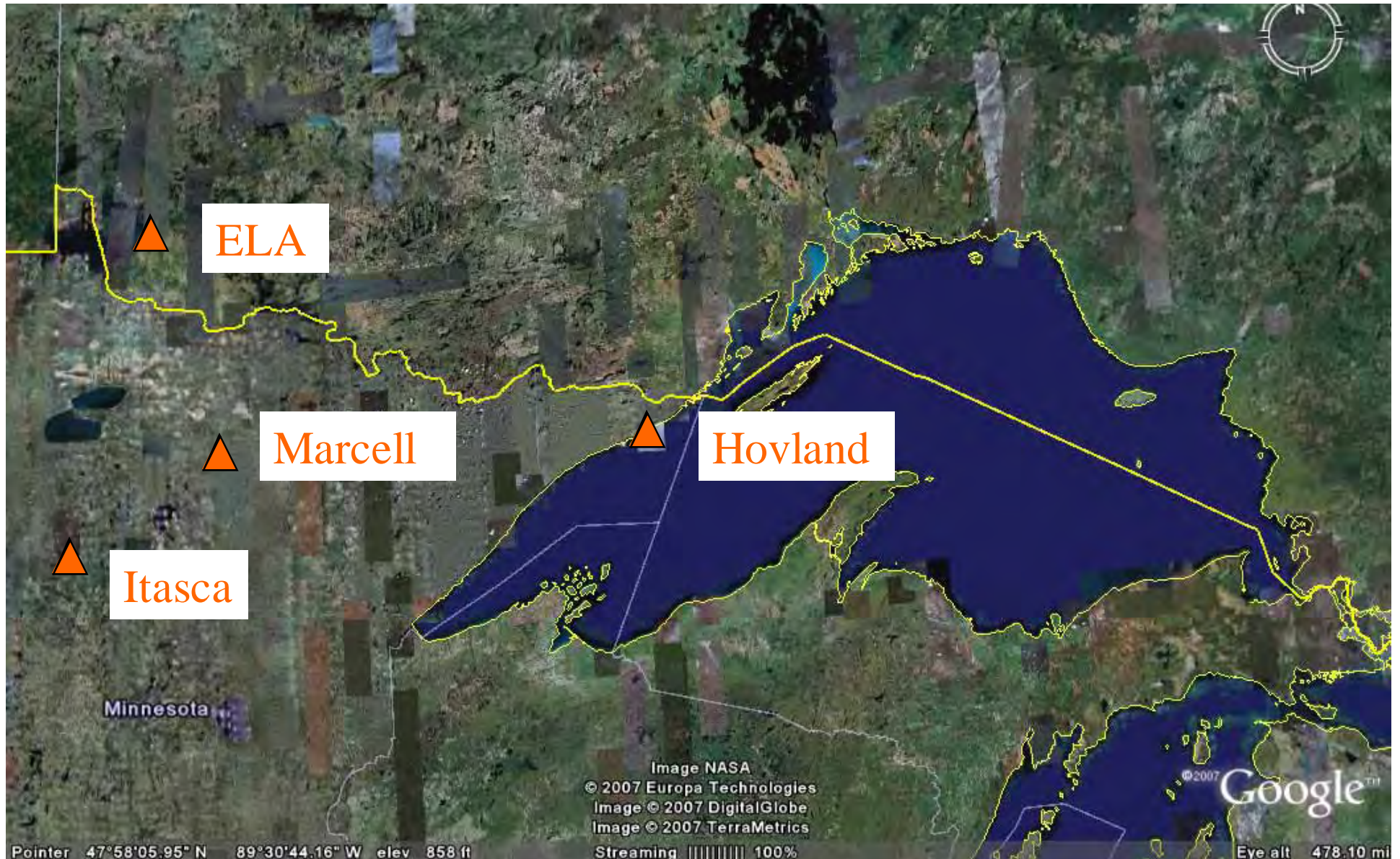
- 1) Lake is coming to steady state with higher but now constant nitrogen inputs
- 2) Nitrogen Inputs are declining: Examine atmospheric record because it now dominates total N inputs (2/3 of total)
- 3) Primary productivity and N sedimentation are increasing;
- 4) Increased rates of microbial processing, e.g. higher denitrification rates

INPUTS?

To determine if inputs are changing, ideally we would have a long monitoring record for all sources and forms of nitrogen entering the lake.

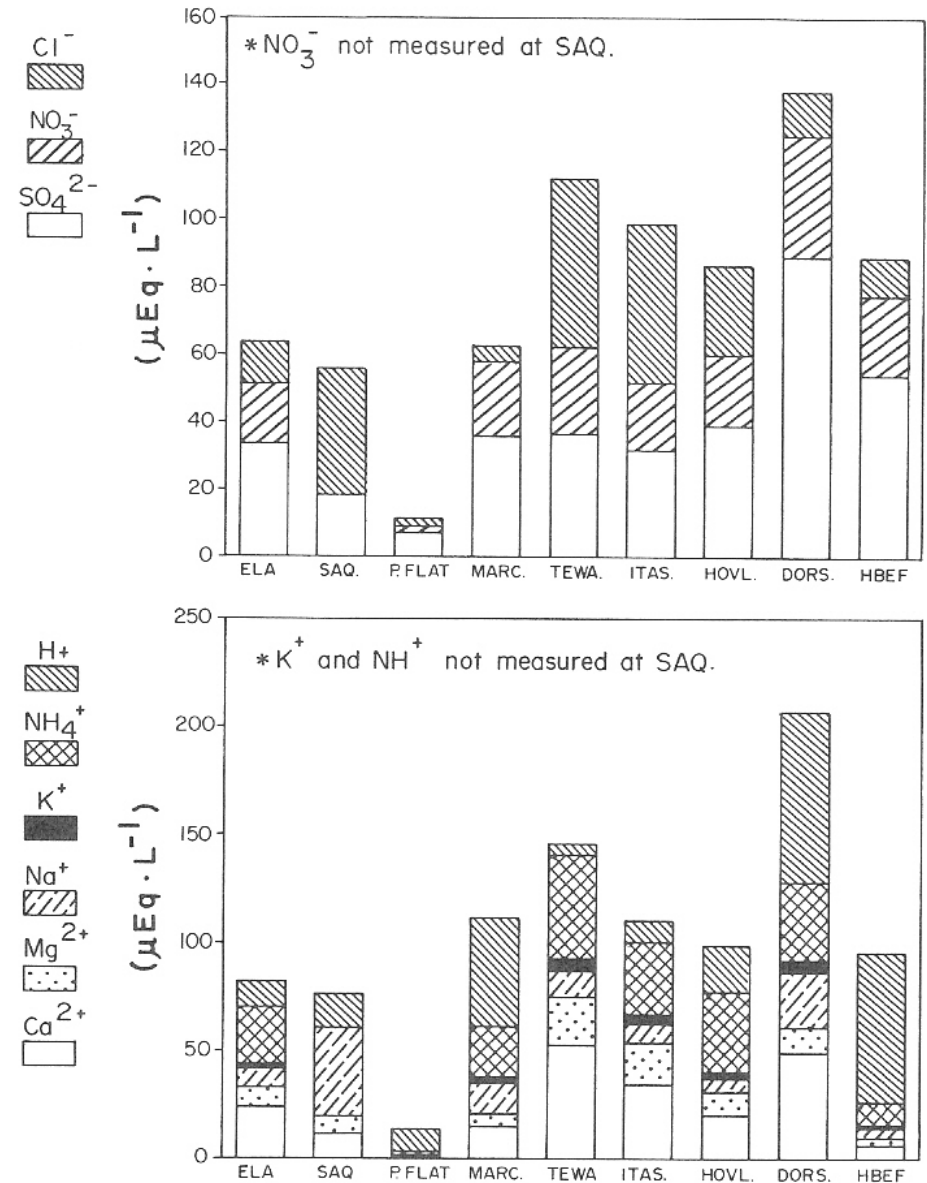
Longest comprehensive data (all forms of nitrogen) set is for atmospheric deposition at Experimental Lakes Area in north west Ontario

Some precipitation chemistry monitoring stations relevant to Lake Superior: Oldest is ELA and it is most comprehensive, all N forms as well as other compounds and nutrients such as phosphorus

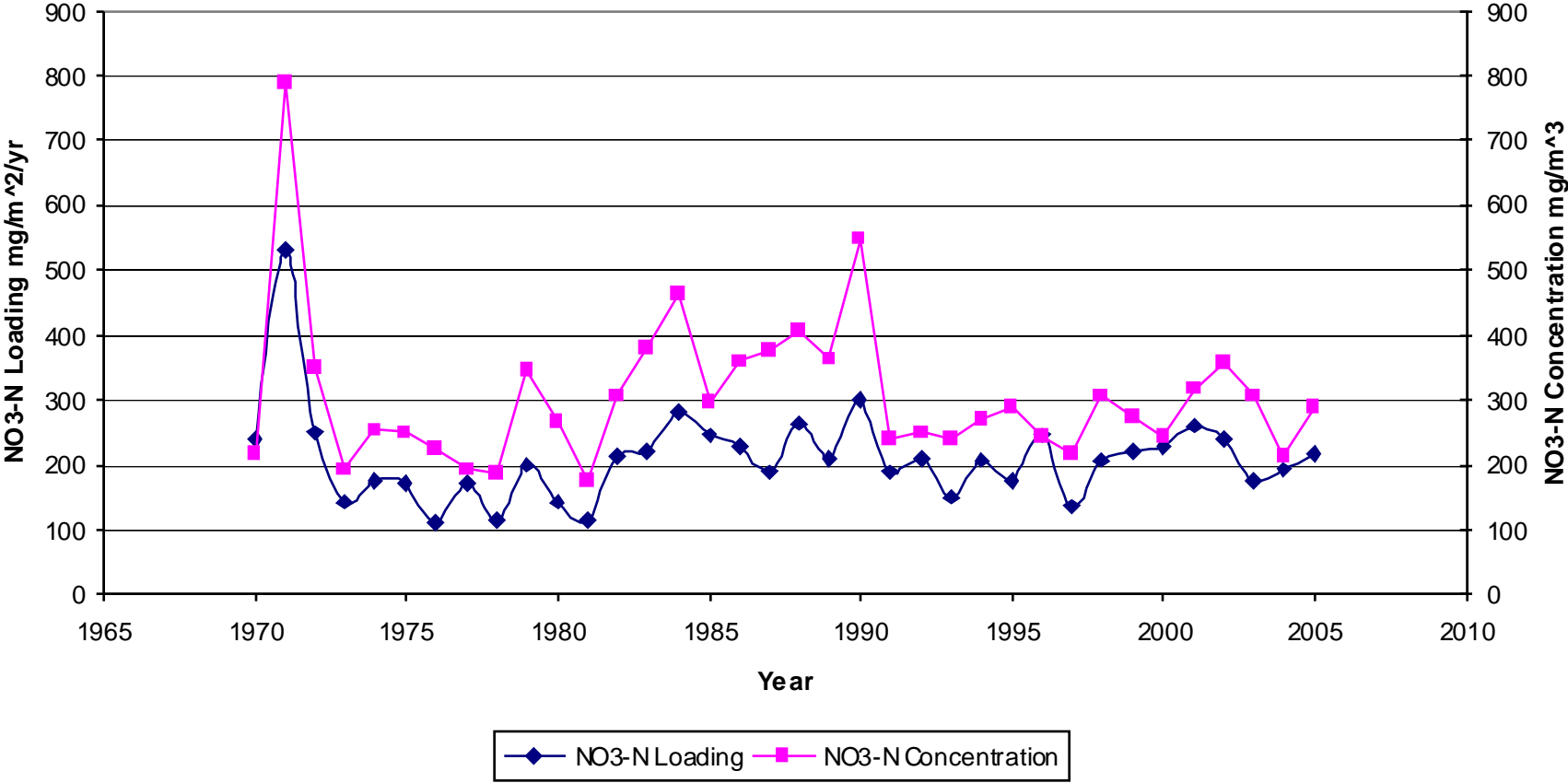


Why ELA?

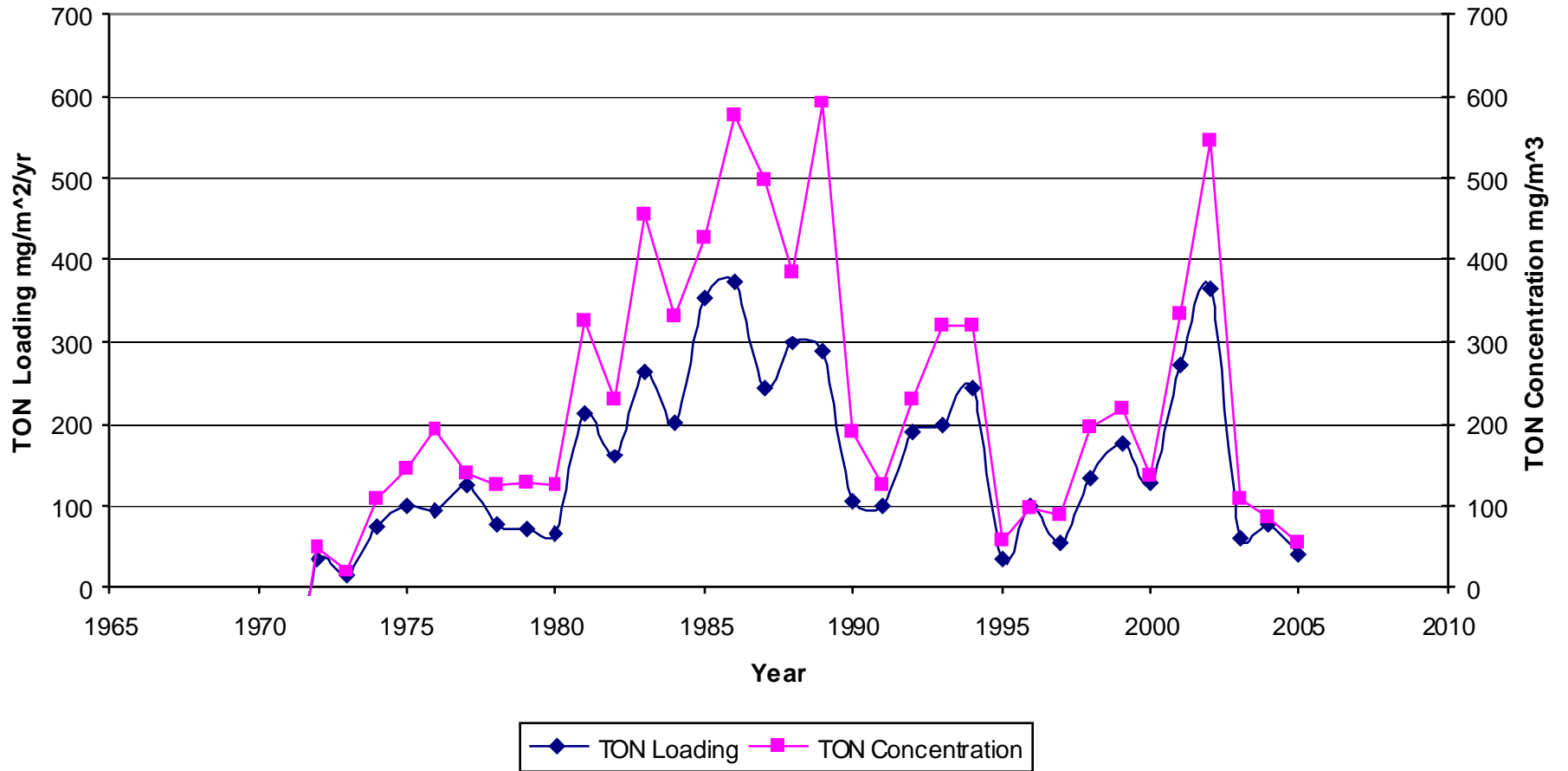
Comparison by Lindsey et al (1987) *Can. J. Fish. Aquat. Sci.* among several sites including several in Minnesota found similar concentrations of nitrate and ammonia in precipitation. Advantage of the ELA record is length, quality, and inclusion of analysis of organic N as well as phosphorus compounds.



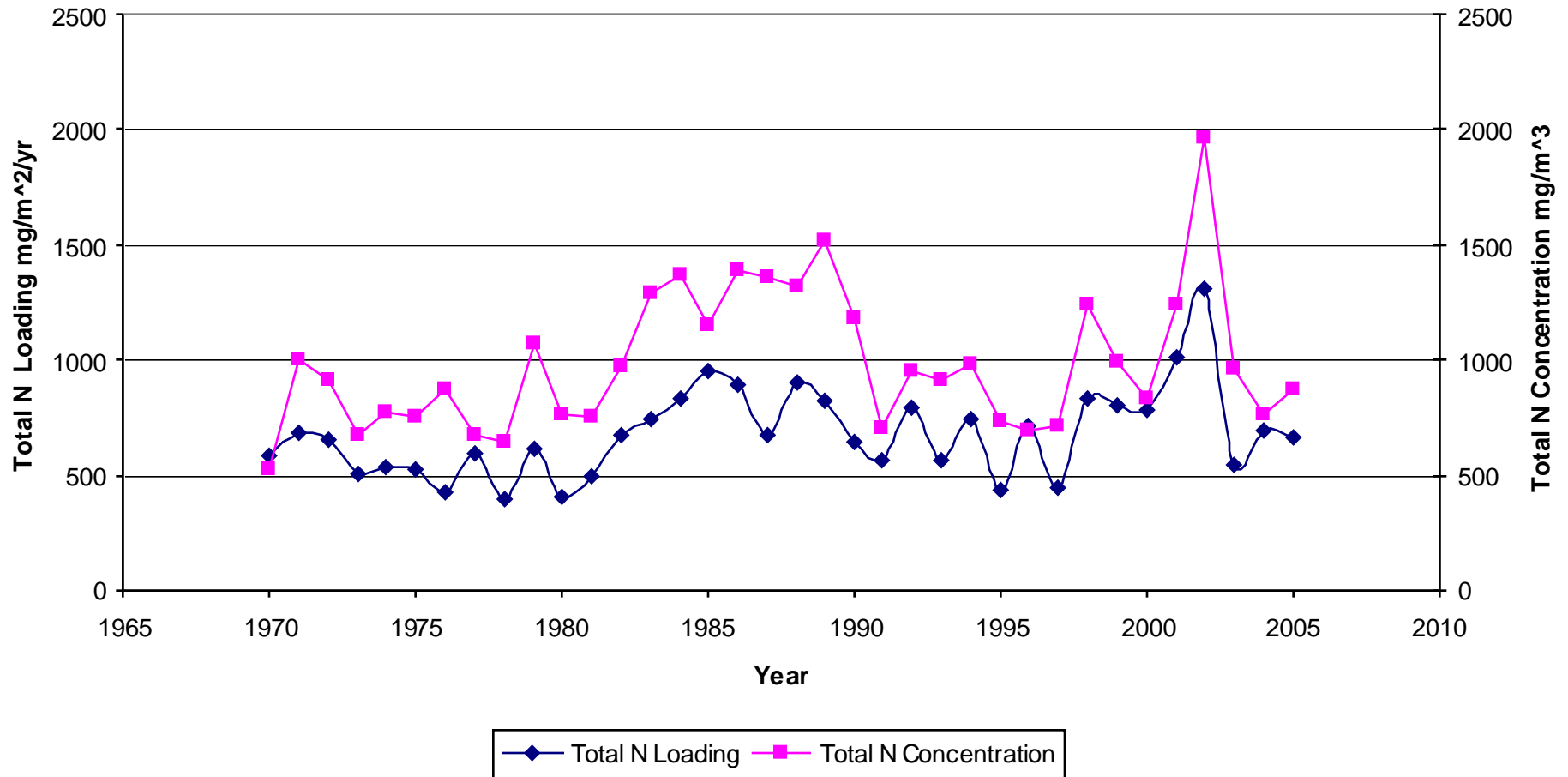
ELA Bulk Precipitation Loading and Concentration



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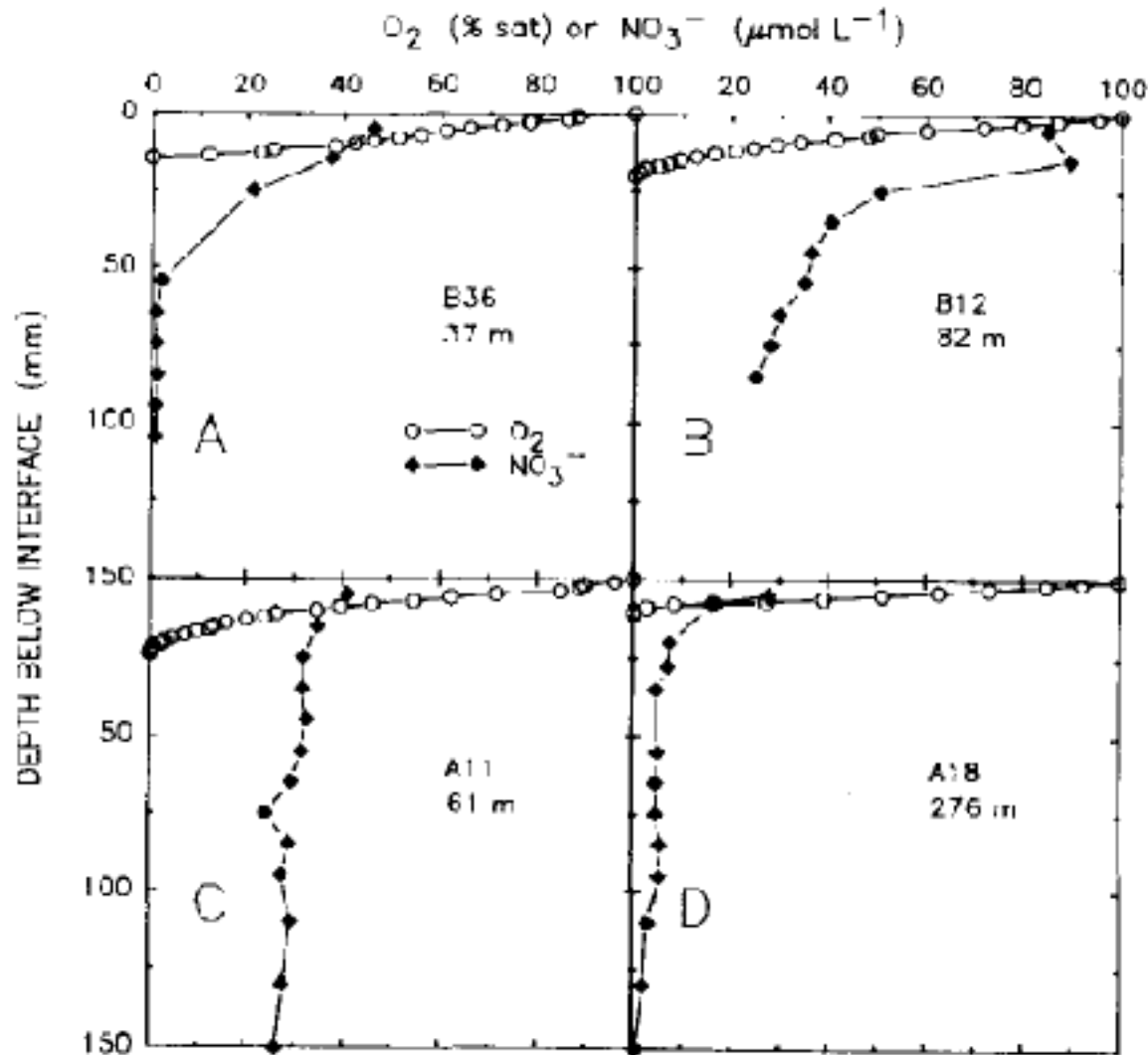


ELA Bulk Precipitation Loading and Concentration



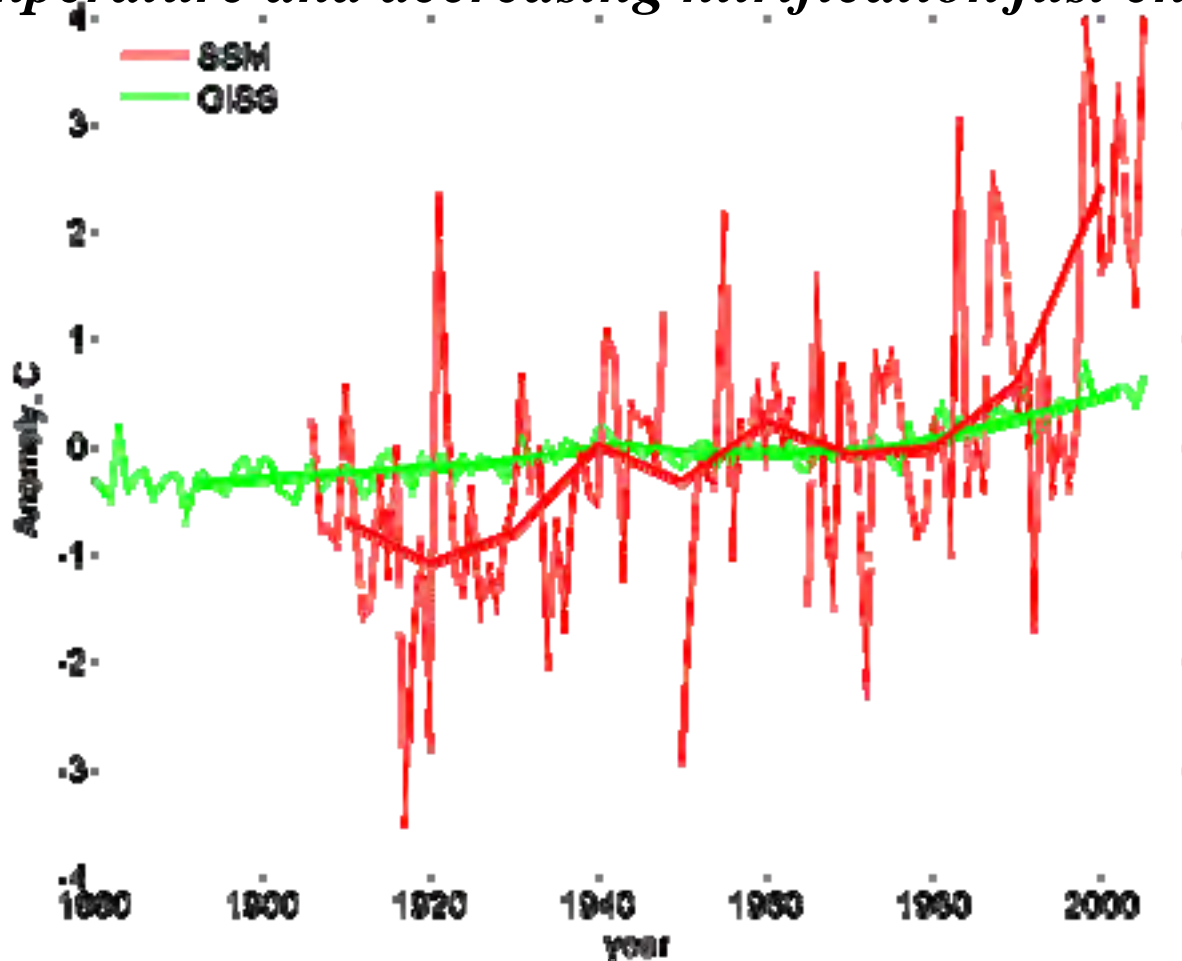
Conclusion on atmospheric N loading: No evidence for decline at ELA atmospheric deposition of fixed nitrogen species since 1970; Minnesota stations show similar result for nitrate and ammonia since 1980

Denitrification rates are limited by temperature and rate of supply of nitrate and oxidizable organic substrate *so it may be increasing* especially at shallow depths where rates are highest



Carlton et al. 1987. *J. Great Lakes Res.*

Rising temperatures in Superior may lead to higher primary productivity (and N sedimentation) and higher denitrification rates and possibly reduced rates of nitrate increase in Lake Superior. *Is synchrony of increasing temperature and decreasing nitrification just chance?*



Austin and Colman (submitted) *Limnol. Oceanogr.*

Conclusions:

- 1) There is no evidence that atmospheric loading of N to Lake Superior has changed in the last 40 years—concentrations may finally be coming to steady state with these now constant and artificially high rates
- 2) However, there is substantial uncertainty in the N budget, and it is possible that some of the outputs from the lake such as sedimentation and denitrification may be increasing due to a warming of the lake over the last decades
- 3) Further research will be needed on these loss processes and their sensitivity to lake warming before future trends in nitrate will be predictable

Table 2. Lake Superior Total N Inputs and Outputs^a

Source	mmol m ⁻² yr ⁻¹
<i>Inputs</i>	
NH ₄ ⁺ , direct precipitation	12.9
NH ₄ ⁺ tributary input	3.25
Organic N tributary input	22.6
Organic N, direct precipitation	unknown
NO ₃ ⁻ (Table 1)	24.1
Total N input to lake	62.8+
<i>Outputs</i>	
Outflow	
NH ₄	0.18
Dissolved Organic N	4.7
Particulate Organic N	1.05
NO ₃ ⁻ (Table 1)	22.4
Total N output from lake	28.3
N buildup (from Table 1)	23.4

^aN₂ is not considered. Methods and sources are the same as Table 1. The difference between inputs and the sum of outputs plus buildup (62.8 – (28.3 + 23.4) = 11.1) might be made up by long-term burial or denitrification. N fixation is considered negligible.

From Sterner et al. (2007) GRL

Denitrification rates are poorly known but considered low in Lake Superior but highest rates occur at shallower depths as well as in deep fine grained sediments. Could they have changed over time?

TABLE 2. Results of measured and modeled microbial process rates and surficial particular organic carbon in Lake Superior sediment cores.

Core	A11	A18	B36/B25	B1/B12	B32
Depth (m)	61	276	37	82	105
Oxygen Consumption Mole O ₂ m ⁻² · yr ⁻¹	—	—	1.210	2.740	1.850
Denitrification Acetylene Block Mole NO ₃ ⁻ m ⁻² · yr ⁻¹	—	—	0.027	0.000	—
K _{NO3} yr ⁻¹	0.75	50.0	25.0	25.0	60.0
Denitrification Model Mole NO ₃ ⁻ m ⁻² · yr ⁻¹	0.002	0.039	0.031	0.016	0.024
Sulfate Reduction	—	—	0.000	0.000	0.000
Particulate Organic Carbon 0-1 cm ‰ Mass	1.110	4.040	0.320	0.930	0.400

Carlton et al. 1989 *J. Great Lakes Res.*