Examples of nitrogen compounds in the environment?

Aquatic Ecosystems

23.02.-03.03.2016

Nitrogen and Eutrophication
- Lecture 1 -

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Overview of this teaching unit

- **Lecture 1** today – 10.15 – 12.00
  - Nitrogen (Importance, sources, transformations and recent trends)
  - Environmental Quality Criteria

- **Exercise 1** today – 13.15 -17.00 (likely shorter)
  - Application of the Environmental Quality Criteria and mapping using R

- **Lecture 2** on Thursday – 10.15 – 12.00
  - Feedbacks, interactions, stable states
  - Eutrophication Management (Directives, examples)

Overview of this teaching unit

- **Lecture 2** on Thursday – 13.15 – 15.00
  - ‚Brownification‘ in inland waters
  - Time series analysis using linear mixed effects models
- **Exercises 2 to 5** – Fr 26/02 to Tue 01/03
  - Case studies brownification in lakes, rivers and estuaries
  - Time series analyses, mixed effects modeling, R
- **Final seminar** – Thursday 03/03 – 10.15 – 12.00
  - Presentation of case study results and group discussion

Literature

- Limnology (Jacob Kalff), pp. 270-283
- Limnology (Robert G. Wetzel), pp. 205-235 and pp. 836-841
- European Nitrogen Assessment 2011, Chapters 2, 4, 7, 8
- Articles as indicated (see reference list)

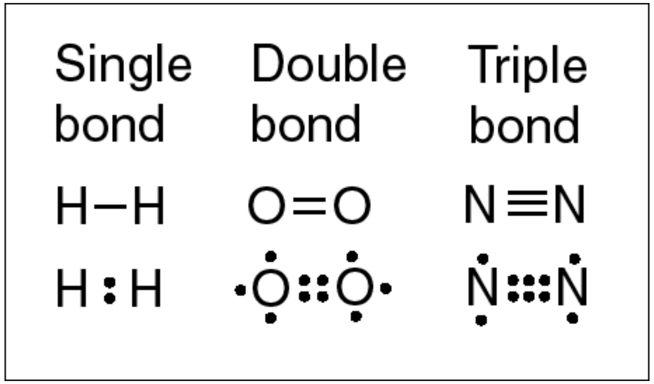
Learning goals

1. Anthropogenic production of reactive nitrogen compounds is a central global change issue
2. Increased atmospheric deposition of reactive nitrogen has changed the nutrient status of lakes
3. Increasing nitrogen concentrations in aquatic systems can cause various environmental problems – e.g. algae blooms
4. Introduction of the Environmental Quality Criteria (Bedömningsgrunder) for lakes and watercourses by the Swedish Environmental Protection Agency (Naturvårdsverket)

Questions welcome at all times!!

Non-reactive and reactive nitrogen

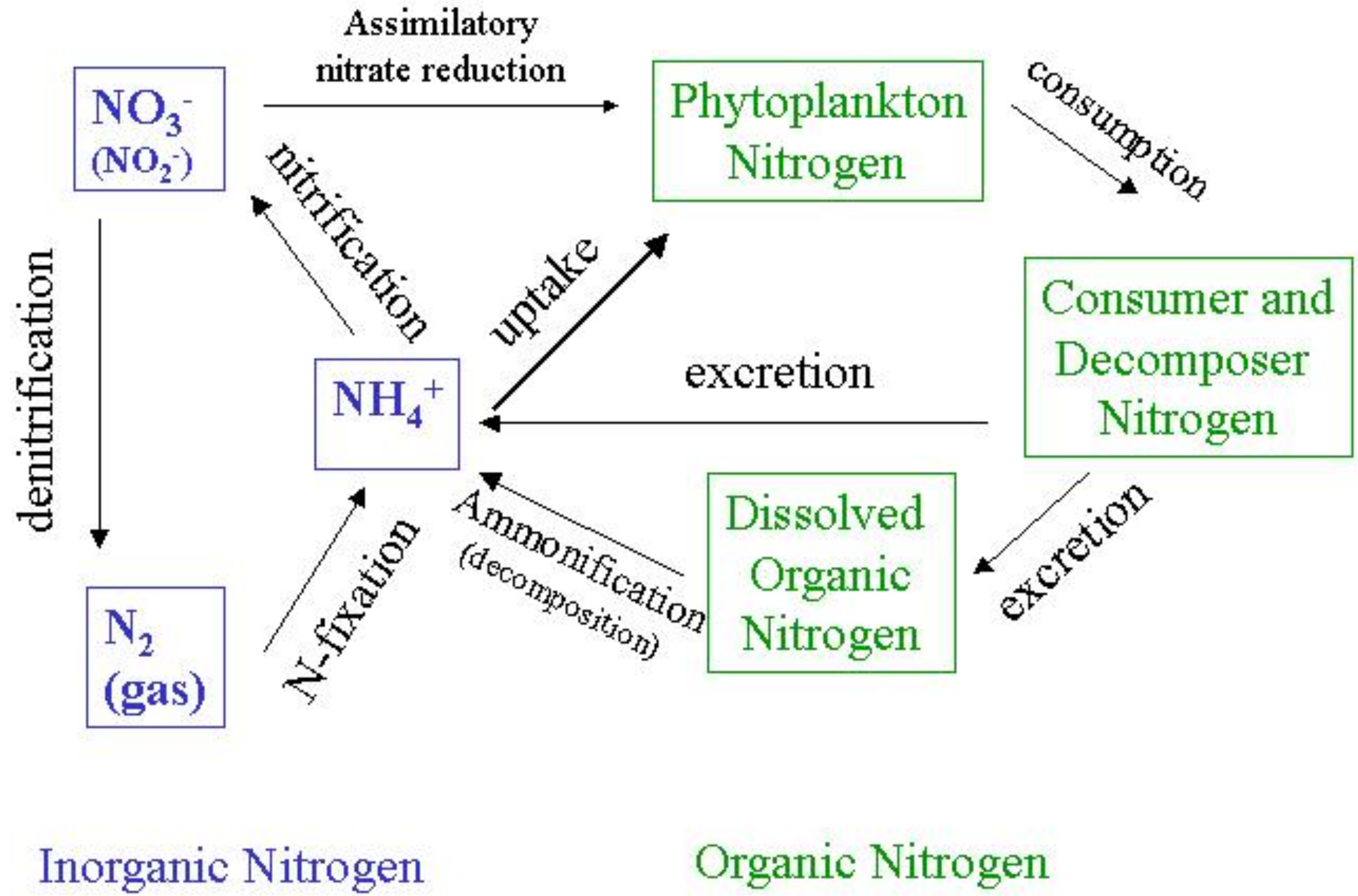
78% of the atmospheric air is ‚non-reactive nitrogen' **(N_2)**



Reactive nitrogen **(N_r)**

- Nitrogen bond to carbon, oxygen or hydrogen
  - e.g. nitrate, ammonium, nitrous oxide

Aquatic Nitrogen Cycle



Haber-Bosch process

Fritz Haber

Industrial synthesis of ammonia at high temperature and high pressure, developed between 1905 and 1913

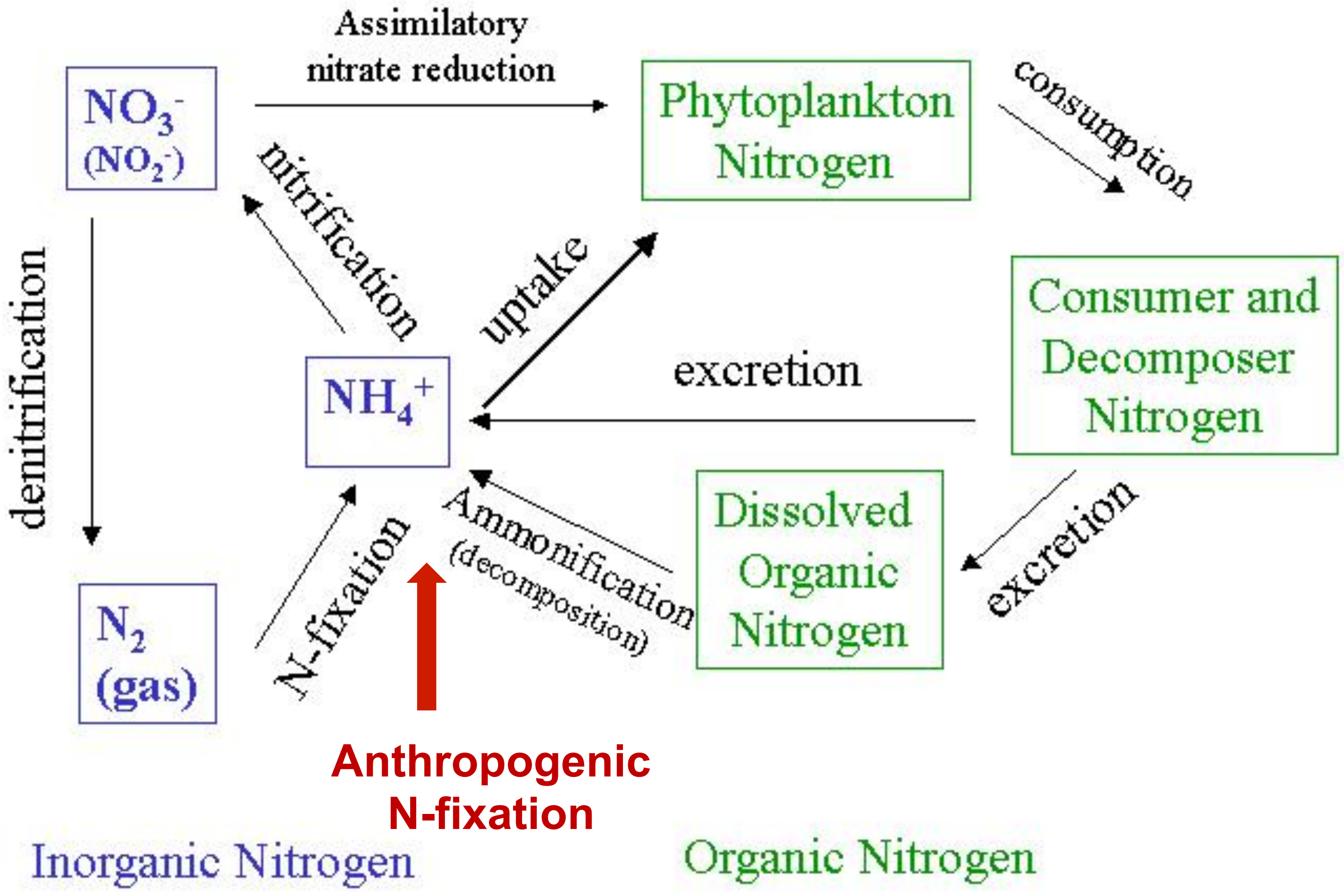
-> Fertilizer

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

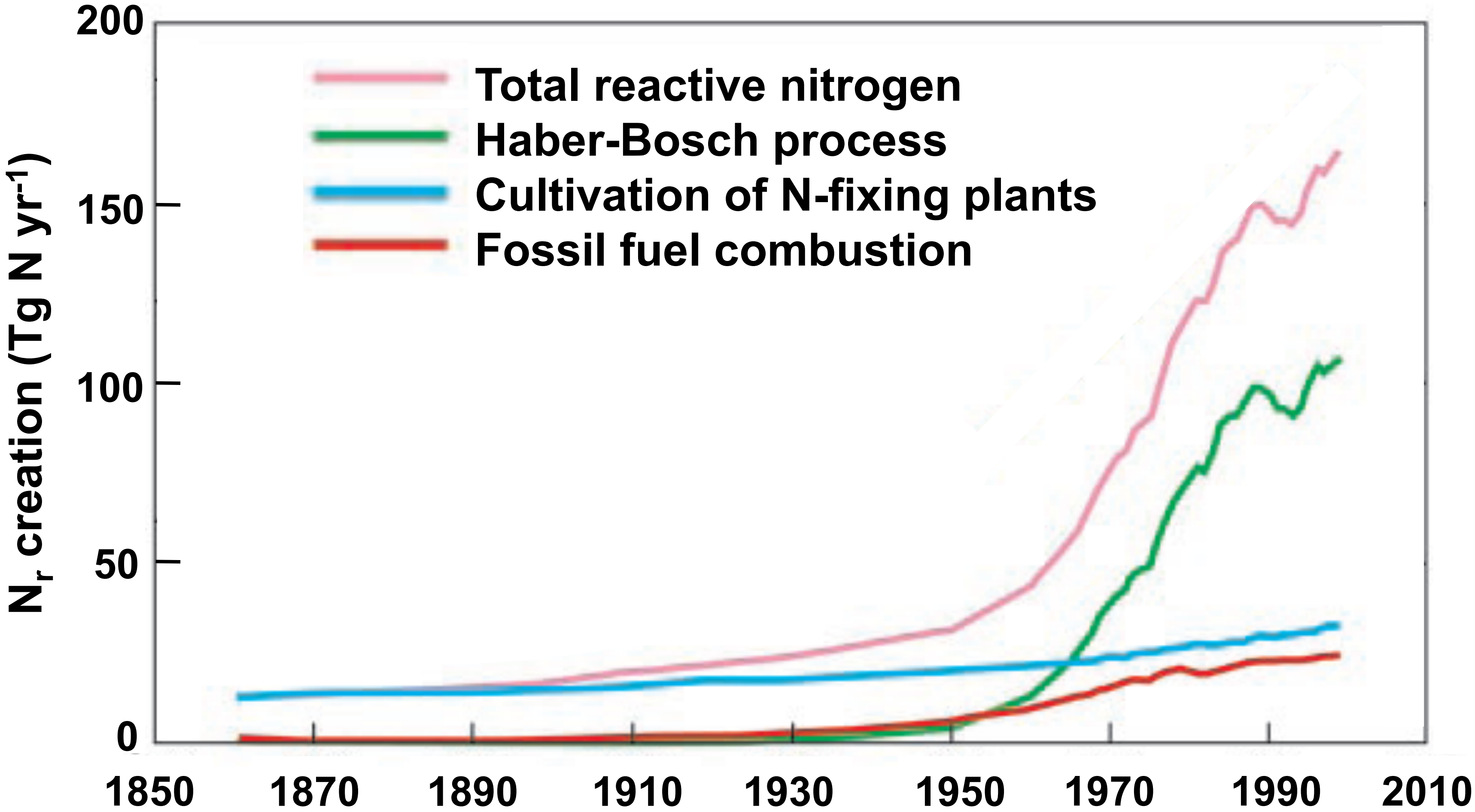
1% of the world's annual energy supply is consumed in the Haber process

Smith 2002

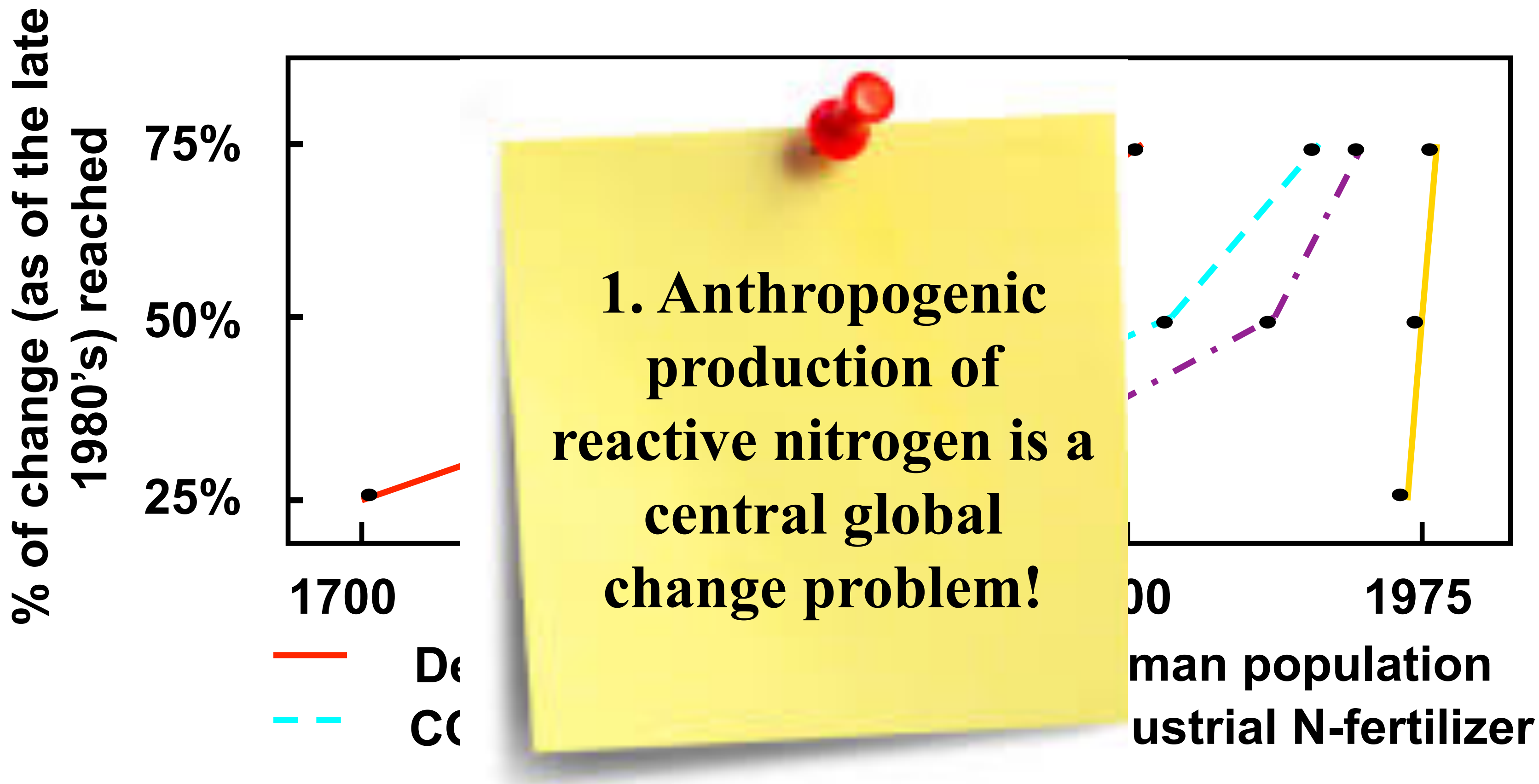
Aquatic Nitrogen Cycle



Anthropogenic production of reactive nitrogen



Galloway *et al.* 2003

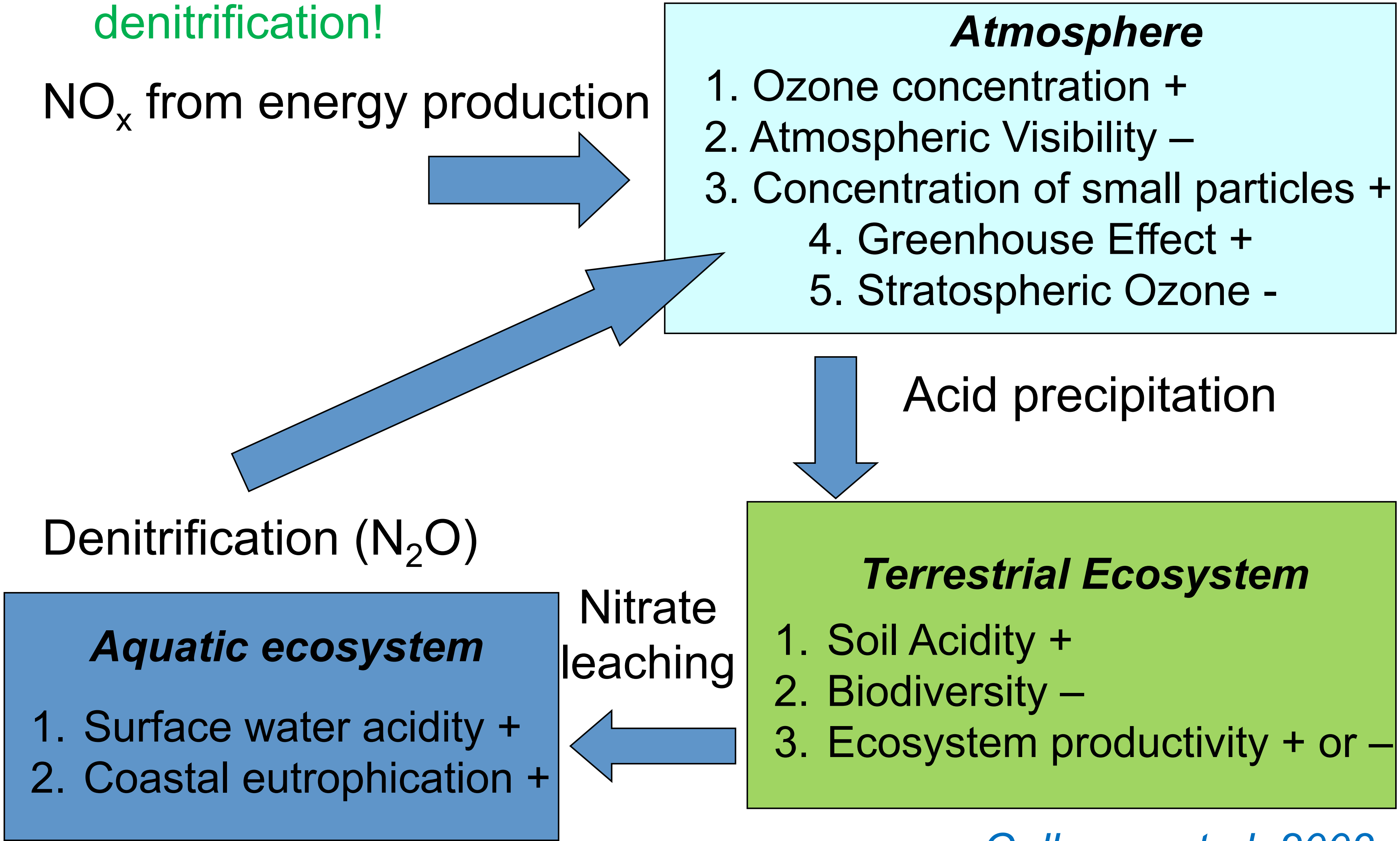


- ➢ Anthropogenic activities release more reactive nitrogen into the biosphere than all natural processes together – **for example 5 times more in Europe!**
- ➢ Europe (covering <3% of the continental area) produces **10%** of the global anthropogenic reactive nitrogen

Vitousek et al, 1997; The European Nitrogen Assessment, 2011

The ‚nitrogen cascade‘

- Each reactive nitrogen atom may cause several effects before denitrification!



Galloway et al. 2003

Dominant forms of nitrogen in fresh waters

- Molecular N_2
- Ammonium (NH_4^+) and ammonia (NH_3)
- Nitrite (NO_2^-)
- Nitrate (NO_3^-)

- Organic compounds (e.g. amino acids, amines, nucleotides, proteins, humic substances)
- Dissolved organic nitrogen to particulate organic nitrogen usually 5:1 to 10:1

Nitrogen supply and losses in LAKES

- **Supply:**
- Inflow with surface water or groundwater (dissolved nitrogen)
- Erosion (nitrogen bound to particles)
- Nitrogen fixation in the water and sediments (N_2 to ammonium)
- Atmospheric wet and dry deposition

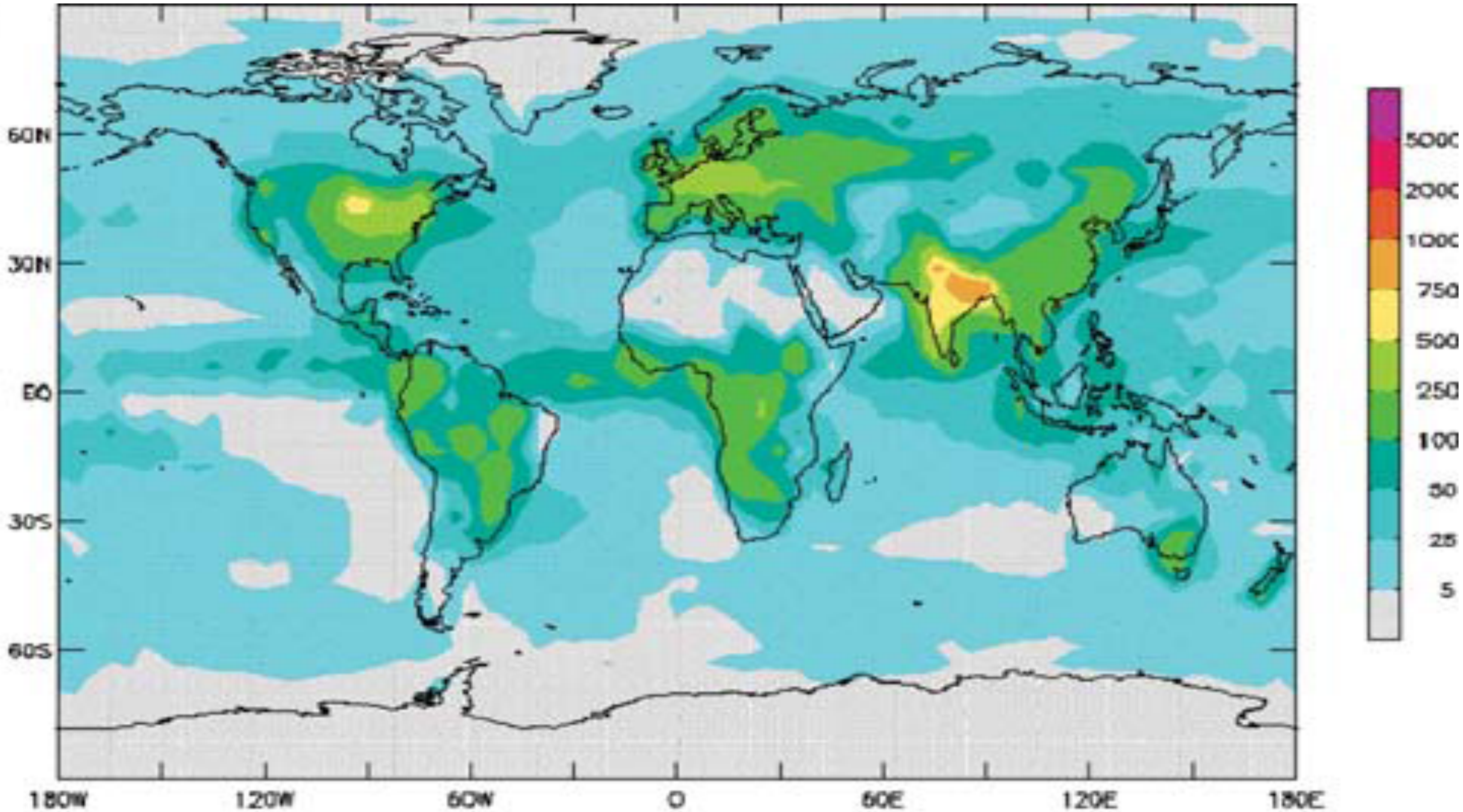
- **Losses:**
- Outflow (dissolved nitrogen)
- Gaseous loss into the atmosphere (e.g. as NO, N_2O, N_2 or as ammonia at high pH)
- Permanent sedimentation (nitrogen bound to particles)

Nutrient limitation characteristics in freshwaters

- **Why is important to know which nutrient limits lake productivity?**
- **Phosphorus** often limits upstream **freshwater** productivity because:
- generally large watersheds which mobilize large amounts of reactive nitrogen relative to phosphorus
- cyanobacteria commonly bloom and fix nitrogen at low availability
- **But:** Lakes with small watersheds more often nitrogen-limited, or N and P co-limited
- **Also:** Different community members can be limited by different nutrients, and may also change in time (e.g. seasons)
- **Current discussion:** Phosphorus limitation in unproductive lakes may be induced by **atmospheric nitrogen deposition** - i.e. ‚naturally' N limitation or co-limitation by N and P

Bergström and Jansson 2006; Elser et al. 2009; Howarth et al., 2011; Paerl, 2009; European Nitrogen Assessment, 2011

Atmospheric nitrogen deposition in 1860 (mg N m^{-2} yr^{-1})

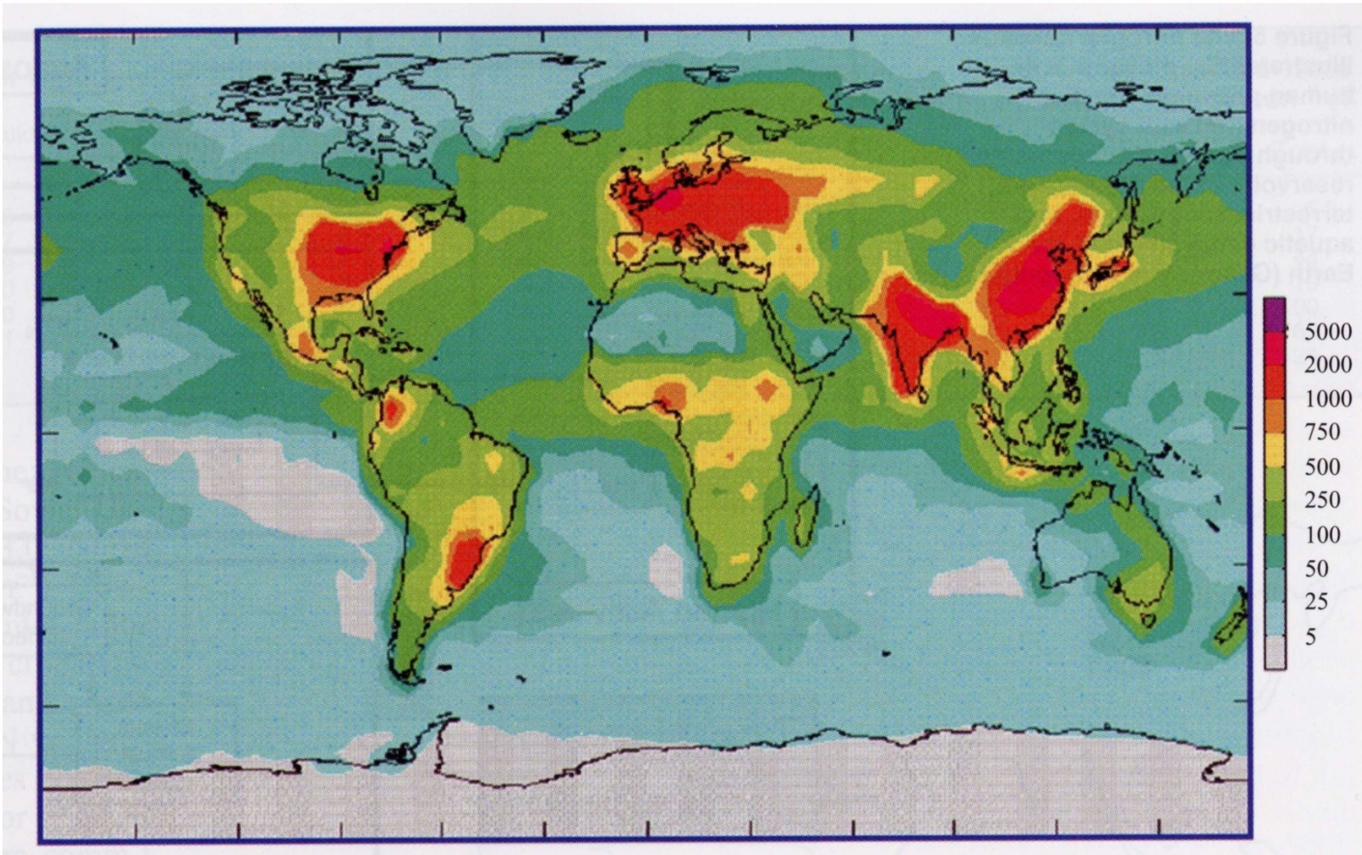


➢Suggested values for nutrient limitation in lakes:

- N limitation at <~25 kg N ha^{-1} yr^{-1}
- N-and-P co-limitation at ~25-50 kg N ha^{-1} yr^{-1}
- P limitation at ~> 50 kg N ha^{-1} yr^{-1}

Galloway and Cowling, 2002; Bergström and Jansson 2006

Atmospheric nitrogen deposition in 1993 (mg N m^{-2} yr^{-1})



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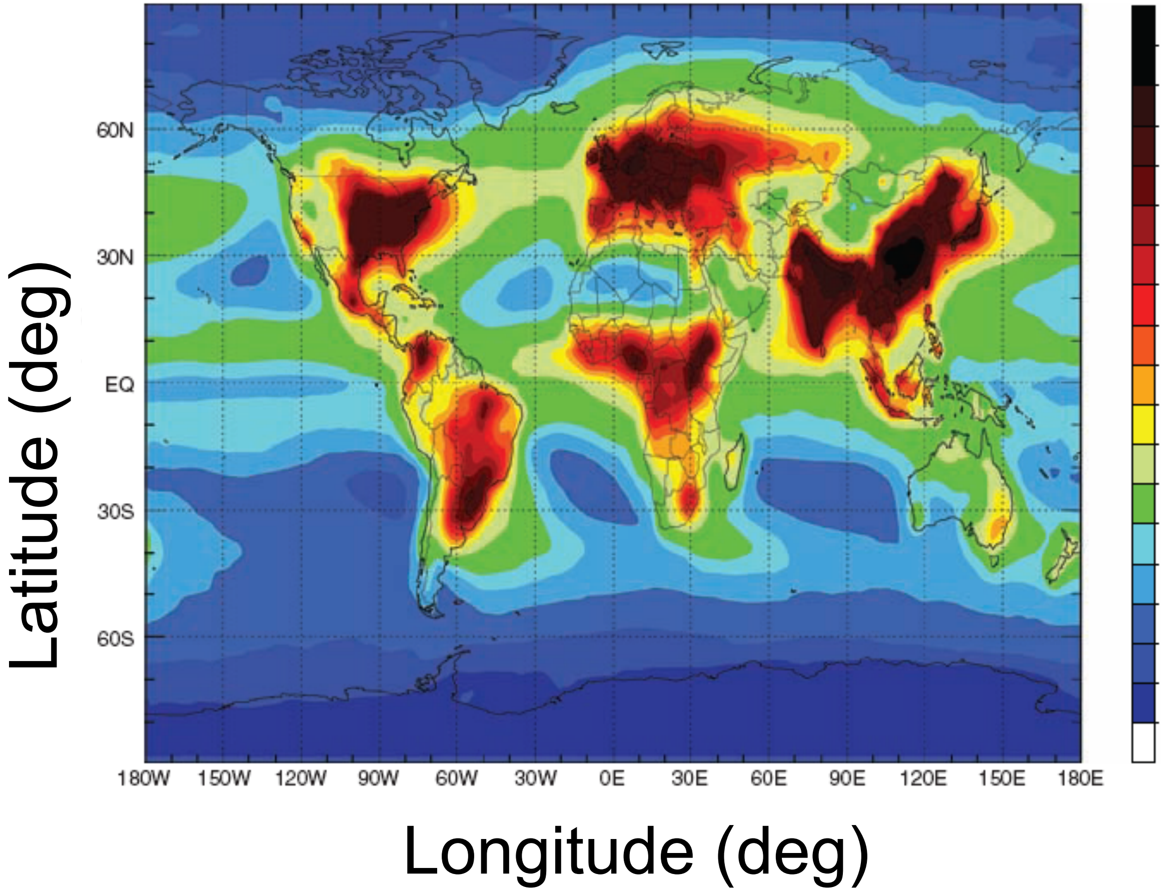
Galloway and Cowling, 2002; Bergström and Jansson 2006

Atmospheric nitrogen deposition in 2000 (kg N ha^{-1} yr^{-1})



2. Increased atmospheric deposition of reactive nitrogen has changed the nutrient status of lakes!

➢Suggested values for nutrient limitation in lakes:

- N limitation at <~25 kg N ha^{-1} yr^{-1}
- N-and-P co-limitation at ~25-50 kg N ha^{-1} yr^{-1}
- P limitation at ~> 50 kg N ha^{-1} yr^{-1}

Bergström and Jansson 2006; Galloway et al., 2008; Dentener et al. 2006

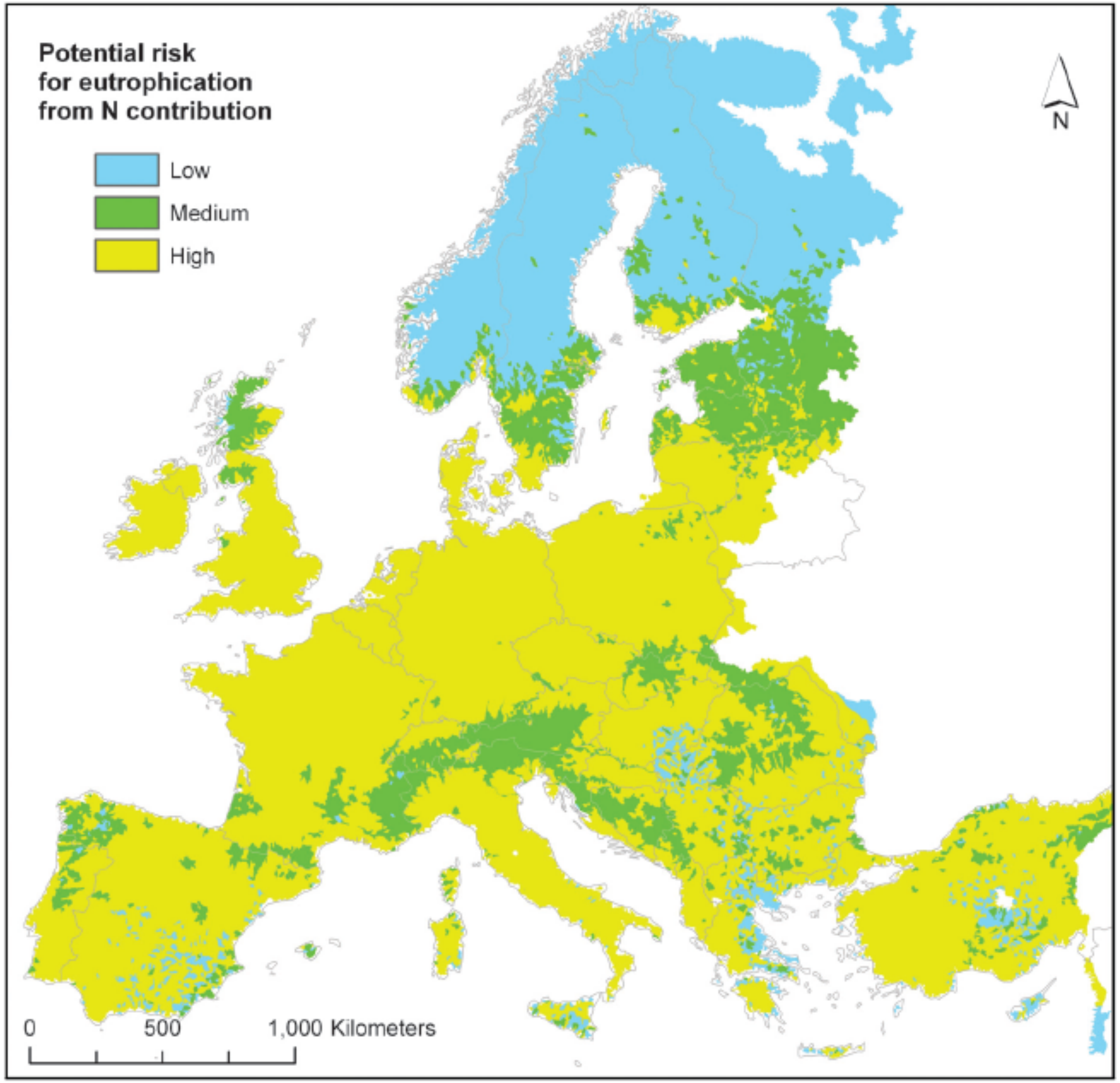


Figure TS.7 Indication of the nitrogen threat to water quality. Potential risk of eutrophication for surface freshwater based on estimated total N_r concentrations. The three classes of risk are: low, <0.5 mg/l; medium 0.5–1.5 mg/l; high >1.5 mg/l as total N_r concentration in water [17.3.3].

European Nitrogen Assessment 2011

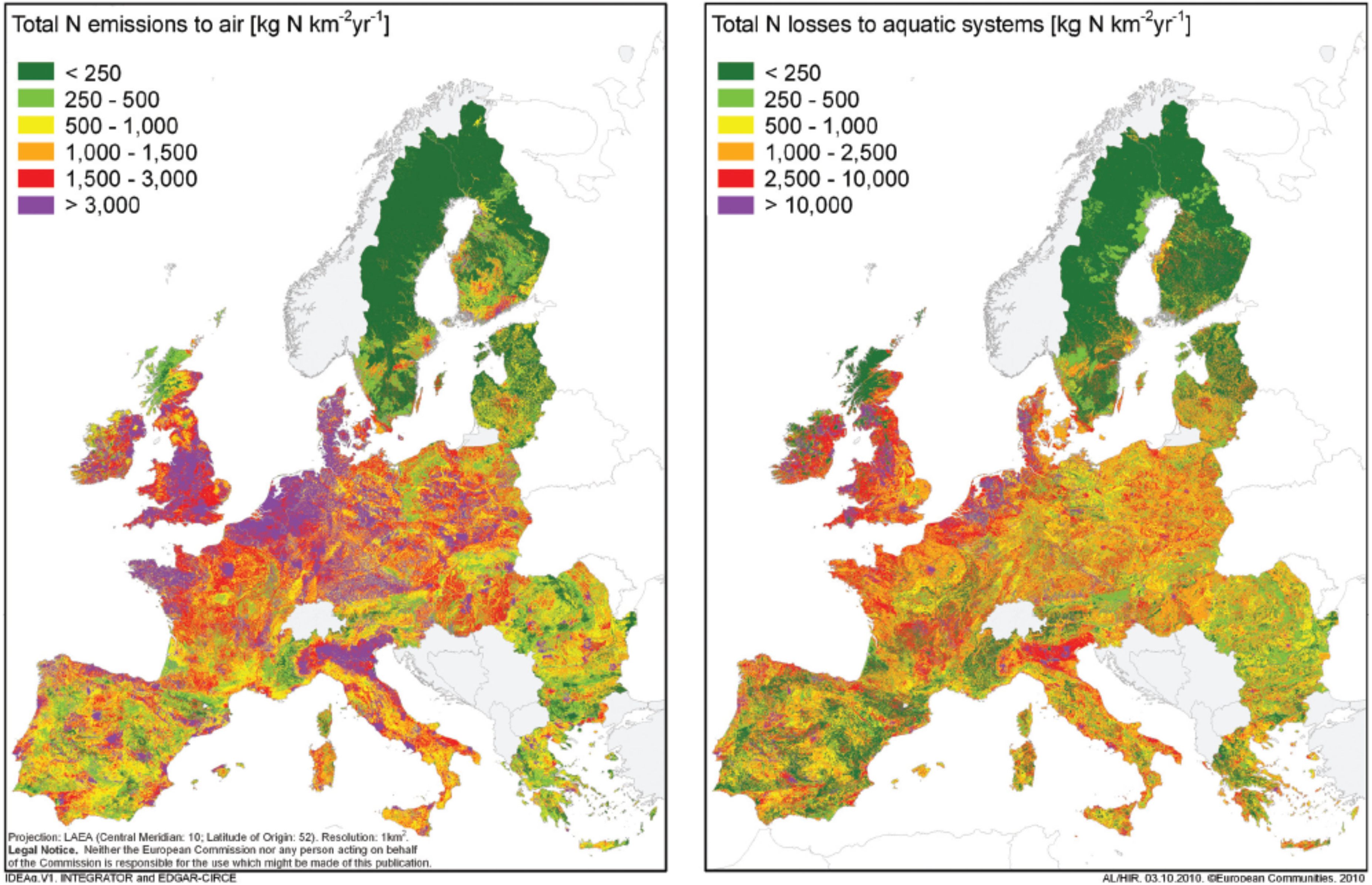


Figure TS.4 Distribution of reactive nitrogen emissions across Europe (kg N per km² for 2000) including emissions to air as NO_x, NH_3 and N_2O, and total losses to aquatic systems, including nitrate and other N_r leaching and wastewaters [16.3].

European Nitrogen Assessment 2011

Increasing nitrogen input to lakes

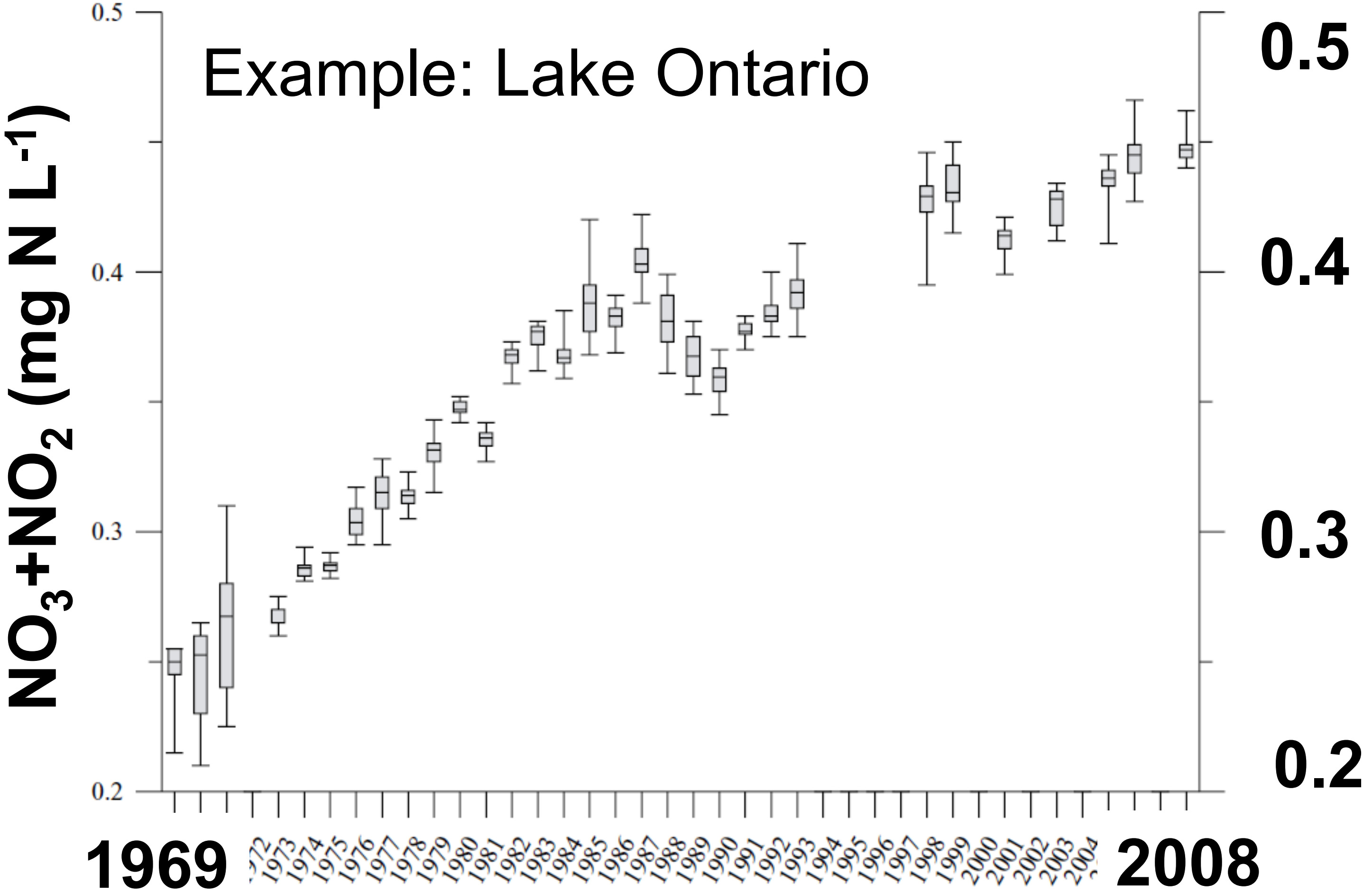


Figure 5. Spring, Surface (1m) Nitrate-plus-Nitrite in Lake Ontario Open Waters, 1969–2008. The solid line within each box is the median; the lower and upper ends of the boxes are the 25th and 75th percentiles, respectively; whiskers show the minimum and maximum values.

Dove et al. 2009

Increasing nitrogen transport to river mouths

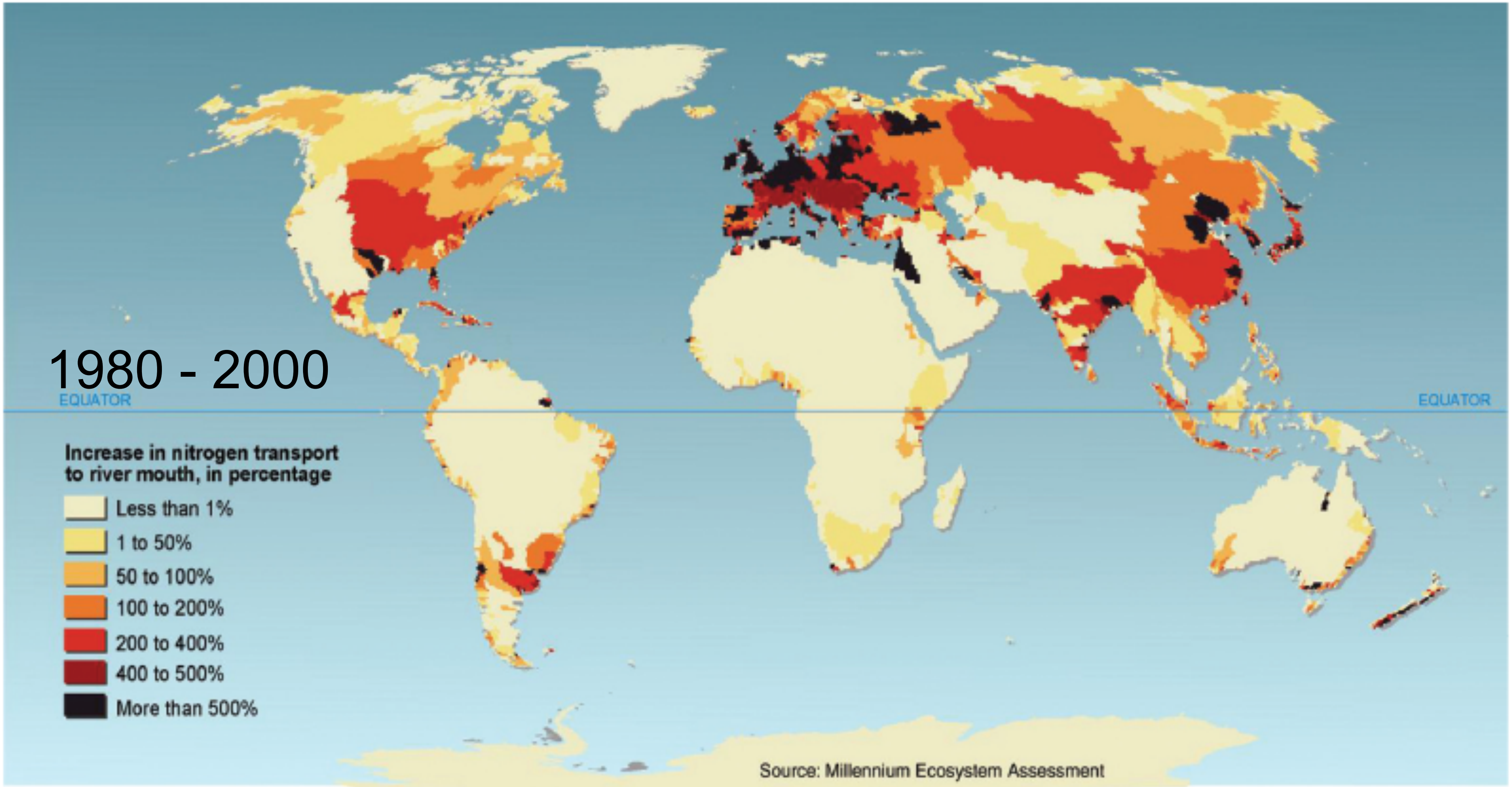


Figure 2.14 Increase in nitrogen transport to river mouth between 1980 and 2000 (Reid *et al.*, 2005).

European Nitrogen Assessment 2011

Dominant nitrogen forms change with nitrogen enrichment:

Nitrate-to-DON-ratios increase

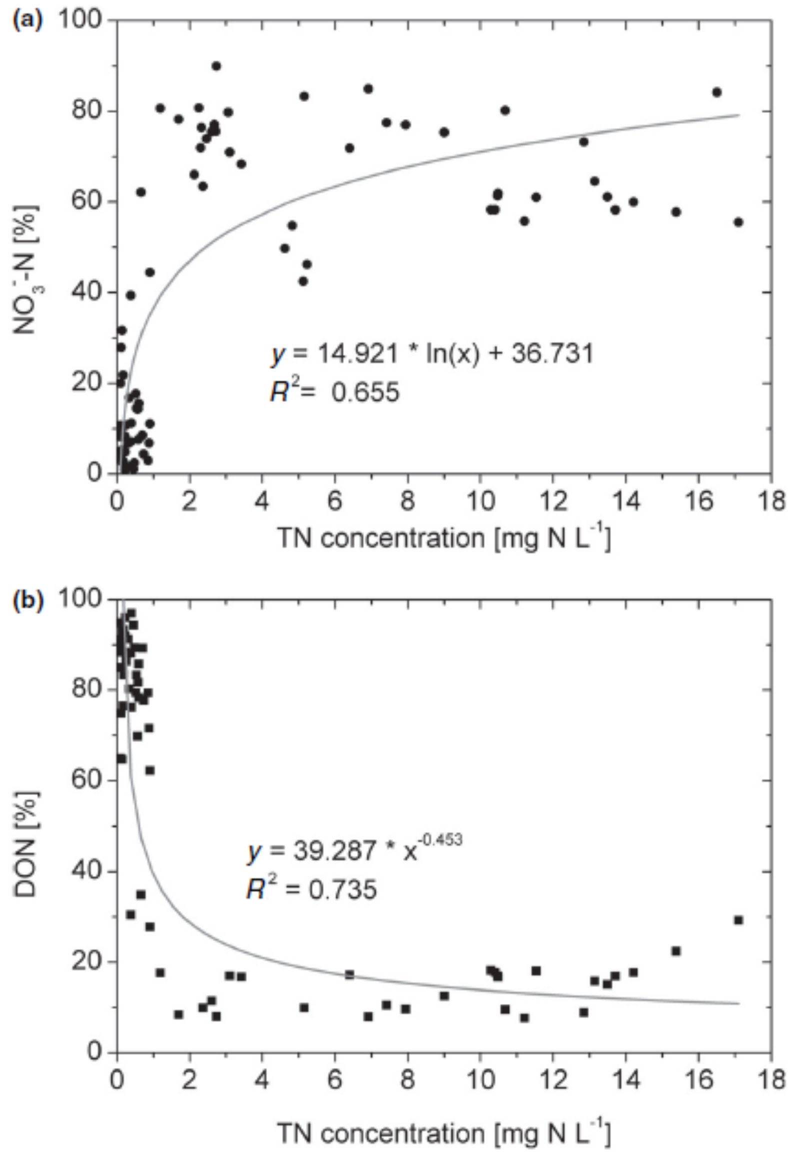


Figure 7.6 Proportion of total N present in the form of (a) nitrate-N and (b) DON in European rivers along a gradient of N enrichment (an explanation of data sources is given in the text).

European Nitrogen Assessment 2011

Consequences of nitrogen enrichment in aquatic ecosystems

- Increased biomass of phytoplankton, macrophytes and consumers; but: Phosphorus-limited algae are poor-quality food, may reduce production at higher trophic levels (e.g. fish)
- Changes in community composition
- High nitrate concentrations in drinking water are toxic
- Hypoxia or anoxia (low to no oxygen) – ‚dead zones‘
- Fish kills
- Increase in unedible or toxic algal blooms -> hear more after fika!
- Acidification
- Decrease in biodiversity
- Loss of critical habitat (e.g. seagrass beds, coral reefs)
- ...

Smith and Schindler 2009; Howarth et al. 2011

FIKA!

3. Increasing nitrogen concentrations in aquatic systems can cause various environmental problems

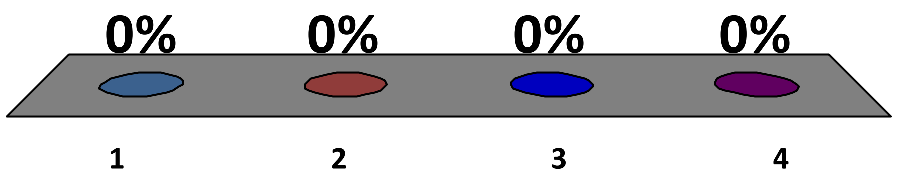
Questions about part 1?

What is the most important reason for the increasing rates of reactive nitrogen cycling and atmospheric nitrogen deposition?

1. Biological N fixation by cyanobacteria has massively increased in the recent decades.
2. The increasing abundance of cattle worldwide.
3. The industrial application of the Haber-Bosch-process.
4. Increasing areas of anoxic zones in the oceans.
5. Emissions from the combustion of fossil fuels.

The nitrogen pool in freshwaters is usually...

1. dominated by particulate compounds.
2. dominated by gaseous compounds.
3. dominated by dissolved compounds.
4. made up by similar proportions of particulate and dissolved compounds.



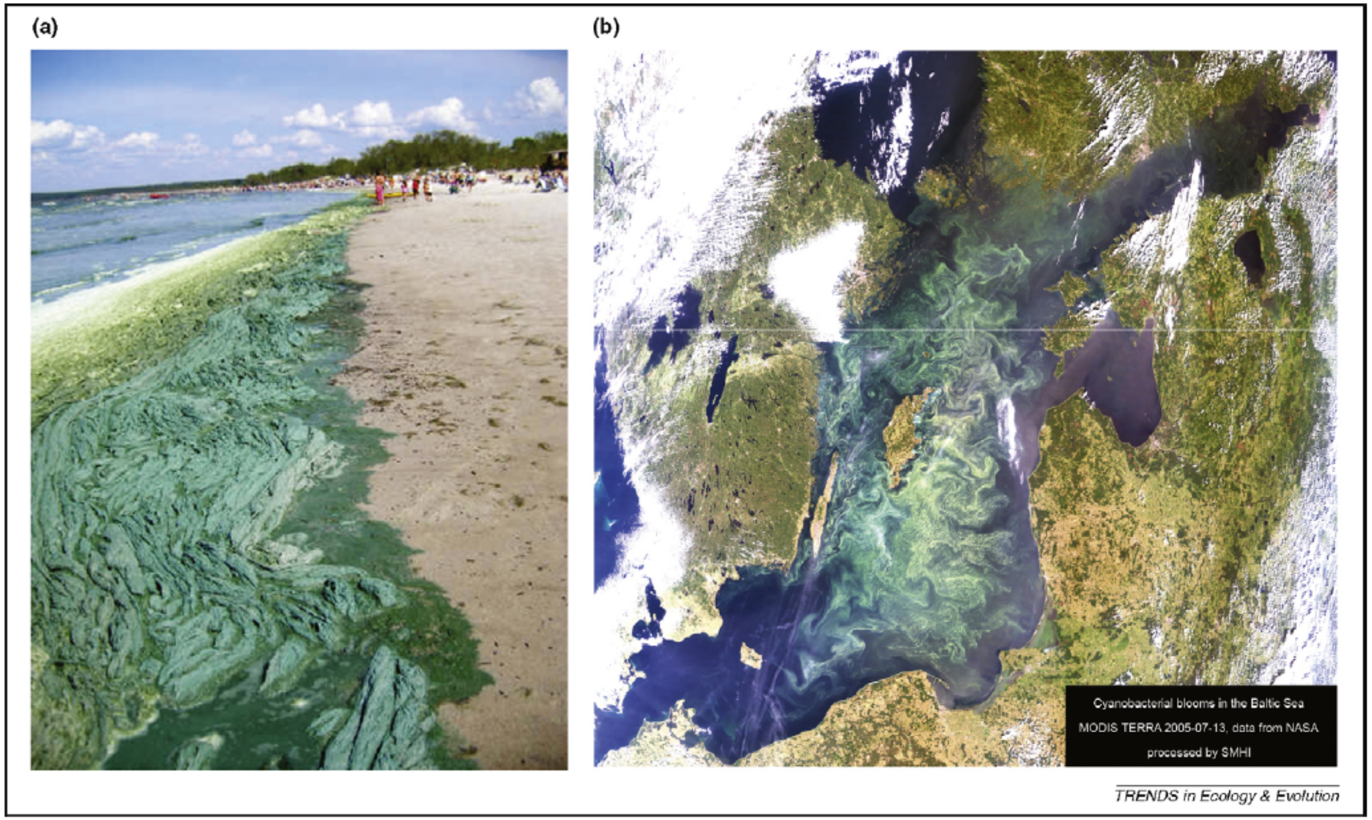
2 times 2 minutes ’speed dating’ with your neighbour

a) What was unclear for you so far?
   2 minuter

b) What was the most interesting for you so far?
   2 minuter

Questions to the big group?

‚Harmful algal blooms‘ (HABs)

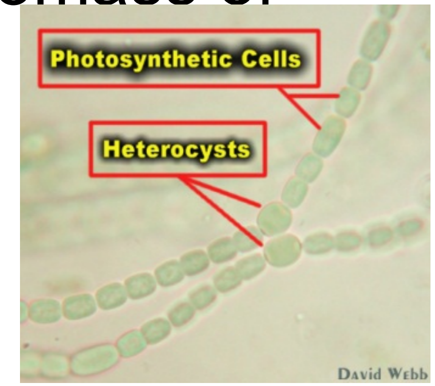


- ‘Red tides’ in US coastal waters created almost $500 million in economic costs between 1987 and 1992
- In the USA, CyanoHABs result in >$2 billion annual losses of water resources

Anderson et al. 2000; Smith and Schindler 2009

Cyanobacteria

- First classified as *Cyanophyta* or blue-green algae before it was clear that they belong to the Empire Bacteria (*Prokaryota*), but with chlorophyll
- ~1350 freshwater species
- Frequently dominate the phytoplankton biomass of nutrient-rich lakes
- Some groups are capable of nitrogen fixation in specialized cells with anoxic conditions (heterocycts)



- Optimal growth rates at relatively high temperatures, usually > 25°C
- Toxins that affect mainly the liver (*hepatotoxins*) or the nervous system (*neurotoxins*)

Cyanobacteria dominate eutrophic systems

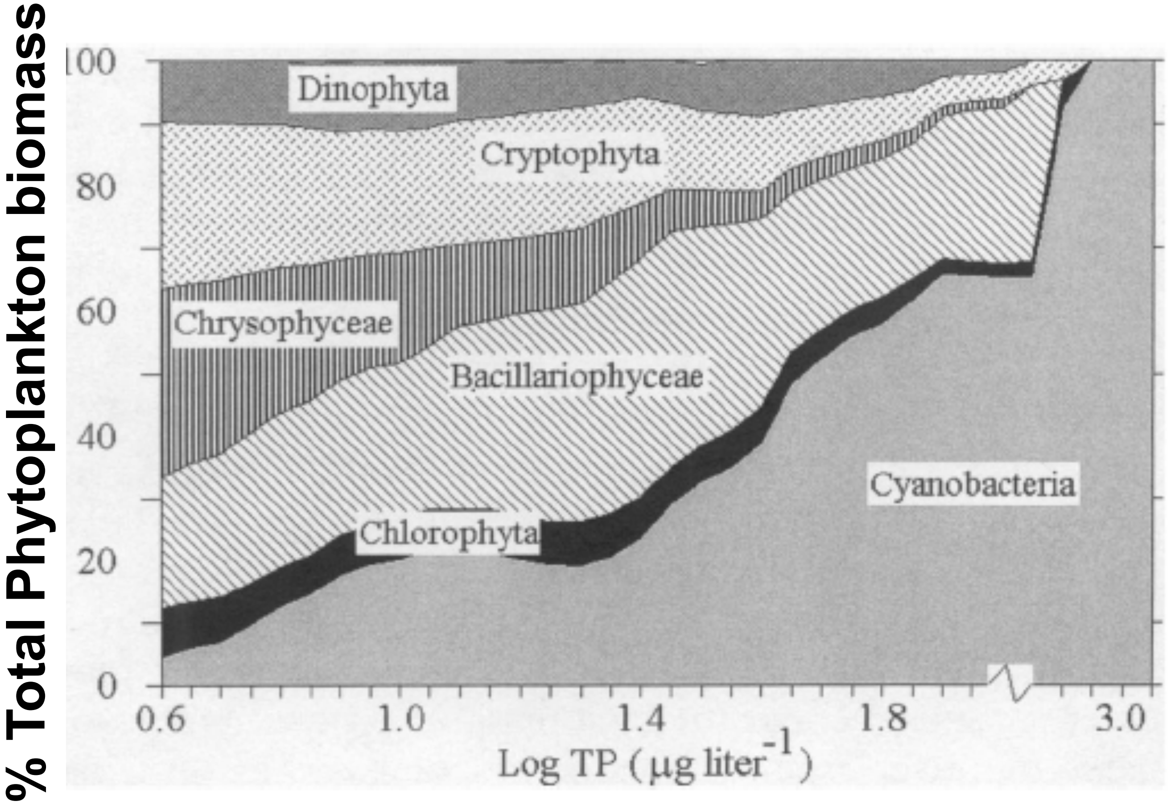


Fig. 4. Area plot of average contribution (%) of individual taxonomic groups to total summer biomass; data fitted with LOWESS smoothing technique.

Dinophyta = Dinoflagellates
Cryptophyta = Flagellates
Chrysophyceae = Golden-brown algae
Bacillariophyceae = Diatoms
Chlorophyta = Green algae

Watson et al. 1997

CAUTION

POSTED ________________: **Based on counts of the cyanobacteria (blue-green algae), MDPH thresholds for recreational waters have been exceeded.**

- Water which looks like the pictures above may contain algae capable of producing toxins that can be dangerous to humans and pets.

- People and pets should avoid contact in areas of algae concentration

- Do not swallow water and rinse off after contact

For further information call:

MA Department of Public Health at 617-624-5757

Cyanobacteria blooms and water treatment

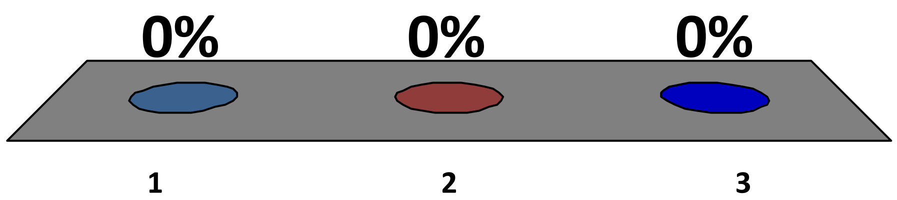
- High cyanobacteria biomasses
- ➢ Clog the filters more easily
- ➢ Give earthy taste and smell
- ➢ Requires expensive treatment for cyanotoxin removal

➢ Current methods:

- Conventional treatment and membrane filtration can remove intact bacteria and thereby **intra**cellular toxins
- Desinfection with chlorine? Problem of potential toxic or carcinogenic by-products!
- Activated carbon adsorption, but it needs to be replaced ususally every couple of months
- Electrochemical oxidation as new technology?

Cyanobacteria are...

1. bacteria which possess chlorophyll.
2. algae which were historically misclassified as bacteria.
3. components of the zooplankton.



What are the negative consequences of eutrophication and of harmful algae blooms, especially of cyanoHABs?

- This much as a first background (more tomorrow), but...

...how do Swedish Environmental agencies/ authorities evaluate the state of eutrophication in Swedish waters...

How do you deal with this in practise...?

Some background on this, then do it yourself in the exercise!

Environmental Quality Criteria

- Download from the Swedish Environmental Protection Agency:

http://www.naturvardsverket.se/Documents/publikationer/620-0148-3.pdf

‚Bedömningsgrunder för sjöar och vattendrag‘

- Chapters 10 and 11
- Background: ‚Förslag till bedömningsgrunder för eutrofierande ämnen‘, Anders Wilander, SLU rapport 19, 2004

Environmental Quality Criteria

- **Calculation of ‚reference nutrient values‘ and comparison to the actual nutrient concentrations**

- **Lakes:**
- Key variable: Total phosphorus concentrations - but total nitrogen concentrations and TN/TP-ratios also considered
- Recommendation: At least 1 year of monthly measurements from May to October; if not available, 3-year average of August-samplings

- **Rivers:**
- Classified according to areal-specific losses of phosphorus and nitrogen
- Recommendation: Use monthly measurements over at least 3 years

State of the aquatic system

Tabell 37. Klassning av tillstånd i sjöar och vattendrag. Koncentration av totalfosfor (µg/l).

Klass	Benämning	Totalfosfor µg/l
1	Låga halter	≤12,5
2	Måttligt höga halter	12,5–25
3	Höga halter	25–50
4	Mycket höga halter	50–100
5	Extremt höga halter	>100

Tabell 2. Tillstånd i sjöar totalkväve/totalfosfor för perioden juni–september enligt Bedömningsgrunder (1999).

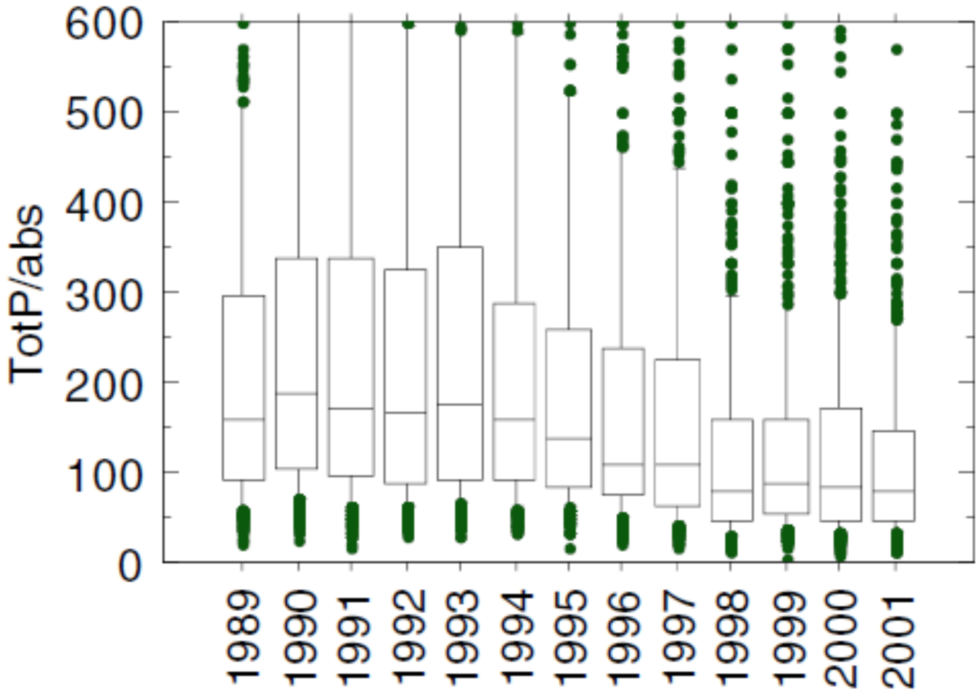
Klass	Benämning	Totalkväve/totalfosfor
1	Kväveöverskott	≥ 30
2	Kväve-fosforbalans	15–30
3	Måttligt kväveunderskott	10–15
4	Stort kväveunderskott	5–10
5	Extremt kväveunderskott	< 5

Tabell 4. Klassning av tillstånd i vattendrag. Arealspecifik förlust av totalkväve och totalfosfor enligt Bedömningsgrunder (1999).

Klass	Benämning	Arealspecifik förlust kg/ha,år	
		Totalkväve	Totalfosfor
1	Mycket låga förluster	≤ 1,0	≤ 0,04
2	Låga förluster	1,0–2,0	0,04–0,08
3	Måttligt höga förluster	2,0–4,0	0,08–0,16
4	Höga förluster	4,0–16,0	0,16–0,32
5	Mycket höga förluster	> 16,0	> 0,32

Continuous development of the system

- Classification method revised in 2004 because of the increases of dissolved organic carbon and water color in Swedish inland waters, which cause changes in the phosphorus-absorbance relationship



Figur 16. Sjöar. Total-P. Förändringar hos kvoten totalfosfor/absorbans för referenssjöar.

Some criticism

- Difficulties and expenses to obtain area-specific nutrient fluxes from the rivers, and the poor coupling with the responses of the biota. Suggestions to replace this system by a system based on concentrations, as for lakes.

- Dependency of the results on the reference values, which are sensitive to recent changes, and how they are obtained. Suggestions to use other information sources, e.g. historical data or paläolimnological data for reference information.

Movie by the European Nitrogen Assessment

http://www.youtube.com/watch?v=uuwN6qxM7BU

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