



**The Abdus Salam
International Centre for Theoretical Physics**



2066-9

**Workshop and Conference on Biogeochemical Impacts of Climate and
Land-Use Changes on Marine Ecosystems**

2 - 10 November 2009

**Anthropogenic impact on the global nitrogen cycle with a special focus on nitrogen
effects along tropical coastal zones**

M. Voss
IOW
Germany

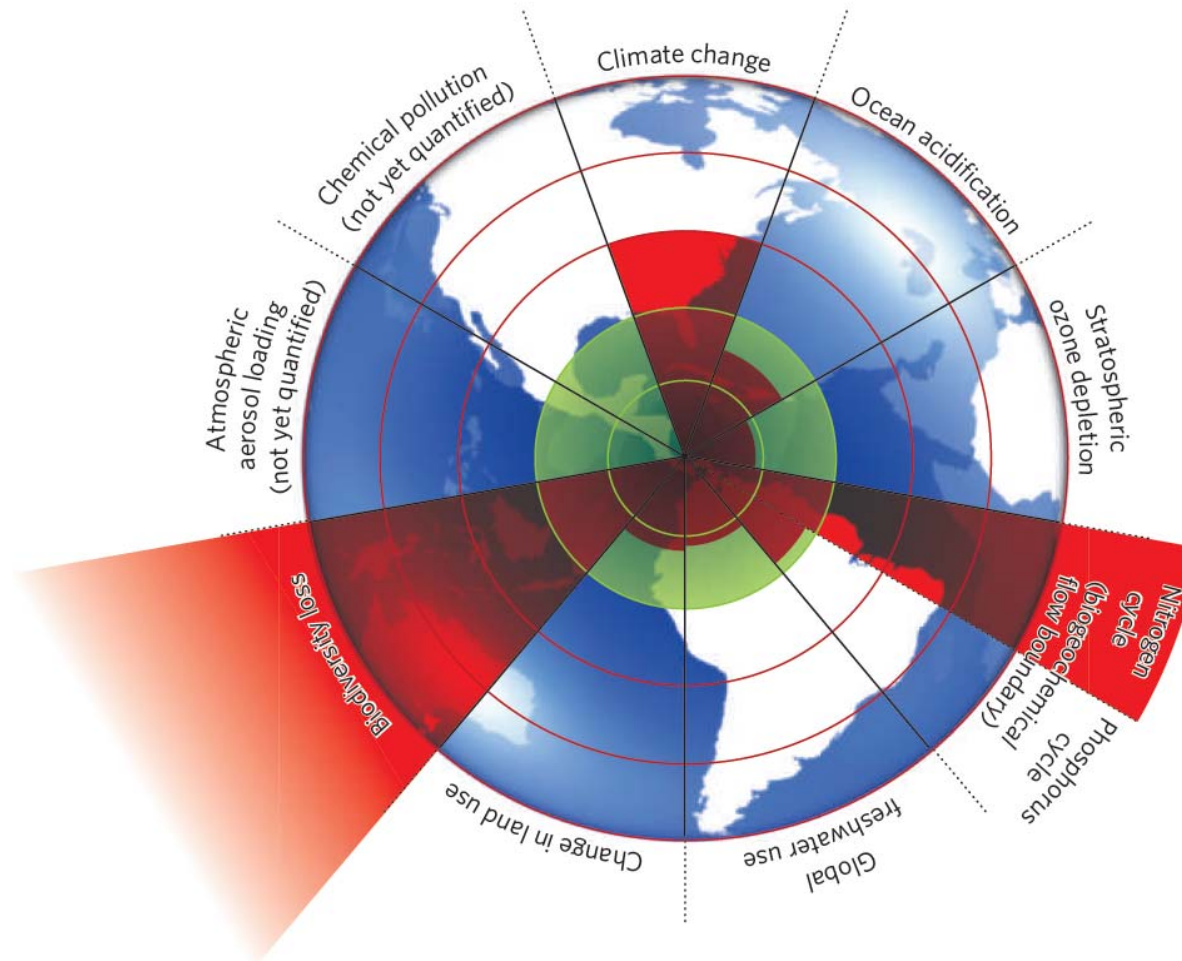
Anthropogenic impact on the global nitrogen (and carbon) cycle

Special focus in nitrogen effects along
tropical coastal zones

Maren Voss and Nicola Wannicke
Leibniz Institute of Baltic Sea Research

- Sources of anthropogenic nitrogen and effects on the environment
- Global impacts of anthropogenic nitrogen
- Nitrogen delivery to the coast
- Feedback to harmful algae blooms
- Algae genera
- N acquisition in HABs
- HAB management
- Anthropogenic effects on the carbon cycle

Nitrogen and biodiversity a key global threat

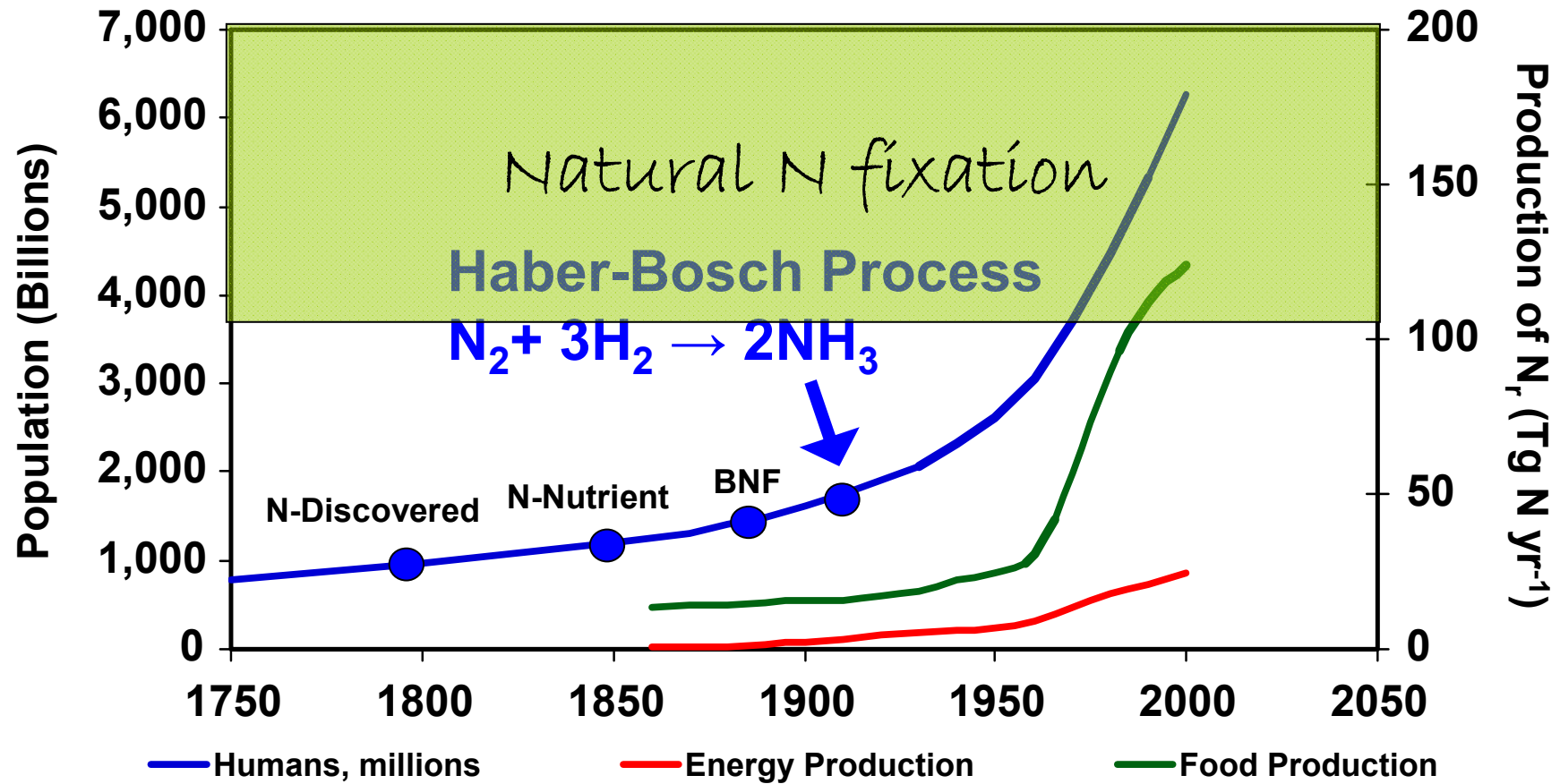


This Feature is an edited summary of a longer paper available at the Stockholm Resilience Centre (<http://www.stockholmresilience.org/planetary-boundaries>)

PLANETARY BOUNDARIES

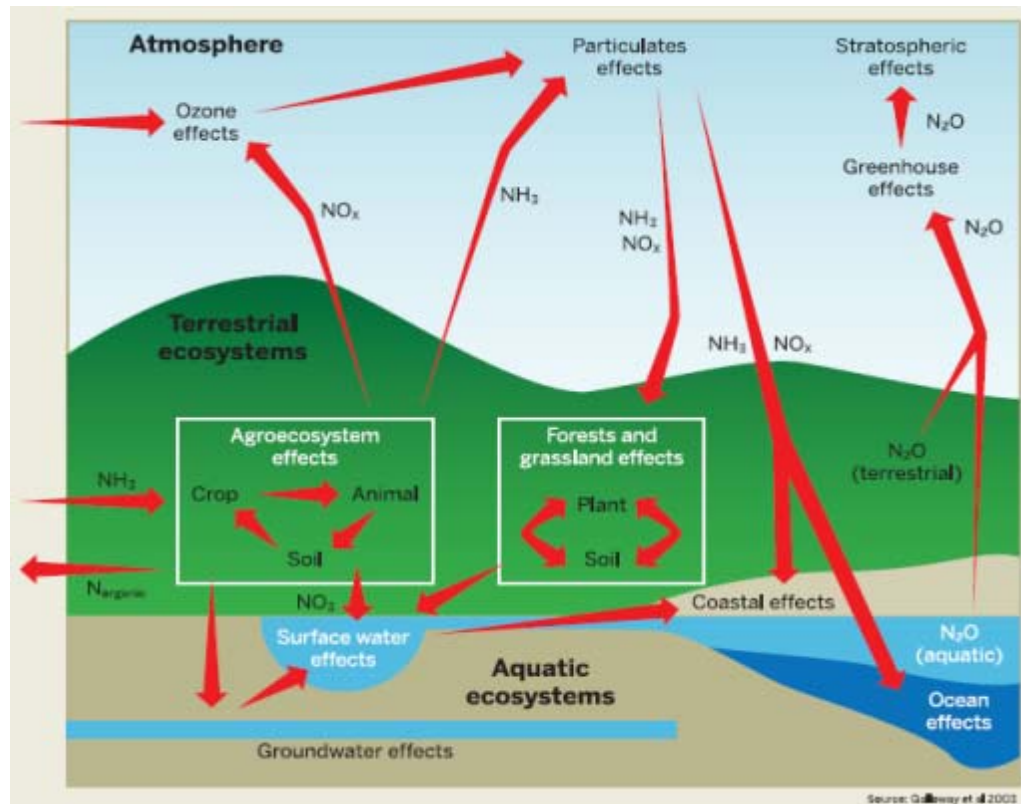
Earth-system process	Parameters	Proposed boundary	Current status	Pre-industrial value
Climate change	(i) Atmospheric carbon dioxide concentration (parts per million by volume)	350	387	280
	(ii) Change in radiative forcing (watts per metre squared)	1	1.5	0
Rate of biodiversity loss	Extinction rate (number of species per million species per year)	10	>100	0.1-1
Nitrogen cycle (part of a boundary with the phosphorus cycle)	Amount of N ₂ removed from the atmosphere for human use (millions of tonnes per year)	35	121	0
Phosphorus cycle (part of a boundary with the nitrogen cycle)	Quantity of P flowing into the oceans (millions of tonnes per year)	11	8.5-9.5	-1
Stratospheric ozone depletion	Concentration of ozone (Dobson unit)	276	283	290
Ocean acidification	Global mean saturation state of aragonite in surface seawater	2.73	2.90	3.44
Global freshwater use	Consumption of freshwater by humans (km ³ per year)	4,000	2,600	415
Change in land use	Percentage of global land cover converted to cropland	15	11.7	Low
Atmospheric aerosol loading	Overall particulate concentration in the atmosphere, on a regional basis		To be determined	
Chemical pollution	For example, amount emitted to, or concentration of persistent organic pollutants, plastics, endocrine disruptors, heavy metals and nuclear waste in, the global environment, or the effect on ecosystem and functioning of Earth system thereof		To be determined	

History of reactive Nitrogen (Nr) development



Modified after Galloway and Cowling 2002

The reactive nitrogen formation and cascade

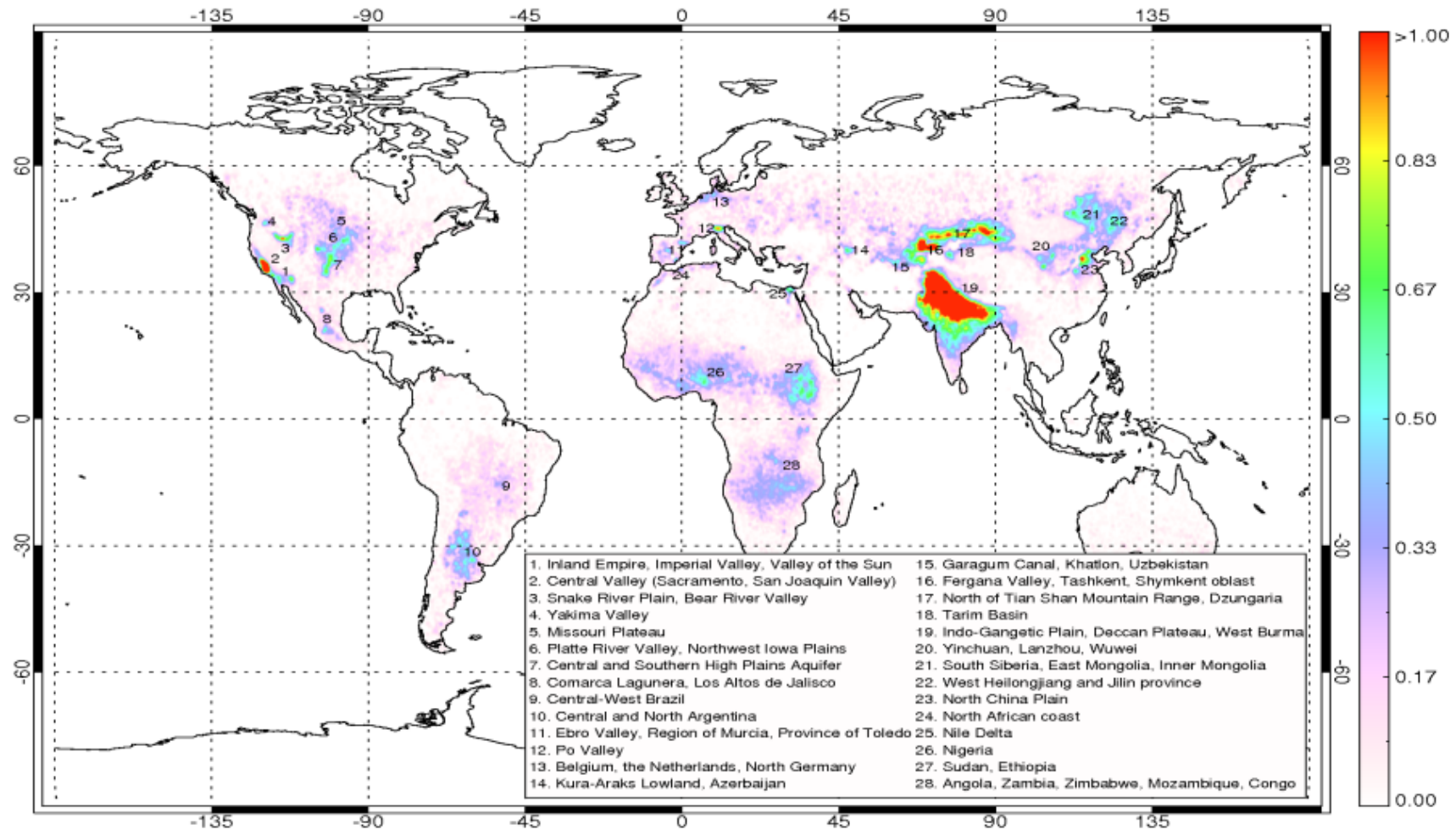


Cascade through the environment

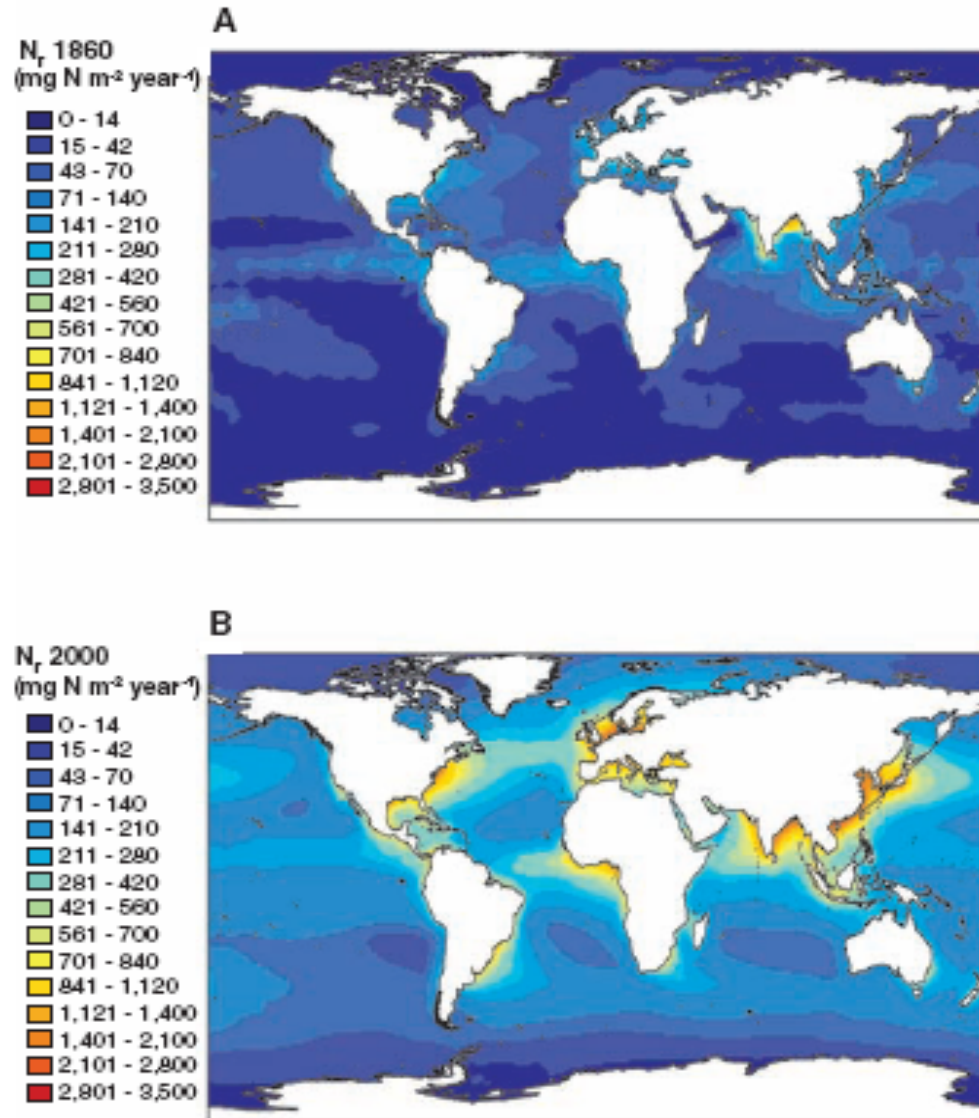
- Agriculture is main N user in EU-27
- Less than 50% of N input is utilized
- Agriculture is main source of N losses in EU-27:
 - NH_3 to air: ~90% of total NH_3 emissions
 - N_2O to air: ~60% of total N_2O emissions
 - N in surface waters: ~40-60% of total N emissions
- Self sufficiency of food in EU-27 is ~100%, but massive import of soya
- Global food production has to increase ~50% by 2050

First satellite based ammonia concentrations

Clarisse et al. 2009



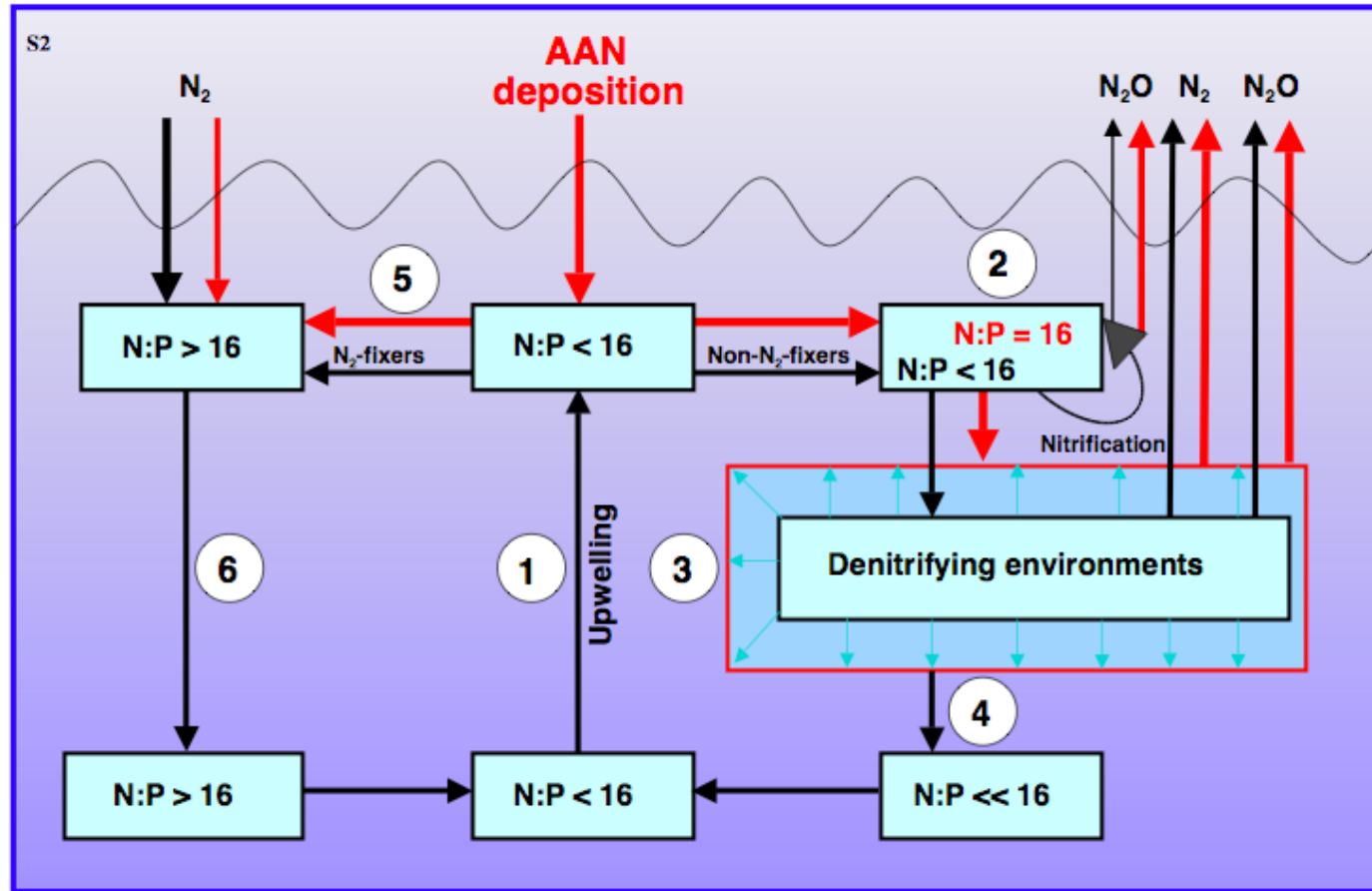
Modelled atmospheric deposition ($\text{mgN m}^{-2} \text{y}^{-1}$)



N_r deposition is not only increasing but also affecting open ocean regions that are currently oligotrophic!



Expected changes in the oceanic N:P ratios from anthropogenic atmospheric deposition

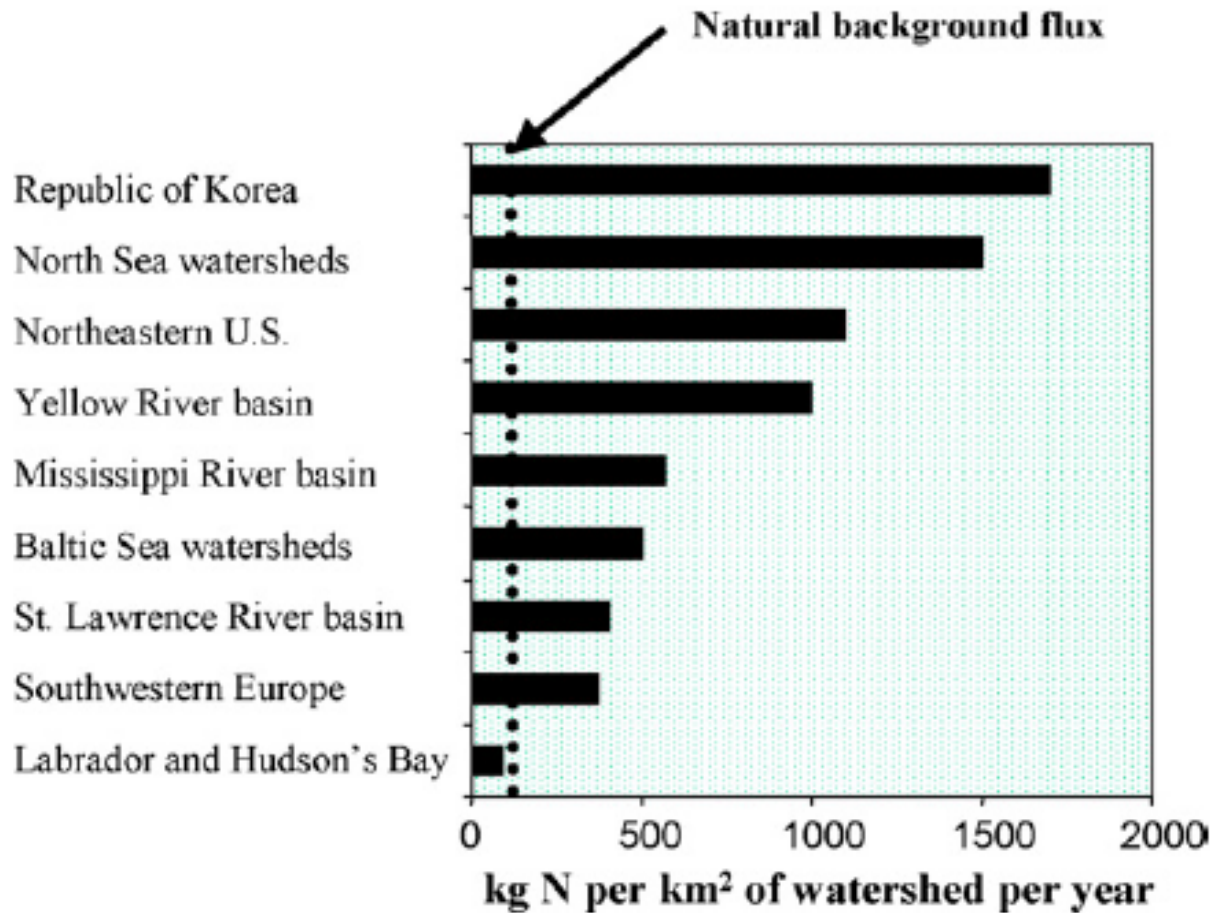


—————→ natural state
 —————→ changes due to AAN

① steps 1 through 6

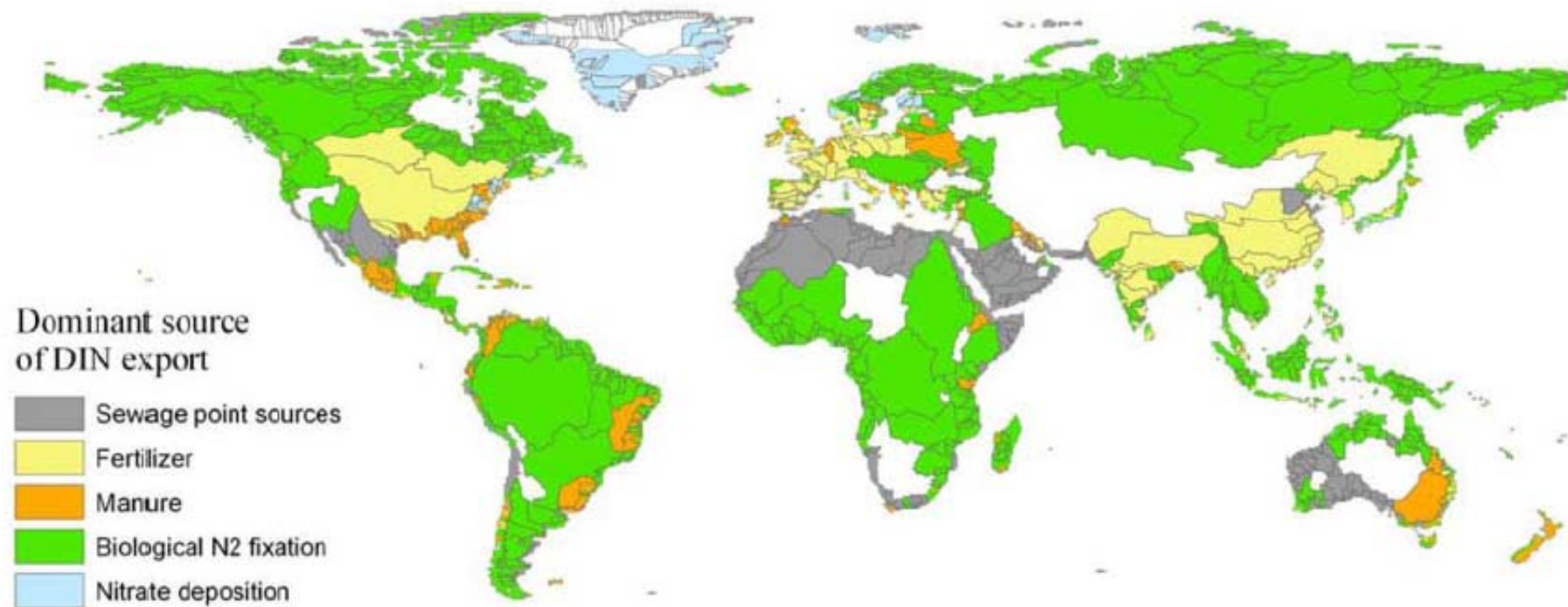
Duce et al. 2008

Riverine input is the most important flux to the coastal ocean

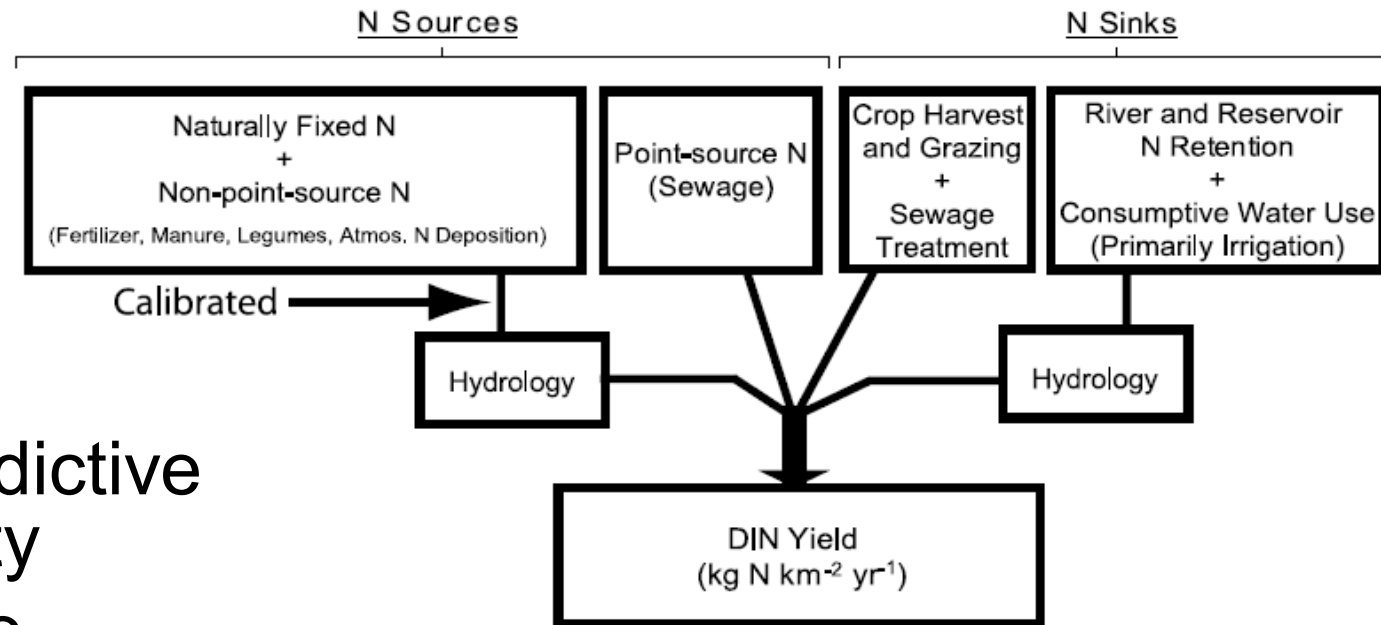


- Many large rivers receive much higher N loads in their catchments than the natural background level.

NEWS-DIN-predicted dominant sources of DIN export



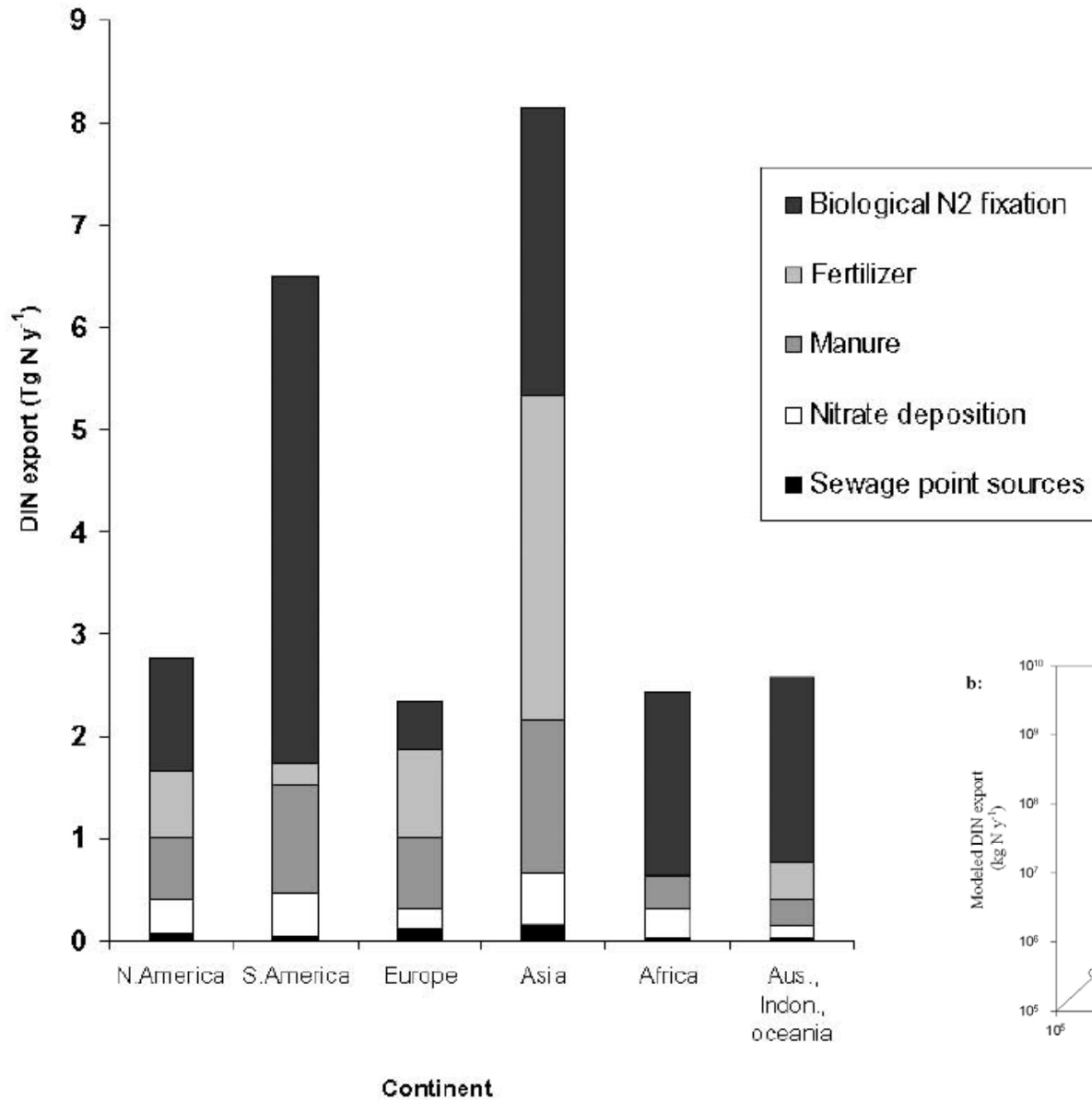
NEWS Model



- No predictive capacity
- No time dependence
- Box model type

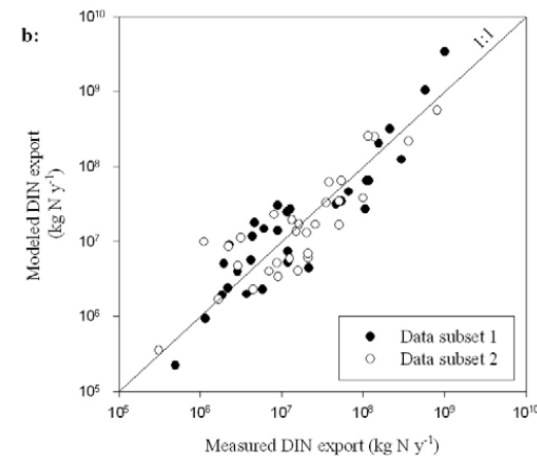
The NEWS - DIN model

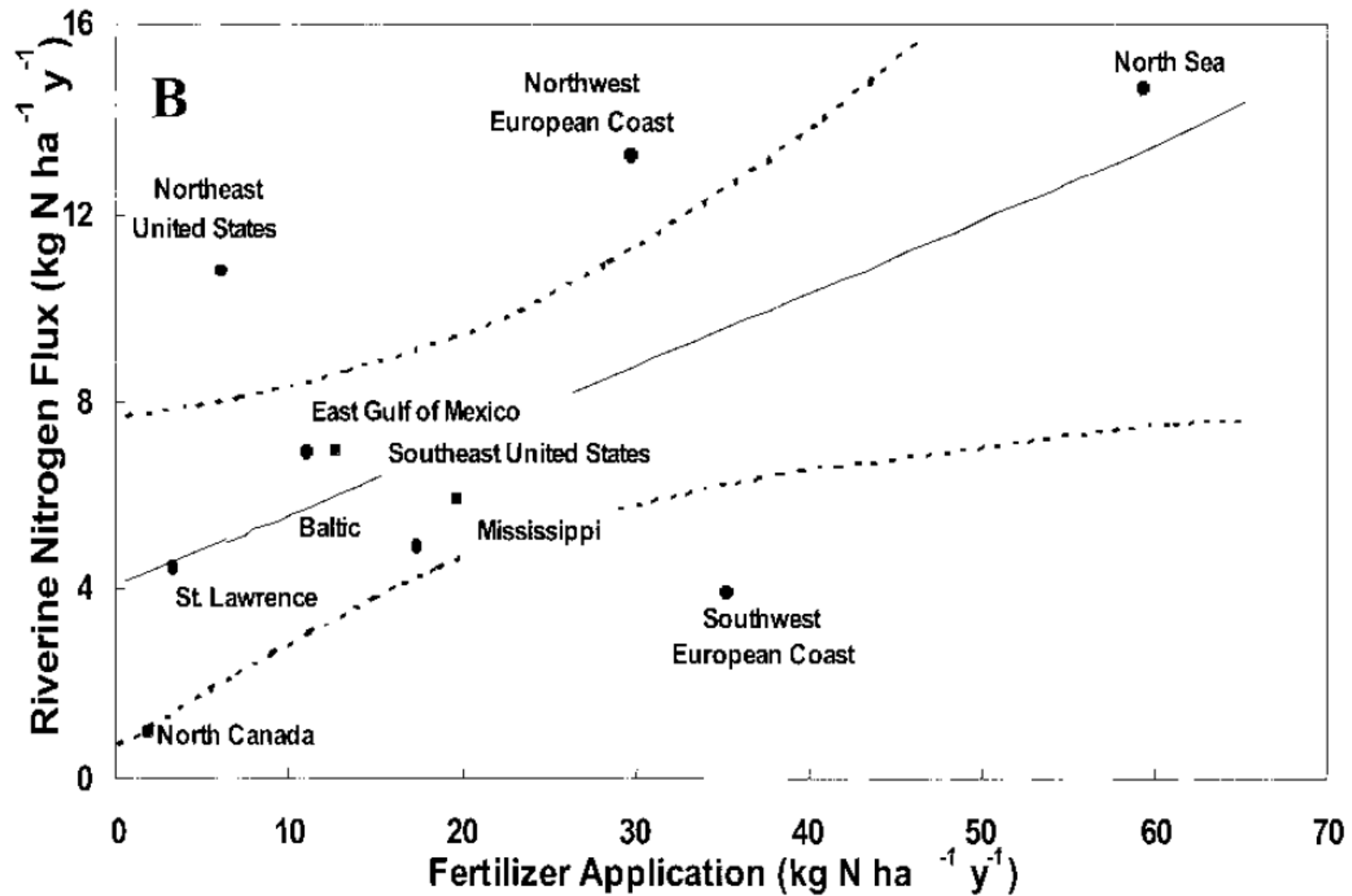
Nutrient Export from Watersheds



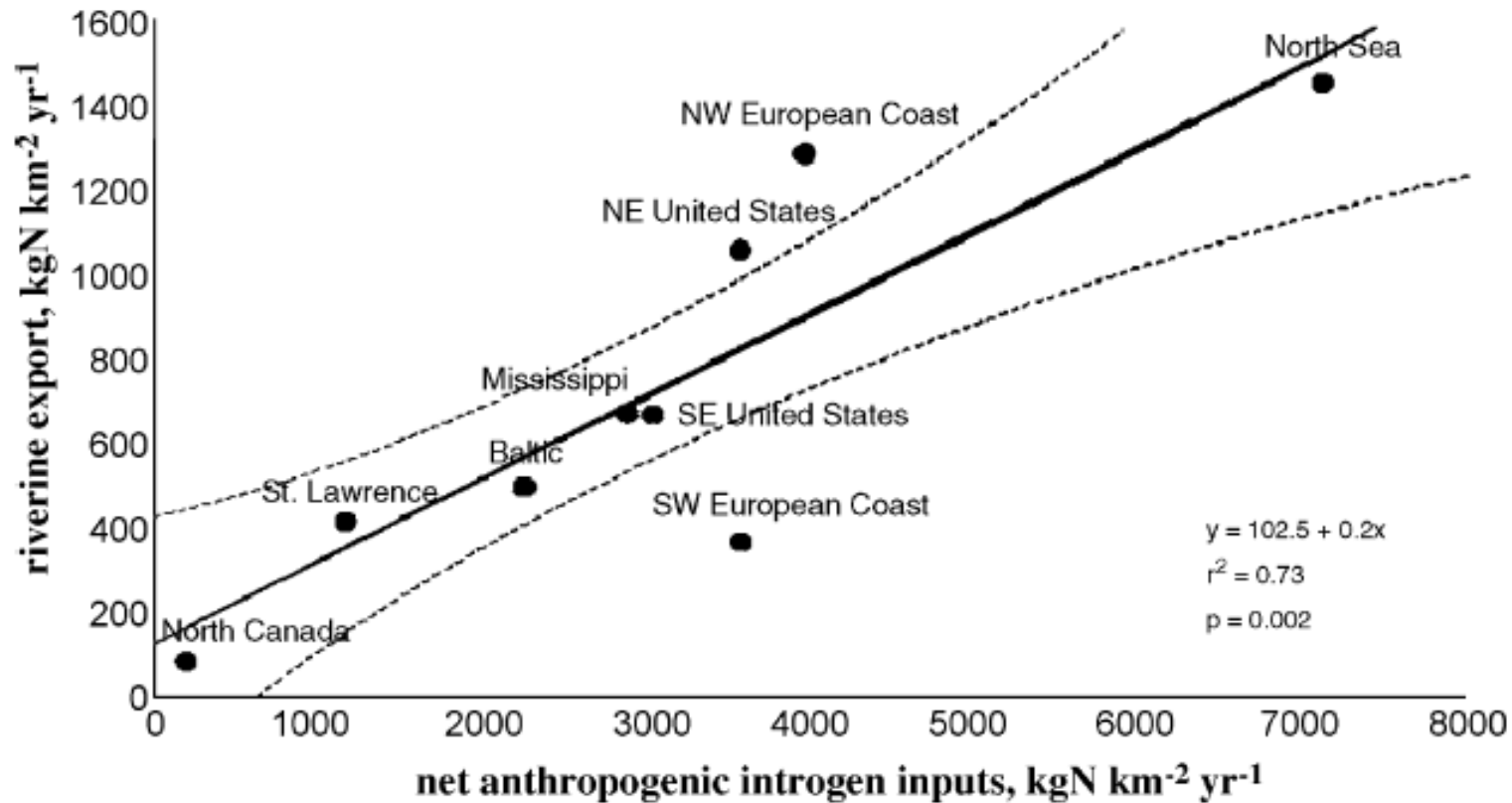
Most DIN is exported from Europe and Asia

The NEWS-DIN model results: 25 TgN y⁻¹ is the global yield, 16 TgN y⁻¹ is of anthr. origin



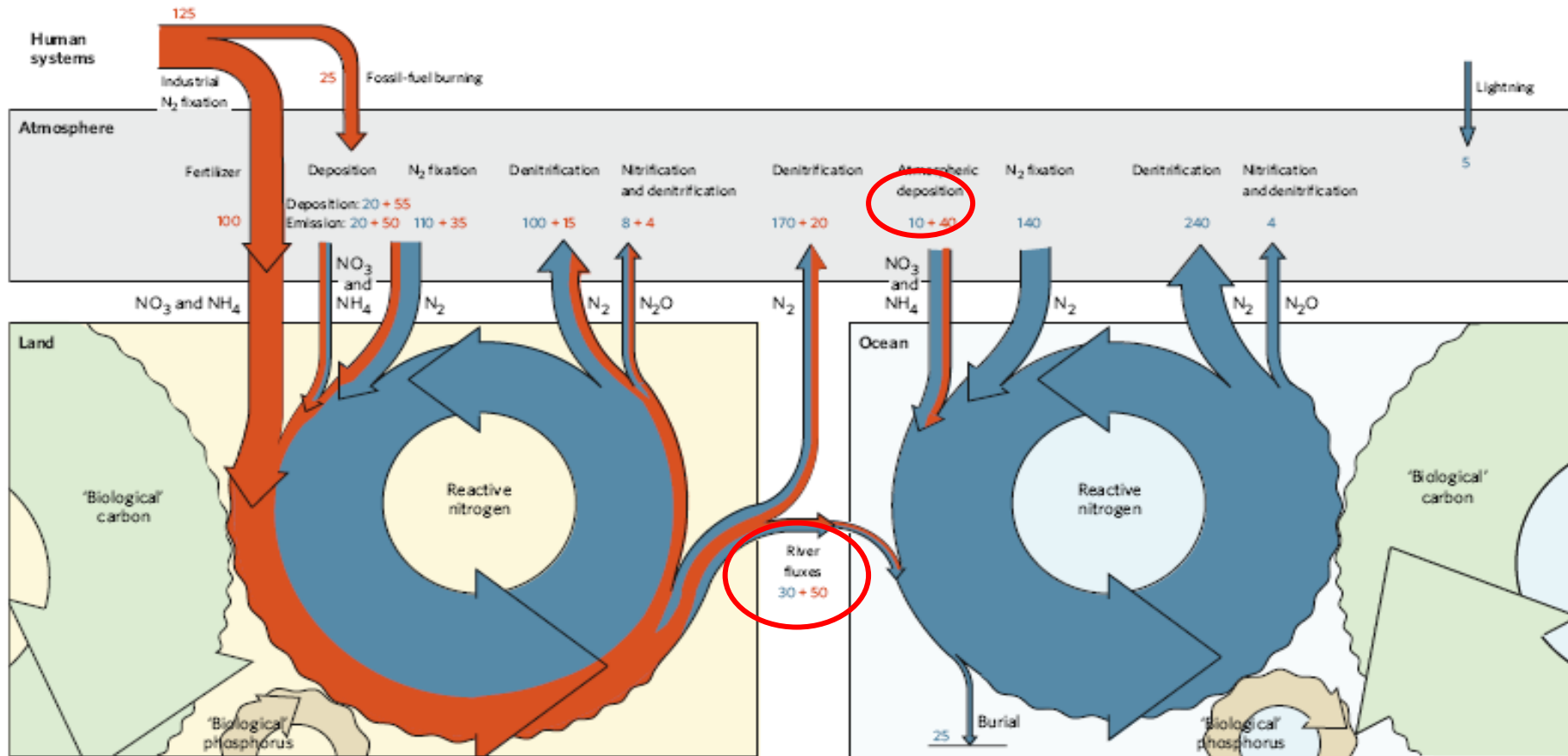


net anthropogenic nitrogen inputs



net anthropogenic nitrogen inputs (NANI):
 defined as the sum of nitrogen inputs as synthetic fertilizer, in nitrogen fixation associated with agriculture, as NO_y deposition, and the net import or export of nitrogen in foods and feeds.

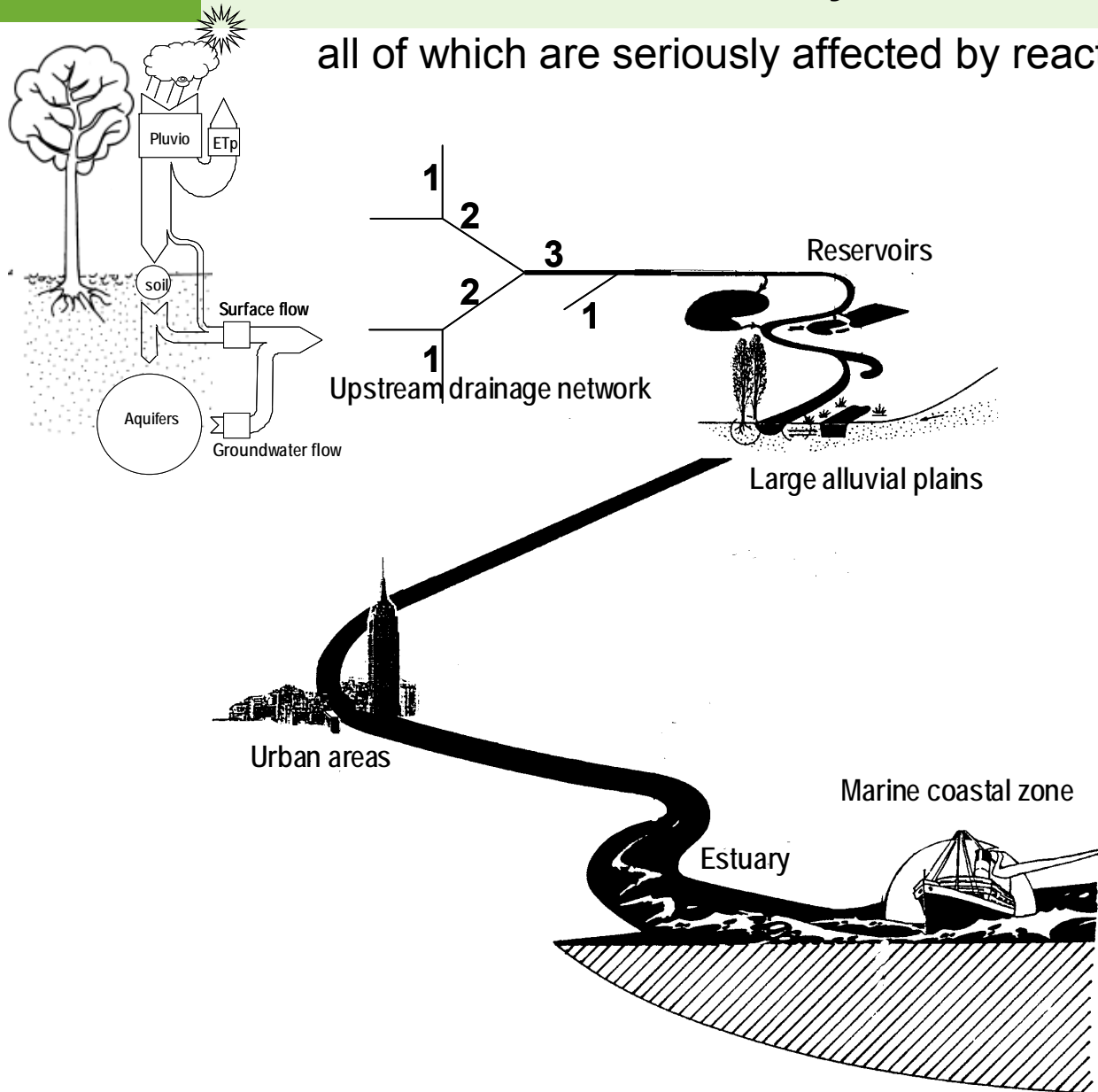
Global N cycle: link between land and ocean



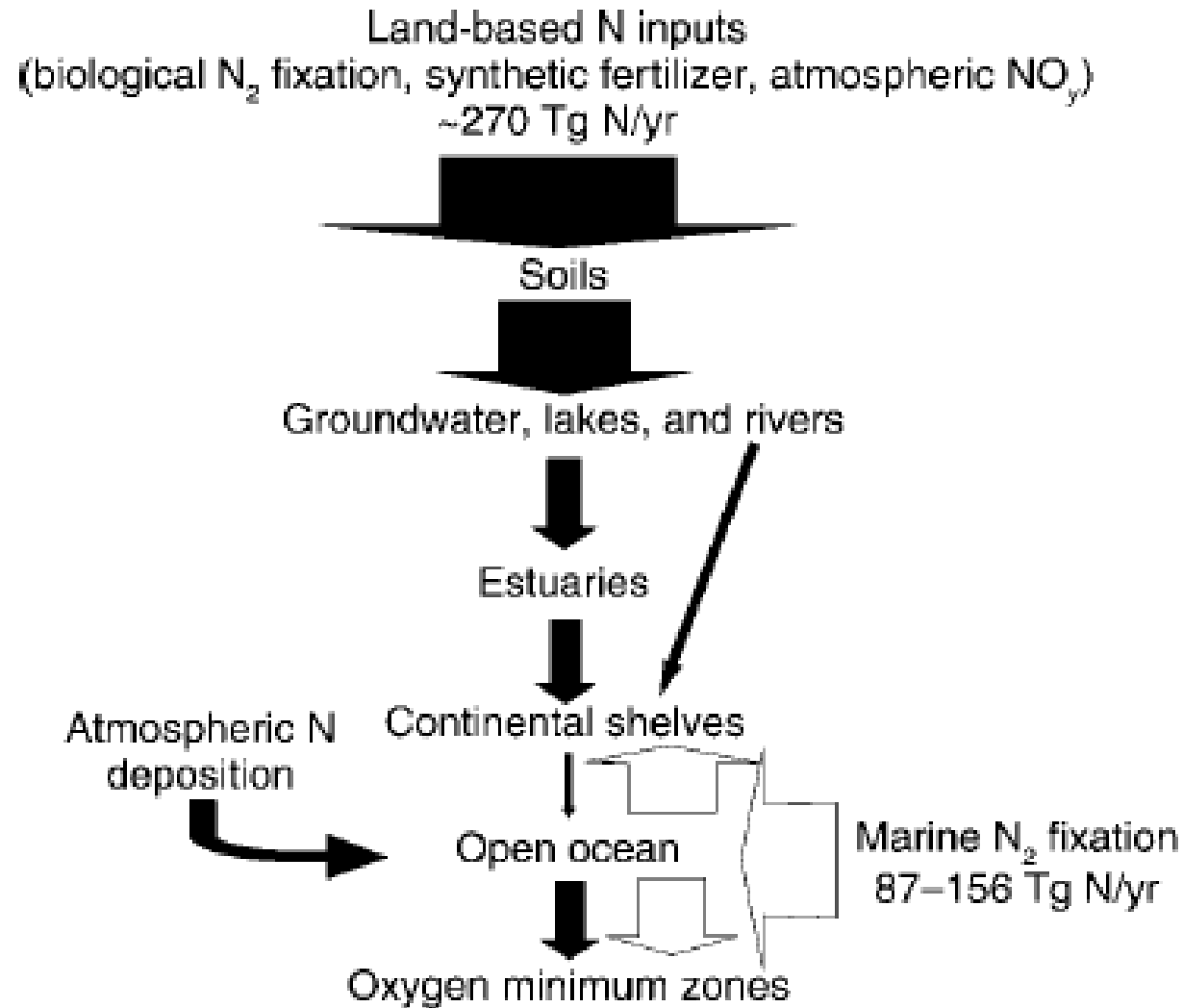


Headwater streams, groundwaters, rivers, estuaries and coastal seas form a **continuum of ecosystems**...

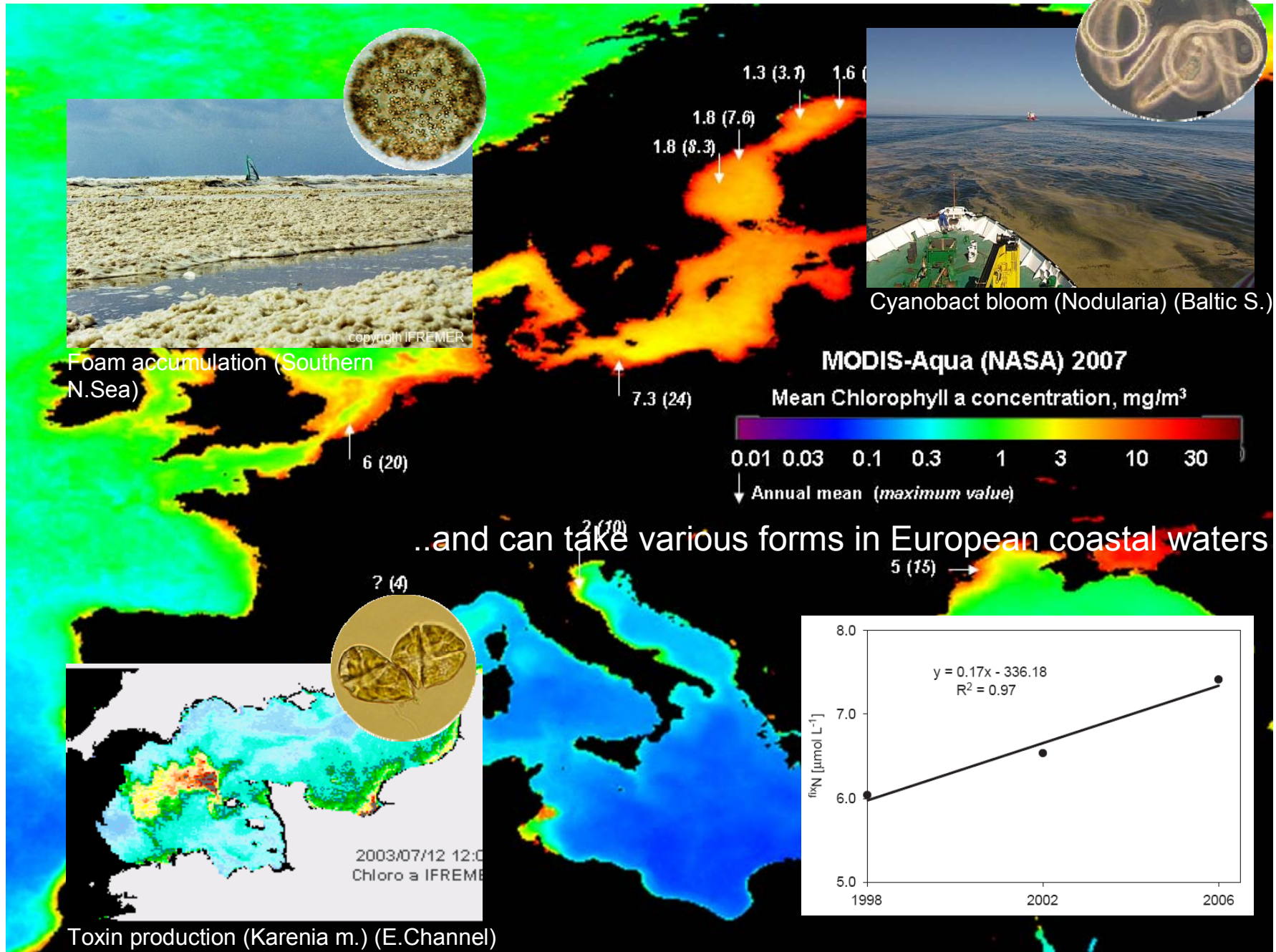
all of which are seriously affected by reactive nitrogen contamination.



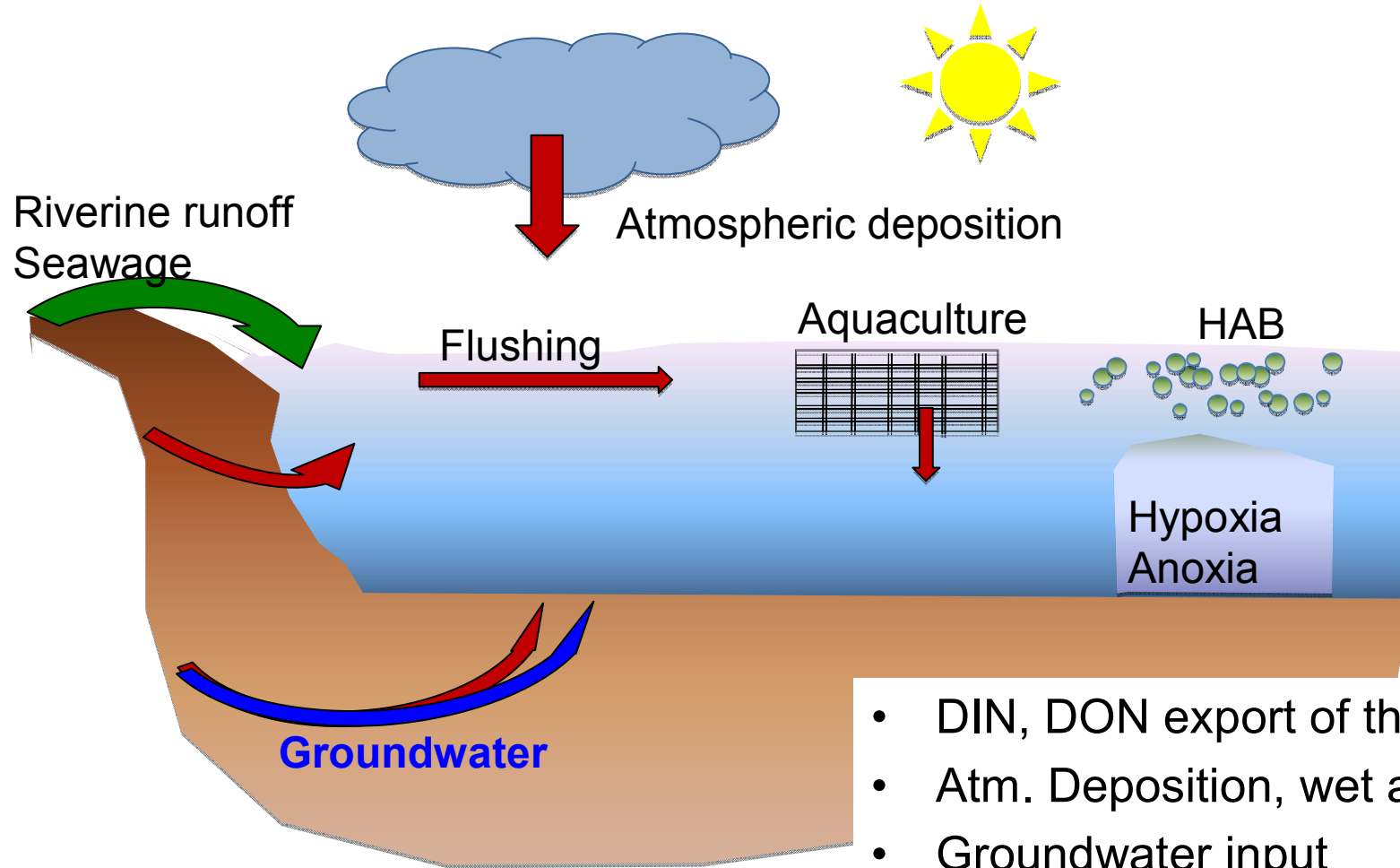
Nitrogen retention in watersheds



Coastal eutrophication is the ultimate manifestation of these perturbations

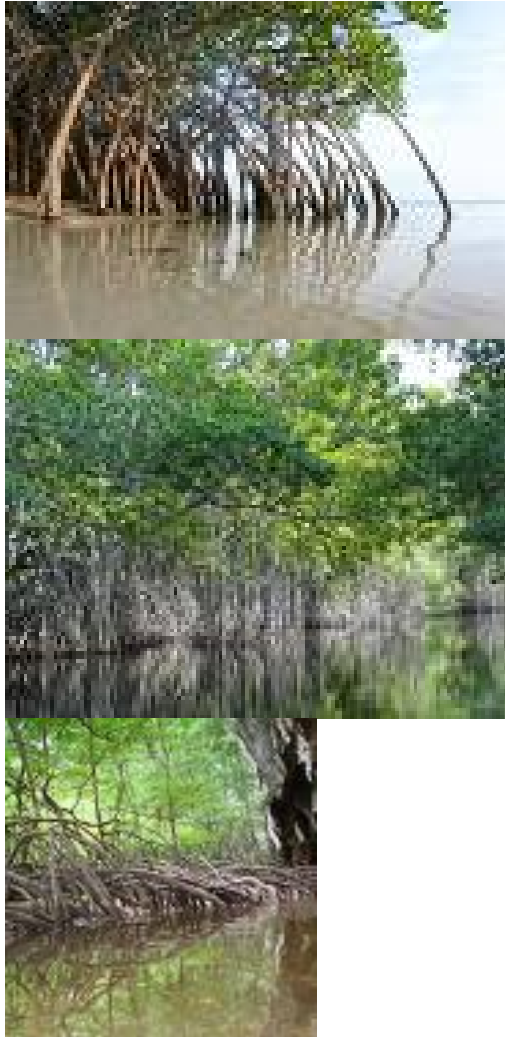


Four major antropogenic N sources for coastal seas



- DIN, DON export of the rivers
- Atm. Deposition, wet and dry
- Groundwater input
- Fish, shrimp etc. farms

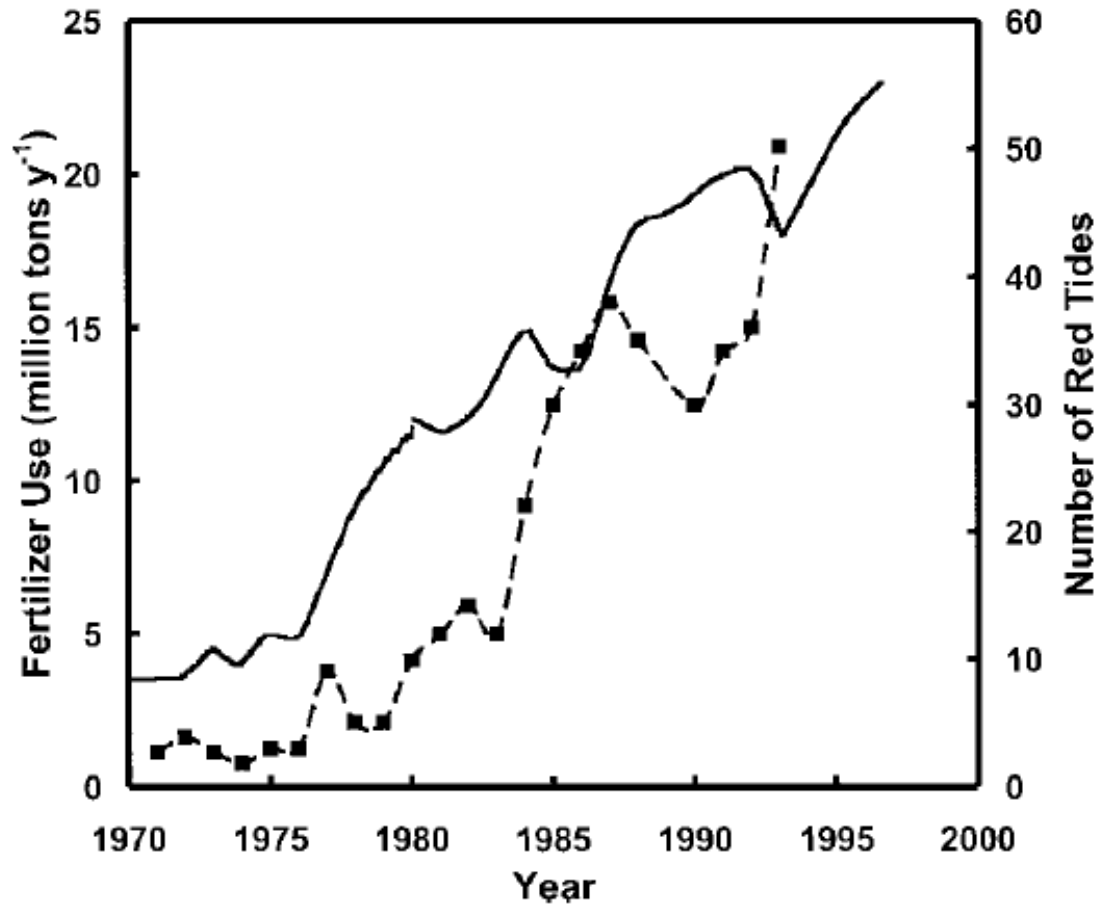
Role of Mangrove forests



- M. fringe 60 – 75% of tropical shores (Spalding et al., 1997) and cover an area of $11 - 24 \times 10^{10} \text{ m}^2$
- They are essential for the regulation of the DIN concentration reaching the coastal ocean.
- In the forests high denitrification rates are encountered.
- M. could strongly reduce DIN concentrations from a polluted river flowing through a mangrove.
- BUT between 35% of dense mangrove areas have been cleared for conversion into shrimp and fish farms, agricultural croplands and urban areas, between 1980 and 2000 globally.

- There are very clear links between the human nitrogen fixation and fertilizer over-application in most countries worldwide – except most countries in Africa.
- Moreover it is clear that coastal eutrophication is a consequence of mainly the diffuse nitrogen input from farming practices.
- Atmospheric deposition plays another important role for eutrophication of inland and coastal waters.

Fertilizer use and number of red tides



The HAB problem is significant and growing worldwide and poses a major threat to public health, ecosystem health, and to fisheries and economic development.

Hamful Algal Blooms (HAB)

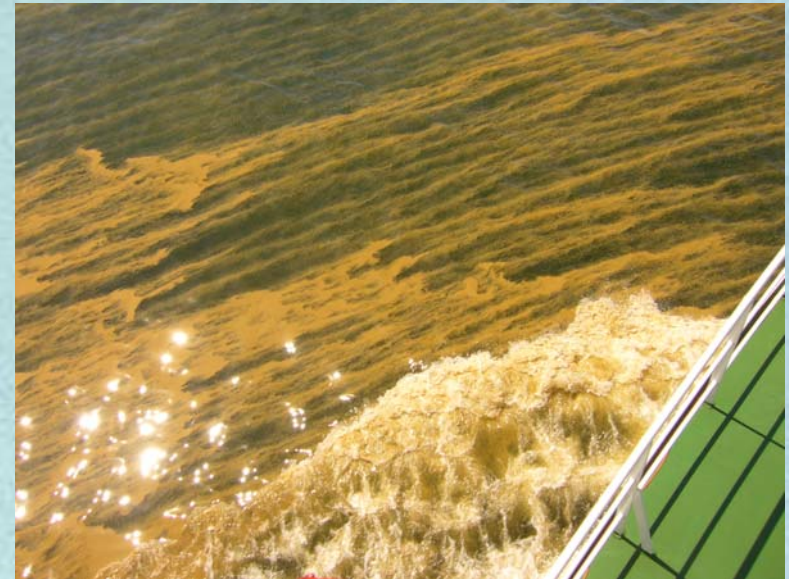
Definition by the scientific community ...

...to describe a diverse array of blooms of both microscopic and macroscopic marine algae which produce toxic effects on humans and other organisms

physical impairment of fish and shellfish; nuisance conditions from odors and discoloration of waters or habitats.

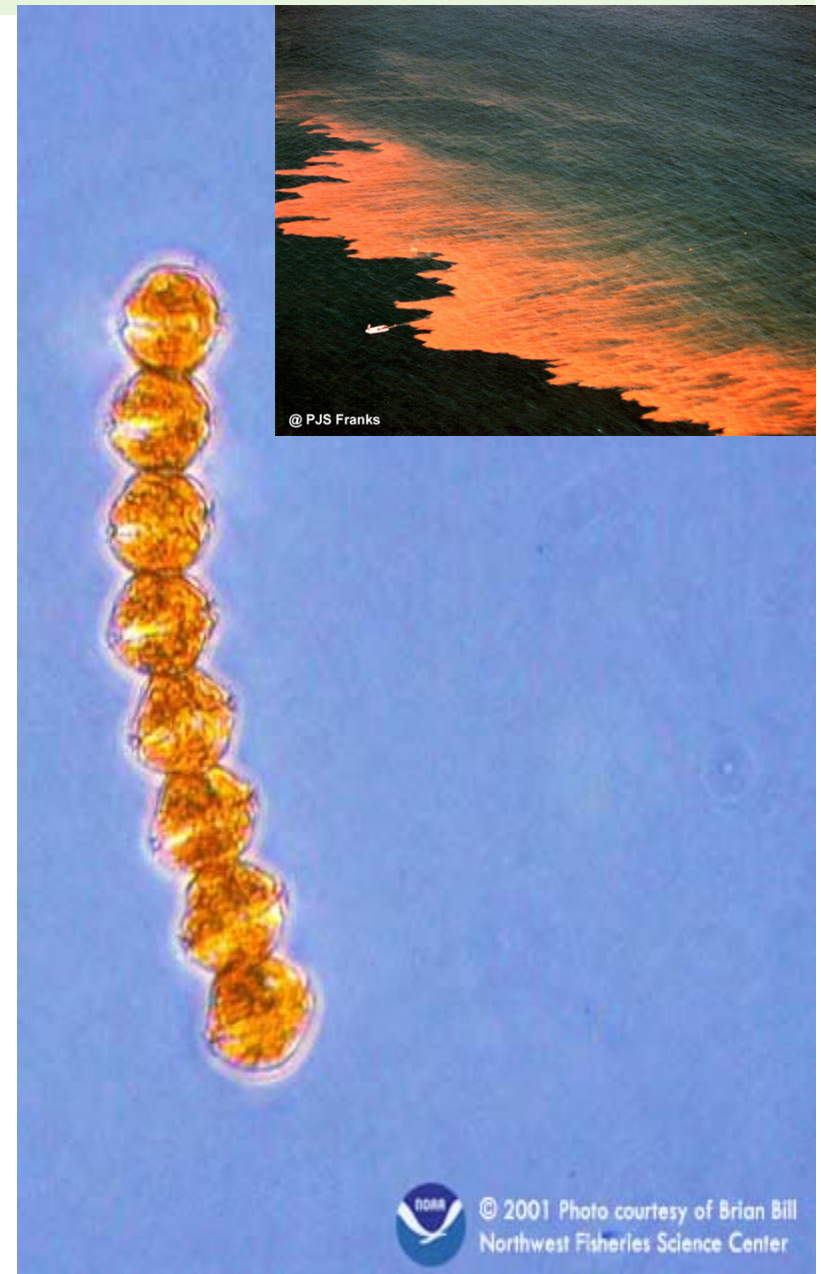
Cyanobacteria- „blue-green algae“

- prokaryotic
- cell wall
- more abundant in freshwater/brackish waters
- able to fix N₂
- heterocystic: *Anabaena*, *Aphanizomenon*
- non-heterocystic: *Trichodesmium*
- unicellular: *Microcystis*
- toxins: Anatoxins, Microcystins, Nodularins, Saxitoxins



Dinoflagellates- „Red tides“

- eukaryotic
- cell wall: cellulose
- more abundant in marine environments
- dormant resting stages
- *Alexandrium*, *Gymnodinium*, *Karenia*
- Paralytic Shellfish Poisoning – (PSP) in *Pfisteria* species
- Other toxins: Brevetoxins, Saxitoxins



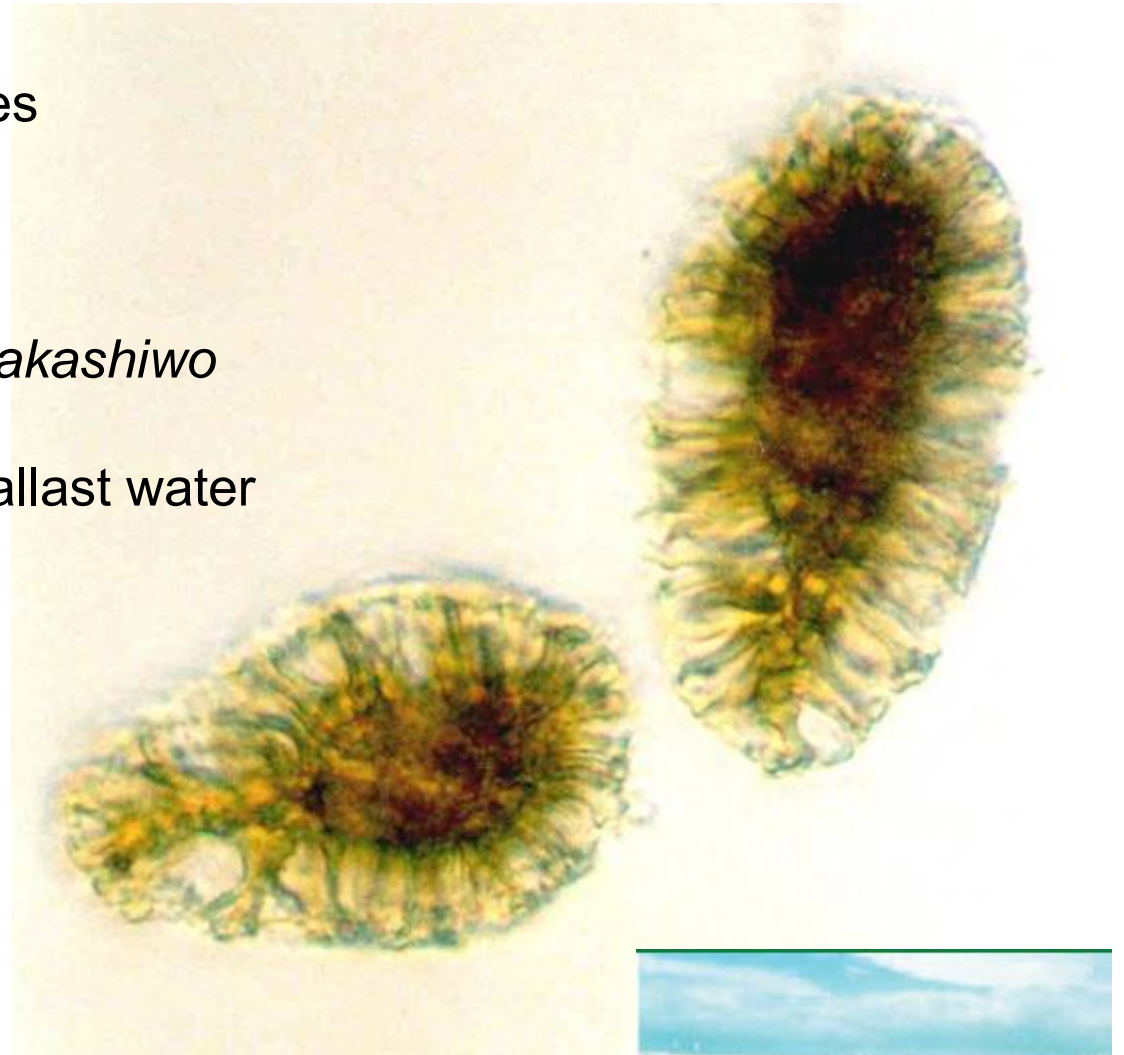
Diatoms- „brown tide“

- eukaryotic
- freshwater+ marine
- single celled
- cell wall: silicate
- *Chaetocerus*, *Skeletonema*
Thalassiosira
- Toxin: domoic acid, food web
transferred neurotoxin
- Amnesic Shellfish Poisoning (ASP)
in *Pseudo-nitzschia*



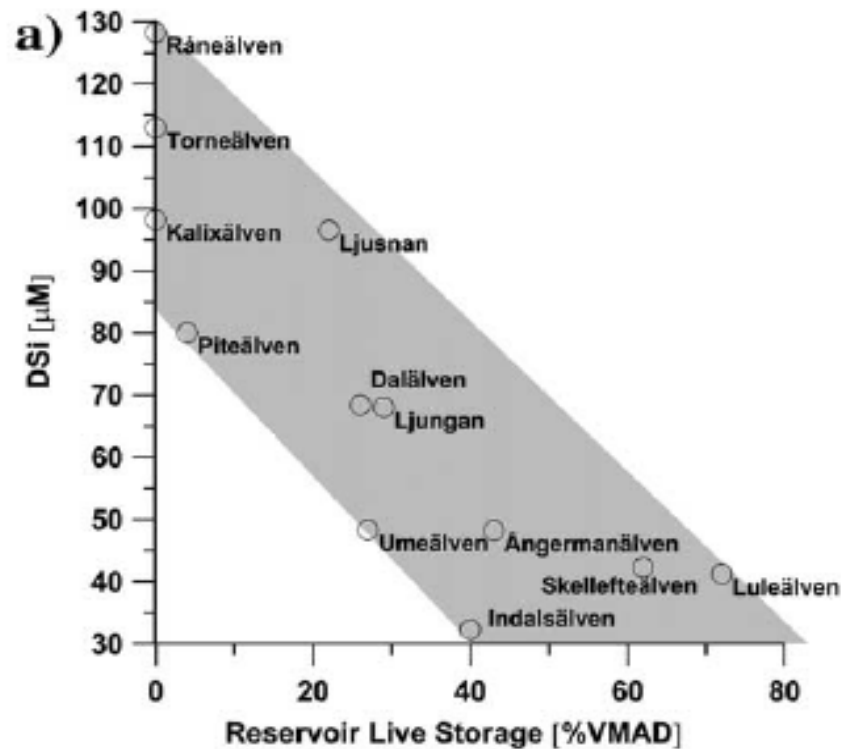
Raphidophytes and Haptophytes

- eukaryotic
- R. no rigid cell wall
- R: *Chattonella*, *Heterosigma akashiwo*
- H: *Emiliana*, *Phaeocystis*
- exotic species allocated by ballast water

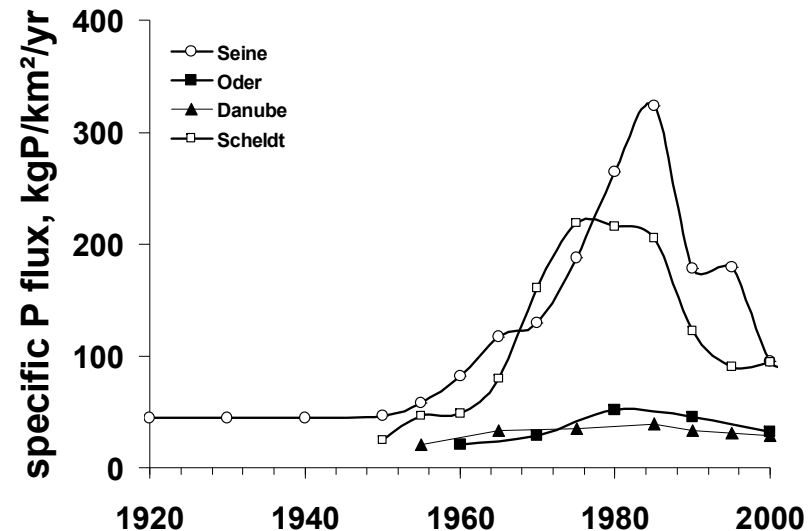
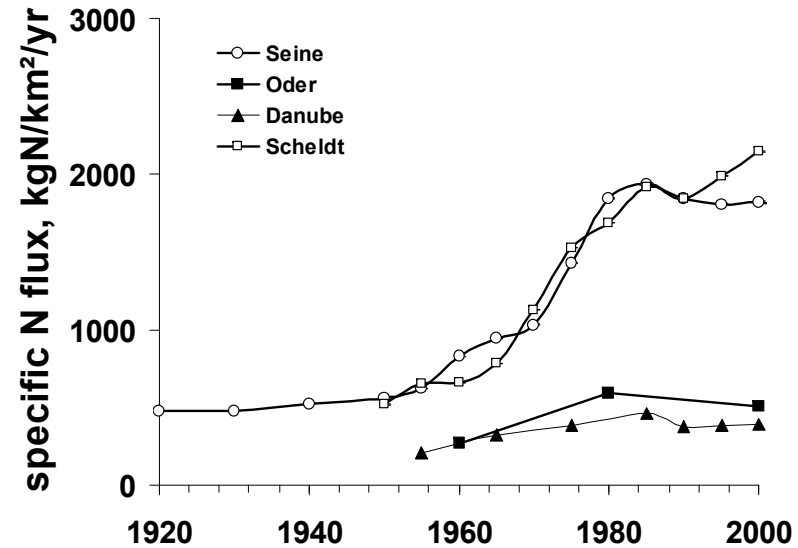


Imbalance between nitrogen (and phosphorus) inputs, changing the N:P ratio

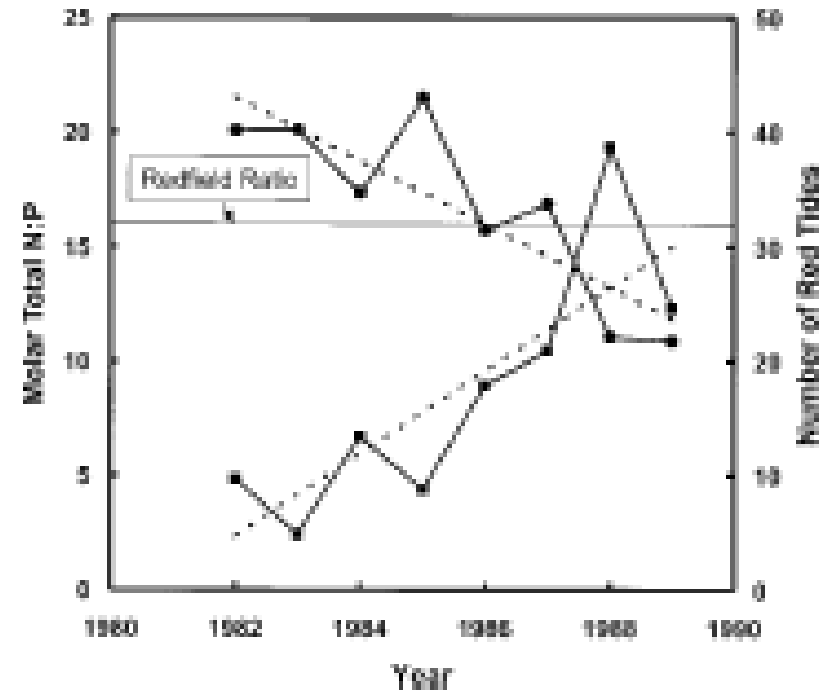
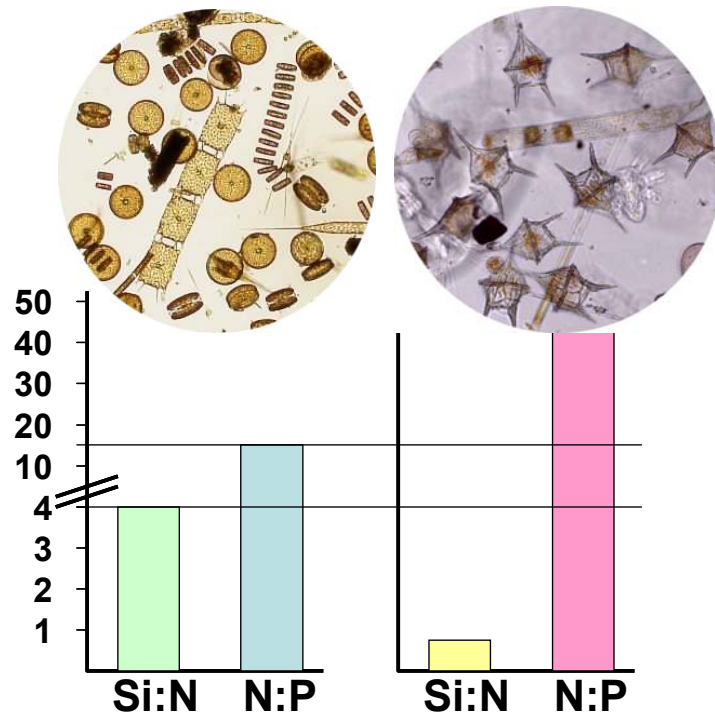
- ...with respect to **silica** inputs, compared to the requirements of diatoms growth
- The trends in river inputs are to decreasing riverine **silica** inputs because of prolonged residence time in reservoirs



increasing riverine **nitrogen** inputs

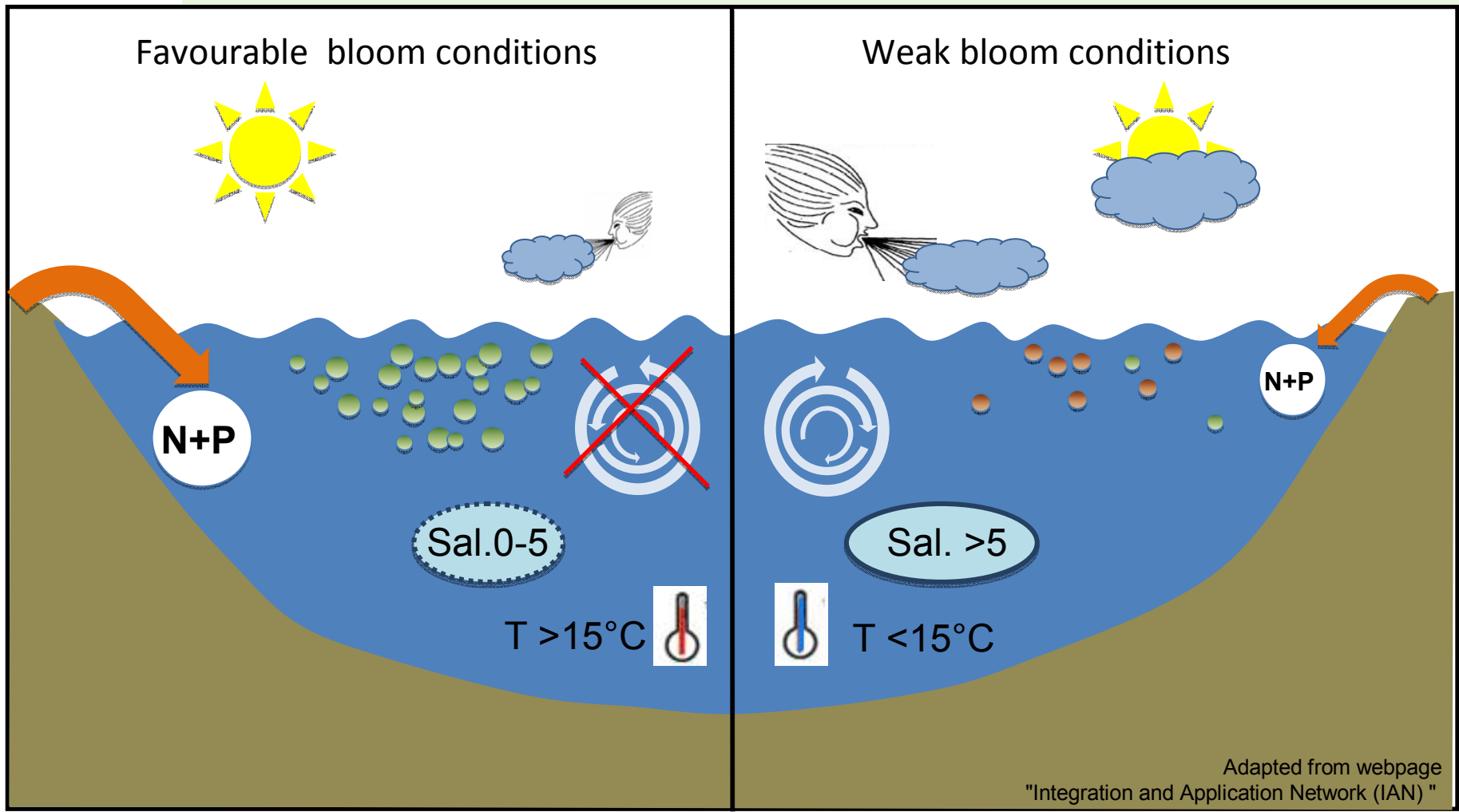


Consequence from the imbalance between nitrogen (and phosphorus) inputs



Imbalanced nutrient inputs lead to drastic changes in the phytoplankton community

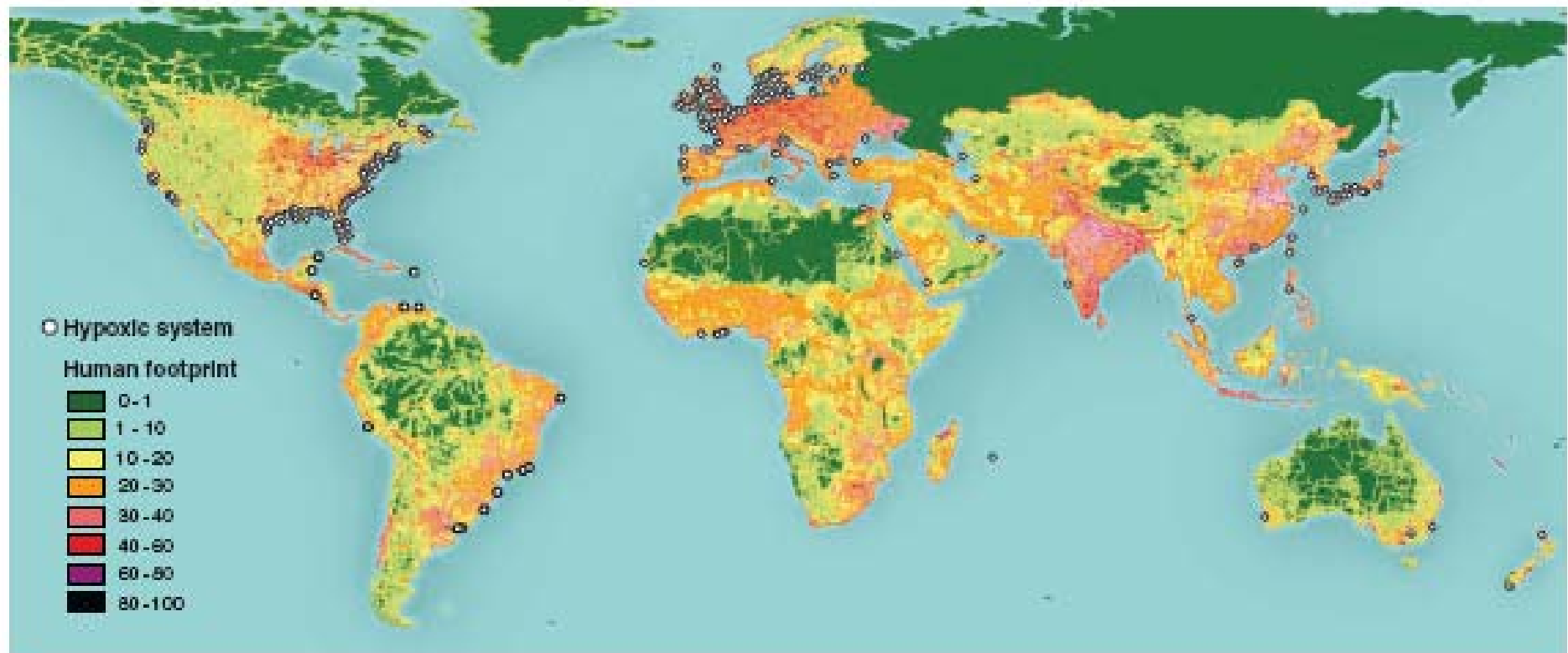
Other possible controls of blooms



Adapted from webpage "Integration and Application Network (IAN) "

	Flow	Water Temp	Mixing	Sunlight	Salinity
Intense blooms:	High flow 	Warm water (>15°C) 	Still water (little wind) 	High light (little cloud) 	Low salinity (NaCl: 0-5%)
No/weak blooms:	Low flow 	Cooler water (<15°C) 	Mixed water (Winds) 	Lower light (cloudy) 	Higher salinity (NaCl: >5%)

Sites with reported eutrophication related dead zones



Diaz and Rosenberg 2008

Top-down control

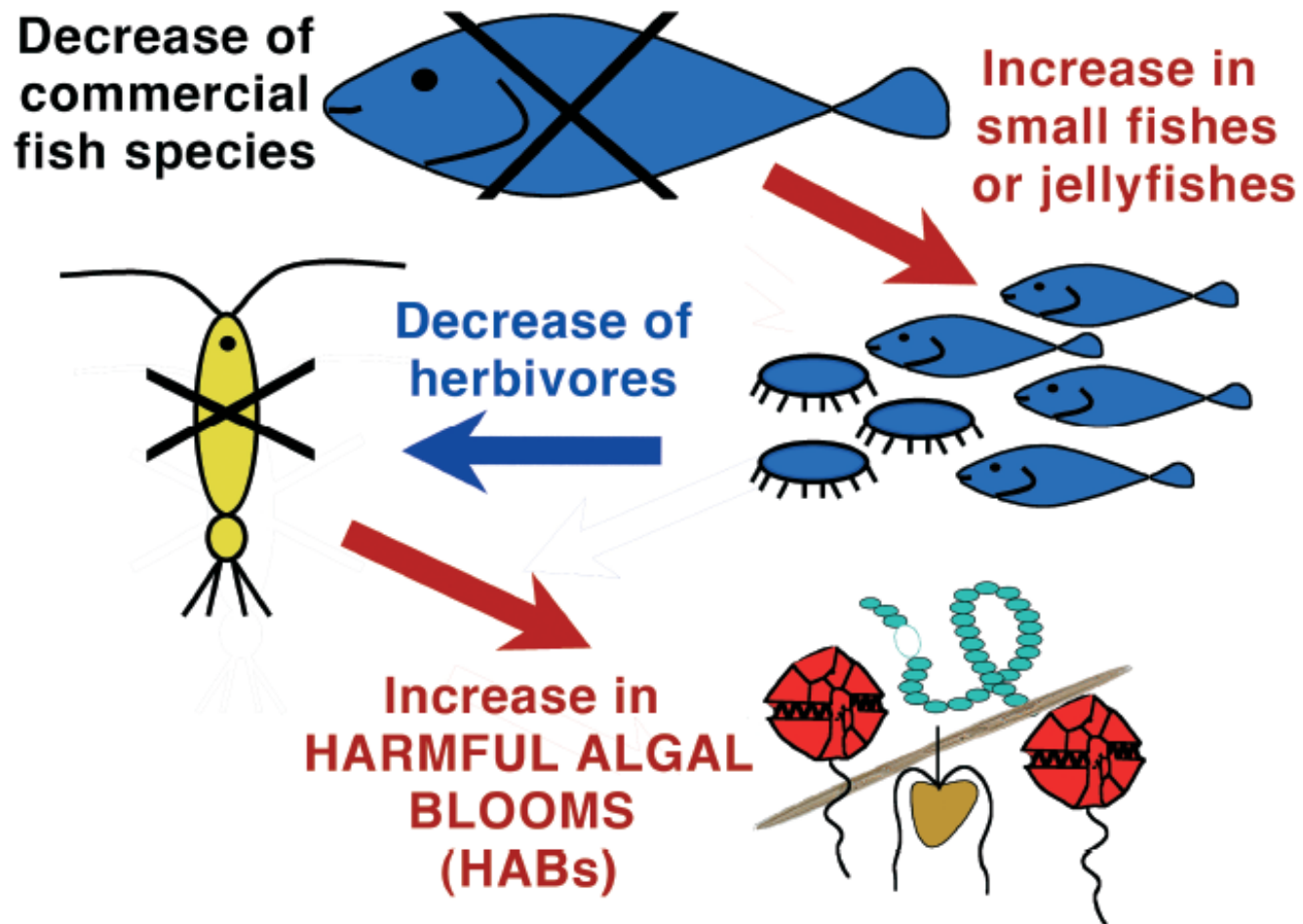


Fig 27.1. Possible pathway for HAB formation when the “top-down control” of the food chain is disrupted, as e.g., by overfishing. (Redrawn from Granéli 2004)



Competitive advantage - Mixotrophy

= Combination of photoautotrophy and heterotrophy

Phagotrophy
= prey ingestion

Osmotrophy
= uptake of dissolved
compounds

TYPE I
"Ideal Mixotrophy"
Balanced phototrophy and phagotrophy

TYPE II
Phagotrophic "Algae"
Primarily phototrophic

IIA
Feed when DIN is limiting

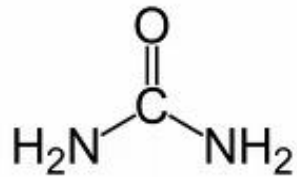
IIB
Feed when a trace organic
growth factor is limiting

IIC
Feed when light is limiting
(to get Carbon)

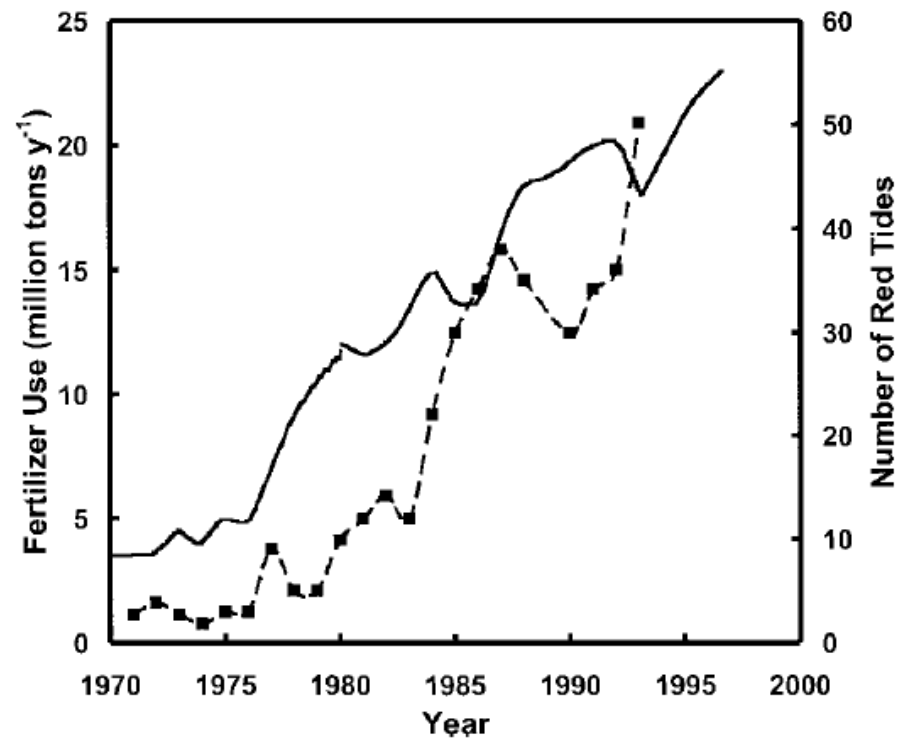
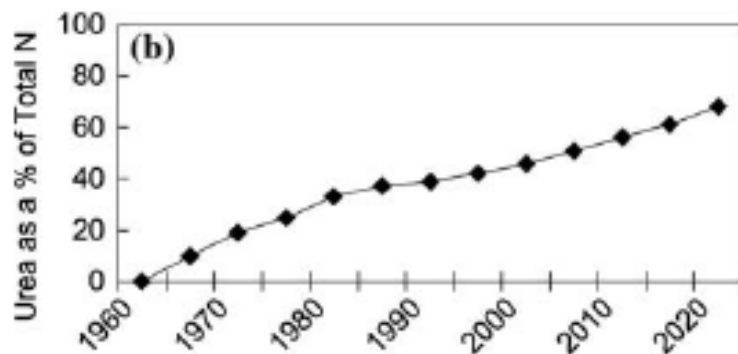
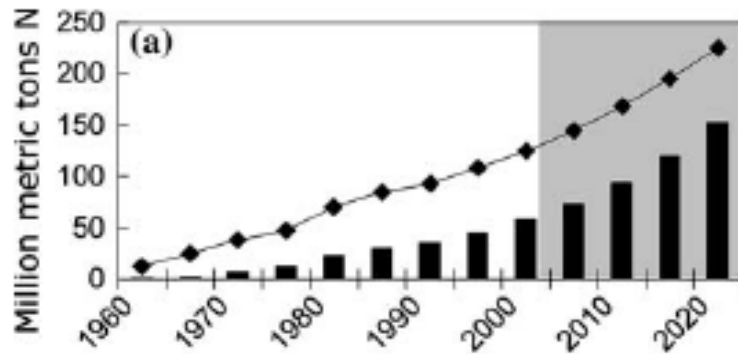
TYPE III
Photosynthetic "Protozoa"
primarily phagotrophic

IIIA
with "own" plastids
Photosynthesis when prey is limiting

IIIB
with harbored algal endosymbionts
Photosynthesis supplements carbon nutrition



Special importance of urea



- Advantages of urea uses over ammonia: less explosive, granulas, easy transportation, 2 N instead of just 1 N per mol, longer residence times in soils
- Urea production increases and is heavily subsidised – 50% of global fertilizer production is nowadays urea!
- China and India account for half of the global consumption.
- India, Pakistan, Bangladesh subsidise the use which leads to heavy over-consumption of urea fertilizer.
- Urea in soils usually hydrolysed and then nitrified, but also it reaches the water unchanged.

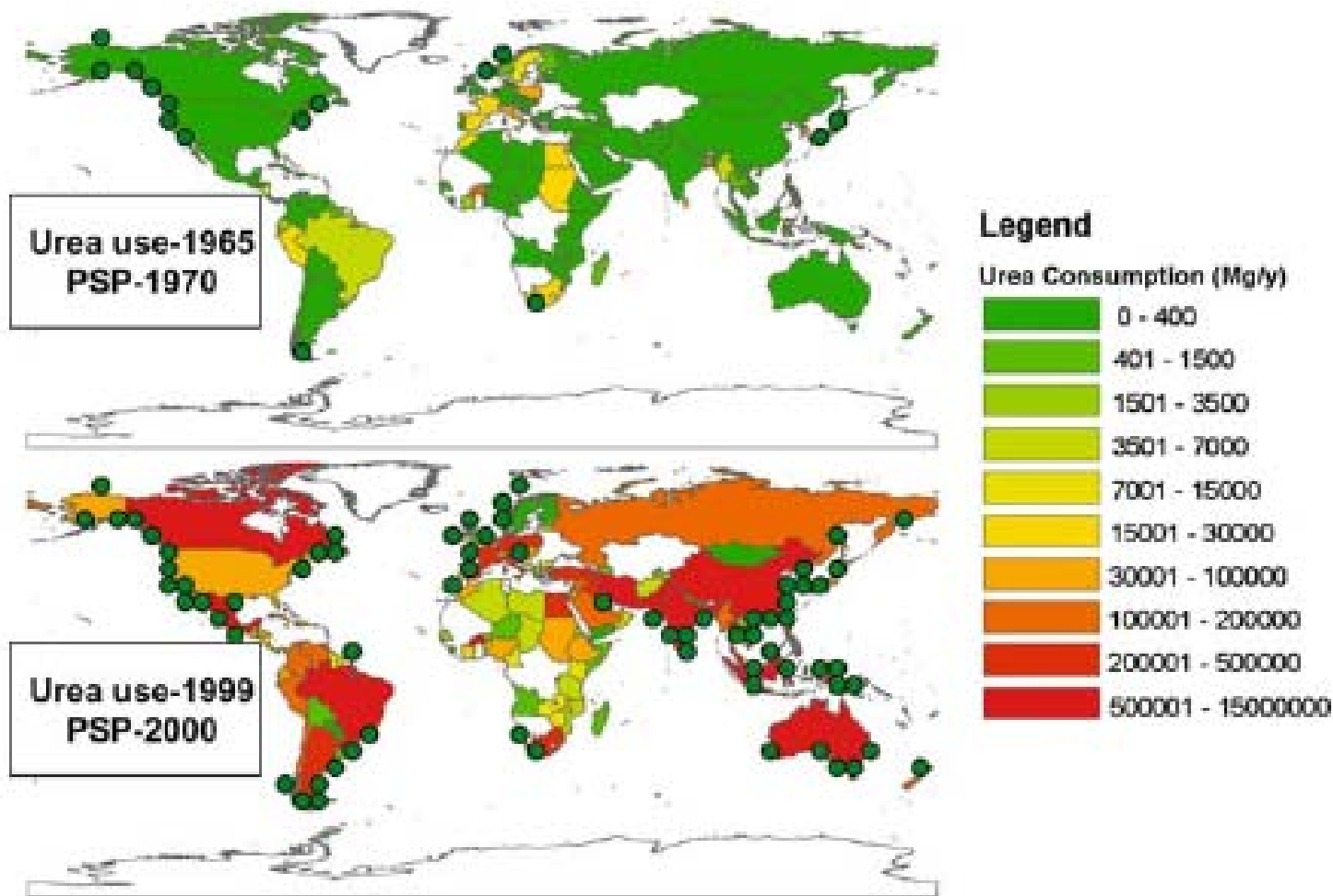
- Used as a feed additive
- Urea-based herbicides and pesticides – this includes direct applications on land and it then enters surface waters
- Spread on oil-spills
- Use in pharmacy eg as moistening additive

Table 1. Range of concentrations ($\mu\text{M-N}$) of urea from some coastal and estuarine sites reported in the literature.

Location	Range of concentration	Reference
Savannah R., Georgia	0.59–8.89	Remsen 1971
Ogeechee R., Georgia	1.26–4.89	Remsen 1971
Great South Bay, New York	0.6–9.4	Kaufman et al. 1983
Mankyung and Dongjin River estuary, Korea	0.6–4.3	Cho et al. 1996
Oslofjord, Norway	0.1–10.0	Kristiansen 1983
Chesapeake Bay, mainstem	< 0.01–8.16	Lomas et al. 2002
Florida Bay, Florida	0.36–1.7	Glibert et al. 2004
Coastal Bays, Maryland	< 0.01–14.4	Glibert et al. 2005a
Kings Creek, Chesapeake Bay, Maryland	0.3–24.2	Glibert et al. 2005a
Chicomicomico R., Chesapeake Bay, Maryland	1.0–23.4	Glibert et al. 2005a
Baltic Sea	0.09–6.91	Stepanauskas et al. 2002
Knysna Estuary, South Africa	0.4–5.8	Switzer, unpub data

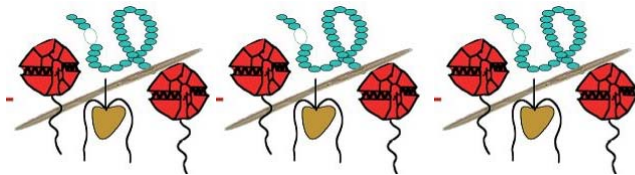
- Urea is an important component of DON in coastal oceans and readily consumed by phytoplankton

Global impact of urea use on HABs reports on increased toxicity



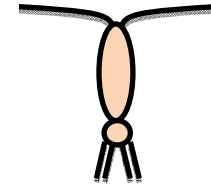
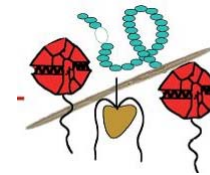
High variability of HABs in occurrence and impact

Large biomass/ low toxicity



- Blockage of respiratory water flow through fish gills
- excessive mucus interference
- Degradation of biomass leads to anoxia

Low biomass/ high toxicity



- Shelfish/fish poisoning
- Respiratory problems
- Drinking water problem
- Accumulation within the food web

Why harmful?- High biomass impact on ecosystem



- massive die-off and decay of algae from a nearshore harmful algal bloom (a "red tide")
- rapid reduction in the water's dissolved oxygen concentration
- driving tens of thousands of rock lobsters to "walk out of the sea" near the coastal town of Elands Bay in South Africa's Western Cape province
- Lobster were stranded while searching for oxygen rich water

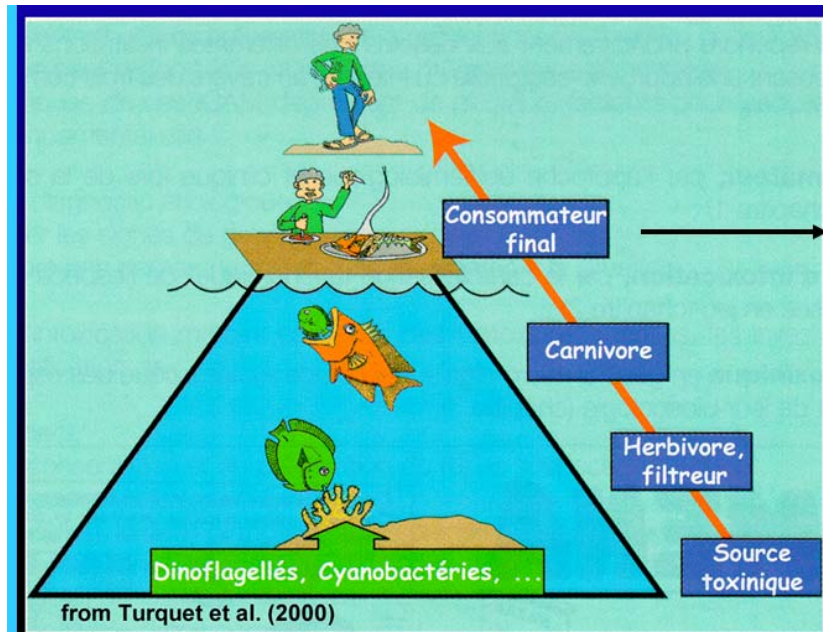
Economic impact

- Human illnesses
- Fish kills in aquaculture industry
- Recreational resources affected through anasthetic water conditions



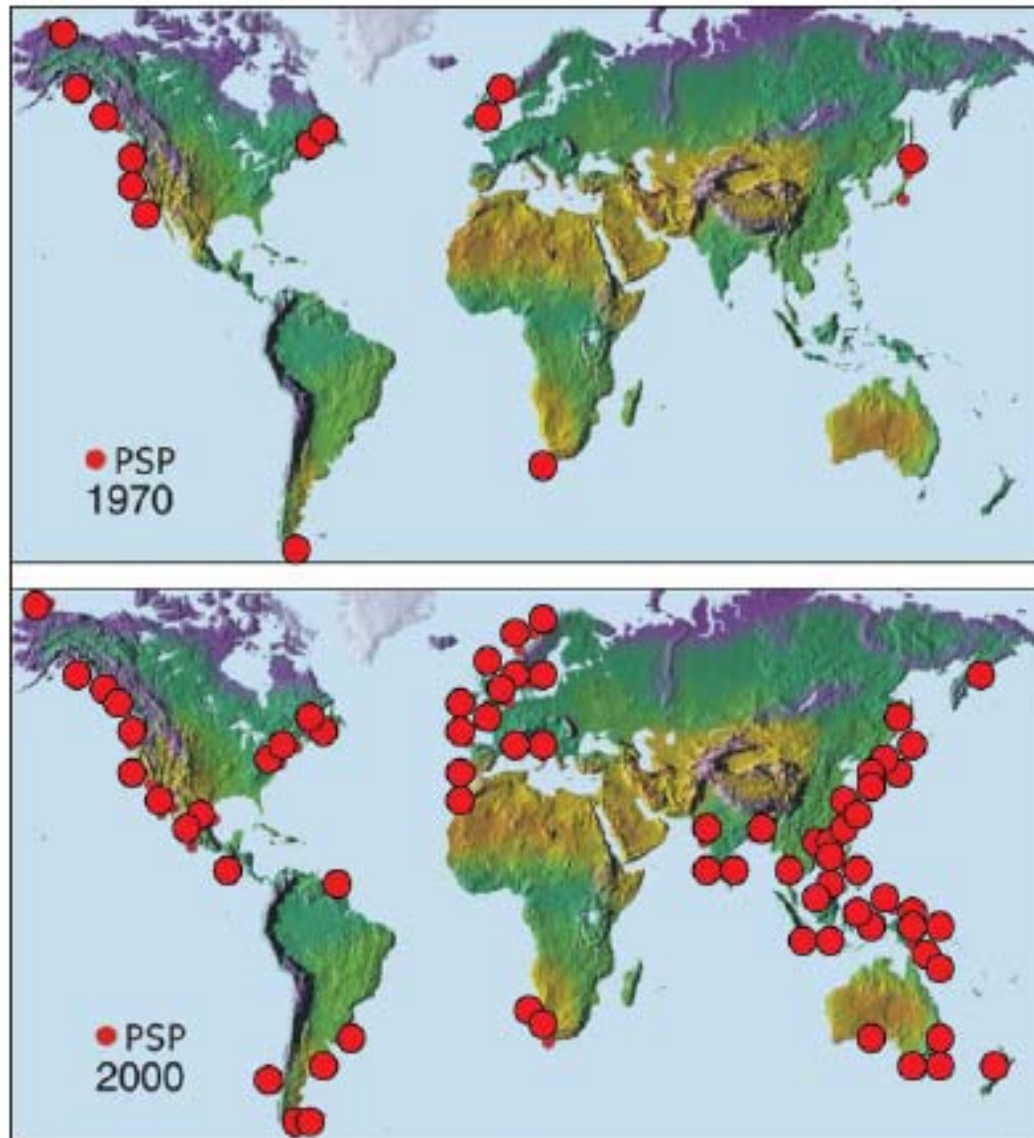
Low biomass but toxic impact on human health

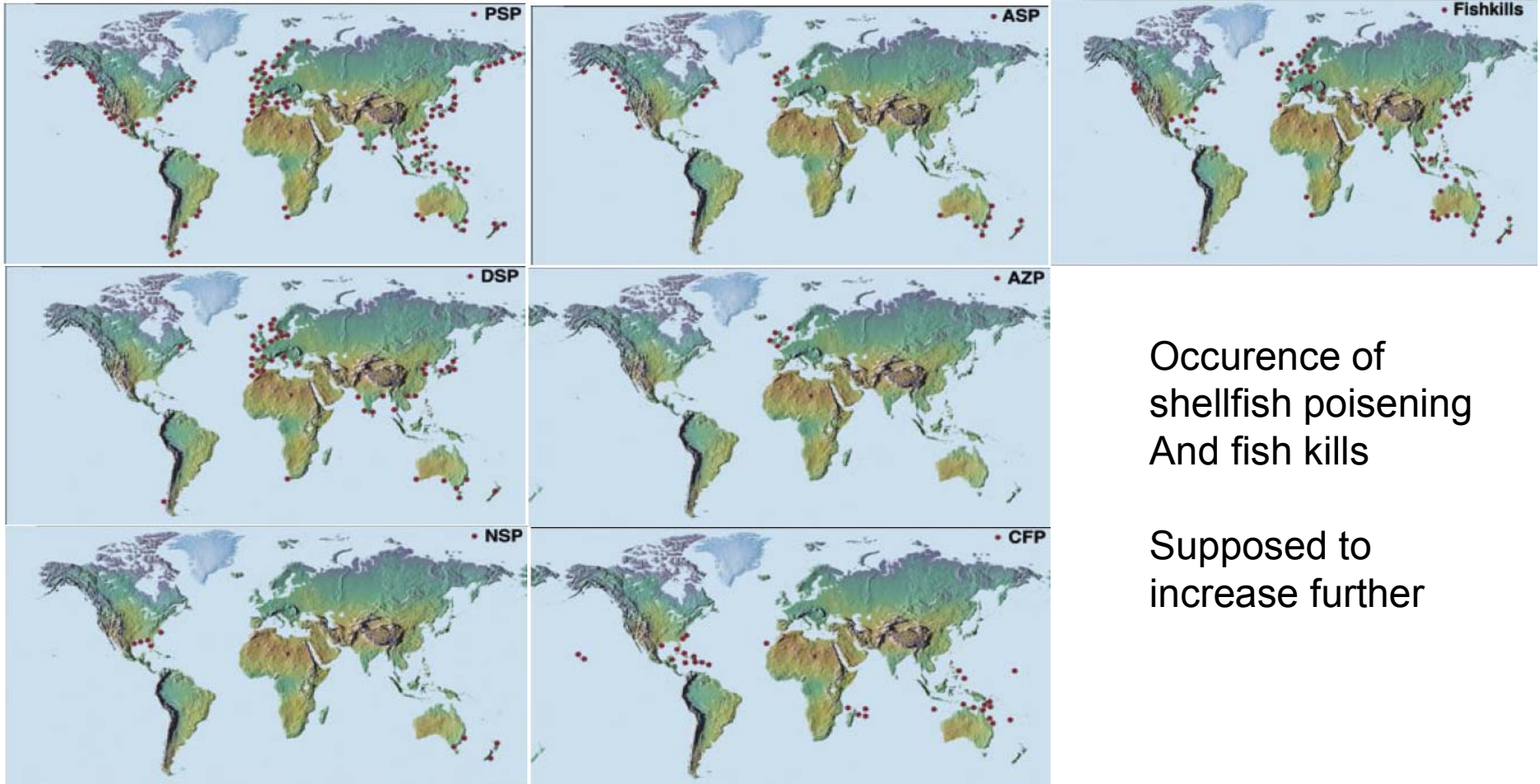
Shellfish Poisoning Syndromes



- PSP paralytic
- DSP diarrhetic,
- NSP neurotoxic
- ASP amnesic
- AZP azaspiracid
- Except for ASP, all are caused by biotoxins synthesized by dinoflagellates, ASP is from diatoms
- ciguatera fish poisoning (CFP) is caused by toxins produced by dinoflagellates that live on surfaces in many coral reef communities

Occurrence of PSP 1970 and 2000



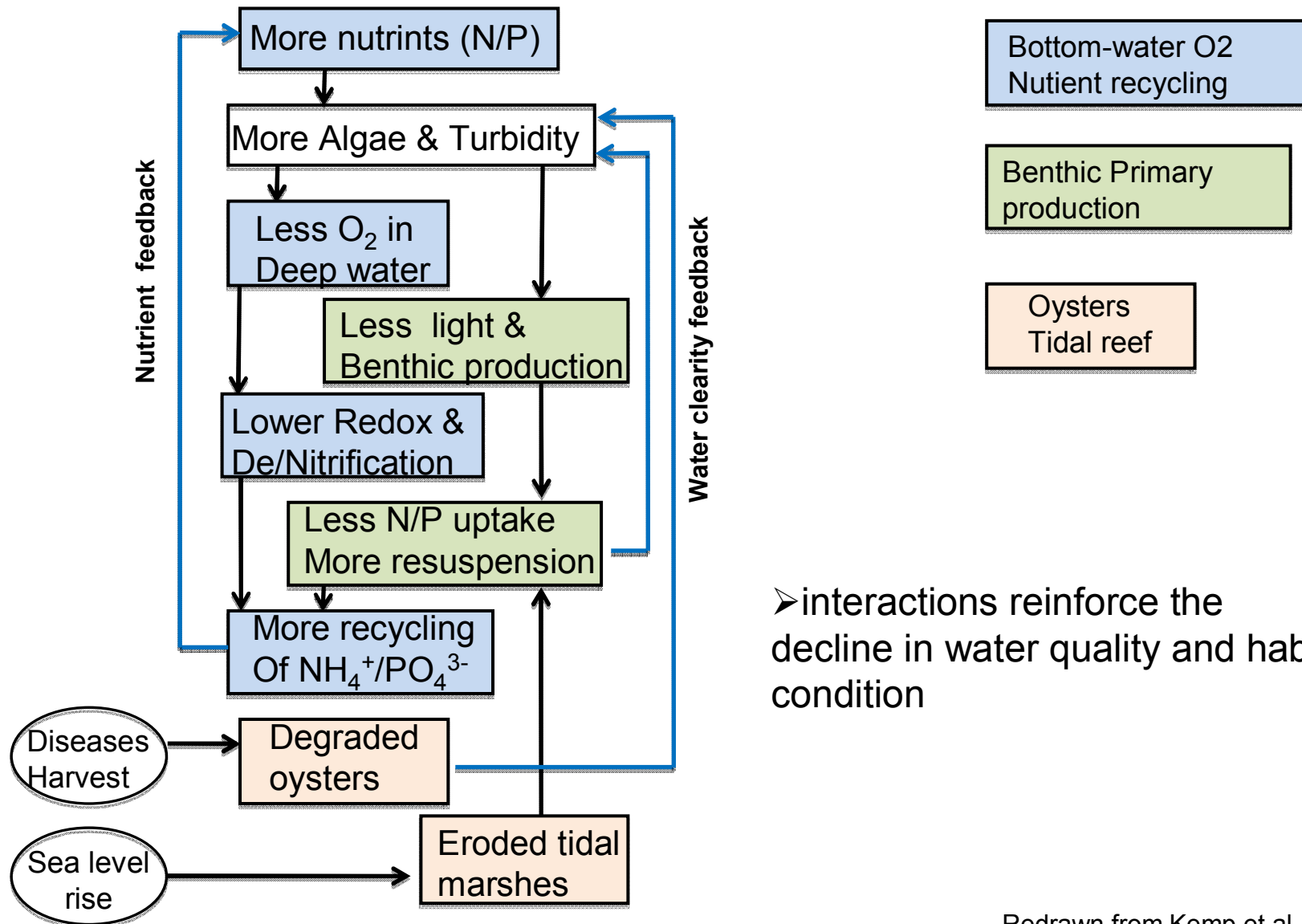


Occurrence of
 shellfish poisoning
 And fish kills

Supposed to
 increase further

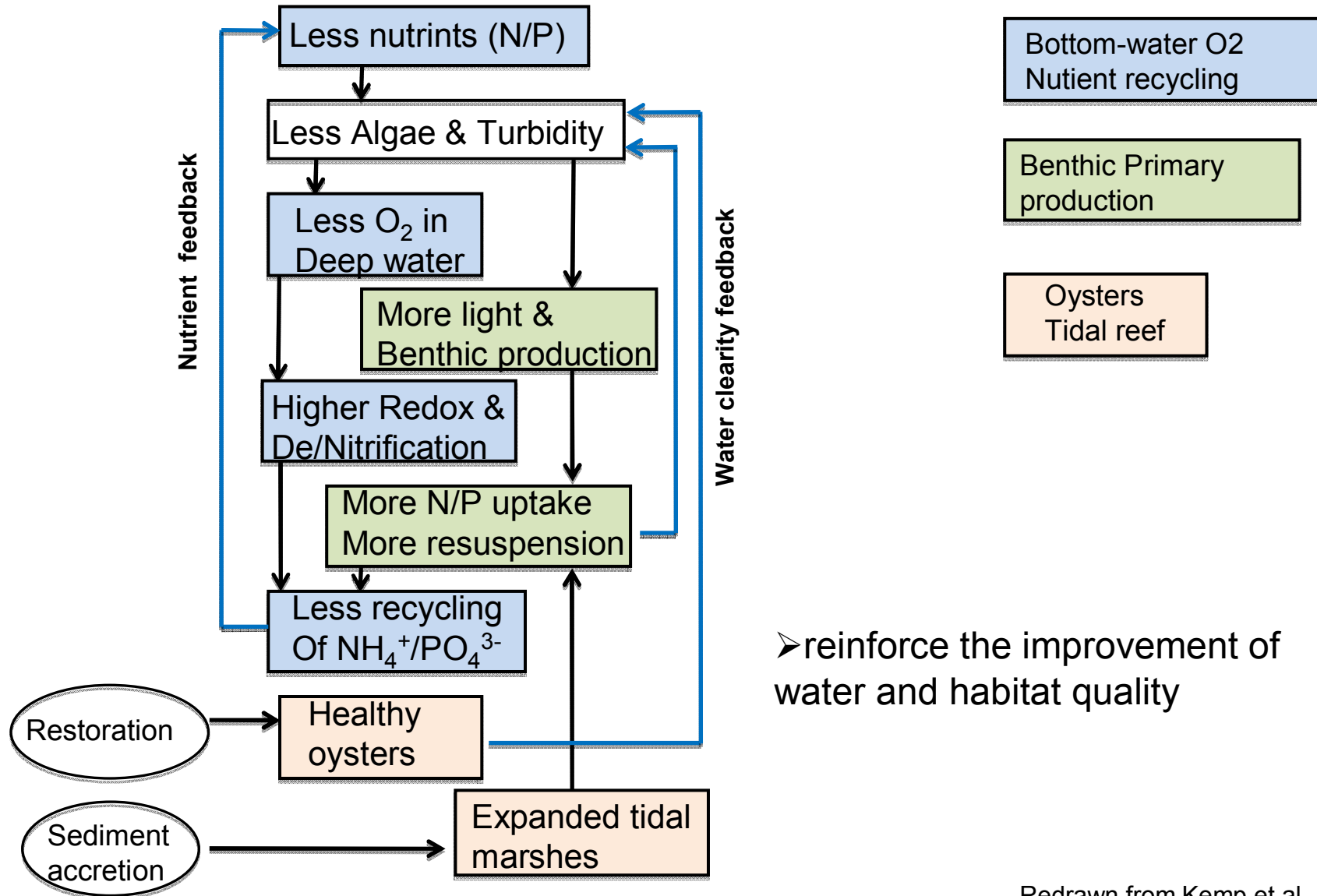
Degradation Trajectory

An example from Chesapeake Bay




➤ interactions reinforce the decline in water quality and habitat condition

Management - Restoration Trajectory




Management and Mitigation

Information

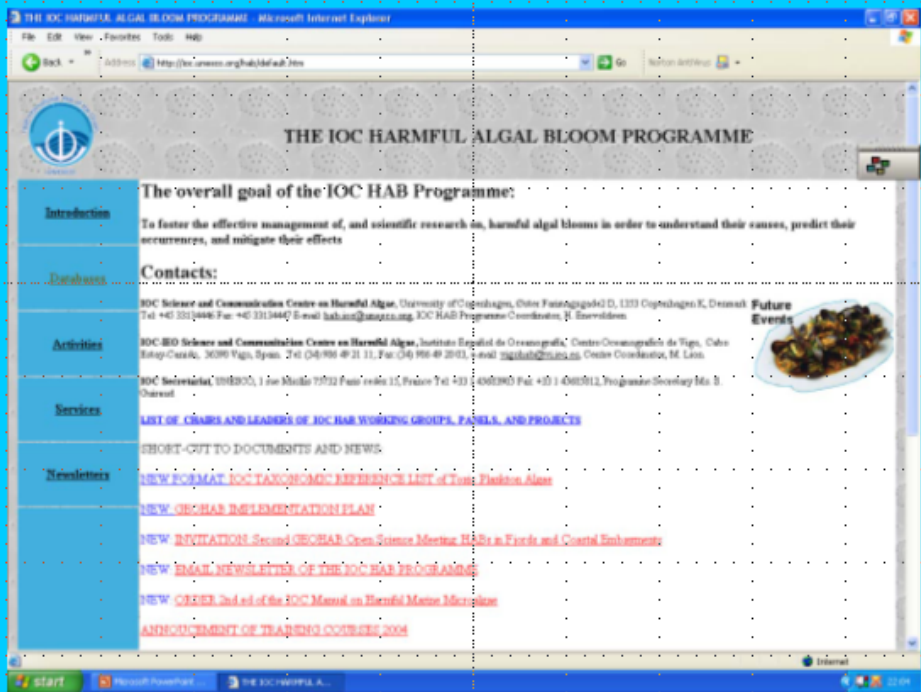


Manual on Harmful Marine Microalgae



Management and Mitigation

Information - visit the IOC homepage: <http://ioc.unesco.org/hab>



THE IOC HARMFUL ALGAL BLOOM PROGRAMME

The overall goal of the IOC HAB Programme:

To foster the effective management of, and scientific research on, harmful algal blooms in order to understand their causes, predict their occurrences, and mitigate their effects

Contacts:

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IOC-Indonesia/UNESCO, Jl. H. Muhsin 17122 Four roads 11, Ploree Tel: 531 480360 Fax: +62 31 4885911, Progresive Secretary Ms. S. Darsani

Future Events

LIST OF CHAIRS AND LEADERS OF IOC HAB WORKING GROUPS, PANELS, AND PROJECTS

SHORT-CUT TO DOCUMENTS AND NEWS

NEW FORMAT IOC TAXONOMIC REFERENCE LIST of Toxic Harmful Algae

NEW OCHRAE IMPLEMENTATION PLAN

NEW INVITATION Second OCHRAE Open Science Meeting HABs in Fresh and Coastal Environments

NEW HABs NEWS LIST of the IOC HAB PROGRAMME

NEW CHECK-List of the IOC Manual on Harmful Marine Microalgae

ANNOUNCEMENT OF TRAINING COURSES 2004

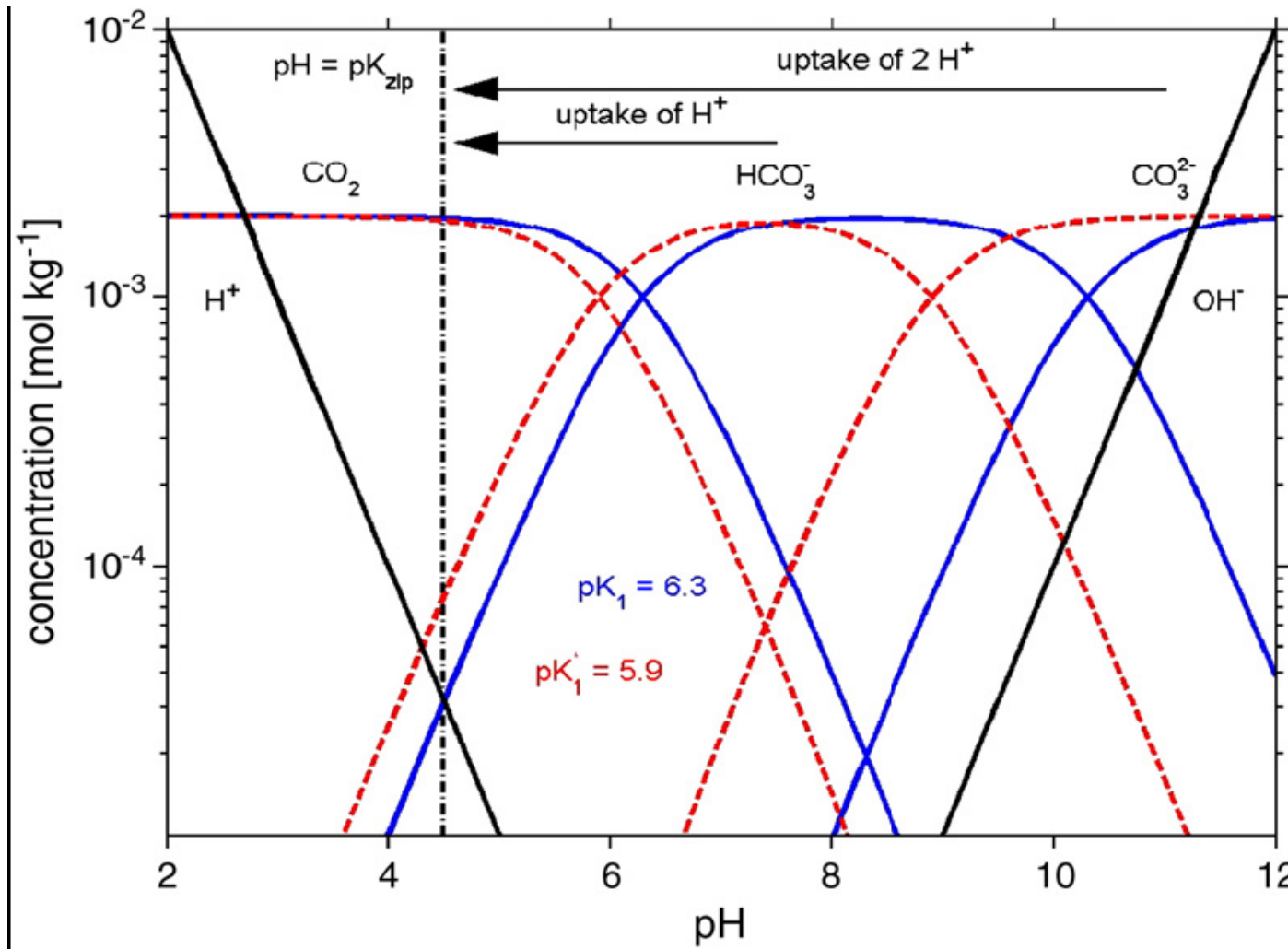


Ocean Acidification

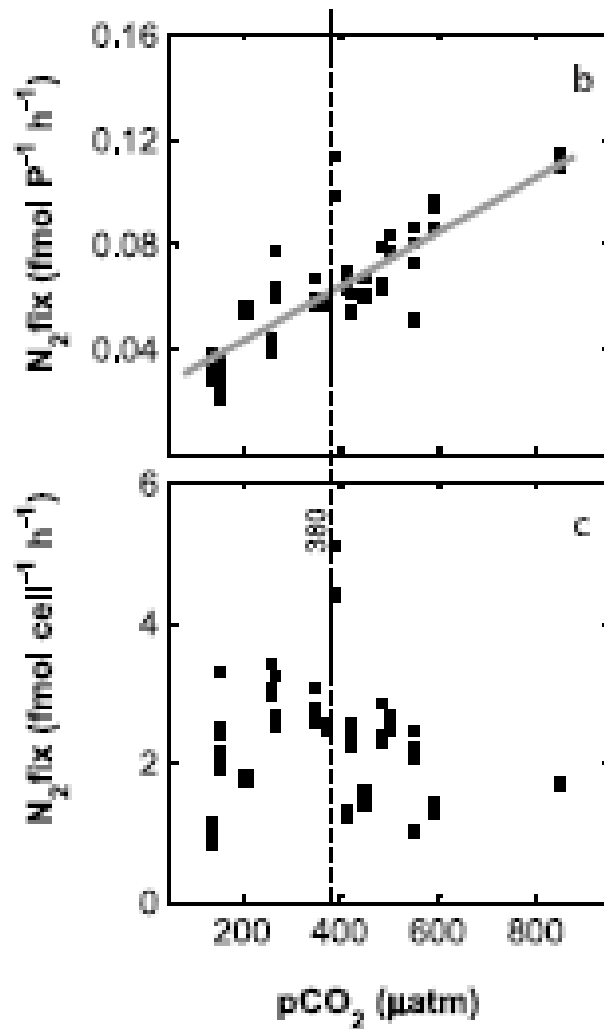
impact in C (and N) cycling

- Over the past decades several hundreds of papers have been published on the effects of OA on biota – most of them in the recent years.
- Large EU projects like Carbocean and Peece have been funded.
- In Sep. 2009 a large German project was launched with a budget of 8.5 mio €. BIOACID will investigate the effects of OA on biota.
- The UK program will soon be launched.
- Also a US program may come soon.

Concentrations of CO_2 , HCO_3^- , CO_3^{2-} , H^+ , and OH^- as functions of pH



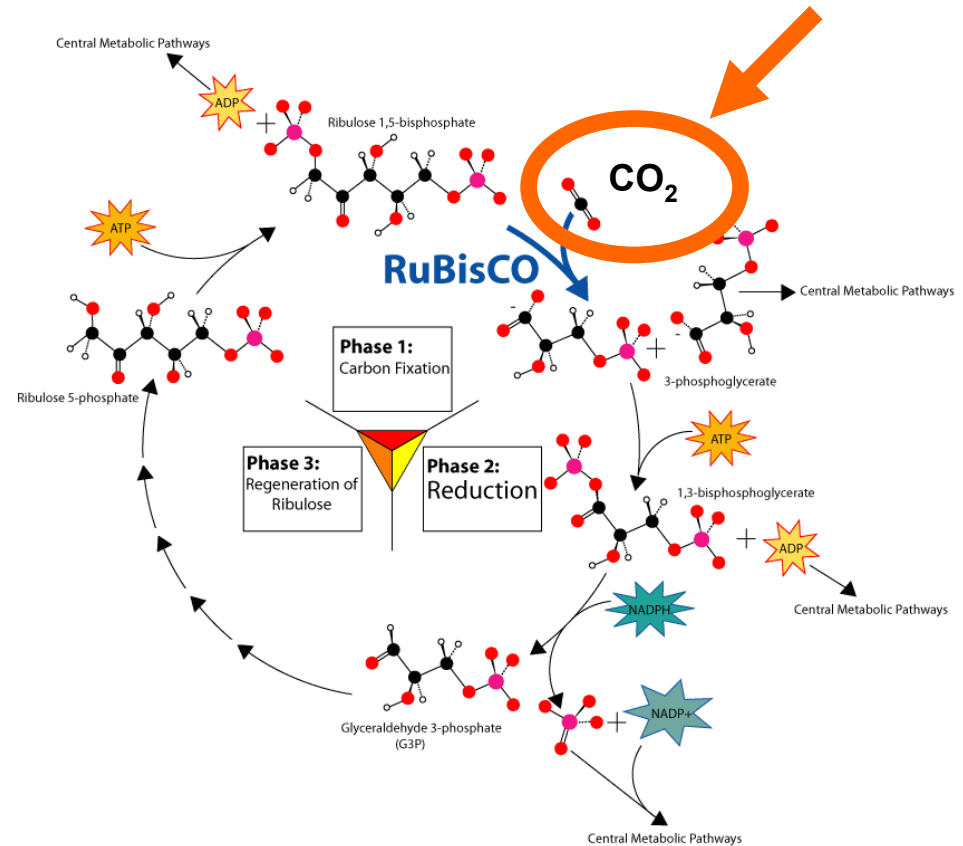
Several studies showed increasing N-fix rates under high CO₂



- Primary production increases under high pCO₂
- Nitrogen fixation increases too

- During primary production CO_2 fixation is mediated by RuBisCO, and takes place in chloroplasts of eukaryotic phytoplankton or in the thylakoid membranes of cyanobacteria
- RuBisCO is unaffected by the pH, but regulated by the CO_2 availability...
- ...the performance of RuBisCo is maximized by the CCM.

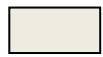
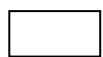

Schematic of the Calvin Cycle:

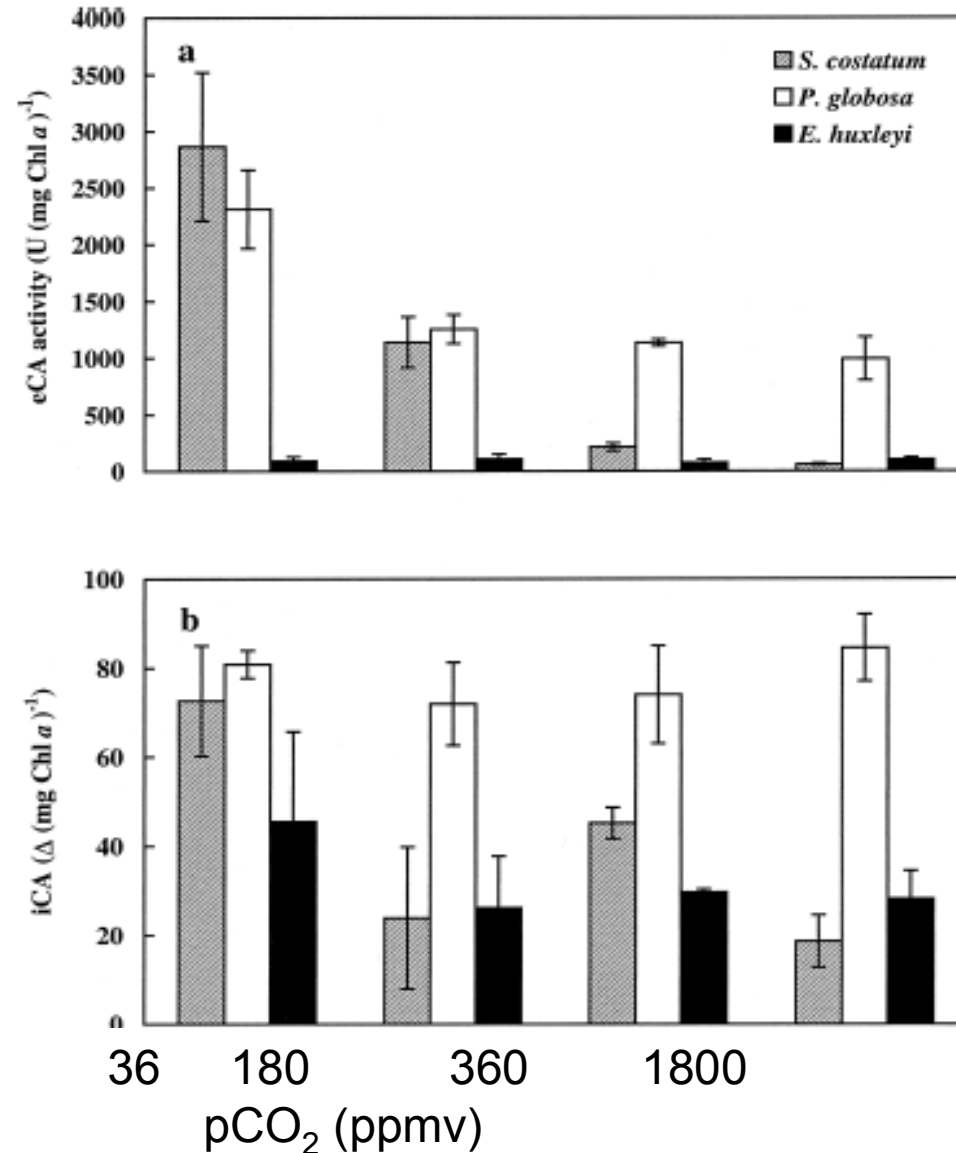


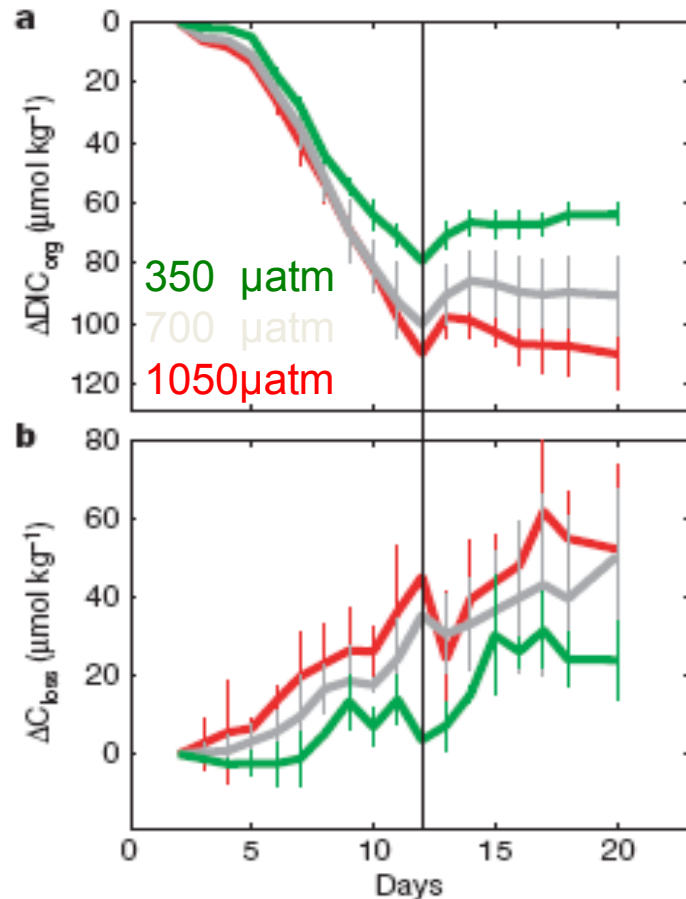
Effect on primary producers

On a species level things are rather unclear.
 Species react differently on different pCO₂ levels

- a) External carbonic anhydrase activity
- b) Internal carbonic anhydrase activity

 *S. costatum*
 *P. globosa*
 *E. huxleyi*

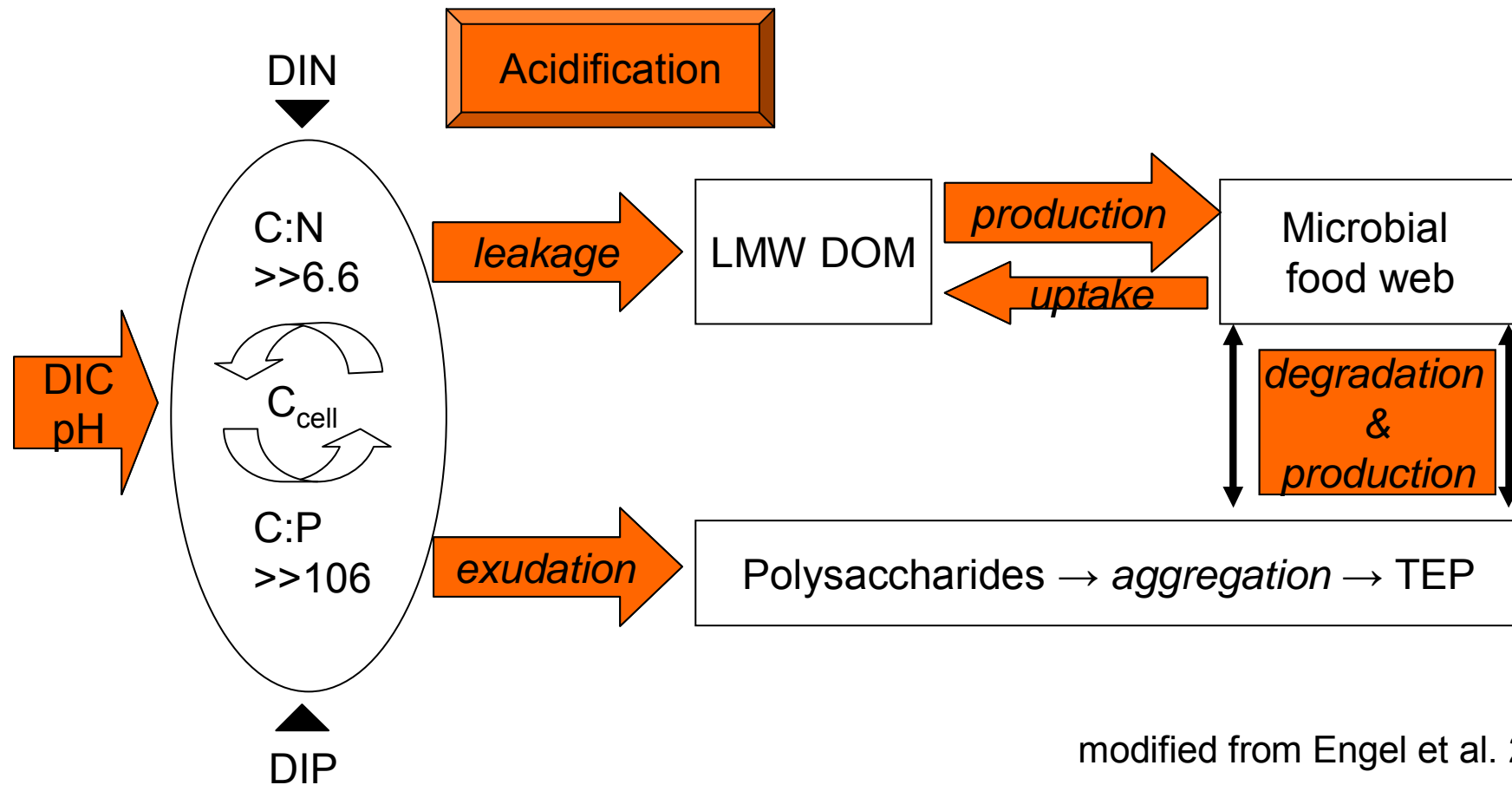




Riebesell et al. Nature, 2007

- Although the same quantities of inorganic nutrients were consumed in all set-ups,
- the carbon consumption exceeded present rates by 27% (at $2 \cdot \text{CO}_2$) and 39% ($3 \cdot \text{CO}_2$).
- The production of TEP (up to fourfold increase) may accelerate particle aggregation and sedimentation.
- Moreover the DOM release may explain the „missing“ organic carbon.

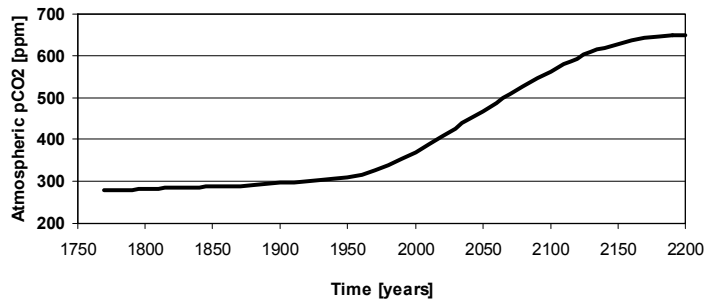
Strong link between C and N



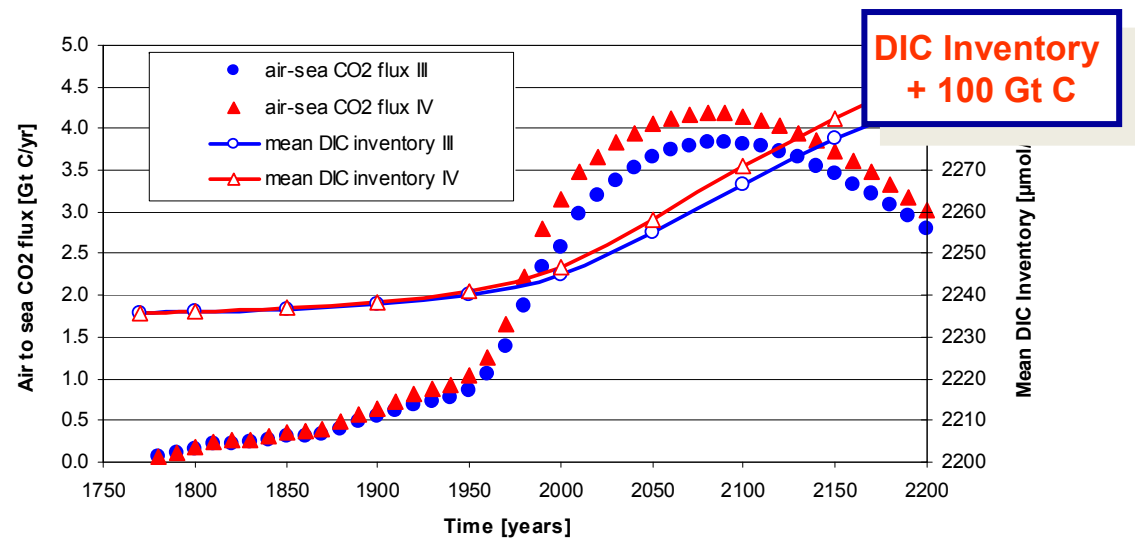
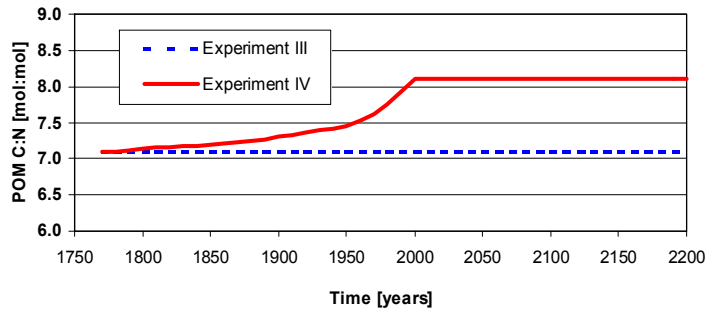
modified from Engel et al. 2004

Results from modelling

pCO₂ increase

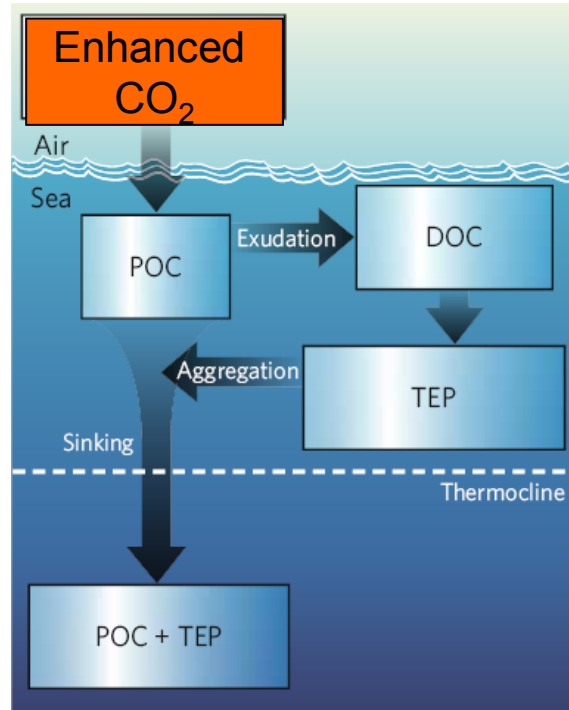
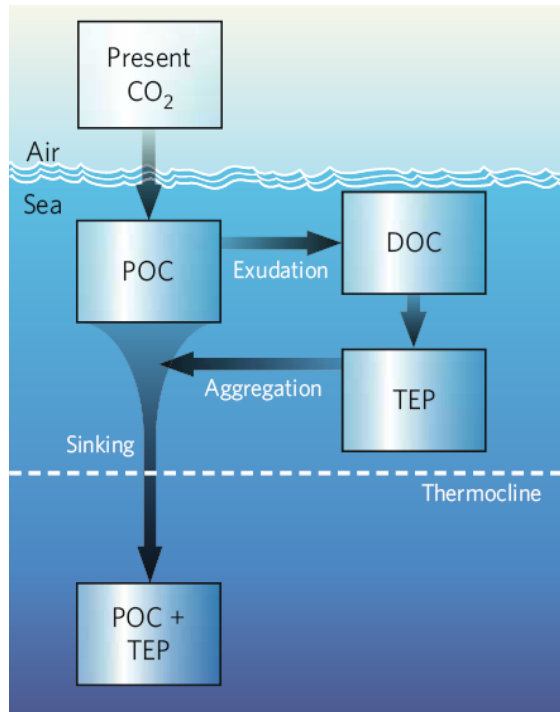


C:N ratio in sinking particles



Schneider et al., 2004

Links from particle production to sedimentation



Arrigo (2007)

- DOC production and decay are sensitive to OA and global warming.
- altered DOC cycling affects particle flux dynamics and carbon export.

- Humans have changed the major elemental cycles considerable with adverse effects for the environment
- Industrial ammonia production has changed the world and is already higher than all natural nitrogen fixation
- This causes unbalanced N:P:Si ratios
- Nutrient concentrations and ratios are reasons for HABs
- One of the effects are HABs producing toxins or harming the environment
- OA needs to be better understood