Aerosols carriers of nutrients to the ecosystems and the role of Atmospheric Chemistry

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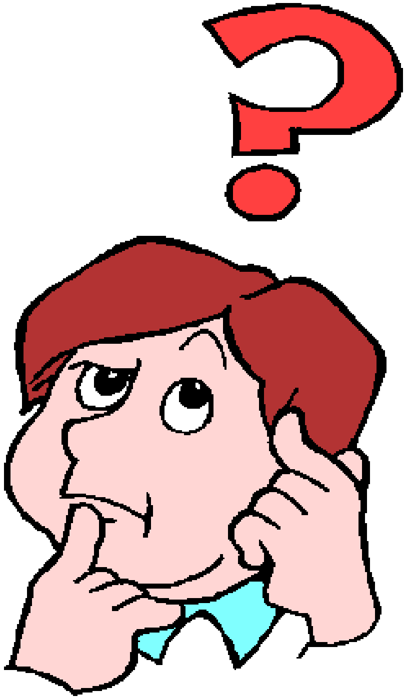
Sao Paolo, 2 Aug 2019

What is a nutrient?
And why we care?



The biomass of all living organisms consists of around 30 of the 92 naturally occurring elements.

All organisms must obtain chemical forms of these essential elements, termed nutrients, from their external environment.

Moore et al NGEO 2013

Examples of 'biological' use of trace metals

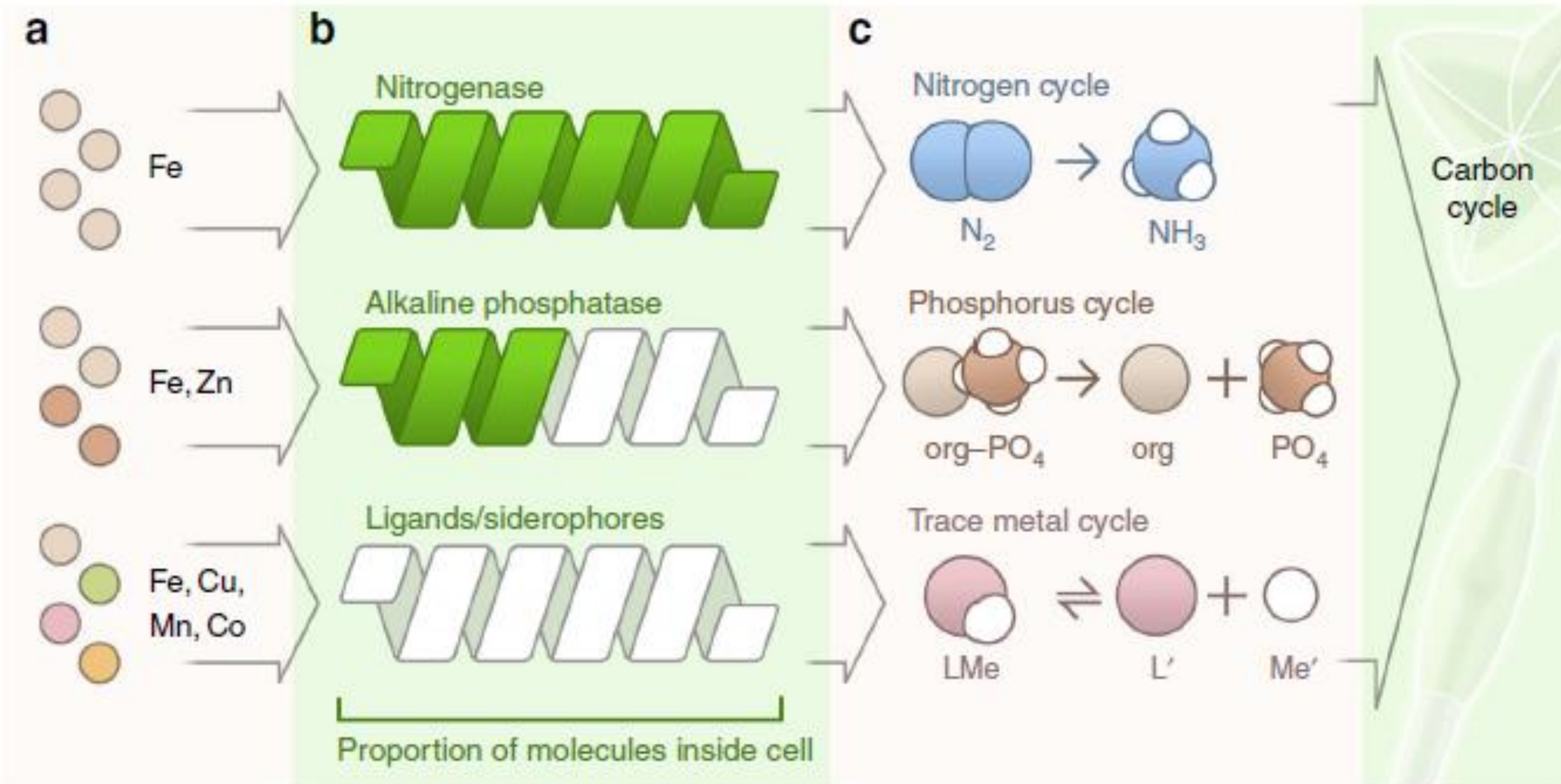
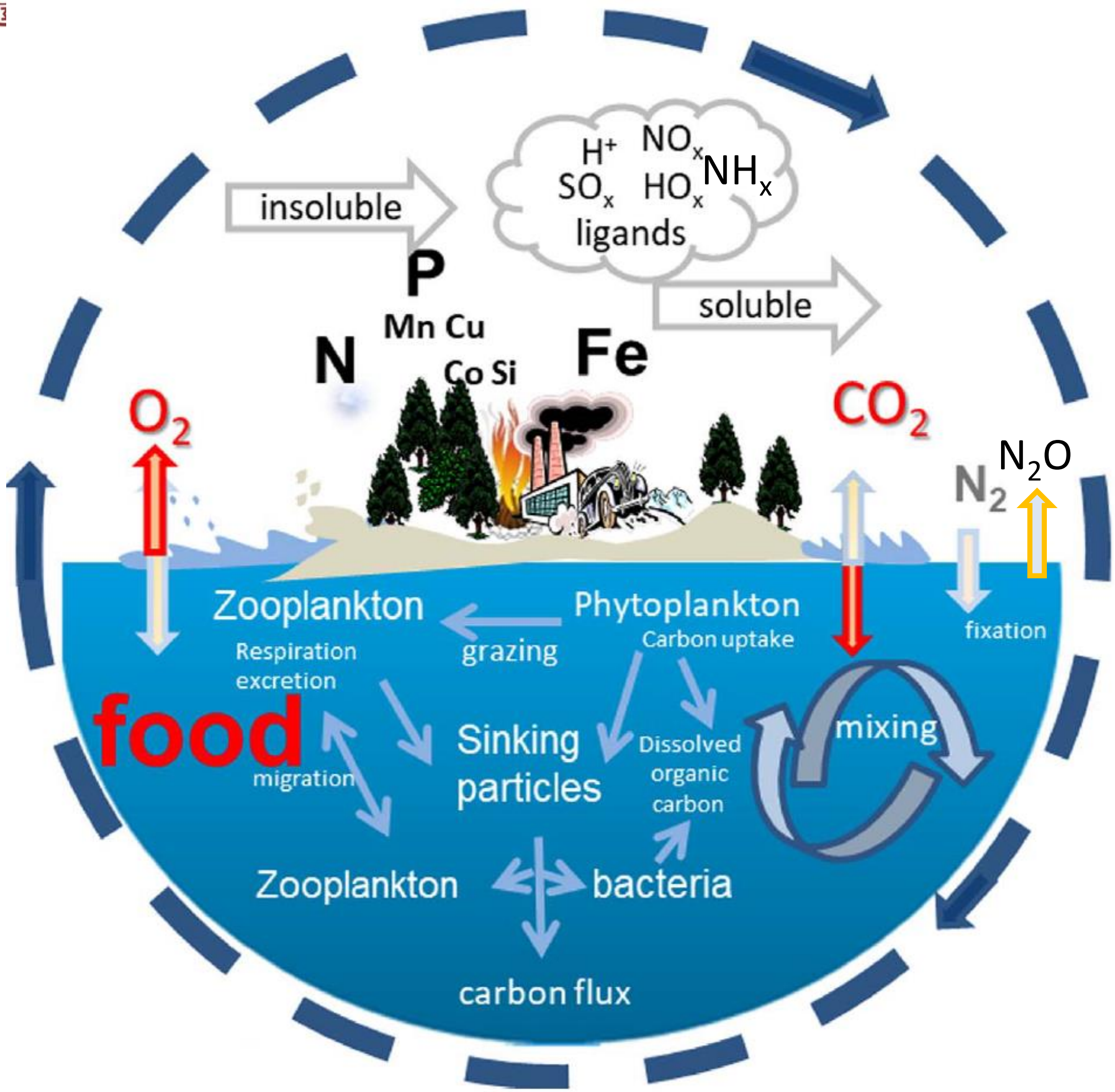


Fig. 6 Biological responses of phytoplankton and bacteria to aerosol trace metals. Trace metals are required as co-factors for many biogeochemically important molecules. Certain aerosol trace metals (**a**) have been shown to stimulate production of nitrogenase[73,77], alkaline phosphatase[91] and metal-binding ligands[70,95,162], and these molecules may remain within the cells (proportion of helix which is green) or be exuded into the sea water (**b**), where they catalyze chemical reactions that influence biogeochemical cycles (**c**). The cycling of N, P, and trace metals in turn affects the carbon cycle by influencing cellular growth rates. See Supplementary table 2 for compilation of studies, which this figure syntheses

Mahowald et al., Nature Communications, 2018

Interaction between ocean and atmosphere



Transfer of energy through currents and evaporation/ condensation of water

Exchange of mass:

- source of O_2 for the atmosphere
- CO_2 sequestration
- Source of N_2O at low oxygen regions
- gases and particles emissions

Kanakidou et al., Environ Research Letters, 2018 doi.org/10.1088/1748-9326/aabcdb

How much nutrients are needed ?

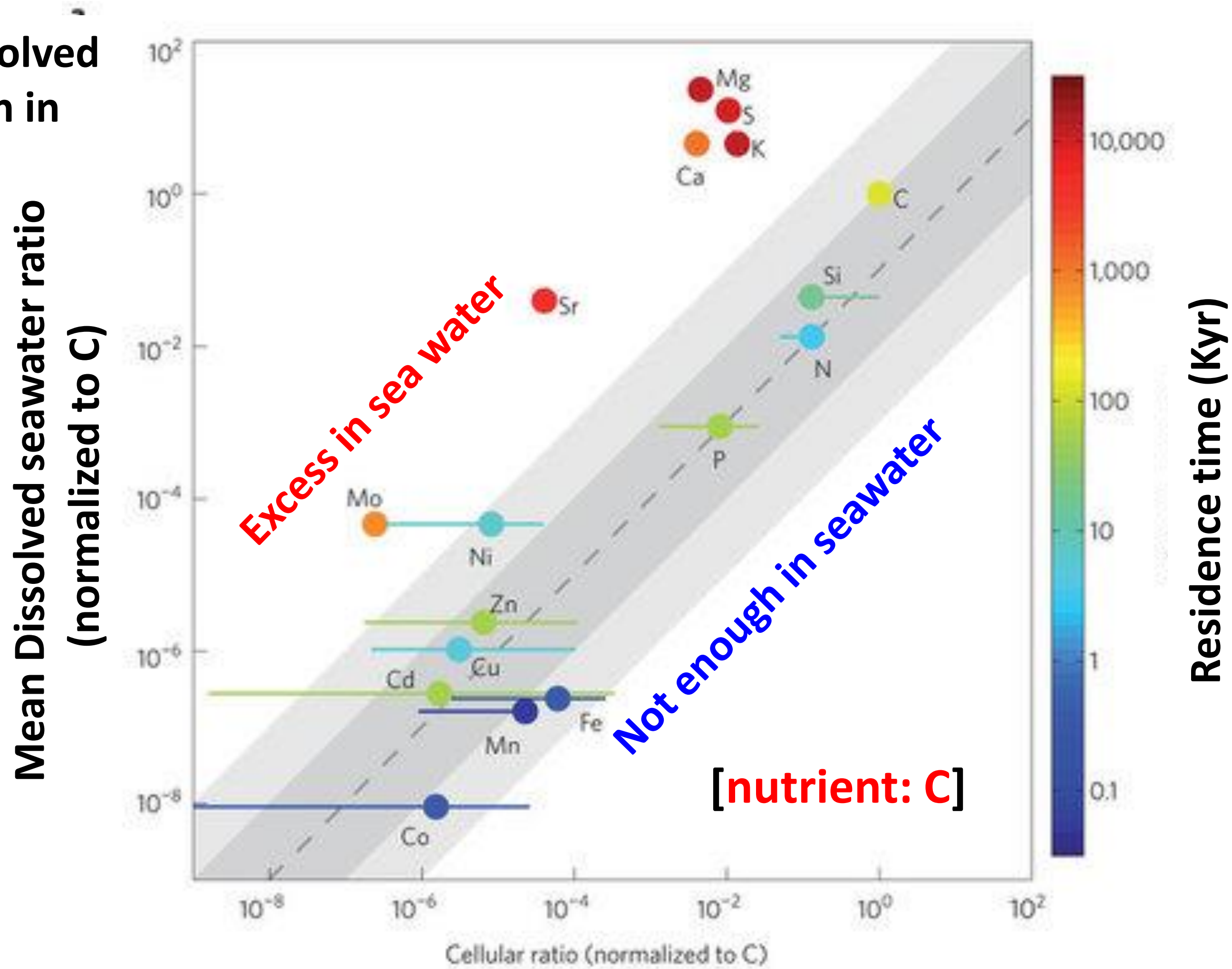
Too much → eutrophication (algae bloom, less O_2 available, loss of biodiversity)

→toxicity

Too little → limitation of growth

What levels of nutrients are needed?

Mean ratio of dissolved nutrient-to-Carbon in the seawater

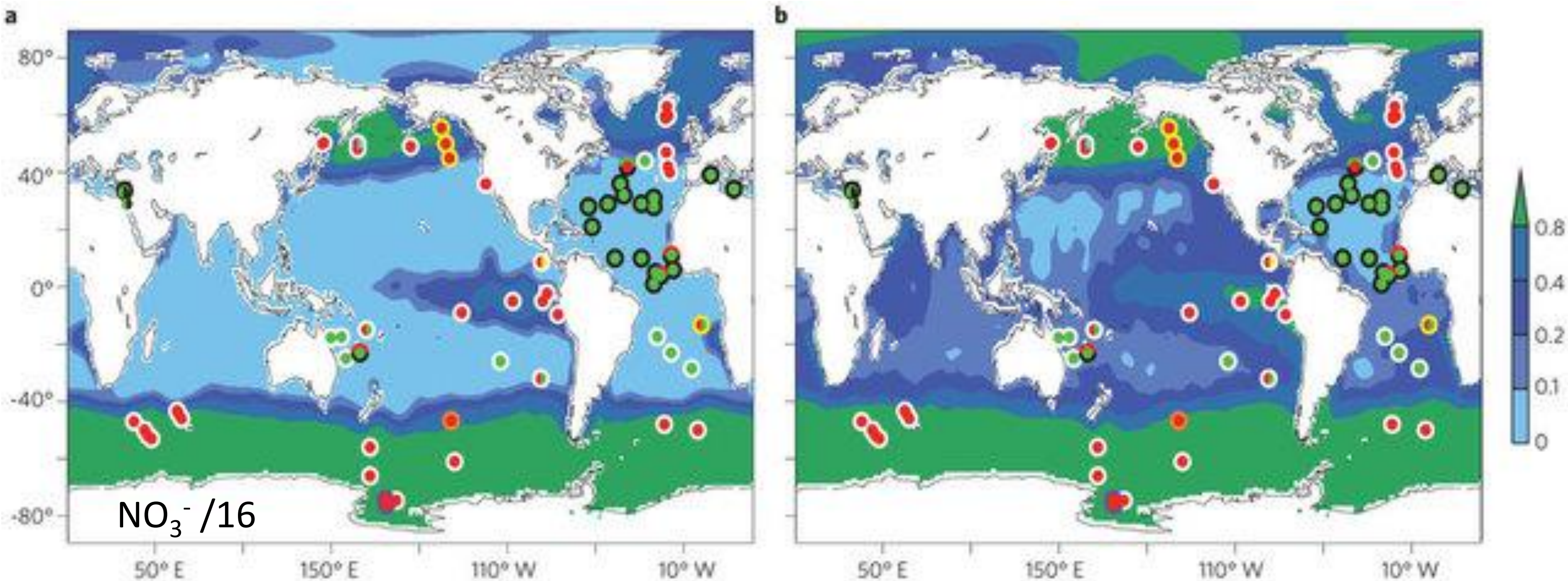


Ratio in the cells

Circles: representative ratios, **bars** : range of observations

Moore et al NGEO 2013

Primary production is limited by the availability of nutrients



Background: Distribution of NO_3^- in seawater

Background: Distribution of PO_4^{3-} in seawater

N (green), P (black), Fe (red), Si (orange), Co (yellow), Zn (cyan) and vitamin B12 (purple). primary (central circles) and secondary (outer circles) limiting nutrients. White outer circles indicate that no secondary limiting nutrient was identified

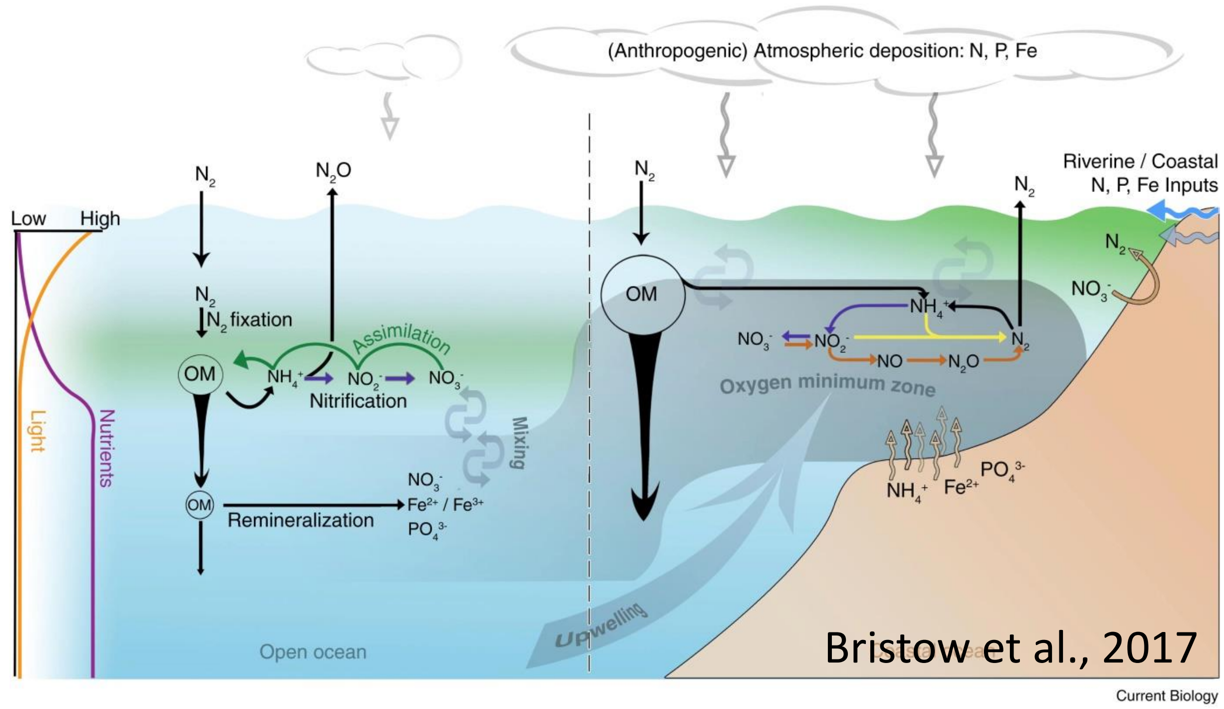
Moore et al NGEO 2013

Sources of nutrients for the marine ecosystems

Where they find the nutrients needed for their growth?

Sources external to the sea
- rivers
- Fixation of atmospheric N_2 (cyanobacteria)
- Atmospheric deposition

Internal oceanic sources
- Decomposition of organic matter
- underground rivers
- Upwelling
- Thermal sources
- sediments



Bristow et al., 2017

Aerosols contain ON and metals

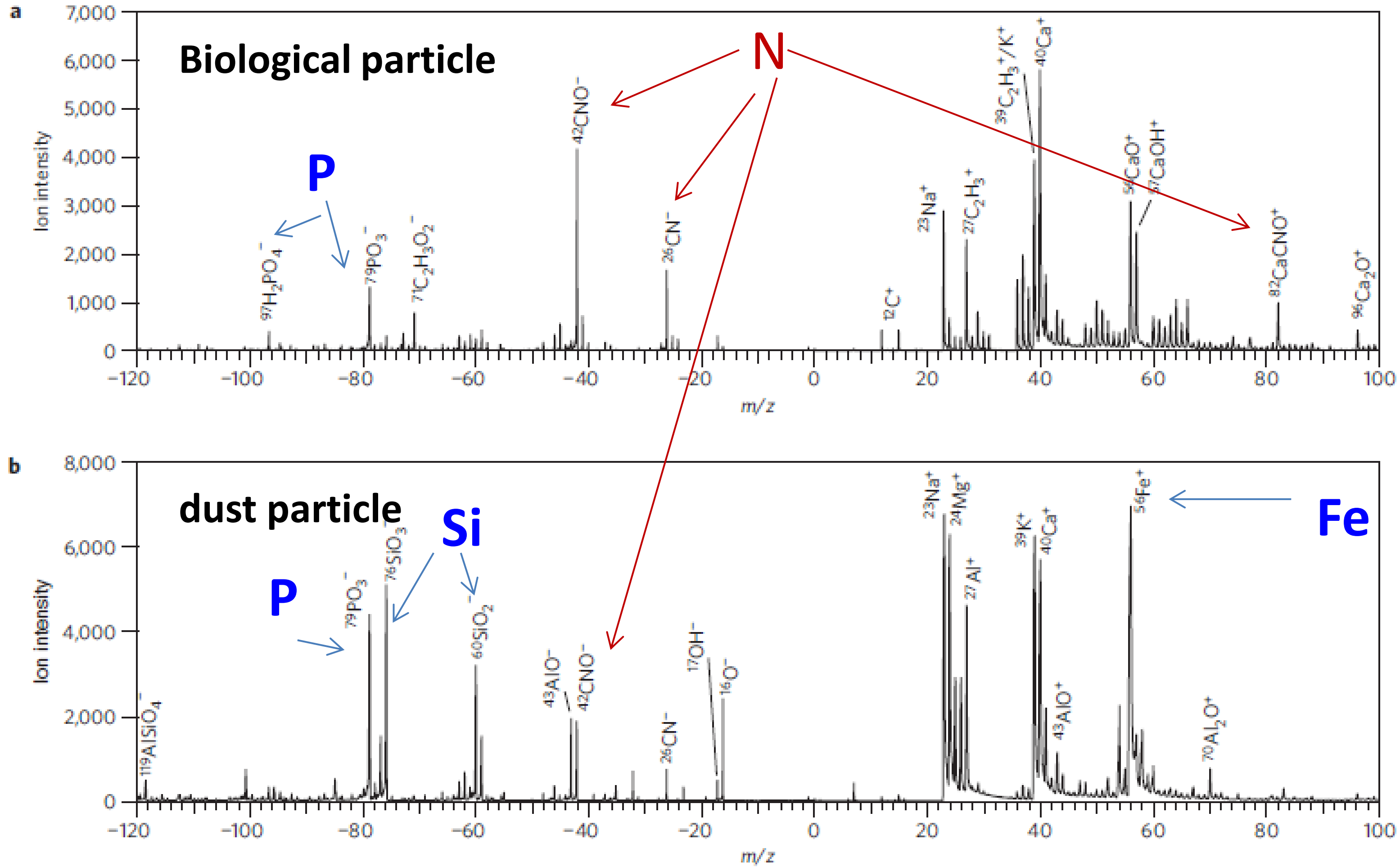


Figure 3 | Representative chemical composition of biological and dust particles. Positive- and negative-ion mass spectra of representative individual biological (**a**) and mineral-dust (**b**) CVI ice residual particles. Wyoming, US

CVI ice residual particles

Pratt et al., 2009 17 MAY 2009 | DOI:10.1038/NGEO521

Experimental evidence of atmospheric deposition impact on marine ecosystems

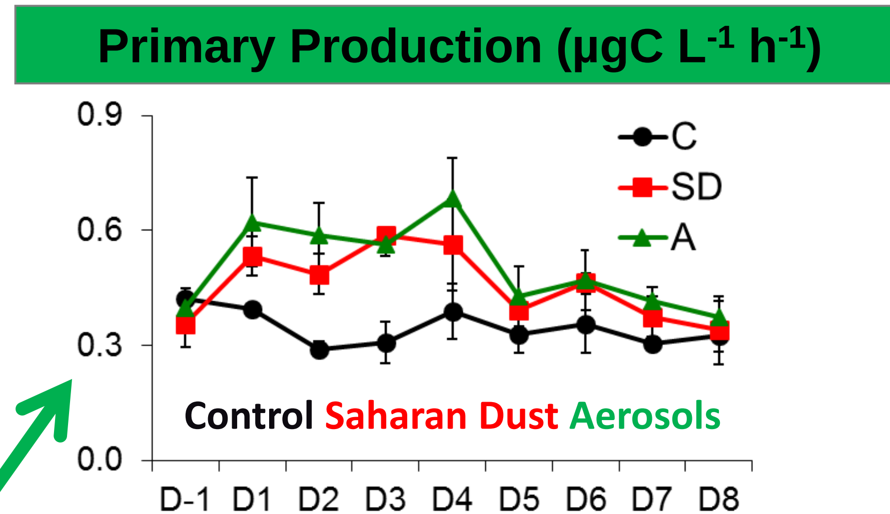
H.C.M.R.

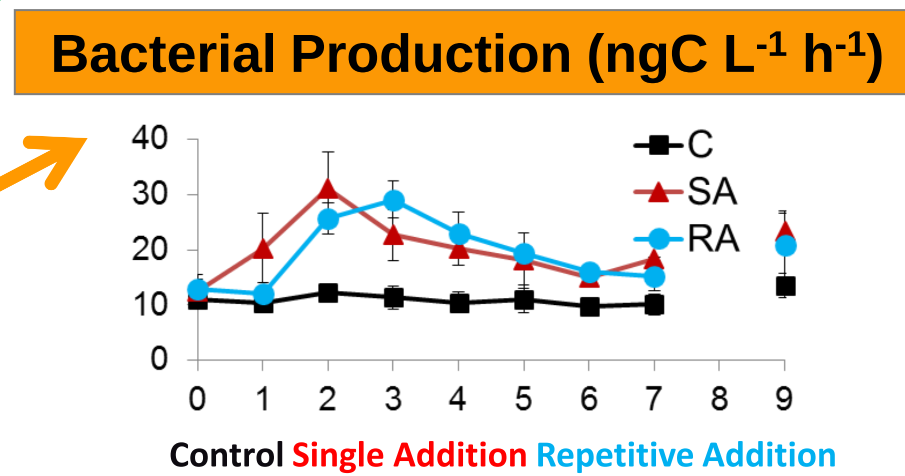
atmospheric deposition and mediterannean sea water productivity

adamant

UNIVERSITY OF CRETE

ENVIRONMENTAL CHEMICAL PROCESSES LABORATORY E C P L

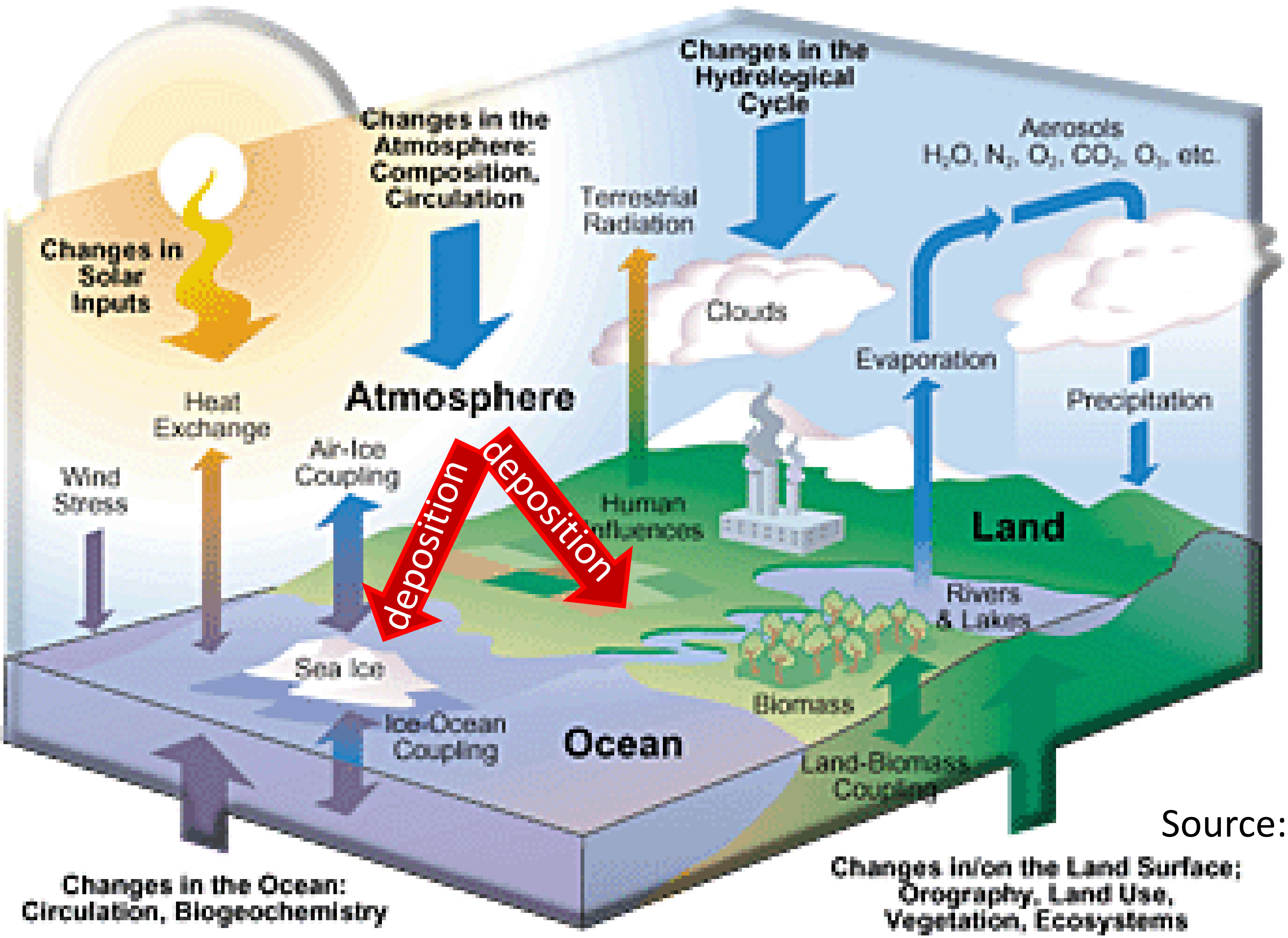




Clear effect on autotrophs and heterotrophs

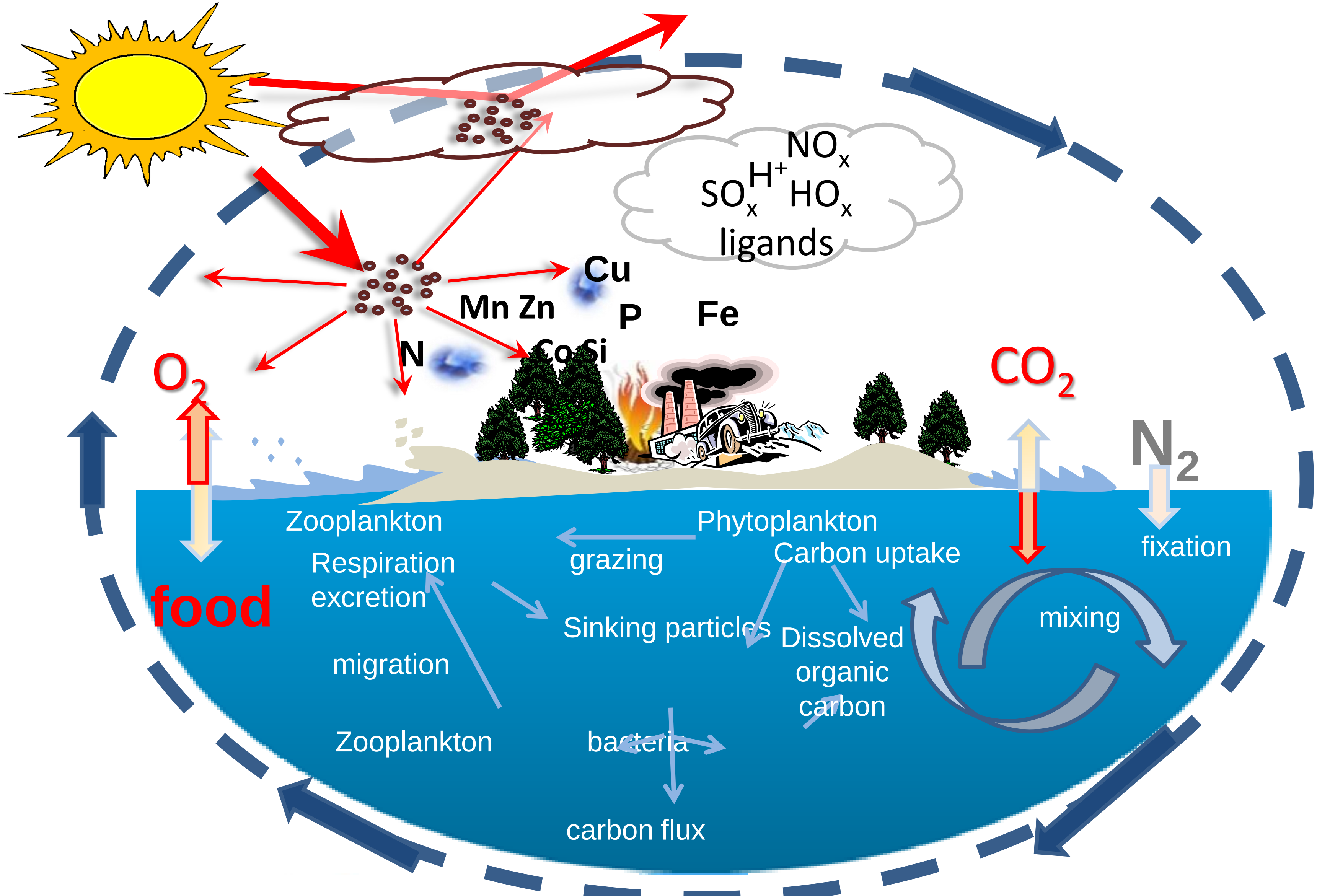
Pitta et al., FMARS, 2017
10.3389/fmars.2017.00117

Global Climate System Components



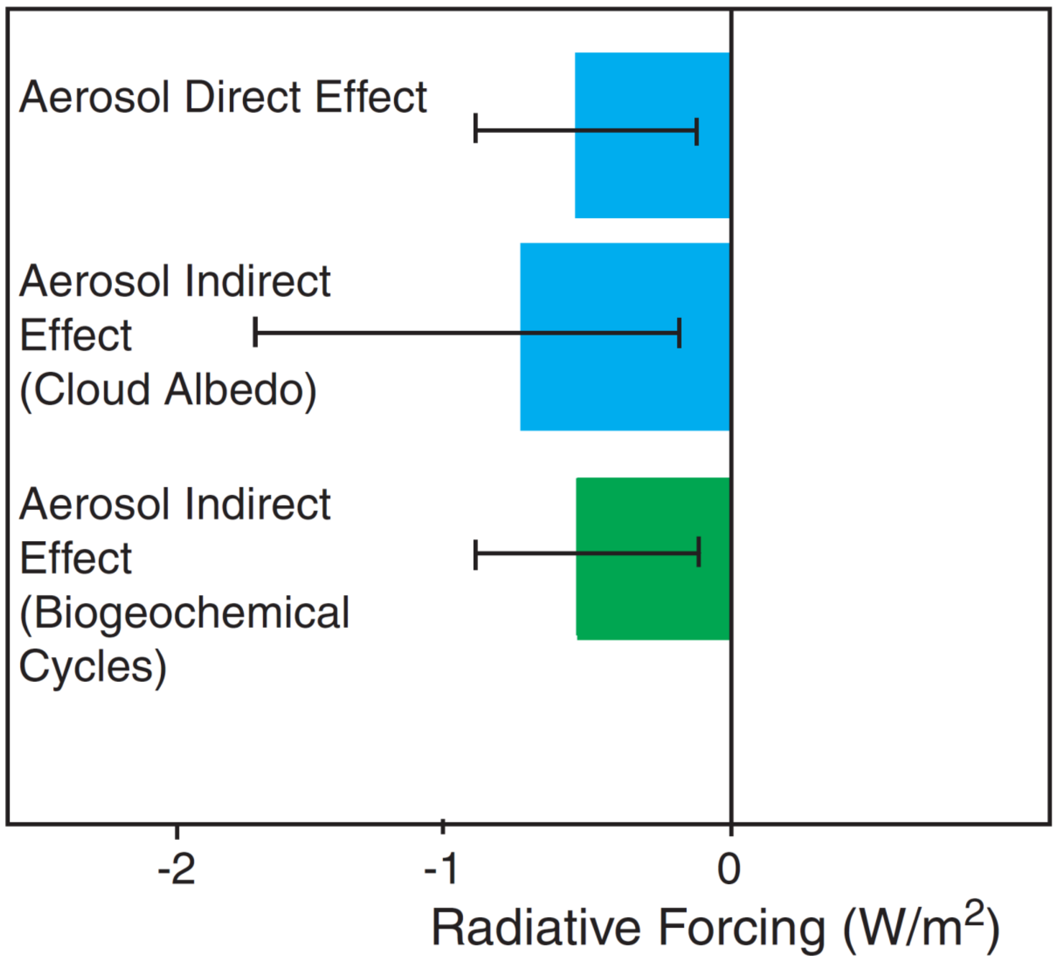
Source: ECMWF

Indirect climate effect of aerosols



Modified from Kanakidou et al. ERL 2018

The neglected indirect effect of aerosols – biogeochemical cycles

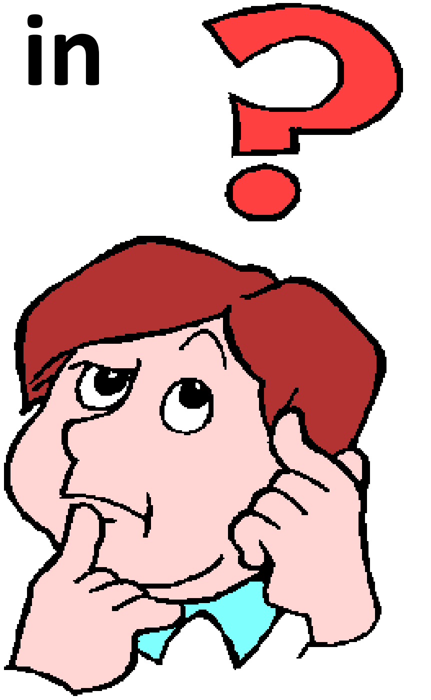


Aerosols through deposition of nutrients affect CO_2 sink and thus exert a cooling effect to the climate

Vey rough estimate accounting both terrestrial and oceanic ecosystems

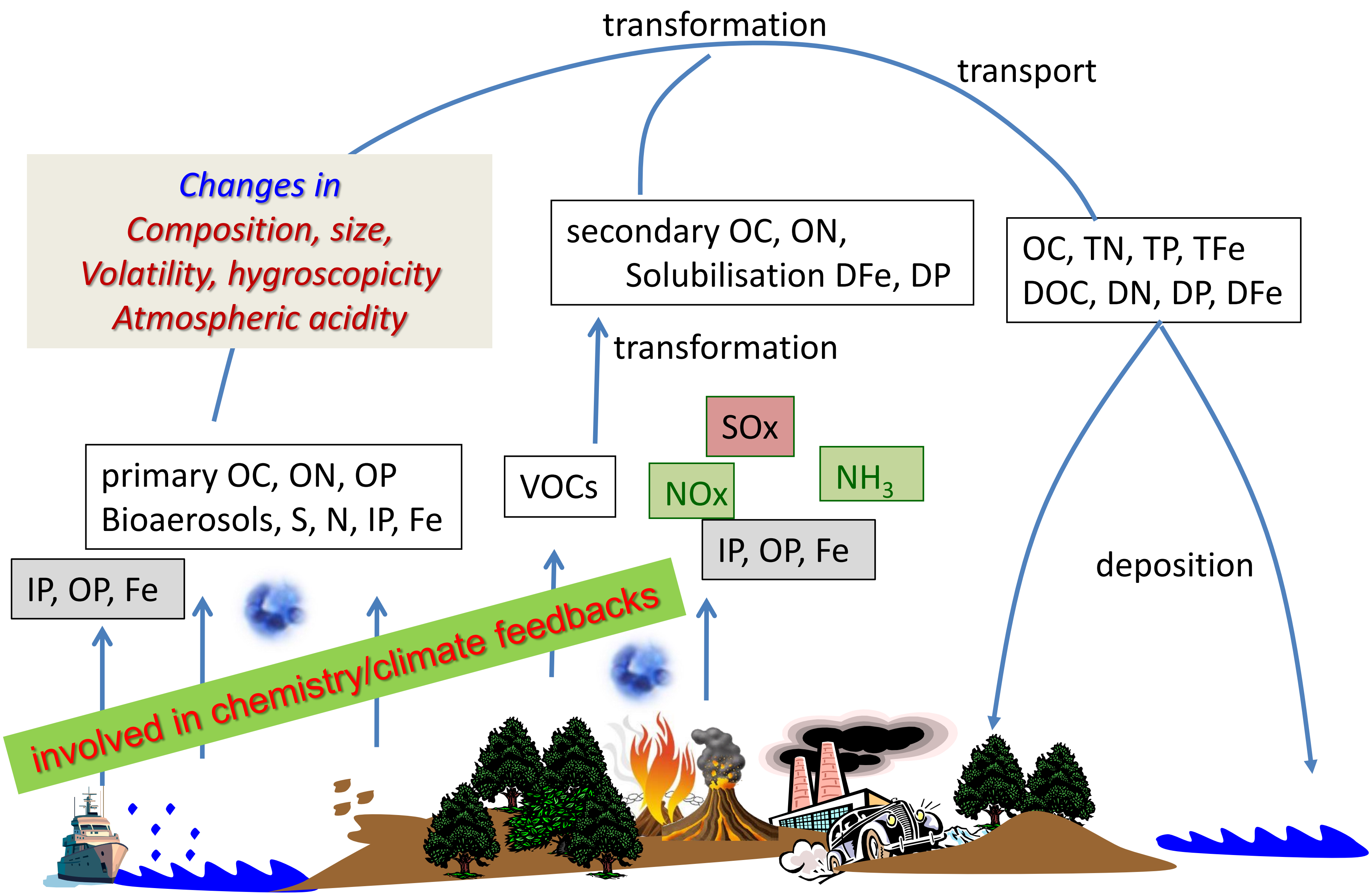
Mahowald, Science, 2011

How the nutrients are found in aerosols



- Chemical fixation
- Primary emissions
  - In soluble form
  - ‘mobilized’ (converted in soluble form) by chemical reactions

Aerosols carriers of nutrients in the Earth System



8/2/2019

Modified from Kanakidou et Global Biogeochemical Cycles 2012

What happens in the atmosphere?

CHEMISTRY !!!

NO + [O_3 / RO_2 (from VOC)] → NO_2 → → [O_3; HNO_3/NO_3^- acid/aerosol; ON; SOA **aerosols** (may contain ON)]

- NO: Mainly anthropogenic
- O_3, RO_2 (from VOC): Mainly natural

O_3

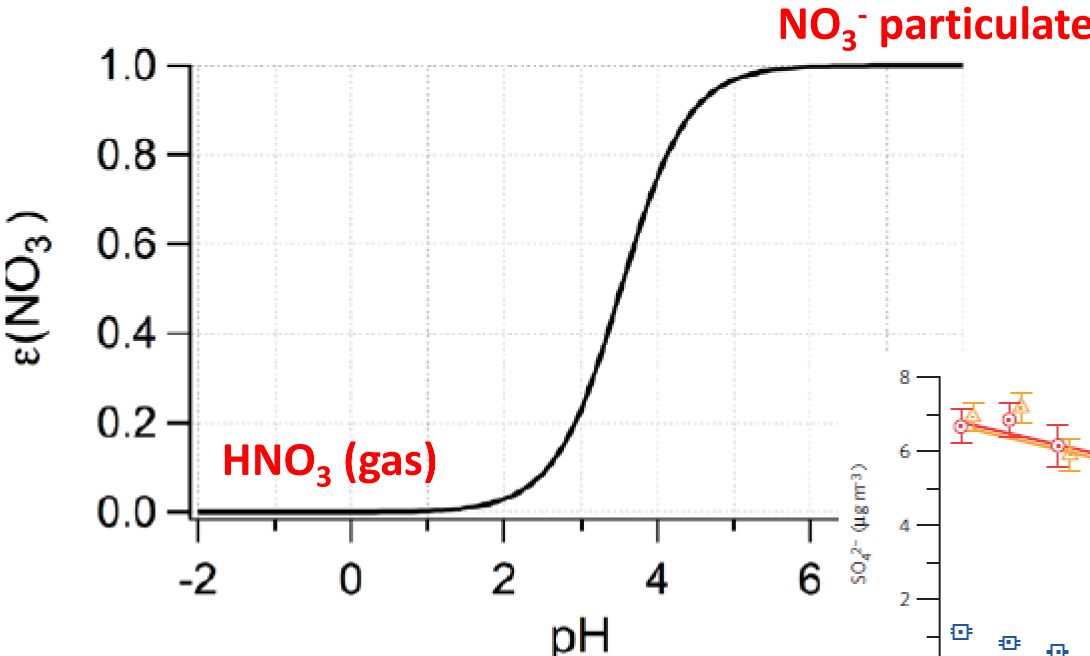
HNO_3/NO_3^-
acid/aerosol

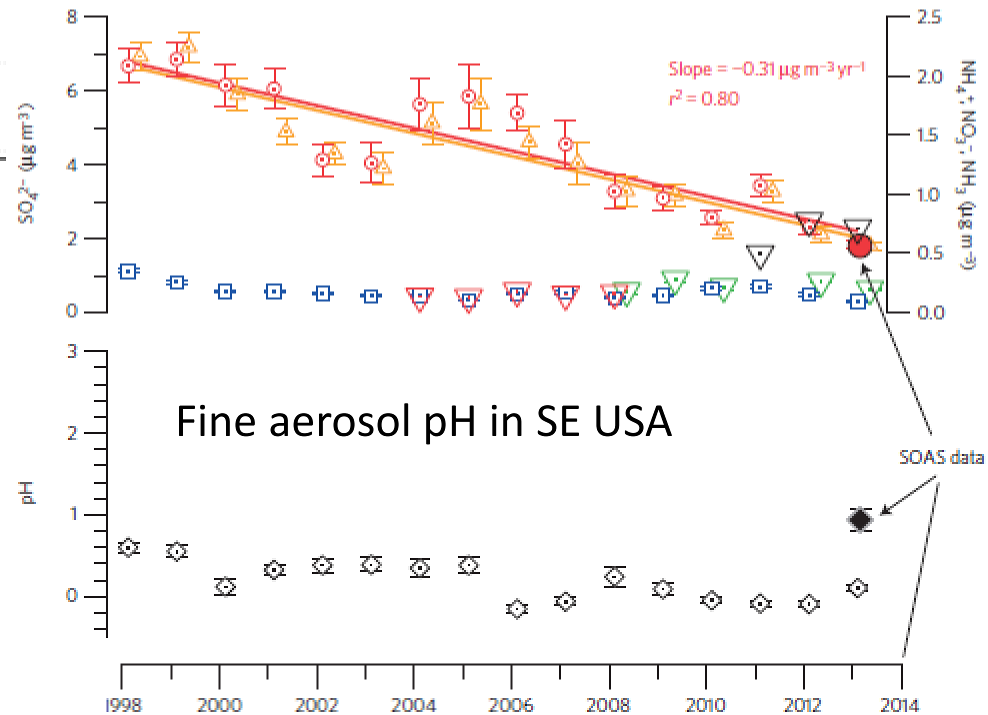
ON

SOA **aerosols** (may contain ON)

NH_3 → neutralizes atmospheric acids → **aerosols**
(NH_4HSO_4 or $(NH_4)_2SO_4$ or NH_4NO_3 – **pH sensitive**)
→ can be involved in nucleation / formation of new particles in the atmosphere

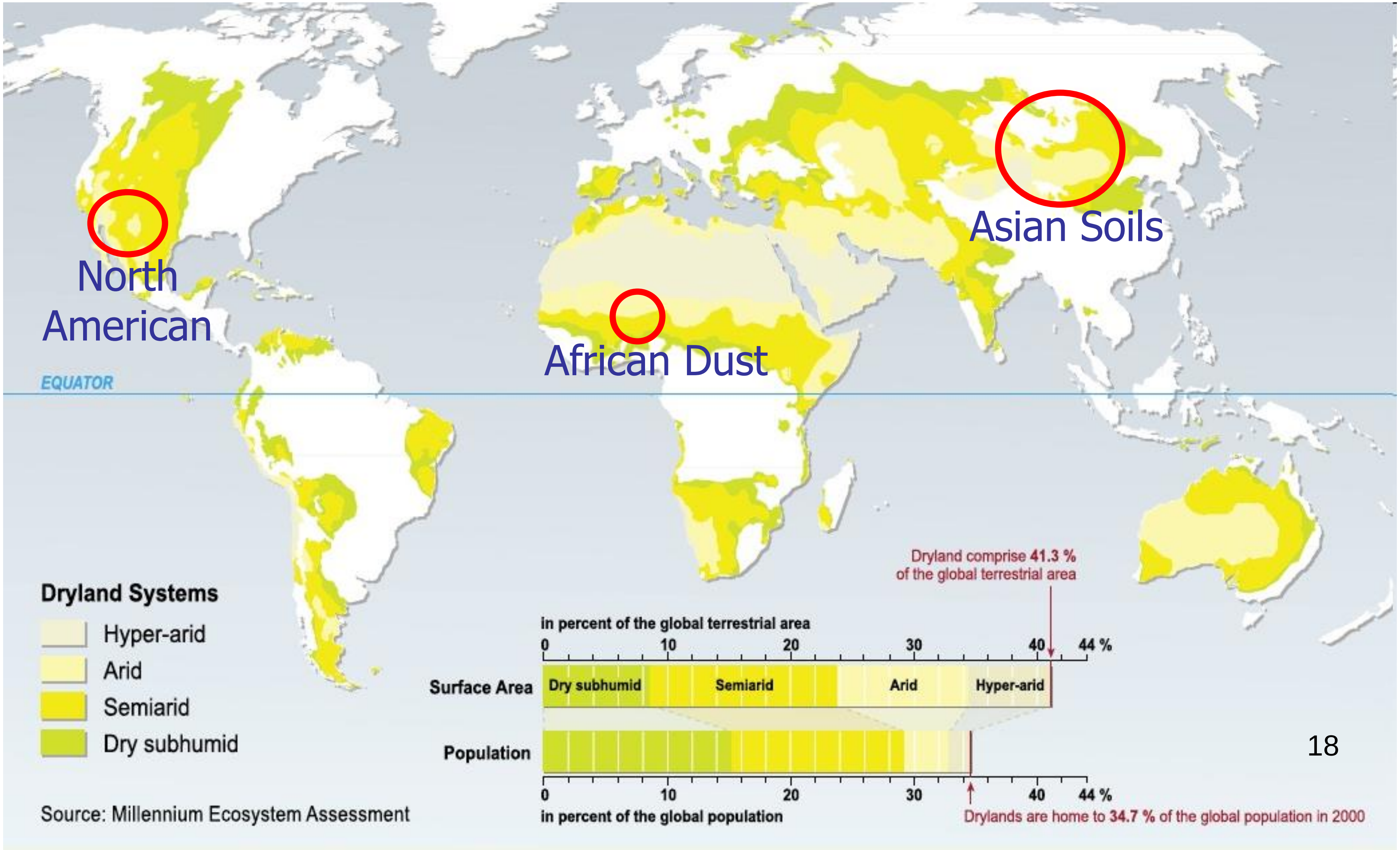
NO_3^-/HNO_3 partitioning is pH sensitive



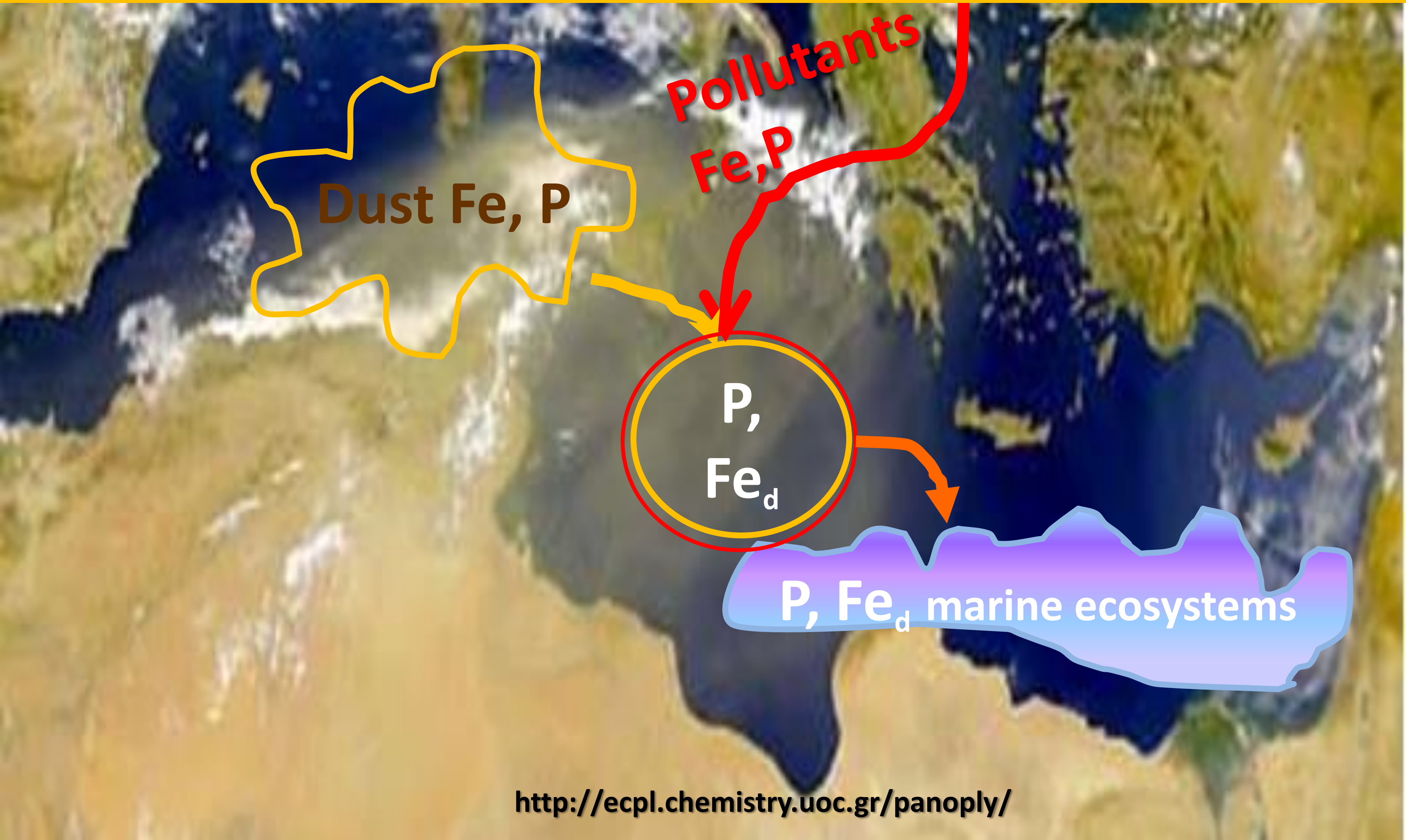


Weber et al., NGEO, 2016

Dust is emitted close to "pollution": opportunity for interaction



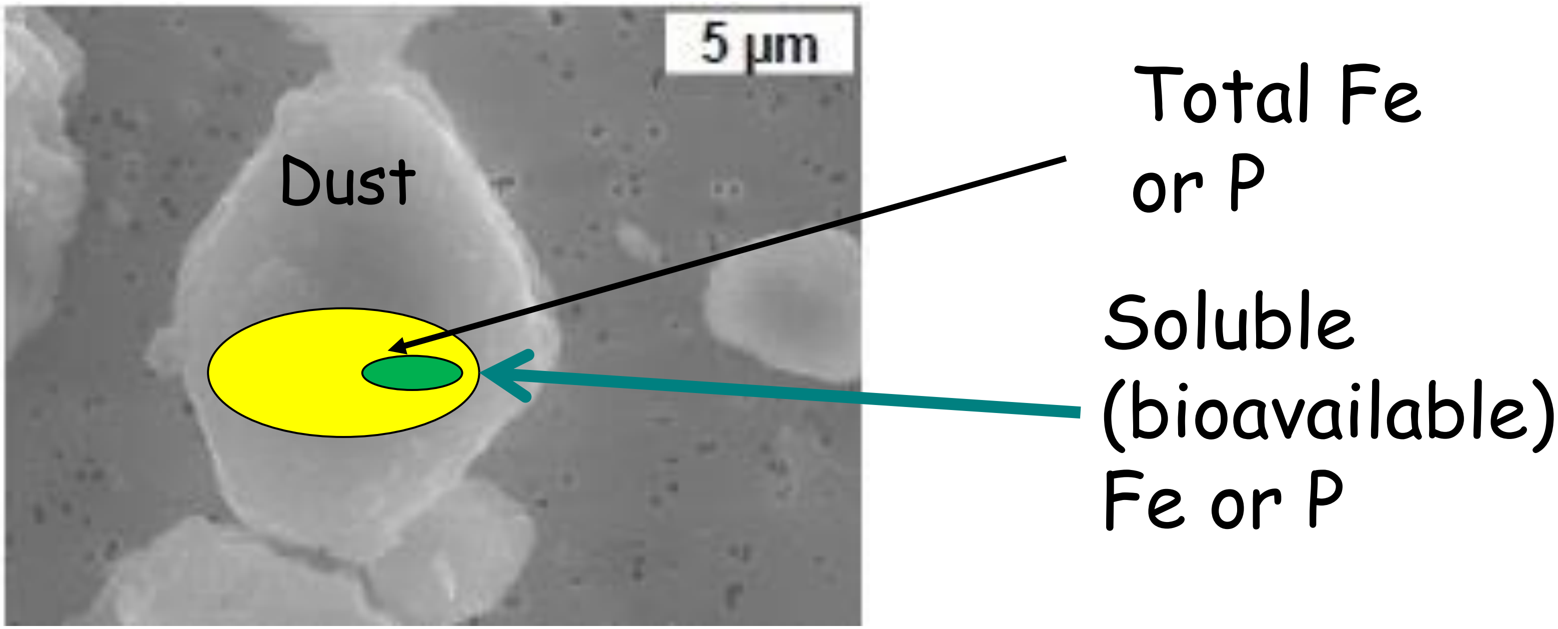
Dust is the most important reservoir of Fe and P that are mobilized by interactions between natural & anthropogenic emissions



http://ecpl.chemistry.uoc.gr/panoply/

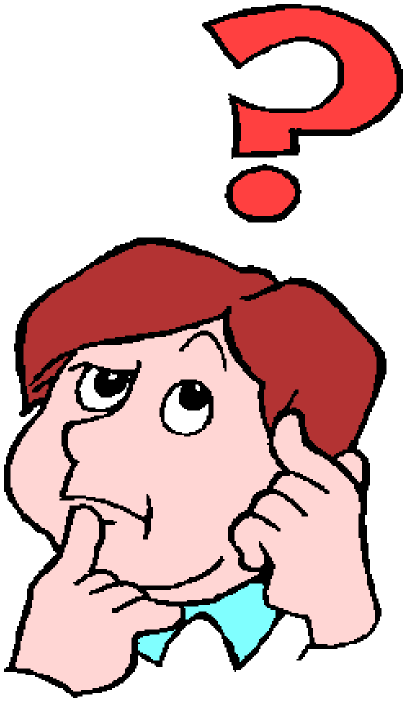
Mineral dust and its content

- Dust interaction with pollution can affect the soluble (bioavailable) fraction of Fe, P in dust (and reactive N).



Courtesy Athanasios Nenes

What is bioavailability?



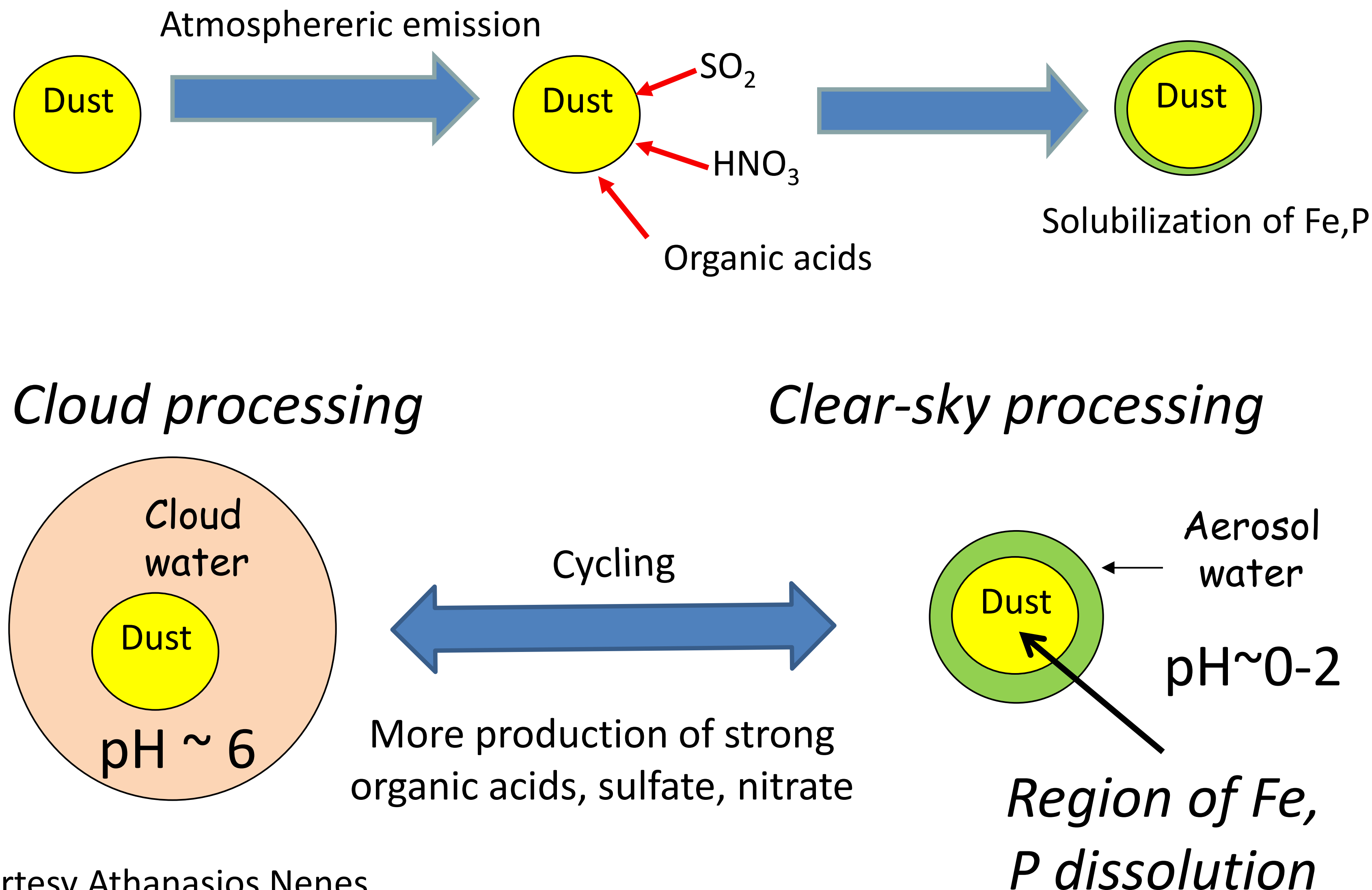
- ‘Bioavailability is sometimes assumed to correspond to a measure of the absolute availability of a given nutrient to the biota.
- Under many circumstances the bioavailability of a chemical species or complexed element may be better described in terms of the community uptake rate.

readily available

- Bioavailability reflects a combined characteristic of both the chemical form of a nutrient and the capabilities of the extant biological community’.

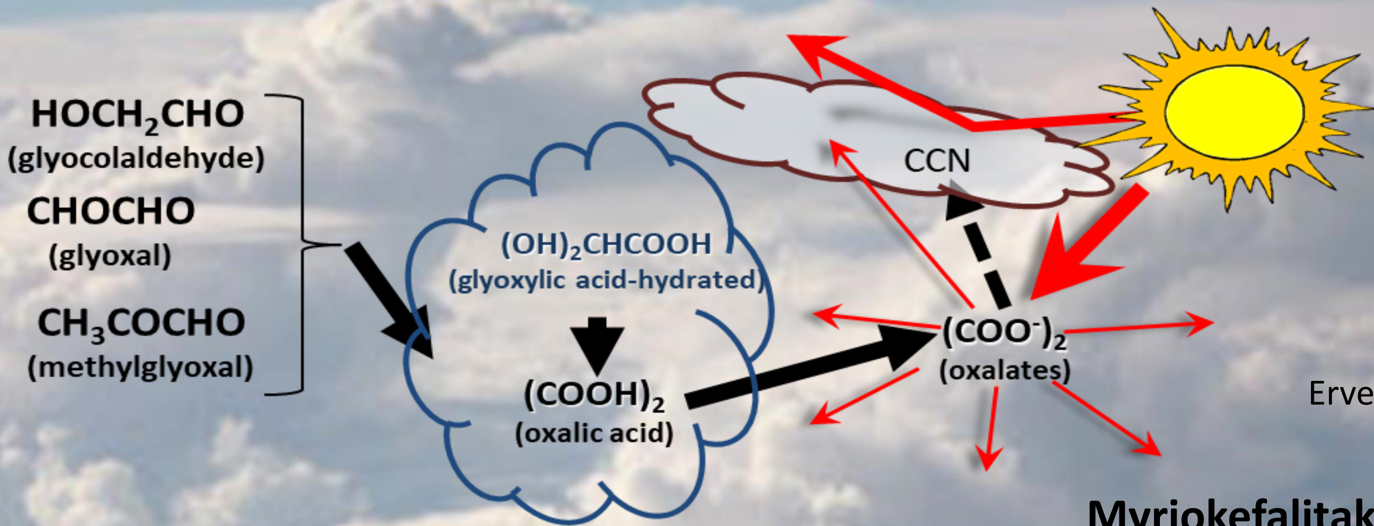
Moore et al. NGEO 2013

How does pollution increase the fraction of soluble Fe, P in dust?



Courtesy Athanasios Nenes

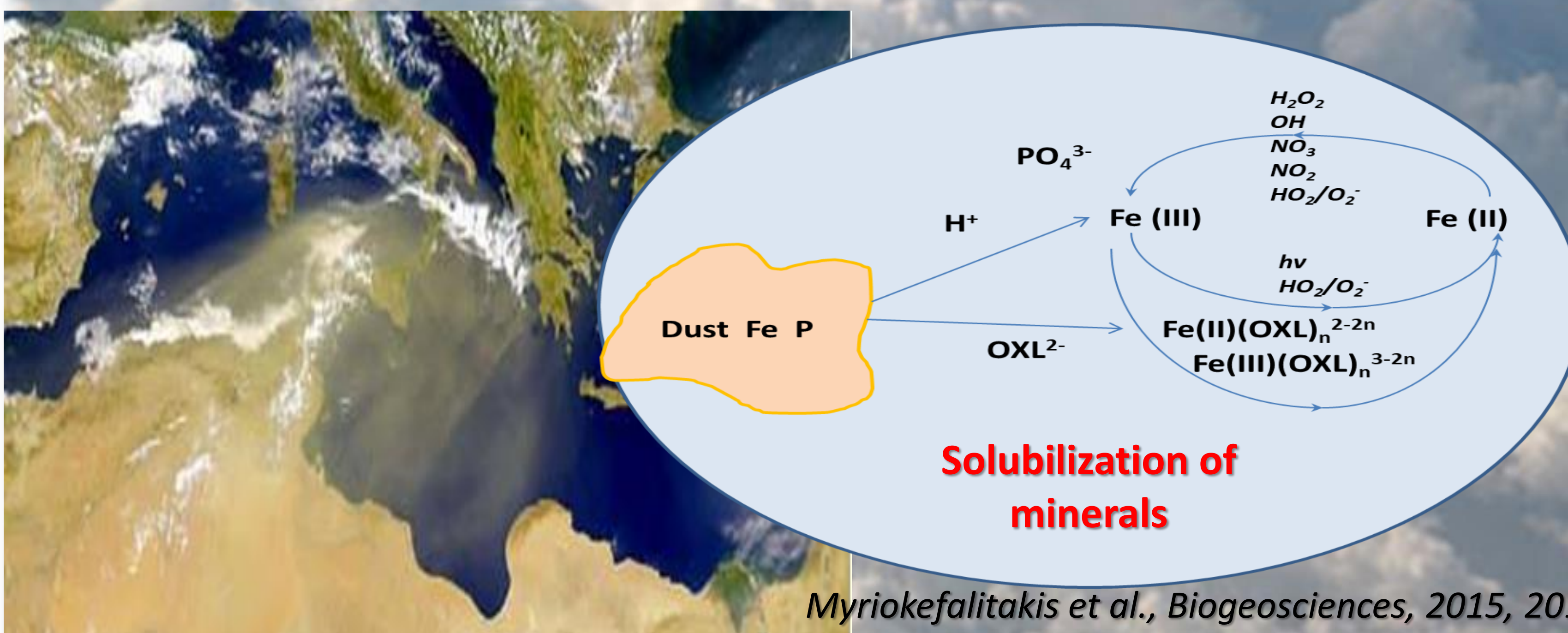
Multiphase chemistry in the global troposphere



Organic ligand formation

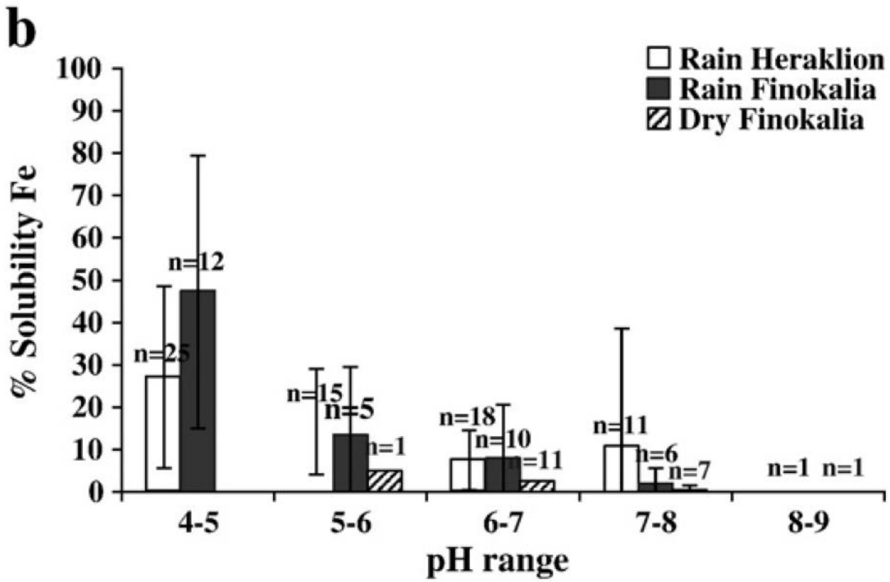
Kinetics from
Lim et al., ACP, 2010
Ervens & Volkamer, ACP, 2010
Noziere et al., 2009

Myriokefalitakis et al., ACP 2011

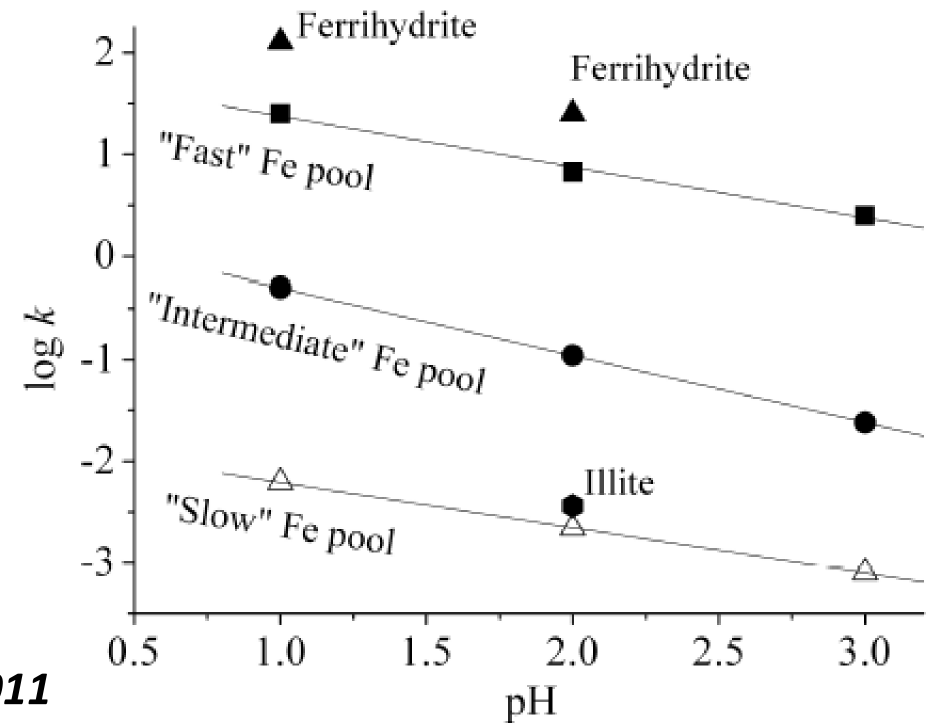


Myriokefalitakis et al., Biogeosciences, 2015, 2016

Fe solubility and pH



Iron solubility - C. Theodosi et al., Marine Chemistry 120 (2010) 154–163

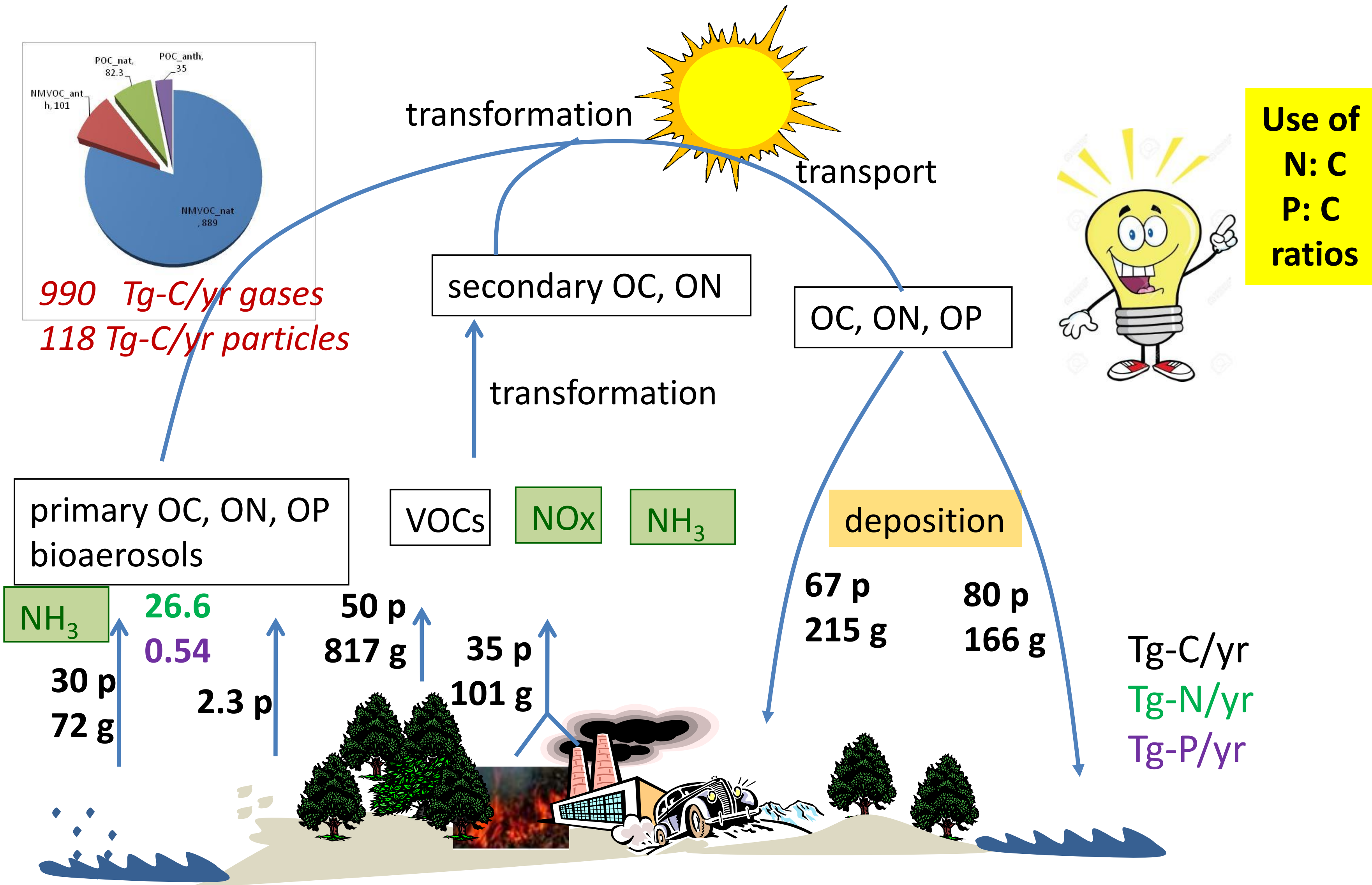


Parameterization based on 3 pools of Fe

Shi et al., ACP, 2011

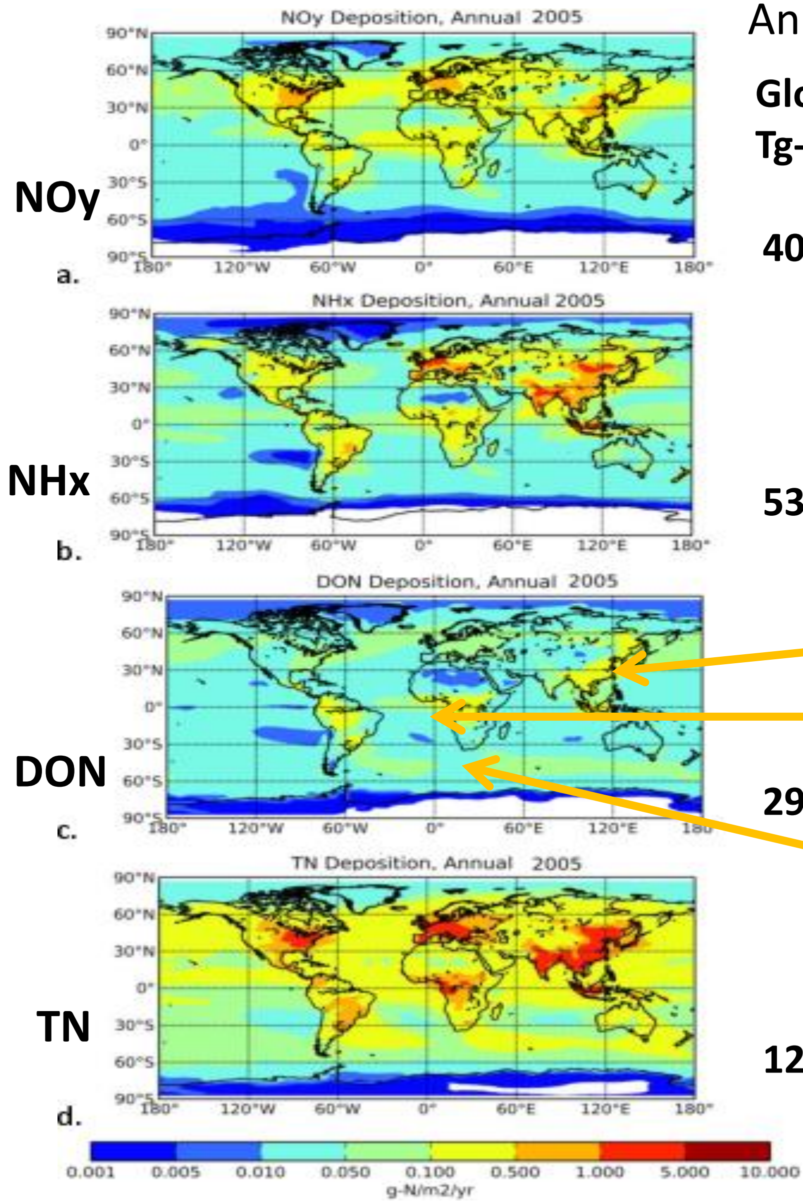
Organic C, N, P in the global atmosphere

Link ON & OP to OC atmospheric cycle



Kanakidou et al., GBC, 2012, doi 10.10.1029/2011GB004277

Atmospheric N deposition



Annual mean deposition

Globe (ocean)
Tg-N/yr

NOy	**40(20)**
NHx	**53(20)**
DON	**29(13)**
TN	**129(54)**

ON source :

- **increases by 20% TN deposition**
- **is by 40% anthropogenic**

ON deposition is 20-25% of TN deposition

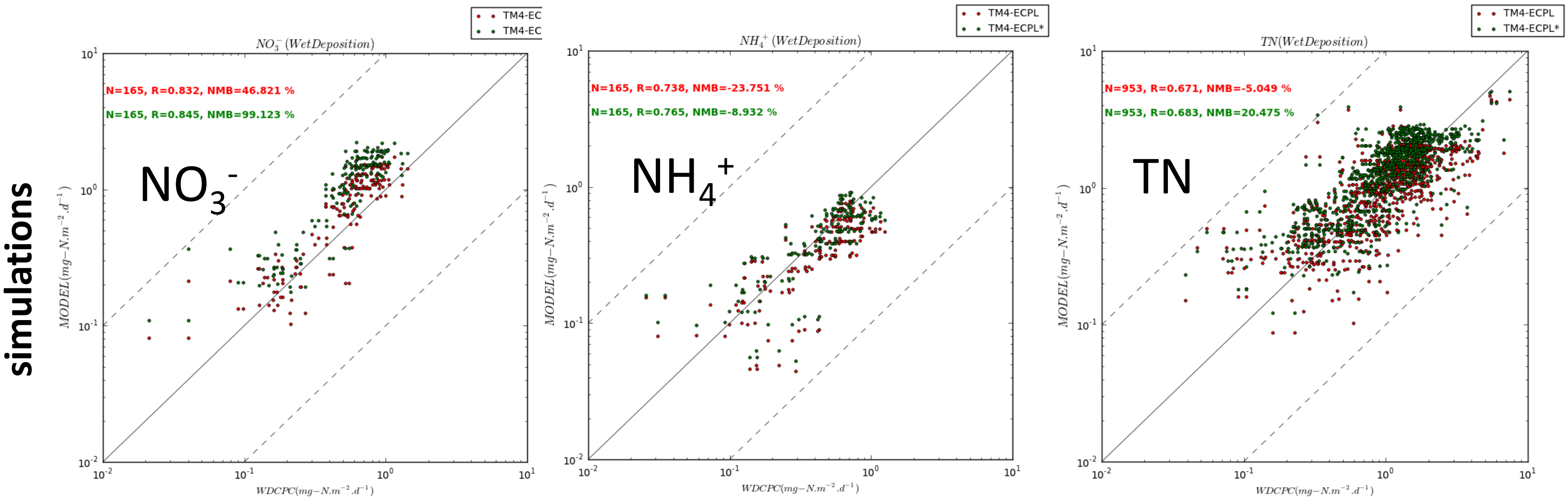
combustion

Primary biological particles
Biomass burning

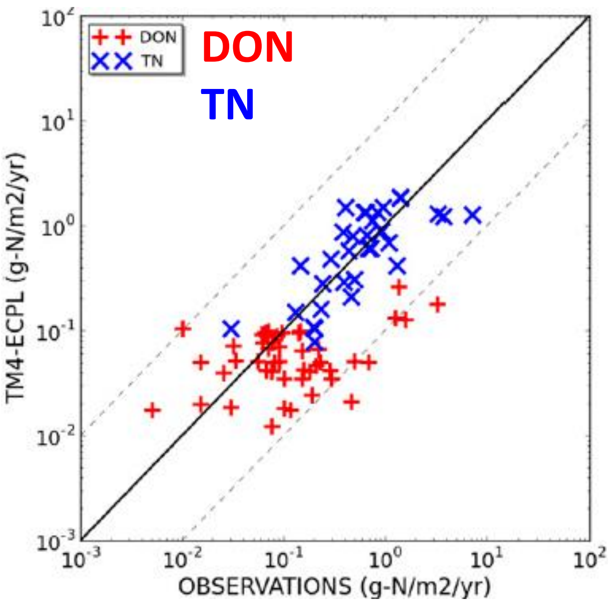
Sea-spray

Kanakidou et al., J. Aerosol Science, D150278, 2016

Atmospheric N deposition- agreement within the order of magnitude: 2- wet deposition fluxes



Observations (mg-N/m²/d) Scale 10^{-2} to 10^{1}

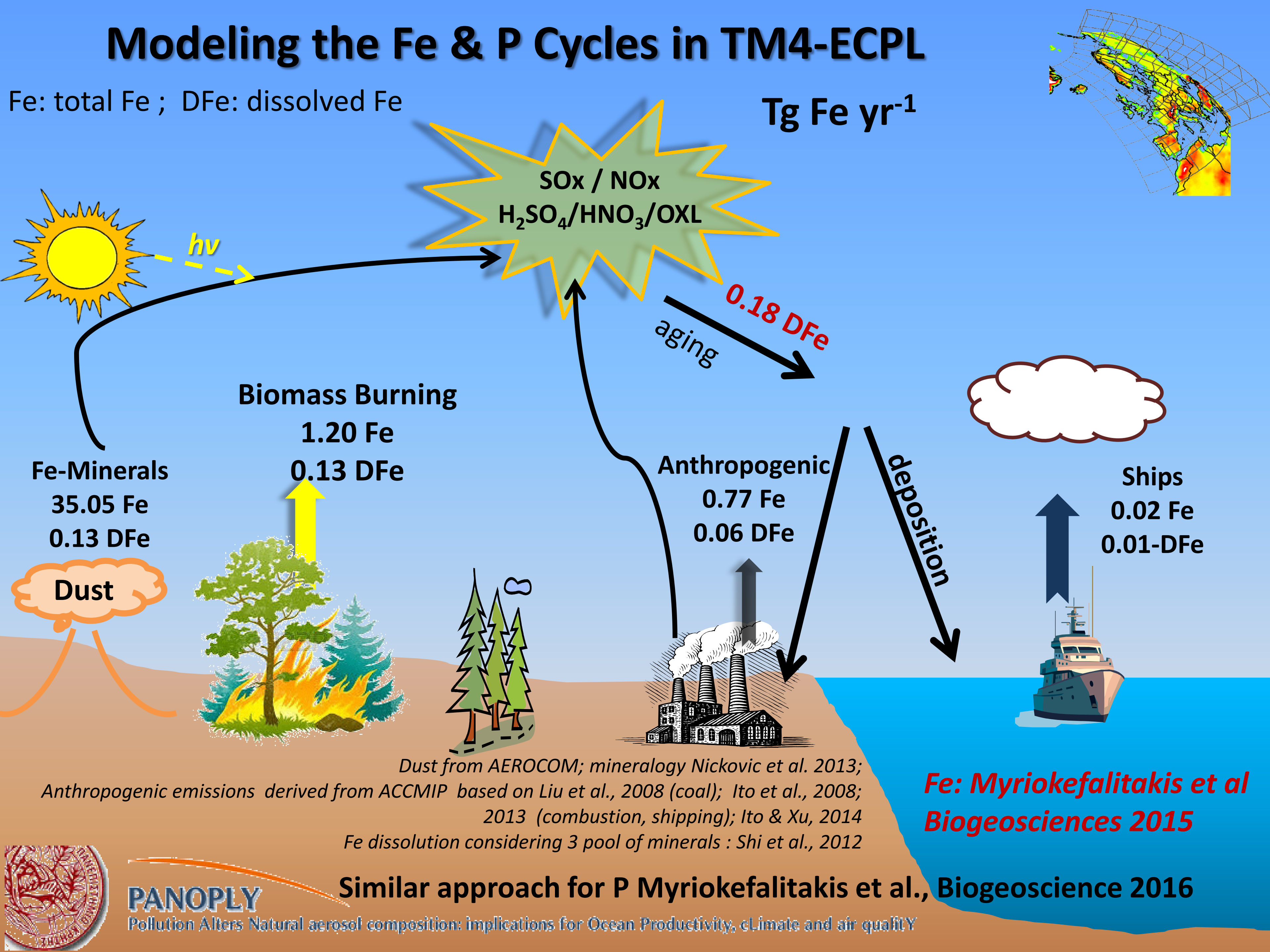


Kanakidou et al., JAS, 2016 suppl

Observations from Vet et al AE (2014)

← *Total deposition fluxes*

Kanakidou et al., JAS, 2016


Modeling the Fe & P Cycles in TM4-ECPL
Fe: total Fe ; DFe: dissolved Fe
Tg Fe yr^{-1}
SOx / NOx
H_2SO_4/HNO_3/OXL
hv
0.18 DFe
aging
Biomass Burning
1.20 Fe
0.13 DFe
Fe-Minerals
35.05 Fe
0.13 DFe
Dust
Anthropogenic
0.77 Fe
0.06 DFe
deposition
Ships
0.02 Fe
0.01-DFe
Dust from AEROCOM; mineralogy Nickovic et al. 2013;
Anthropogenic emissions derived from ACCMIP based on Liu et al., 2008 (coal); Ito et al., 2008; 2013 (combustion, shipping); Ito & Xu, 2014
Fe dissolution considering 3 pool of minerals : Shi et al., 2012
Fe: Myriokefalitakis et al Biogeosciences 2015
Similar approach for P Myriokefalitakis et al., Biogeoscience 2016
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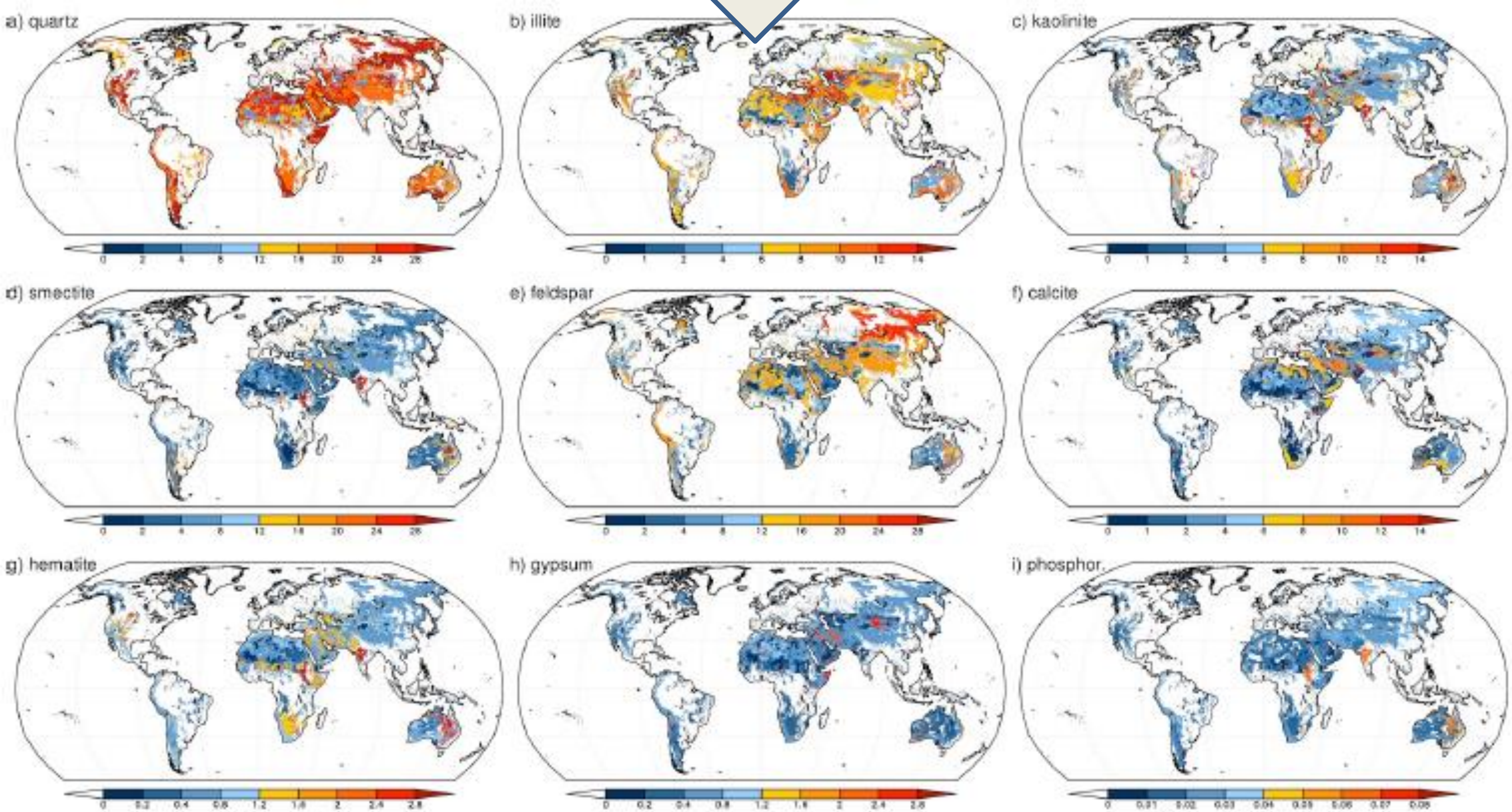
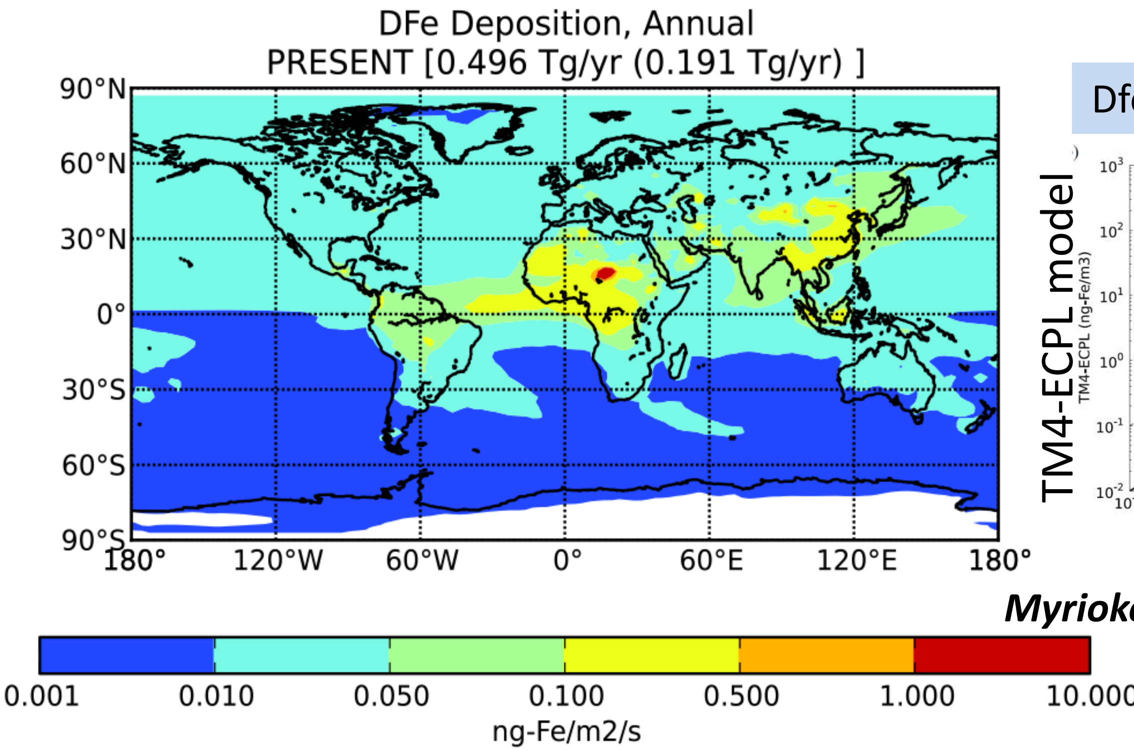
Emissions of Fe and P from dust sources

Dust emissions ✕ Mineralogy
Effective mineral content in soil in % ✕ Fe, P content

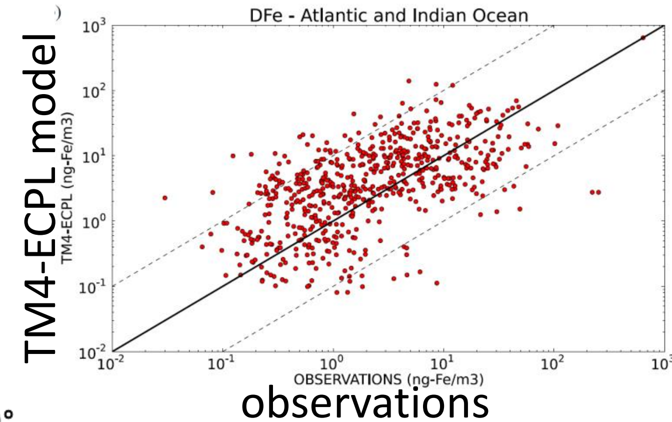


S. Nickovic et al.: High-resolution mineralogical database ACP, 2012

Soluble Fe (DFe) deposition



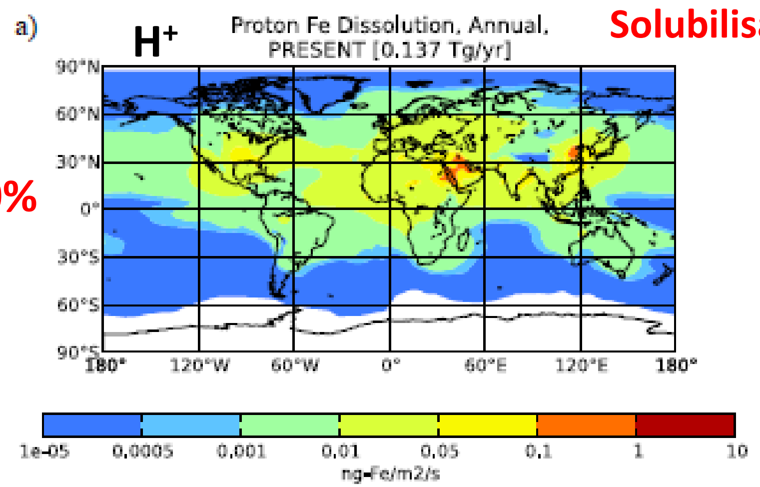
Dfe atmospheric concentrations

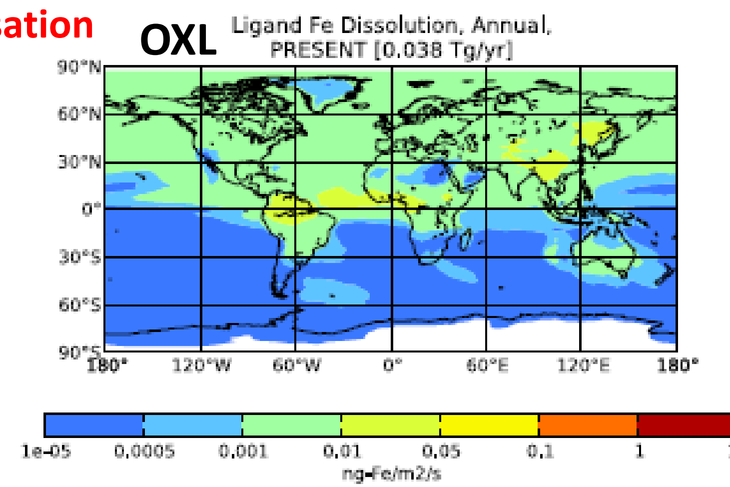


Myriokefalitakis et al Biogeoscience 2015

Solubilisation

80%

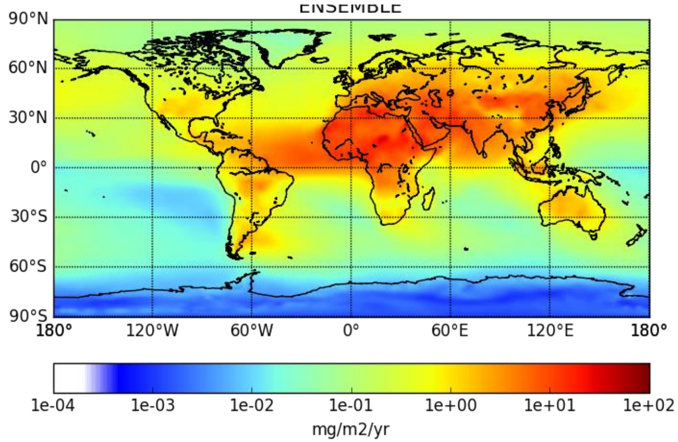




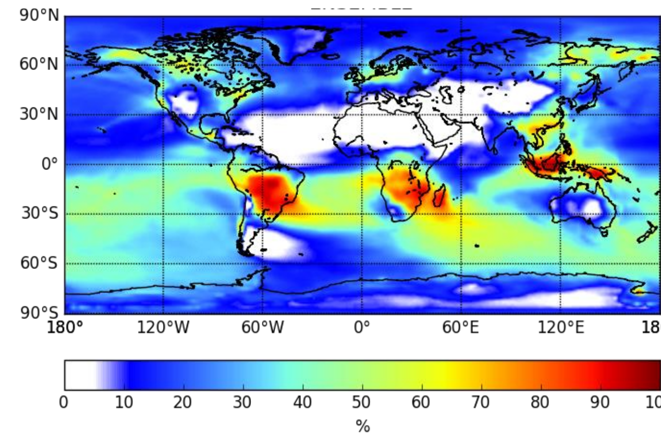
20%

Importance of Fe combustion sources

DFe deposition- annual mean

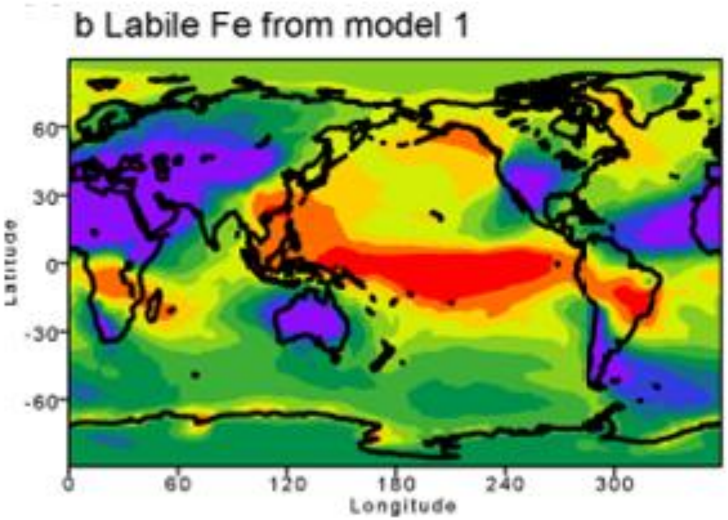


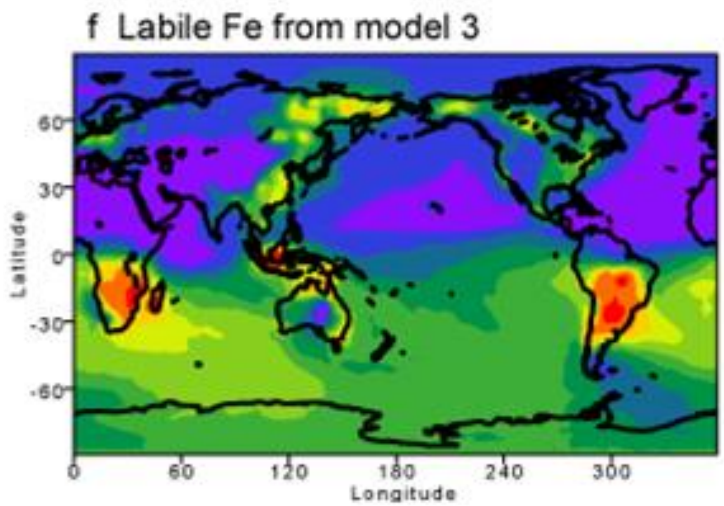
% contribution of combustion



Ensemble of global models Myriokefalitakis et al., Biogeoscience 2018

Large uncertainty – Combustion / Total (combustion + dust)

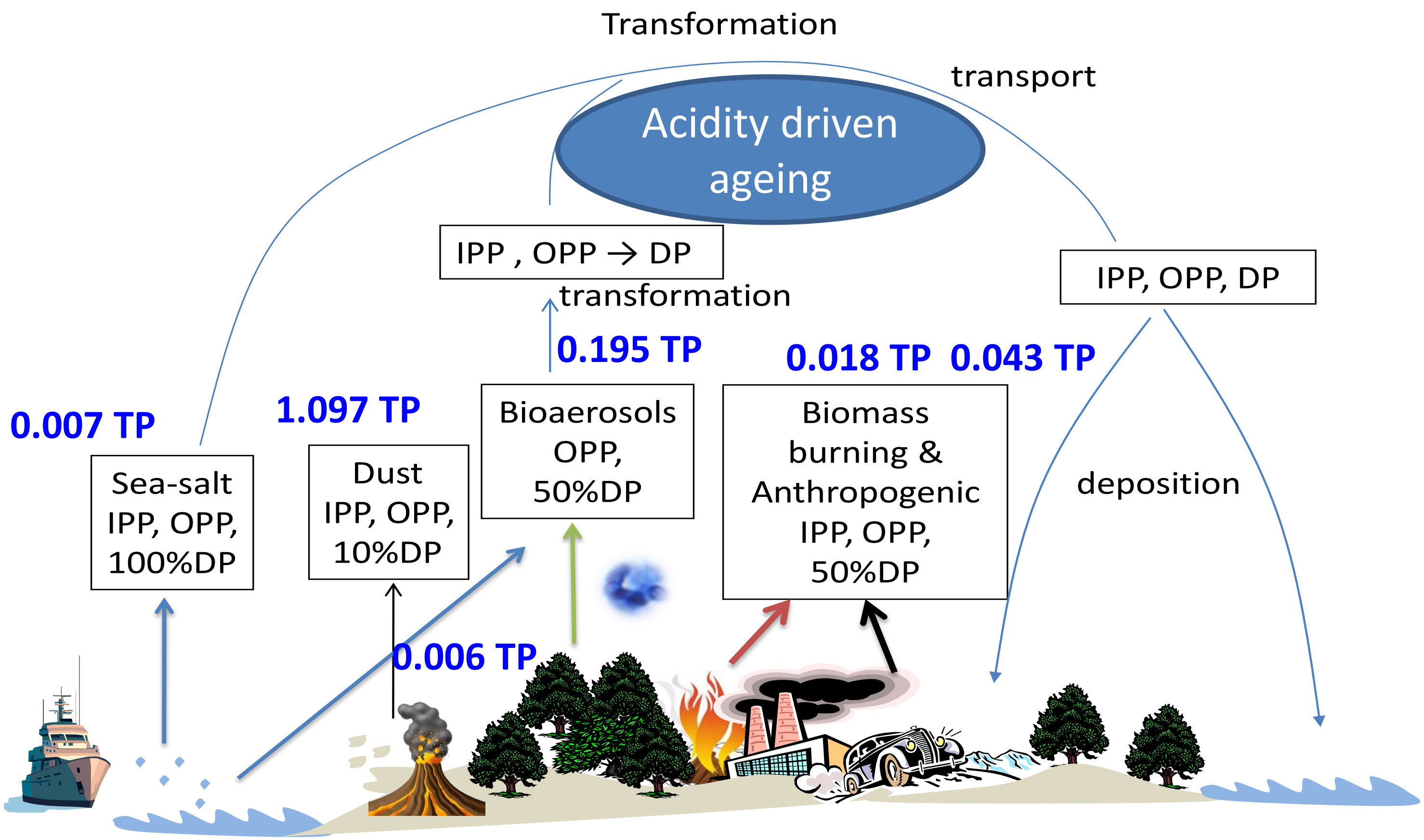




Ito et al., Science Advances 2019

GESAMP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

Atmospheric Phosphorus cycle



IPP: Inorganic P insol. ; OPP: Organic P insol.; DP: Dissolved (IP+OP)

TP: total P in Tg-P/yr

Myriokefalitakis et al. Biogeoscience, 2016

Based on: Nickovic et al., 2012; Zamora et al. 2013; Mahowald et al., 2008; Burrows et al., 2009; Hummel et al., 2015; Hoose et al., 2010 LEVITUS94 World Ocean Atlas

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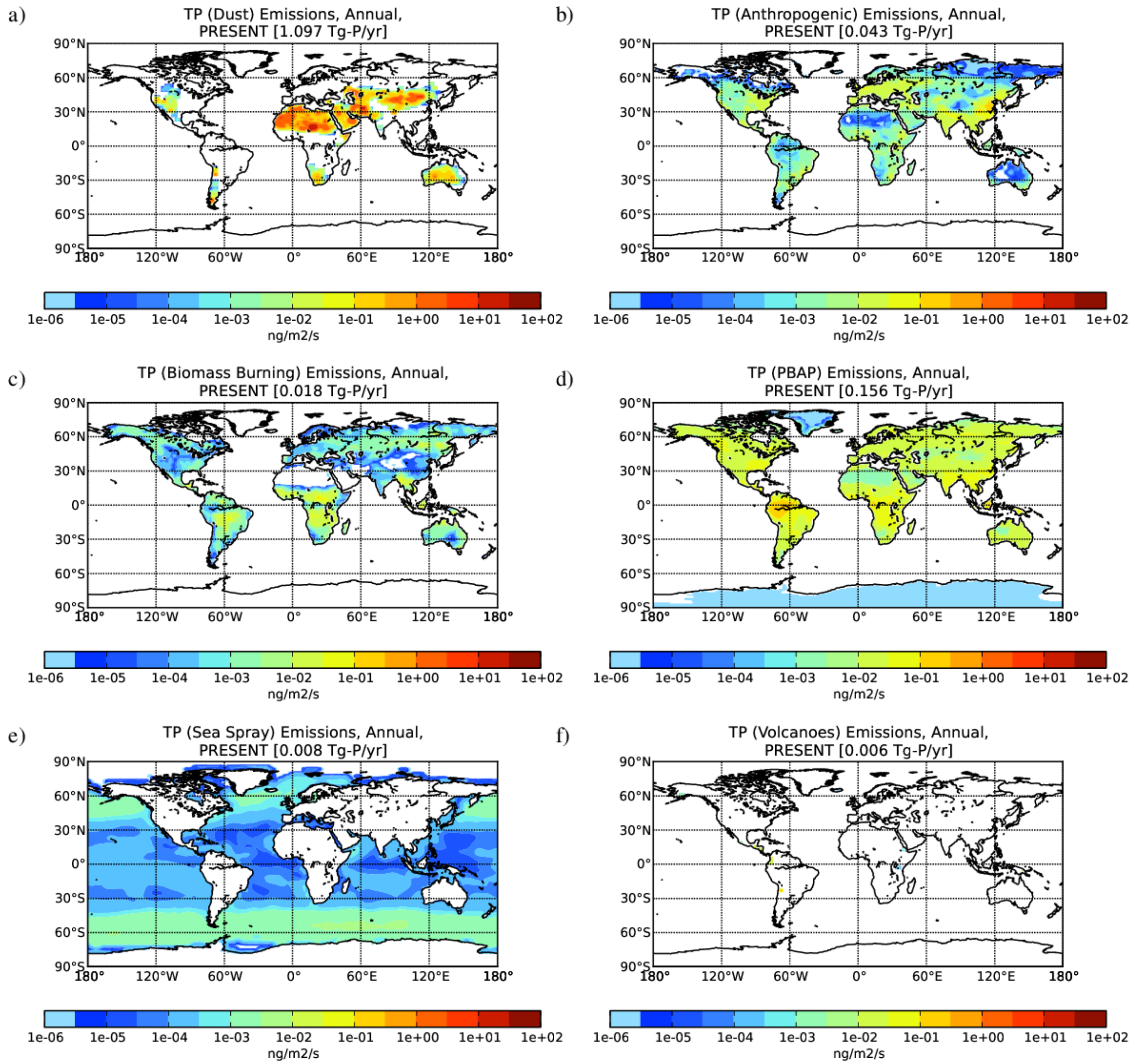
Distribution of P sources

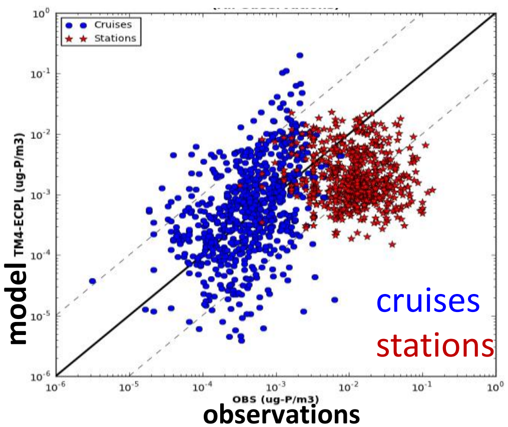


Myriokefalitakis et al, Biogeoscience, 2016

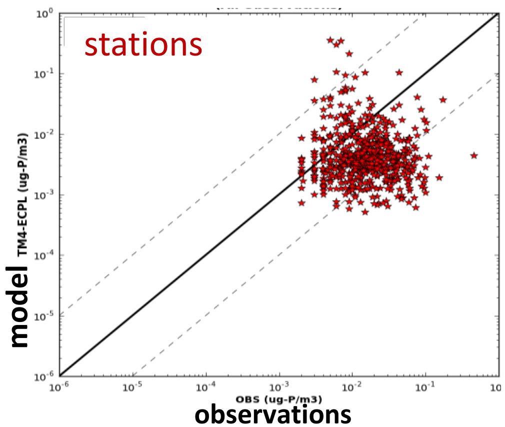
Atmospheric soluble Phosphorus (DP) deposition

P atmospheric concentrations

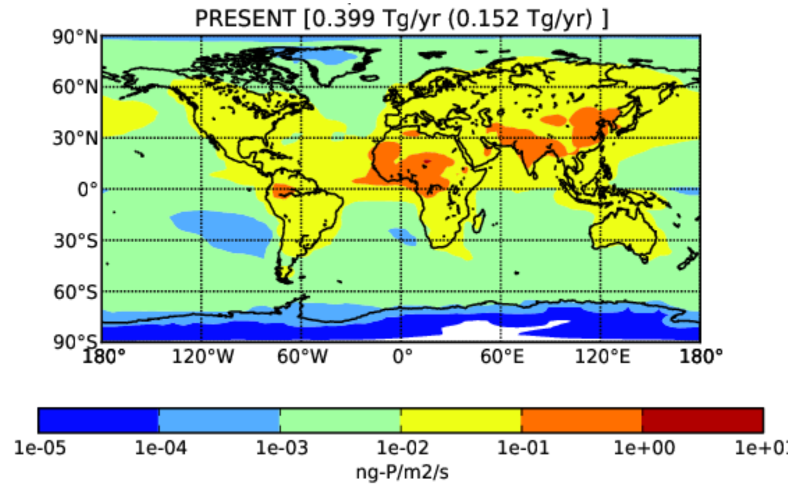
DP aerosol concentrations



TP aerosol concentrations

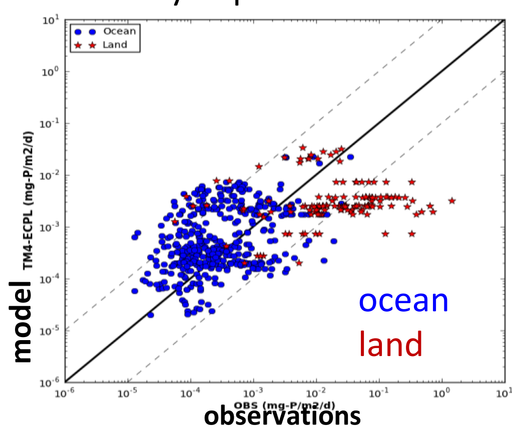


Soluble P (DP) deposition

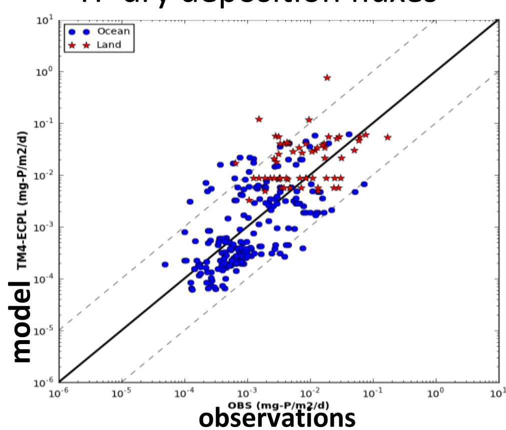


P atmospheric deposition fluxes

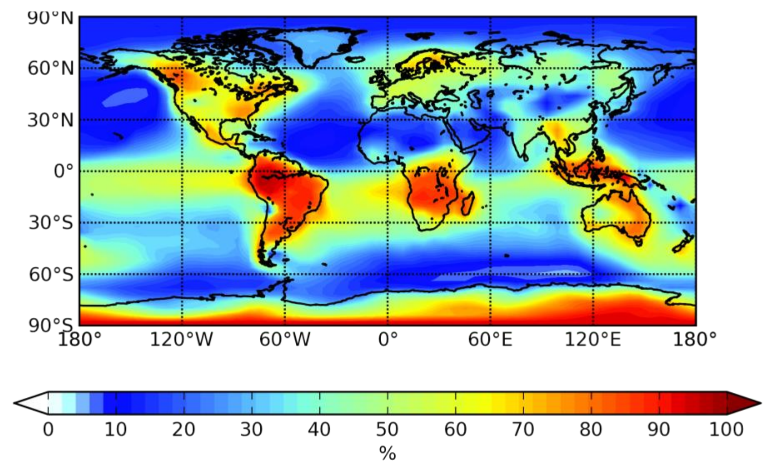
DP dry deposition fluxes



TP dry deposition fluxes



soluble organic P/total soluble P (DOP/DP)



Data from Vet et al., AE 2014; Baker et al., 2006; Mihalopoulos et al. unpublished

Myriokefalitakis et al. Biogeoscience 2016

- ✓ ***3 times higher P mobilization in aerosol water than in clouds***
- ✓ ***Importance of bioaerosols***

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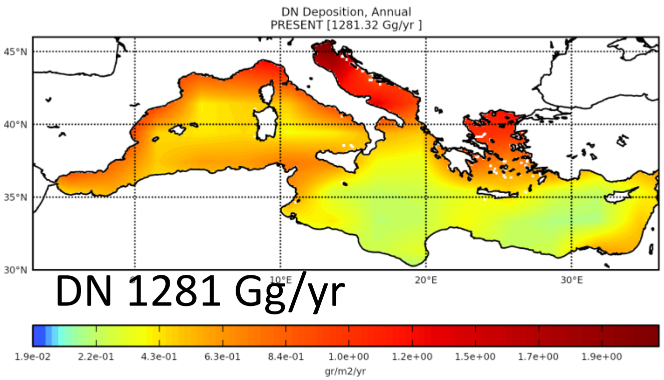
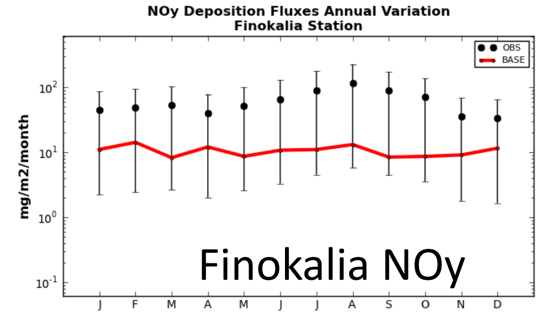
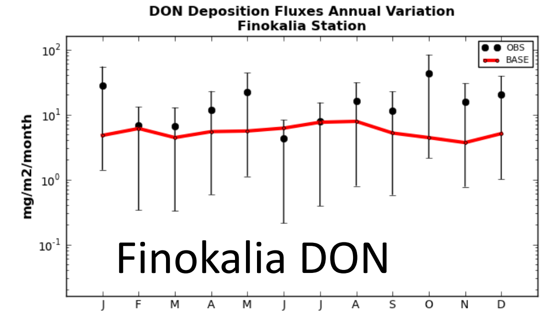
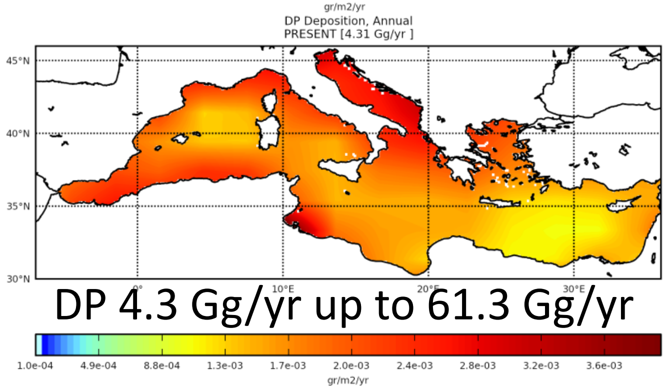
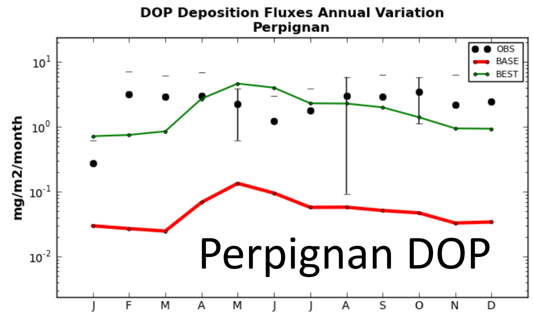
Annual deposition of soluble nutrients to the Mediterranean

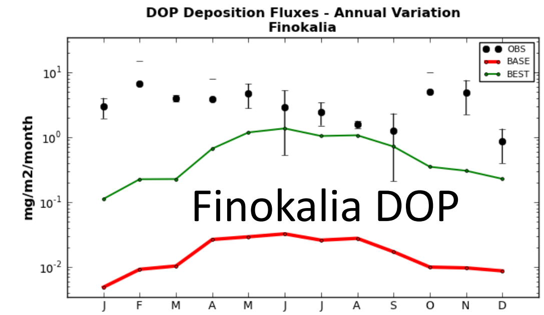


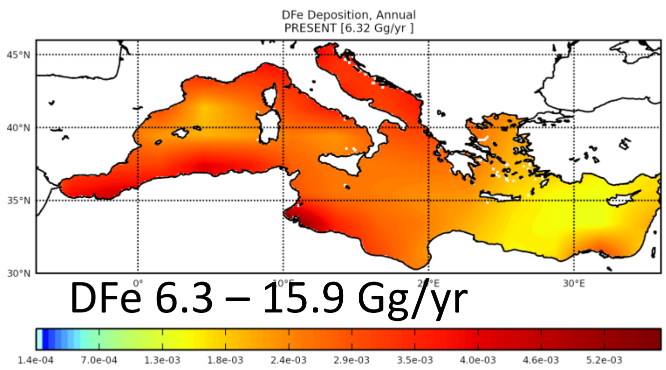


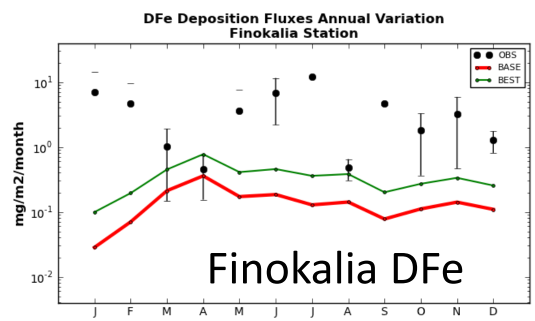








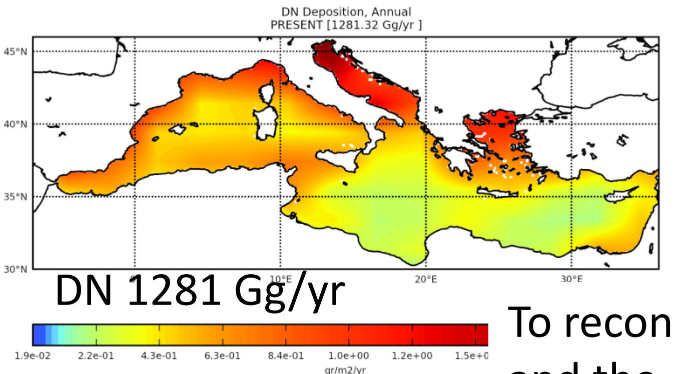


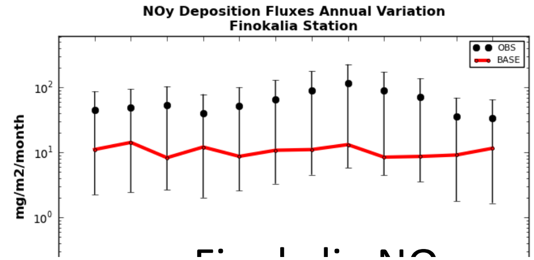


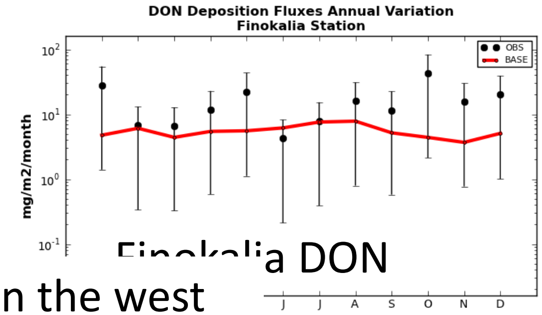
Red lines base case
Green lines :
2.5 times higher flux of DFe
(5x combustion as in Matsui et al 2018; 2x dust Fe emissions as in Myriokefalitakis et al., 2018)
~14 times higher flux of DP (2x dust P – following Fe emissions 50x bioaerosol –P within the uncertainty range (Depres et al,, 2012; Kanakidou et al 2012)

Kanakidou et al, Dep Sea Res. II, 2019
doi.org/10.1016/j.dsr2.2019.06.014

Annual deposition of soluble nutrients to the Mediterranean

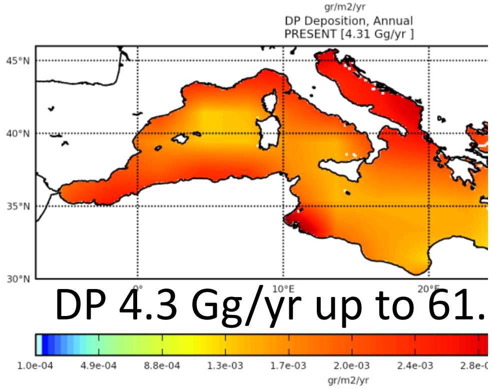


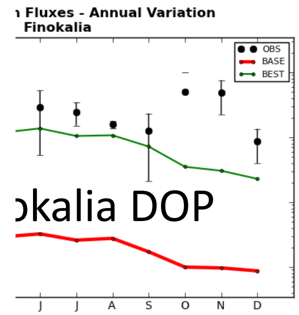


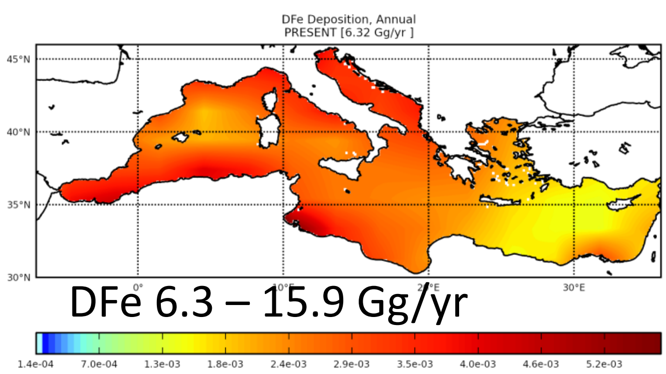


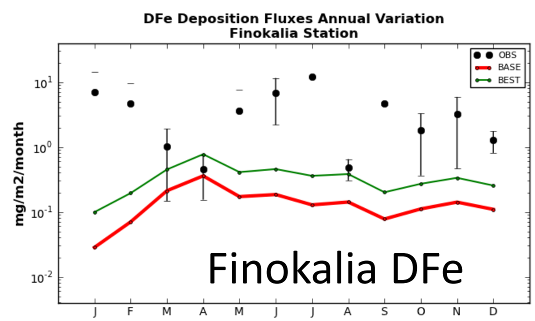
To reconcile with the observed fluxes in the west and the east Mediterranean, ~14 times higher flux of DP ,in particular DOP, and at least 2.5 times higher flux of DFe need to be considered in the model.

These could be linked to combustion and bioaerosols as well as to dust dissolution rates









Green lines :
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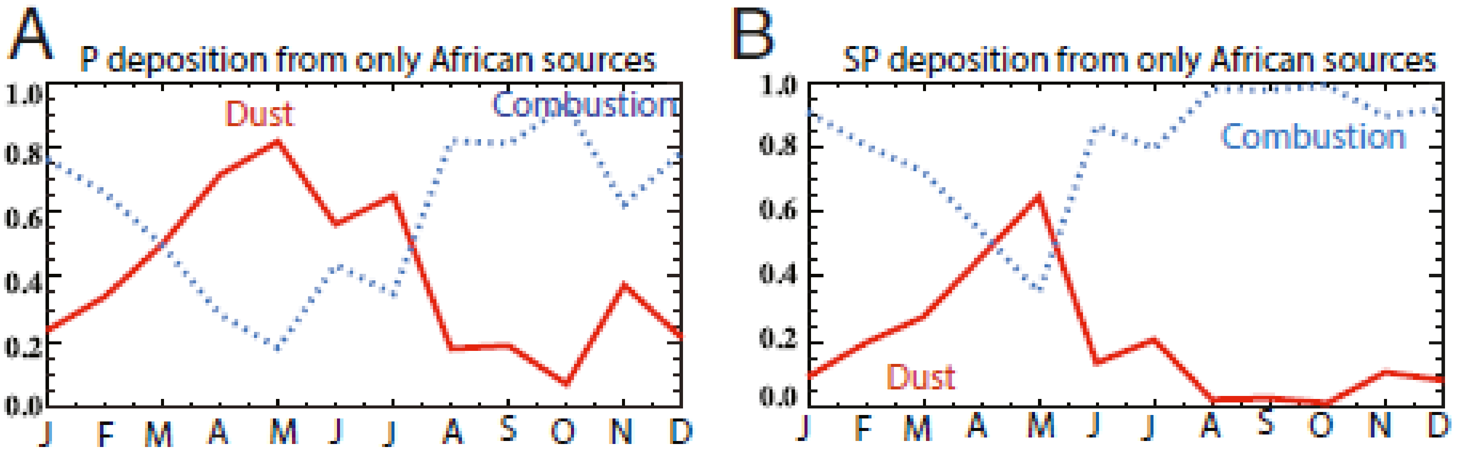
Kanakidou et al, Dep Sea Res. II, 2019
doi.org/10.1016/j.dsr2.2019.06.014

African biomass burning is a substantial source of phosphorus deposition to the Amazon, Tropical Atlantic Ocean, and Southern Ocean



Boreal spring → Dust major supplier of P (5% soluble)

Boreal fall → Biomass burning from S. Africa supplies about half of the P deposited annually to the Amazon from transport African aerosols

Barkley et al., PNAS 2019

Πηγές ατμοσφαιρικού N, Fe και P

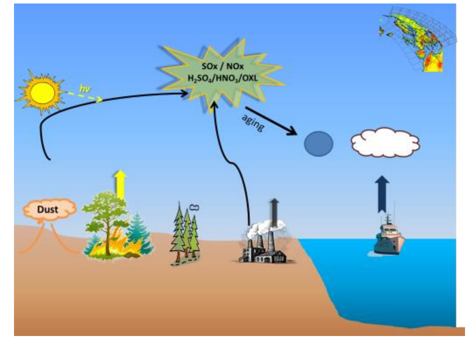
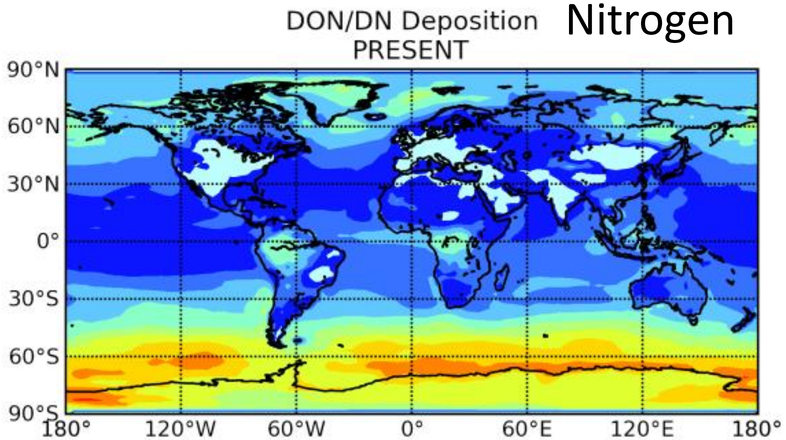


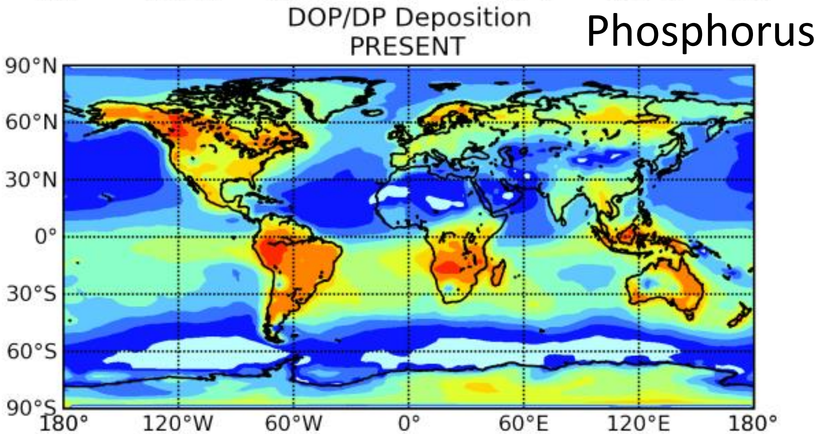
Table 1. Summary of source estimates for total N (NO_x/NO_3^-, NH_3/NH_4^+, organic N), P(inorganic and organic P) and Fe (in Tg N yr^{-1}, Tg P yr^{-1} and Tg Fe yr^{-1}, respectively). A range is provided, where available, with a suggested estimate in parenthesis. For details see in the text and the table footnotes.

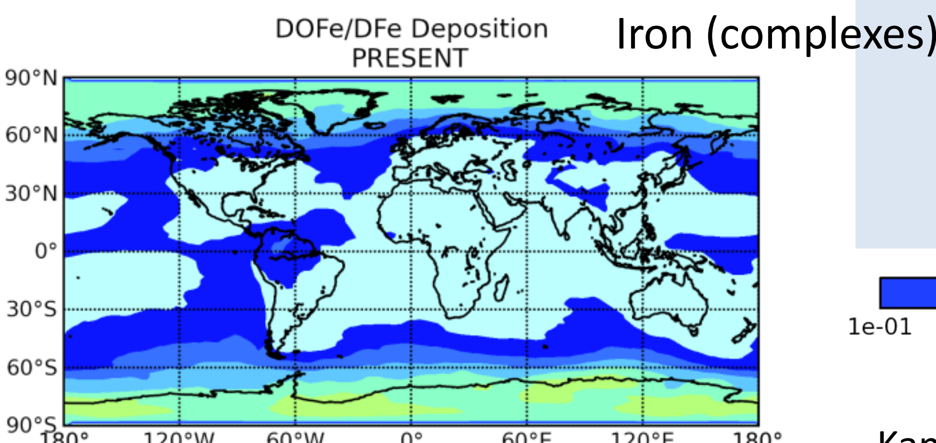
Sources	Nitrogen[a]	Phosphorus	Iron
Desert dust	0.1–4.2 (0.3)	0.23[c]–3.8[b] (1.1)	35–115 (35)[b]
Soil and lightning	6–23[d] (14)		
Ocean (gases and sea spray)	8.9–34.7 (14.4)	0.005–2.71 (0.01)[g]	
Bioaerosols	0.6–18.6 (9.0)	0.002–2.13 (0.156)	0.001–0.05 (0.001)
Volcanoes	0.4–1.3 (0.9)[h]	0.006–0.218 (0.01)[h]	0.008–0.305[i]
Biomass burning	15.6–44.06 (19.4)	0.071–2.5[e,f] (0.1)	1.07–5.3[e] (1.2)
Terrestrial anthropogenic	60.3–77.3 (62.5)		0.66–0.77
Shipping	5.3		0.015–0.016
Total	105.2–198.2 (126)	0.5–9.5 (1.38)	36.8–121.4[e] (42.1[b])

Kanakidou et al. ERL, 2018

Organic fraction of soluble nutrient deposition



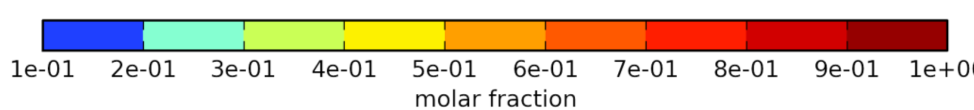




Important contribution of organic nitrogen, organic phosphorus and organic complexes of iron to the respective nutrient total soluble deposition

20-40% (nitrogen)
35-45% (phosphorus)
7-18% (iron)

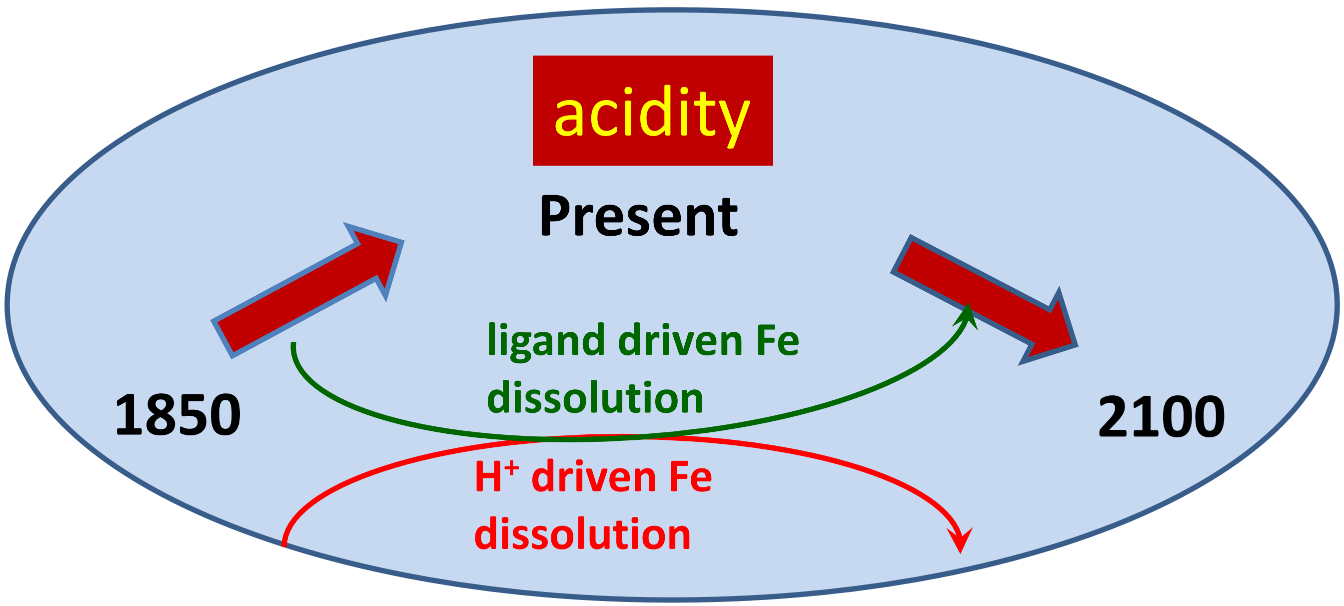
Important contribution of bioaerosols to ON and OP



Kanakidou et al. , *Environ. Res. Lett.* 13 (2018) 063004

What is the impact of emission changes on atmospheric acidity and on nutrients?

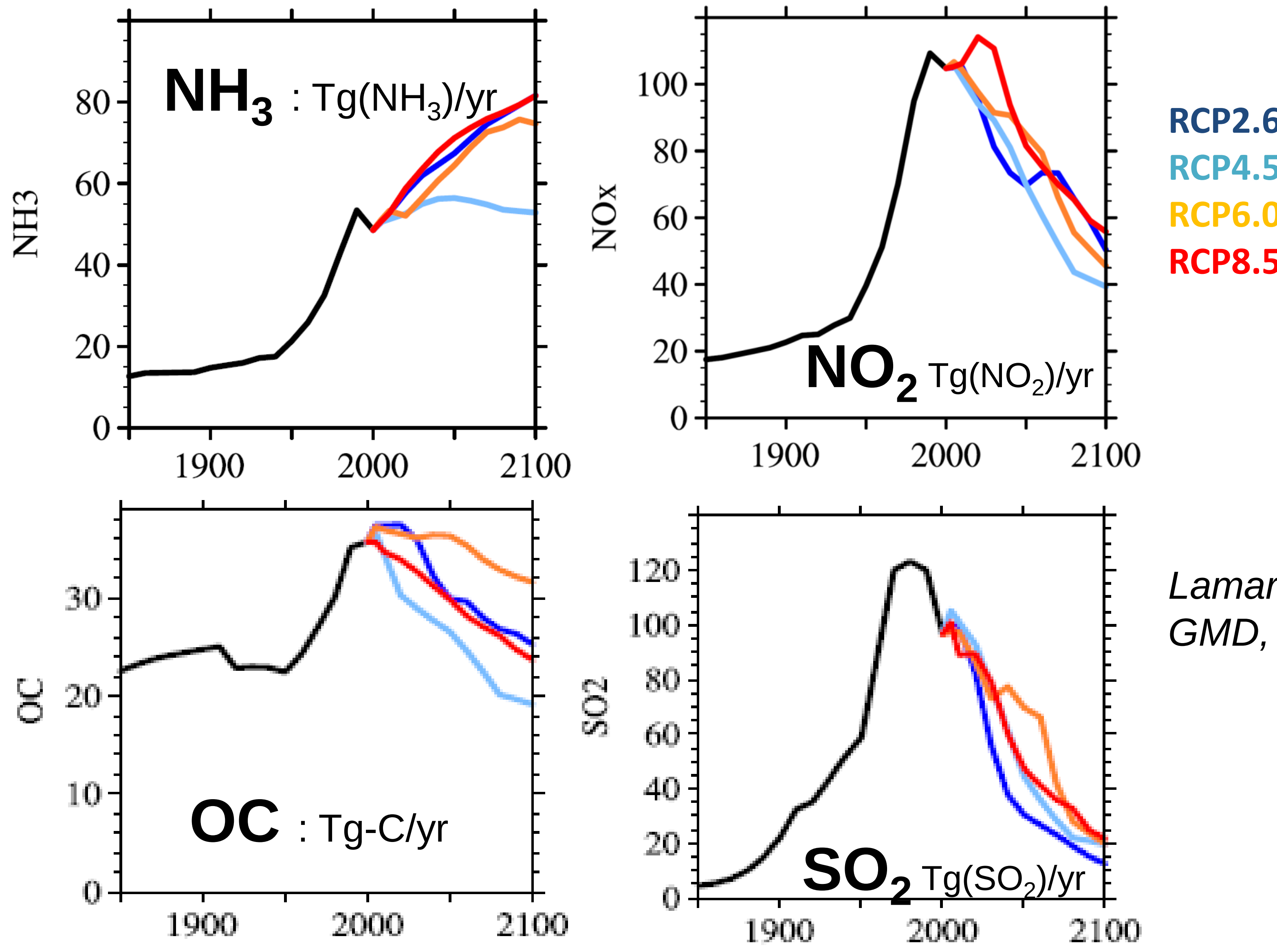
Simulations : Past-present-future emissions
& constant present day meteorology



Myriokefalitakis et al., BG 2015

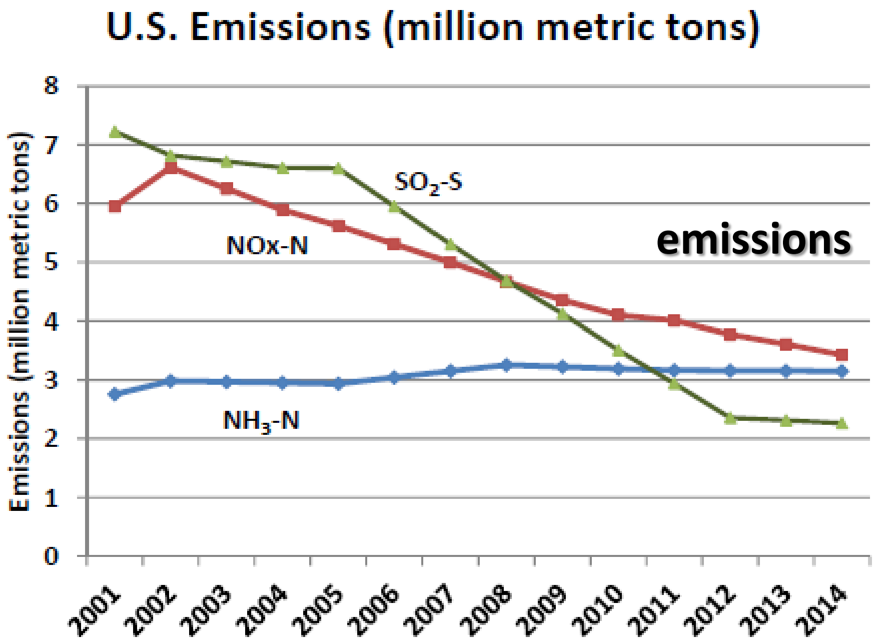
Development of emissions

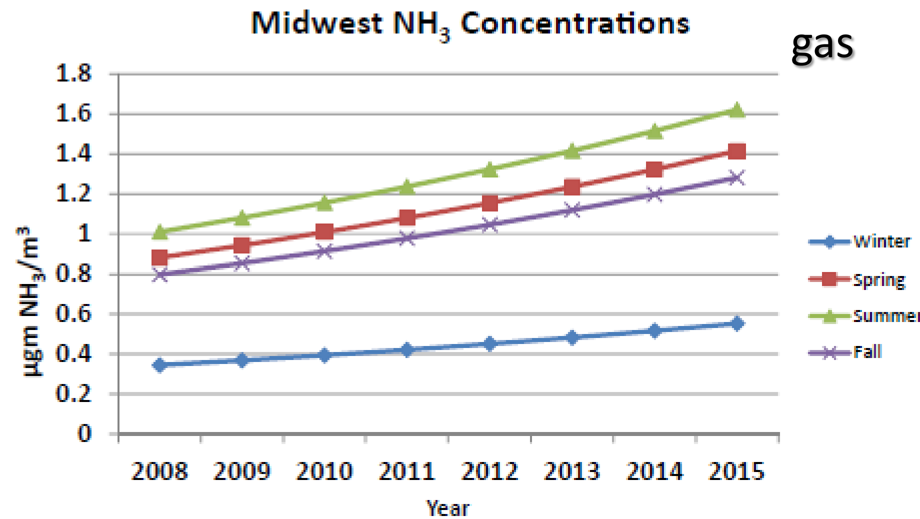
Global anthropogenic & biomass burning emissions

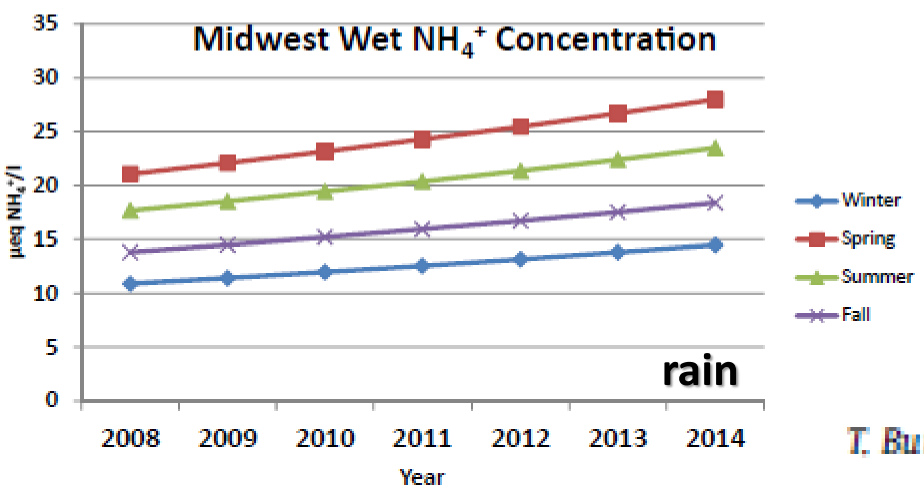


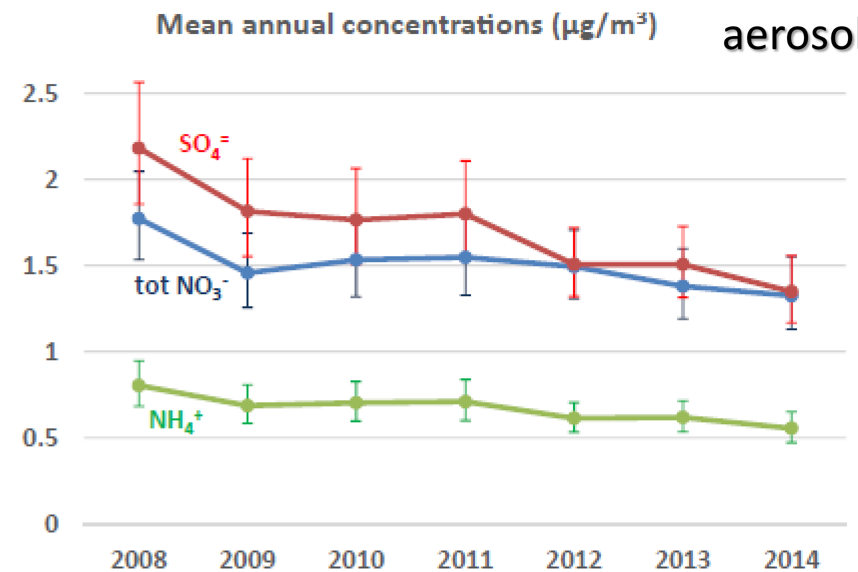
Lamarque et al. GMD, 2013

Recently observed variations



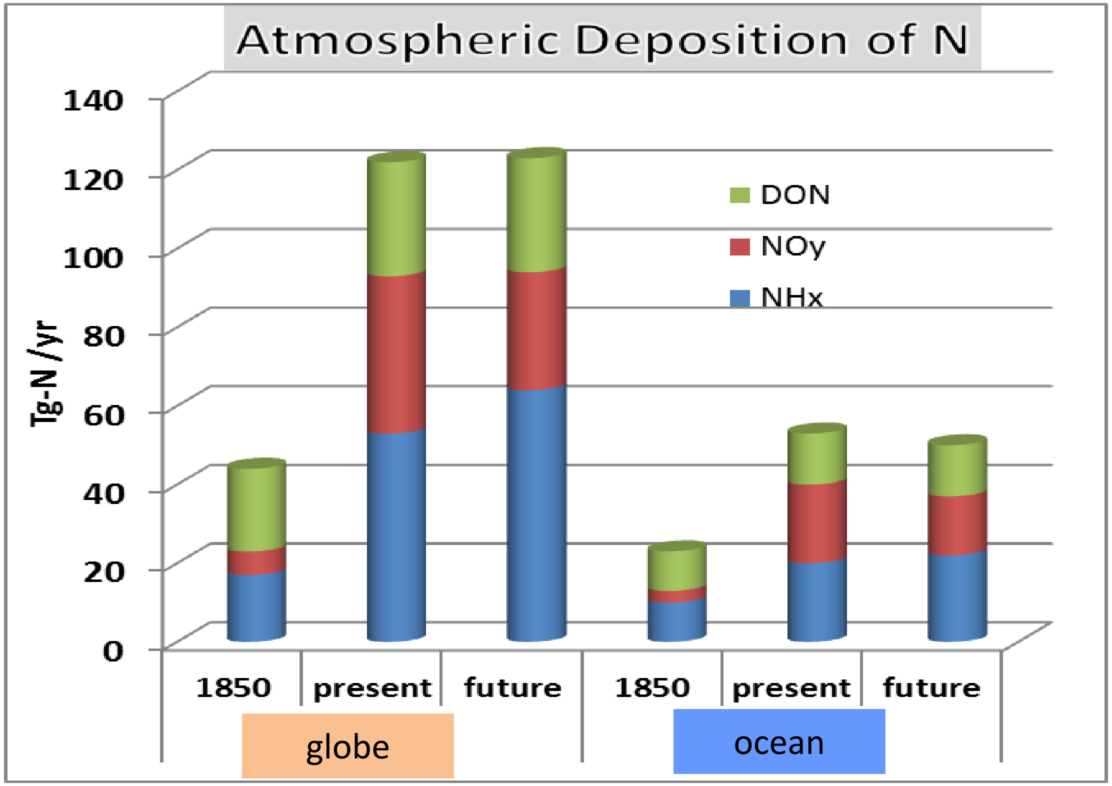






T. Butler et al. / Atmospheric Environment 146 (2016) 132–140

Atmospheric N deposition changes



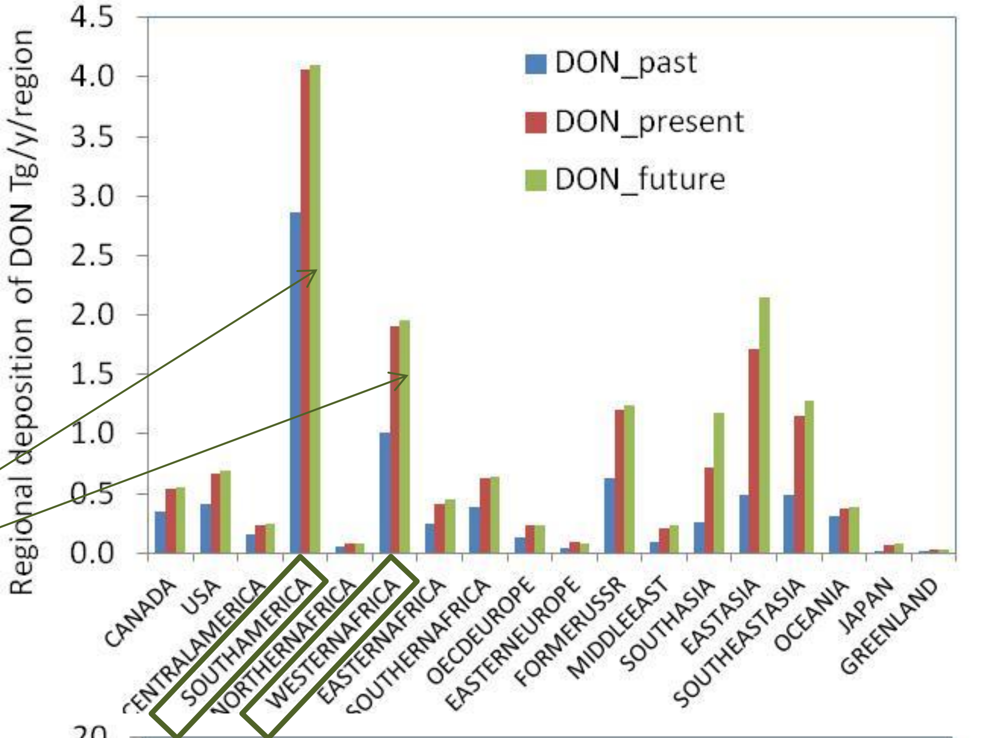
Kanakidou et al., JAS 2016

- Large uncertainties associated with the estimates
- What is the impact on the ecosystems?

Regional deposition of soluble N

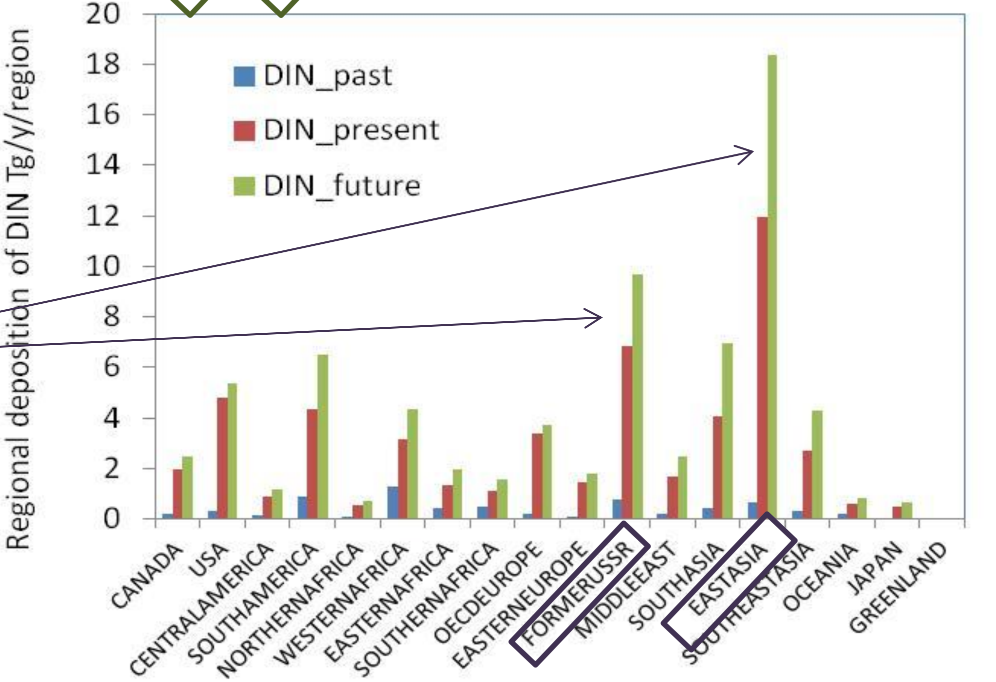
Soluble organic nitrogen

Vegetation driven sources



Soluble inorganic nitrogen

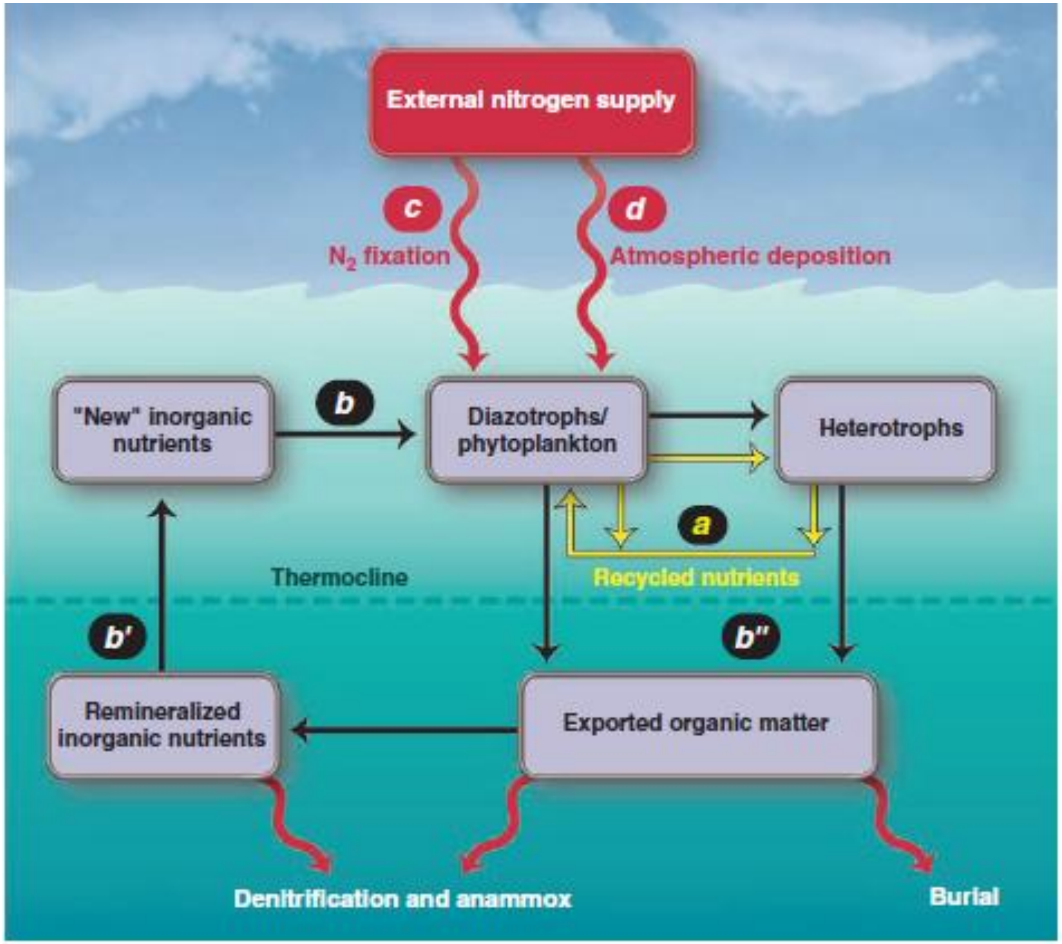
Human driven sources



mariak@uoc.gr

Aerosols & biogeochemical cycles

Deposition provides nutrients needed for ecosystems growth.



Duce et al., Science, 2009, Impacts of atmospheric Anthropogenic Nitrogen Deposition in the Open Ocean

Importance of atmospheric deposition compared to other N sources external to the ocean

Table 3. Nitrogen Inputs to the Total Oceans Including the Continental Shelf and to the Open Ocean Beyond the Shelf Break[a]

Source	Total Ocean Flux (Tg N yr^{-1})	Flux to the Open Ocean (Tg N yr^{-1})
Atmospheric	39	>30
Fluvial	DIN 23, DON 11	DIN 17, Don >0 to <11
N fixation	164	164

Fluvial from Sharples et al., GBC, 2016]; N fixation by PlankTOM10 model *Jickells et al ., GBC, 2017*

The calculations here suggest that the impacts of atmospheric deposition on ocean biogeochemistry can result in a net increase in primary production and CO_2 uptake of 0.15 Pg C yr^{-1}. However, the resulting reduction in radiative forcing will be offset slightly by increases in N_2O emissions from some regions of the oceans [*Suntharalingam et al.*, 2012].

The analysis and model calculations presented here highlight that this conclusion is very sensitive to four feedbacks which we identify—recycling of ammonia and organic nitrogen from seawater to the atmosphere, inhibition of nitrogen fixation by atmospheric nitrogen deposition, and the denitrification sink for nitrogen.

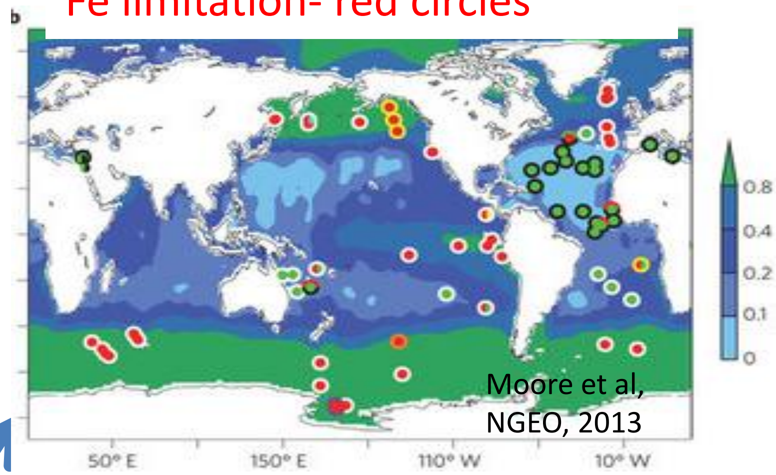
GESAMP
Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

An update of the study by Duce et al Science 2008

Jickells et al ., GBC, 2017

DFe Deposition changes over the ocean

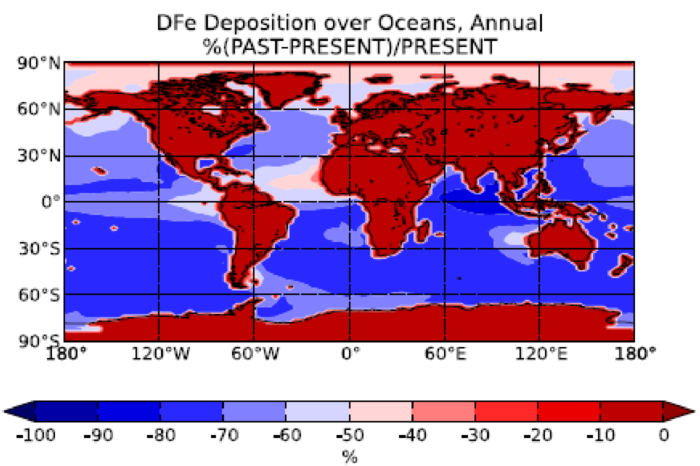
Fe limitation- red circles



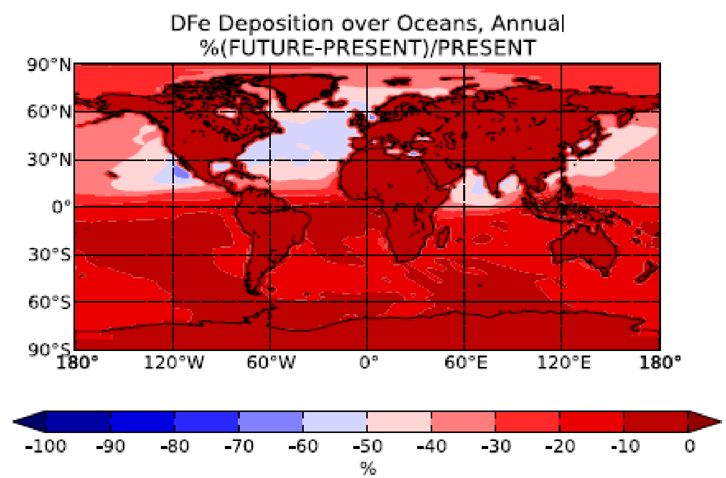
has increased (3x) due to anthropogenic emissions (emis. & diss.) **(~50% over HNLC)**

is expected to decrease (~30%) due to air pollution regulations

% (PAST-PRESENT)/ PRESENT

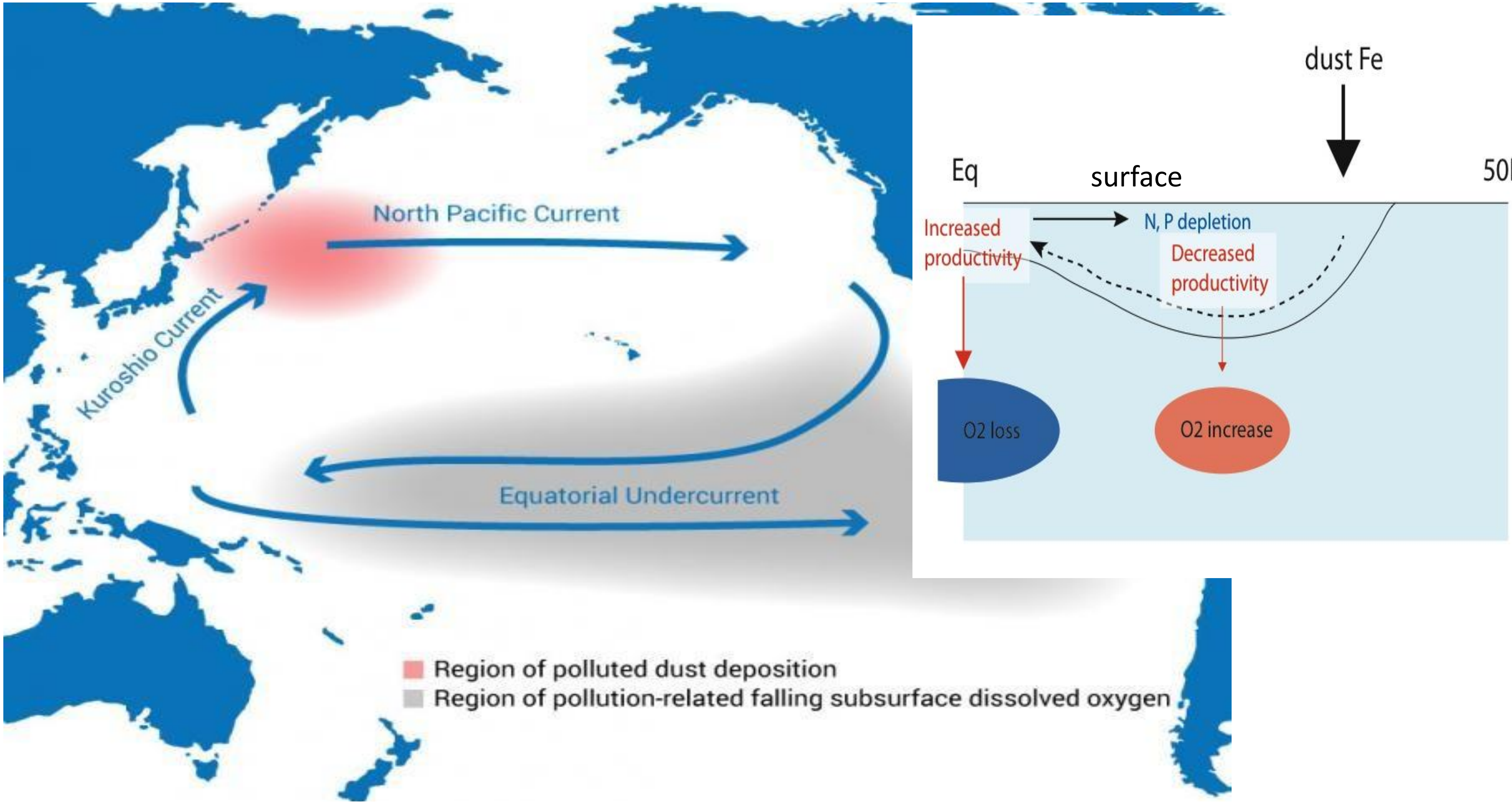


% (FUTURE-PRESENT)/ PRESENT



Myriokefalitakis et al, Biogeosciences, 12, 3973, 2015

To evaluate the impact of Fe atmospheric deposition an ocean circulation model is needed



Acceleration of oxygen decline in the tropical Pacific over the past decades by aerosol pollutants

T. Ito[1*], A. Nenes[1,2,3,4], M. S. Johnson[5], N. Meskhidze[6] and C. Deutsch[7]

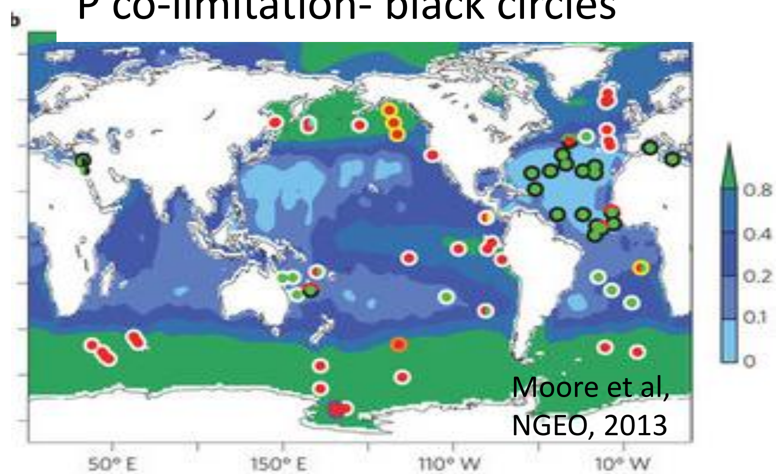
16 MAY 2016 | DOI: 10.1038/NGEO2717

DP Deposition changes over the oceans

DP deposition has an important natural component & has increased due to anthropogenic emissions

No large changes are projected due to air pollution regulations

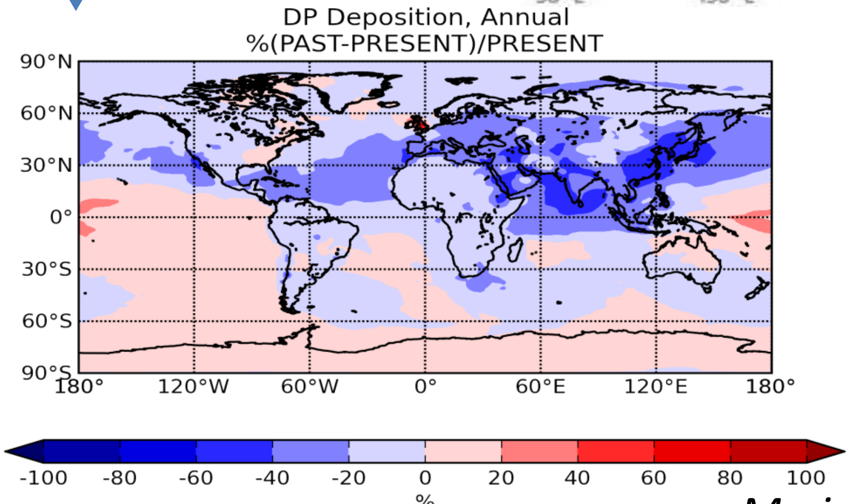
P co-limitation- black circles

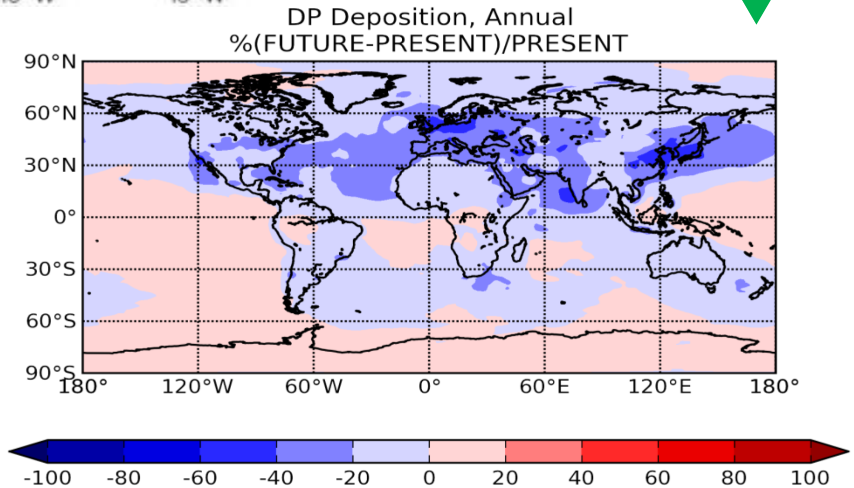


Global ~ 19%
Ocean ~ 21%

Global ~ -18 %
Ocean ~ -16%

Large uncertainties



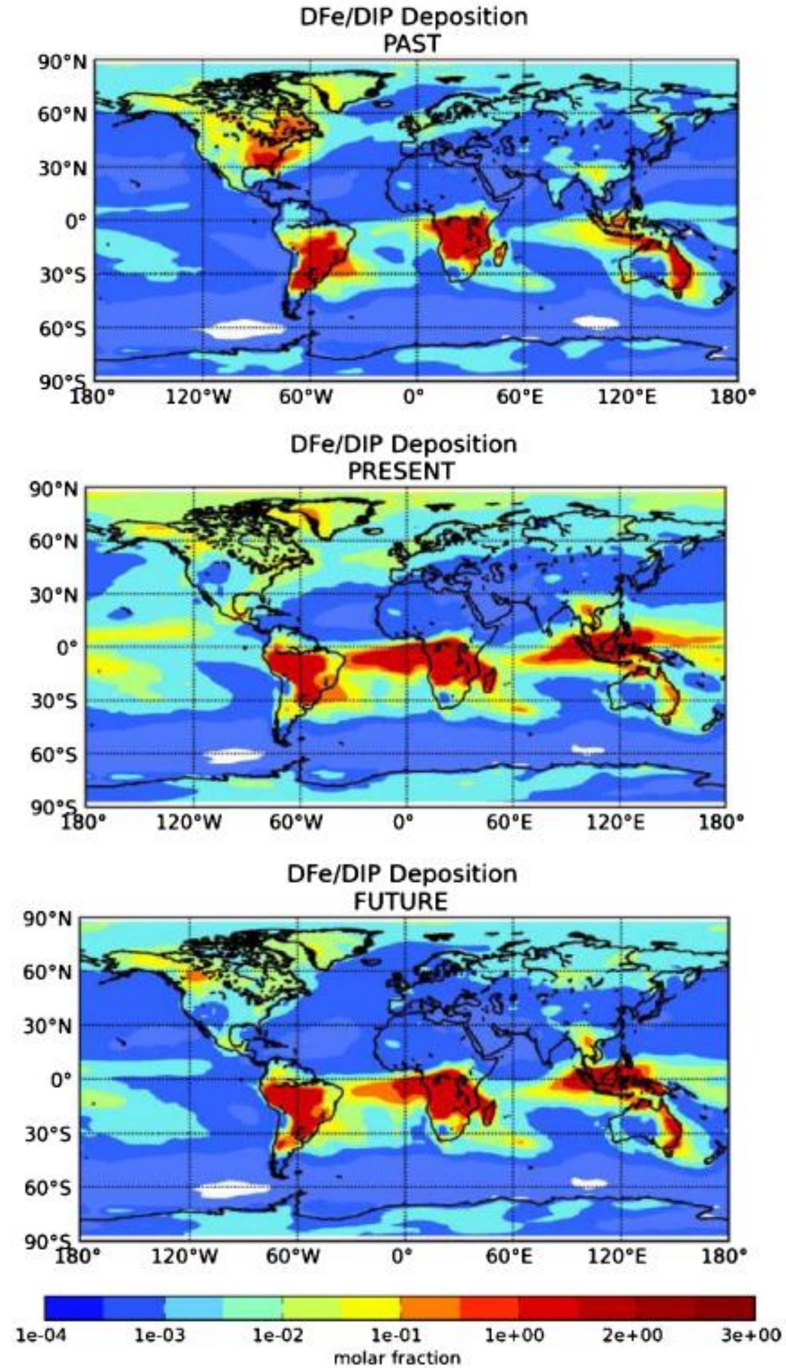


Myriokefalitakis et al., Biogeoscience, 2016

Changes of atmospheric deposition relative composition in nutrients

Ratios of deposition fluxes of DFe/DIP (soluble Fe to soluble inorganic P from all sources)
past = emission year 1850,
present = emission year 2008,
future = emission year 2100

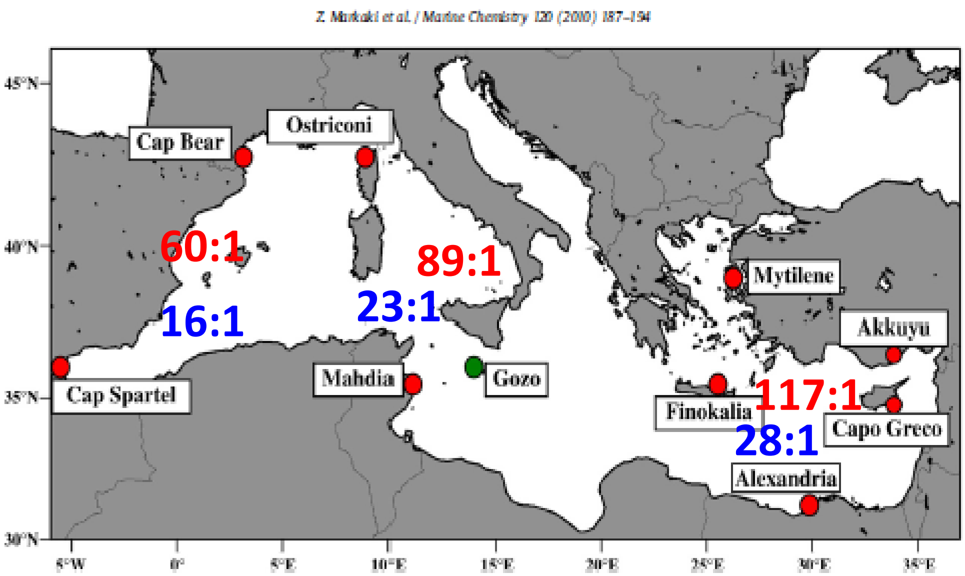
How do they affect ecosystem's growth and biodiversity ?



Kanakidou et al. , *Environ. Res. Lett.* 13 (2018) 063004

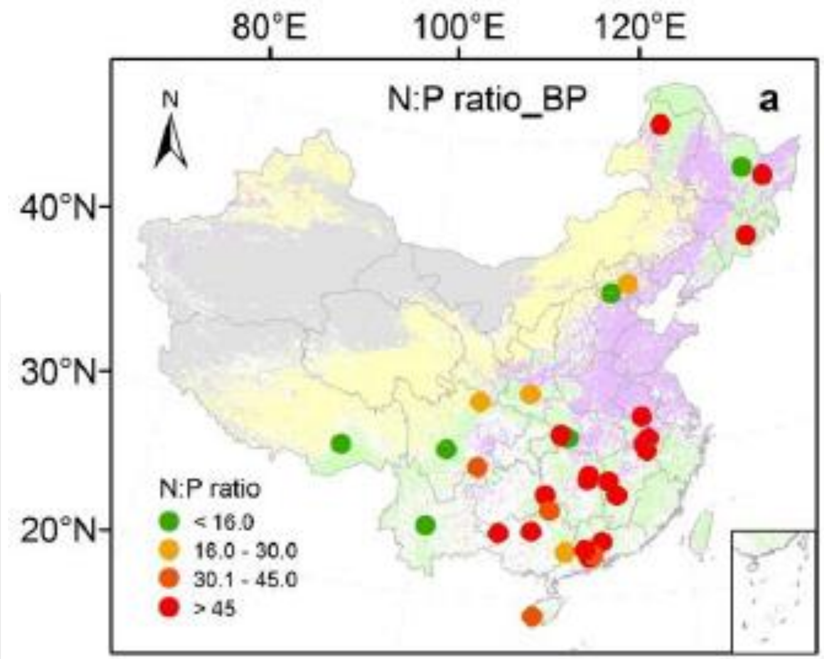
Imbalanced N/P atmospheric deposition

- Atmospheric deposition provides N in excess to P : **China's forests →**
- Mediterranean Sea ↓



N:P ratio in the sea **N:P ratio in deposition**

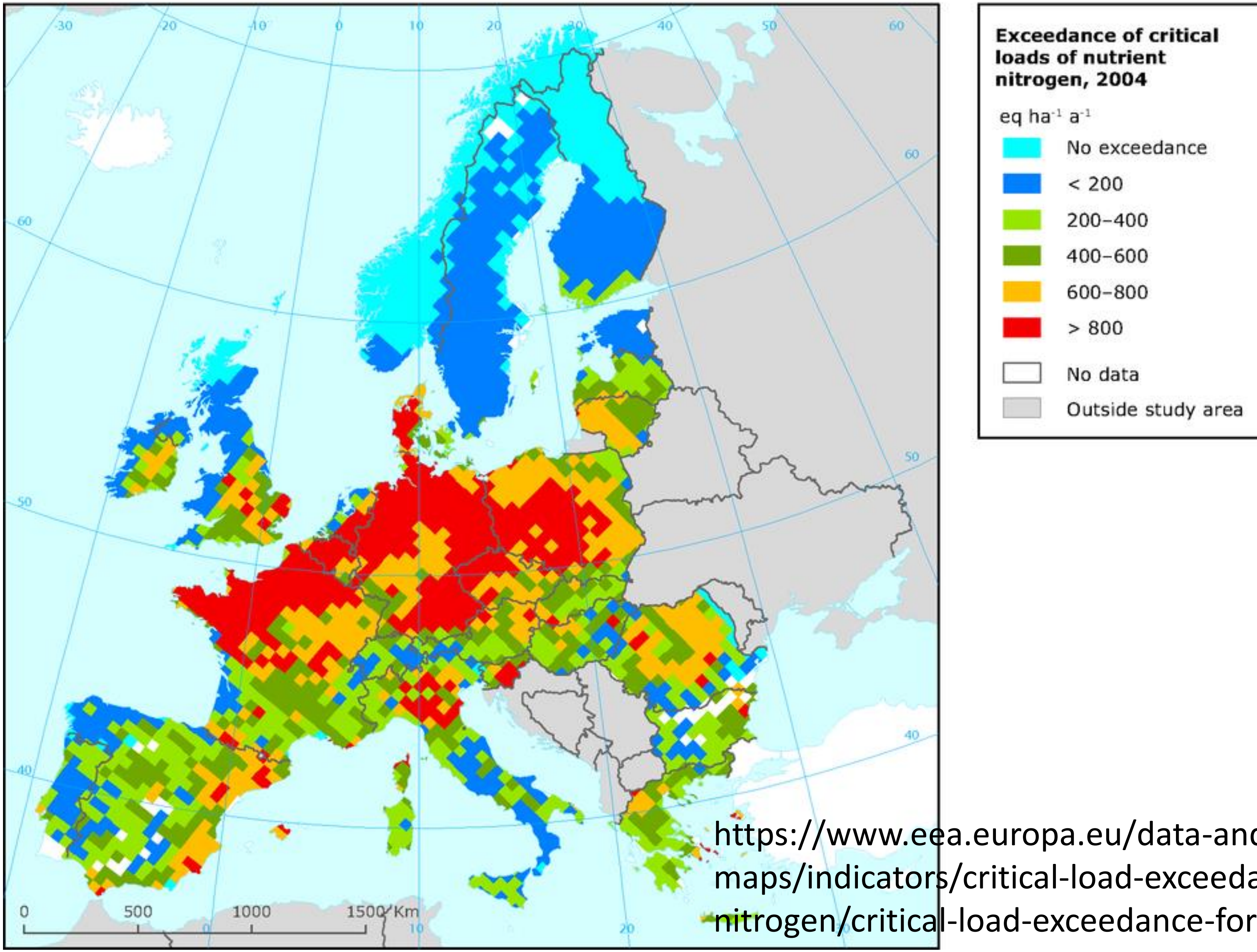
Markaki et al., Marine Chemistry, 2010



N:P ratio in Bulk Precipitation (BP) over China's Forests

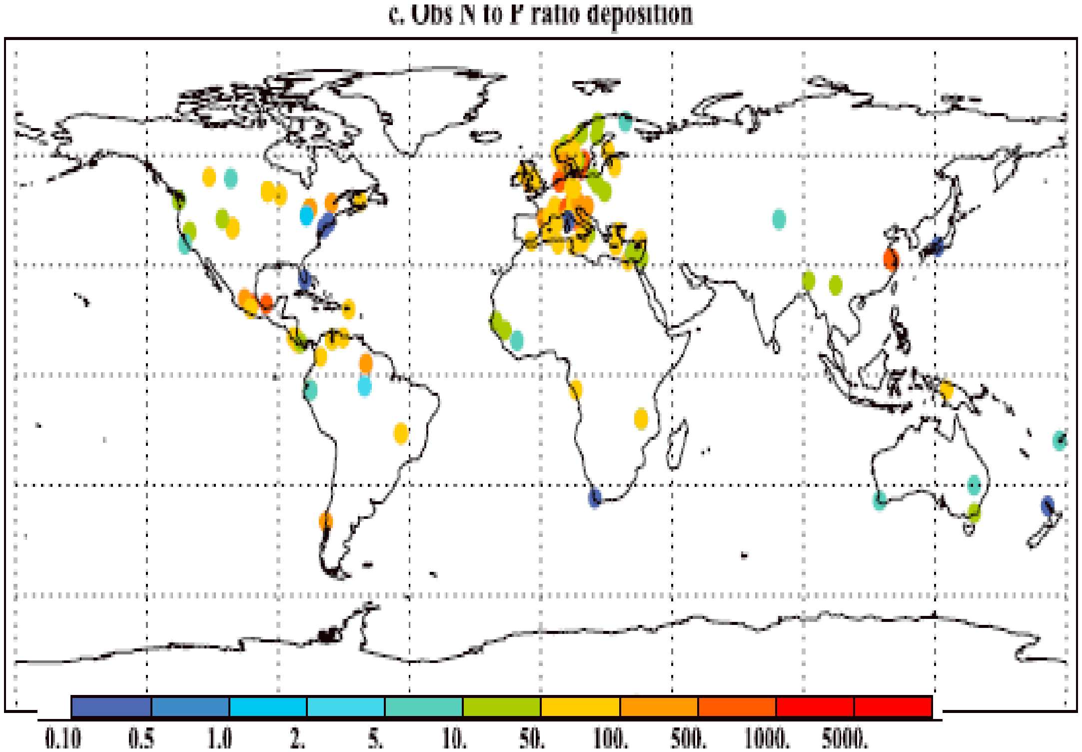
Du E. et al., ACP, 2016

Human induced P limitation?



https://www.eea.europa.eu/data-and-maps/indicators/critical-load-exceedance-for-nitrogen/critical-load-exceedance-for-nitrogen

Observed N:P ratio in atmospheric deposition over lakes



Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry?

GBC, 2016 10.1002/2015GB005137

Janice Brahney[1], Natalie Mahowald[2], Daniel S. Ward[2], Ashley P. Ballantyne[3], and Jason C. Neff[4]

Coupling of biogeochemical cycles

- C/N/P cycles are coupled, mainly through photosynthetic fixation of these elements by biological activity.
- C, N and P are main constituent of proteins and living organisms.
- *Biological productivity relies on the availability of these nutrients*
- There is increasing evidence that a significant fraction of N and P deposition occurs as ON and OP.
- *Human activities have modified the atmospheric content and deposition fluxes of OC, ON and OP*
- Critical biochemical feedbacks might exist between chemistry/climate/ terrestrial and marine biosphere that involve the coupling of the C/N/P cycles.

BNMOC (+) → Dep ON (+) + dep OP(+) +SOA (+) + CO_2 uptake (+) → T (-) → BNMOC (- or +) SOA(-) →

T(+) + dep ON (-) + dep OP (-) → ?

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ευχαριστω
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Thank you!