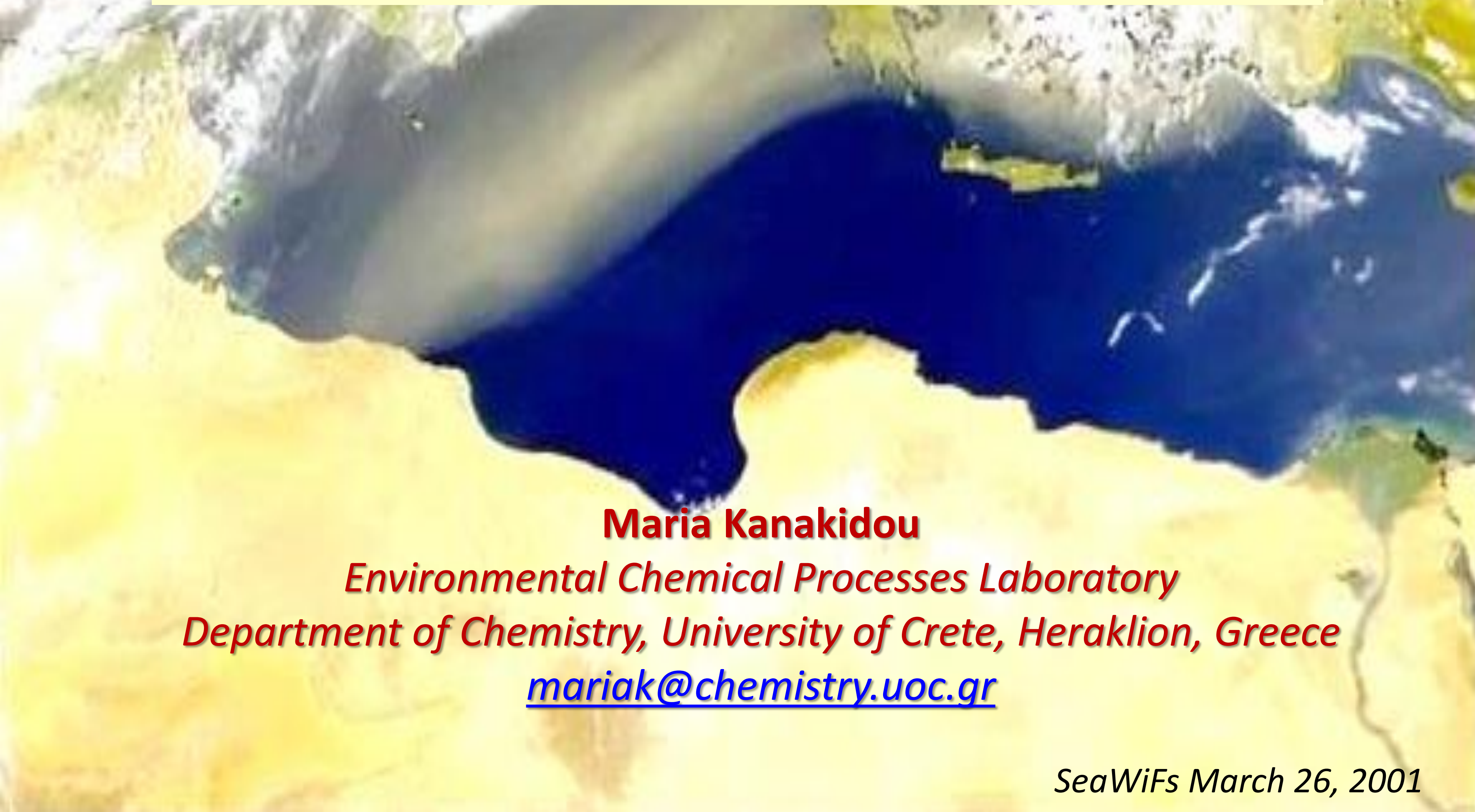
Atmospheric Deposition of nutrients and its impact on the marine environment

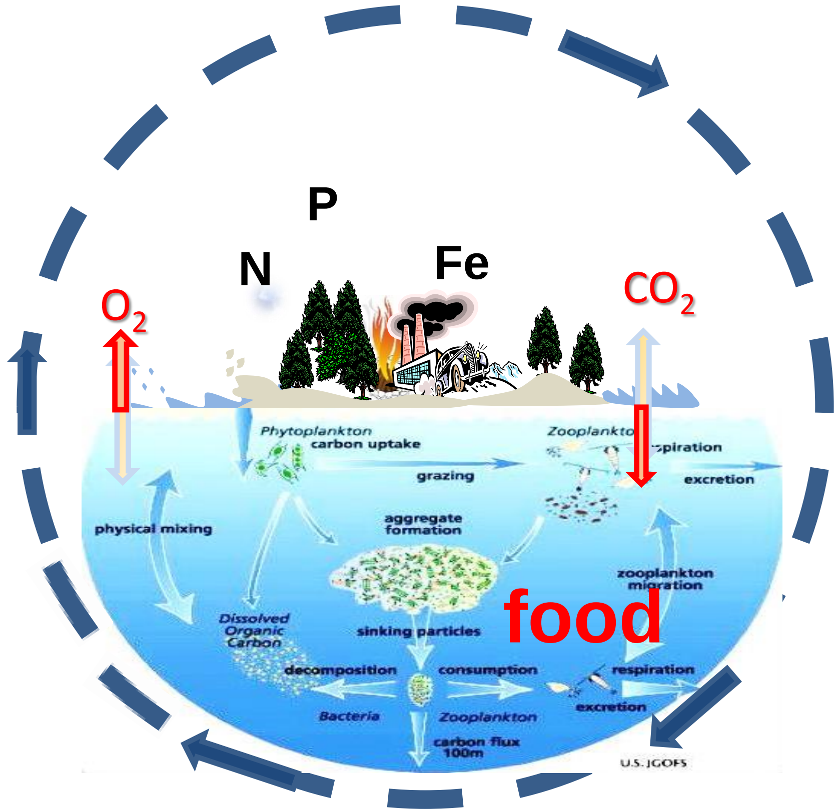


Maria Kanakidou
Environmental Chemical Processes Laboratory
Department of Chemistry, University of Crete, Heraklion, Greece
mariak@chemistry.uoc.gr

SeaWiFs March 26, 2001

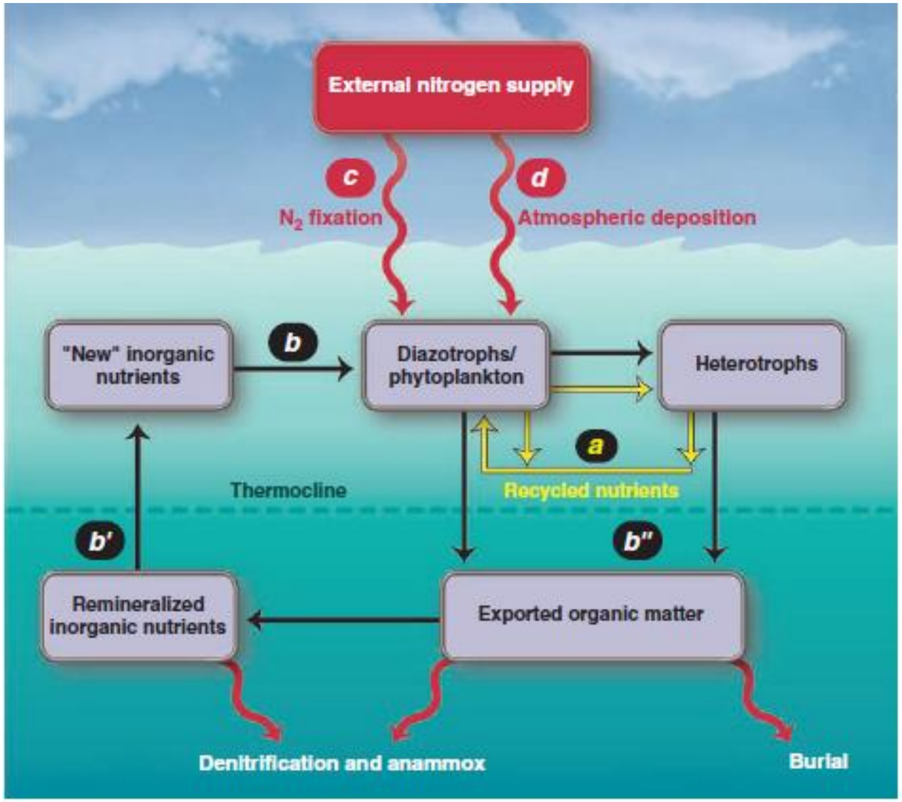
Importance of the Ocean - Atmosphere coupling

Mass and Energy transfer



Atmospheric deposition & biogeochemical cycles

Deposition provides nutrients needed for ecosystems growth.



N deposition Could be responsible of

About 1/3 of external flux of N to the ocean

About 3% of annual new marine primary production

Large Uncertainty

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

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NSRF 2007-2013 programme for development
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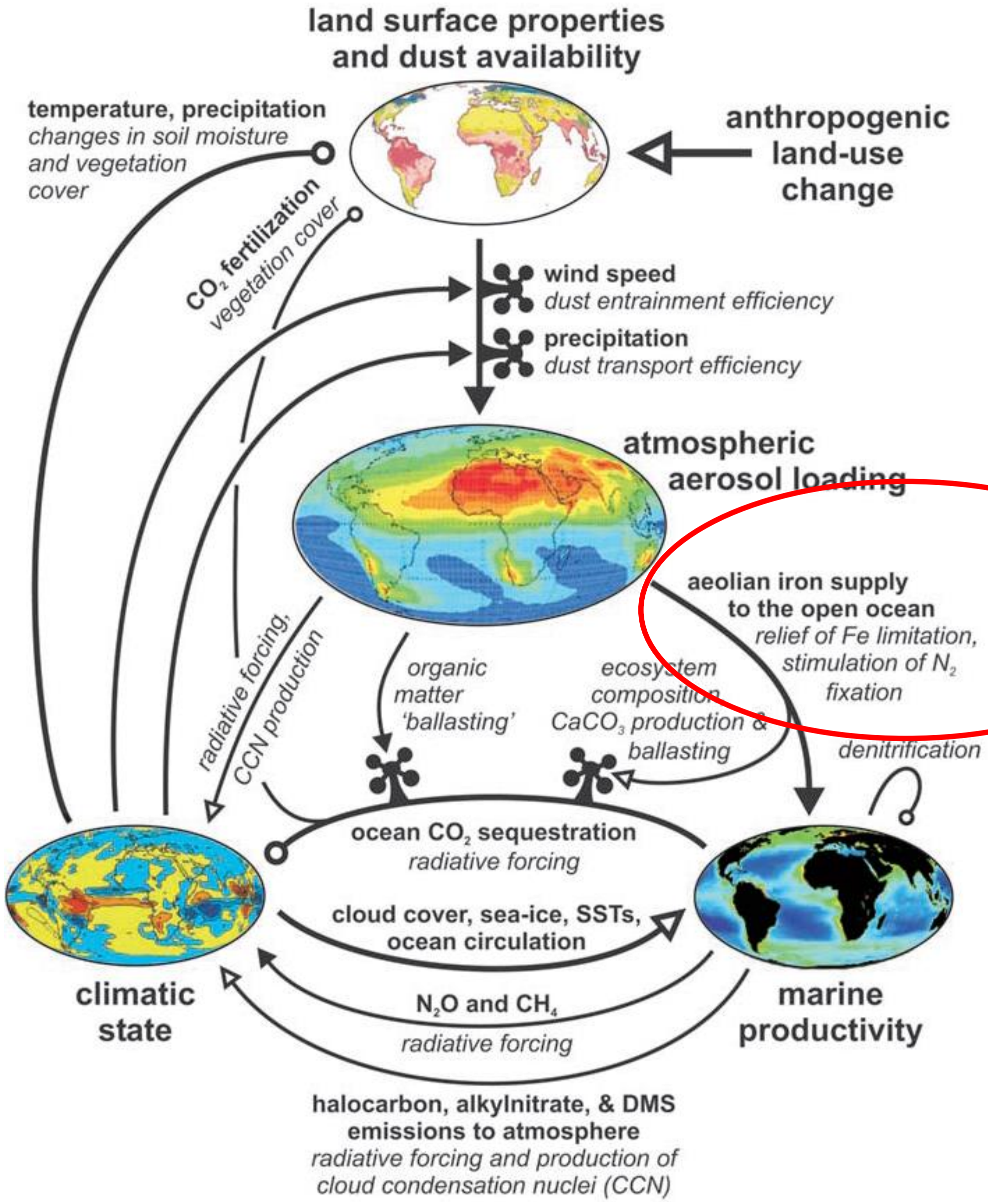
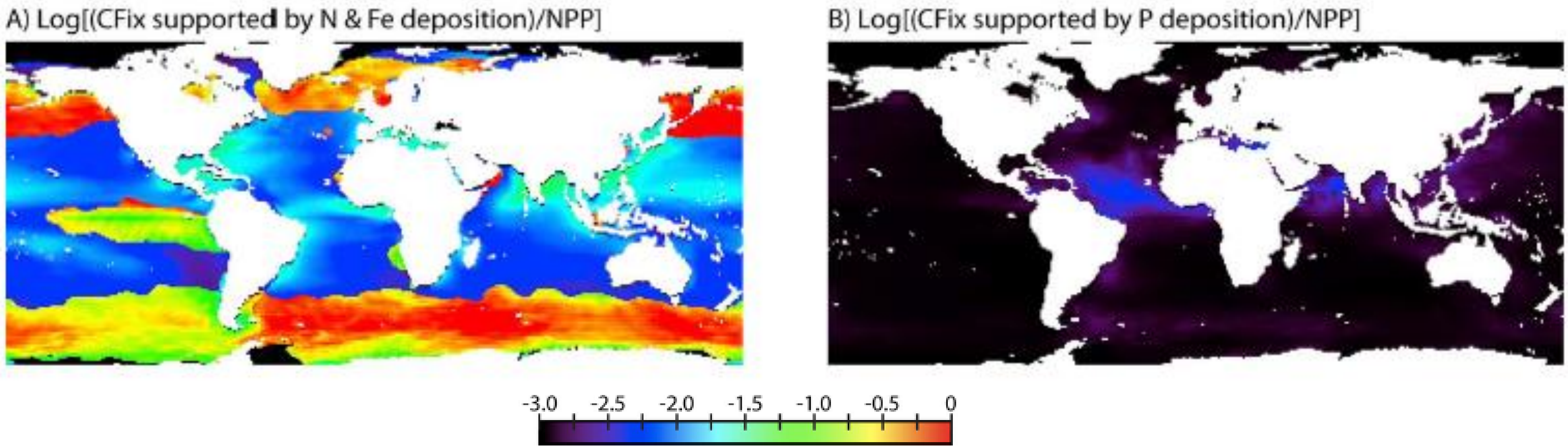
Aerosol deposition & biogeochemical cycles



Global Iron Connections Between Desert Dust, Ocean Biogeochemistry, and Climate
T. D. Jickells, *et al.*
Science **308**, 67 (2005);
DOI: 10.1126/science.1105959

Fraction of phytoplankton seen by satellites that could be sustained by atmospheric deposition of N & Fe and P

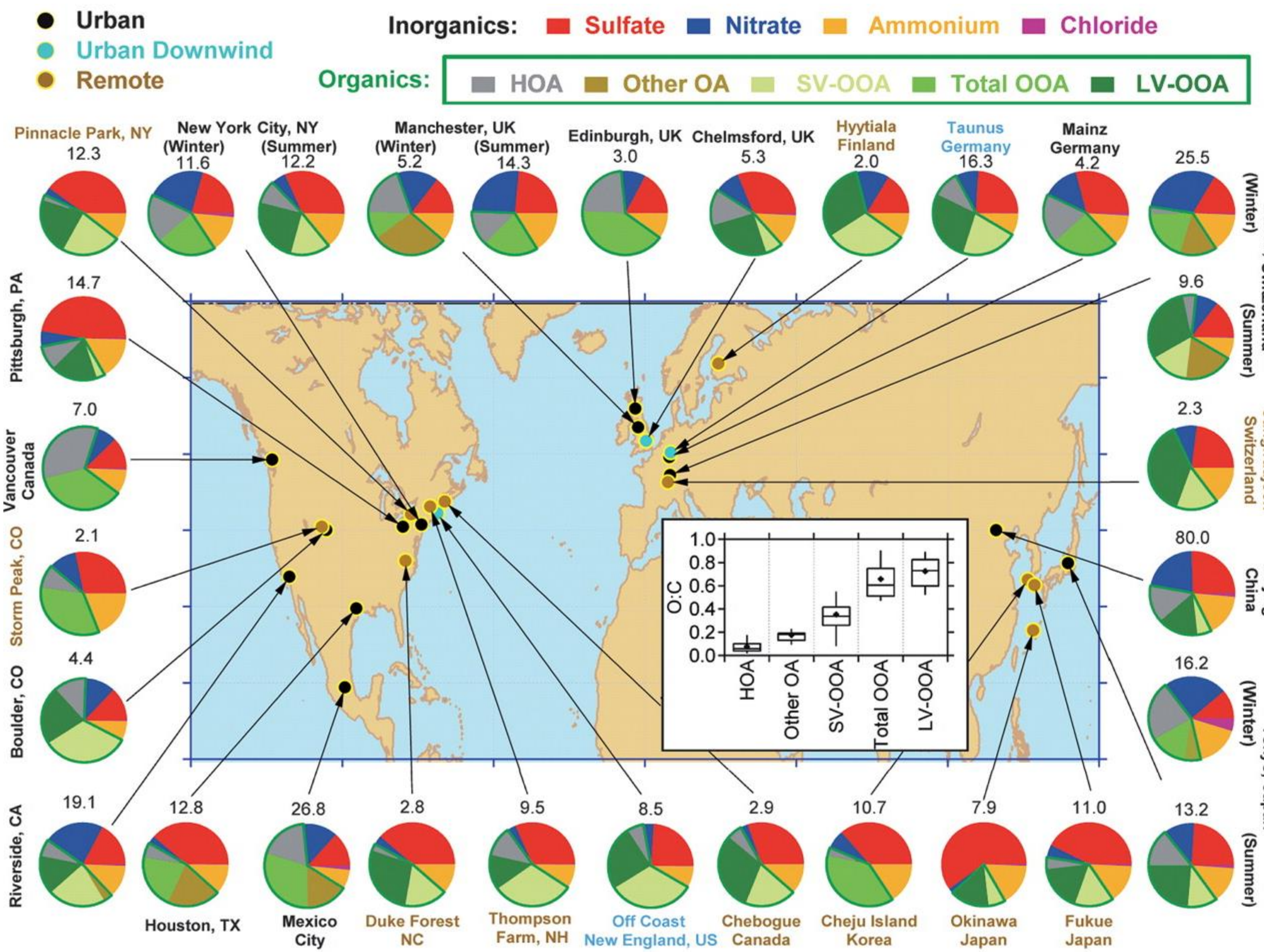


1‰ 10% 100%

OKIN ET AL.: ATMOSPHERIC DEPOSITION TO OCEANS

GBC, 2011

PM1 Aerosol Composition Worldwide



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Aerosols contain ON and metals

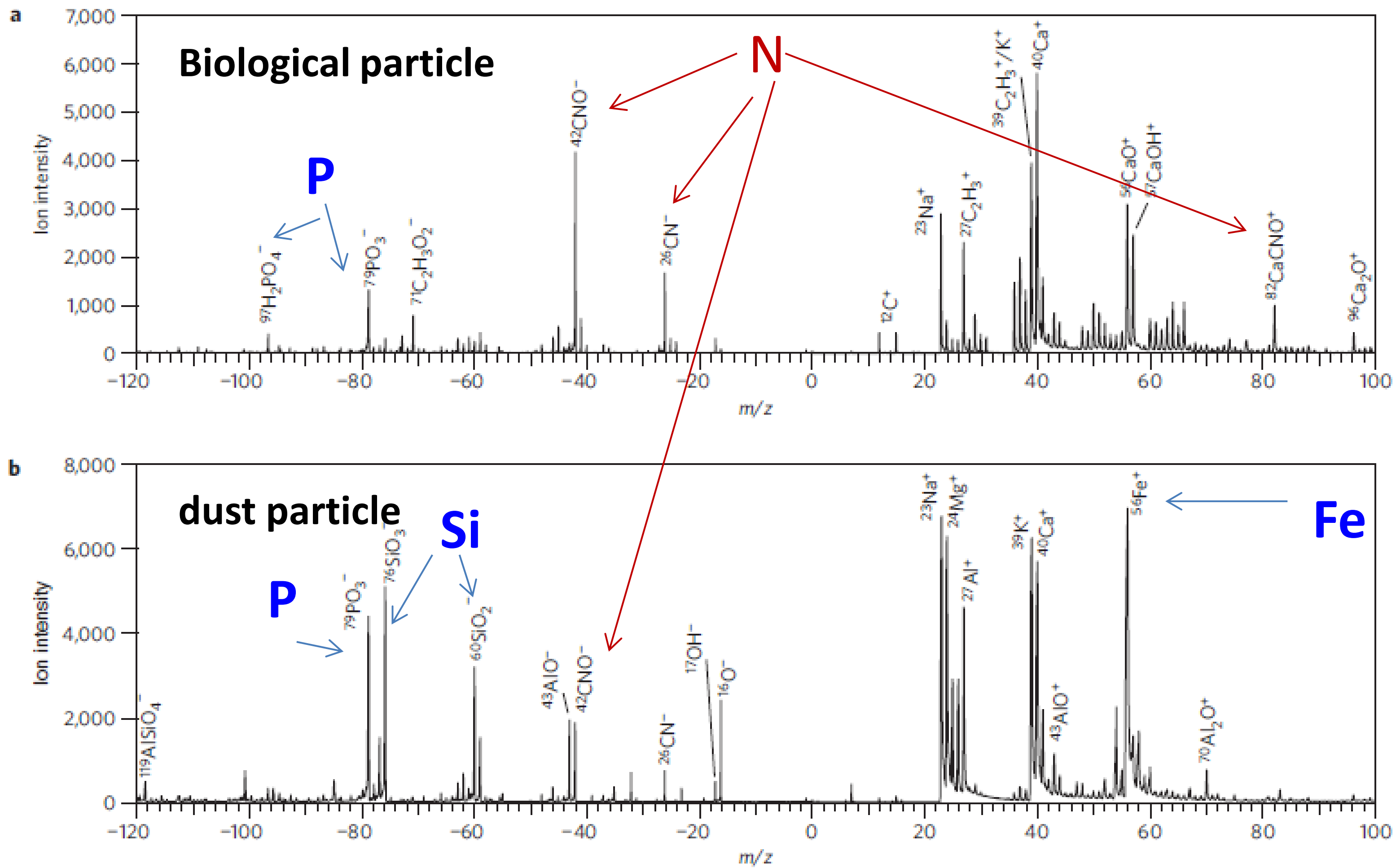


Figure 3 | Representative chemical composition of biological and dust particles. Positive- and negative-ion mass spectra of representative individual biological (**a**) and mineral-dust (**b**) CVI ice residual particles. Wyoming, US

CVI ice residual particles

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

Aerosols & biogeochemical cycles

Large uncertainties exist in the amounts and 'quality' of atmospheric deposition

Estimate:

- The atmospheric global deposition of nutrients: N, Fe and P (inorganic + organic)
- How the deposition of dissolved N, Fe and P has been and will be affected by humans

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3-d global modeling of atmospheric composition and deposition – TM4-ECPL

Methodology

- **Oxidants/gases/aerosols/multiphase chemistry**

  VOC /NOx/oxidants / oxalate & all major aerosol components including POA/SOA, coupled with ISORROPIA II *(Myriokefalitakis et al., ACP, 2008, Advances in Meteorology 2010, ACP, 2011; Tsigaridis et al., ACP, 2003; 2005; 2006; Daskalakis et al ACP, 2015; 2016)*

- **Nitrogen and Organic P deposition**

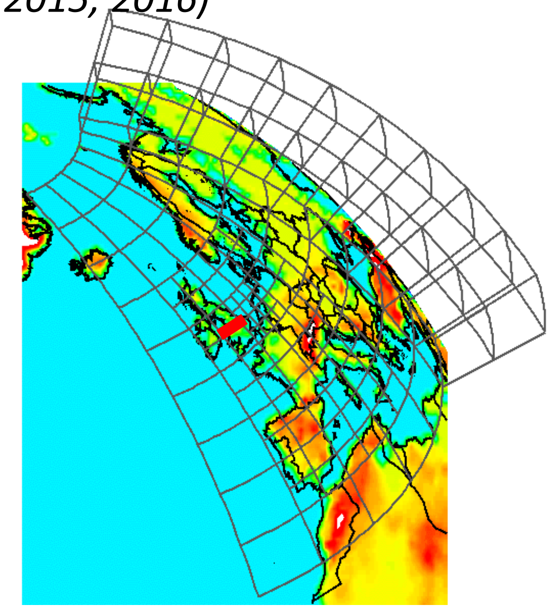
  (*Kanakidou et al., GBC 2012*
  Kanakidou et al., JAS 2016)

- **Fe & P atmospheric cycles**

  (*Myriokefalitakis et al Biogeosc 2015; 2016)*

- AEROCOM OA intercomparison

  (*Tsigaridis et al., ACP, 2014)*



- **Interannual emissions -** ACCMIP anthropogenic emissions

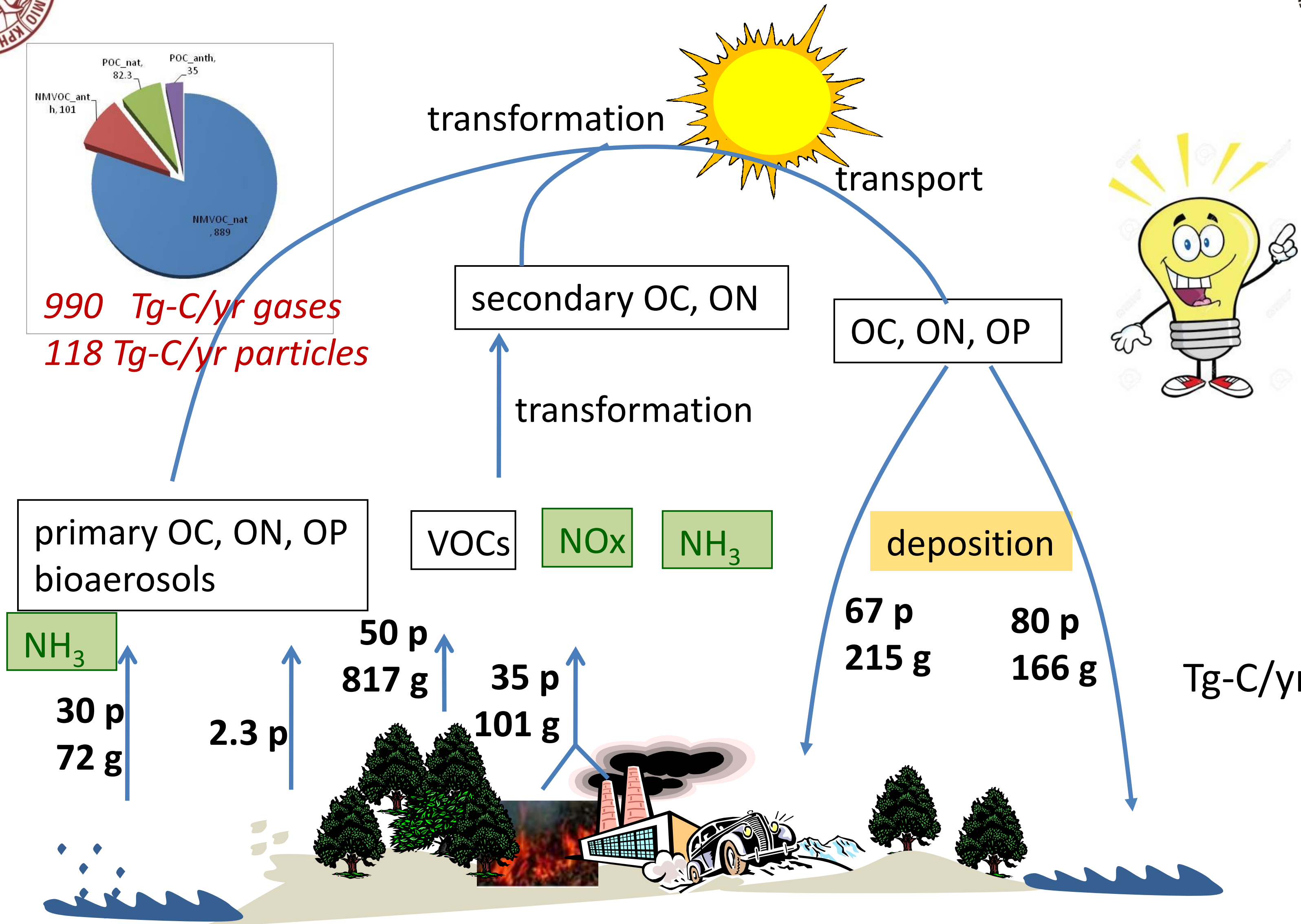
  MEGAN MACC biogenic, ACCMIP anthropogenic, ACCMIP fire emissions, *(Daskalakis et al., ACP, 2015)*

- **Interactive dust, sea-salt, marine POA, bioaerosol emissions**

- **Meteorology ERA-Interim**

Organic C, N, P in the global atmosphere

Link ON & OP to OC atmospheric cycle

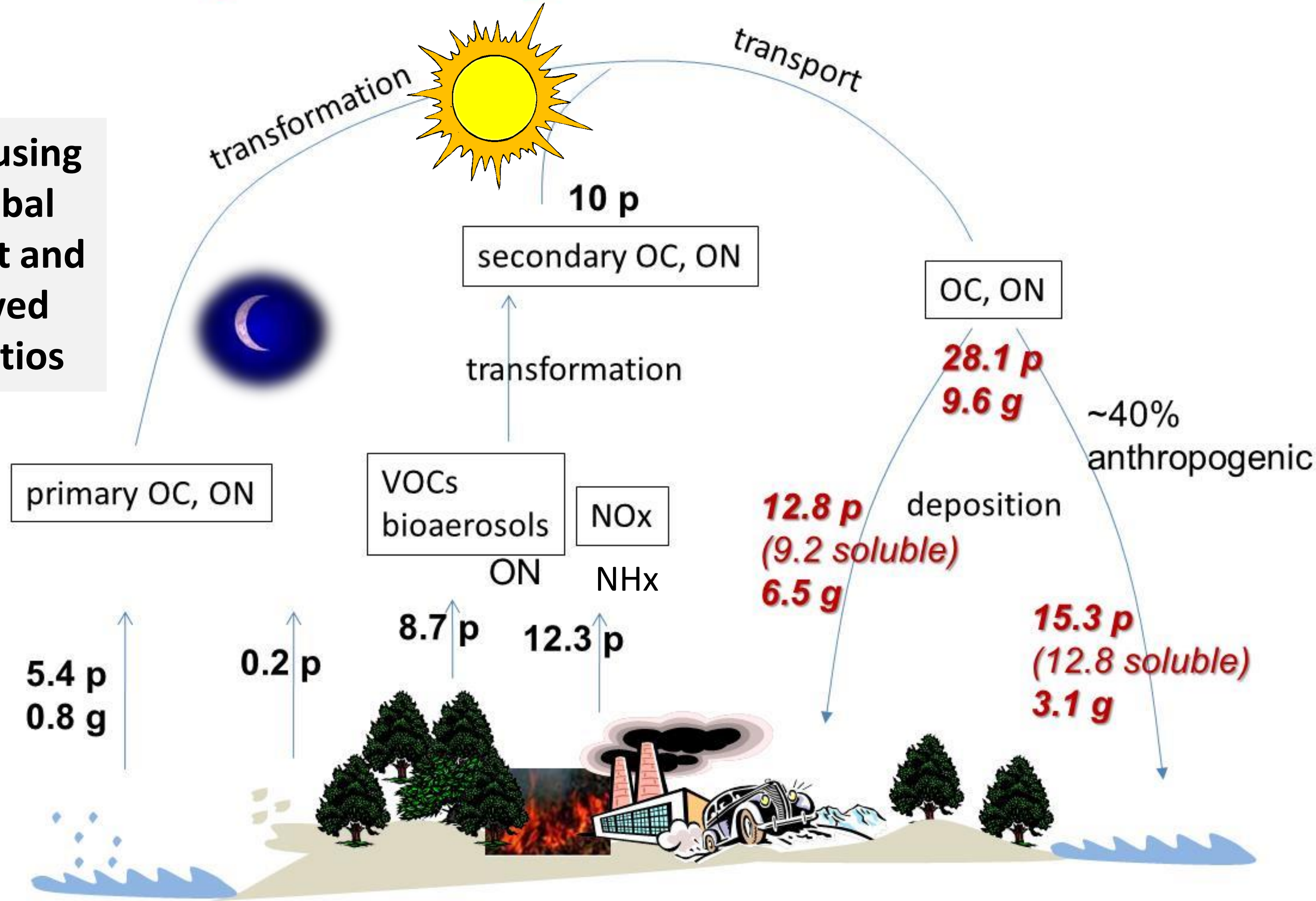


Use of
N: C
P: C
ratios

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

Organic Nitrogen global budget Tg-N/yr

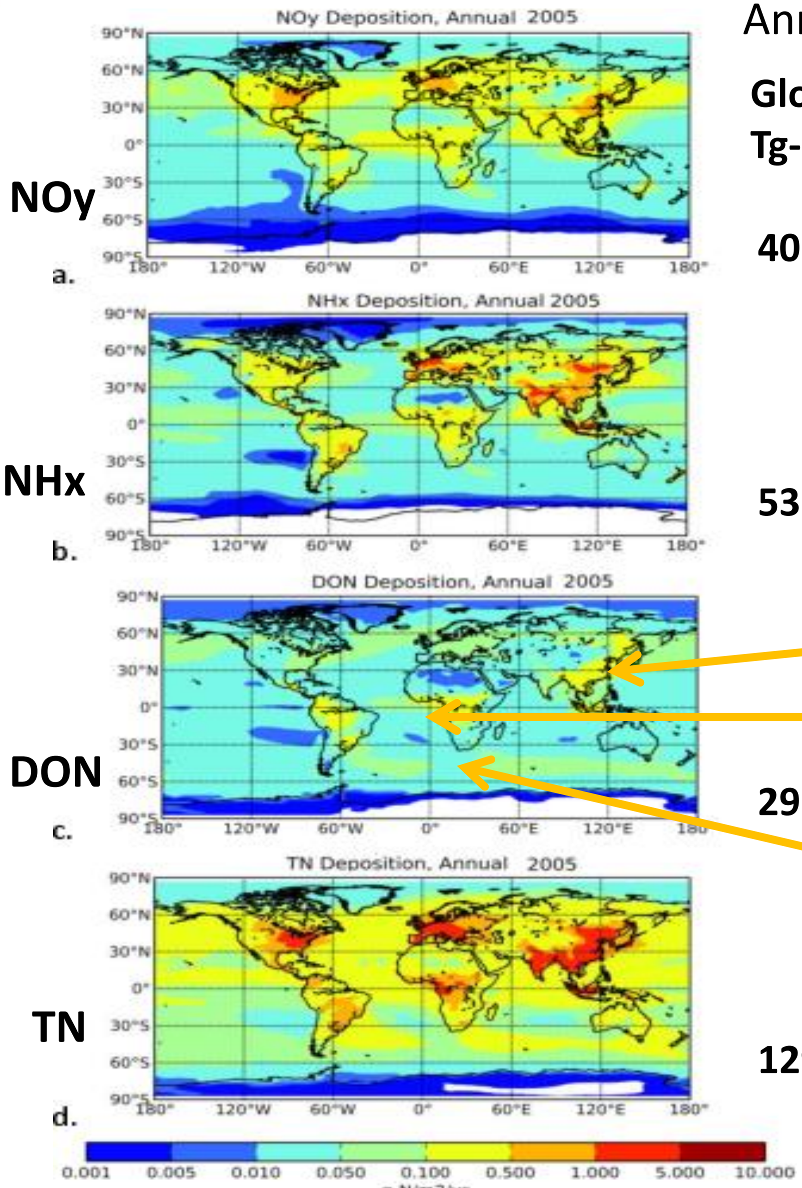
How: using OC global budget and observed N/C ratios



Kanakidou, et al. Global Biogeochemical Cycles, 2011GB004277, 2012

emissions **deposition**

Atmospheric N deposition



Annual mean deposition

Globe (ocean)
Tg-N/yr

Species	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**
- **is by 40% from bioaerosol**

ON deposition is 20-25% of TN deposition

combustion

Primary biological particles
Biomass burning

Marine source

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

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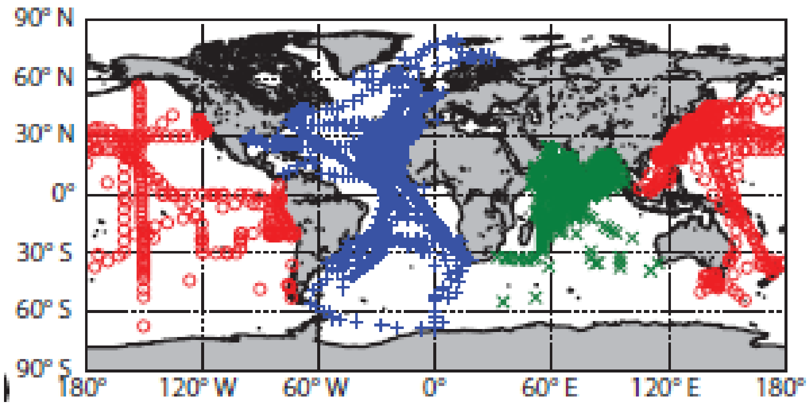
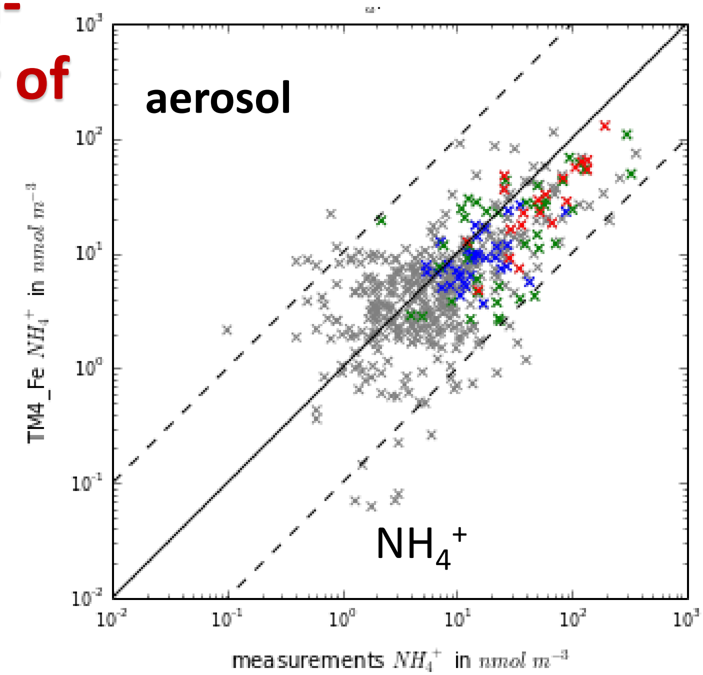
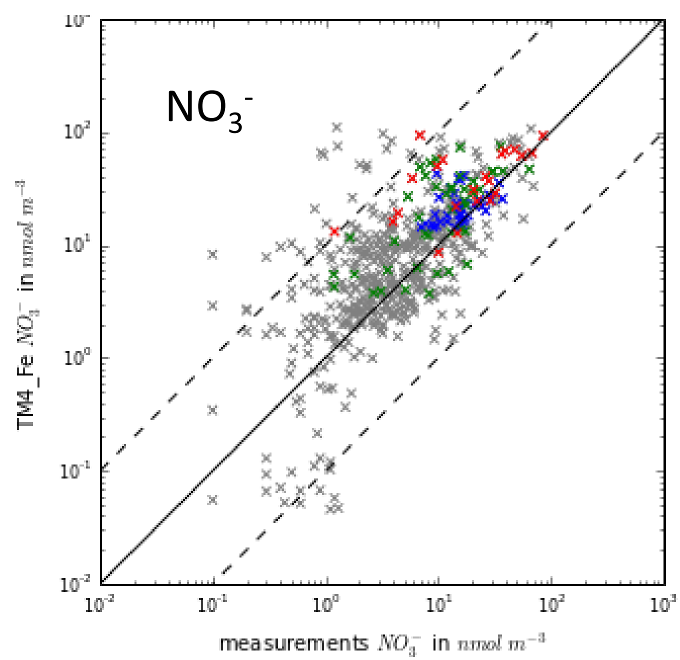
Atmospheric N deposition- agreement within the order of magnitude
1. Aerosol data



data compilation ~3000 samples
cruises & island stations
Baker et al. ACP, 17, 8189, 2017

Kanakidou et al., JAS-150278, 2016





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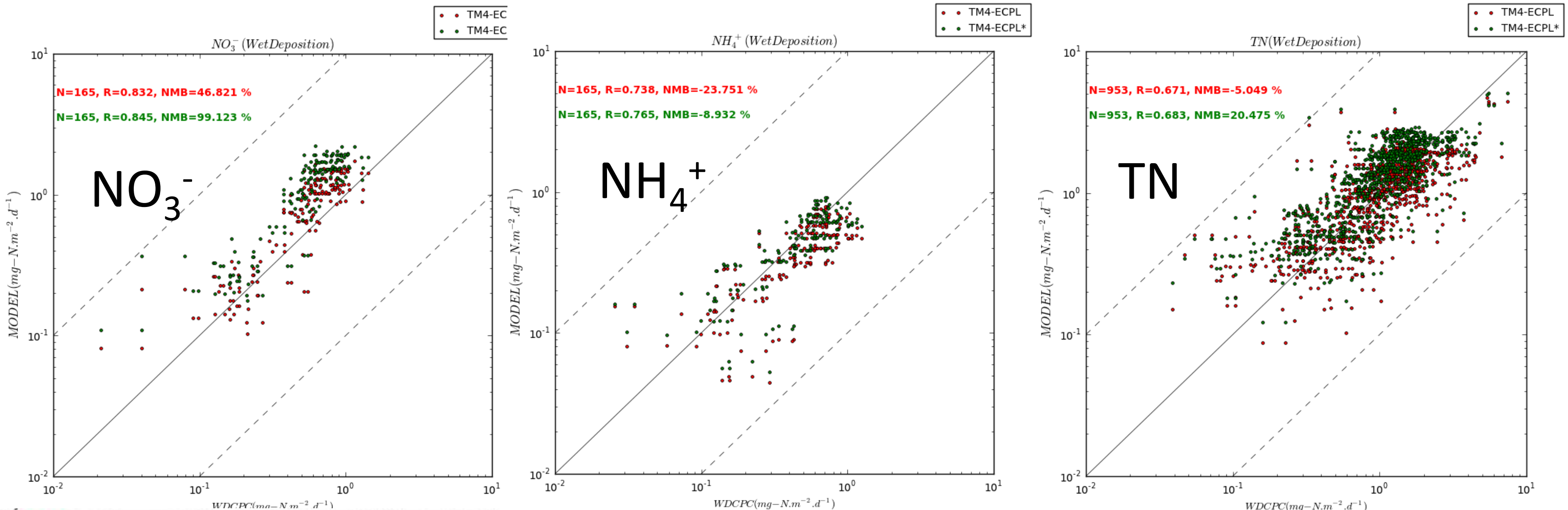
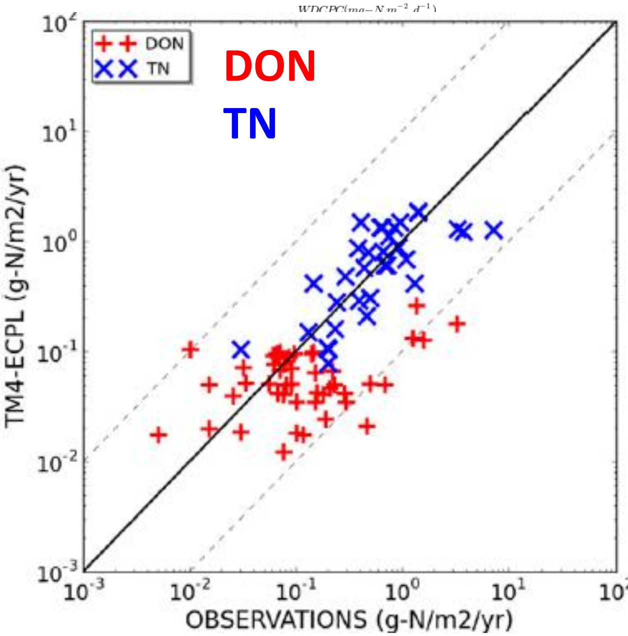
Atmospheric N deposition- agreement within the order of magnitude: 2- deposition fluxes

simulations



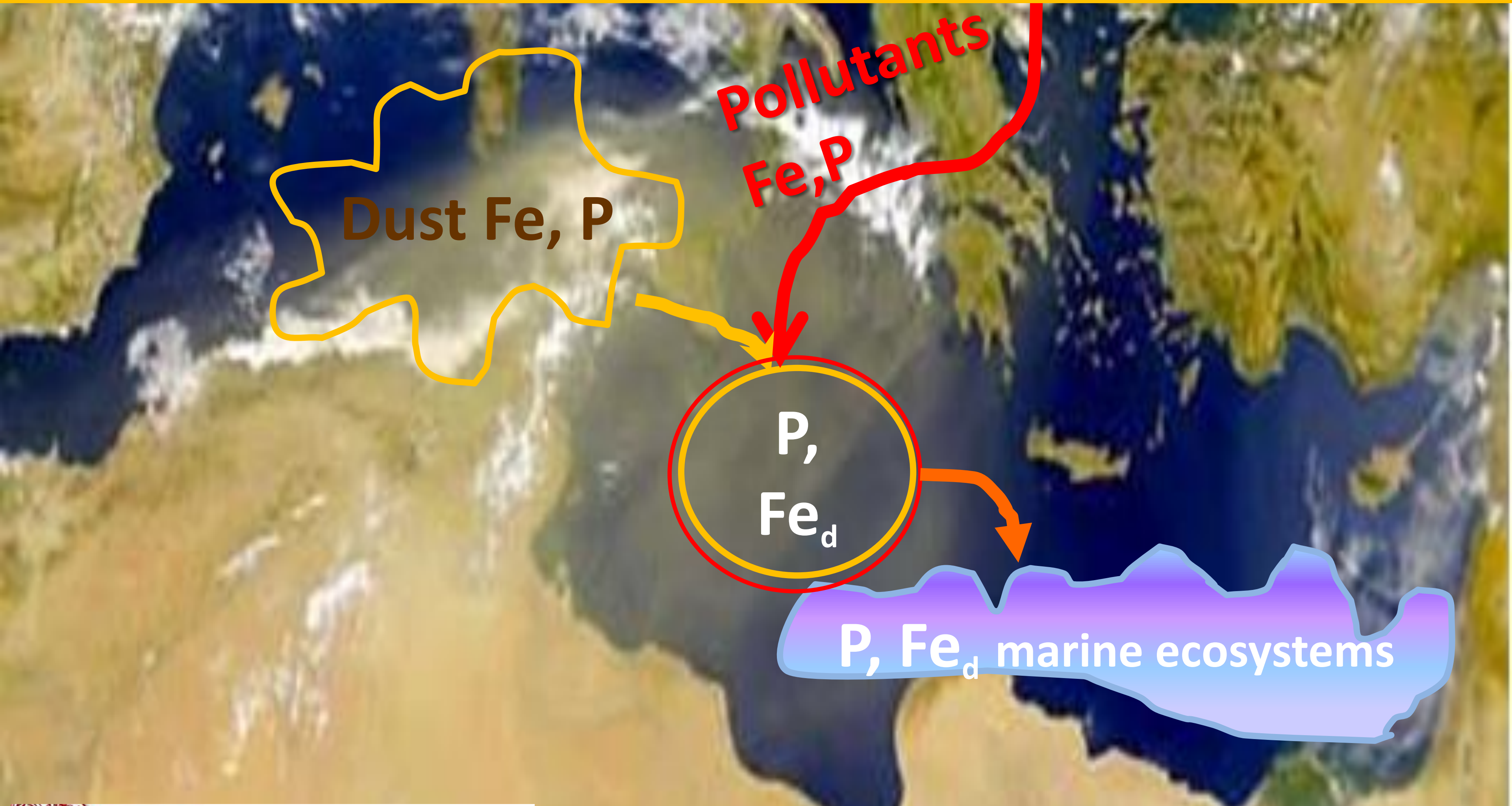
Observations (mg-N/m²/d) Scale 10^{-2} to 10^{1}



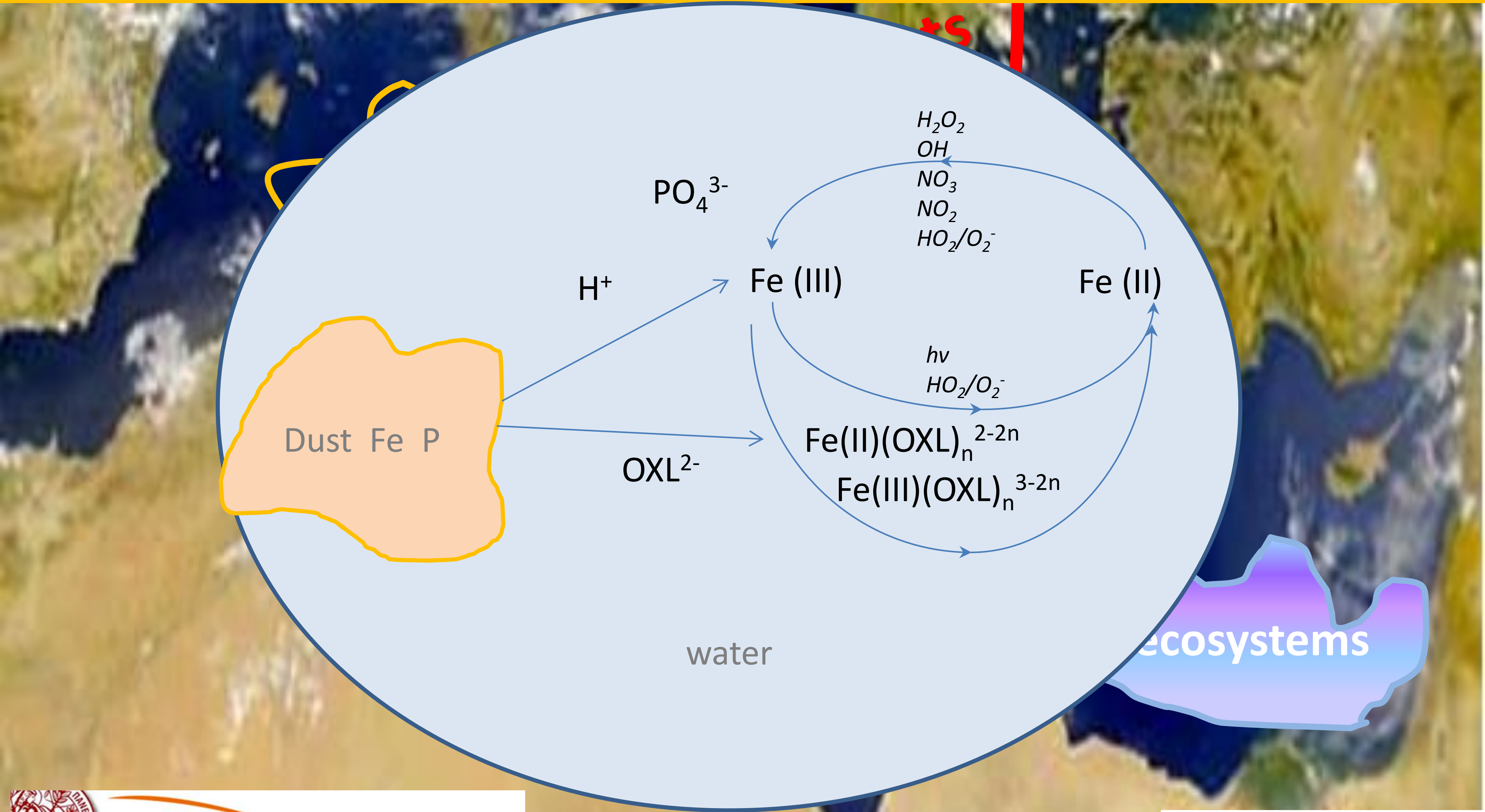
Kanakidou et al., JAS-150278, 2016 suppl
Observations from Vet et al AE (2014)

← *Total deposition fluxes*
Kanakidou et al., JAS-150278, 2016

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



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



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

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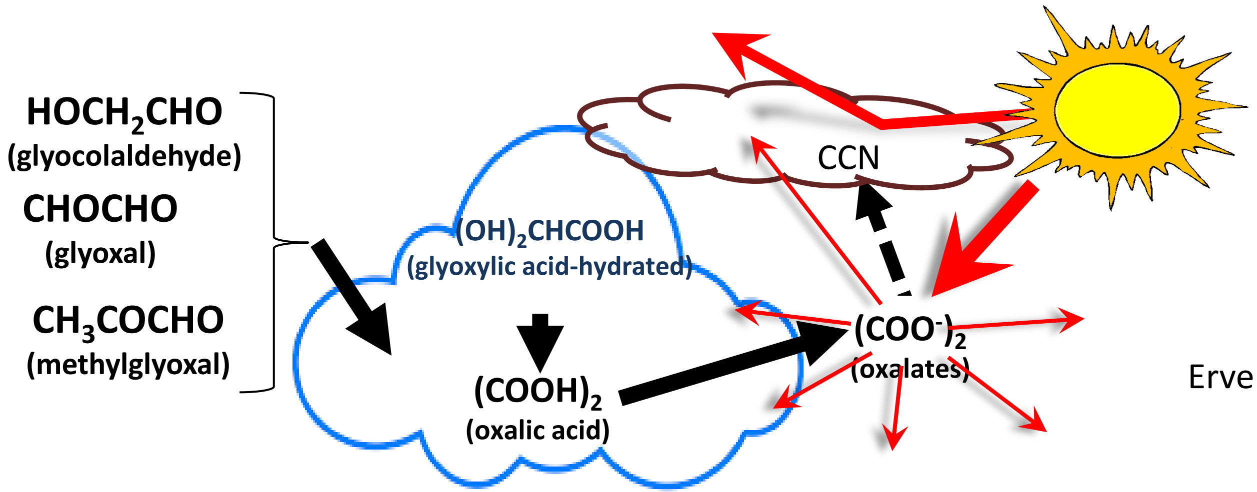
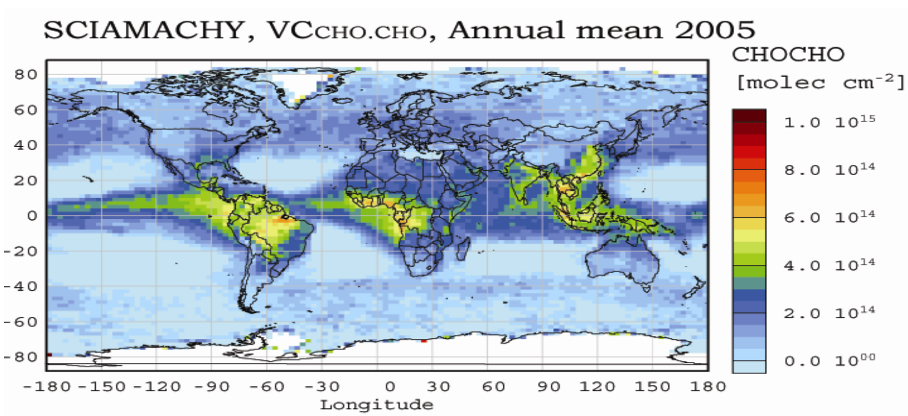
Oxalate in the global troposphere

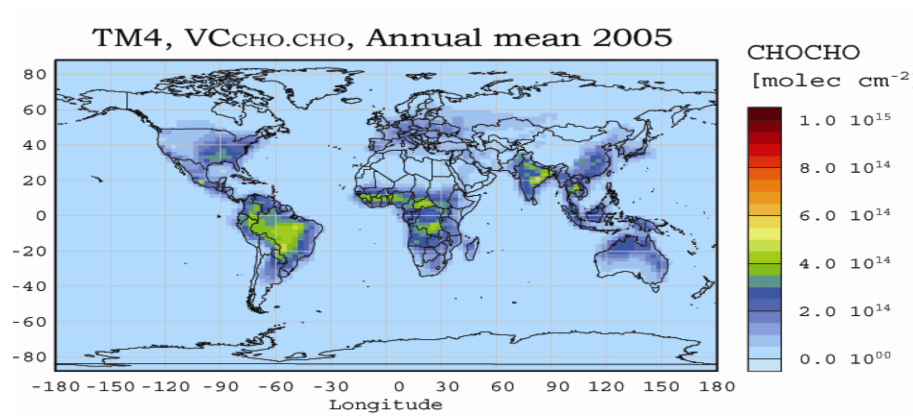


Kinetics from
Lim et al., ACP, 2010
Ervens & Volkamer, ACP, 2010
Noziere et al., 2009

Myriokefalitakis et al., ACP, 2011

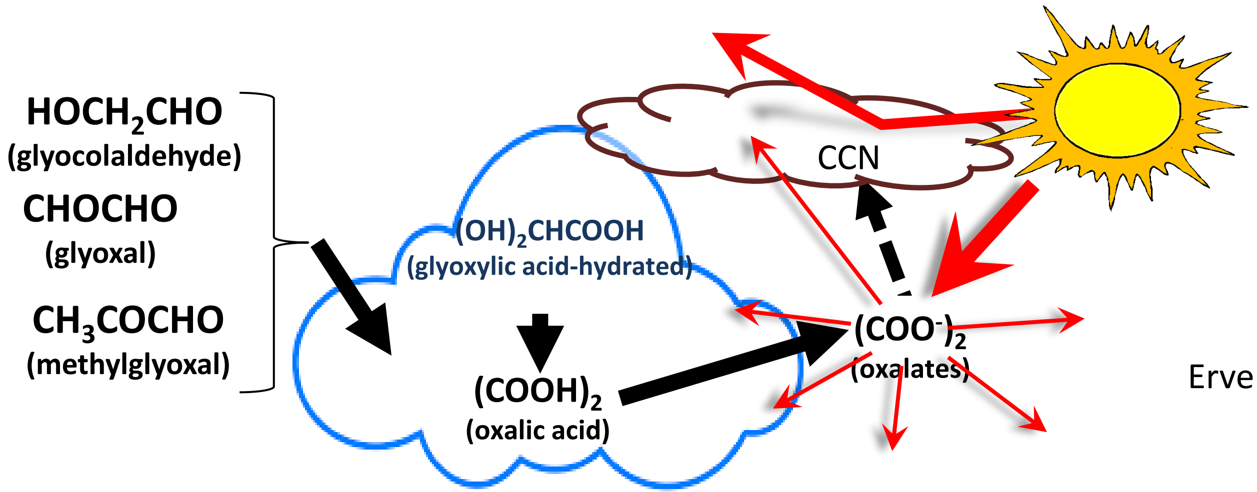
CHOCHO
global distribution – first retrievals (IUP) and TM4 modeling



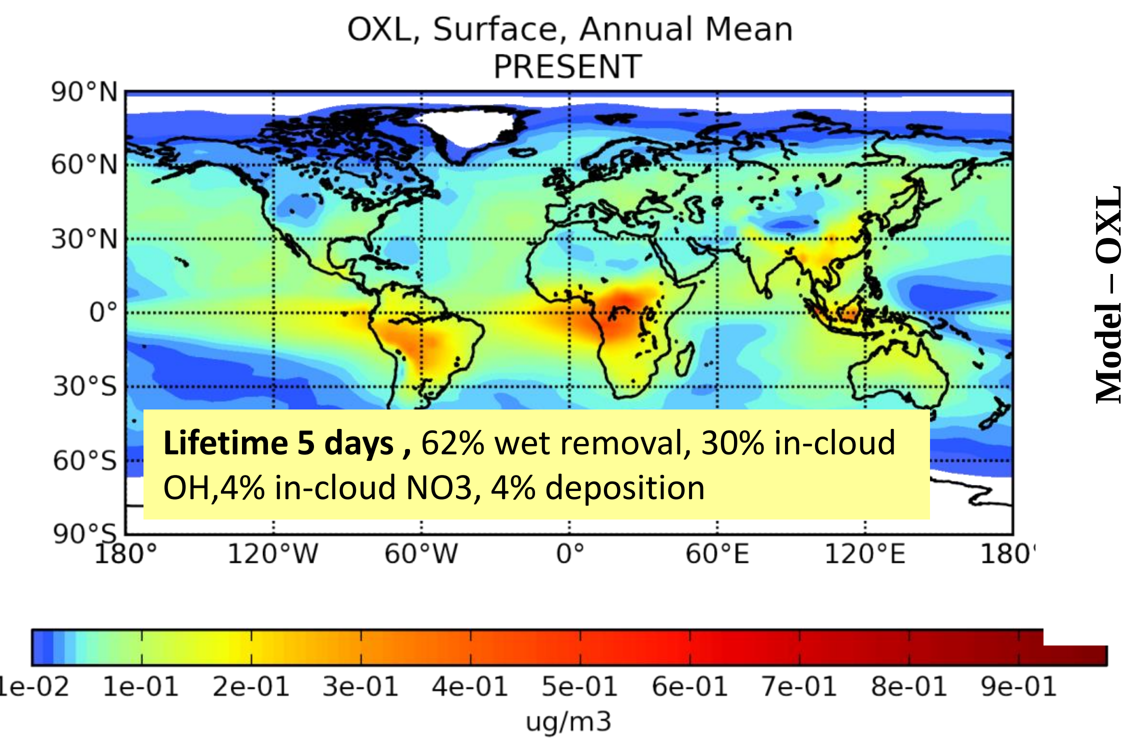


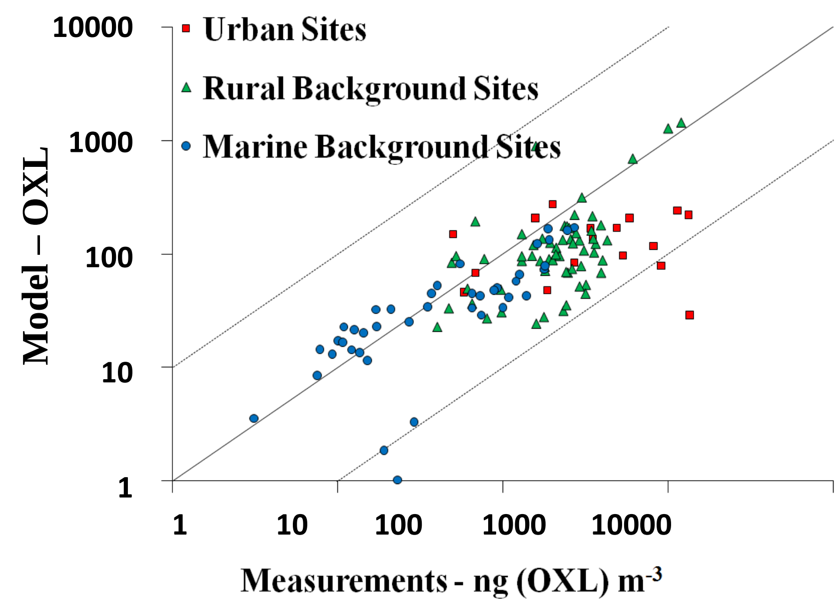
Myriokefalitakis et al., ACP, 2008

Oxalate in the global troposphere



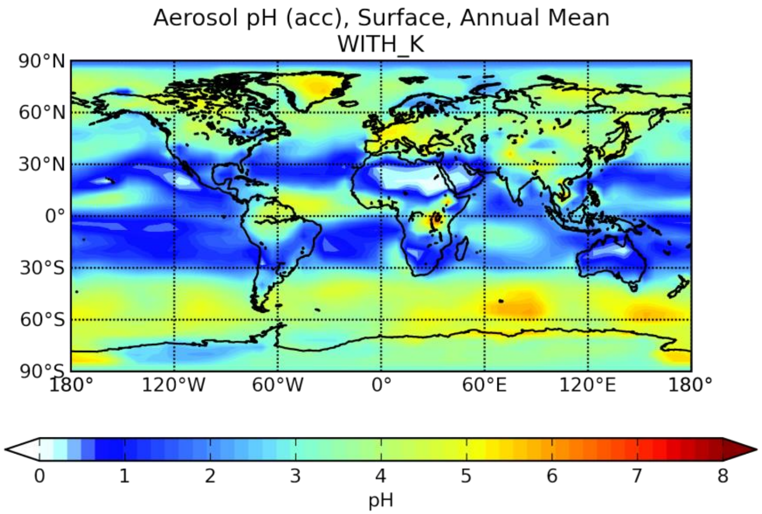
Kinetics from
Lim et al., ACP, 2010
Ervens & Volkamer, ACP, 2010
Noziere et al., 2009

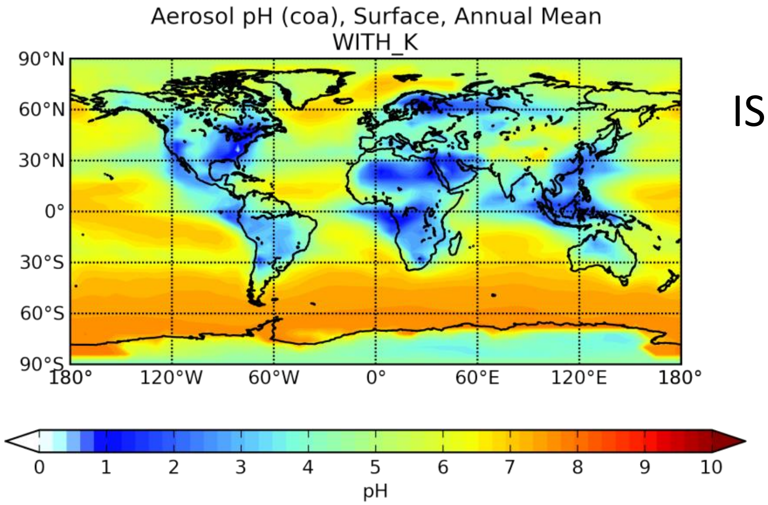




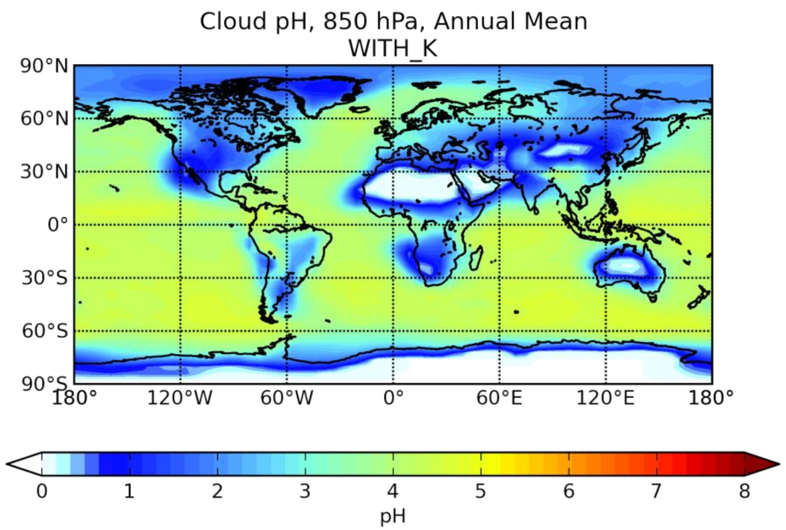
Myriokefalitakis et al., ACP, 2011

Simulated Aerosol & Cloud pH – TM4-ECPL





ISORROPIA II

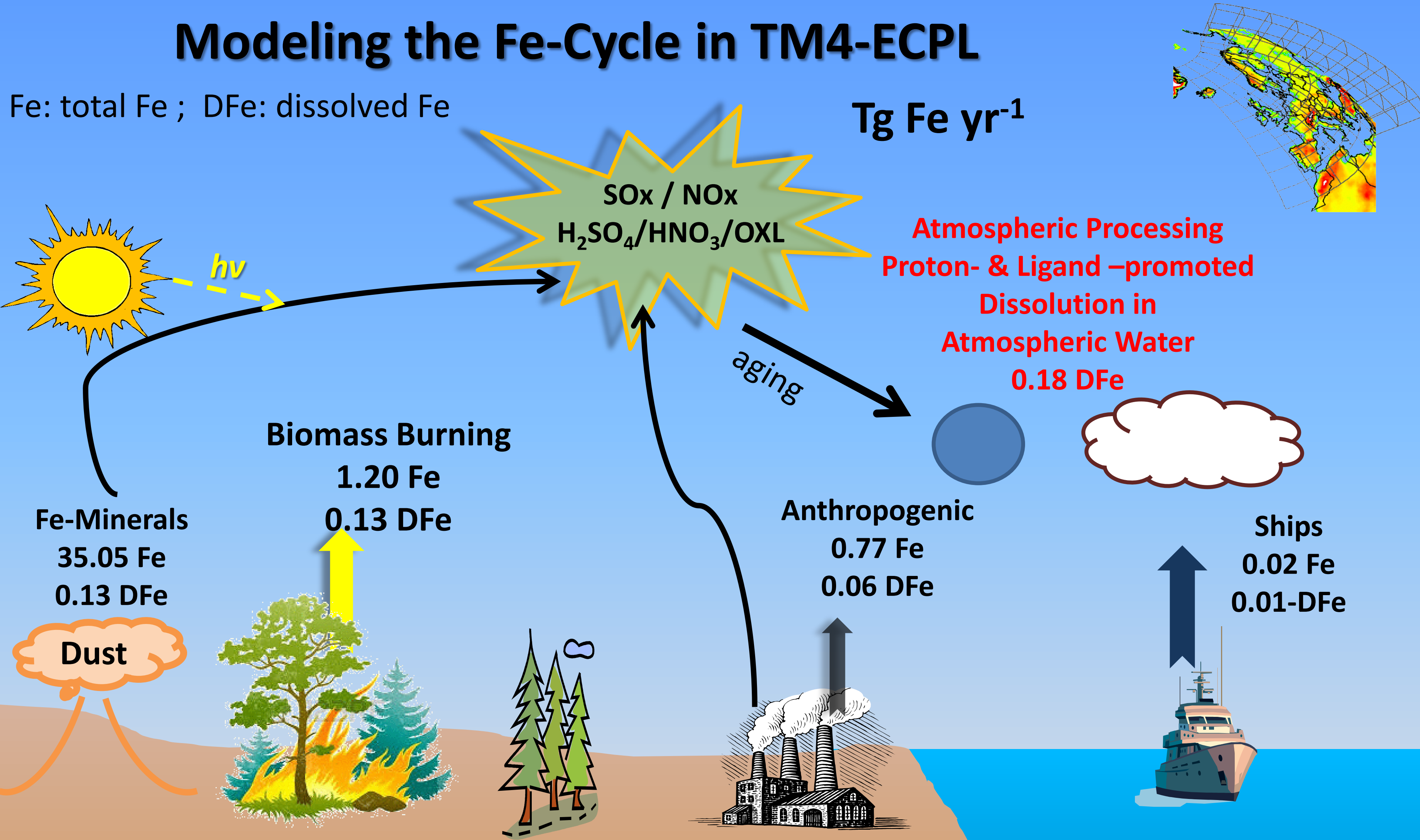


CO_2, SO_2, NH_3, ions of strong acids & Oxalate

Modeling the Fe-Cycle in TM4-ECPL

Fe: total Fe ; DFe: dissolved Fe

Tg Fe yr^{-1}



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

Myriokefalitakis et al Biogeosciences 2015

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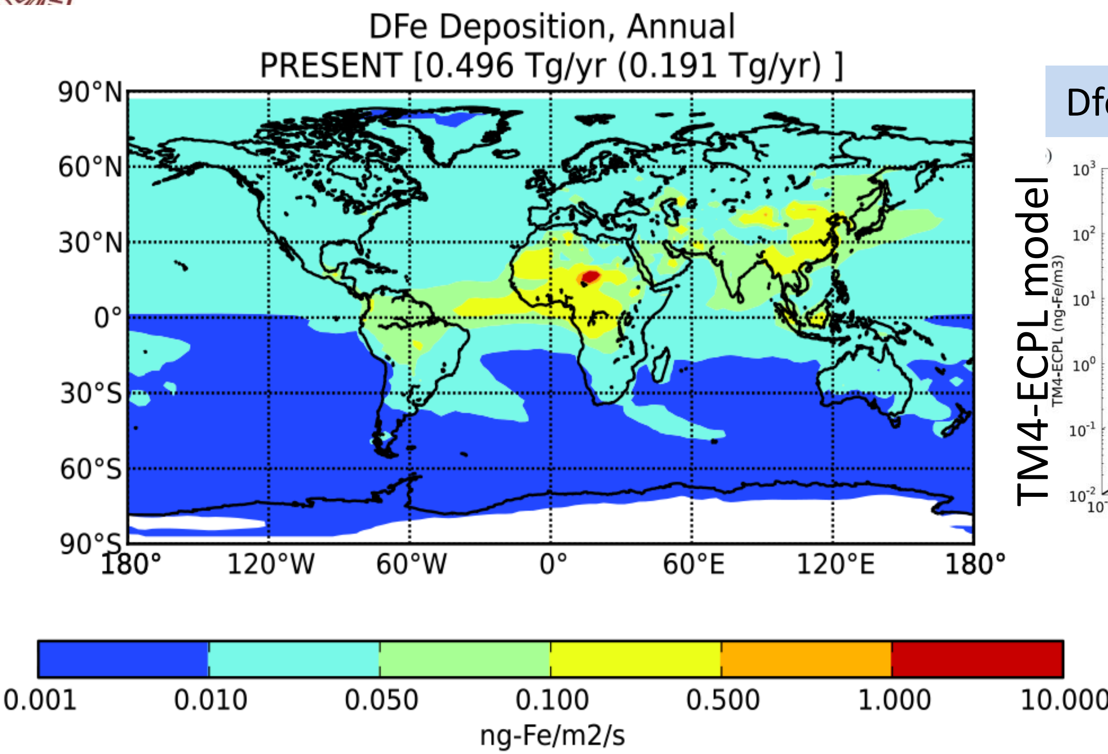
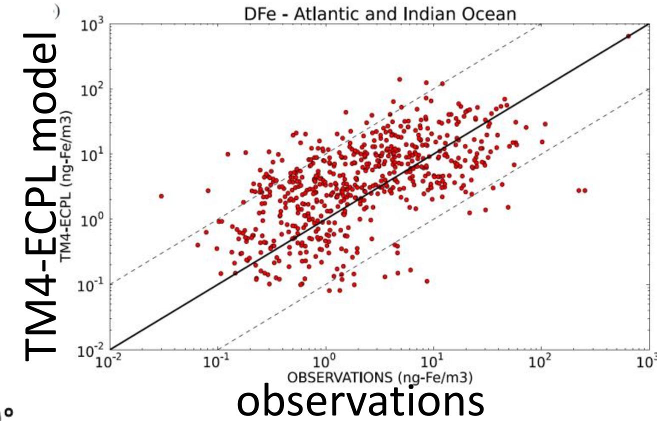
Dissolved Fe deposition



Dfe atmospheric concentrations

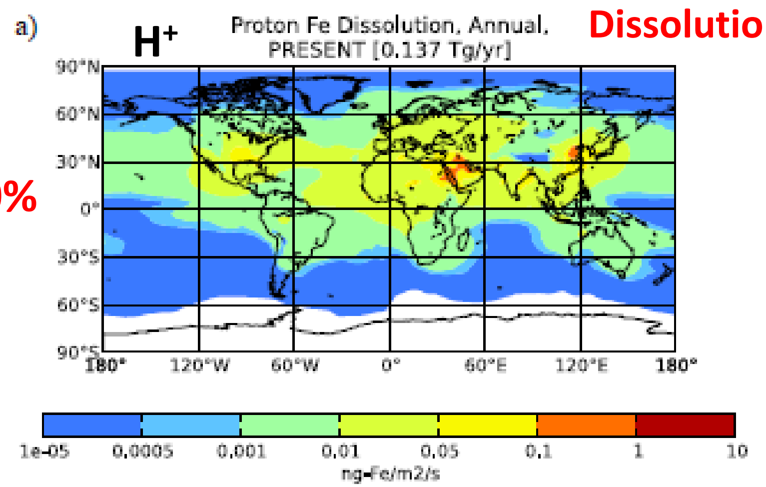


Myriokefalitakis et al Biogeosciences 2015

Dissolution flux

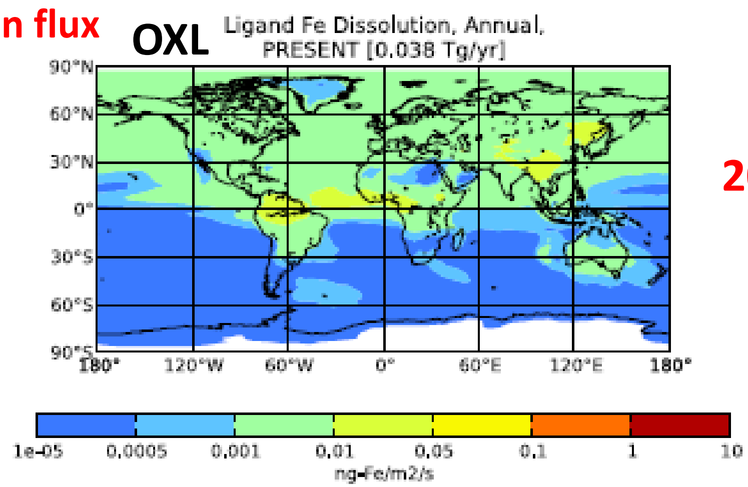
H+

80%

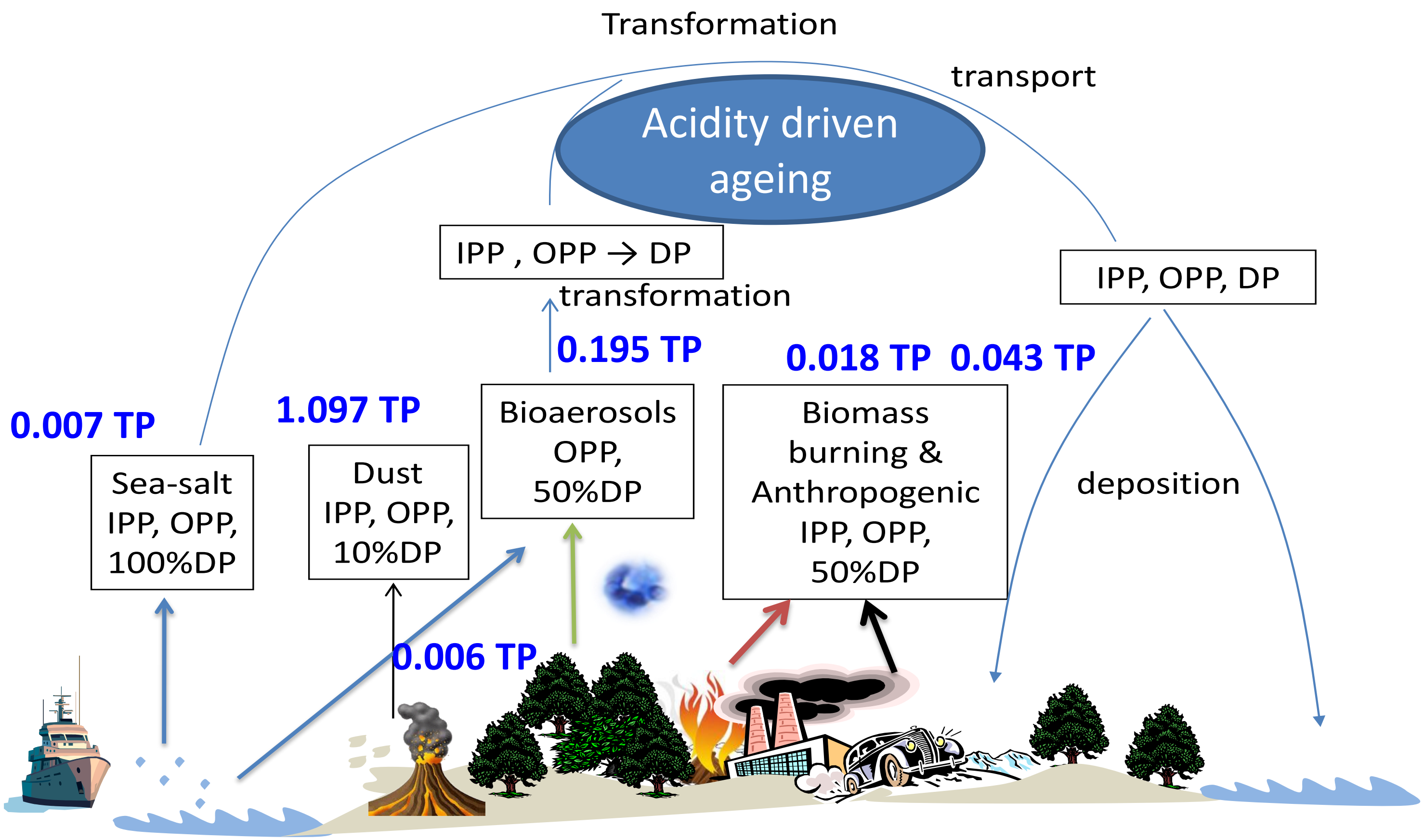


OXL

20%



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 ; solubility Guidry and Mackenzie, 2003; van Cappellen and Berner (1991).

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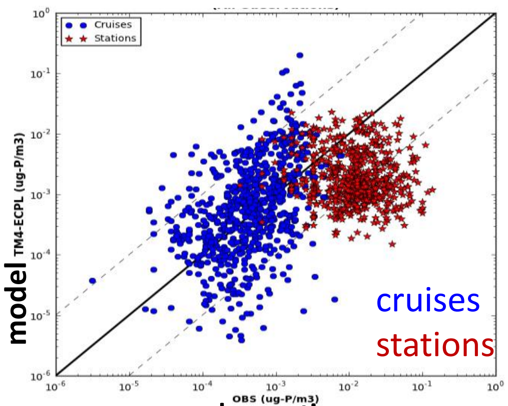
Fluoroapatite and hydroxyapatatite

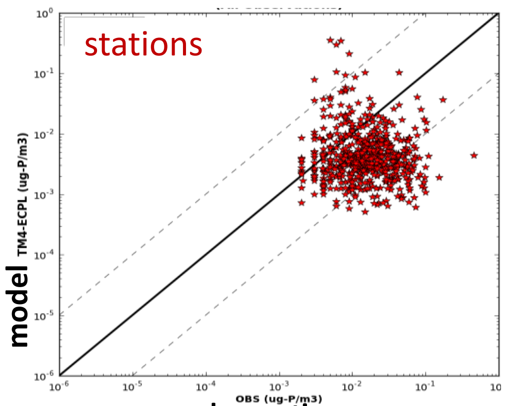
Atmospheric Dissolved Phosphorus deposition

P atmospheric concentrations

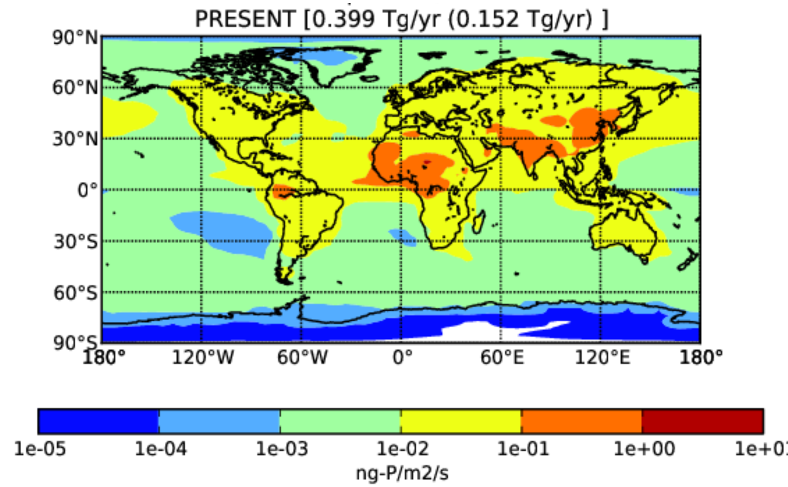
DP aerosol concentrations



TP aerosol concentrations

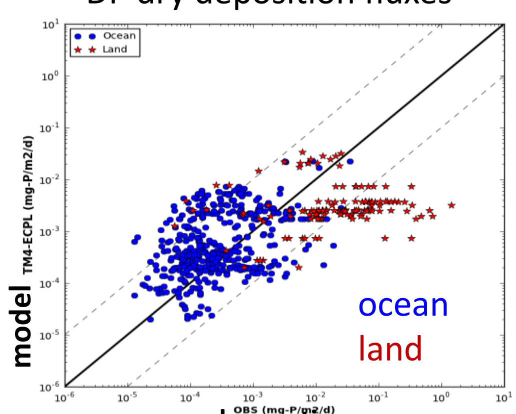


Dissolved P deposition

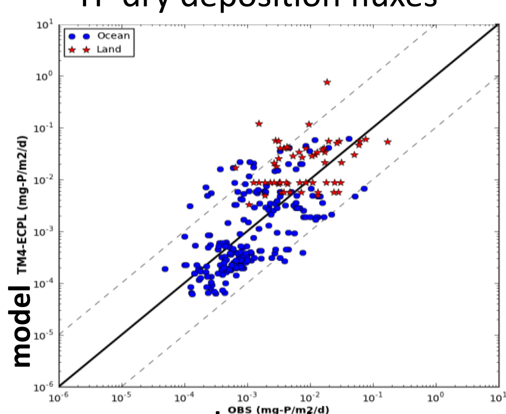


P atmospheric deposition fluxes

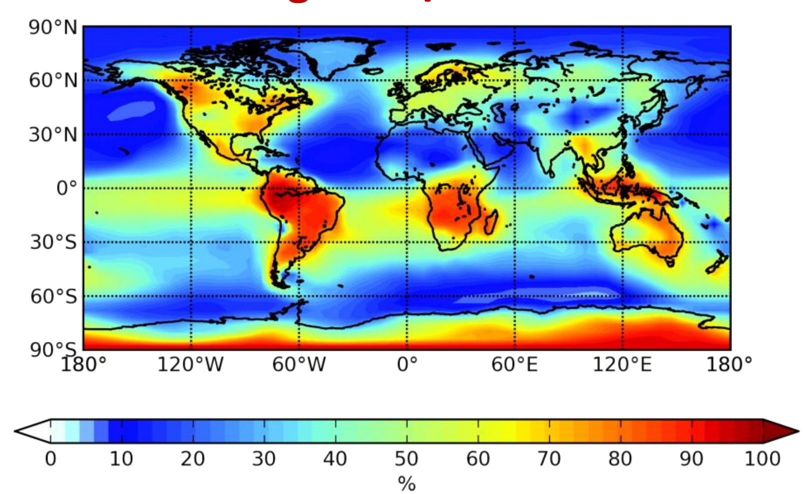
DP dry deposition fluxes



TP dry deposition fluxes



Dissolved Organic P/total Dissolved P



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

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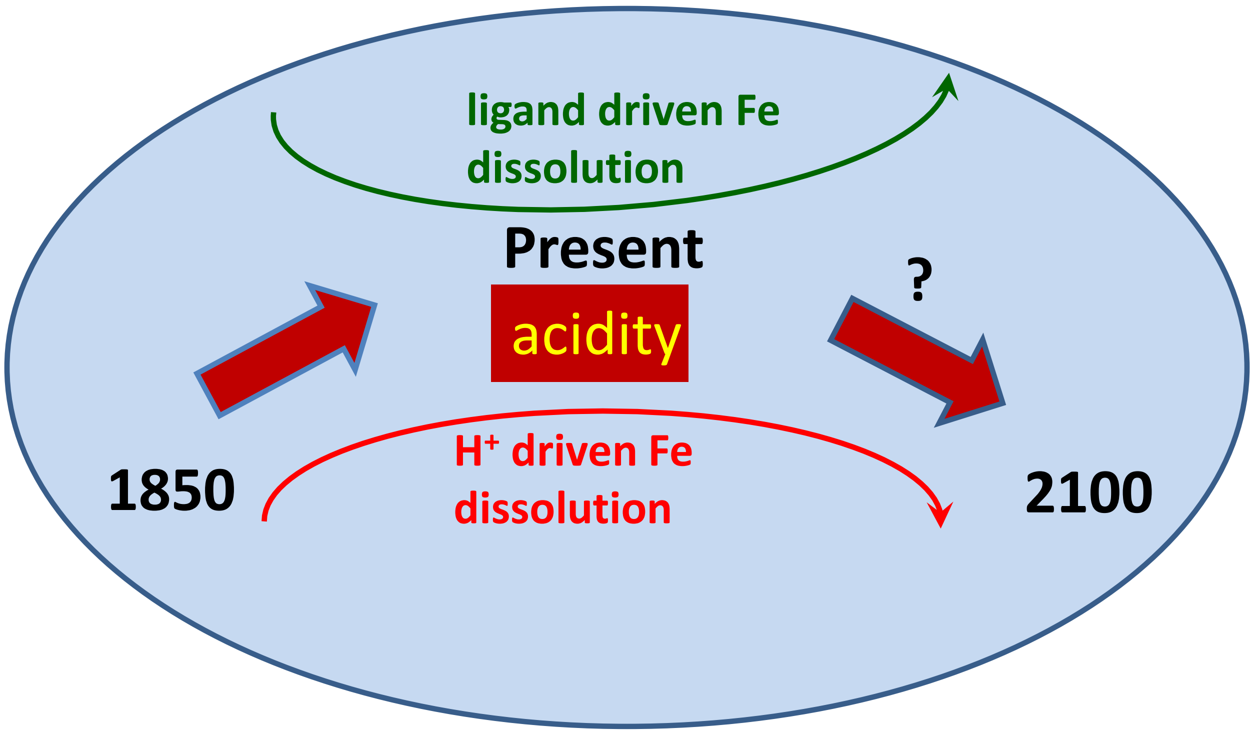
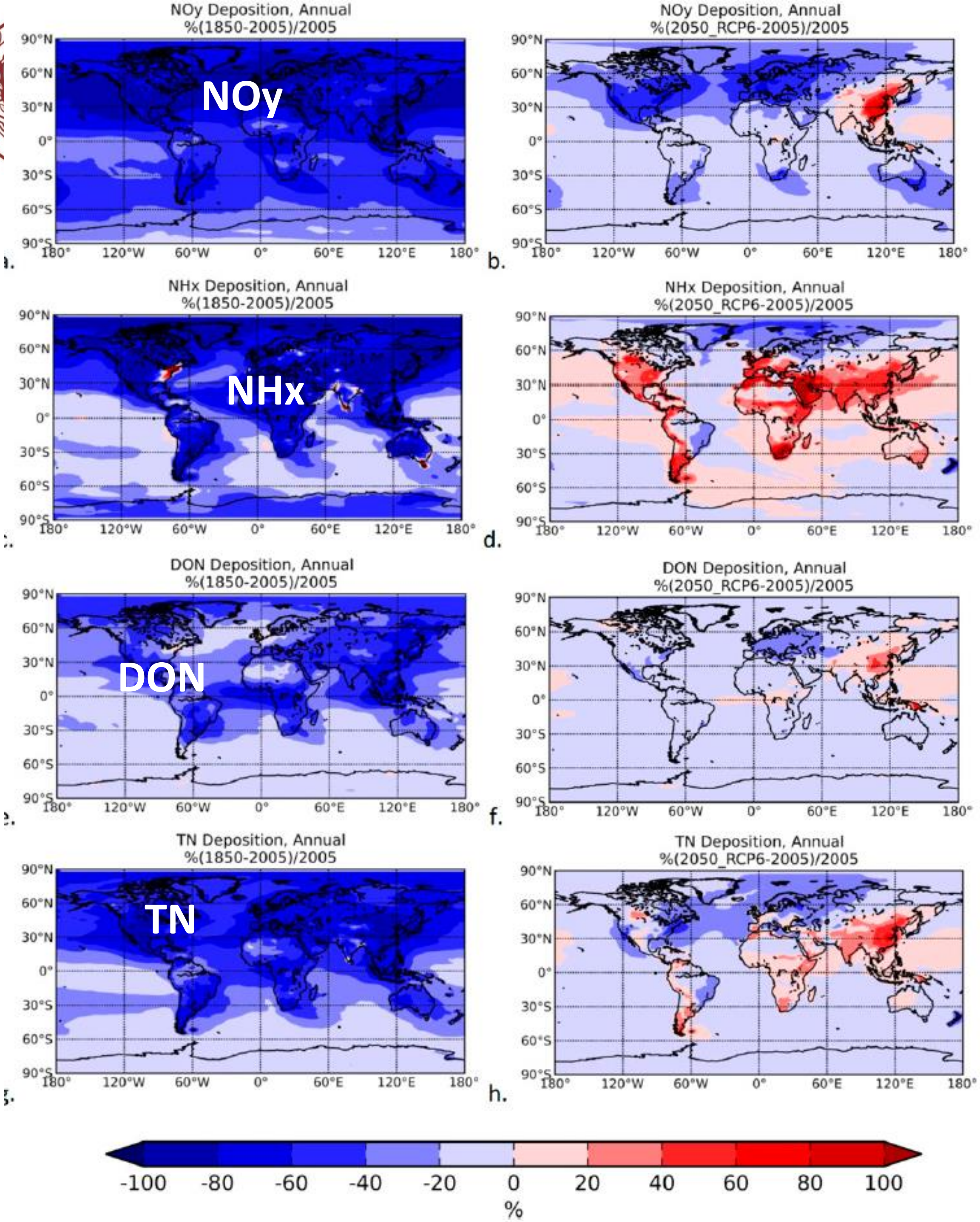
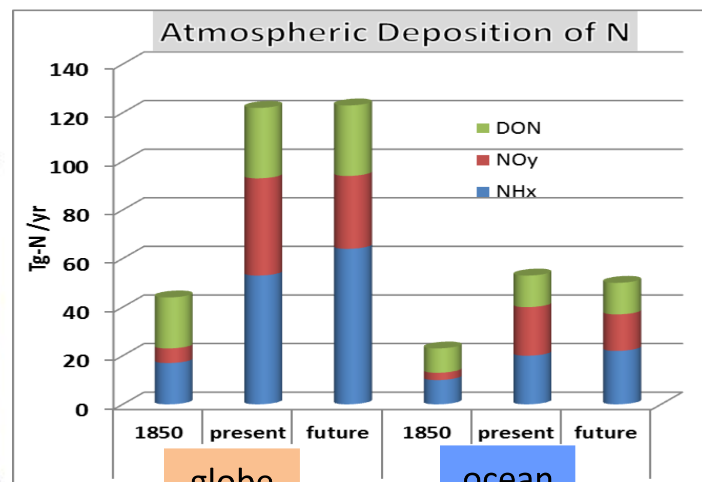
Changes in the importance of multiphase chemical pathways of Fe Dissolution



Myriokefalitakis et al Biogeosciences 2015

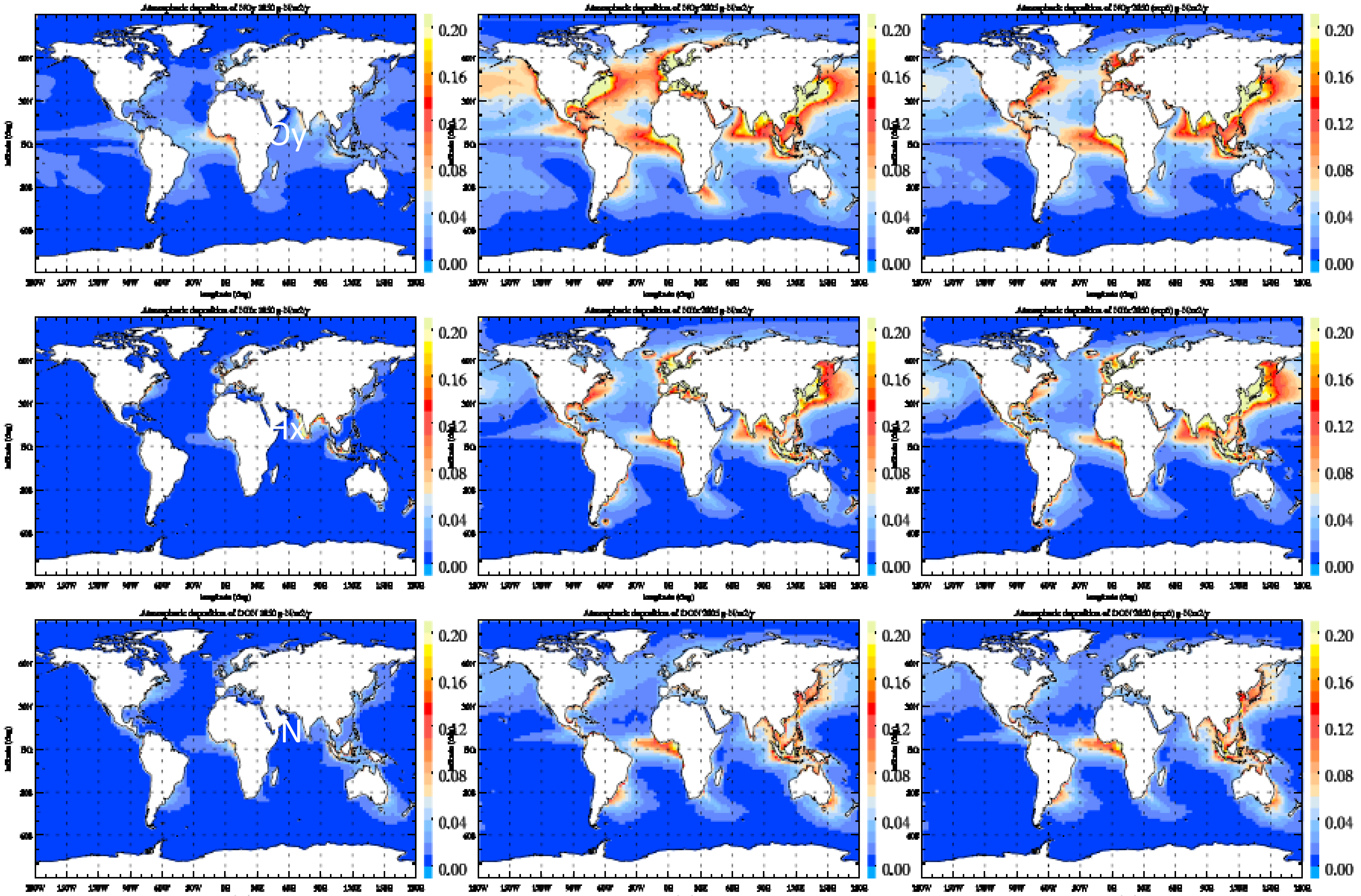


Changes (%) in total deposition since 1850 and projected (2050, RCP6)



Kanakidou et al., JAS 2016

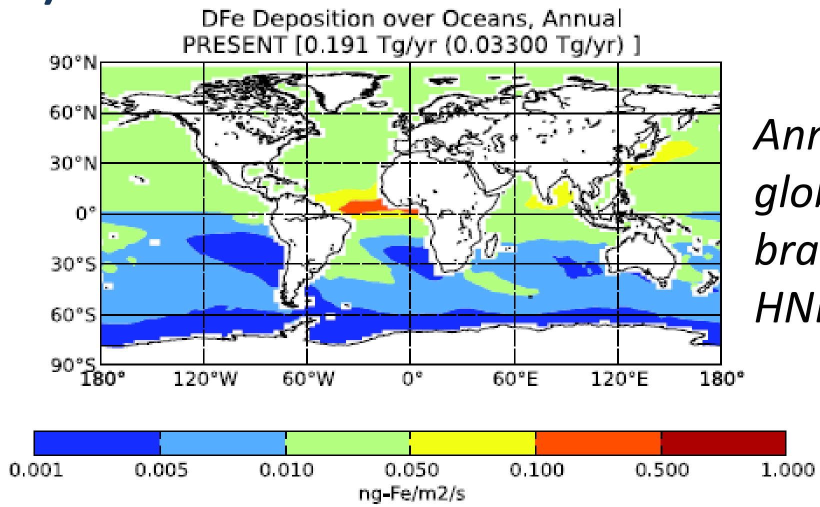
Past Present Future



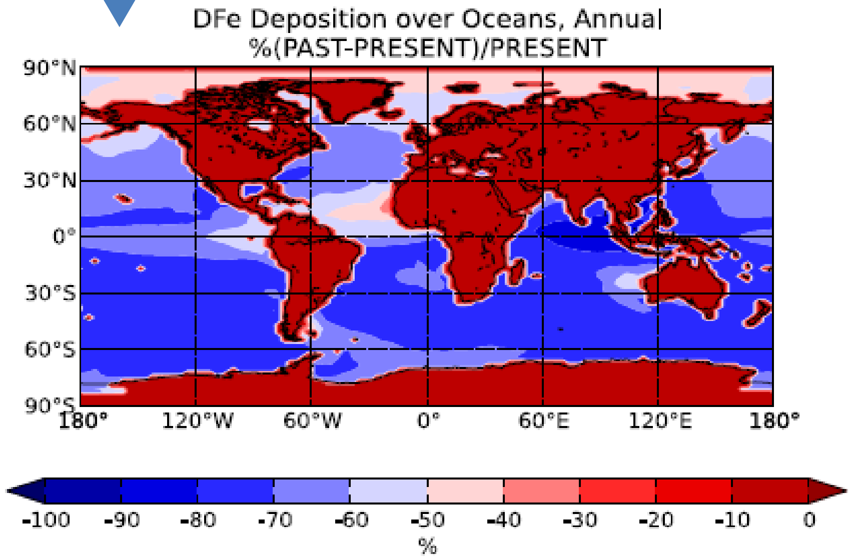
Jickells et al ., GBC, 2017 as calculated by Kanakidou et al., JAS 2016

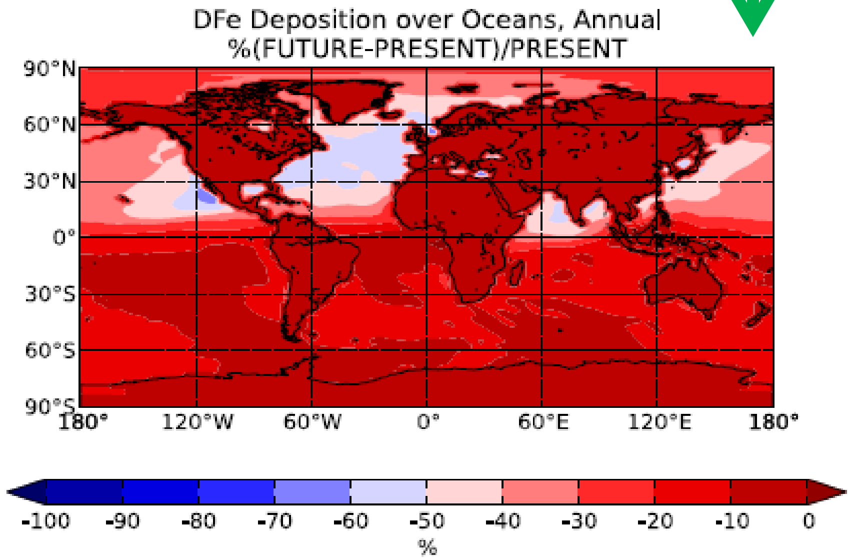
DFe Deposition changes over oceanic areas

has increased (3x) due to anthropogenic emissions (emis. & diss.) **(~50% over HNLC)** **is expected to decrease (~30%) due to air pollution regulations**



Annual flux over the global ocean & in brackets only over HNLC



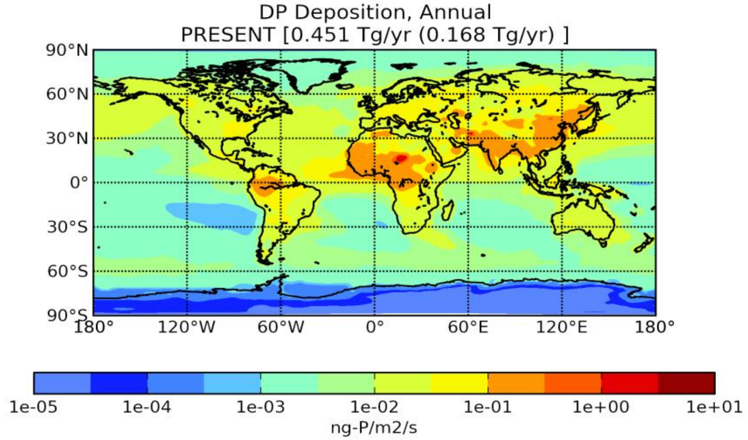


Myriokefalitakis et al, Biogeosciences, 12, 3973, 2015

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

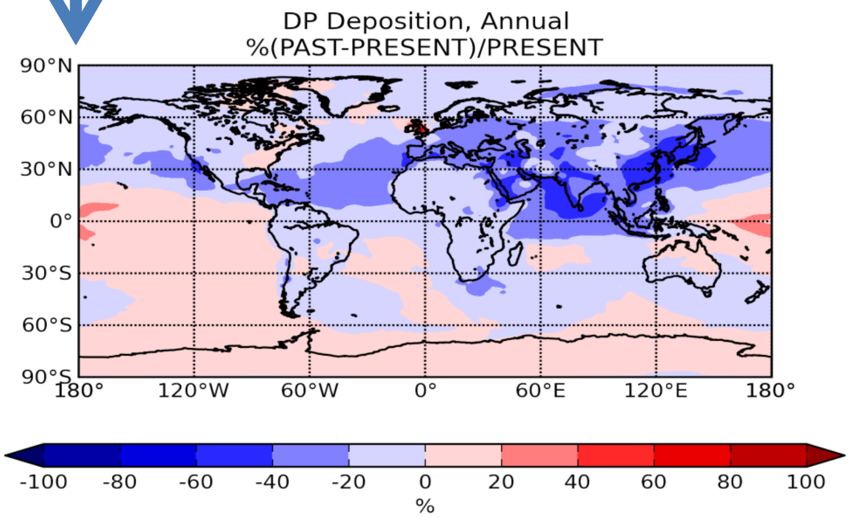


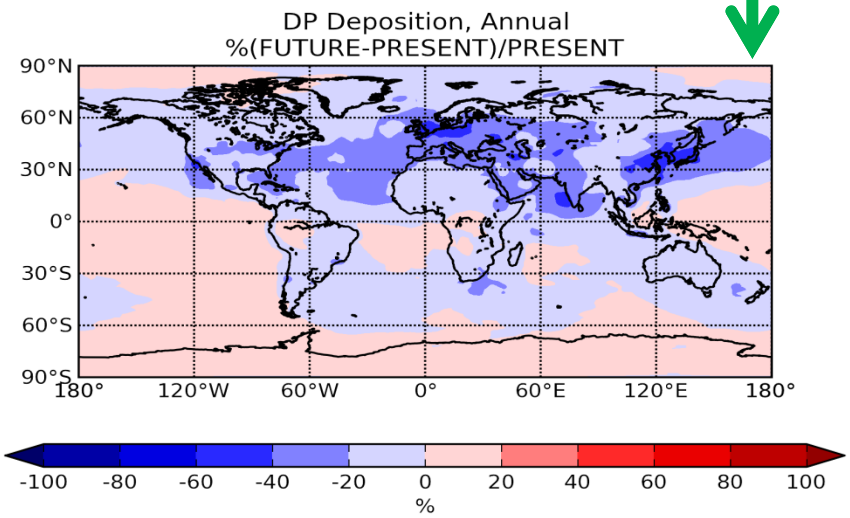
Annual flux over the Globe & in brackets only over oceans

Global ~ 19%
Ocean ~ 21%

Global ~ -18 %
Ocean ~ -16%

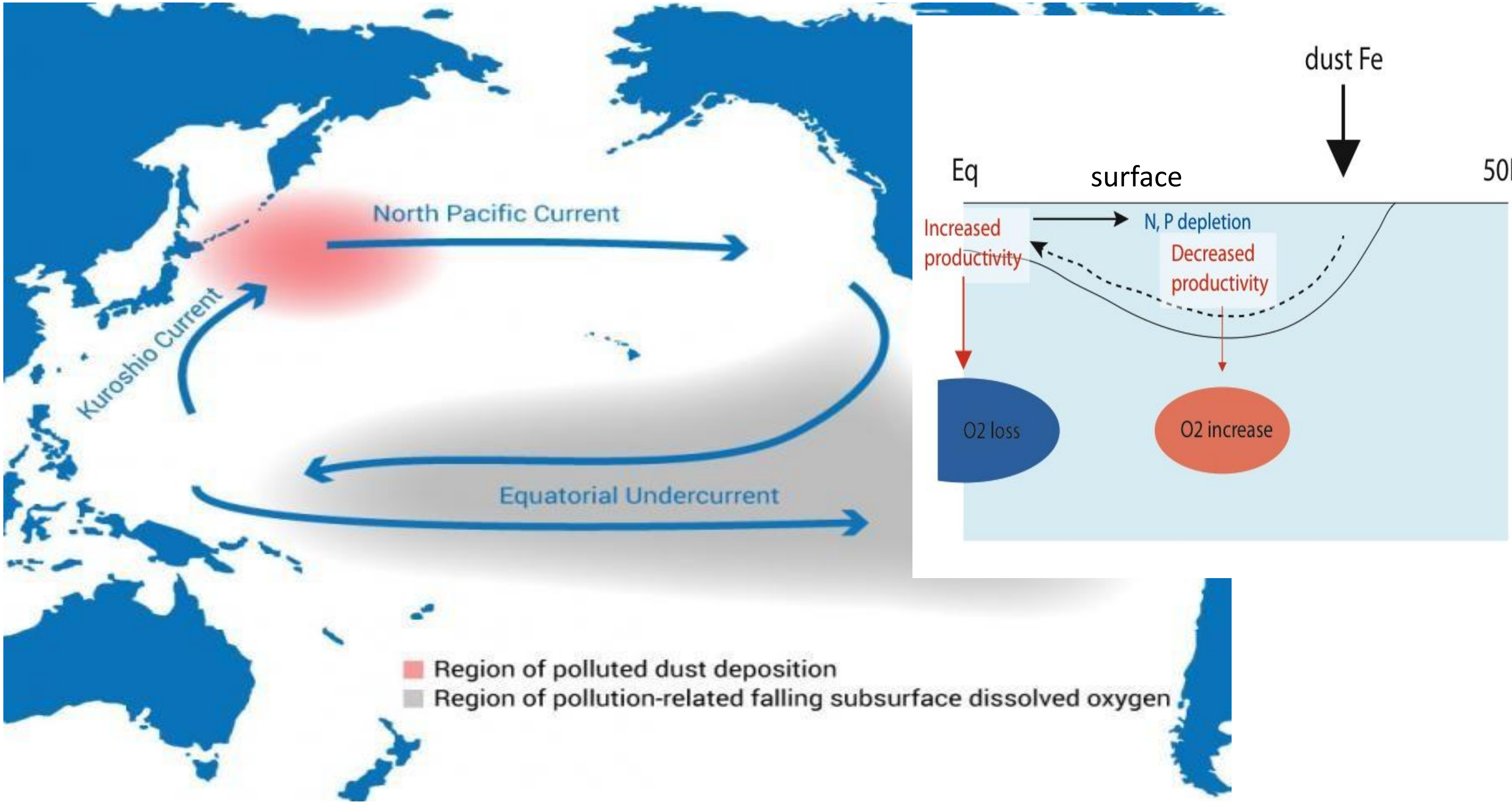
Large uncertainties





Myriokefalitakis et al., Biogeoscience Disc., 2016

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

Importance of atmospheric deposition compared to our 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

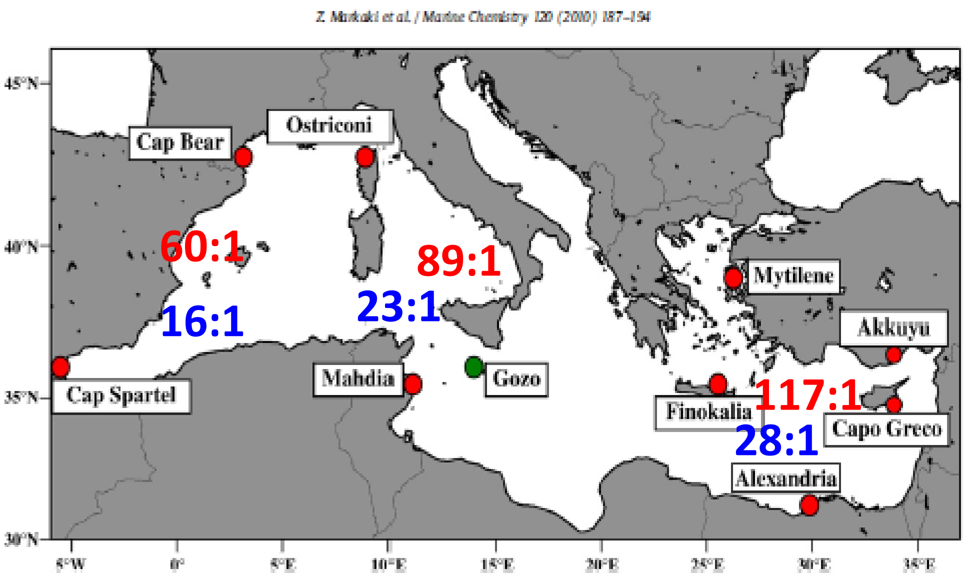
The calculations here suggest that the impacts of atmospheric deposition on ocean biogeochemistry can result in a net increase in primary production and CO_2 uptake of 0.15 Pg C yr^{-1}. However, the resulting reduction in radiative forcing will be offset slightly by increases in N_2O emissions from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

Jickells et al ., GBC, 2017

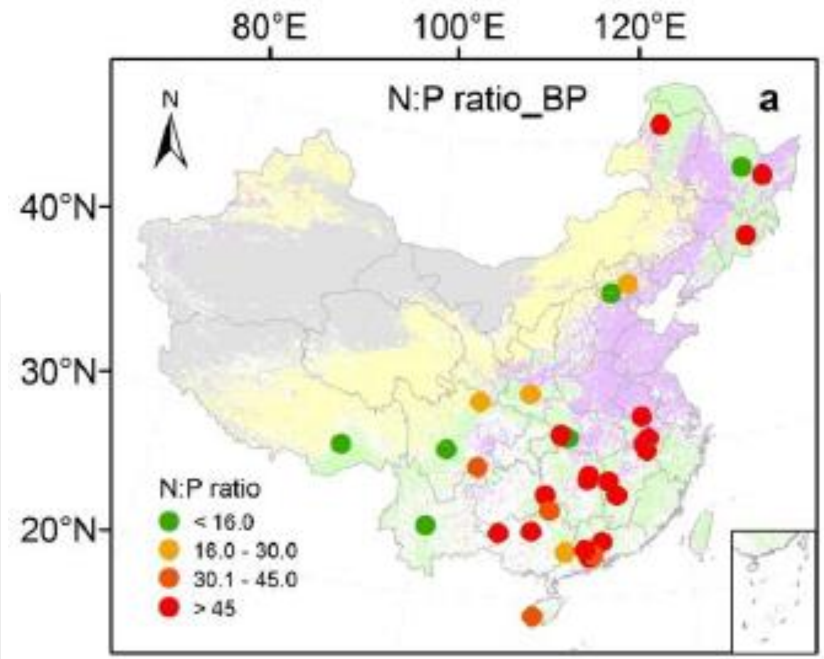
Imbalanced N/P atmospheric deposition

- 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

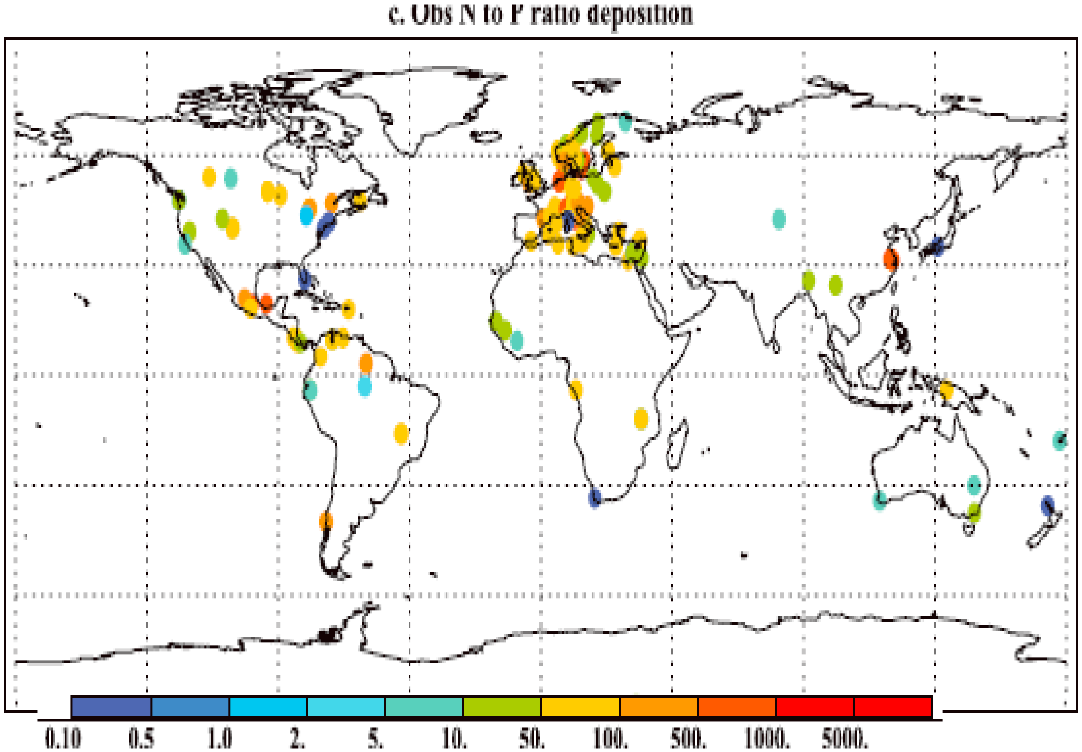


N:P ratio in Bulk Precipitation (BP) over China's Forests

Du E. et al., ACPD, 2016

Human induced P limitation?

Observed N:P ratio in atmospheric deposition over lakes

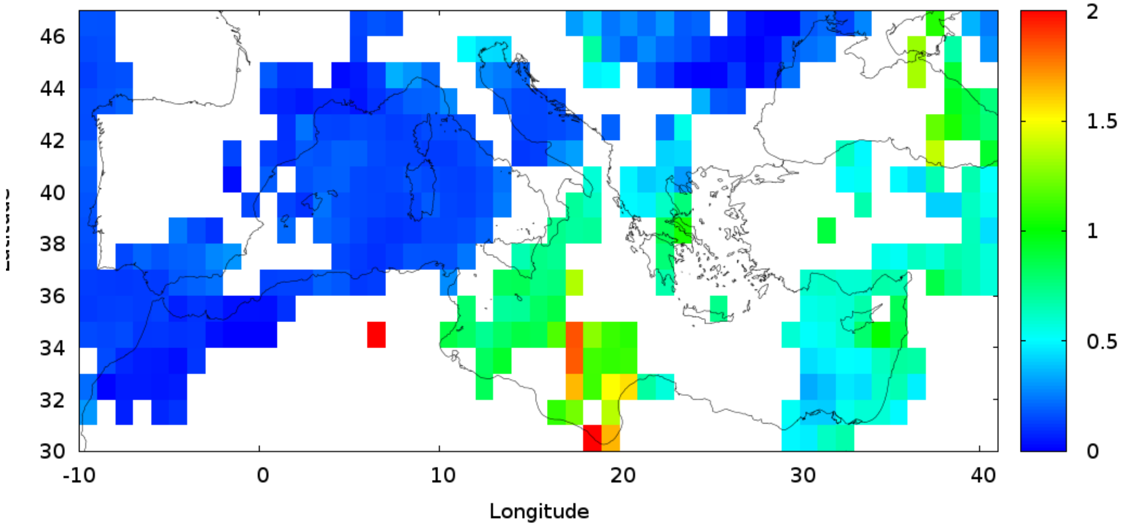


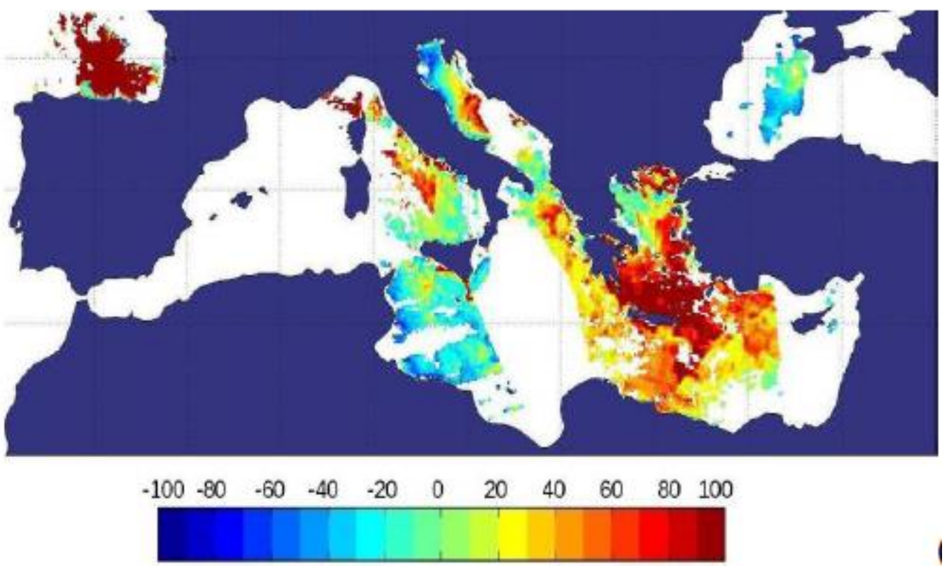
Is atmospheric phosphorus pollution altering global alpine Lake stoichiometry?

GBC, 2016 10.1002/2015GB005137

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

Linking AOD with Chl-a





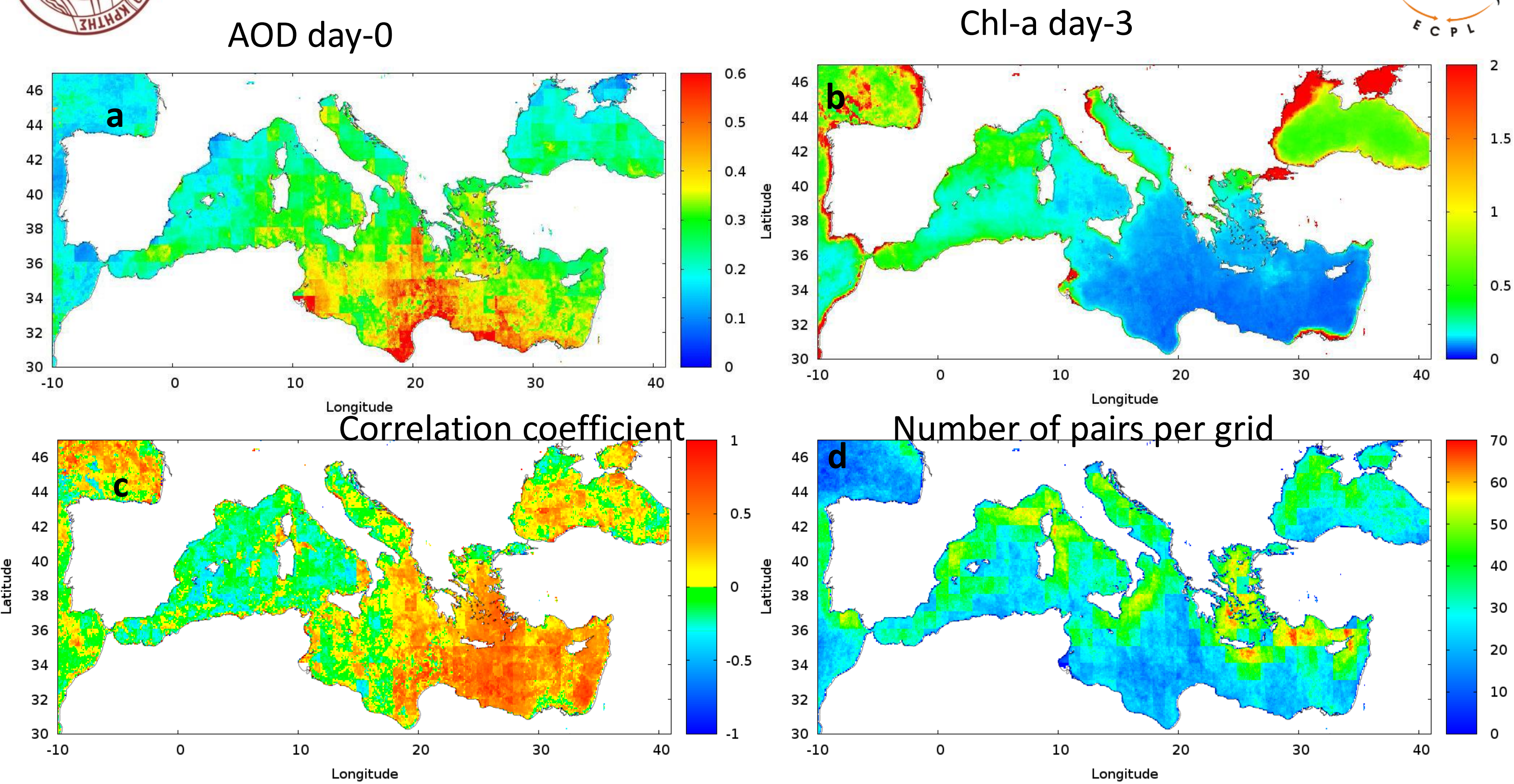
Case study of dust link to chlorophyll concentration in the Mediterranean basin on April 13, 2008 (day 104).

(a) AOD550nm values for April 13, 2008 (day 104)

(b) Chl-a concentration anomalies in percentage values (with respect to 2003-2014 mean) three days after the dust episode, i.e. on April 16, 2008 (day 107).

Papadimas et al submitted

MODIS Aqua – daily 9km x 9km



(a) Average spatial distribution of AOD550nm for dust episodes (day-0) over the Mediterranean during 2003-2014,

(b) as in (a) but for Chlorophyll and for three days after the episode (day-3),

(c) correlation coefficients between AOD550nm for day-0 and Chlorophyll-anomalies for day-3 based on concurrent observations (common days with available data) for both cases (d) number of pairs per grid used for the correlation.

Take home messages

- ✓ **Multiphase chemistry is** important for atmospheric oxidants and nutrients deposition
- ✓ The **acidity** of the media is critical for accurate predictions of atmospheric deposition
- ✓ Atmospheric deposition of soluble nutrients to the ocean could have **increased due to human activities** and projections are sensitive to emission controls and changes in atmospheric acidity.
- ✓ Important quantities of nutrients are in **organic form** and in aerosols → to be considered to understand ecosystem functioning. **Bioaerosols** are important contributors to ON and OP budget
- ✓ Impact of aerosol deposition to the marine productivity can be seen by satellites
- ✓ **Large uncertainties remain** @ in heterogeneous reactions rates parameterisations with globally applicability @ the N content of SOA and the properties of these particles. This affects the $O_3/NO_x/NH_3$ chemistry in the atmosphere @ nutrient dissolution kinetics @ nutrient chemical forms @ sources @ impact to the ecosystems

Perspectives …….

Dr. Stelios Myriokefalitakis – now at Utrecht
Dr. Nikos Daskalakis –moving to IUP
Dr. Giorgos Fanourgakis – UoC
Dr. Sylvia Christodoulaki – now at HCMR
Dr. Kostas Tsigaridis – now at Uni. Columbia
Dr. Ch. Papadimas – now private company
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Prof. John Burrows and coworkers - IUP
Prof. Bob Duce – TAMU, Texas
Prof. Alex Baker – UEA, UK
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Prof. Nikos Mihalopoulos – Univ Crete & NOA
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Benedicte Ardouin

Thank you!