



*modelling the effect of air pollution on ocean biogeochemistry  
in an Earth System Model*

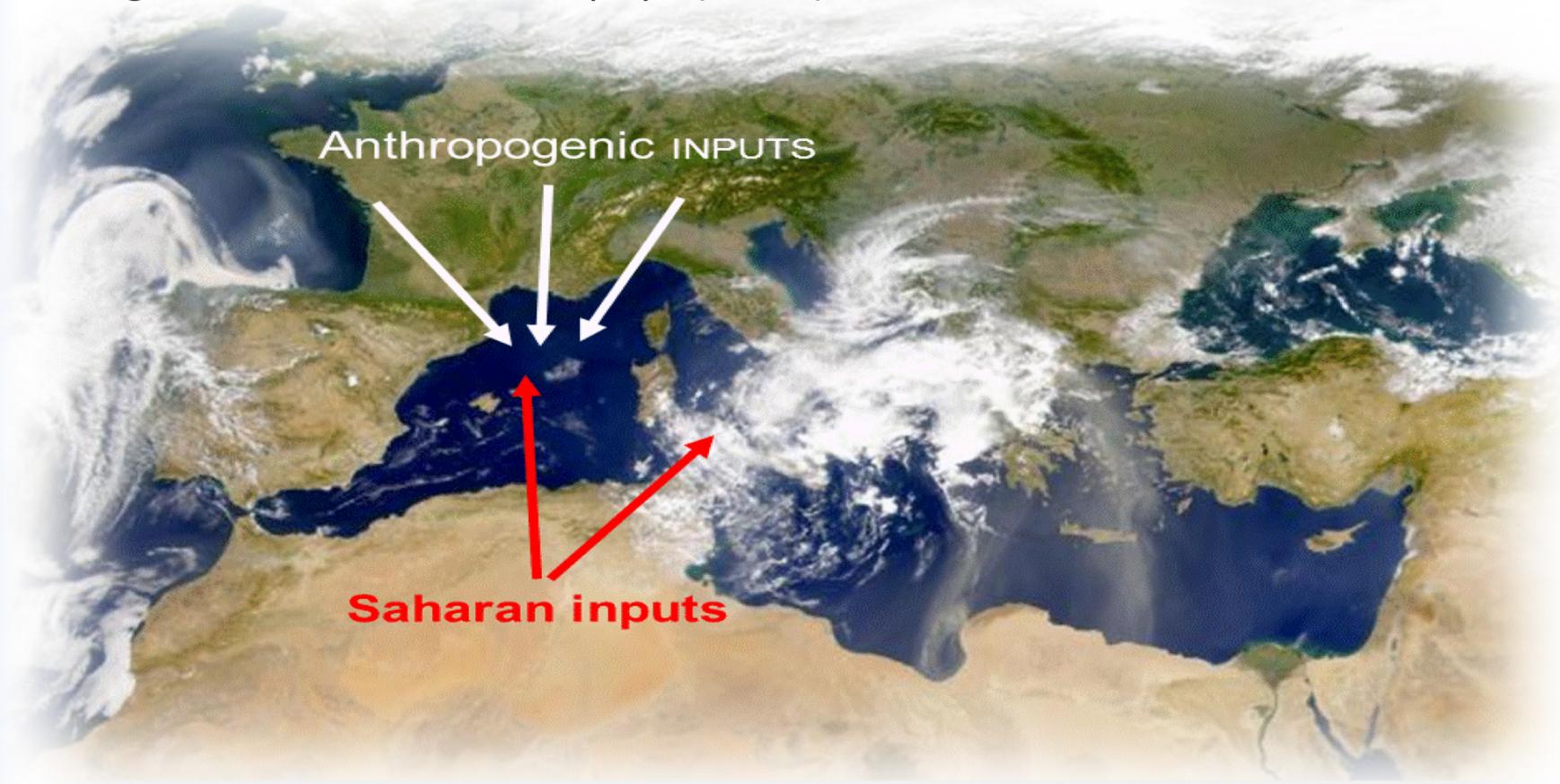
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# Outlook

- 1. The role of Fe deposition over the global ocean**
- 2. State-of-the-art**
- 3. The objectives of the ODEON project**
- 4. Current status of TM5-MP**

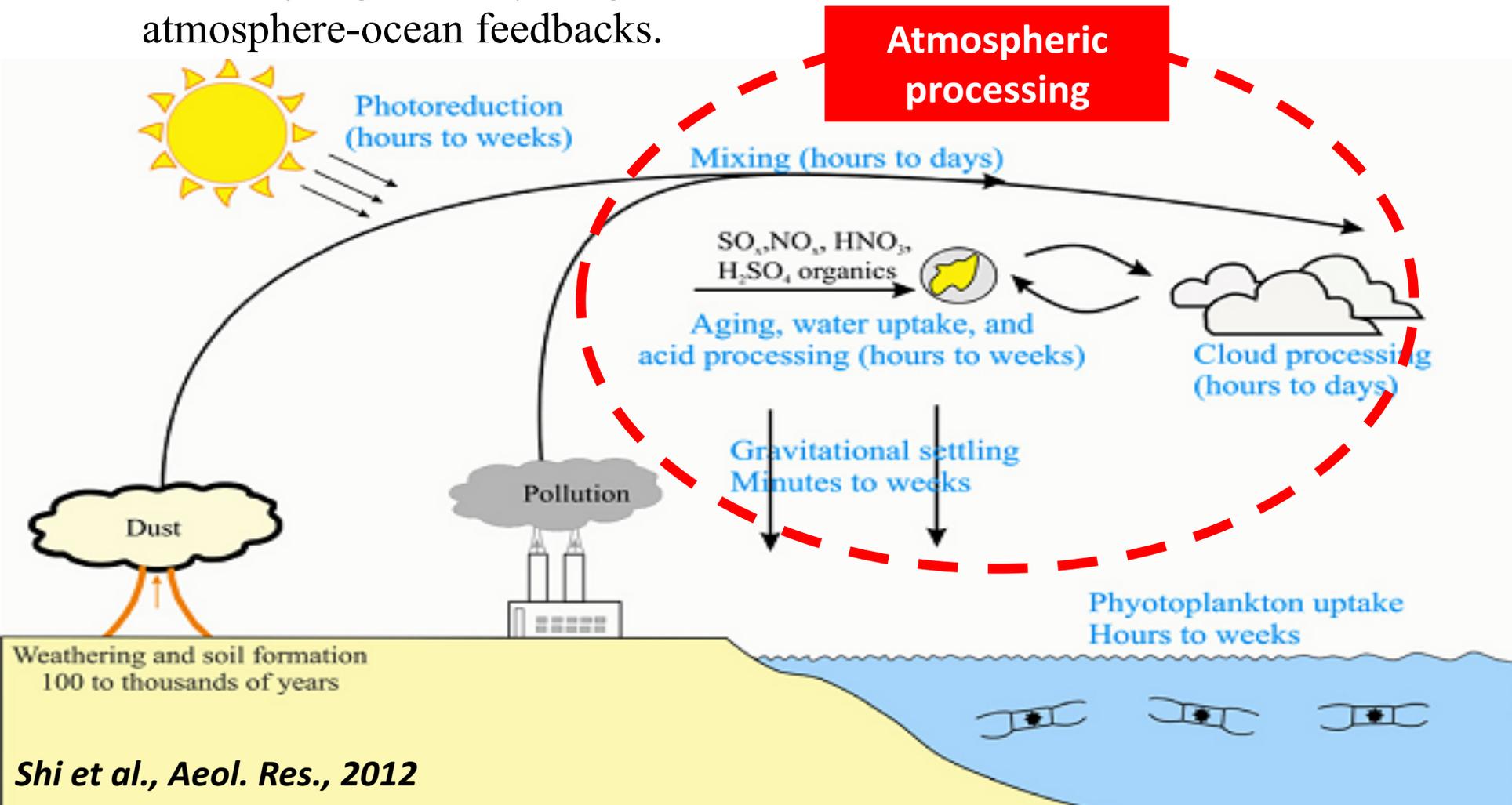
# Atmospheric inputs to the ocean

- ❖ The *surface ocean* ecosystem comprises essential sources and sinks for carbon cycle.
- ❖ Atmospheric deposition of macro- and micro-nutrients (e.g. Fe, P, Si, ...) set important controls on marine ecology and biogeochemistry.
- ❖ Iron (**Fe**) is a key micronutrient that modulates gross primary production in High-Nutrient-Low-Chlorophyll (**HNLC**) oceans.



# The Atmospheric Fe Cycle

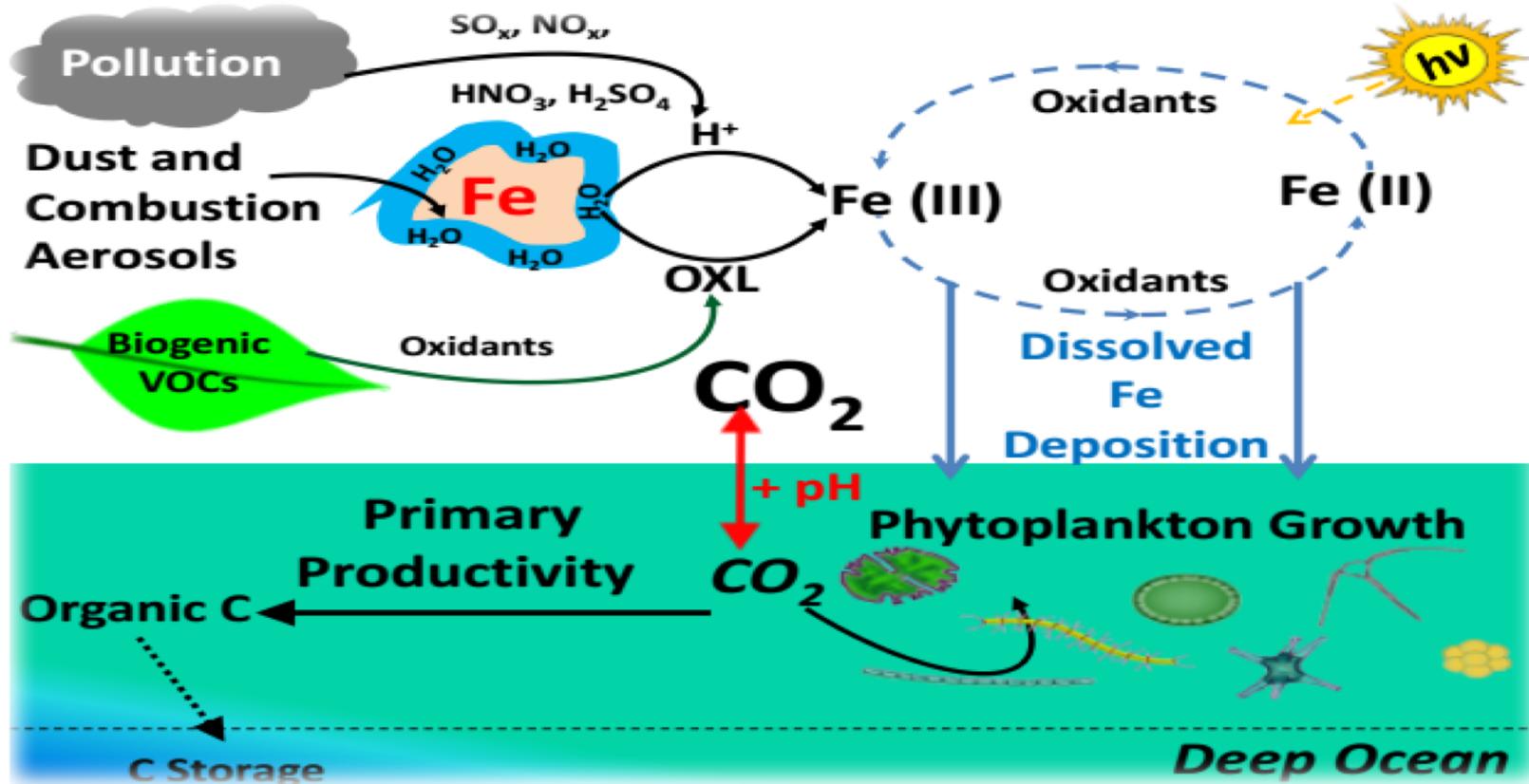
- ✓ Fe carried by atmospheric dust and combustion aerosols is transported and deposited over remote oceans.
- ✓ Dissolved Fe (DFe) is a significant nutrient for marine biota (i.e. bio-available).
  - DFe may regulate key biogeochemical interactions and influence climate via atmosphere-ocean feedbacks.



# Atmospheric Fe input to the ocean

➤ Atmospheric processes related to air-quality convert insoluble Fe to more soluble forms (*and thus bioavailable...*)

➤ **Strong acids and organic ligands** that coat minerals transform part of the contained insoluble forms of Fe (e.g.  $\text{Fe}_2\text{O}_3$ ) into **soluble forms** (e.g. Fe(II), inorganic soluble species of Fe (III), organic Fe-complexes) during atmospheric processing.



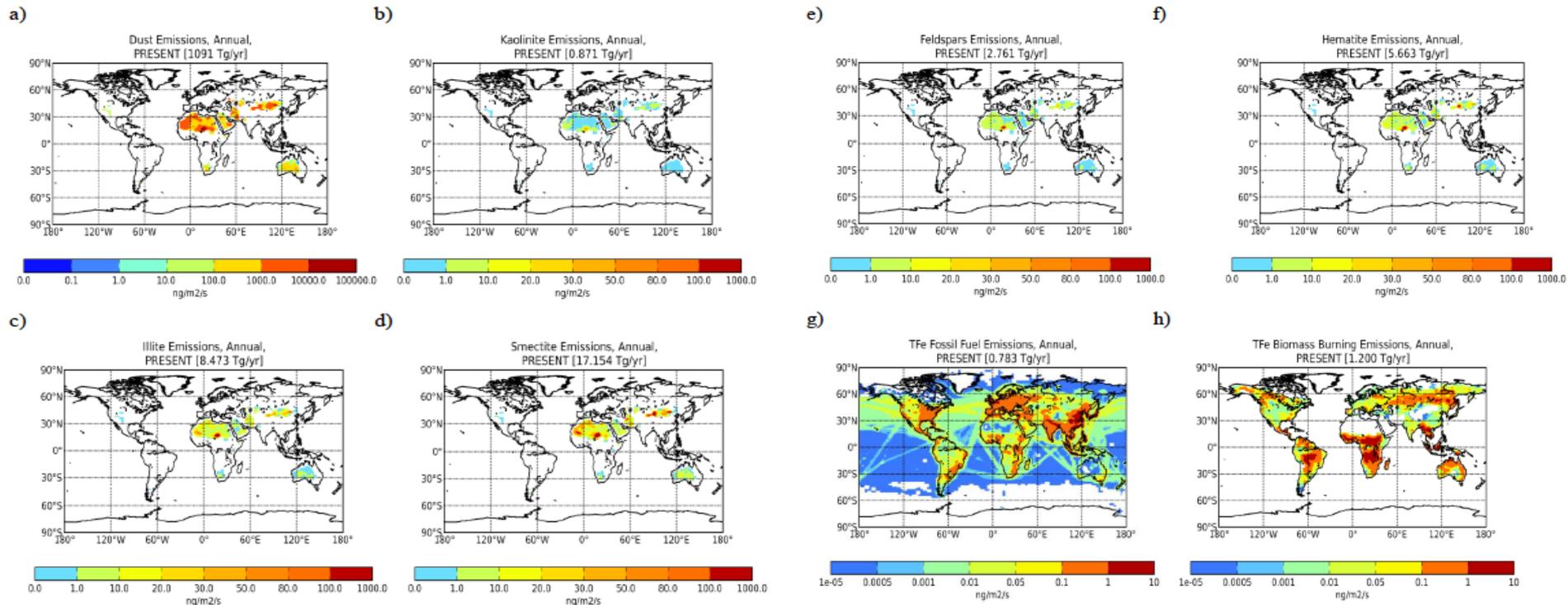
➤ **Uncertainty remains on the impact of atmospheric composition and climate on the marine Fe-limitations and consequently on the oceanic carbon-cycle !!!**



# The Atmospheric Fe-Cycle in TM4-ECPL

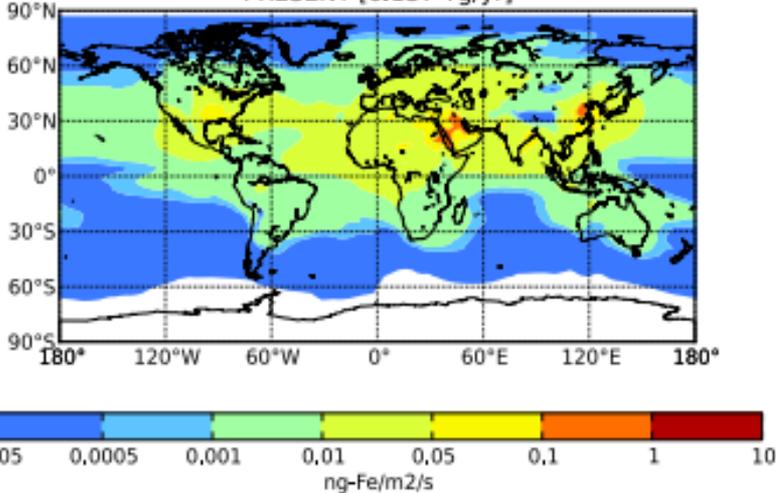
# Global Fe Emissions

- TM4-ECPL takes into account  $\sim 8 \text{ Tg Fe yr}^{-1}$  Illite,  $\sim 1 \text{ Tg Fe yr}^{-1}$  Kaolinite,  $\sim 16 \text{ Tg Fe yr}^{-1}$  Smectite,  $\sim 3 \text{ Tg Fe yr}^{-1}$  Feldspar and  $\sim 6 \text{ Tg Fe yr}^{-1}$  Hematite and Goethite (Nickovic et al., ACP, 2013)
- Fe emissions from combustion processes (biomass burning, coal and ships oil combustion) are equal to  $\sim 2 \text{ Tg Fe yr}^{-1}$  (Luo et al. GBC, 2008; Ito, GBC, 2013).
- The extractable Fe emissions  $\sim 0.3 \text{ Tg Fe yr}^{-1}$  are prescribed a) in the initial dust sources as 4.3% Fe is in the form of impurities in soils (Ito and Xu, ACP, 2014) and b) 4% in combustion Fe emissions.

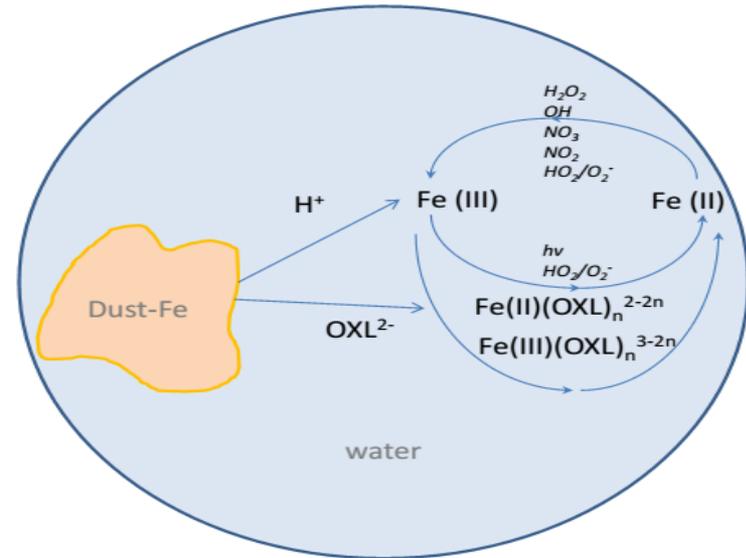
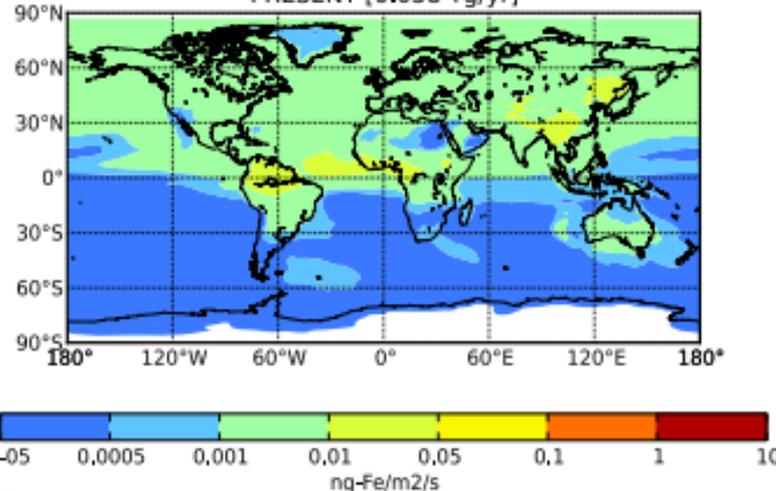


# Mineral-Fe mobilization fluxes: Estimations with the TM4 model

Proton Fe Dissolution, Annual,  
PRESENT [0.137 Tg/yr]



Ligand Fe Dissolution, Annual,  
PRESENT [0.038 Tg/yr]



The model calculates the dissolution of Fe-containing minerals, both in aerosol water and cloud droplets, as a kinetic process that depends on the concentrations of:

- i)  $H^+$  (proton-promoted Fe dissolution; *Lasaga et al., Geochim. Cosmochim., 1994*) and
- ii) Oxalate ( $OXL$ ) (organic ligand-promoted Fe dissolution; *Paris et al., Atmos. Environ., 2011; Johnson and Meskhidze, GMD, 2013*)

# Fe atmospheric chemical processing

## PROTON PROMOTED MOBILIZATION

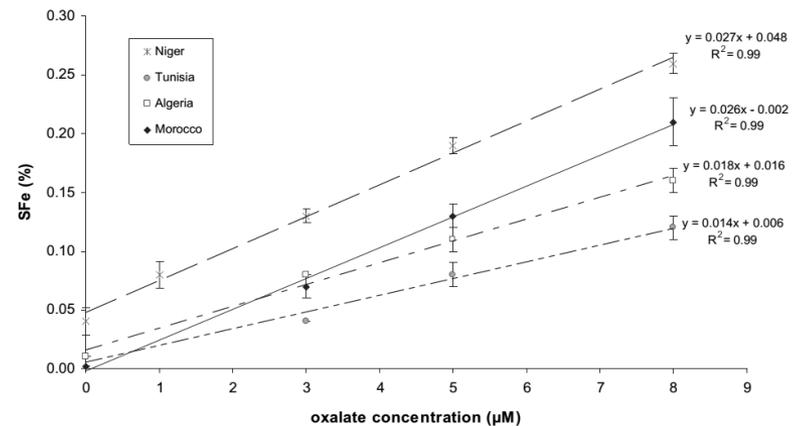
$$R_{Fe} = NFe_{MIN} \cdot K_{MIN}(T) \cdot a(H^+)^m \cdot f_{MIN} \cdot A_{MIN} \cdot [MIN]$$

*Lasaga et al., Geochim. Cosmochim., 1994*

- $R_{Fe}$  is the mineral dissolution rate ( $\text{mol Fe gr}_{MIN}^{-1} \text{s}^{-1}$ )
- $NFe_{MIN}$  is the stoichiometric number of moles of Fe per mole of mineral
- $K_{MIN}$  is the mineral's temperature (T) dependent dissolution reaction coefficient ( $\text{mol m}^{-2} \text{s}^{-1}$ )
- $a(H^+)$  is the  $H^+$  activity in the solution
- $m$  is the reaction order with respect to aqueous-phase protons
- $f$  accounts for the variation of the rate with deviation from equilibrium
- $A_{MIN}$  is the specific surface area of the mineral ( $\text{m}^2 \text{g}^{-1}$ )

## OXALATE PROMOTED MOBILIZATION

- Experimental studies support a positive linear correlation between iron solubility and oxalate concentrations (*Paris et al., Atmos. Env., 2011; Paris and Desboeufs, ACP, 2013*)



*Myriokefalitakis et al., Biogeosciences, 2015*

# Fe Deposition *Estimations*

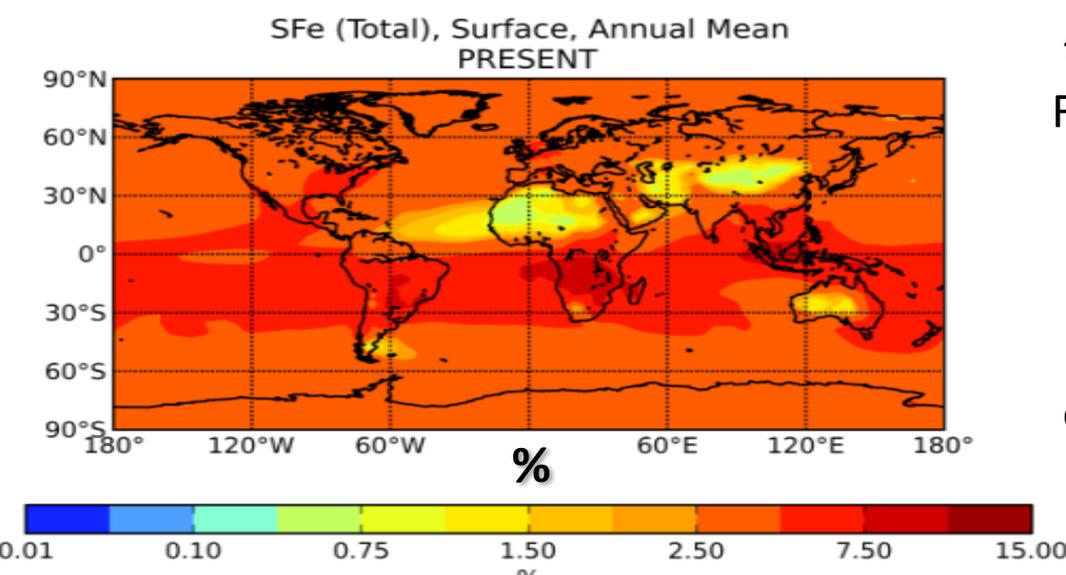
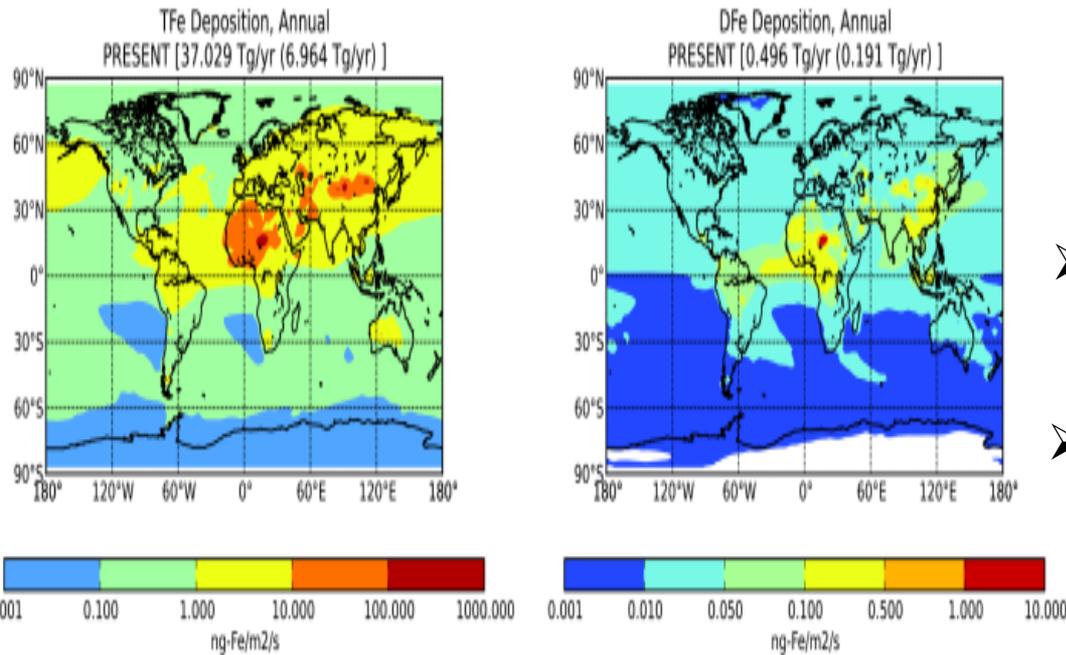
➤ State-of-the-art chemistry-transport modelling (CTM) studies calculate a total **oceanic** Fe deposition flux of 7-10 Tg-Fe/yr.

➤ TM4 calculates that **~37 Tg Fe yr<sup>-1</sup>** of TFe are deposited on Earth's surface.

➤ Global DFe deposition is calculated to be **~0.5 Tg Fe yr<sup>-1</sup>** of which **~0.2 Tg Fe yr<sup>-1</sup>** is deposited over the oceans.

➤ State-of-the-art CTMs clearly support the view that air-quality affects dissolved Fe deposition flux over oceans (0.1-0.3 Tg-Fe/yr).

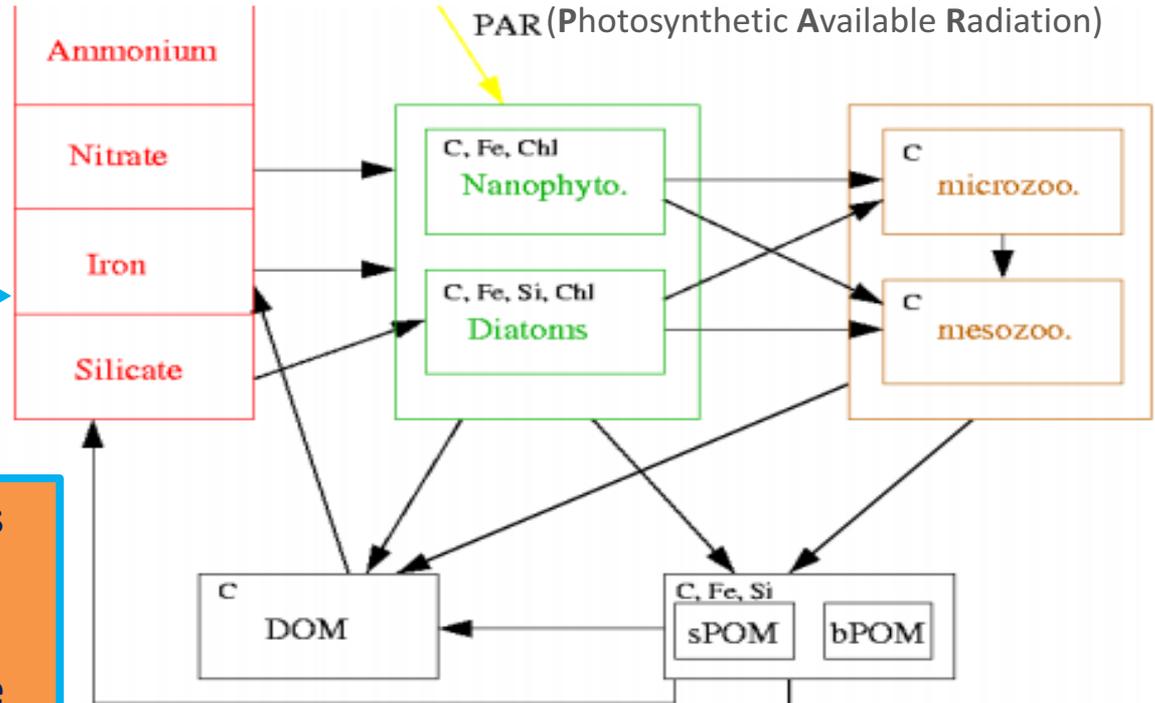
➤ Fe solubility (SFe = %DFe/TFe) is calculated to vary spatially with minima over the dust sources (~ 1%) and maxima over remote (equatorial) regions (~ 5%).



# Fe parameterization in the PISCES model

- The model can include the atmospheric supply of Fe, Si, P and N.
- Fe, Si and P sources are dependent on each other as they are computed from the same dust input file.

There are 4 modeled limiting nutrients for phytoplankton growth



- The Fe content of dust is set to a constant valued (default value is 3.5%)
- The total bioavailable Fe concentration is equal to the total dissolved Fe concentration

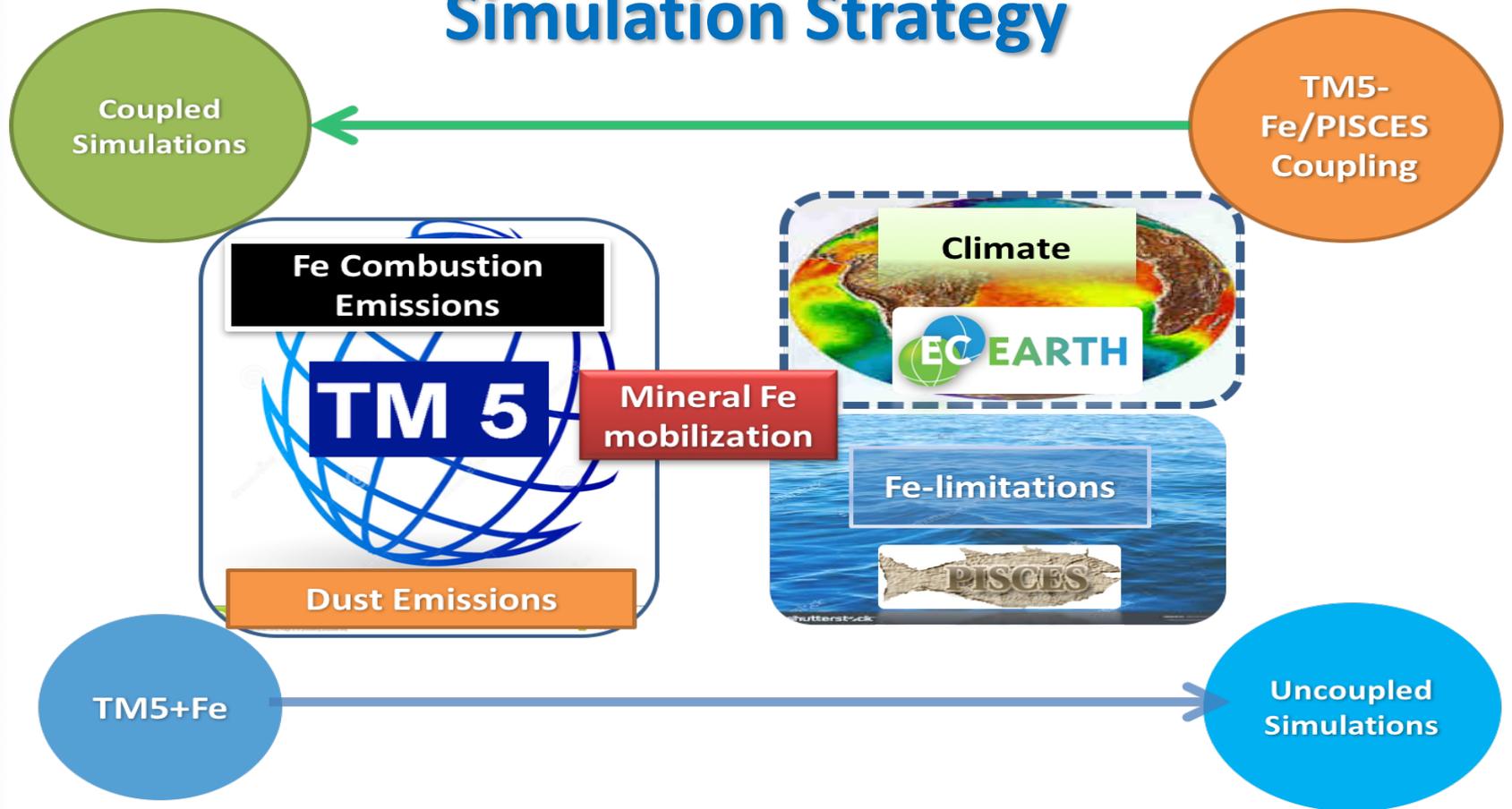
The solubility of dust-Fe in sea water can be either set to a constant value or can be read from a file.  
→ Roughly 0.01% of the particulate Fe dissolves per day

# ODEON Objectives

1. Implementation and evaluation of the atmospheric Fe-cycle in TM5.
2. Cause-effect linkages between climate and atmospheric Fe-mobilization.
3. Atmospheric Fe-cycle coupling to marine bio-geochemistry in EC-Earth.
4. Impact estimations of air-quality changes on the marine primary productivity



# Simulation Strategy



•The couplings of air-quality and Fe-supply into the oceanic biogeochemistry and climate (between IFS, TM5 and PISCES) will be activated in a stepwise approach via Uncoupled (U) and Coupled (C) configurations of the oceanic Fe input

•10-years time-slice simulations for preindustrial (1846-1855), the present day (2001-2010) and the end of the century (2091-2100) for the medium-high (e.g. RCP6.0) and the high (e.g. RCP8.5) forcing scenarios

# Current status of ODEON

- **Fe emissions**

Fe-dust emissions based on an updated iron mineralogy dataset on emissions (Perlwitz et al., 2015) for accumulation and coarse dust particles

Current model species: FeH\_aci, FeH\_coi, FeO\_aci, FeO\_coi, ILL\_aci, ILL\_coi, SME\_aci, SME\_coi, HEM\_aci, SME\_coi, Fep3\_acs, Fep3\_cos, Fep2\_acs, Fep2\_cos

Combustion Fe emissions (not yet fully implemented)

Current model species: FeC\_aai, FeC\_ais, FeC\_aci, FeC\_acs, FeC\_coi, FeC\_cos

- **Fe chemistry**

TM5-MP is coupled with a multiphase Fe-mobilization scheme in cloud droplets.

(wetS subroutine is now replaced with the (standalone) AQHEM module; aerosol water still under development for the global simulation)

New feature: KPP solver for aqueous phase chemistry is now implemented (with the contribution of Giorgos Fanourgakis from M. Kanakidou group)

- **To do...**

- **Finish aqueous-phase chemistry reactions budgets calculations (budrw)**
- **Thermodynamic calculations for both accumulation and coarse particles**
- **Model Fe evaluation**
- **Coupling the ECPL detailed gas-phase chemical scheme (?)**



**The End**



# Aqueous-phase Fe Chemical Scheme

Reactions	$K_{298}$ ( $M^{-n+1}s^{-1}$ )	Ea/R (K)	References
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + \cdot OH$	$5.24 \times 10^1$	5050	Kremer, 2003
$Fe^{2+} + O_2^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2$	$1.00 \times 10^7$	5050	Rush and Bielski, 1985
$Fe^{2+} + HO_2 + H^+ \rightarrow Fe^{3+} + H_2O_2$	$1.20 \times 10^6$	5050	Jayson et al., 1973b
$Fe^{2+} + OH \rightarrow Fe(OH)^{2+}$	$4.60 \times 10^8$	1100	Christensen and Sehested, 1981
$Fe^{2+} + NO_3 \rightarrow Fe^{3+} + NO_3^-$	$8.00 \times 10^6$		Pikaeu et al., 1974
$Fe^{2+} + NO_2 + H^+ \rightarrow Fe^{3+} + HONO$	$3.10 \times 10^4$		Epstein et al., 1982
$Fe^{2+} + O_3 (+ H_2O) \rightarrow Fe(OH)^{2+} + OH + O_2 (*)$	$8.20 \times 10^5$		Logager et al., 1992
$Fe^{3+} + hv (+ H_2O) \rightarrow Fe^{2+} + OH + H^+$	$6.41 \times 10^{-6}$		Benkelberg and Warneck, 1995
$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH$	$4.51 \times 10^{-3}$		Benkelberg and Warneck, 1995
$Fe(OH)_2^+ + hv \rightarrow Fe^{2+} + OH + \cdot OH$	$5.77 \times 10^{-3}$		Benkelberg et al., 1991
$Fe(OH)^{2+} + O_2^- \rightarrow Fe^{2+} + O_2 + \cdot OH$	$1.50 \times 10^8$		Rush and Bielski, 1985
$Fe(OH)^{2+} + HO_2 \rightarrow Fe^{2+} + O_2 + H_2O$	$1.30 \times 10^5$		Ziajka et al., 1994
$Fe^{3+} + SO_4^{2-} \rightarrow Fe(SO_4)^+$	$3.20 \times 10^3$		Jayson et al., 1973b
$Fe(SO_4)^+ \rightarrow Fe^{3+} + SO_4^{2-}$	$2.70 \times 10^1$		Jayson et al., 1973b
$Fe(SO_4)^+ + hv \rightarrow Fe^{2+} + SO_4^-$	$6.43 \times 10^{-3}$		Lin et al., 2014
$Fe^{3+} + C_2O_4^{2-} \rightarrow Fe(C_2O_4)^+$	$7.50 \times 10^6$		Lin et al., 2014
$Fe(C_2O_4)^+ \rightarrow Fe^{3+} + C_2O_4^{2-}$	$3.00 \times 10^{-3}$		Lin et al., 2014
$Fe(C_2O_4)^+ + C_2O_4^{2-} \rightarrow Fe(C_2O_4)_2^-$	$1.89 \times 10^4$		Lin et al., 2014
$Fe(C_2O_4)_2^- \rightarrow Fe(C_2O_4)^+ + C_2O_4^{2-}$	$3.30 \times 10^{-3}$		Lin et al., 2014
$Fe(C_2O_4)^+ + O_2^- \rightarrow Fe(C_2O_4) + O_2$	$1.00 \times 10^6$		Sedlak and Hoigne, 1993
$Fe(C_2O_4)^+ + HO_2 \rightarrow Fe(C_2O_4) + O_2 + H^+$	$1.20 \times 10^5$		Sedlak and Hoigne, 1993
$Fe(C_2O_4)_2^- + O_2^- \rightarrow Fe(C_2O_4)_2^{2-} + O_2$	$1.00 \times 10^6$		Sedlak and Hoigne, 1993
$Fe(C_2O_4)_2^- + HO_2 \rightarrow Fe(C_2O_4)_2^{2-} + O_2 + H^+$	$1.20 \times 10^5$		Sedlak and Hoigne, 1993
$Fe(C_2O_4) + H_2O_2 \rightarrow Fe(C_2O_4)^+ + OH + \cdot OH$	$5.24 \times 10^4$		Sedlak and Hoigne, 1993
$Fe(C_2O_4)_2^- + hv (+ O_2) \rightarrow Fe^{+2} + C_2O_4^{2-} + 2CO_2 + O_2^-$	$2.47 \times 10^{-2}$		Lin et al., 2014
<b>Equilibrium</b>	<b>Keq (mol kg<sup>-1</sup>)</b>		<b>References</b>
$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$	$1.10 \times 10^{-4}$		Ervens et al., 2003
$Fe(OH)^{2+} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$	$1.40 \times 10^{-7}$		Ervens et al., 2003

(\*) For simplicity  $FeO^{2+}$  formation is neglected and formation of  $Fe(OH)^{2+}$  is here considered.