Dust iron solubility, ocean side:
A question of timescales?

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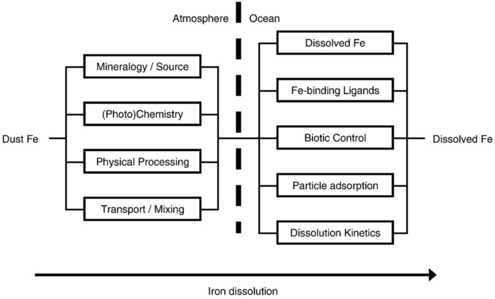
Dust workshop
Telluride, 31 June 2018

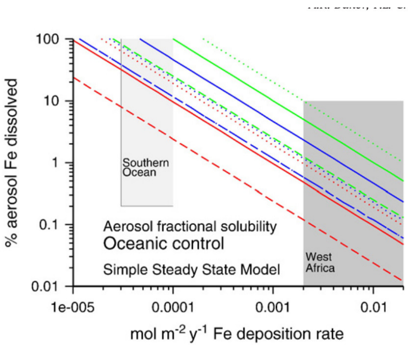
ATMOSPHERIC AND OCEANIC CONTROLS



(Baker and Croot, 2010)

conceptual model for processes affecting solubility of dust-deposited iron

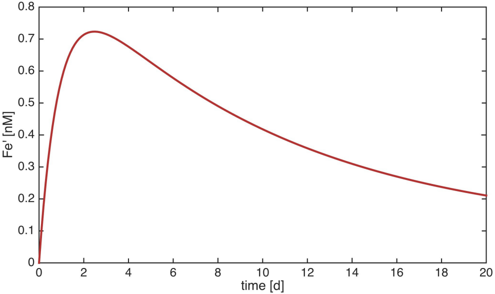
STEADY STATE SOLUBILITY FOR DIFFERENT RESIDENCE TIMES



(Baker and Croot, 2010)

predictions of solubility assuming a constant product (residence time * mixed layer depth) for different processes determining solubilization

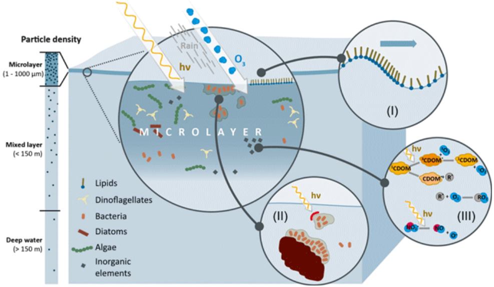
WHAT CAN KINETICS DO?



idealized model for release of iron from dissolvalble dust:
fast release, followed by a small reversible loss to particle surfaces
predicts intial rise of dFe above final equilibrium

but is that final equilibrium ever reached?
depends (amongst others) on the residence time of particles in the surface mixed layer!
aim of the talk: what can we say about timescales from a bit of modelling/calculations?

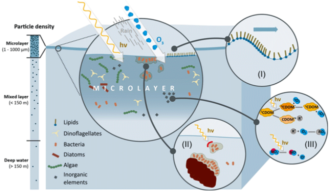
THE FIRST OCEANIC LAYER



(Wurl et al, 2017)

yes, the microlayer is a region of extremes:
high concentration of organics, strong UV radiation,...
but: how long do particles stay there?

RESIDENCE TIME IN THE μLAYER



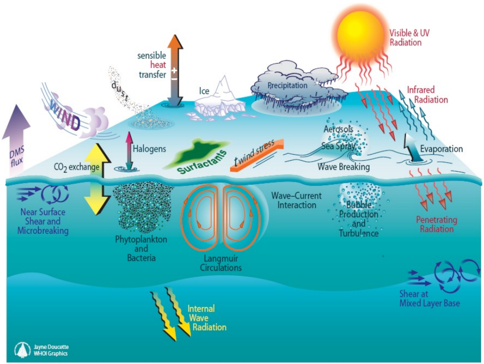
(Wurl et al, 2017)

How long do particles stay within the μlayer?

Residence time estimates:
Chester (2003): 1-15 hours
Ebling and Landing (2017): 1-4 minutes after dust deposition event

has to be seen in relation to timescales for (organic-assisted) dissolution; but seems short

BELOW THE μLAYER: THE MIXED LAYER

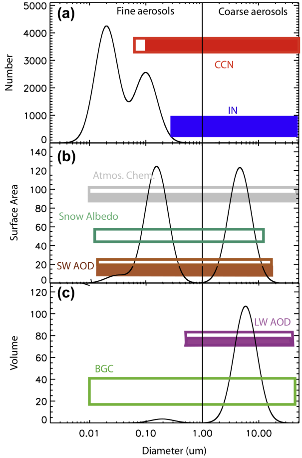


(Jayne Doucette, WHOI)

mixed by shear-induced turbulence and internal wave breaking on time-scales of a day or so (Denman and Gargett, 1983)

species with longer timescales (e.g. particle concentrations) get homogenized
species with short life-times (photochemical species, e.g. O_2^-) have gradients within ML

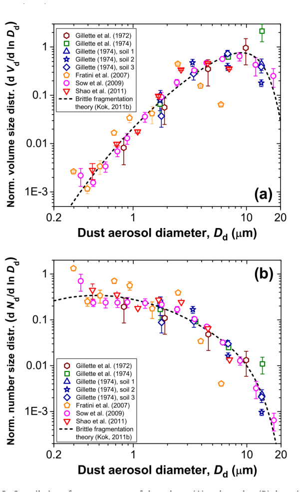
RESIDENCE TIME OF PARTICLES: SIZE DISTRIBUTION



(Mahowald et al, 2013)

For a typical 3-modal dust size-distribution
surface area is both detemined by a fine and a coarse mode
mass is determined by the coarse mode

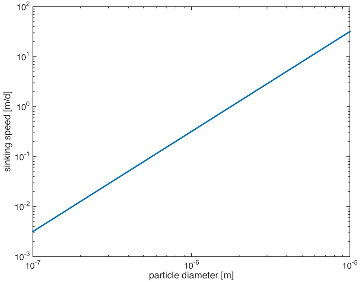
RESIDENCE TIME OF PARTICLES: SIZE DISTRIBUTION



(Mahowald et al, 2013)

For a typical 3-modal dust size-distribution
surface area is both detemined by a fine and a coarse mode
mass is determined by the coarse mode

RESIDENCE TIME OF PARTICLES: STOKES LAW



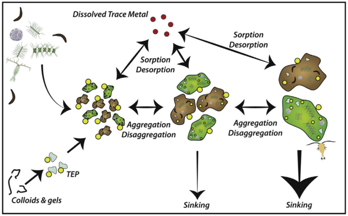
sinking speed of spherical quartz particles, calculated from $v = \frac{2}{9}\frac{r^2 g \Delta\rho}{\eta}$

sinking speed of fine-mode particles: < 0.1 m/d
sinking speed of coarse mode particles (3 μm): ≈ 2 m/d

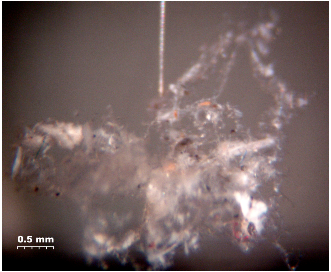
at these speeds, residence time in ML would be months

but: particles aggregate, increasing their sinking rate!

PARTICLE DYNAMICS



aggregation processes (Jackson and Burd 2015)



typical marine aggregate (Iversen, pers. comm.)

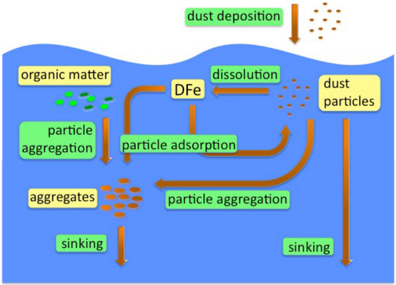
dust brings in mostly μmeter-sized particles

these hardly sink on their own

sinking dominated by larger, mixed organic/inorganic aggregates

MODEL SETUP

global biogeochemical model REcoM including the iron cycle (Hauck et al. 2013, Völker and Tagliabue 2015)



added model for lithogenic particles with two size classes (fine dust and faster-sinking aggregates)

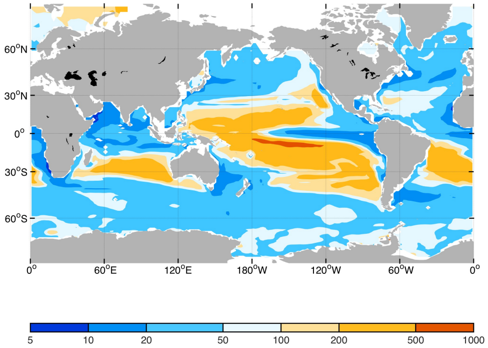
quadratic aggregation and linear disaggregation of particles

lithogenic particles included as additional scavenging agents for dissolved iron

scavenging proportional to particle concentration

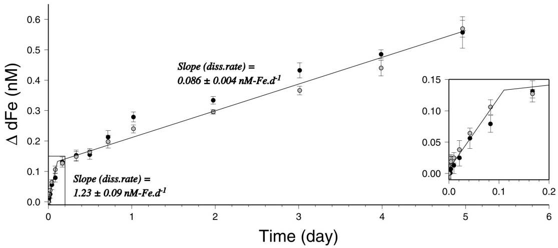
rate equal for organic and lithogenic particles

RESIDENCE TIME OF PARTICLES: MODEL RESULTS



average residence time of lithogenic particles (days) in upper 100m, calculated from model taking aggregation into account

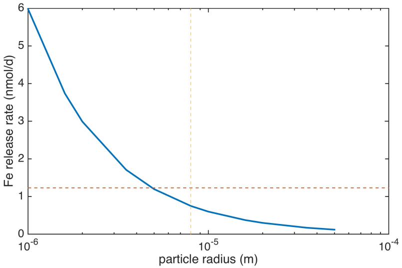
DUST FE DISSOLUTION KINETICS



(Wagener et al, 2008)

• linear increase of DFe with two different slopes; two different pools? • but time-scale short compared to sinking loss • increase in dFe covaries with ligand/DOC concentrations in seawater, in contrast to Fishwick et al. 2014 • Wagener: linear increase insufficient for a mechanistic description. is that so?

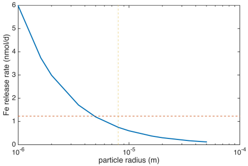
CAN WE UNDERSTAND WAGENER ET AL. RATES?



calculated release rate $R = k_d \cdot sa \cdot c_p$

- FeOOH dissolution rate in medium at pH=8 in presence of DFOB (Akafia et al. 2014): $k_d = 1.2 \cdot 10^{-11}$ mol Fe m^{-2} s^{-1}
- estimate specific surface area *sa* (in m^2 kg^{-1} from equivalent spherical particle radius
- particle concentration in Wagener et al. (2008): $c_p = 5$ mg L^{-1}

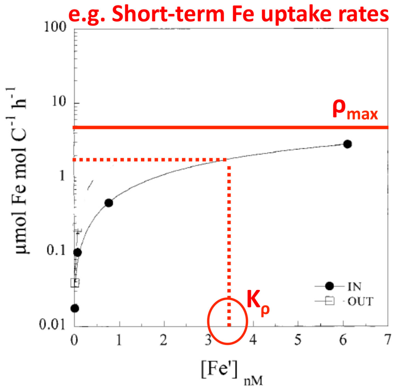
CAN WE UNDERSTAND WAGENER ET AL. RATES II?



measured fast release ≈ calculated release, assuming that dissolved phase is fresh FeOOH and that ligands are present in excess

if the dust particles have an FeOOH coating that is first dissolved, then one would expect a linear release of Fe, until the coating is gone

SHORT-TERM UPTAKE VS. GROWTH



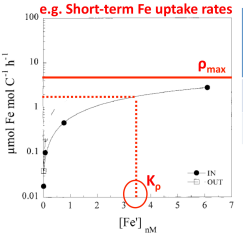
(from a talk by M. Maldonado, 2017)

distinguish between growth and short-term iron uptake

both follow Michaelis-Menten kinetics wrt. Fe, i.e.
$\mu = \frac{\mu_{max} Fe}{Fe + K_\mu}$ and $\rho = \frac{\rho_{max} Fe}{Fe + K_\rho}$
but $K_\rho \approx 3\text{nM} \gg K_\mu < 0.05\text{nM}$

implies that iron input may not directly lead to a strong reaction in cell numbers, but nevertheless will lead to an immediate increase in Fe uptake

TIME-SCALE FOR SHORT-TERM UPTAKE



uptake is described by

$$\frac{d}{dt}Fe = -\rho \cdot B$$

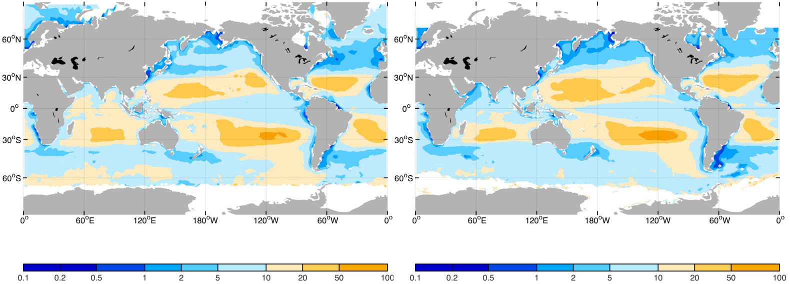
where B is phytoplankton biomass (mol C m^{-3}) and ρ is the short-term uptake rate (μmol Fe (mol C)$^{-1}$ h^{-1})

Inserting

$$\frac{d}{dt}Fe = -\rho_{max}\frac{Fe}{Fe + K_\rho} \cdot B \approx \frac{-\rho_{max}B}{K_\rho}Fe$$

we obtain an e-folding time-scale for uptake of $\tau_{up} = K_\rho/(\rho_{max}B)$

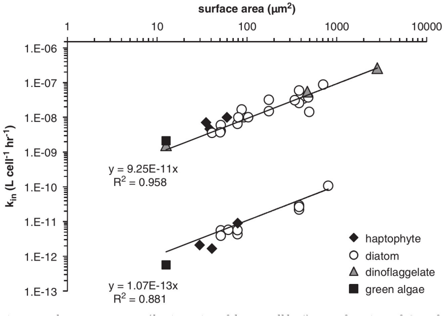
ESTIMATING UPTAKE TIME-SCALE



$\tau_{up} = K_\rho/(\rho_{max}B)$ (d^{-1}) in april and october

- estimate biomass from satellite Chl, using a C:Chl ratio of 60 mol/mol
- use 'typical' values $\rho_{max} = 4\,\mu$molFe molC$^{-1}h^{-1}$ and $K_\rho = 3\,\mu$molFe m^{-3}

MAXIMUM UPTAKE RATES FOR DIFFERENT SPECIES

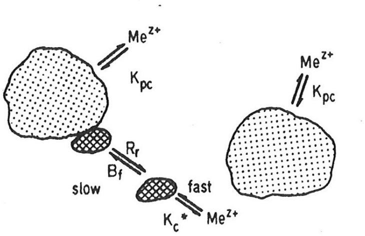


(Lis et al, 2014)

what determines maximum uptake rates?

uptake rates per cell scale predictably with cellular surface area
uptake rates for inorganic Fe 3 orders of magnitude higher than for organically complexed Fe

SCAVENGING: A COMPLEX PROCESS PARAMETERIZED SIMPLY



(Honeyman & Santschi 1989)

conceptually, scavenging occurs mostly through a colloidal intermediate, the 'colloidal pumping mechanism'

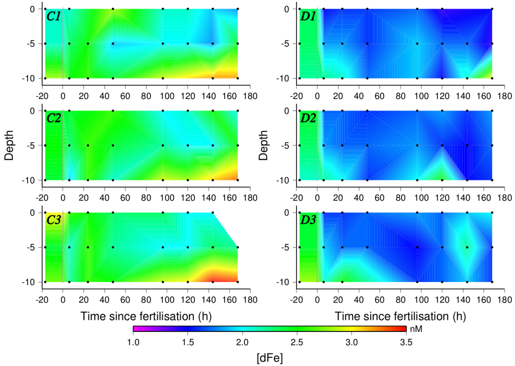
but models usually do not distinguish between soluble/colloidal Fe

first parameterization of scavenging: a constant lifetime $\approx$ 200 yrs.

only later, formulations were made dependent on (biogenic) particle concentrations, dust mostly ignored

almost every model has a different formulation of scavenging!

DUST ALSO SCAVENGES DISSOLVED IRON

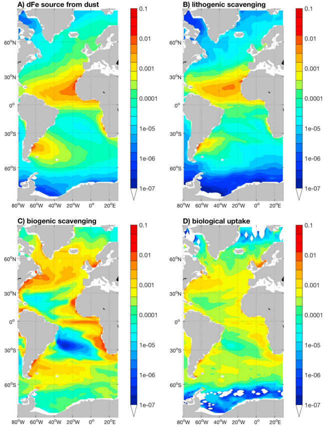


(Wagener et al. 2010)

dissolved iron decreases after dust addition in mesocosms;
dust can act as dFe sink

is that important in the open ocean, where often biogenic particles dominate?
needs understanding & modelling of particle dynamics!

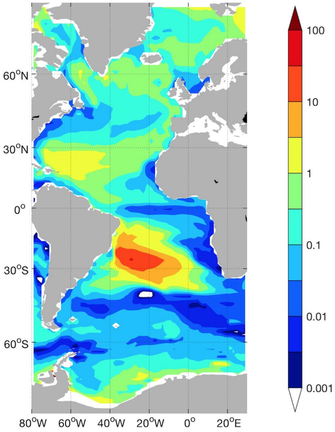
MODELED SOURCES/SINKS OF DFE



sources and sinks of dissolved Fe from Ye and Völker, 2017

under the Saharan dust plume, dust scavenging similar to dust release (assumes constant solubility, though)
in the deep ocean, lithogenic particles act as scavengers

COMBINED RESIDENCE TIME OF DFE



- residence time (stock/total loss rate in years) of dissolved iron varies by several orders of magnitude
- affected by scavenging on dust/biological particles and biological uptake
- distribution of residence time agrees quite well with data-based estimates (Usher et al. 2013)

HOWEVER:

Table 2. A Summary of the Magnitude of the Fe Sources, the Total and Average Fe Inventories, and the Residence Time of Fe Across the FeMIP Models

	Fe Sources (Gmol yr^{-1})							
Model	Dust	Sediment	Hydrothermal	Rivers	Total	Fe Inventory (×10^{11} mol)	Average Fe (nmoles L^{-1})	Residence Time (years)
BEC	21.9	84.6	17.7	0.34	124.5	10.1	0.74	8.1
BFM	1.4	0	0	0.06	1.4	8.8	0.65	626.3
BLING	3.3	9.1	0	0	12.4	5.3	0.37	42.4
COBALT	32.5	155	0	0	182.5	6.8	0.50	3.7
GENIE	1.8	0	0	0	1.8	10.1	0.48	560.0
MEDUSA1	2.7	0	0	0	2.7	6.3	0.46	232.0
MEDUSA2	3.4	2.9	0	0	6.8	4.8	0.35	69.9
MITecco	3.5	104	0	0	107.5	8.8	0.65	8.2
MITigsm	1.4	194	0	0	195.4	9.0	0.66	4.6
PISCES1	32.7	26.6	11.3	2.5	71.0	8.1	0.59	11.5
PISCES2	32.7	26.6	11.3	2.5	71.0	11.2	0.81	15.7
REcoM	3.7	0.6	0	0	4.3	12.5	0.73	291.6
TOPAZ	13.8	74.8	0	0	88.6	6.8	0.50	7.6
				Mean	66.9	8.3	0.58	144.7
				Standard deviation	67.1	2.2	0.14	175.8

different biogeochemical models for Fe have orders of magnitude different Fe sources
nevertheless, mean dFe concentrations are similar
why? because scavenging is used for tuning

questions predictive capability of models for other climate states
→ progress in the description of scavenging is badly needed!

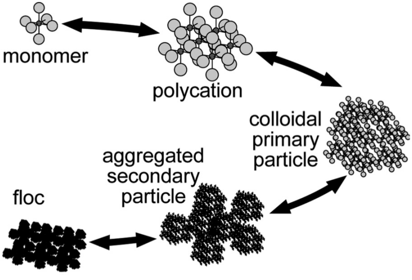
KINETIC DESCRIPTION OF THE BASIC PROCESSES

precipitation of Fe can be described as a three step process:
nucleation → crystal growth → formation of sinking flocs

kinetic measurements (Rose and Waite, 2003, Pham et al, 2006, Rose and Waite, 2007): rate law for loss of $Fe(OH)_3$ monomers:

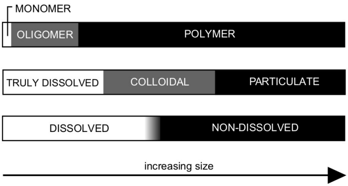
$$\frac{d}{dt}\mathrm{Fe}' = -k_f \cdot \mathrm{Fe}' \cdot \mathrm{Fe_T}$$

with $k_f \approx 2 \cdot 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$
→ timescale for loss after 1 nM addition of Fe: 50 s!



(Rose, 2013)

TWO BUTS:



(Rose and Waite, 2007)

but I: still a disconnect between the different process descriptions: rate law for loss of $Fe(OH)_3$ monomers:

$$\frac{d}{dt}\mathrm{Fe}' = -k_f \cdot \mathrm{Fe}' \cdot \mathrm{Fe}_\mathrm{T}$$

only describes the very first step
can we use scaling arguments to go to a set of soluble/colloidal formation rate laws, a la Smoluchovsky?
but II: what to do with organic colloids, etc?

SOME CONCLUSIONS

- models start to resolve lithogenic particle residence times
- both aggregation and disaggregation important
- iron release: not hopeless to bridge measurements with fundamental understanding; also measure surface properties!
- biological uptake timescales comparable to particle residence times
- some progress in the description of scavenging, but urgent need for more process description, keeping models honest