Prognostic modelling of iron-binding ligands
– what are the processes driving the ligand cycle?

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Why prognostic?

- after realising the importance of organic complexation, the global iron models started with constant ligand concentrations;

- this does not agree with the observations of ligands (Fig. 1) and leads to the distortion of the iron picture (Fig. 2)

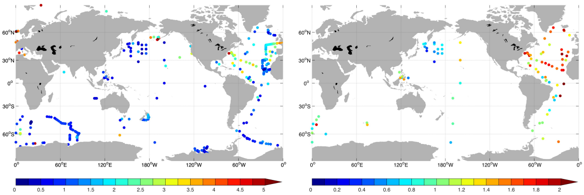

Fig.1 Measured ligands (nM) in the upper 50 meters and below 1000 meters.

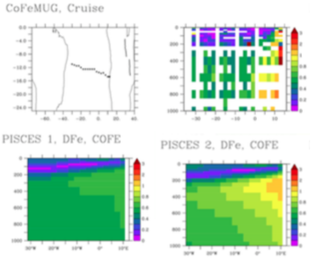

Fig.2 CoFeMUG (Tagliabue et al., 2015)

Why two ligands?

Measurements

two or more ligand classes often measured with different conditional stability constants as well as biological and chemical properties:

- one produced by degradation in the deep ocean, more refractory;
- another one in the surface by bacteria, more labile

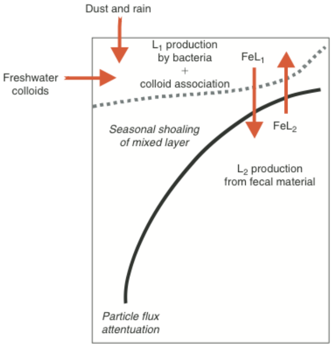

Fig. 3 The idealised ligand cycle (Hunter and Boyd, 2007).

Why two ligands?

Model with one variable ligand

Deep ocean: a long life time of ligand needed

Surface ocean: fast sink processes needed

- even considering a temperature dependence of microbial degradation, we need high photodegradation rates, leading to an unrealistic distribution pattern (Fig. 4)

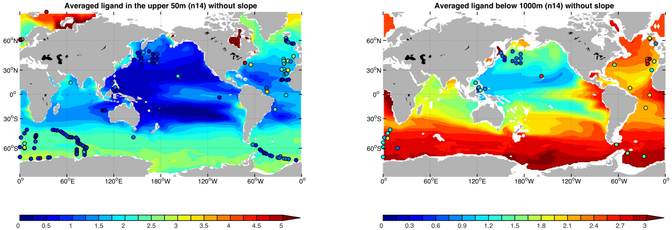

Fig. 4 Ligand distribution (nM) in the upper 50 m and below 1000 m (1L run).

→ separating the sources and sinks for two different ligands might be a more reasonable description of the ligand cycle

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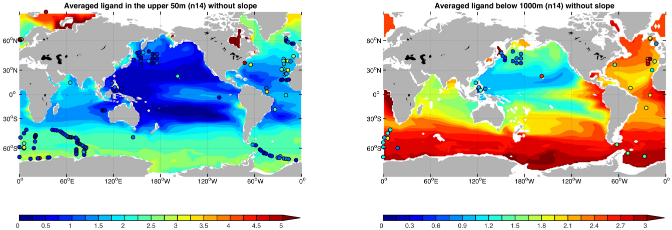


Averaged ligand in the upper 50m (n14) without slope

Averaged ligand below 1000m (n14) without slope

Fig. 4 Ligand distribution (nM) in the upper 50 m and below 1000 m (1L run).

→ separating the sources and sinks for two different ligands might be a more reasonable description of the ligand cycle

A prognostic model with two ligands

Weak ligand (L2)

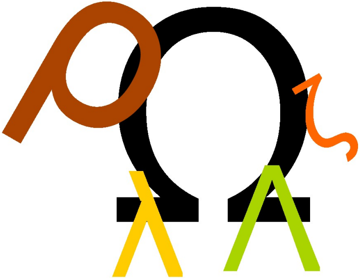
+ POC degradation a_2
+ photochemical destruction of L1 κ_1
- microbial degradation $1/\tau_2$
- photochemical destruction κ_2
- colloidal aggregation p

Strong ligand (L1)

+ DOC excretion by PHY and ZOO a_1
- microbial degradation $1/\tau_1$
- photochemical destruction κ_1
- colloidal aggregation p

$$\begin{aligned}
\frac{\partial}{\partial t} L_2 + \mathbf{U} \cdot \nabla L_2 &= a_2\, rD + \kappa_1 I(z,t) L_1 - 1/\tau_2\, L_2 - \kappa_2 I(z,t) L_2 - p\gamma L_2 \\
\frac{\partial}{\partial t} L_1 + \mathbf{U} \cdot \nabla L_1 &= a_1\, E_{DOC} - 1/\tau_1\, L_1 - \kappa_1 I(z,t) L_1 - p\gamma L_1
\end{aligned}$$

Help!



a model elephant

“With five parameters, we can build an elephant” — Dirk Olbers

Can we infer some parameter values from lab studies or in situ observations?

the ligand:carbon ratio

- Wagener et al. (2008): ligand:DOC correlation in the mediterranean surface waters: $\approx 10^{-4}$ mol mol^{-1}
- Schlosser and Croot (2009): ligand:PO_4 correlation below the mixed layer in the Mauritanian upwelling: $\approx 10^{-3}$ mol mol^{-1}
- Kuma et al. (1998): ligand:PO_4 correlation but in the deep North Pacific, with a 10-fold smaller slope: $\approx 10^{-4}$ mol mol^{-1}
- Boyd et al. (2010): ligand:Fe increase ratio in POC incubation: ≈ 3 mol mol^{-1}

→ Using Redfield ratios C:N:P:Fe, this translates into a ligand:C range: $10^{-6} \sim 10^{-4}$ mol mol^{-1}, but more likely $10^{-5} \sim 10^{-4}$ mol mol^{-1}: lower values (Kuma et al., 1998) probably biased by ligand degradation in 'old' waters

the ligand degradation time-scale below 100 m

- total POC export over 100 m $\approx$ 10 PgC yr^{-1}, most of that remineralized in water column
- assume a ligand:carbon ratio of 10^{-5} mol mol^{-1}
- estimate the average ligand concentration in the deep ocean: 1 nM

Assuming that all ligands produced below 100 m are remineralized there, we arrive at an average life-time of ligands of 200 yr (and shorter if the ligand:carbon ratio is higher)

Do we have similar estimates for the photochemical degradation of ligands? For the fate of ligands when the ligand-bound iron is taken up?

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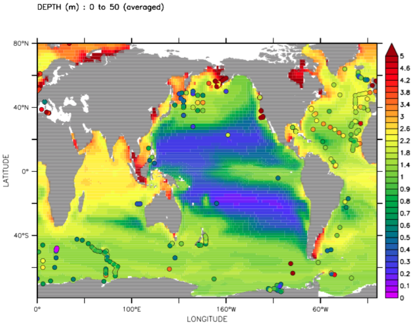
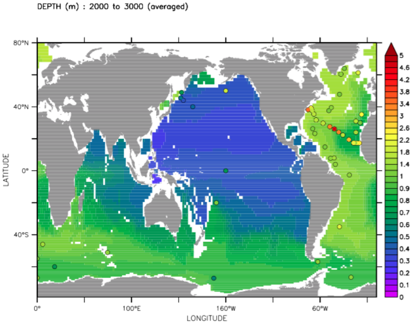
Modelled ligand shows significant variability



DEPTH (m) : 0 to 50 (averaged)

Ligand (nM)



DEPTH (m) : 2000 to 3000 (averaged)

Ligand (nM)

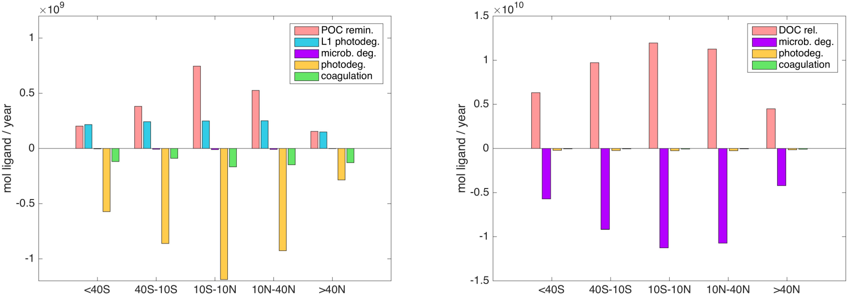
surface ocean $>$ 1 nM in the most parts of the global ocean, exceptions in the subtropical gyres; Indian Ocean $>$ Atlantic $>$ Southern Ocean $>$ Pacific;

deep ocean: controlled by lateral advection, $<$ 1 nM in the Pacific and a part of the Indian Ocean

bias and rms [L] = 1 nM: -0.8 and 3.4 nM; 2 variable ligands: -0.4 and 1.5 nM

What drives the modelled ligand distribution?

Pacific Ocean as example:



Modelled ligand dynamics integrated for the upper 100 meters

L2 dominant sink is photodegradation; similar strength of POC rem. and photodegr. of L1 in the high latitudes (L1 is more sensitive to photochemical destruction)

L1 dominant sink is microb. degradation; faster cycled than L2

Is this the reality?

- Results of this kind of analysis depend strongly on our assumptions on parameters.
- We can have more confidence by inferring them from laboratory or in situ studies.
- Model is a good tool to test the impact of the rate constants determined in experiments on the global ligand cycle and further on the iron cycle.

More measurements planned? And thank you!

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