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

OSM 2016, New Orleans

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24 Feb 2016
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)
Modelling of iron-binding ligands

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).](image)

→ 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](image1)

![Averaged ligand below 1000m (n14) without slope](image2)

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Fig. 4 Ligand distribution (nM) in the upper 50 m and below 1000 m (1L run).
A prognostic model with two ligands

Weak ligand (L2)
+ POC degradation $a_2$
+ photochemical destruction of L1 $\kappa_1$
  - microbial degradation $1/\tau_2$
  - photochemical destruction $\kappa_2$
  - colloidal aggregation $p$

Strong ligand (L1)
+ DOC excretion by PHY and ZOO $a_1$
  - microbial degradation $1/\tau_1$
  - photochemical destruction $\kappa_1$
  - colloidal aggregation $p$

\[
\frac{\partial}{\partial t} L_2 + U \cdot \nabla L_2 = a_2 rD + \kappa_1 I(z, t)L_1 - 1/\tau_2 L_2 - \kappa_2 I(z, t)L_2 - p\gamma L_2
\]

\[
\frac{\partial}{\partial t} L_1 + U \cdot \nabla L_1 = a_1 E_{DOC} - 1/\tau_1 L_1 - \kappa_1 I(z, t)L_1 - p\gamma L_1
\]
“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: $\approx 3$ 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?
Modelling of iron-binding ligands

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Modelled ligand shows significant variability

- **Surface ocean**: $> 1 \text{ nM}$ 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, $< 1 \text{ nM}$ in the Pacific and a part of the Indian Ocean

**Bias and rms** $[L] = 1 \text{ nM}$: -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
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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