

Representation of organic complexation in biogeochemical models and its effect on the cycling of iron



or: from fudge factor towards
mechanistic understanding

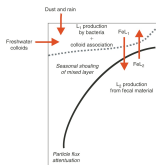


Fig. 5. Microbial cycle for ligands L_1 and L_2 in the ocean.

Christoph Völker¹, Alessandro Tagliabue²

¹Alfred Wegener Institute for Polar and Marine Research

²University of Liverpool

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A DISAPPOINTMENT

unlike speciation modellers, global biogeochemical modellers are not interested in ligands *per se*, their properties, intricacies of titrations etc. at all..

instead they are interested in ligands as a means to get the iron cycle right, i.e. to limit unrealistic scavenging of iron

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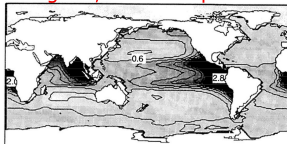
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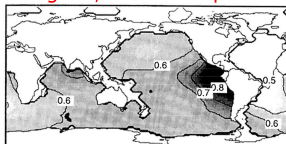
this begins already with the first global model of the iron cycle, Archer & Johnson (2000).

ARCHER & JOHNSON (2000)

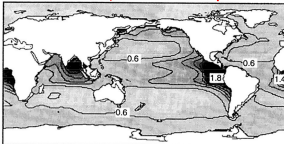
a no ligand, 350 m depth



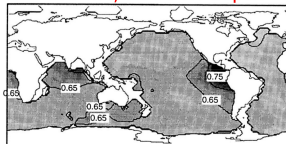
b no ligand, 2500 m depth



c L = 0.6 nM, 350 m depth

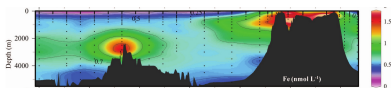


d L = 0.6 nM, 2500 m depth

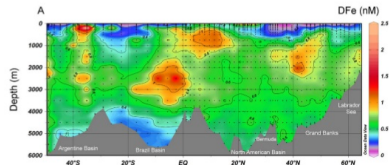


- only iron source: dust deposition
 - scavenging = Fe' / τ
 - no ligand case: $\tau = 650$ years
 - ligand = 0.6 nM case: $\tau = 100$ years
- conclusion back then: ligands prevent unrealistic inter-basin gradient

ALONG CAME GEOTRACES



iron concentration across the South Atlantic (Noble et al., 2012)



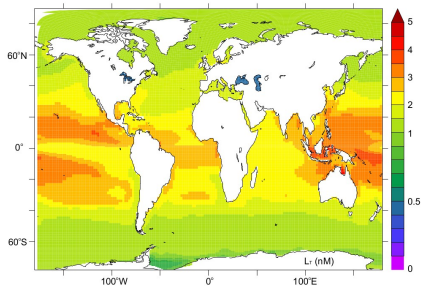
iron concentration along a section through the Western Atlantic (Rijkenberg et al., 2014)

some insights since 2000:

- deep iron distribution less homogenous than thought before
 - often maximum in oxygen minimum zones
 - sediments and hydrothermalism are important iron sources
- these features are not reproduced well with constant ligand concentration

but still, the assumption of a constant ligand concentration is made in almost all global biogeochemical models

LINKING L TO DOC: TAGLIABUE & VÖLKER (2011)



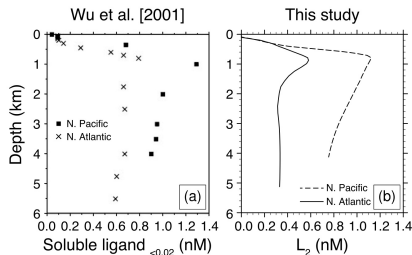
Ligands at 100 m depth, calculated from DOC following Wagener et al. (2008)

motivation: Wagener et al. (2008): correlation between L and DOC in mediterranean waters

model assumptions:

- $DOC = DOC_{refr}$ (prescribed, 40 nM) + DOC_{sl} (modelled)
- $L_1 = DOC_{sl} \cdot 0.06$
- $L_2 = 0.4 \text{ nM} + DOC_{sl} \cdot 0.03$

LINKING L TO AOU: MISUMI & AL. (2013)



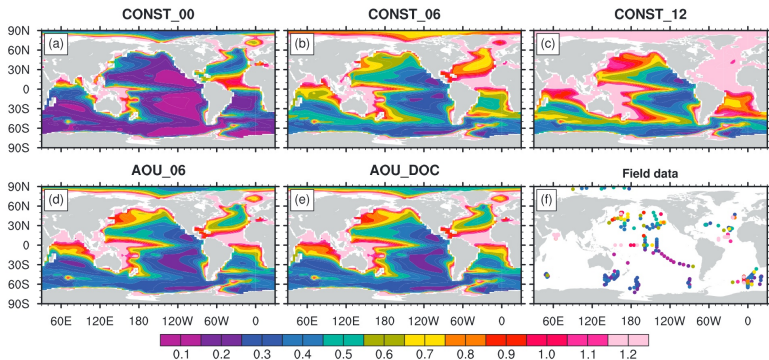
soluble ligands from Wu et al. (2000), and from assuming a linear relationship with AOU

motivation: Wu et al. 2000:
ligands are elevated in oxygen minimum zones

model assumption:

- $L_2 = \alpha + \beta \cdot \text{AOU}$
- several combinations of α and β tested
- DOC taken from climatology, not from the model
- one run combining their AOU and our DOC dependency

LINKING L TO AOU: MISUMI & AL. (2013)

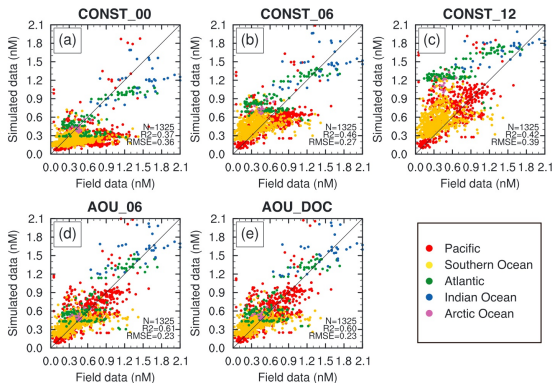


modelled dFe between 200 m and 1000 m depth

model was mainly evaluated by comparing modeled with observed Fe; no real ligand validation

→ keep on measuring ligands! we need a larger database

LINKING L TO AOU: MISUMI & AL. (2013)



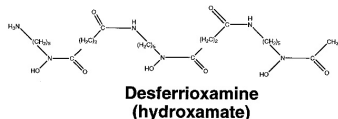
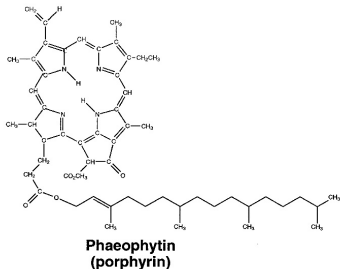
observed vs. modelled dFe below 200 m

best fit to dFe observations by making L dependent on both AOU and DOC

but: not a causal relation, can we trust it for other climate states?

→ we need a prognostic model for ligands!

WHERE DO FE-BINDING LIGANDS COME FROM? WHAT IS THEIR FATE?



Witter et al., 2000

two main types of ligands proposed: degradation products, such as porphyrins, and siderophores, produced by bacteria under iron limitation

production / degradation pathways probably as varied as ligand origins

IDEALIZED LIGAND MODEL

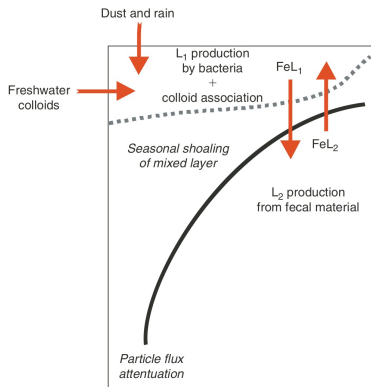
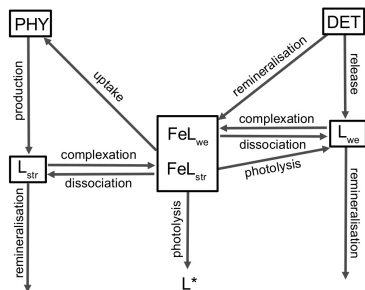


Fig. 5. Idealised cycle for ligands L_1 and L_2 in the ocean.

summarized by Hunter and Boyd 2007 as a simple model for iron-binding ligands:

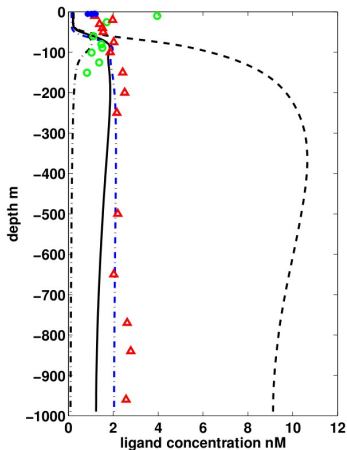
two classes of ligands, one produced by degradation in the deep ocean, more refractory, another one in the surface by bacteria, more labile

PROGNOSTIC MODELLING: YE ET AL. (2009)



Ye et al., 2009

ligand sources: remineralization,
DOC production
ligand sinks: bacterial &
photochemical degradation, iron
uptake



but: local study in NE tropical
Atlantic only

A SLIGHTLY SIMPLER MODEL, BUT GLOBAL

only one ligand

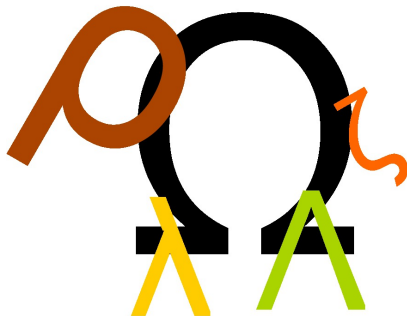
two sources: POC degradation + DOC excretion by phytoplankton and zooplankton

four sinks: bacterial degradation (with nonconstant time-scale τ) + photochemical destruction + iron uptake + colloidal aggregation

$$\frac{\partial}{\partial t}L + \mathbf{U} \cdot \nabla L = a(E_{DON} + rD) - 1/\tau L - \kappa I(z, t)L - \begin{cases} \alpha U_{Fe} & \text{if } L > 0 \\ 0 & \text{if } L \leq 0 \end{cases} - p\gamma L$$

several unknown parameters: **ligand:carbon ratio in fresh DOC** a , **bacterial degradation timescale** τ **photochemical destruction rate** κ , **fraction of ligand destroyed in iron uptake** α , **colloidal fraction of ligand** p

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?

LIGAND:CARBON RATIO

- Wagener et al. (2008): ligand:DOC correlation in mediterranean surface waters: ligand:DOC $\approx 10^{-4}$ mol mol⁻¹
- Schlosser and Croot (2009): ligand:PO₄ correlation below mixed layer in mauritanian upwelling: ligand:PO₄ $\approx 10^{-3}$ mol mol⁻¹
- Kuma et al. (1998) similar ligand:PO₄ correlation, but in deep North Pacific, with 10-fold smaller slope: ligand:PO₄ $\approx 10^{-4}$ mol mol⁻¹
- Boyd et al. (2010): Ligand:Fe increase rate in POC incubation ≈ 3 mol mol⁻¹

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

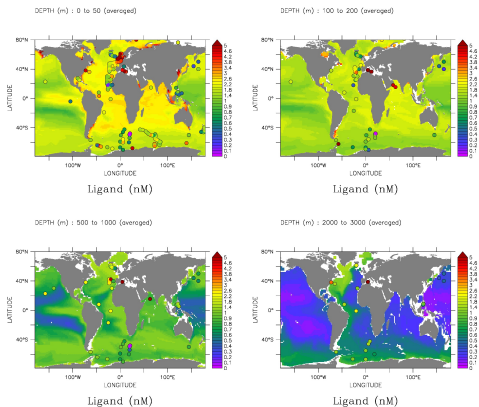
LIGAND DEGRADATION TIME-SCALE BELOW 100 M

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

Assuming that all ligands produced below 100 m are 'eaten' 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 ligand-bound iron is taken up?

THE RESULTING LIGAND DISTRIBUTION



Völker and Tagliabue, 2014

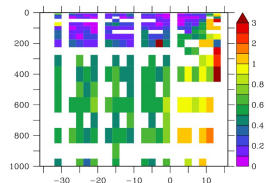
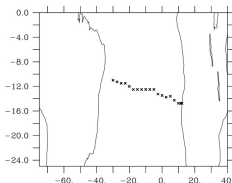
some assumptions made:
 “ligand continuum”: some fractions of ligand degraded much faster than other fractions
 higher degradation rate when concentration of ligand is high
 a fraction of the ligand aggregates with sinking particles

comparison with data:
 bias = -0.1 nM, RMSE = 1.4 nM

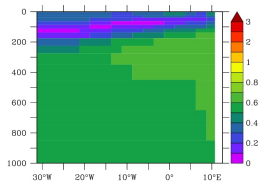
THE EFFECT ON MODELED IRON

CoFeMUG, Cruise

I

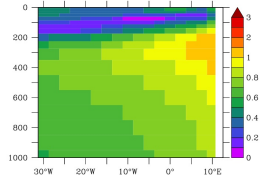


PISCES 1, DFe, COFE



PISCES 2, DFe, COFE

I



dFe along the CoFeMUG cruise; lower left constant ligands; lower right variable ligands

SOME CONCLUSIONS

- a model for global ligand distribution based on conceptual understanding
- still some ad-hoc parameterizations that mask lack of knowledge on processes, such as the “ligand continuum” approach
- some ligand sources missing: rivers, sediments, hydrothermal?
- comparison to ligand data base o.k., room for improvement; larger data base will help
- improvements in the description of the iron distribution; but re-assessment of iron loss processes needed (→ Phil’s talk)
- more sensitivity studies needed! (→ Ying’s talk!)