Sensitivity of the iron cycle to cycling of organic ligands in a 3D biogeochemical model

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Surface Ocean Processes in the Anthropocene

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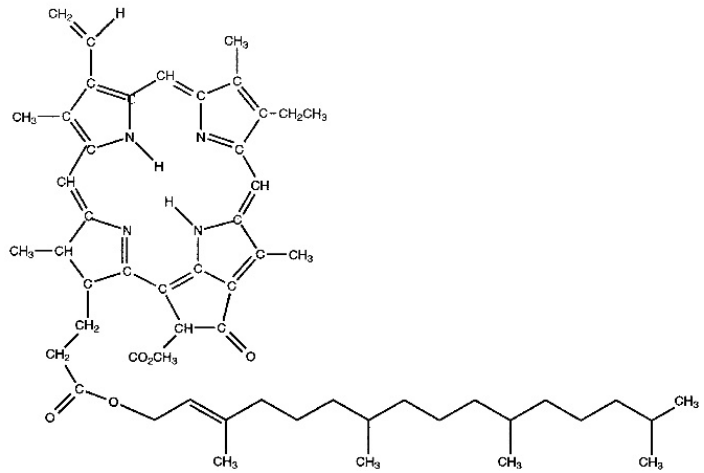
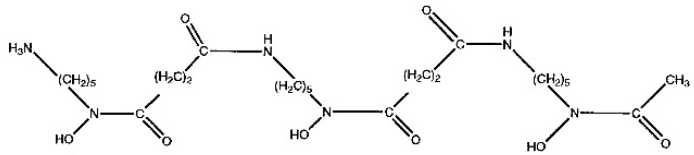
WHERE DO FE-BINDING LIGANDS COME FROM? WHAT IS THEIR FATE?



Phaeophytin (porphyrin)



Desferrioxamine (hydroxamate)

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

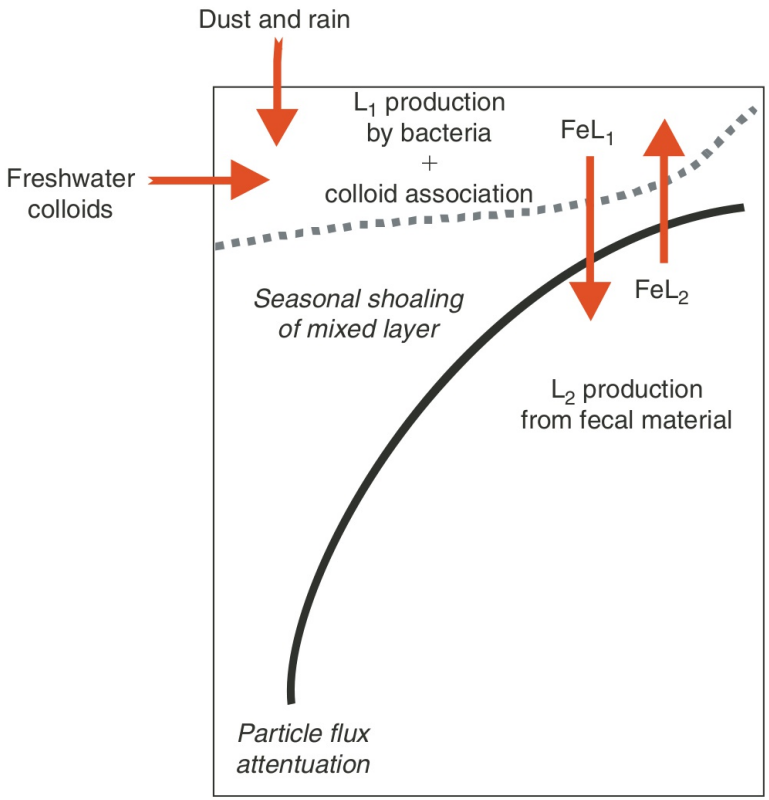


Fig. 5. Idealised cycle for ligands L_1 and L_2 in the ocean.

Hunter and Boyd, 2007

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

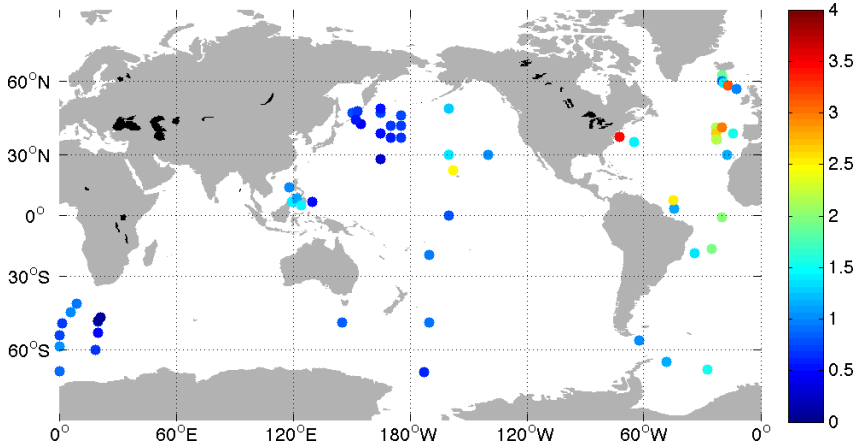
two classes of ligands, one produced by degradation in the deep ocean, more refractory, another one in the surface by bacteria, more labile

Is this model able to reproduce observations?

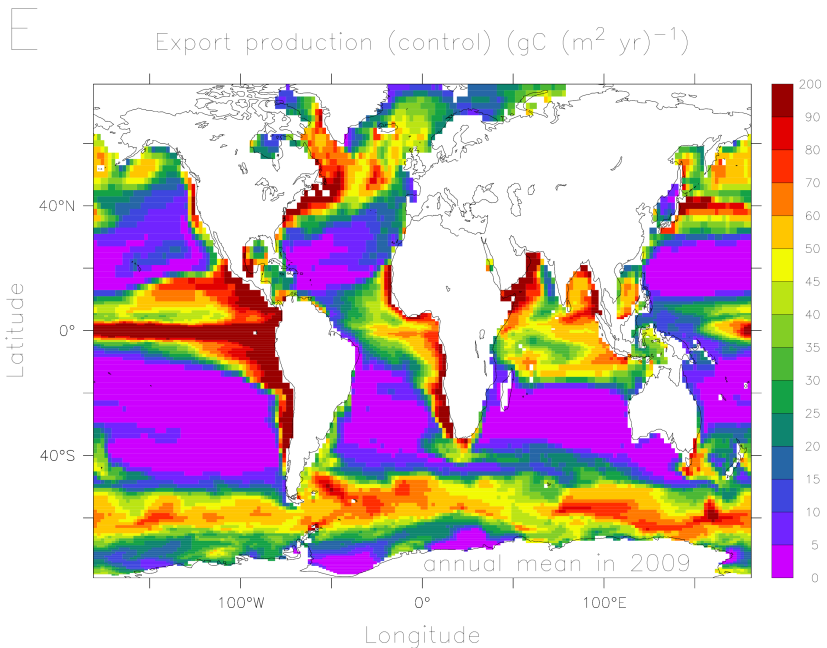
LIGANDS MATTER

- models so far use constant background ligand to prevent excessive scavenging loss
- typically assumed to be in the L1 class and present at 0.6 nM
- doubling or halving of this constant ligand $\rightarrow \approx 5$ ppm $p\mathrm{CO}_2$ changes, same as glacial/interglacial dust change (Tagliabue et al. 2014)
- models have problems with some features in the iron distribution, especially too low Fe at the depth of the AOU maximum
- connection to the assumption of constant ligands, i.e. do models overestimate scavenging at this depth?
- on the other hand: assumption of relatively low Lig may result in an underestimation of the scavenging rate for Fe

THIS IS WHAT WE DO:



ligand observations below 1000m depth



export production from model

1) compile total ligand observations
regardless of the method,
electrochemistry vs. solubility,
analytical window
other ways of aggregating data?
only free ligand?

2) make assumptions on ligand origin and fate
use global biogeochemical model to calculate ligand distributions
compare this to the available ligand distributions

THE SIMPLEST SET OF ASSUMPTIONS

source: remineralization of sinking detritus
sink: bacterial degradation

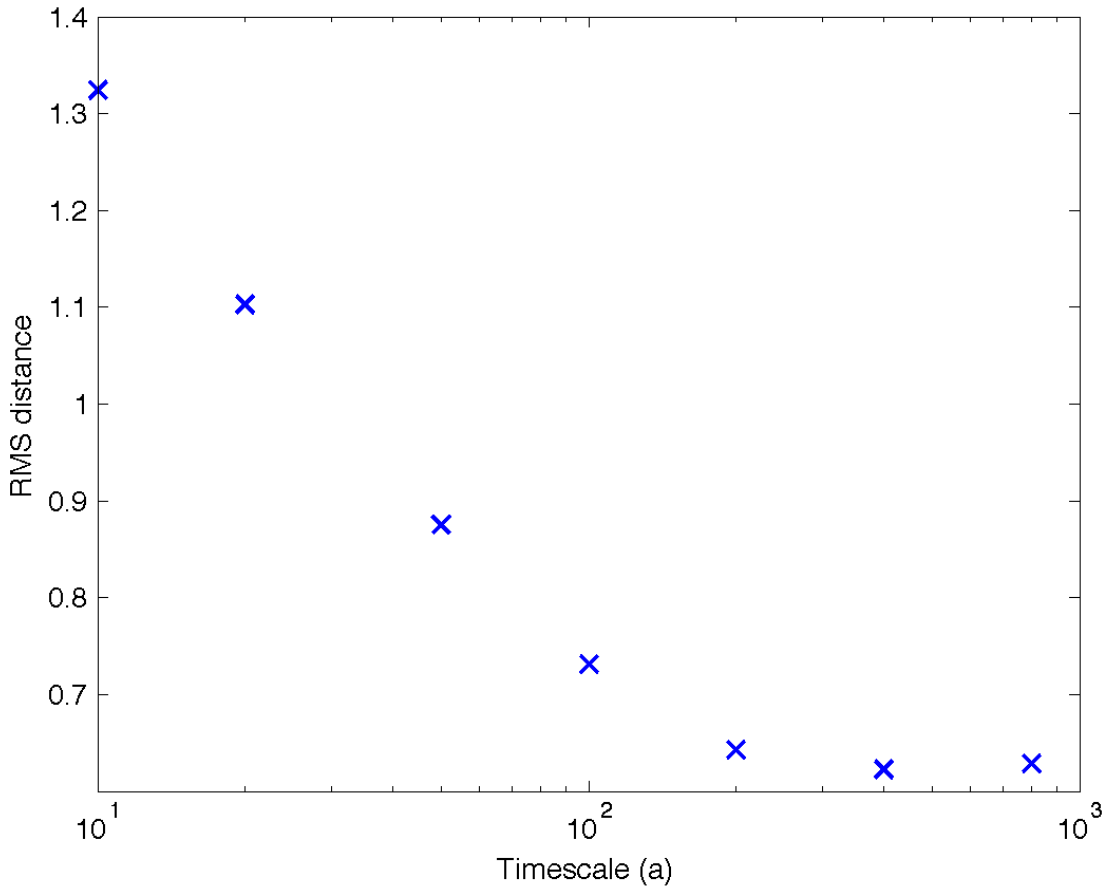
$$\frac{\partial}{\partial t} L + \mathbf{U} \cdot \nabla L = a\, rD - 1/\tau\, L$$

contains two unknown parameters: ligand:nitrogen (or carbon) ratio in detritus remineralization a, and bacterial degradation timescale τ.

Scaling invariance: a can be estimated *post festum*

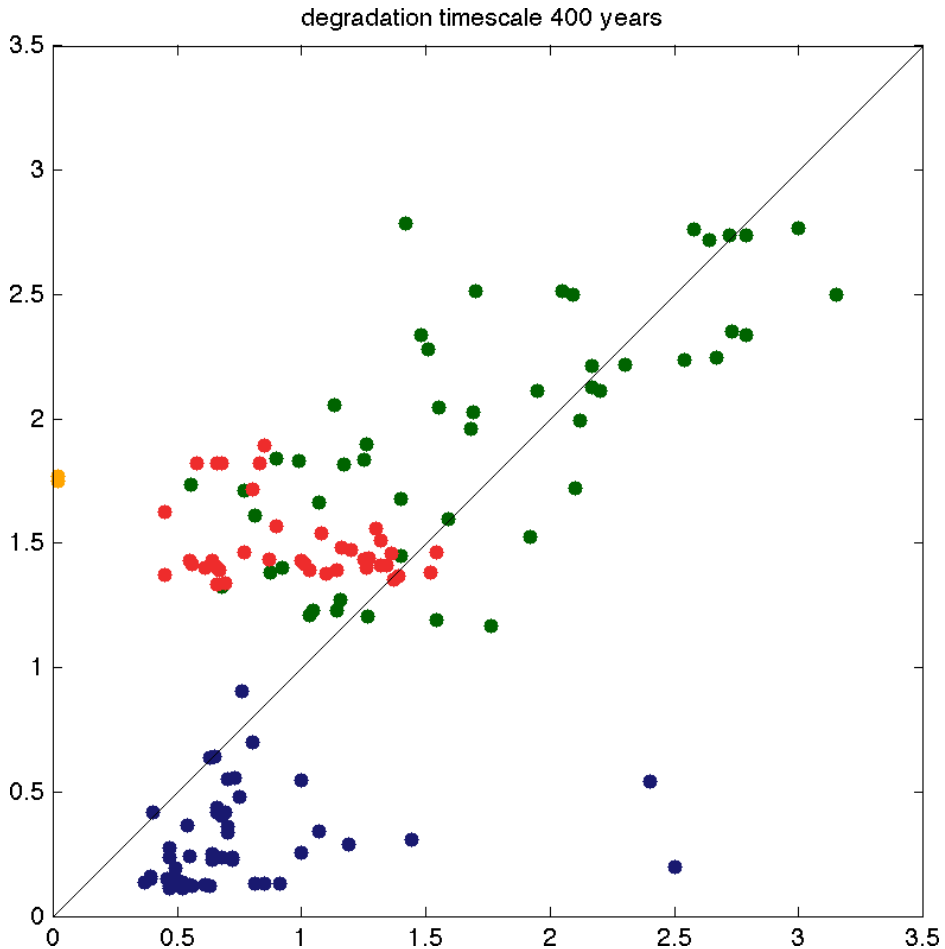
we vary τ from 10 years to 800 years

ROOT-MEAN-SQUARE DIFFERENCE MODEL-DATA BELOW 1000 M



run model with different degradation timescale τ;
best fit to data for $\tau = 400$ years

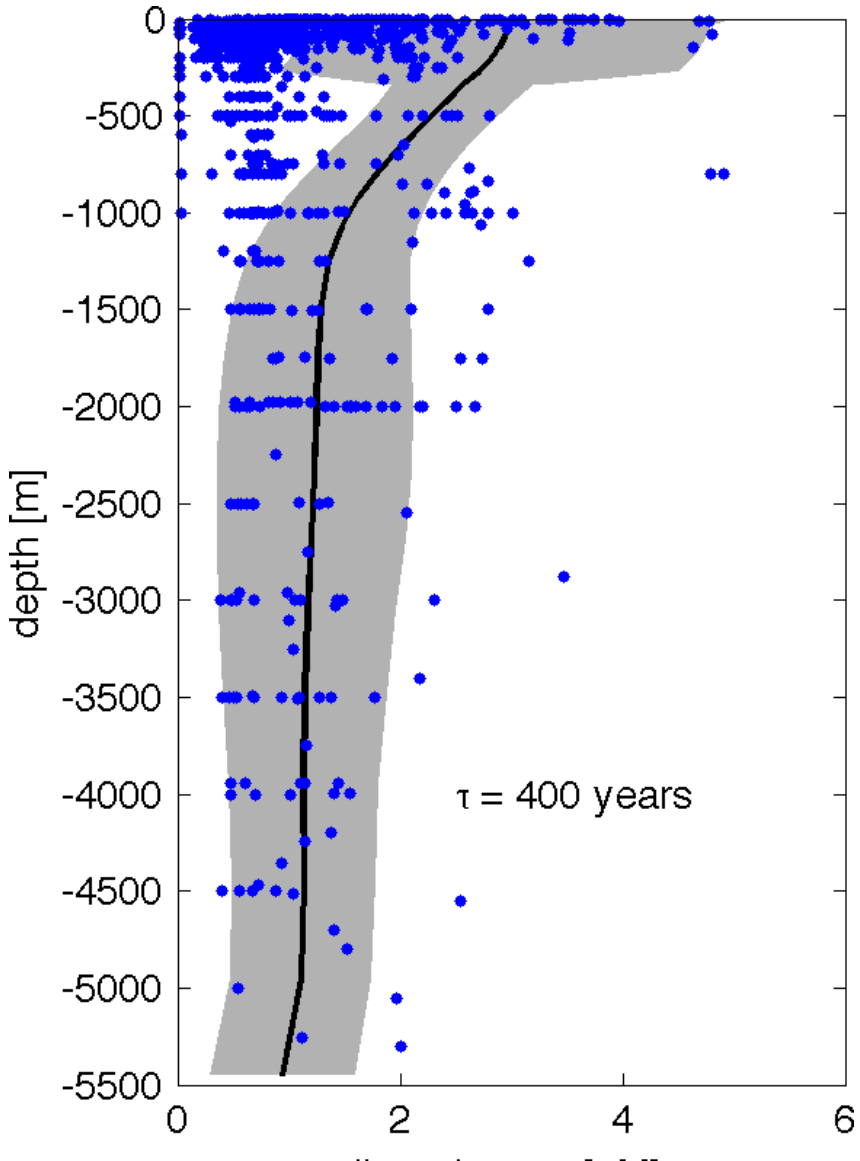
LIGANDS GT. 1000M DEPTH, MODEL VS. DATA



green: Atlantic
red: Southern Ocean
blue: North Pacific
yellow: Indian

best fit for $\tau = 400$ years, a = $1.27 \cdot 10^{-5}$ mol ligand:mol N

BUT THIS CANNOT BE ALL!



modeled ligand concentrations are too high in upper 1000 m

we are missing loss processes there!

some candidates:

- photochemistry
- ligand destruction during phytoplankton Fe uptake
- faster bacterial degradation of parts of the ligand pool

A MORE GENERAL SCENARIO / MODEL

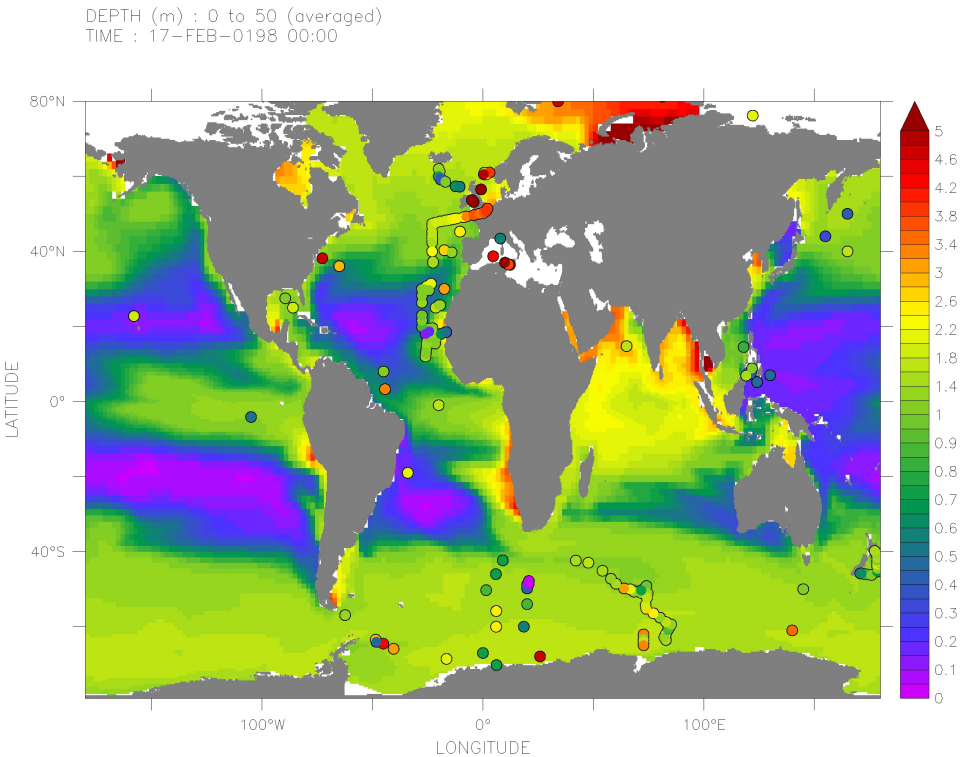
Two sources: PON degradation + DON excretion by phytoplankton and zooplankton
Three sinks: bacterial degradation (possibly with nonconstant time-scale τ) + photochemical destruction + iron uptake

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

excretion of DON by phytoplankton/zooplankton, photodegradation, and iron uptake happen only in euphotic zone

four unknown parameters: ligand:nitrogen ratio in fresh DON a, bacterial degradation timescale τ photochemical destruction rate κ, and fraction of ligand destroyed in iron uptake α.

PHOTOCHEMISTRY

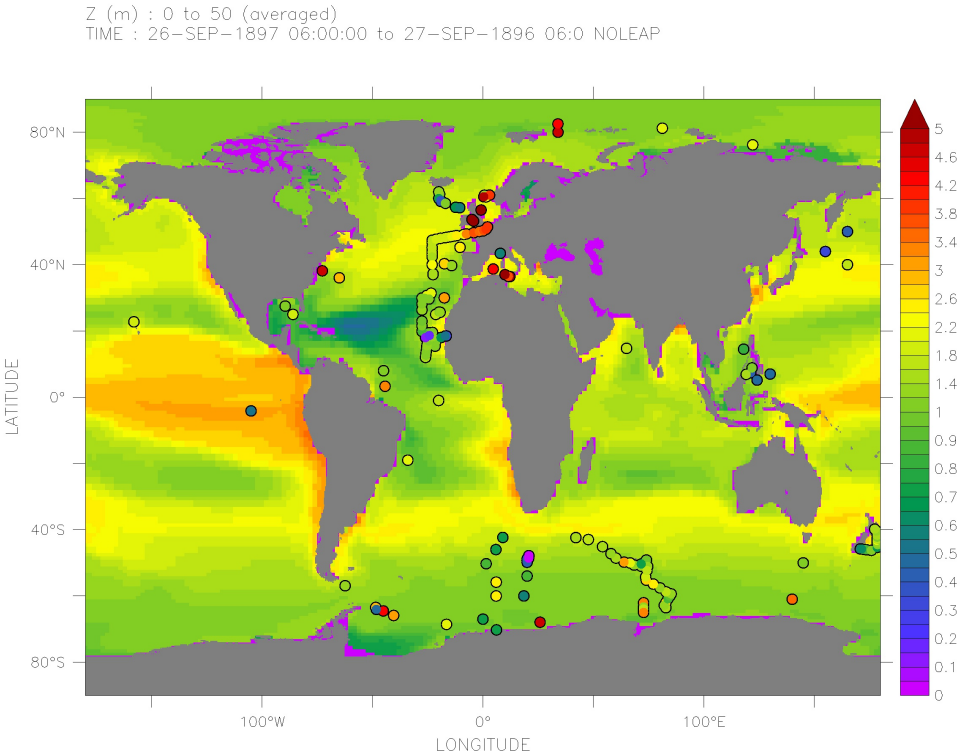


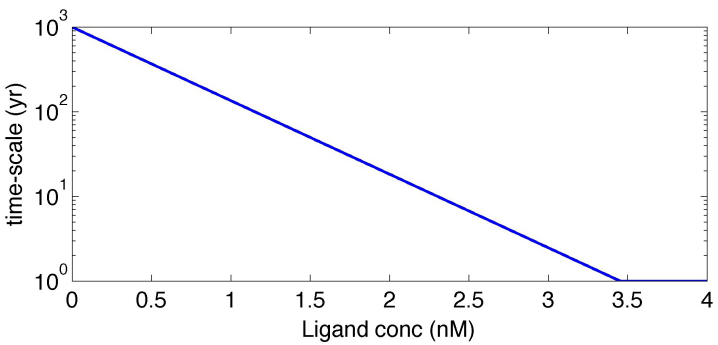
L1 ligand (nM)

Photochemistry can reduce suface Lig concentrations to observed values;

but tends to reduce ligands most in subtropical gyres (no production, fast degradation);

LIGAND 'CONTINUUM'





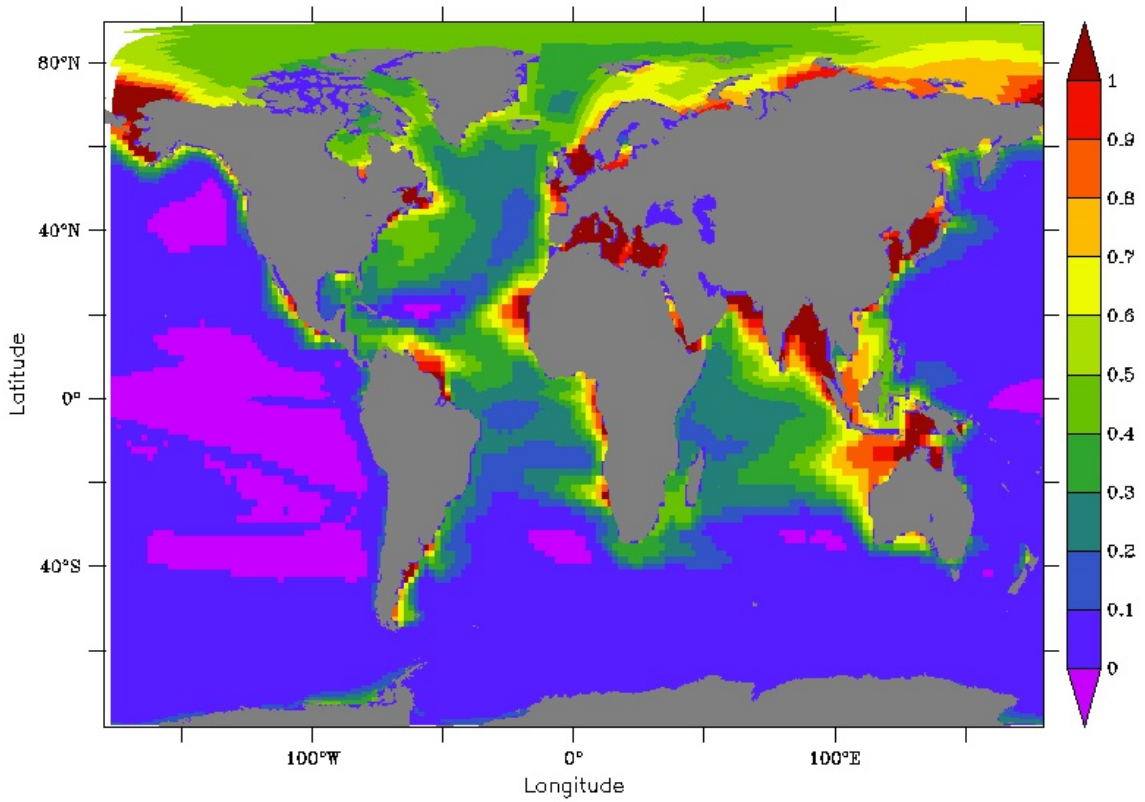
parameterize that some fractions of Lig degraded much faster than others;

higher degradation rate when concentration of ligand is high;

a fraction of the ligand tends to aggregate with sinking particles;

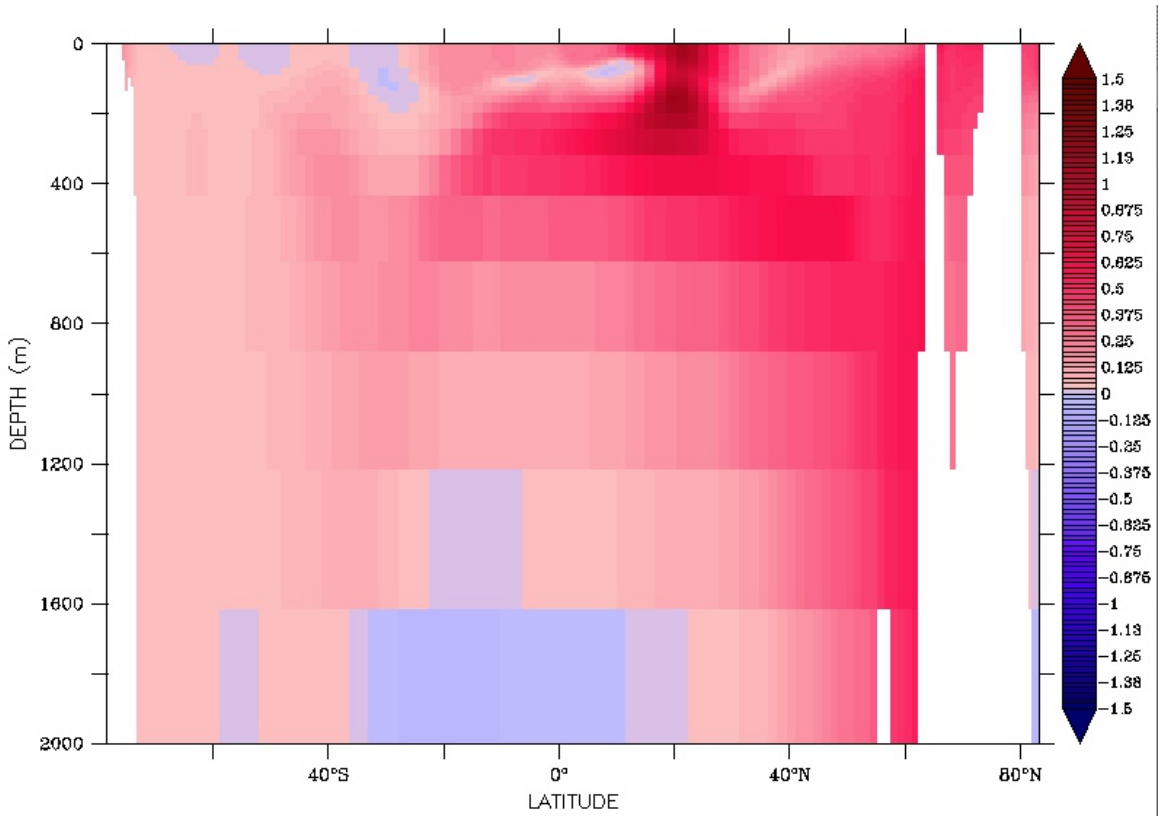
makes surface concentration more homogenous and reduces strong sensitivity to ligand:carbon (or nitrogen) ratio

HOW IS THE FE DISTRIBUTION AFFECTED BY THIS?



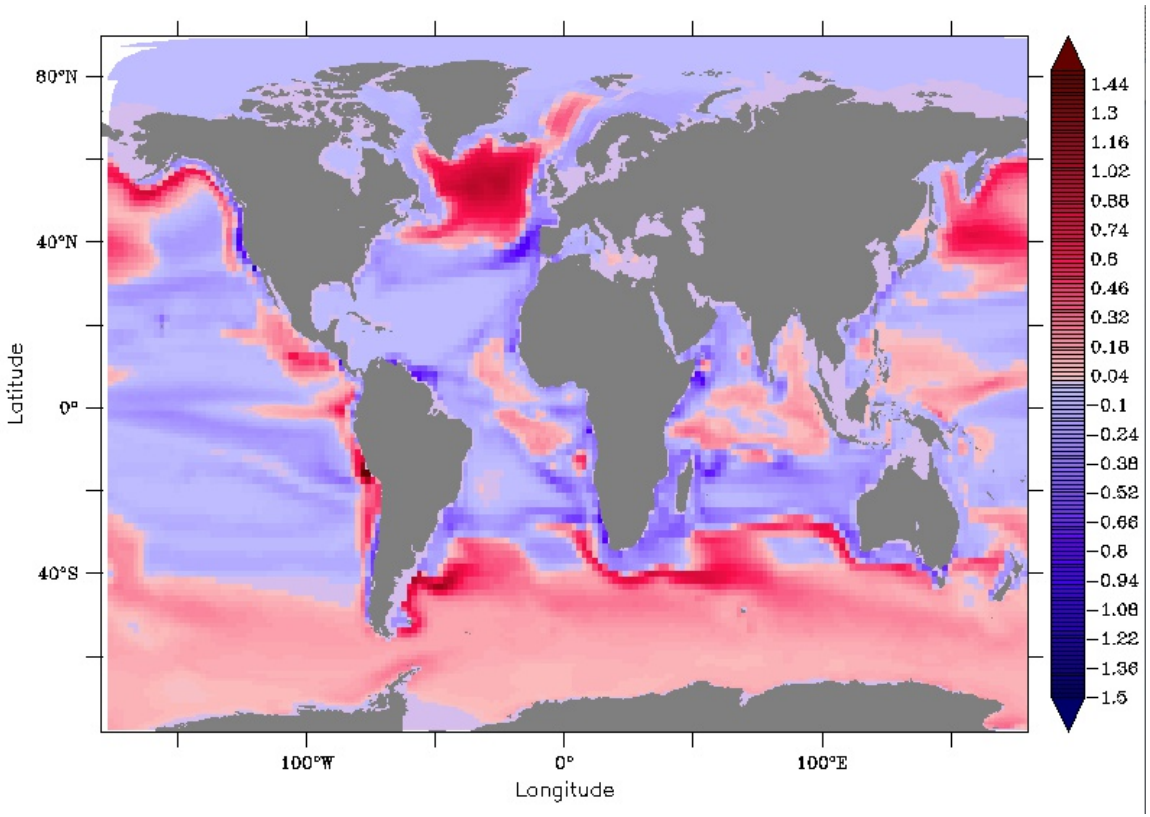
Surface: increase in Fe in high-productivity regions

HOW IS THE FE DISTRIBUTION AFFECTED BY THIS?



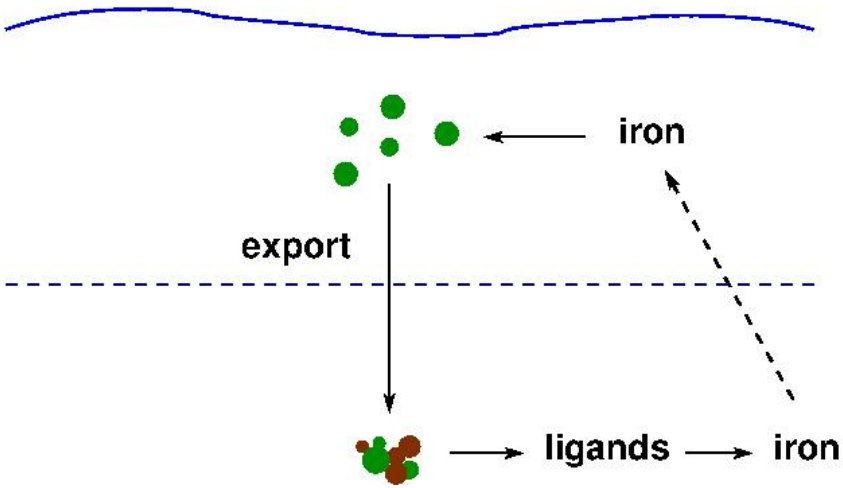
Atlantic zonal section (30N): increase in Fe around 500m

WHAT DOES THAT DO TO BIOLOGY?



leads to some increase in export (mol C m^2 yr^{-1}) in upwelling, subpolar gyres and Southern Ocean; decrease in subtropical gyres

FEEDBACK IN IRON-LIMITED SYSTEMS



- more ligand
- less scavenging of iron
- increased iron concentration in upwelling
- higher biological productivity
- more production of ligand from remineralization

feedback works both ways $\rightarrow$ possibility of runaway iron limitation

SUMMARY SO FAR

- Remineralization source and bacterial degradation can explain deep ligands
- More complex model needed to account for faster ligand loss near surface
- Model can create 'realistically-looking' surface ligand distributions; but some freedom in which process is how important
- This is changing with the upcoming data from GEOTRACES
- Some model parameters constrained from process understanding; but not all $\rightarrow$ need for mechanistic studies
- Feedback between ligand production $\rightarrow$ iron concentration $\rightarrow$ biological activity $\rightarrow$ ligand production