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Stability of dissolved and soluble Fe(II) in shelf sediment pore waters and release to an oxic water column

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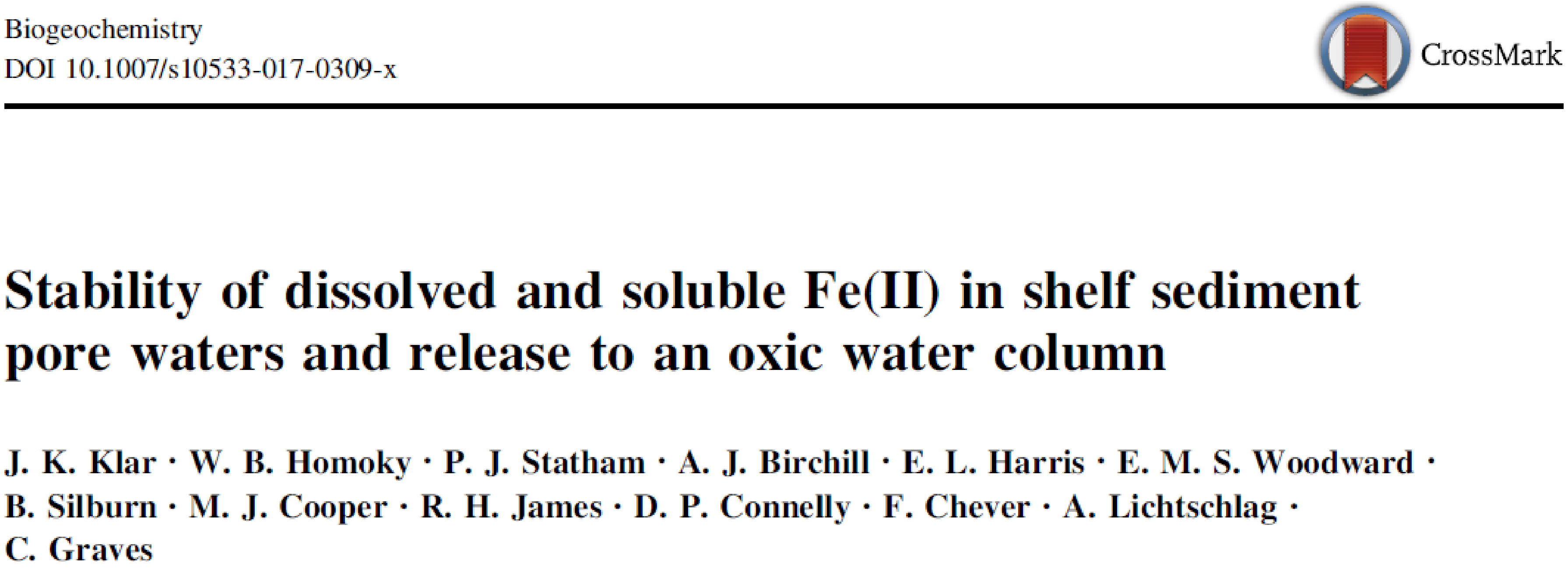

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Stability of dissolved and soluble Fe(II) in shelf sediment pore waters and release to an oxic water column

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Part of Biogeochemistry special issue due to be released…

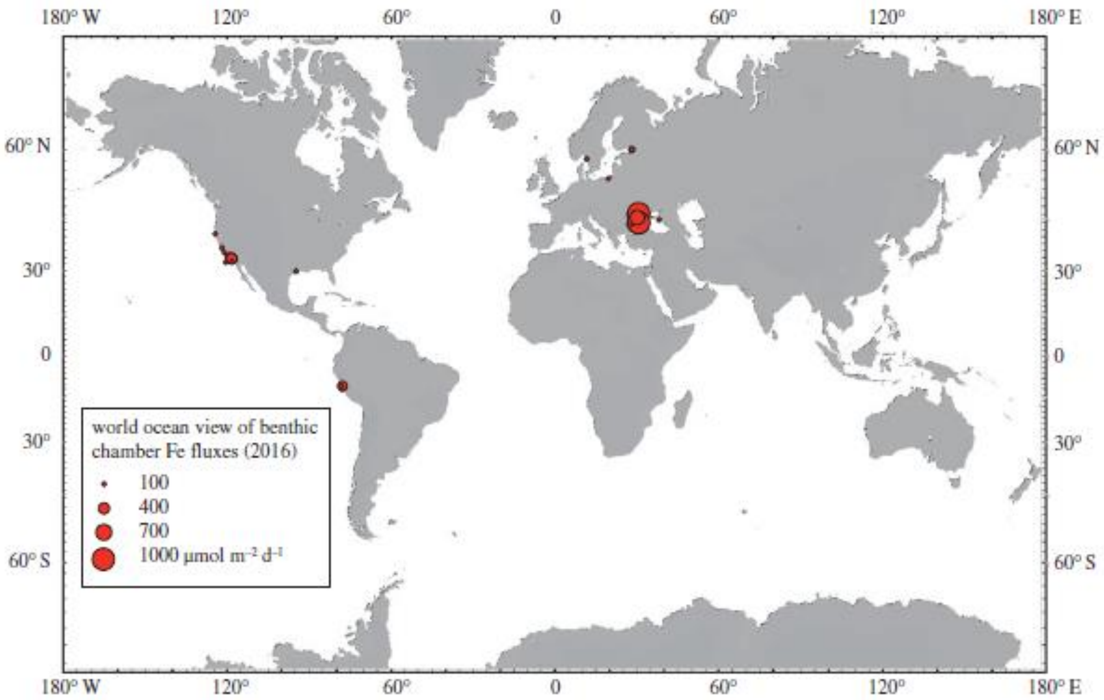
Talk overview

Part 1 – Findings in the field –
Jessica Klar

Part 2 – Flux modelling –
Will Homoky

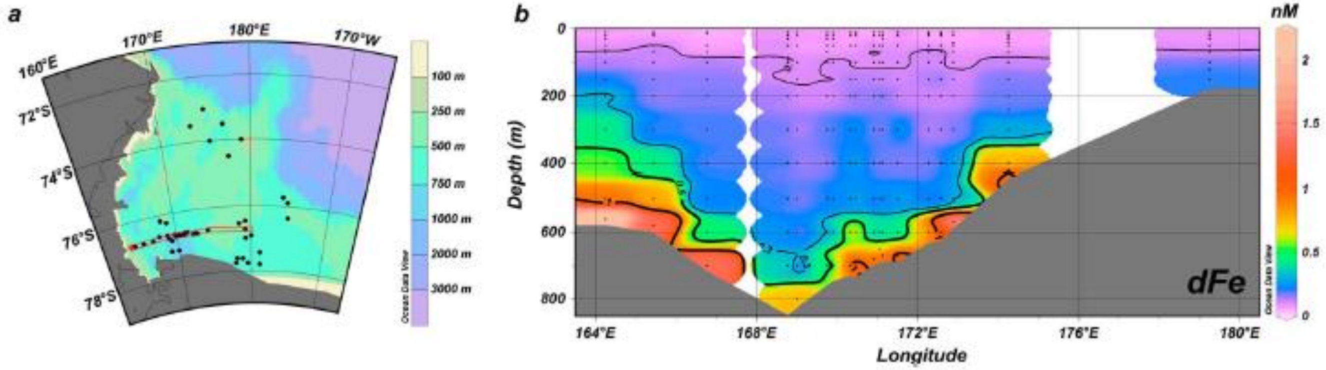
Introduction

- Sediments are recognised to be an important **source** of dFe to the ocean
- Previous studies targeted areas of low bottom water O_2 concentrations and high org C → high rates of dFe release
- Oxic shelf waters with increased dFe concentrations → what is the importance of benthic Fe supply to the ocean?
- In which **form** is Fe released from sediments and how is it transformed thereafter?
- What are the effects of **seasonal** changes in C supply to the seafloor?
- What role plays **sediment type**?



Homoky et al., 2016 *Phil. Trans. R. Soc. A*, 374

Marsay et al., 2014 *GRL*, 41



Study area

Extensive shallow (~100 m) shelf with oxic water column

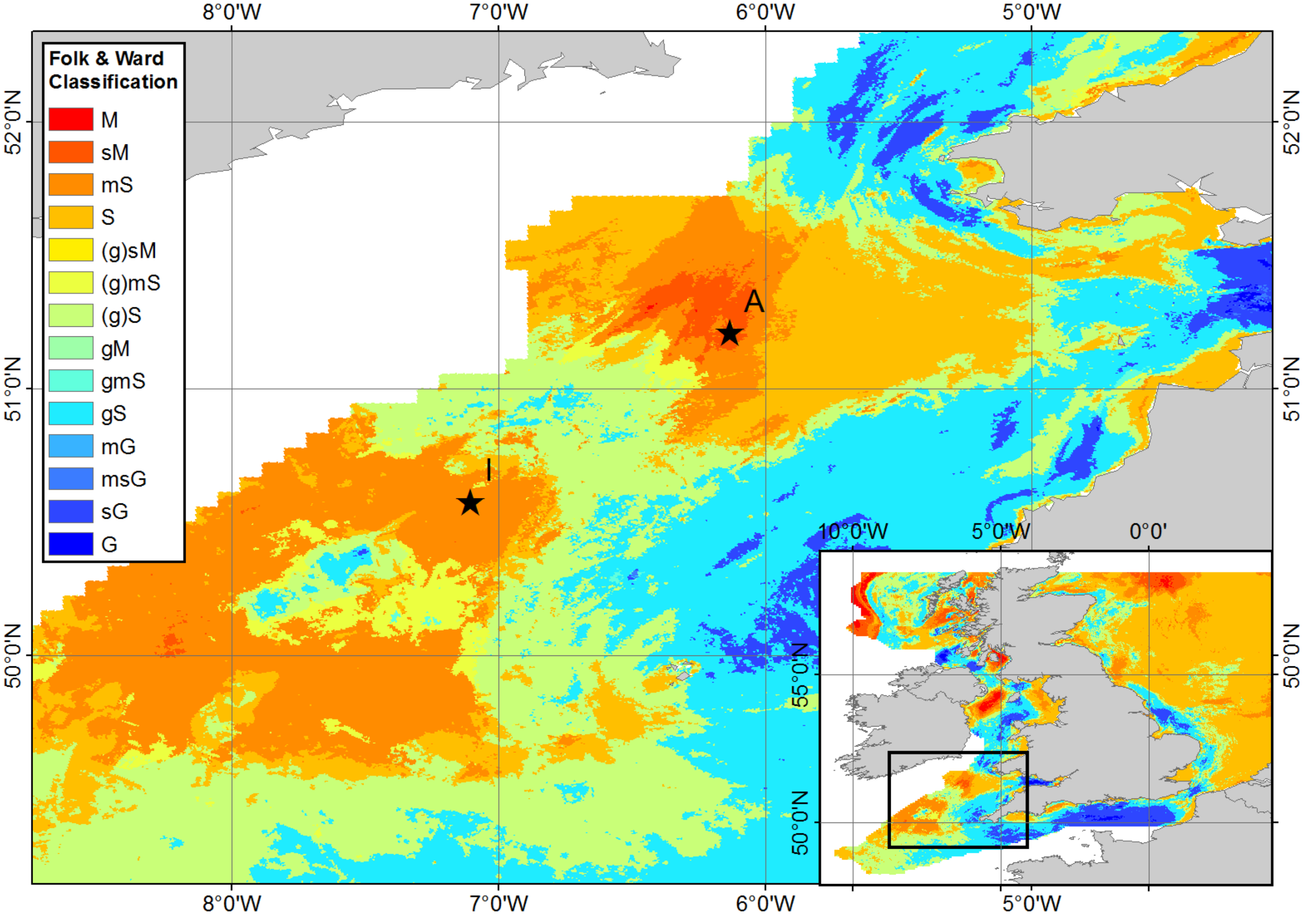
4 benthic cruises to capture seasonal changes

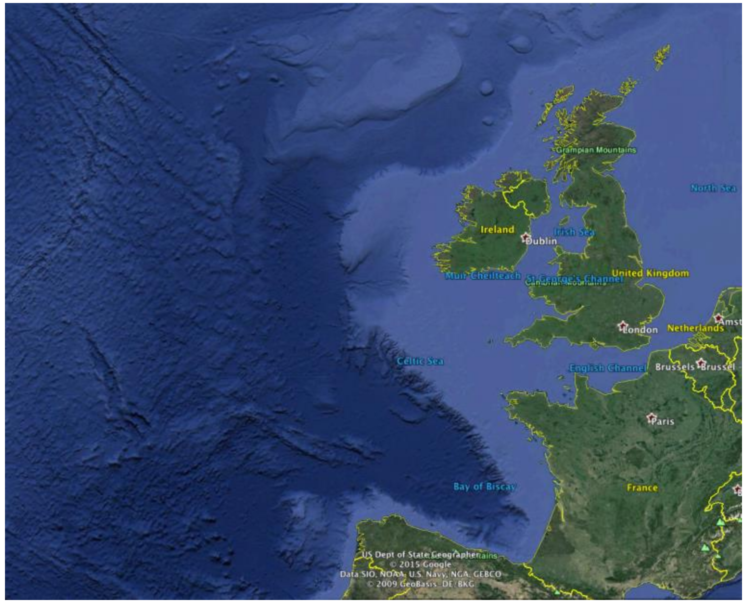
Data from 2 cruises in 2015

- **Late spring (DY030)**
- **Late summer (DY034)**

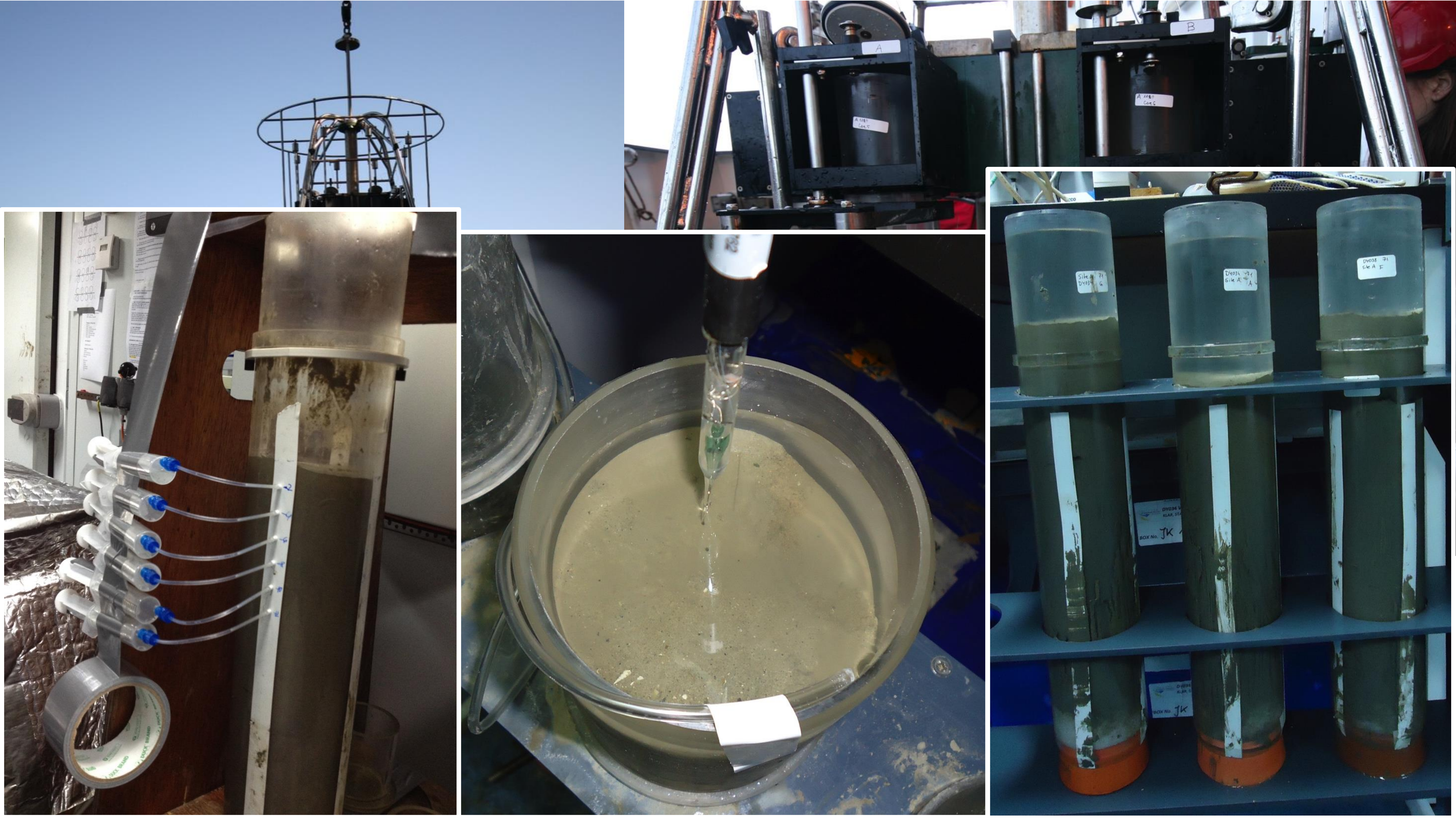
4 benthic sites to capture varying sedimentology

Paper focussed on Site A (sandy mud - cohesive)





Sampling in the Celtic Sea with a new ship!


A
B
BOX No. JK
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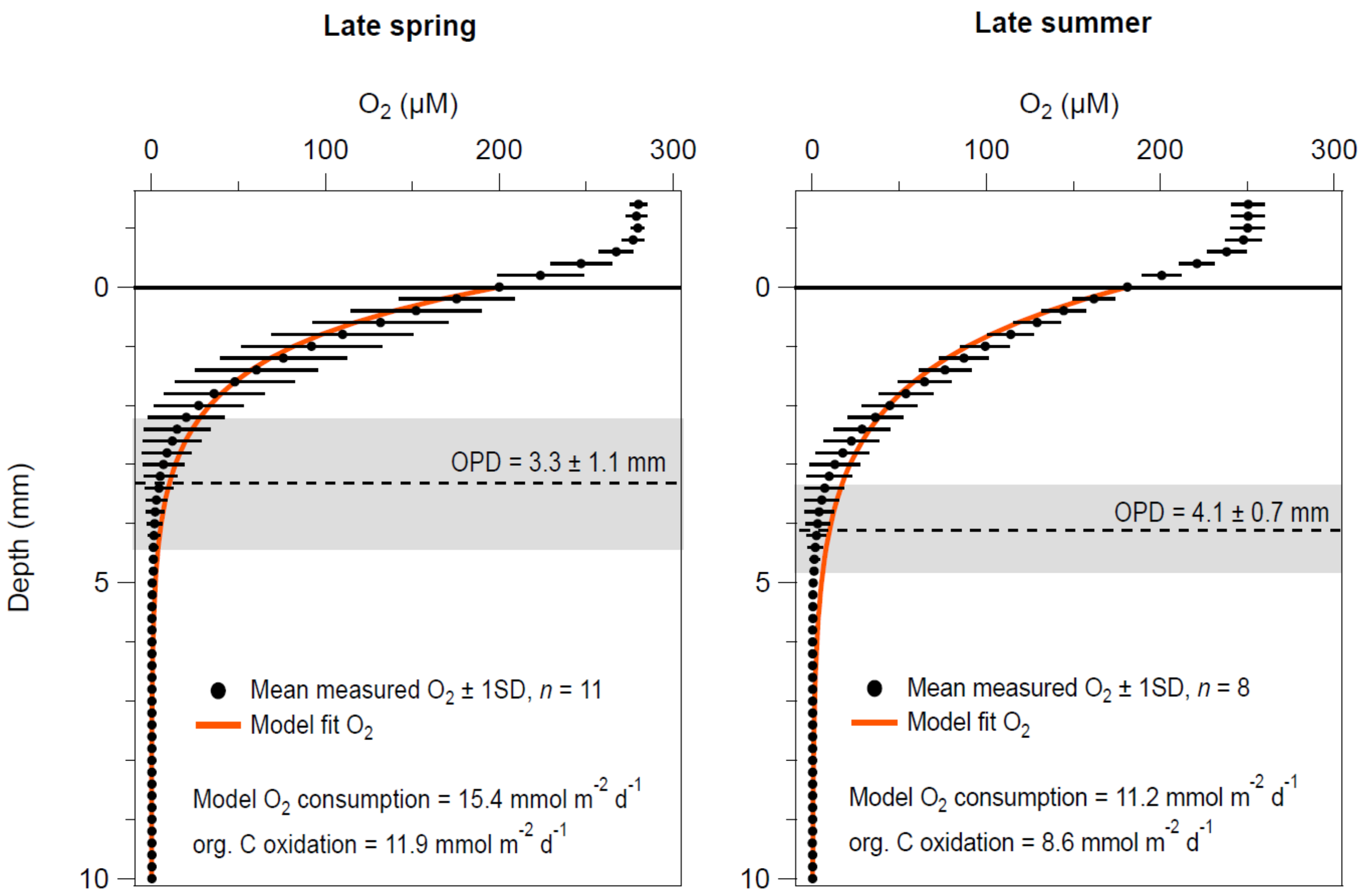
What we found

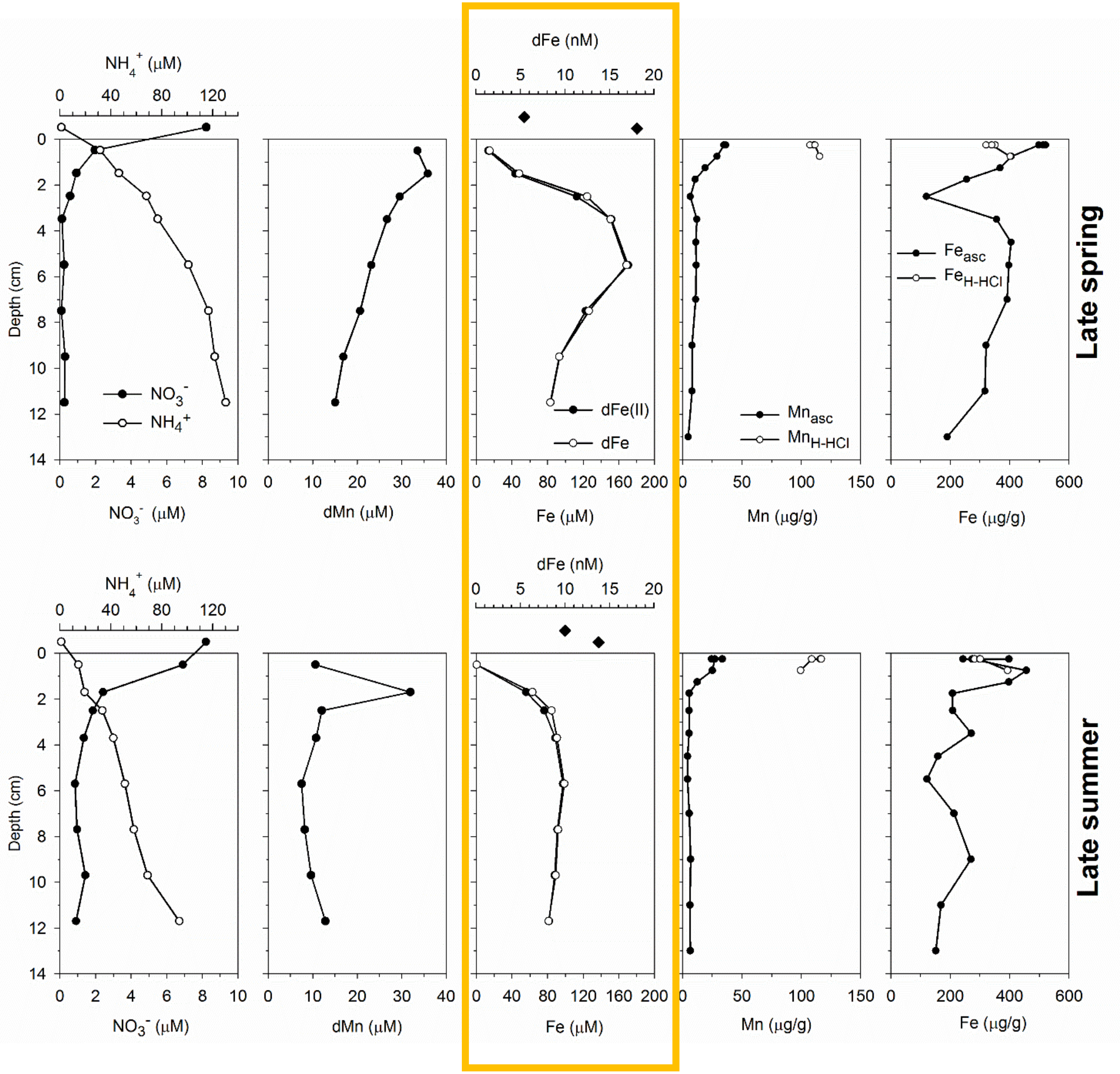
Seasonal change in oxygen penetration



Enhanced supply of organic carbon after the bloom

- Peak chlorophyll – MODIS satellites
- Surface sediment POC highest in spring (1.25% vs 1.14% in summer)
- Higher O_2 consumption
- Higher org C oxidation (Berner, 1980; 1-D steady-state oxygen diffusion-consumption model)

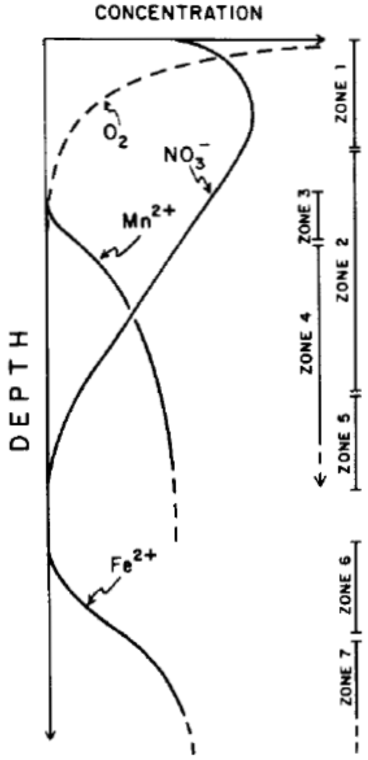
Classical biogeochemical zonations



- Sequential reduction of electron acceptors with depth

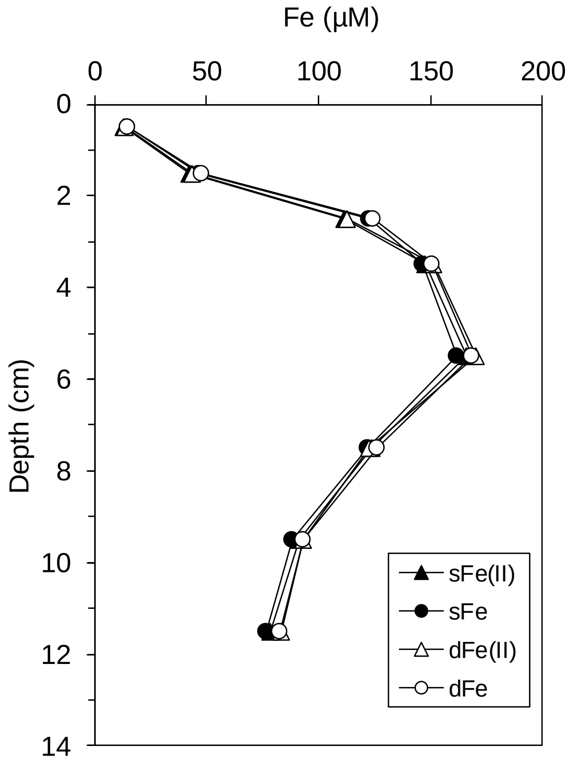
O_2 – NO_3^- - Fe(III) – Mn(IV) – SO_4^{2-}

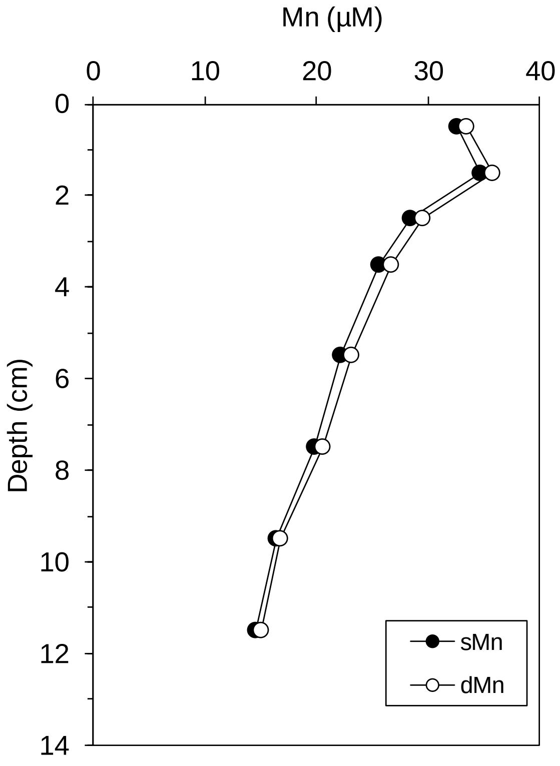
- Sulphide was not detected but must be present further downcore
- Ascorbic leach – easily reducible oxide phases (i.e., amorphous ferrihydrite)
- Acetic acid – hydroxylamine - HCl leach – extracts other amorphous oxide phases as well as ferryhydrite
- dFe(II) >85 % of dFe, d < 3cm
- dFe(II) = 100 % of dFe, d > 3cm



Froelich et al., 1979

Dissolved Fe and Mn is soluble and reduced



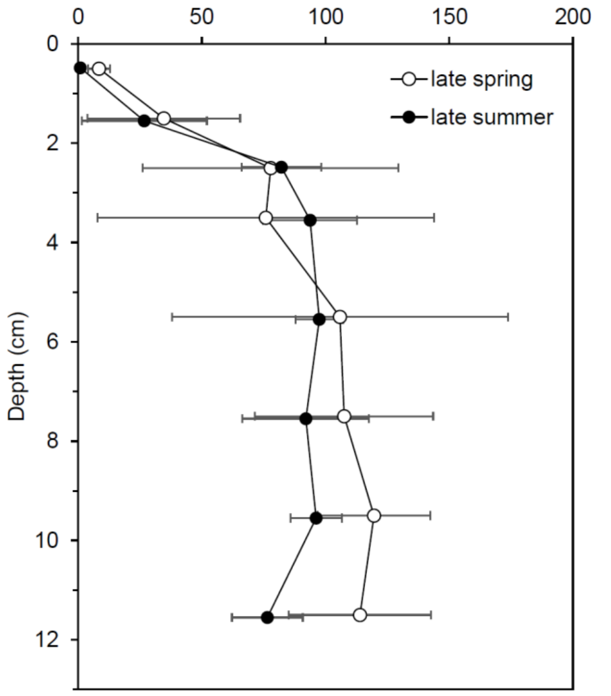


Soluble phases (<0.2 µm)
sFe > 85% of dFe(II)
sMn = 100% of dMn

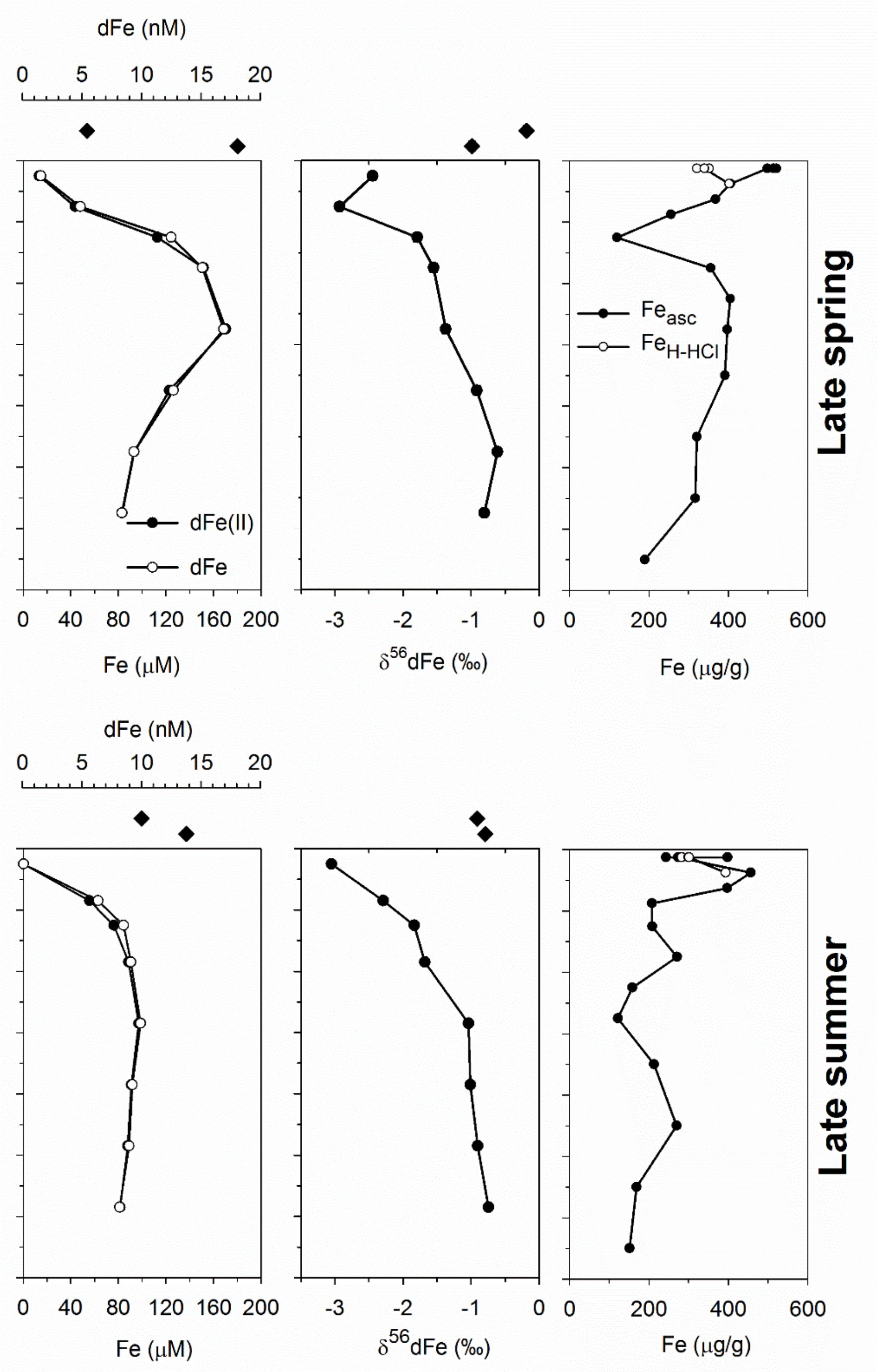
	Late spring*	Late summer
Subsurface dFe(II) maxima	150 ± 20 µM	110 ± 10 µM
Surface layer dFe(II)	5 - 13 µM	0.3 - 1.2 µM

*Enhanced supply of org C in late spring

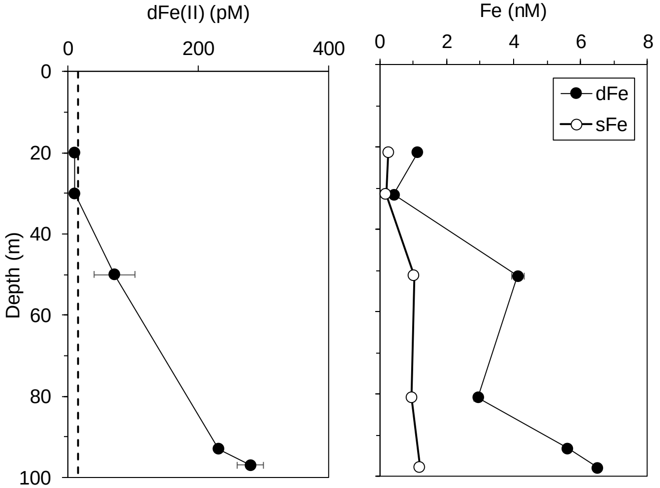
dFe(II)



Seasonal mean values from multiple cores



Fe isotopes to trace processes



- Surface: reactive consumption to Fe(II) oxidation
  - Oxidation Fe(II) to Fe(III) incorporation of heavier isotopes into Fe(III) phases
- Mid-depth maxima: Fe(II) production by Dissimilatory Iron Reduction (DIR)
- Depth: reactive consumption to Fe-sulphides
  - FeS incorporates light isotopes

- Shift towards heavier isotopes near surface and in CTW and BW:

  → Fe-ligand (FeL) formation?
- Significant fraction of upward diffusing Fe(II) is able to escape the oxidative trap in surface sediments and enter the oxic water column

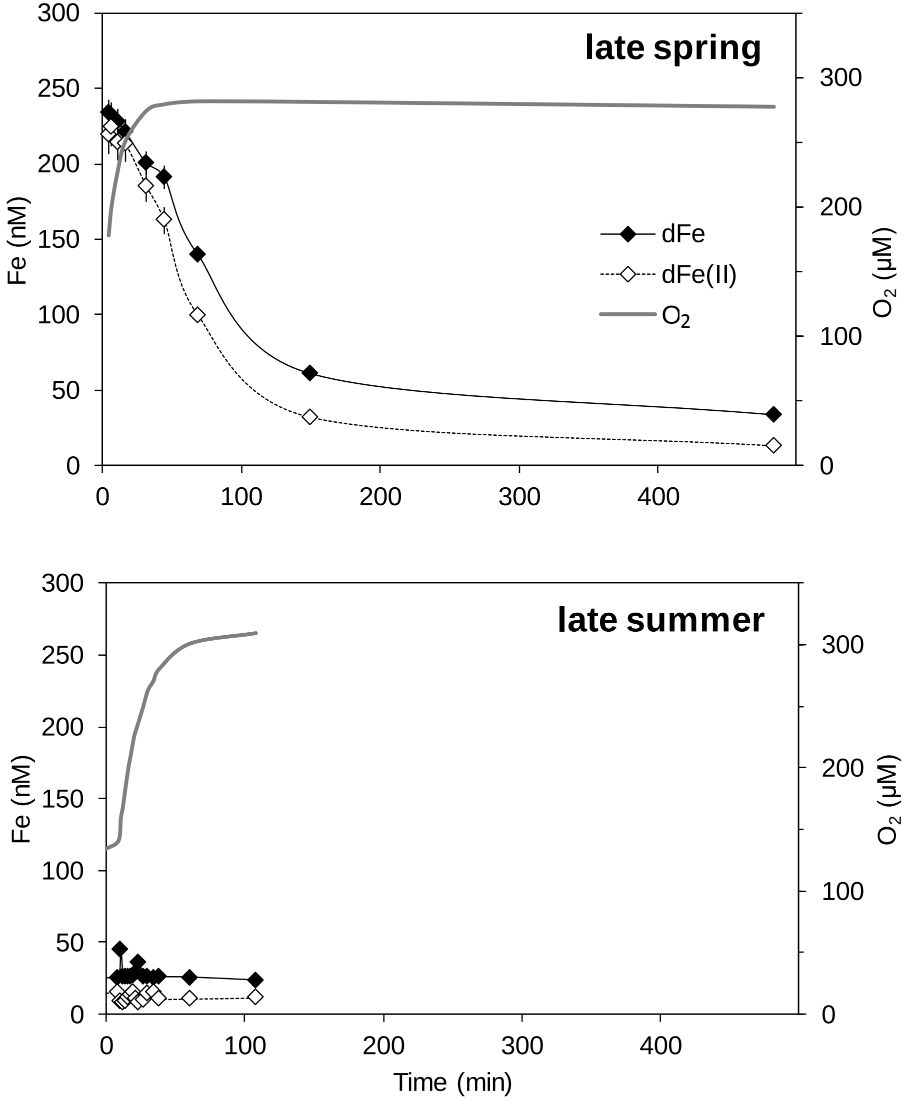
  CTW: dFe(II) = 70 % of dFe

  BW: sFe(II) = 4% of dFe

  } Organic ligands?

Experiments to investigate the presence of Fe(II) in oxic sediment surface layer and core top water

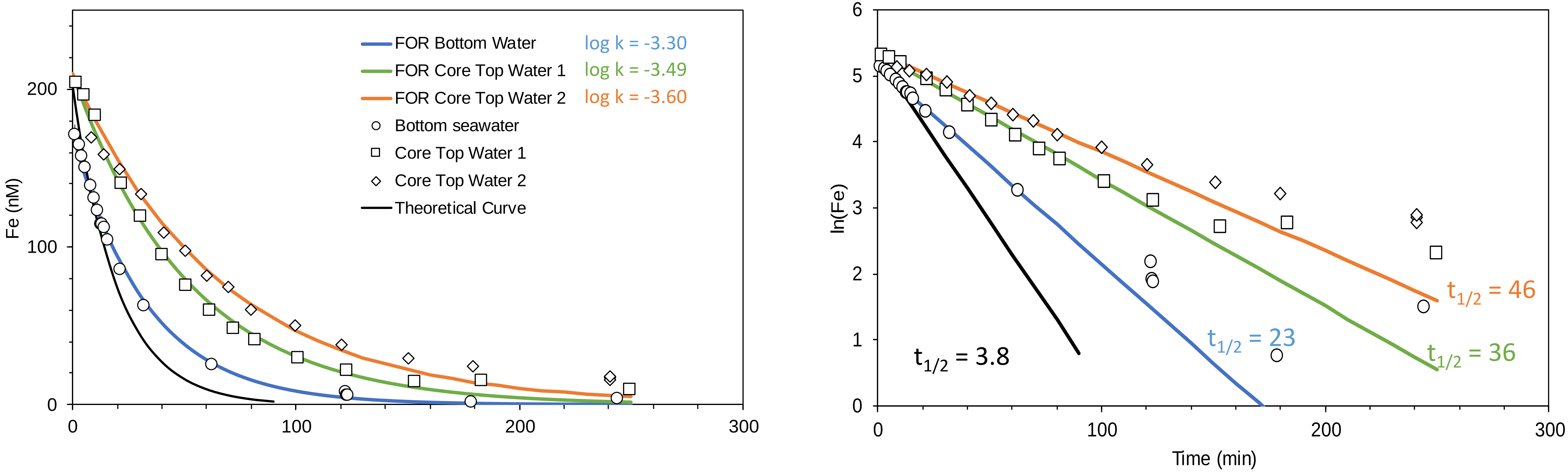
Seasonal decrease of bottom water O_2



- Other areas of the North Sea undergo seasonal decrease in bottom water O_2 → effect on Fe release?
- Seasonal differences in surface porewater Fe concentration and OPD are important controls on the release of dFe to bottom waters
- Enhanced Fe release in late spring
- Residual dFe concentration of 25 – 30 nM (30 – 50 % dFe(II))
- Hypothesis: Fe(II) and Fe(III) stabilisation by organic ligands
- Organic ligands supplied by sediments, especially post-bloom

Fe(II) oxidation rates slowest in seawater closest to sediments

- Slower oxidation rates in CTW and BW
- Do not follow first order kinetics
- Residual dFe and dFe(II) → Fe-L formation
- Sediments provide a source of dFe to the overlying water column
- Fe(II)-L → oxidation to Fe(III)-L



Key findings – from in the field

- Elevated soluble Fe(II) inventory in sediments, even in surface porewaters
- Higher benthic Fe inventory in the late spring after the phytoplankton bloom
- The deposition of org C on the seafloor leads to higher release of Fe(II) in surface sediments and across the sediment-water boundary
- A significant fraction of Fe(II) resists the oxidative trap and is observed in overlying oxic bottom waters, where Fe(II) persists oxidation
- Hypothesis: Fe(II) released from sediments is stabilised with organic ligands in the water column
- What are the implications of benthic Fe supply to the Fe inventory in the overlying water column?

4 key findings implicate dynamic benthic flux of iron in Celtic Sea:

1. Rich pool of soluble Fe(II) in subsurface porewater

2. High [Fe(II)] in shelf waters near sediments

3. Seasonal growth in porewater Fe(II) inventory and drop in size of the oxic surface trap

4. Ligand inhibition of Fe(II) oxidation rates nearest sediments

A theoretical approach to quantify Fe(II) efflux

$$\text{Flux Fe(II)}, J = \frac{\varphi (D_s K_1)^{0.5} C_p}{\sinh[(K_1/D_s)^{0.5} L]}$$ (Raiswell and Anderson, 2005)

Diffusion coefficient, $D_s = \varphi^{1.7}(3.31+0.15T)10^{-6}$

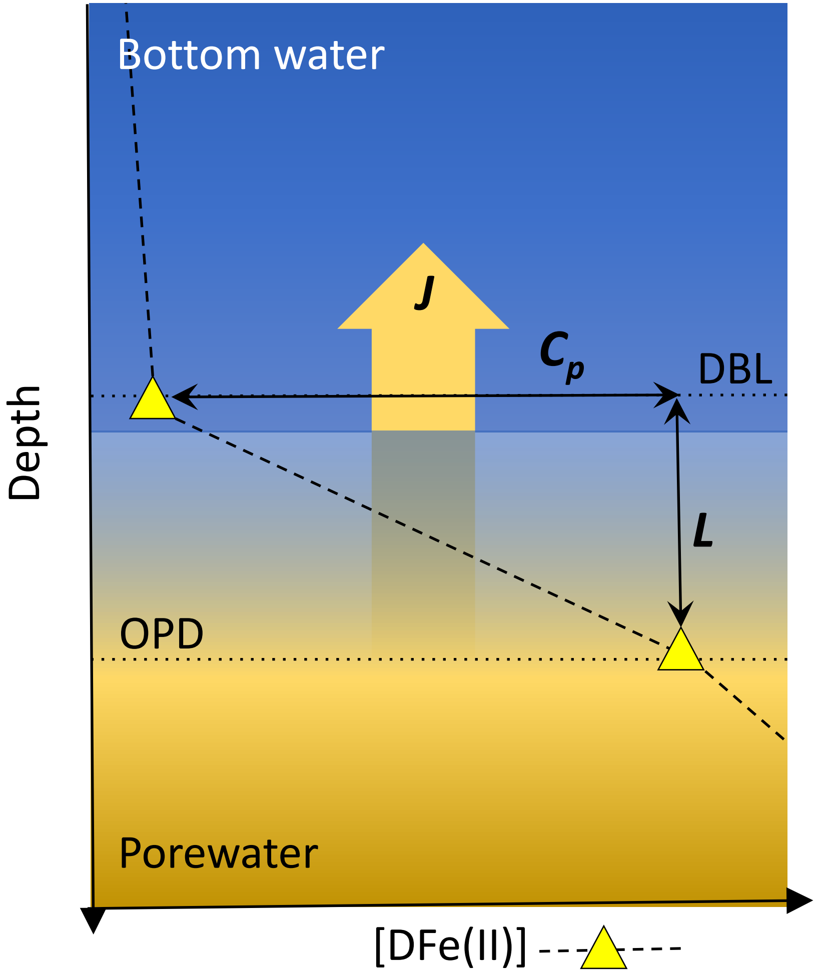
Reaction constant, $k_1 = k[O_2][OH^-]^2$

$\log k = 21.56 - 1545/T - 3.29I^{0.5} + 1.52I$ (Millero, 1987)

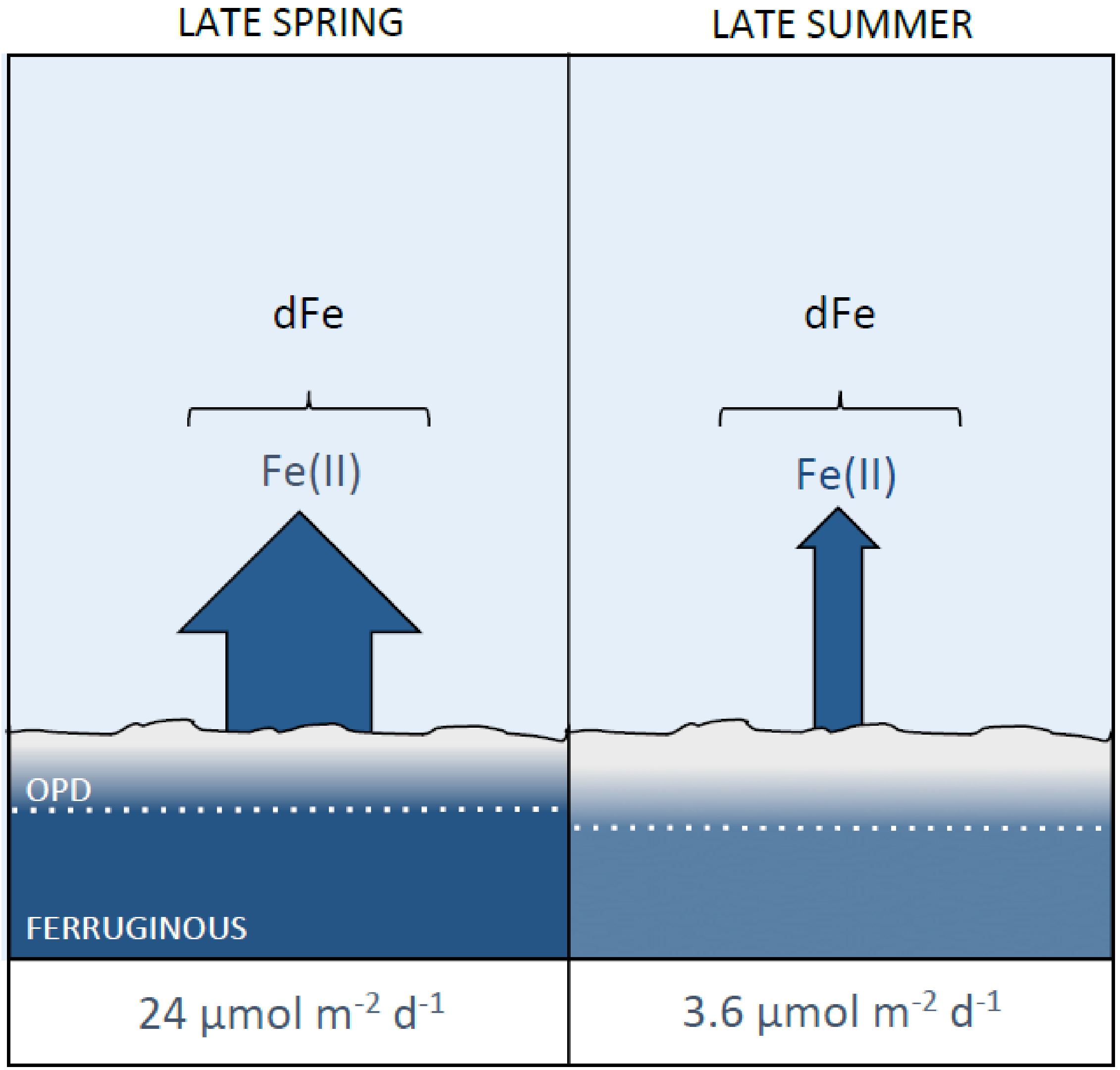
Porosity, φ

Reactive layer thickness (OPD+DBL), L

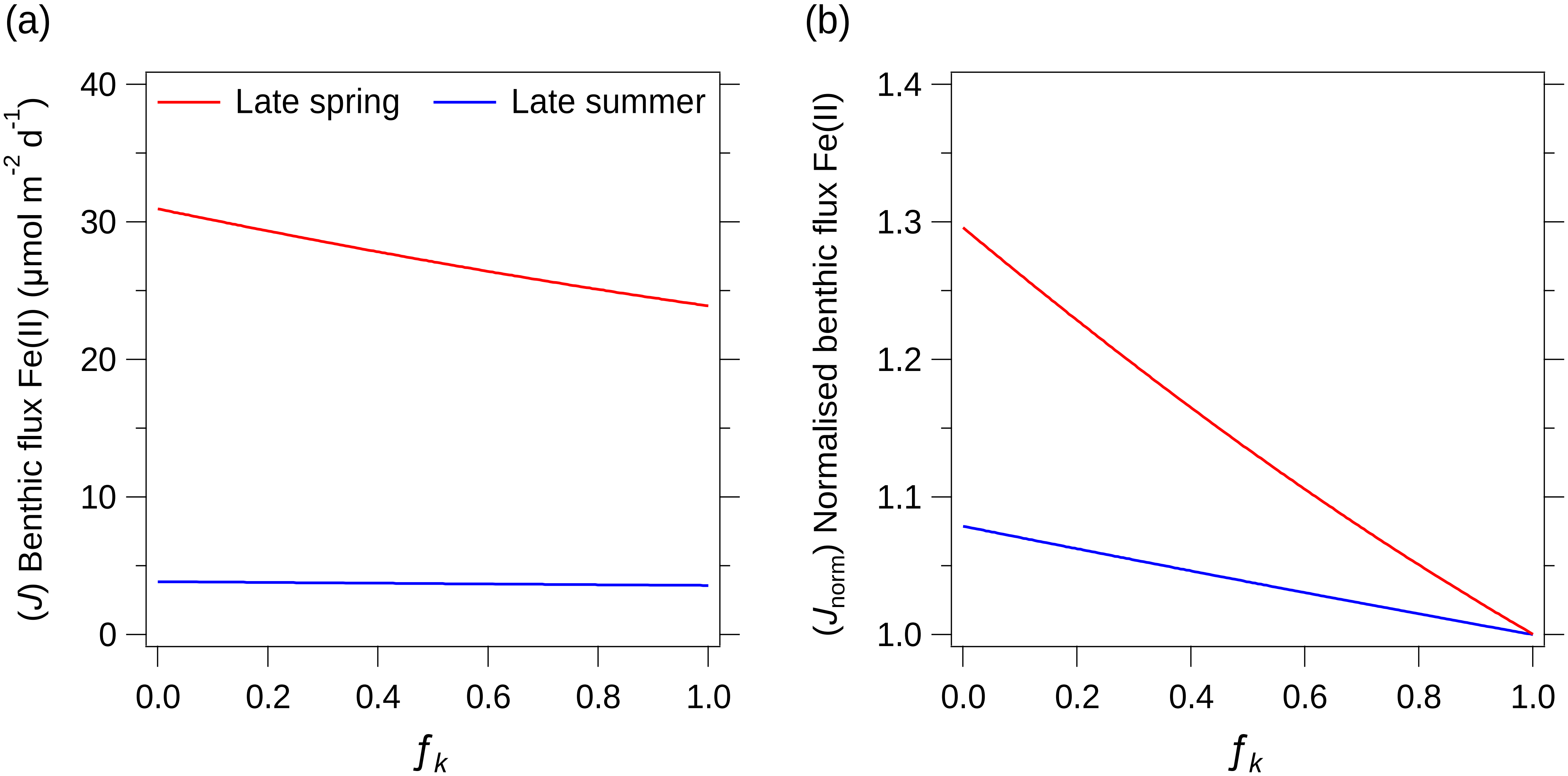
Δ[Fe(II)] across L*,* C_p



A seasonal benthic Fe flux



Resultant fluxes from inhibition of *k*



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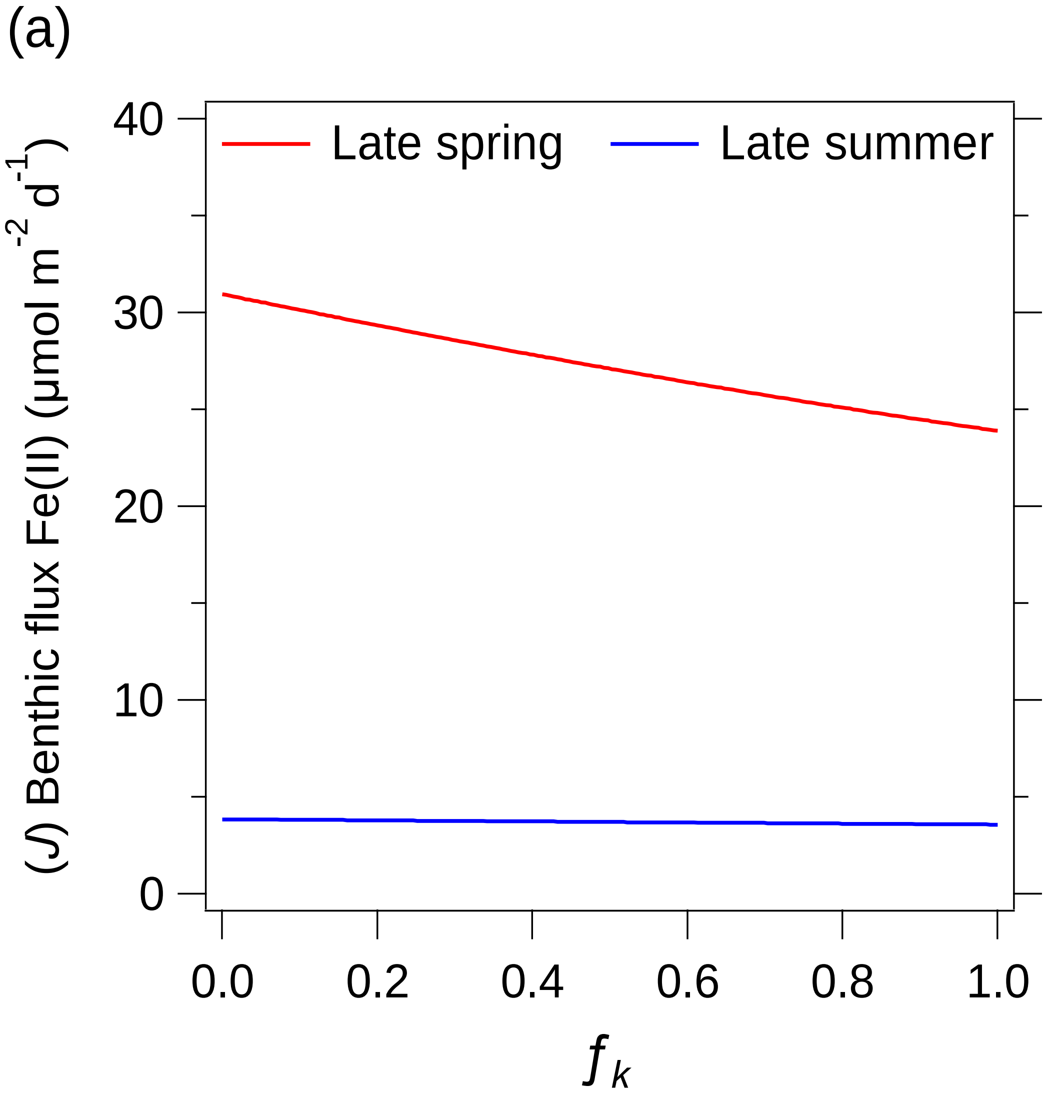
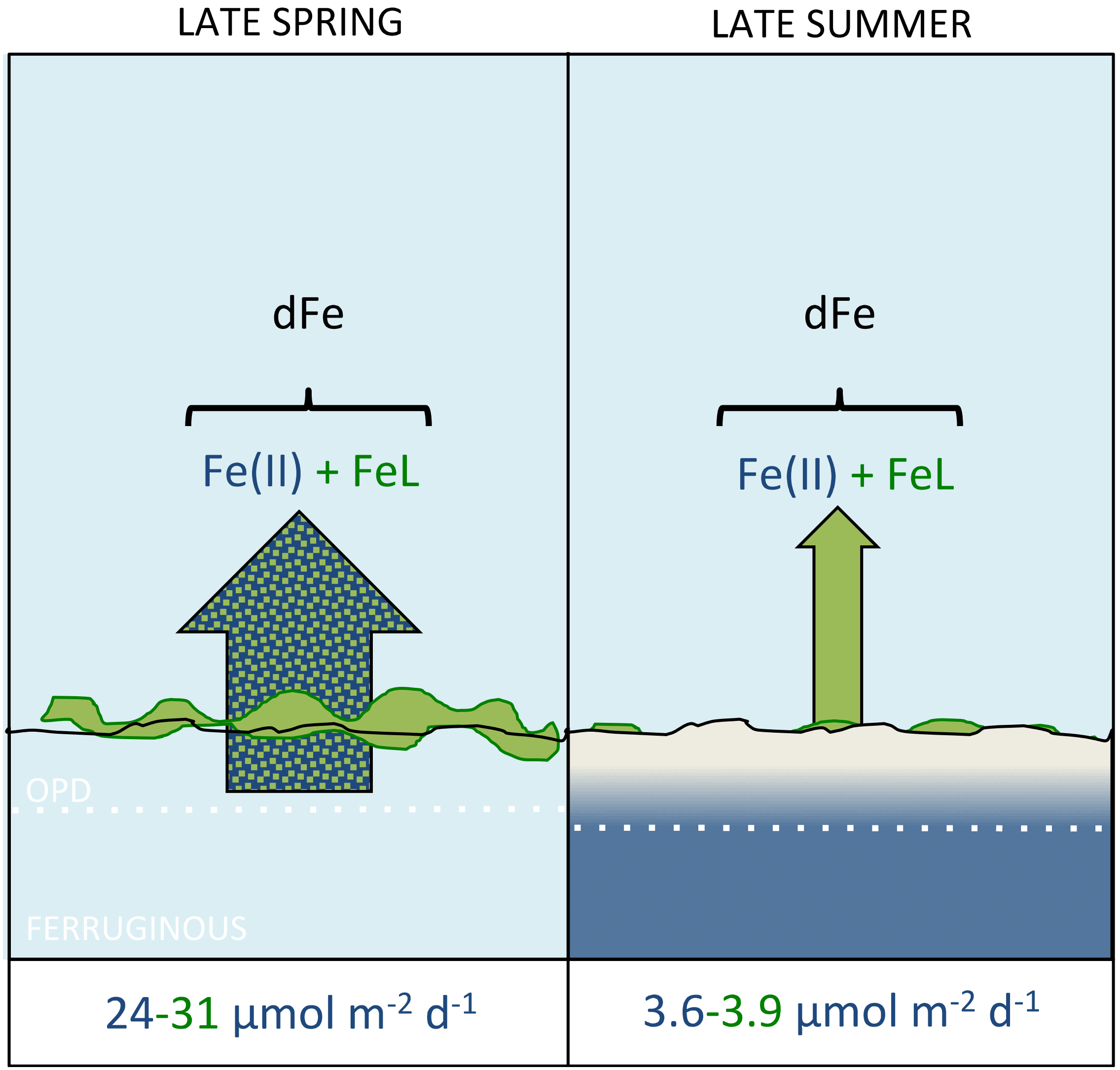
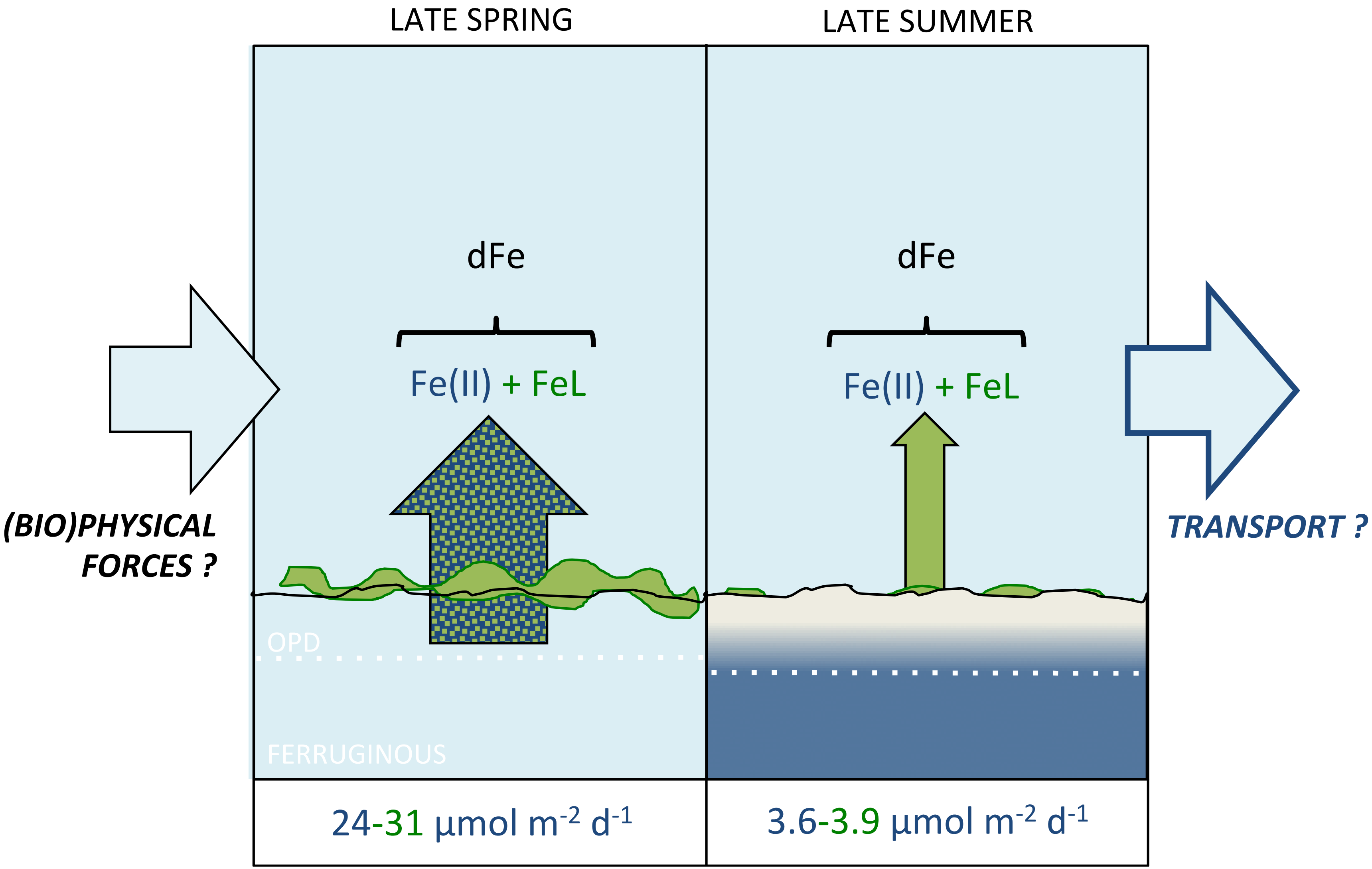
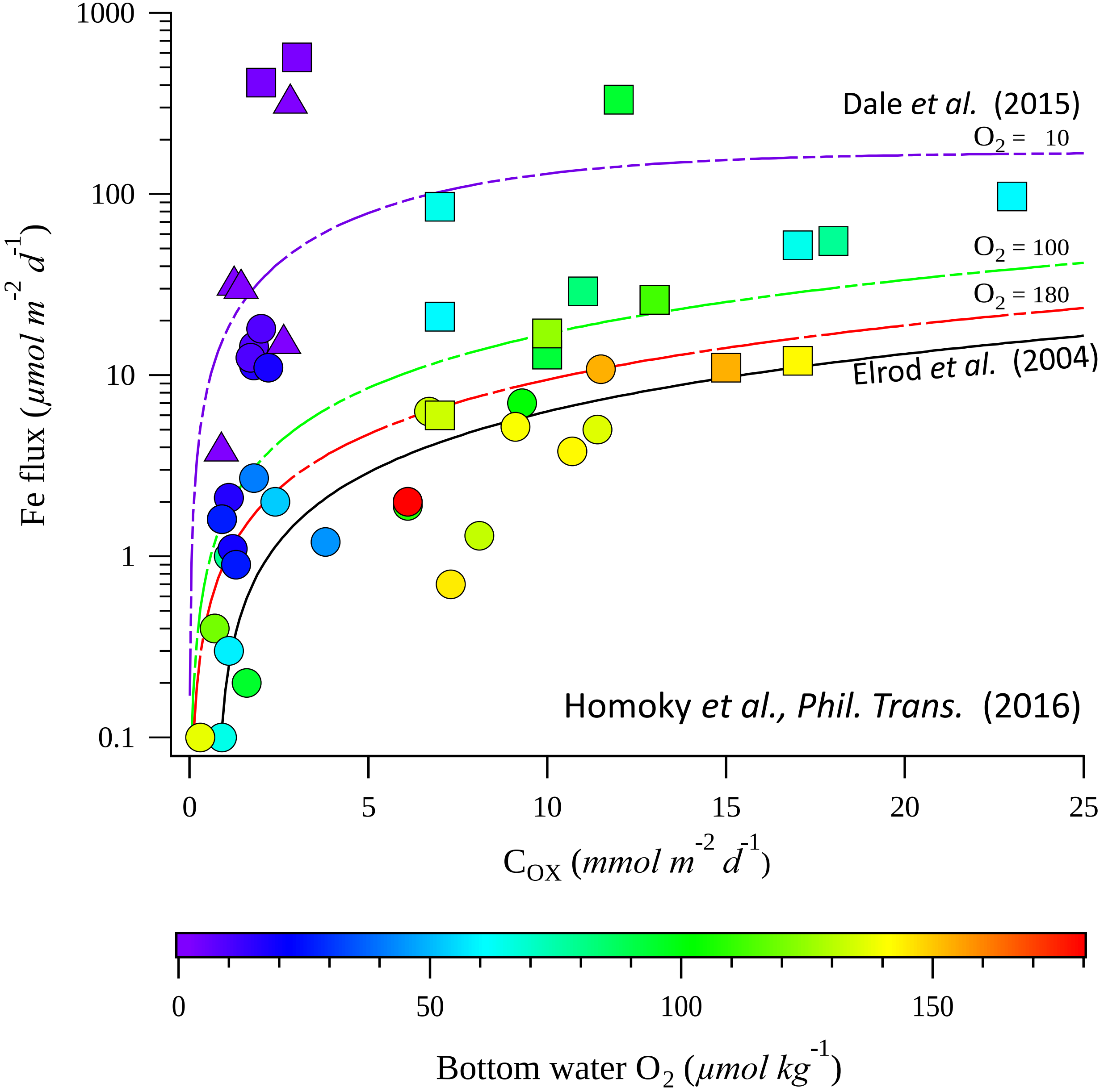




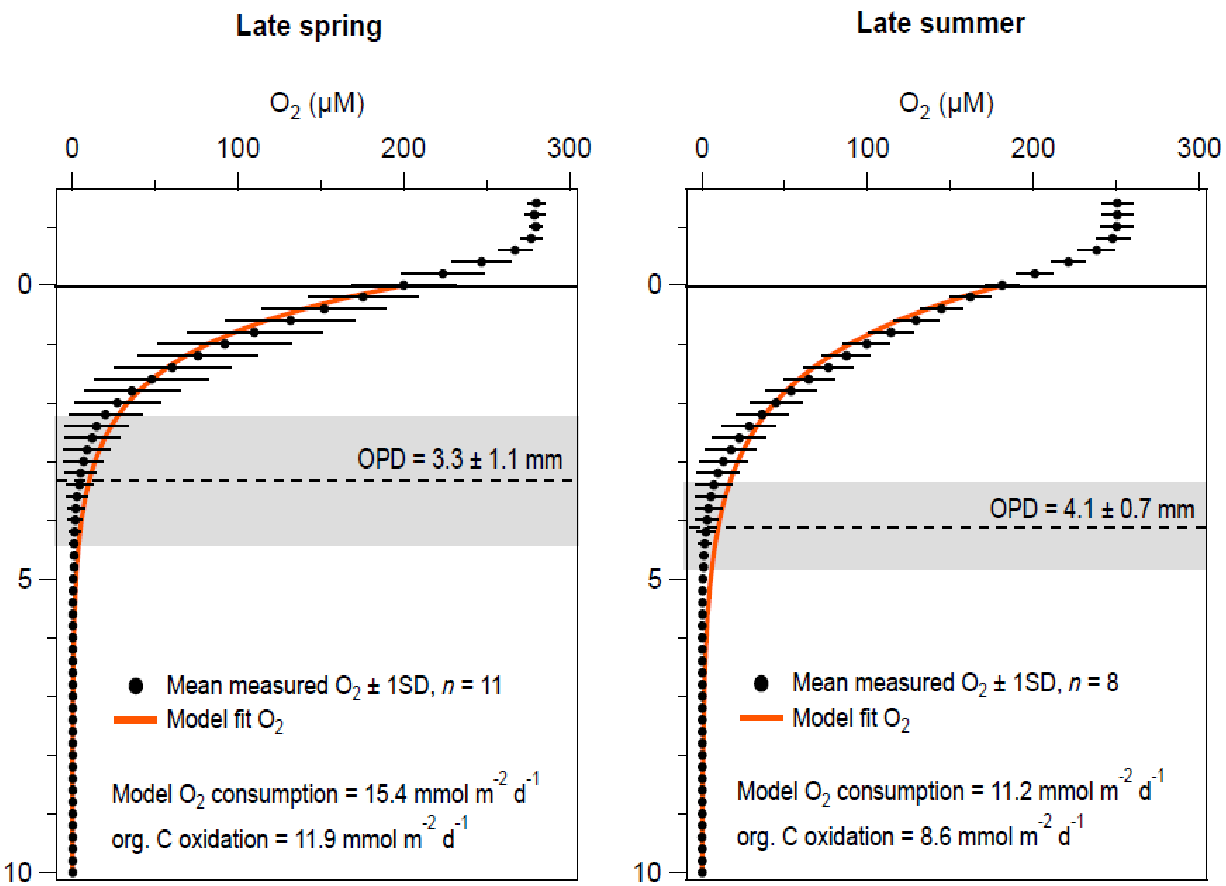
Seasonal and ligand-promoted benthic Fe flux



Comparison to global Fe flux relationships



$$\text{Fe flux} = 170 \bullet \tanh\left(\frac{C_{ox}}{O_{2BW}}\right)$$



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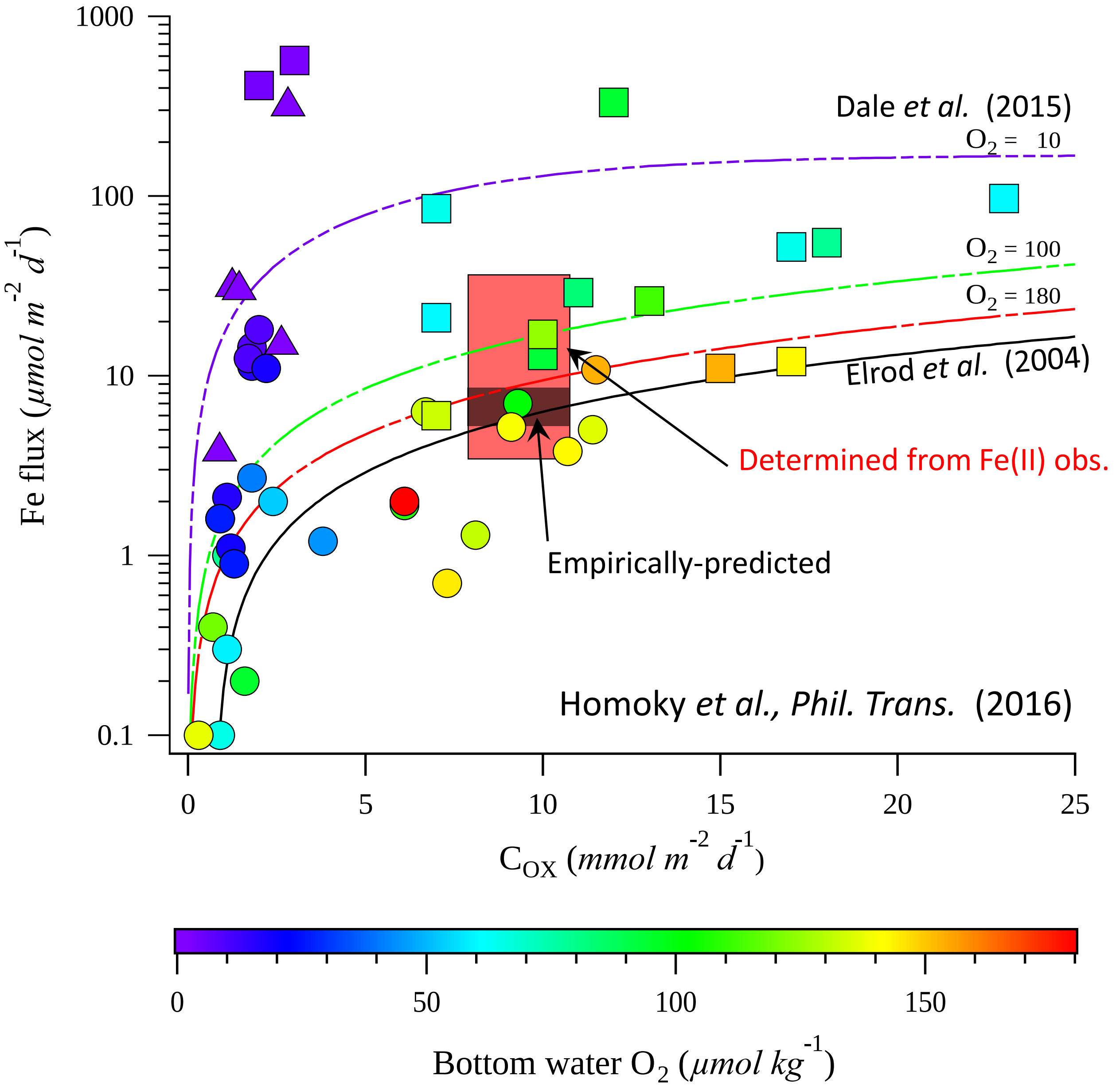


Dale *et al.* (2015)

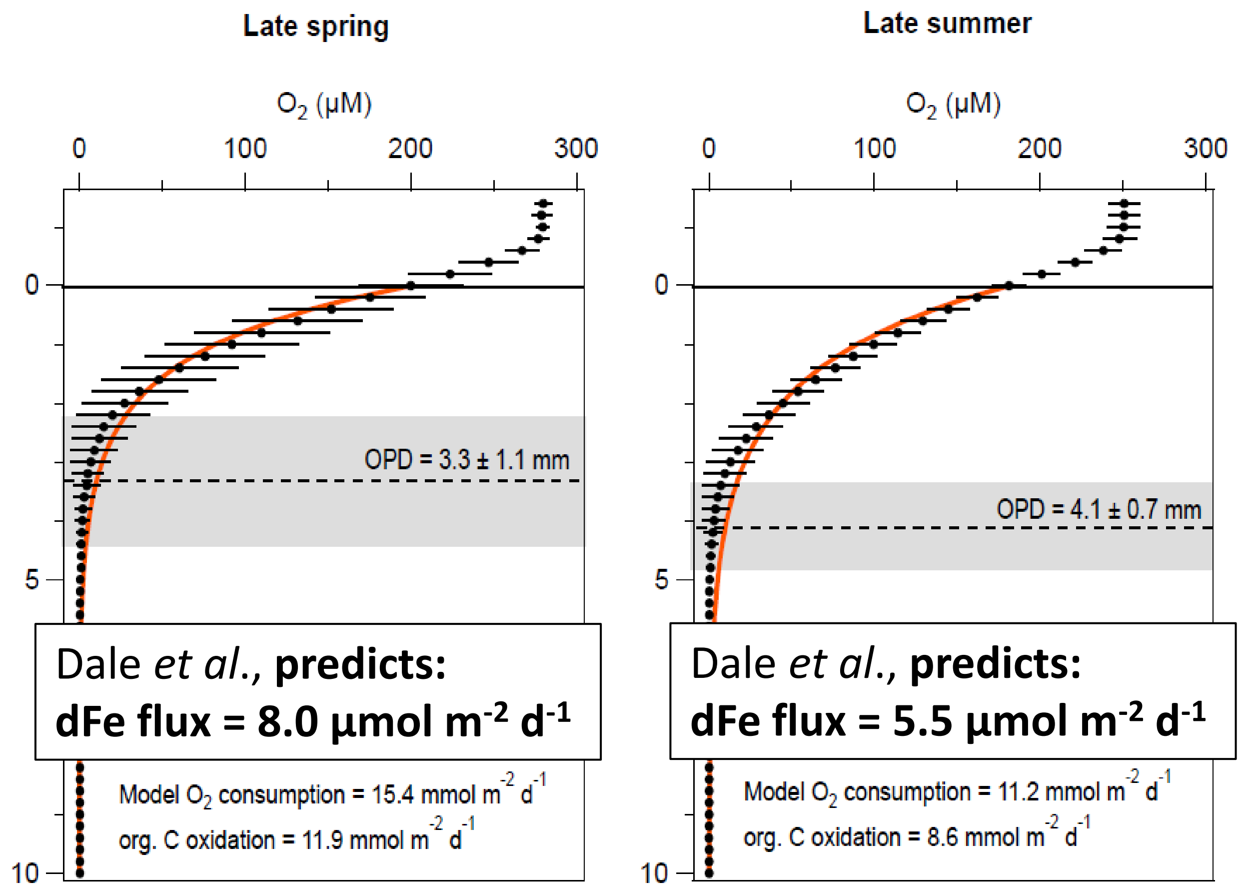
Elrod *et al.* (2004)

Determined from Fe(II) obs.

Empirically-predicted

Homoky *et al., Phil. Trans.* (2016)

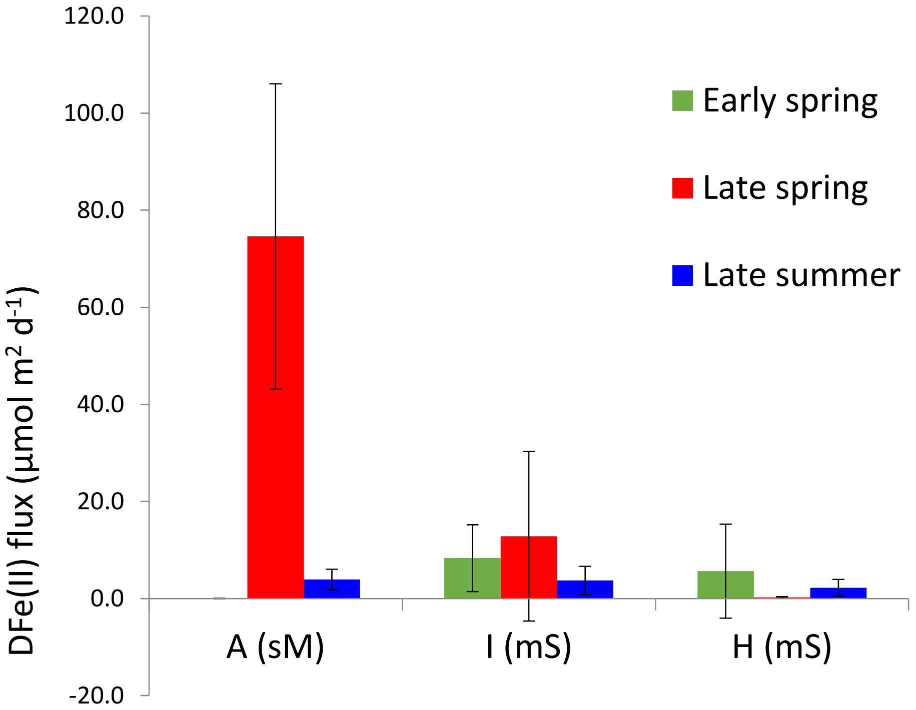
$$\textit{Fe flux} = 170 \bullet \tanh\left(\frac{C_{ox}}{O_{2BW}}\right)$$



Dale *et al.*, **predicts:**
dFe flux = 8.0 µmol m^{-2} d^{-1}

Dale *et al.*, **predicts:**
dFe flux = 5.5 µmol m^{-2} d^{-1}

Diffusive calculations bias importance of muds



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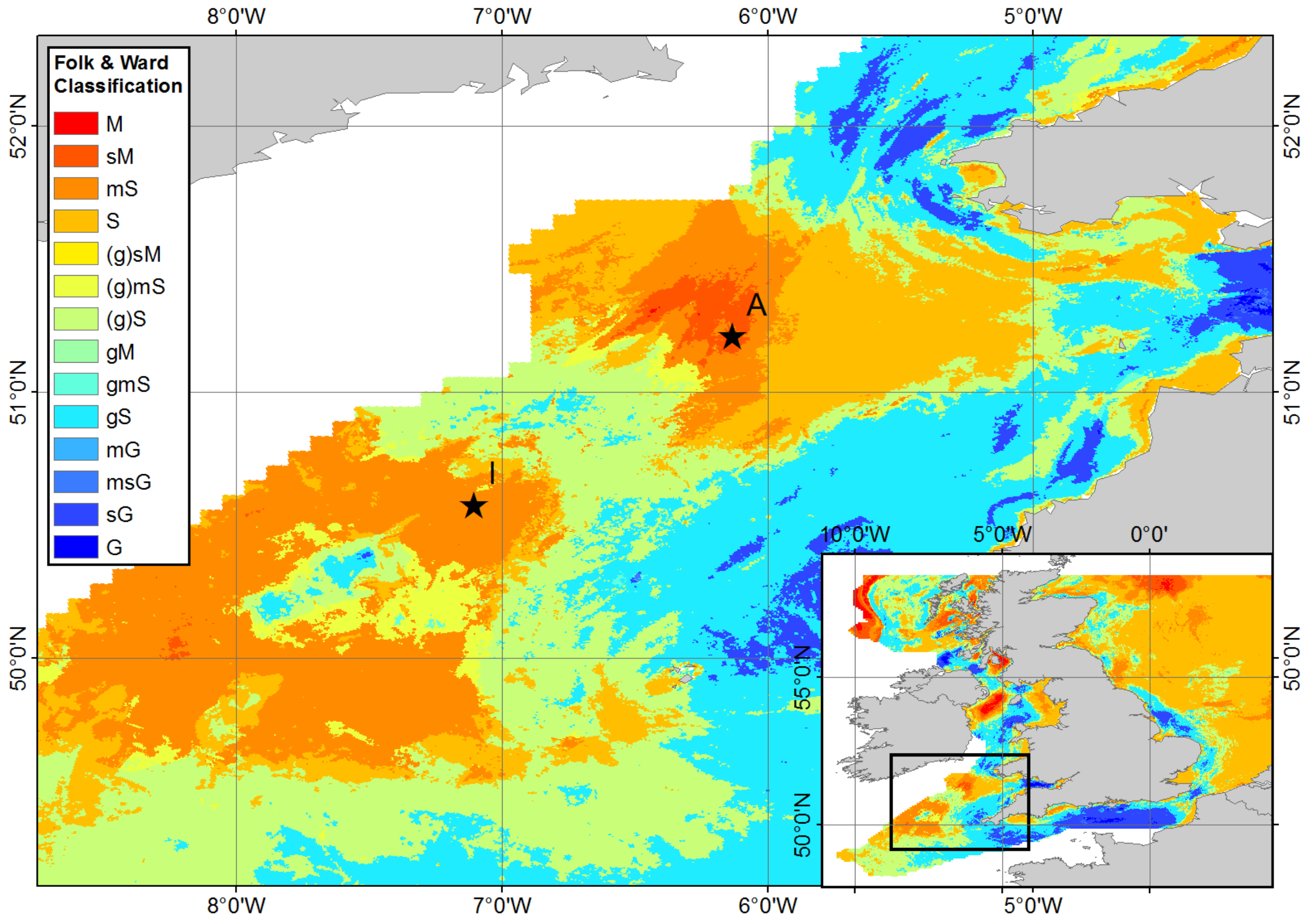
Klar *et al., BGC*
(2017)



Conclusions

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1. Org. C. in Celtic Sea sediments promotes inventory of isotopically light, reduced and soluble Fe(II) in shallow porewaters.

2. Org. ligands reasoned to account for abundance and longevity of Fe(II) in bottom waters

3. Benthic fluxes of Fe(II) from a steady-state diffusion-reaction model are 4-24 µmol m^2 d^{-1}; first order similarity to empirical predictions, but…

4. We show pronounced seasonality of Fe(II) fluxes in a temperate shelf, and suggest fluxes could be 10-30% greater (up to 33 µmol m^2 d^{-1}) if ligands inhibit Fe(II) oxidation.

5. By combing (bio-physical) advection-dominated transport studies of Fe (e.g. Annett et al., Reynolds et al., In prep etc.), the SSB programme is poised to integrate new mechanistic knowledge of Fe supply rates from temperate shelf seas to the oceans.

Thank you