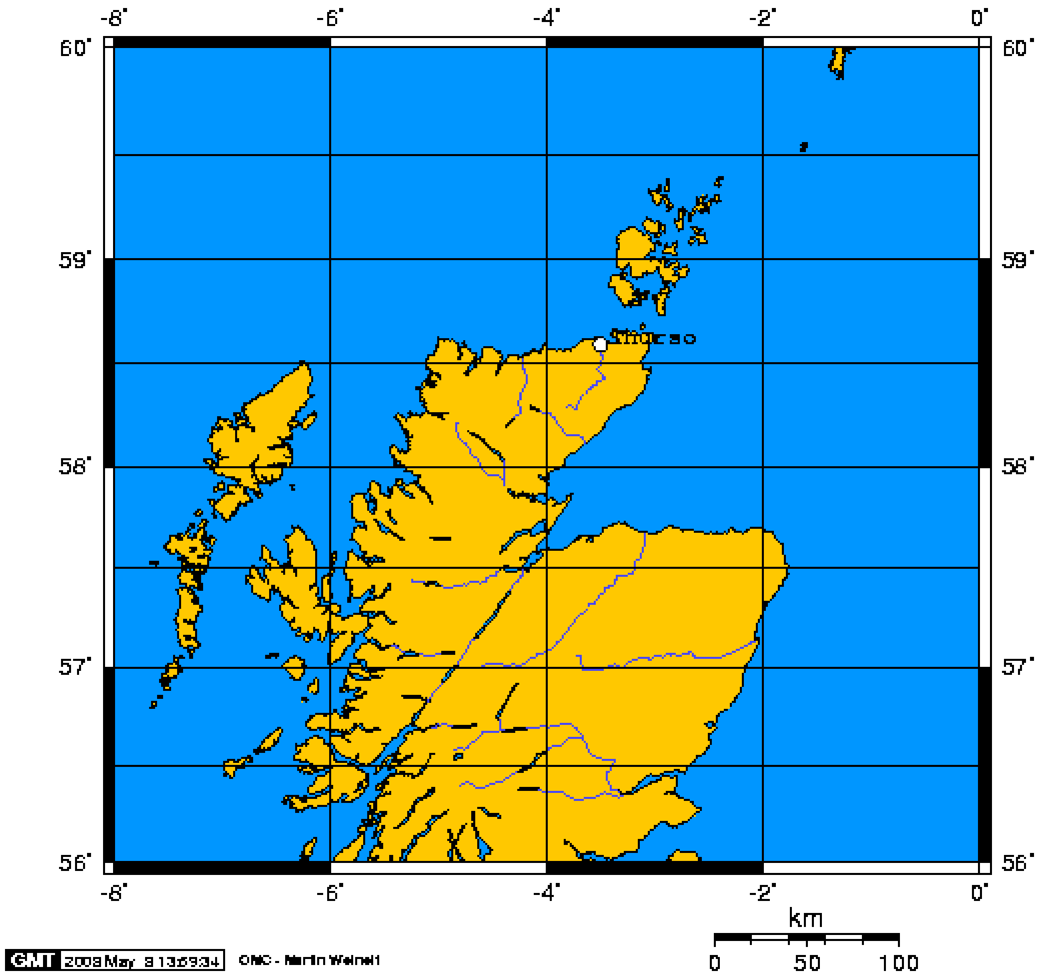
Fluorescence, fractionation behaviour and iron binding properties of colloidal organic matter from a black water estuary

Silvia Batchelli

Environmental Research Institute
Thurso, Scotland, UK

Introduction



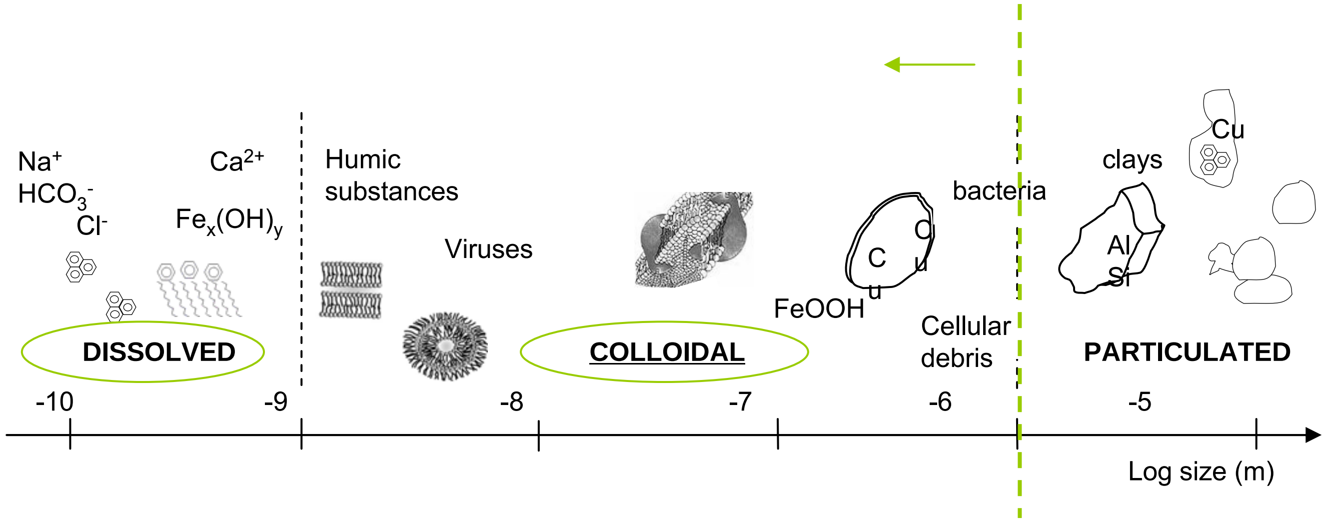
Introduction

- Large quantities of natural organic mater (drainage of Peatlands)
- Fast flow (~10.8 $m^3 s^{-1}$)
- Low microbial activity

↓

Conservative estuarine mixing of bulk properties
(i.e. DOM)

Introduction



COLLOIDS

- Wide range of entities with at least one dimension between 1 nm – 1 µm. Chemically heterogeneous and polydisperse.

- binding properties affecting the physicochemical forms and the bioavailability of trace metals

Objectives

- Study the relationship between colloidal architecture, molecular weight and metal-binding properties
- Determine how this relationship changes along the estuarine mixing zone, so as to be able to predict colloidal and metal behaviour and fate

1. Characterization of colloids
2. Characterization of colloid-metal interactions

Methods - Sampling

Natural estuarine samples

Salinity	pH
0.1	8.4
4.0	8.2
12.6	8.6
33.8	8.3

Solutions of Nordic Natural Organic Matter (NOM)

1kDa freshwater (ml) [NOM] = 30 mg l^{-1}	1kDa seawater (ml)	Measured salinity	pH
1500	0	0.1	8.2
1350	150	4.3	8.0
950	550	12.7	8.1
100	1400	33.3	8.5

Isolation of colloids

COLLOID ISOLATION - Cross-flow filtration (CFF)

- Bulk sample (B): <0.45 μm

- Permeate (P): Truly dissolved (LMM) <5 kDa
- Retentate (R): Colloidal fraction (5 kDa – 0.45 μm)

Methods

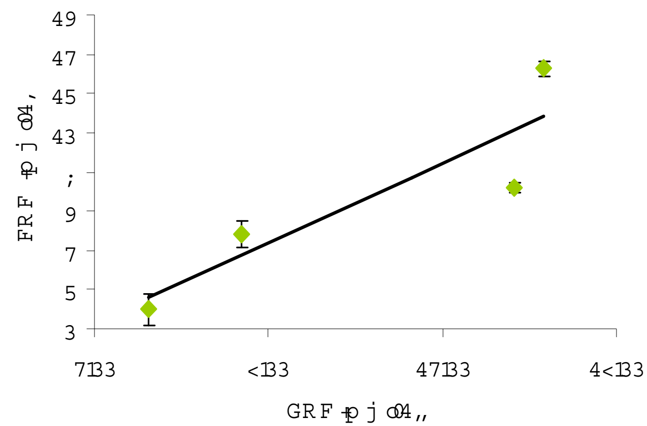
COLLOID CHARACTERIZATION – Analytical techniques

- UV-absorption measurements 320-720 nm
- Fluorescence measurements (3D-EEM)
- Inorganic and organic carbon determinations
- Estimation of average diffusion coefficients and hydrodynamic radii by:
    - dynamic light scattering (DLS)
    - flow-field flow fractionation (FIFFF)

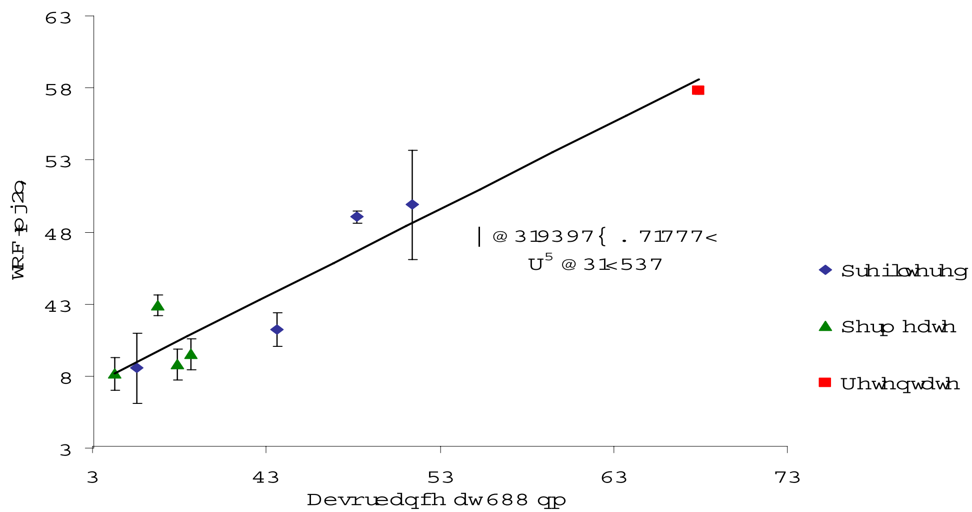
Results

Colloidal organic carbon

40-60% of the organic carbon is found to be colloidal in the estuary, with the exception of high salinities where the values decrease under 20%



TOC-Absorbance (355 nm)

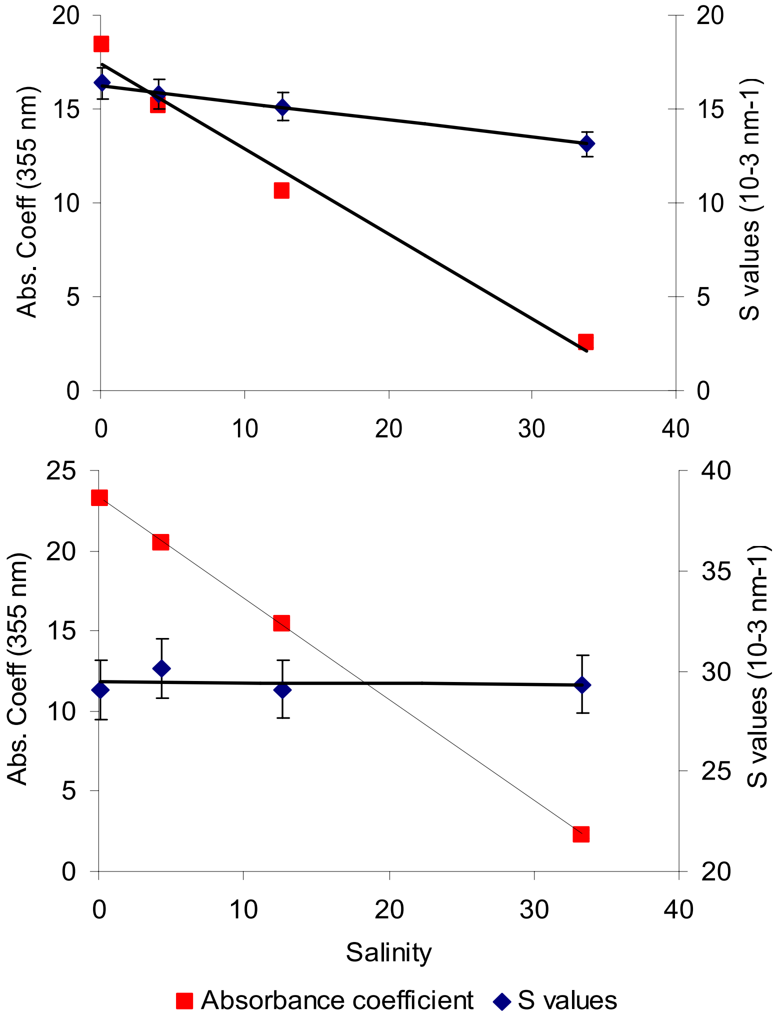


Results

Absorbance coefficients and slope (S) values

River Thurso

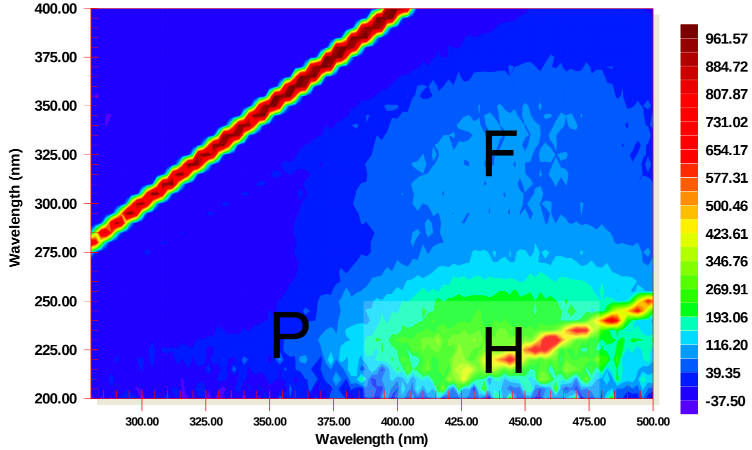
Nordic NOM Samples



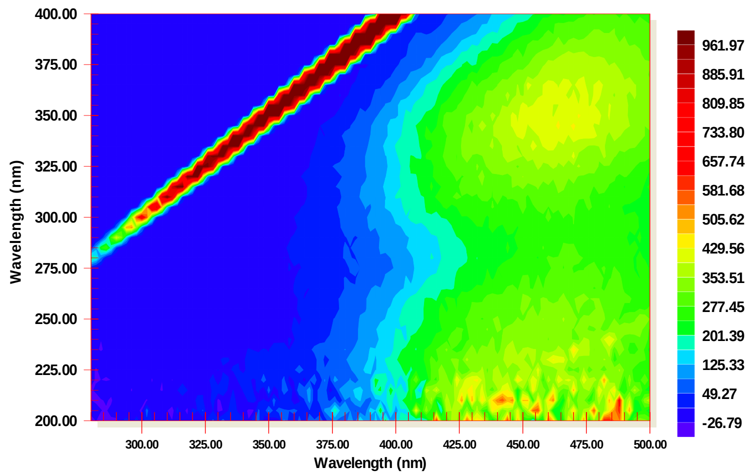
Results

Fluorescence

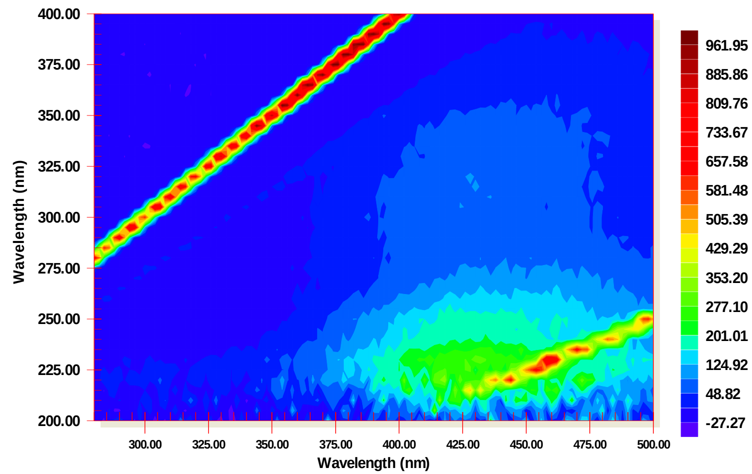
Bulk



Retentate

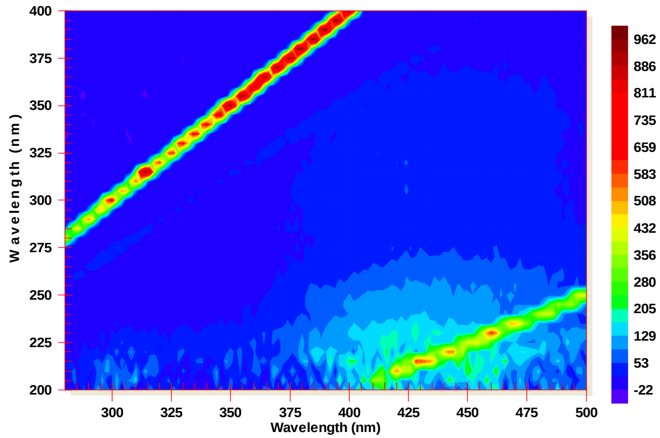


Permeate

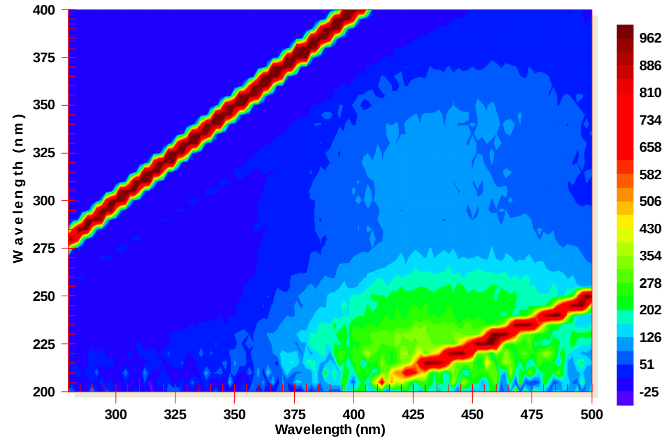


Results

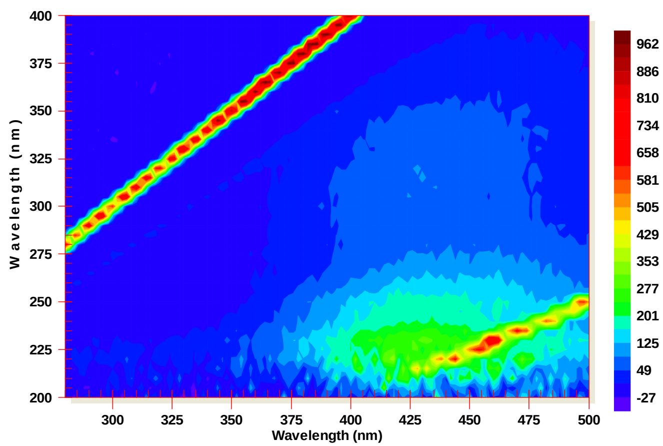
Fluorescence – Truly dissolved fraction (P)



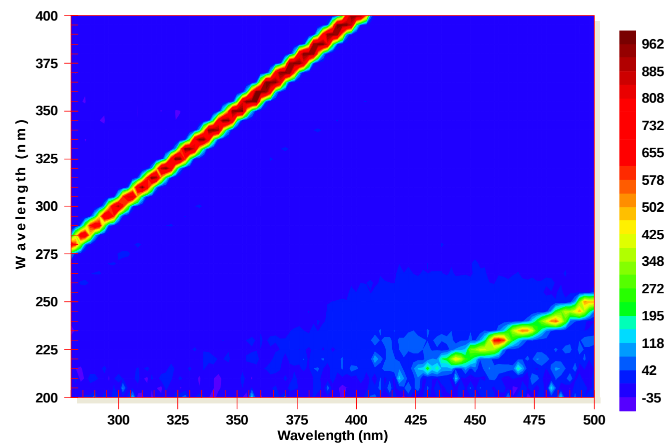
S=0.1



S=4.0



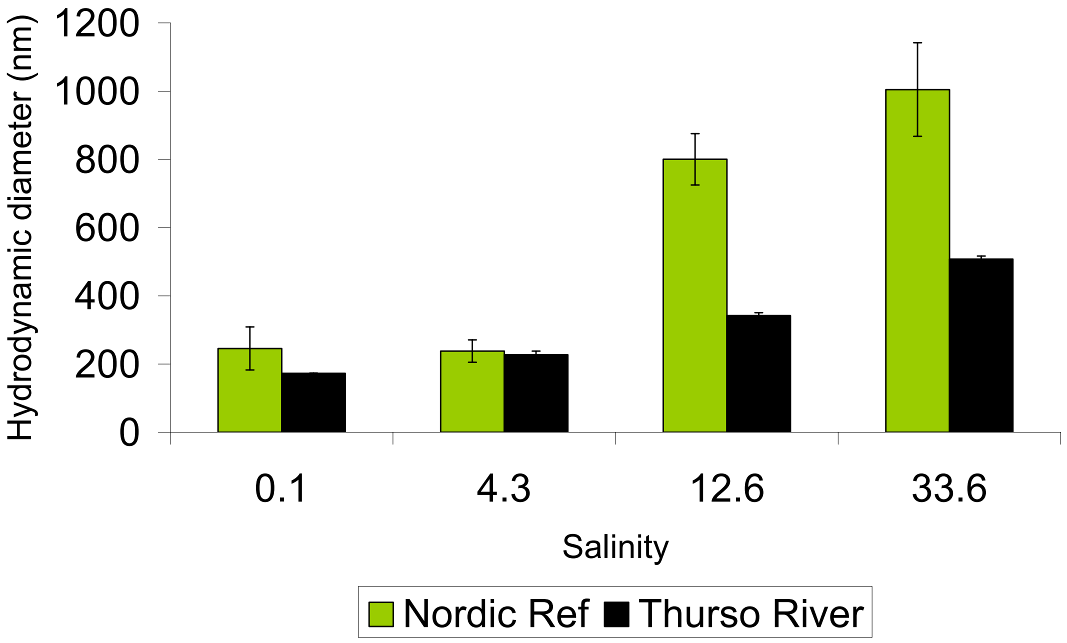
S=12.6



S=33.8

Results

Colloidal size characterization (DLS results)



Results

Colloidal size characterization (FIFFF results)

	Salinity	d_n	d_w/d_n
Thurso River retentate	0.1	2.11 ±0.04	1.21 ±0.04
	4.3	2.47 ±0.09	1.35 ±0.09
	12.6	2.46 ±0.07	1.31 ±0.03
	33.6	2.99 ±0.36	1.37 ±0.10
Nordic NOM retentate	0.1	2.79 ±0.17	1.44 ±0.09
	4.3	2.82 ±0.04	1.42 ±0.13
	12.6	2.87 ±0.10	1.33 ±0.08
	33.6	3.79 ±0.52	1.57 ±0.13

Objectives

1. Characterization of colloids

2. Characterization of colloid-metal interactions

C= 30 mg/l

Fe= 0.23 mg/l

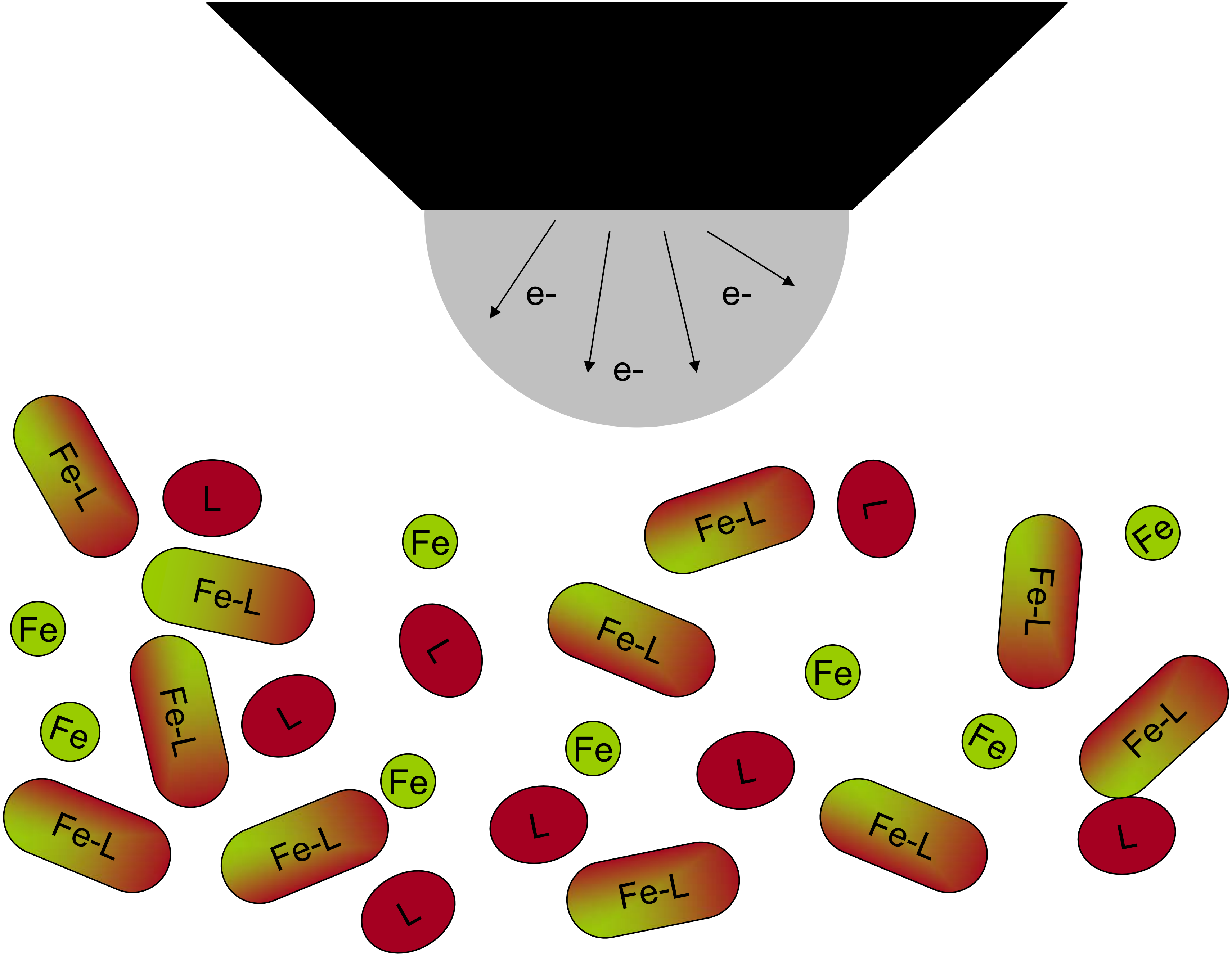
→ Fe and organic matter are likely to interact

Methods

COLLOID-METAL INTERACTIONS – Analytical techniques

- Total Fe determination by ICP-OES

- Direct detection of NOM-Fe associations by Adsorptive Cathodic Stripping voltammetry (Laglera et al. 2007)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Fe-L

Methods

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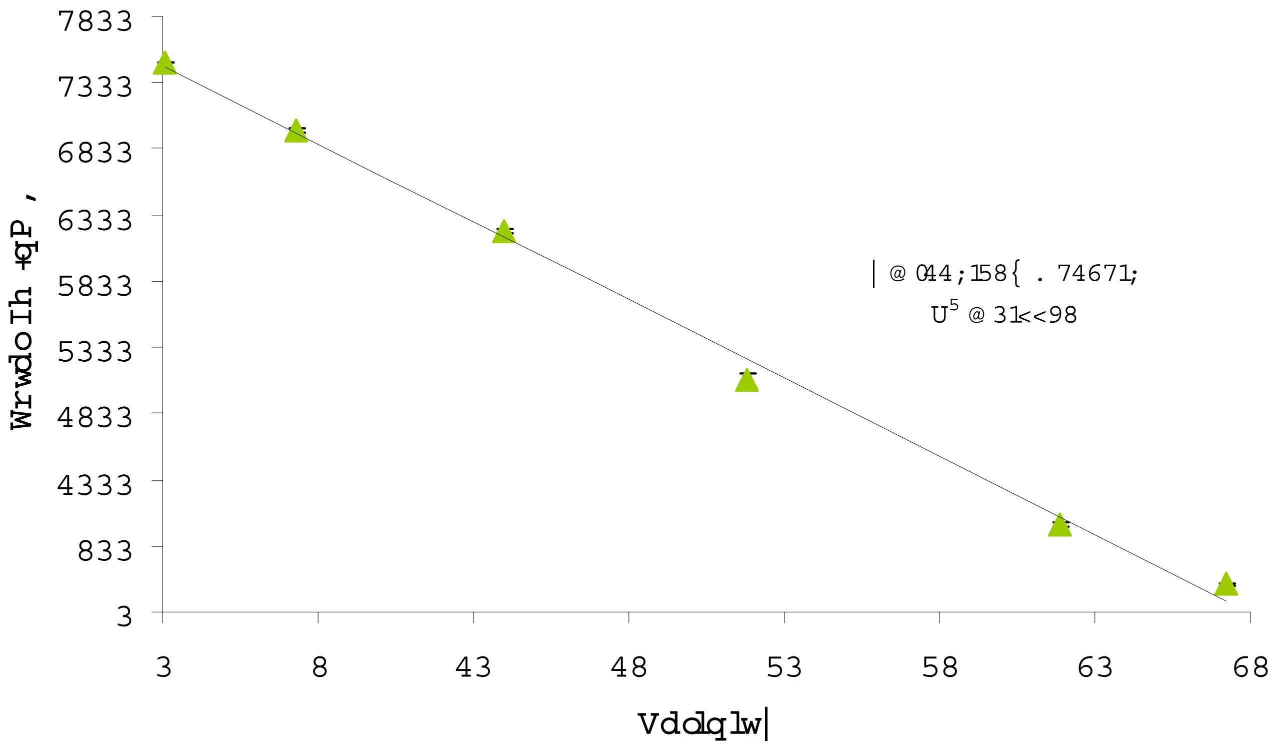
Results

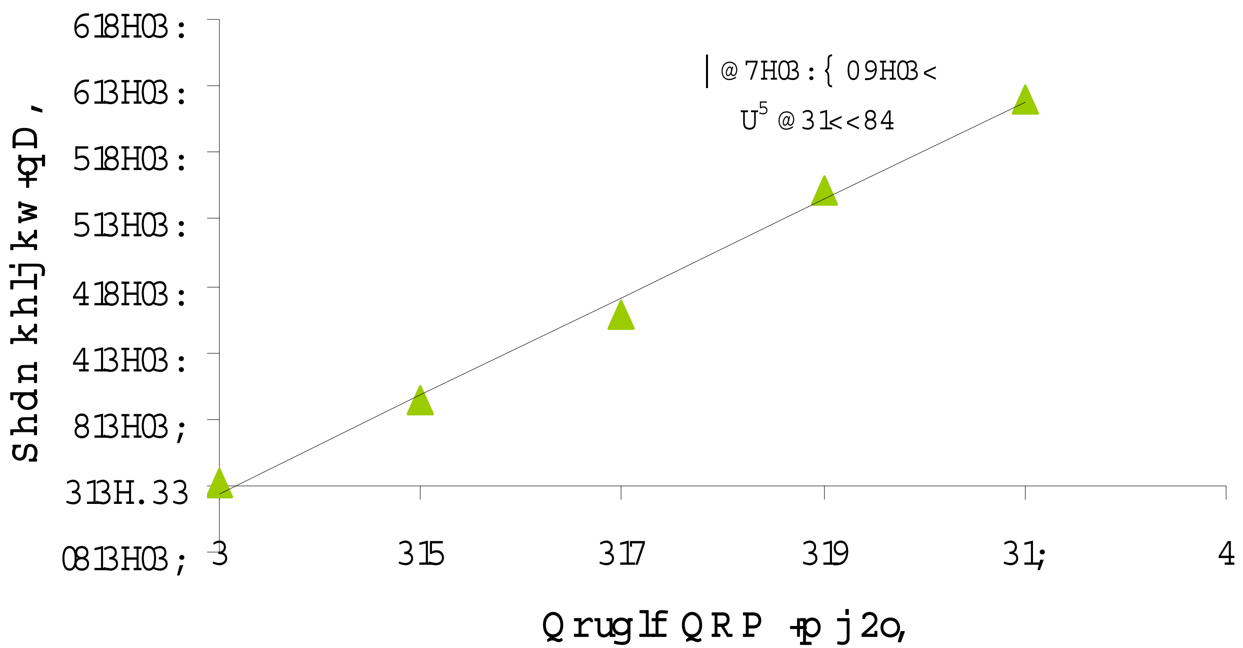
1. Introduction
2. Objectives
3. Colloid characterization
   - Methods
   - Results
4. Colloid-metal interactions
   - Methods
   - Results
5. Conclusions
6. Further work

Iron estuarine mixing behaviour (Total Fe)



Results

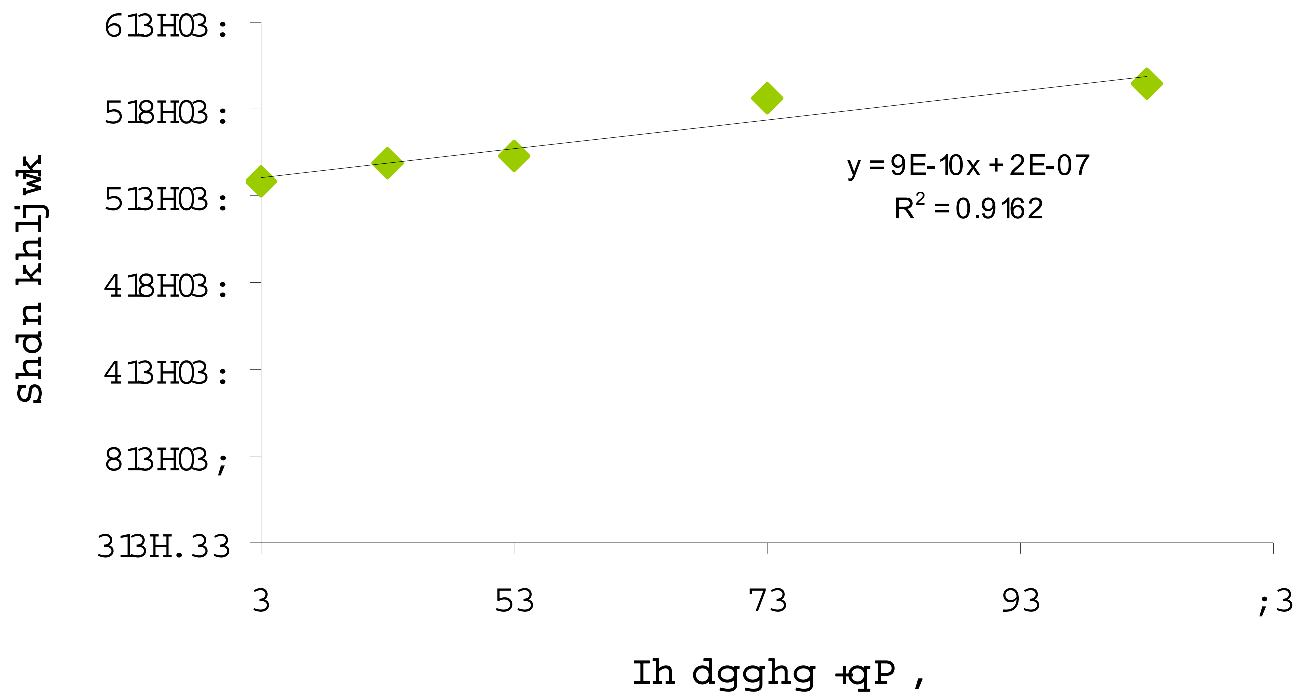
NOM-Fe binding properties



Bulk fraction (<0.4 µm) S= 34.5; pH=8.1 Fe added=20 nM

Results

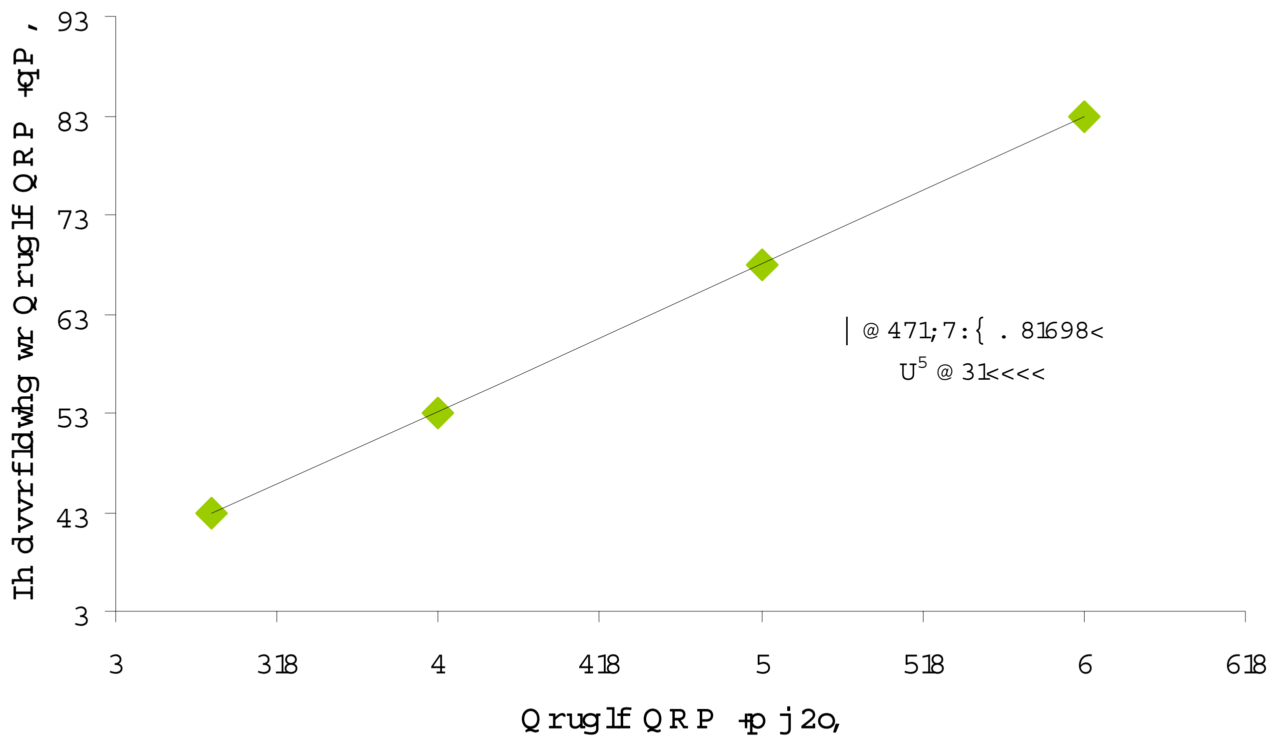
NOM-Fe binding properties



Bulk fraction (<0.4 µm) S= 34.5; pH=8.1 NOM= 0.6 mg/l

Results

NOM-Fe associations – LMW (permeate)



Low molecular weight fraction S= 34.5; pH=8.1

Conclusions

- Fluorescence results reveal a dynamic, salinity driven, exchange between the colloidal and the dissolved pools of organic matter.

- Large quantities of unaltered terrestrial organic matter reach the marine environment where they may be subject to photochemical or microbial degradation.

- Colloidal size tends to increase with salinity, in accordance with the colloidal pumping theory developed by Honeyman & Santschi (1989). This may have far-reaching implications for the reactivity of associated minor and trace elements.

- Added Fe reacts rapidly and strongly with the naturally occurring NOM, and the electroactive complex formed produces a signal which is proportional to both Fe and NOM.

Further work

- Since the colloidal fraction is too concentrated for the voltammetric method presented, the CFF system should be operated in the diafiltration mode whereby colloids are kept at the same (or more dilute) concentration while being transferred to a synthetic medium.

- There is a need to identify a synthetic ligand that will establish a balanced competition for Fe with the natural organic ligands and be measurable at a different potential.

- The fate of Fe-colloids in the coastal environment remains to be investigated. Which are the most important transport pathways and removal processes? Can terrestrial colloids provide a source of iron and reactive organic carbon to the North Sea?

Acknowledgements

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THANK YOU!

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