

Supporting information

The role of natural organic matter in controlling the size and oxidation state of Fe in natural waters

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8 pages of supporting information containing detailed methods, 3 tables and 1 figure.

Ensuring the molarity of base used in laboratory simulations

0.01M NaOH was prepared once from a sealed supply of 2M stock (Analar, BDH) and immediately transferred to a burette which it completely filled. The burette was sealed with a molecular sieve that allowed air pressure equalisation and pumping of the titrant but prevented its contact with CO₂.

The molarity of the base was checked before each titration, as the autotitrator measured its pH. The pH was also calibrated prior to each titration.

Defining an upper limit to the potential amount of Fe (II) production by reduction of Fe(III) during the ferrozine assay

Waters containing Fe and OC at all the Fe concentrations and Fe:OC ratios relevant to both laboratory and field investigations were prepared using both Fe³⁺ (added as an acid solution to water containing HA – resultant pH 6.5) and Fe(OH)₃ (precipitated by titration to pH 6.5 of an acid solution prior to addition of water containing HA – resultant pH 6.5) as the starting materials. The resulting Fe speciation is shown in Table S-1.

Controlling the interference of OC on the colorimetric measurement of ferrozine at 562nm

Rather than several calibration curves being prepared, each appropriate for water of a particular OC concentration, a single curve was prepared from Fe(II) in DIW. When analysing samples the optical effects of any OC present were removed by subtracting from the absorbance of the sample that of a blank, before reading the Fe(II) concentration from the calibration curve.

It was determined that the absorbance of ferrozine alone at the concentration used in these tests was equivalent (within error at 95% confidence, n=3) to DIW (Table S-2). Therefore, the absorbance of one or other of the following was used as the blank and subtracted from the absorbances of the samples:

- for the laboratory systems – water containing the same concentration and type of OC as the sample but diluted with a volume of DIW equivalent to the aliquot of ferrozine that would be added to the test sample
- for the field samples – the water sample diluted with a volume of DIW equivalent to the aliquot of ferrozine that would be added to the test sample.

To verify that correction of each sample by subtraction of blanks rather than preparing calibration curves for each type of water was accurate, the absorbance of several dilutions of a sample containing Fe(II), ferrozine and OC are shown in Figure S-1. The appropriate summed blanks have been subtracted from these absorbances and this results in their equivalence (within error at 95% confidence, n=3), throughout the concentration range measured in this work, to the absorbance of samples without OC.

Ultrafiltration method and quality assurance

The procedure of Ross and Sherrell (1) has been followed; for each filter plate the proportion of Fe / C in permeate and retentate were calculated by subtracting the mass in the filtrate from the starting mass:

$$(1) \text{ cR} = \text{S} - \text{P}$$

Where cR is the calculated retentate mass, S the starting mass and P the permeate mass. Figures are drawn using proportions calculated from cR.

For quality control, however, the amount of Fe / C trapped within the filter units was calculated by measuring the retentate mass:

$$(2) \text{ T} = \text{S} - (\text{P} + \text{mR})$$

Where T is the trapped mass, S the starting mass, P the permeate mass and mR the measured retentate mass. The mass balance for each sample and each filter plate is shown in Table S-3 we also include a mass balance amended by addition of Fe / C recovered from each plate in a series of washings (recirculation of 100ml DIW then 100ml DIW adjusted to pH 2 with conc. HNO₃, both for 40 minutes) subsequent to sample processing.

References

- (1) Ross, J. M.; Sherrell, R. M. The role of colloids in tracemetal transport and adsorption behaviour in New Jersey pineland streams. *Limnol. Oceanogr.* **44**, 1019-1034.

		A Measured	B Potential corrections				C Corrected
Fe as	Fe:OC mg/l : mg/l	Fe(II)	Fe ³⁺		Fe(OH) ₃		Fe(II)
		% Fe(II)	% Fe(II)	Error +/-	% Fe(II)	Error +/-	% Fe(II)
Fe / HA	1 : 12	77	37.2	5.7	6.8	2.8	34.1
Fe / HA	5 : 12	9.8	2.8	1.8	3	1.8	5.2
Fe / HA	5 : 19	14.2	5.9	0.3	4.1	1	8.0
Fe as		Unknown (Field)					
P low	2.1 : 6.3	61.1	4	1.8	4.3	1.9	54.9
P high	1.2 : 9.7	67.3	21.8	7.9	8.3	0.5	37.6
PM low	0.39 : 3.56	71.6	38.4	11.2	15.9	12.1	22.0
PM high	0.46 : 9.15	86.7	47	13.3	19.1	6.1	26.4

Table S-1: (A) Variations in the proportion of total Fe present as bound Fe(II) when Fe in the form of Fe(II), is mixed with HA in a range of concentration ratios, and also, in field samples in which Fe would have been in an unknown form initially. (B) Variations in the proportion of total Fe present as bound Fe(II) when Fe in the form of Fe(III) or Fe(OH)₃ is mixed with HA. These proportions represent the maximum amount of Fe(II) that may have been present in the corresponding samples in (A) as a result of Fe(III) reduction by HA rather than binding of Fe(II) to HA. (C) The proportions from (A) corrected by subtraction of the greatest corresponding proportion in (B) including +ve error (confidence limits at 95%, n=3).

HA (mg l ⁻¹)	Absorbance at 562nm								
	DIW	Fz	Error +/-	HA	Error +/-	HA + Fz (separate)	Error +/-	HA + Fz (mixed)	Error +/-
3.5	0.008	0.01	0.005	0.017	0.008	0.019	0.009	0.015	0.005
6	0.008	0.01	0.005	0.025	0.005	0.027	0.007	0.026	0.007
10	0.008	0.01	0.005	0.036	0.001	0.038	0.005	0.042	0.006
12	0.008	0.01	0.005	0.041	0.003	0.043	0.006	0.043	0.010
19	0.008	0.01	0.005	0.068	0.007	0.070	0.008	0.069	0.007

Table S-2: Humic acid (HA) colorimetric response. Error expressed at 95% confidence limits, n = 3.

DIW denotes de-ionised water and Fz denotes ferrozine.

Sample	Element	Start Mass	% mass balance (No washings)			% mass balance (With washings)		
			0.2µm	50kD	10kD	0.2µm	50kD	10kD
AA	C	2.38	79.5	98.4	-	87.6	114.6	-
HA	C	2.75	61.5	84.1	-	67.8	109.1	-
P	C	3.52	97.7	97.3	111.3	102.8	106.3	122.1
PM	C	3.78	78.5	109.4	74.4	89.7	118.0	88.2
30HA	C	1.23	75.3	94.4	-	76.3	96.4	-
50HA	C	1.83	79.7	99.8	-	97.7	129.0	-
30AA	C	1.32	92.3	95.6	-	103.6	117.9	-
50AA	C	1.99	86.6	89.9	-	104.0	123.3	-
P	Fe	0.32	100.9	83.9	53.1	113.6	96.2	67.7
PM	Fe	0.19	75.8	98.9	61.5	85.1	110.9	77.4
30HA	Fe	0.5	80.2	75.5	-	84.4	81.5	-
50HA	Fe	0.5	76.1	82.4	-	84.1	88.8	-
30AA	Fe	0.5	85.0	85.0	-	89.3	92.7	-
50AA	Fe	0.5	69.5	73.0	-	73.5	80.0	-

Table S-3: Deviations from mass balance (100%) for each filter plate. Each % is calculated as a proportion of the initial starting mass which is shown in the third column. Mass balances into which have been included the material recovered by washing are also shown.

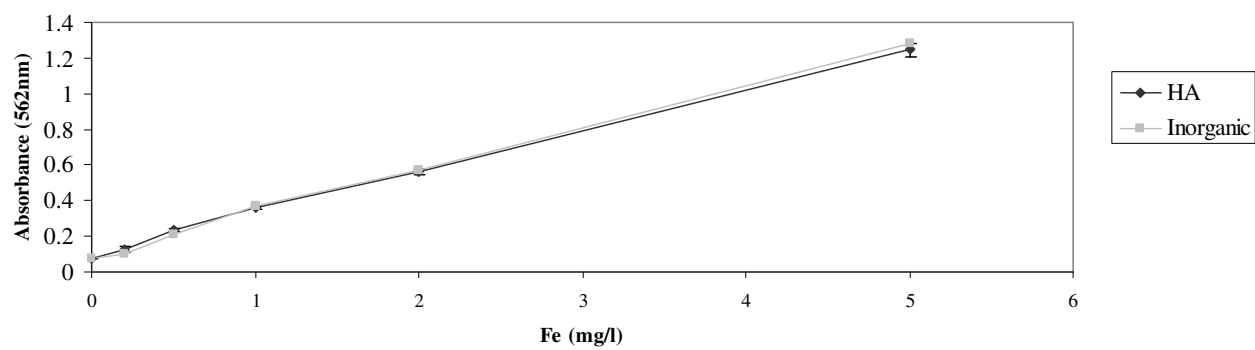


Figure S-1: Calibration curve constructed with Fe(II) standards made up in DIW (Inorganic) and containing different concentrations of OC (HA) at pH 2.