

Article (refereed)

Lofts, Stephen; Tipping, Edward; Hamilton-Taylor, John.
2008 The chemical speciation of Fe(III) in freshwaters.
Aquatic Geochemistry, 14 (4). 337-358.
doi:10.1007/s10498-008-9040-5

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4 **The chemical speciation of Fe(III) in**
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7 **freshwaters**
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4 Abstract

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7 Dialysis and chemical speciation modelling have been used to calculate activities of Fe^{3+}
8 for a range of UK surface waters of varying chemistry (pH 4.3-8.0; dissolved organic
9 carbon 1.7-40.3 mg l^{-1}) at 283K. The resulting activities were regressed against pH to
10 give the empirical model:

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$$\log a_{\text{Fe}^{3+}} = 2.93(\pm 0.40) - 2.70(\pm 0.06) \text{ pH}$$

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16 Predicted Fe^{3+} activities are consistent with a solid-solution equilibrium with hydrous
17 ferric oxide, consistent with some previous studies on Fe(III) solubility in the laboratory.
18 However, as has also sometimes been observed in the laboratory, the slope of the
19 solubility equation is lower than the theoretical value of three. The empirical model was
20 used to predict concentrations of Fe in dialysates and ultrafiltrates of globally distributed
21 surface and soil/ground waters. The predictions were improved greatly by the
22 incorporation of a temperature correction for $a_{\text{Fe}^{3+}}$, consistent with the temperature-
23 dependence of previously reported hydrous ferric oxide solubility. The empirical model,
24 incorporating temperature effects, may be used to make generic predictions of the ratio of
25 free and complexed Fe(III) to dissolved organic matter in freshwaters. Comparison of
26 such ratios with observed Fe: dissolved organic matter ratios allows an assessment to
27 be made of the amounts of Fe present as Fe(II) or colloidal Fe(III), where no separate
28 measurements have been made.

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36 *Iron; speciation; solubility; freshwater; dialysis; ultrafiltration*

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39 **1 Introduction**

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42 Iron is one of the most abundant elements on Earth, and is considered
43 essential for living organisms. It is highly reactive in the freshwater
44 environment, has an oxidation-reduction chemistry that is an important
45 aspect of its aquatic cycling behaviour, and has been shown to have a
46 number of significant roles in the cycling and bioavailability of other
47 elements. In oxic freshwaters the +3 oxidation state is the
48 thermodynamically stable form (Davison, 1993). Iron(III) influences the
49 speciation and bioavailability of phosphorus in lakes (Jones et al., 1993),
50 promotes the decomposition of dissolved organic carbon in surface waters
51 by photochemical means (Stumm and Morgan, 1996), and forms
52 particulate oxides and hydroxides (hereafter collectively referred to as
53 hydrous ferric oxide, HFO) capable of sorbing and transporting trace
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4 metals and anionic species (Dzombak and Morel, 1990) and dissolved
5 organic matter (DOM) (Tipping, 1981). More recently, the importance of
6 iron in limiting phytoplankton growth in the oceans has increased interest
7 in riverine fluxes to the oceans (Turner et al., 2001). Additionally, iron
8 influences the aquatic speciation and bioavailability of trace metals by
9 competing for common ligands such as natural organic matter (Tipping et
10 al., 2002). Clearly, knowledge of the speciation of Fe(III) is key in
11 developing a quantitative understanding of these processes.
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18 Our knowledge of inorganic Fe(III) chemistry indicates that in the range of
19 pH (6-9) of the majority of surface waters, the concentration of free and
20 complexed dissolved Fe(III) concentration should be very low due to
21 extensive hydrolysis and precipitation to form HFO. In practice, measured
22 concentrations of dissolved (i.e. filtered) Fe in such waters tend to be
23 larger, sometimes by several orders of magnitude, than concentrations
24 predicted by assuming equilibrium of Fe(III) with an HFO phase. The
25 presence of this additional dissolved Fe has been variously attributed to
26 dissolved organic complexes of Fe(III) (e.g. Perdue et al., 1976; Koenings,
27 1976) or to the presence of small particles of HFO, perhaps stabilised by
28 surface coatings of natural organic matter (e.g. Shapiro, 1966; Cameron &
29 Liss, 1984; Laxen and Chandler, 1983), but evidence for the relative
30 importance of these forms is somewhat lacking. Recent work on the
31 speciation of iron in natural waters (e.g. Rose et al., 1998; Olivie-Lauquet
32 et al., 1999; Benedetti et al., 2003; Allard et al., 2004) suggests that iron in
33 colloidal phases (variously defined with a lower nominal cutoff in the range
34 5-30 kDa) can exist both as organic complexes and small hydroxide
35 particles. Lyven et al. (2003) used flow field-flow fractionation to
36 demonstrate the presence of two distinct iron forms in a surface water- a
37 small fraction (largely below a nominal molecular weight of 30kDa)
38 associated with organic C, and a larger fraction rich in Fe itself. These
39 results are strongly suggestive of the presence of Fe(III) as a mixture of
40 organic complexes and an HFO phase, and also indicate that a reliable
41 size separation method can differentiate the two forms. Sophisticated
42 methods such as flow field-flow fractionation can provide invaluable fine
43 scale information on physical speciation, but are complex and not
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4 amenable to high sample throughput. A simpler separation technique,
5 amenable to use on large numbers of samples, is needed to investigate
6 spatial and temporal trends in Fe(III) speciation in surface waters.
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8 Ultrafiltration is reasonably well-established yet issues remain regarding
9 artefacts, such as the blockage of filter pores by suspended material, and
10 the formation of 'gel' layers at the filter surface. Dialysis, on the other
11 hand, is relatively simple and non-invasive, and has previously been used
12 to isolate small size fractions of metals (e.g. Benes and Steinnes, 1974;
13 Jansen et al., 2001).
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19 The ability to quantitatively separate the Fe in the size range below that in
20 which HFO is encountered would be highly useful in the study of whether
21 and how HFO controls the combined concentrations of free and
22 complexed Fe(III) (hereafter referred to as truly dissolved Fe(III)).
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24 Laboratory studies on synthetic forms of HFO indicate that for the solubility
25 equilibrium
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30 values for the standard solubility product K_{so} are in the range 10^{25} - 10^{50}
31 Allard et al. (2004) showed that the concentrations of colloidal organically-
32 complexed Fe(III) in waters from the Amazon region were consistent with
33 an equilibrium between the Fe^{3+} ion and an HFO with a single solubility
34 product within this range. However there has been no extension of this
35 work to other environments, particularly to temperate regions and to
36 soil/ground waters. Chemical speciation of a small size fraction from which
37 HFO has been removed would allow the Fe^{3+} activity to be estimated and
38 thus allow controls on Fe(III) solubility to be assessed. This would in
39 principle enable a general model of Fe(III) chemistry in freshwaters to be
40 constructed.
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52 The modelling of the binding of a metal such as Fe(III) to aquatic dissolved
53 organic matter (DOM) is complex, and a clear conceptual picture of the
54 binding properties of the DOM is required. Some workers consider the
55 binding to be to specific organic ligands, while others consider the binding
56 to be controlled by binding sites on the bulk of the organic matter, in
57 competition with protons and other trace metals. In the second hypothesis
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4 the degree of binding may in principle be related to the total concentration
5 of DOM whereas in the first hypothesis the concentrations of specific
6 ligands are not necessarily related to the total DOM concentration. In
7 previous work, Tipping et al. (2002) characterised the binding of Fe(III) to
8 isolated humic and fulvic acids using the WHAM/Model VI model and used
9 the parameterised model to simulate Fe(III) speciation in a limited number
10 of field samples, under the assumption that Fe(III) binding to DOC could
11 be related to its binding to fulvic acid. The model was able to describe
12 speciation in the data, if some reasonable variability in model parameters
13 among samples was allowed. There is, however, a pressing need to
14 further assess model performance against field data.
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23 In the work reported here, we have sampled and dialysed natural waters,
24 giving a dialysate excluding fine particulates in which the Fe(III) should be
25 present only in truly dissolved form. We have used WHAM/Model VI to
26 calculate Fe^{3+} activities in these samples, and used the results to produce
27 an empirical expression for the variation in Fe^{3+} activity with pH and
28 temperature. We have compared this expression with predictions of Fe^{3+}
29 activity derived from laboratory studies of Fe(III) solubility, and we have
30 shown how our results may be incorporated into speciation models either
31 empirically or by assuming equilibrium with an HFO-type phase. We then
32 make predictions of truly dissolved Fe(III) in dialysates and ultrafiltrates of
33 surface and soil/ground waters, reported in the literature. We have also
34 investigated the use of the Fe:DOM ratio in the truly dissolved fraction as a
35 means of assessing Fe speciation, and illustrated this using an extensive
36 dataset on UK surface waters.
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48 **2 Study sites**

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51 Surface water samples were obtained from 10 sites in the northwest of
52 England. Of the sites, seven are situated in the upland areas of the
53 Pennines and the Forest of Bowland. These areas are dominated by
54 blanket peats and rankers (relatively shallow organic-rich soils usually
55 developed directly over the underlying rock). Landscape types include acid
56 grassland, blanket bog and upland heathland. The underlying geology
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4 comprises both acidic and alkaline rock types. The remaining sites are
5 situated in the lowlands. Two of these (the River Lune and the River
6 Ribble) drain upland areas and were sampled close to their tidal limits.
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8 The third lowland site, Roudsea Wood, drains a complex of raised lowland
9 peat bogs. Two samples were obtained from seven of the sites. Of these,
10 four (the Rivers Hodder, Lune and Ribble, and the Whitray Beck tributary)
11 were sampled under high flow conditions in November 2003 and low flow
12 conditions in January 2004.
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19 **3 Experimental**

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22 Deionised water (conforming to the ASTM Type 1 standard) was used for
23 all dilutions and washings. Sample vessels of 5L or 10L volume were
24 used. All sampling vessels were soaked in 1% v/v nitric acid (BDH
25 'Aristar' grade) for 24 hours, followed by deionised water for 24 hours. On
26 return to the laboratory, bags of dialysis membrane (SpectraPor 7
27 regenerated cellulose, Spectrum Laboratories Inc., 3.5kDa, 10kDa and
28 15kDa molecular weight cutoff) containing deionised water were
29 suspended directly into the solution. All dialysis membranes were
30 thoroughly rinsed with deionised water prior to use. The solution volume
31 within each set of dialysis bags was 2% of the sample volume. Samples
32 containing dialysis bags were stirred at 10°C in the dark for seven days.
33 The dialysis bags were removed, rinsed thoroughly with deionised water
34 and the dialysate solutions removed. A portion was acidified with 5M
35 hydrochloric acid (BDH 'Spectrosol' grade; 200ml per 10ml sample) for
36 colorimetric analysis of total Fe and Fe(II). The remaining dialysate was
37 stored unaltered for analysis of dissolved organic carbon (DOC) and
38 monomeric aluminium. A portion of the outer sample solution was
39 retained for analysis of pH and conductivity. All solutions were stored in
40 the dark at 4°C until analysis.
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55 Field samples for the analysis of water chemistry were obtained at the
56 same time as experimental samples. Samples for the measurement of pH
57 were collected in thoroughly rinsed airtight glass vessels and analysed
58 within 24 hours. Samples for the analysis of major ions, alkalinity, DOC,
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4 monomeric aluminium and acid-reactive aluminium were taken in single-
5 use polyethylene terephthalate (PETE) bottles. Unfiltered samples were
6 analysed for alkalinity, monomeric aluminium and acid-reactive
7 aluminium. On return to the laboratory a portion of sample was filtered
8 (GF/F filters, Whatman Inc.) for the analysis of major ions, monomeric
9 aluminium and acid-reactive aluminium. Samples for the analysis of total
10 Fe and Fe(II) were taken in PETE bottles previously soaked in 1% (v/v)
11 nitric acid (BDH 'AnalaR' grade) and rinsed thoroughly with deionised
12 water. The samples were filtered (0.451µm cut-off filters, Whatman Inc.)
13 immediately on return to the laboratory and acidified with 5M hydrochloric
14 acid (BDH 'Spectrosol' grade; 200ml per 10ml sample) prior to storage for
15 analysis of total Fe and Fe(II). All samples were stored in the dark at 4°C
16 prior to analysis.
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26 Total Fe and Fe(II) were analysed colorimetrically using Ferrozine®
27 (Sigma-Aldrich Chemie GmbH) Gibbs (1979) in an acetic acid/sodium
28 acetate buffer at a wavelength of 562nm. Calibration was done using
29 solutions prepared from stock iron(III) nitrate standards (BDH 'Aristar'
30 grade). For the analysis of total iron, a reducing agent
31 (hydroxylammonium chloride) was added to standards and samples to
32 reduce Fe(III) to Fe(II), and a contact time of 10 minutes was allowed prior
33 to analysis. For the analysis of Fe(II), reducing agent was not added and
34 a contact time of 30s was allowed. Prior to analysis, the recovery of Fe(II)
35 from mixed Fe(II)/Fe(III) solutions (1:1 w/w) was analysed; the mean
36 recovery of 501Jg dm⁻³ (895nM) and 2501Jg dm⁻³ (4476nM) Fe(II) from
37 mixed solutions was 105.0%. Quality standards were prepared from an
38 independent iron(III) nitrate stock solution (BDH 'Aristar' grade). The
39 detection limit of the method (calculated as twice the standard deviation of
40 control samples), for both Fe(II) and total Fe, was 21Jg dm⁻³ (36nM) for a
41 cell path length of 4cm (Hitachi U-2000 spectrophotometer). All
42 determinations were performed within three days of sampling.
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56 Monomeric and acid-reactive Al were determined by the method of Seip
57 et al. (1984). Measurements of pH were made following the procedures
58 recommended by Davison (1990) using a GK2401C combination electrode
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4 (Radiometer Inc.). Major cations (sodium, magnesium, potassium and
5 calcium) were measured by ICP-OES (Perkin Elmer Optima 4300 DV) on
6 filtered samples after acidification. Major anions (chloride, nitrate,
7 sulphate) were measured by ion chromatography (DX 100, Dionex Corp.).
8 Alkalinity was measured by Gran titration, using a 702 SM Titrino
9 (Metrohm AG). Dissolved organic carbon was measured by flame
10 combustion (TOC-V CPH/CPN analyser, Shimadzu Corp.).
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16 17 **4 Speciation modelling**

18 19 20 21 **4.1 Nomenclature**

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23 In presenting and discussing the modelling, we will use the term 'truly
24 dissolved' Fe(III) to refer to the modelled sum of the free ion, inorganic and
25 organic complexes, and 'colloidal' to refer to filterable Fe(III) that is
26 predicted to be precipitated as HFO or to be complexed to organic matter
27 that is not ultrafiltered or dialysed. Where reference is made to modelling
28 in equilibrium with the atmosphere, this refers to the use of a carbon
29 dioxide partial pressure of 3.65×10^{-4} atm for the purpose of simulating the
30 carbonate system.
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38 39 40 **4.2 WHAM/Model VI**

41 Speciation modelling was done using WHAM/Model VI (Tipping, 1994;
42 Tipping, 1998; Tipping et al., 2003). For the purposes of this work the
43 model can be considered as combining a standard model of
44 thermodynamic equilibria among solution ions, with a model for the
45 equilibrium complexation of ions with fulvic acid (Model VI). Model VI
46 considers complexation of cations to fulvic acid by complexation at
47 discrete sites and by electrostatic accumulation. The model contains 80
48 specific binding site types. The formulation of binding strengths is
49 structured such that the binding of each metal is described by two metal-
50 specific parameters: K_{MA} , which describes binding to relatively weak,
51 abundant sites, and IJK_2 , a modifying parameter which accounts for
52 binding to relatively strong, scarce sites. It is assumed that only the free
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4 metal ion and its first hydrolysis product can bind, with the same
5 parameter values, and the model has been parameterised on this basis.
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7 Tipping (1998) calculated a value of 2.4 for logKMA for Fe(III) by linear
8 regression of calculated logKMA values for fulvic acid against those for
9 humic acid. Tipping et al. (2002) calculated a logKMA of 2.8 for the binding
10 data of Langford and Khan (1975) and proposed a new default logKMA of
11 2.6 for fulvic acid binding, which we shall use here.
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16 Thermodynamic parameters for Fe(III) solution species are shown in Table
17 1. The formation reactions for the Fe(III) dimer $\text{Fe}_2(\text{OH})_2^{4+}$ and trimer
18 $\text{Fe}_3(\text{OH})_4^{5+}$ were included to test for the possible importance of these
19 species in the samples studied. In practice calculated concentrations of
20 these species were found to be negligible.
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25 26 **4.3 Model inputs**

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28 Dissolved organic matter (DOM) comprises a wide range of classes of
29 compound, of which the most important from the metal binding point of
30 view are the humic substances (humic and fulvic acids). WHAM/Model VI
31 has previously been shown to provide adequate descriptions of metal
32 binding to uncharacterised DOM samples, by adjustment of the proportion
33 of dissolved DOM considered to be chemically 'active' with respect to
34 binding (e.g. Bryan et al., 2002; Tipping et al, 2002). Thus, within ranges
35 of pH, DOM concentrations and metal concentrations previously studied,
36 the use of humic substances as a surrogate for bulk dissolved NOM has
37 been shown to be reasonable for the simulation of metal binding. NOM
38 was assumed throughout to comprise 50% C. It was also assumed
39 throughout that DOM was 65% chemically 'active', i.e. that it behaved as
40 though composed of 65% fulvic acid and 35% inert material with no
41 binding properties, after Bryan et al. (2002). Thus, we make the
42 assumption that binding properties of DOM do not vary among samples.
43 We argue that the assumptions are further justified if it can be shown that
44 the resulting chemical modelling successfully provides a coherent picture
45 of Fe(III) speciation across a broad range of water types.
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4 In order to assess the effect that variability in DOM 'activity' might have
5 upon model outcomes, model calculations were done using bootstrapping.
6 For each sample 10000 speciation calculations were done each with a
7 different 'activity', calculated at random assuming the 'activity' to have a
8 standard deviation of 15%, to give 10000 estimates of the output variable
9 of interest (either $\log a_{\text{Fe}^{3+}}$ or total Fe(III)). The standard deviation is based
10 on the range of DOM 'activities' found by Bryan (2001), based on copper
11 binding to UK freshwaters. The 10000 estimates of the output variable of
12 interest were used to calculate its standard deviation.
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21 **4.4 Literature data**

22 *4.4.1 USA surface waters (Babiarz et al.)*

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26 Babiarz et al. (2001) filtered 23 surface water samples from the northern
27 and southern U.S.A. using conventional filtration (0.41 μm) and tangential-
28 flow ultrafiltration (10kDa cutoff), and measured organic C, Fe and Al in
29 both filtrates. Ultrafiltration was done at ambient temperature. The
30 conductivity and pH of bulk samples were also measured. pH ranged from
31 3.8 to 8.2 and DOC from 0.2 to 26.5 mg dm⁻³. Concentrations of major
32 ions (Na, Mg, K, Ca, Cl, NO₃, SO₄, F, and HCO₃) were estimated for 20 of
33 the sites from the United States Geological Survey (USGS) via the
34 National Water Information System (2008) to derive relationships between
35 each major ion and conductivity, from time series samples for the sites
36 closest to those sampled by Babiarz et al. (2001). Stream water
37 temperatures were estimated from the available data by taking the mean
38 of all measured temperatures for the sampling month. For two samples
39 taken in the Florida Everglades, pH, concentrations of DOC, Na, Mg, K,
40 Ca, Cl, SO₄ and alkalinity were taken from the United States Geological
41 Survey South Florida Information Access Service (2008). Major ions at
42 two further Everglades sites were estimated by scaling the available
43 concentrations to the conductivity measurements made at these sites by
44 Babiarz et al. (2001). Surface water temperatures at these four sites were
45 estimated from the mean temperature for the sampling month at the
46 closest site on National Water Information System (2008).
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4.4.2 Amazon surface waters (Kuchler *eta/.*)

KUchler et al. (1994) filtered samples of two Amazon waters (Rio Negro and Rio Solimoes) at 11-1m and successively ultrafiltered subsamples using a hollow fibre column with nominal cutoffs of 100, 10 and 3kDa. Concentrations of Mg, Al, K, Ca, Fe and DOC in the 1OkDa and 3kDa ultrafiltrates were given. Water temperatures were not given; values of 303K were assumed, based on the mean monitored temperature for the River Solimoes during the months of sampling (GEMStat, 2008). Values of pH were estimated from the data of Seyler and Boaventura (2001). These authors listed a pH of 4.90 in the Rio Negro at a location close to that of KUchler et al. (1994), which was used here. The pH at six locations on the River Solimoes was given, ranging from 7.02 to 7.44; the mean of 7.25 was used. Equilibrium with atmospheric CO₂ was assumed for modelling. Both 1OkDa and 3kDa filtrates were modelled.

4.4.3 River Awout, Cameroon (Dupre *eta/.*)

Dupre et al. (1999) sampled the Awout River (Cameroon) (pH 4.7) and performed sequential tangential filtration (0.21Jm) and ultrafiltration (300kDa and 5kDa nominal cutoff). A subsample of the 0.21Jm filtrate was acidified to pH 3.0 and ultrafiltered (1kDa nominal cutoff). Concentrations of DOC, Mg, Al and Fe were given for both the 5kDa and 1kDa samples. Concentrations of Na, K, Ca, Cl and SO₄ were also given for the 5kDa sample; these concentrations were used for the 1kDa sample *in lieu* of measured concentrations. pH was measured only in the 0.21Jm frontal filtrate; this value was used for both ultrafiltrates. Equilibrium with atmospheric CO₂ was assumed for modelling.

4.4.4 Cameroon surface and ground waters (Viers *eta/.*)

Viers et al. (1997) sampled surface waters of the Sanaga (pH 7.4) and Mengong (pH 4.6) rivers of Cameroon, along with three groundwaters within the Mengong catchment (pH 4.7-5.5). Samples were filtered successively at 0.221Jm, 0.0251Jm or 300kDa, and 5kDa. Concentrations of Na, Mg, Al, K, Ca, Fe, Cl, NO₃, SO₄, alkalinity and DOC were measured

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4 in 5kDa filtrates. The pH was measured in 0.221Jm filtrates only. Two of
5 the groundwater samples had DOC concentrations below the detection
6 limit so were not used.
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10 4.4.5 *Brazil surface waters (Eyrolle et al.)*

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12 Eyrolle et al. (1996) sampled surface waters from three locations in Brazil
13 (pH 4.1-7.1). Samples were filtered successively at 0.21Jm, 100kDa,
14 20kDa and 5kDa. Samples taken from the Parana system were not
15 modelled due to the low recoveries of Fe obtained, which the authors
16 attributed to the use of old ultrafiltration membranes. Speciation was
17 modelled in the 20kDa and 5kDa fractions. Concentrations of Mg, Al, Ca,
18 Fe and DOC were measured in the 20kDa and 5kDa size fractions.
19 Measurements of pH and alkalinity were done on unfiltered samples.
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27 4.4.6 *Brazil, Venezuela and Cameroon surface waters (Deberdt et al.)*

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29 Deberdt et al. (2002) sampled surface waters from locations in Brazil,
30 Venezuela and Cameroon (pH 5.6-7.7). Samples were filtered
31 successively at 0.21Jm, 300kDa, 100kDa, 10kDa and 5kDa. Measurements
32 of pH, alkalinity and temperature were done in the field. Measurements of
33 Fe, Al, Na, Mg, K, Ca, Cl, NO₃, SO₄ and DOC were done on ultrafiltrates.
34 Both 10kDa and 5kDa filtrates were modelled.
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42 4.4.7 *Russia soil waters (Pokrovsky et al.)*

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44 Pokrovsky et al. (2005) performed filtrations and ultrafiltrations of soil
45 solutions from four locations near Moscow, Russia. The solutions were
46 acidic (pH 3.9-4.7) and high in DOC (39-58 mg dm⁻³ in 0.221Jm filtrates).
47 pH, DOC and major ions including Na, Mg, Al, K, Ca, Fe, Cl, NO₃ and SO₄
48 were measured. Data for filtrates of 0.221Jm filter pore size, and for
49 ultrafiltrates of 10kDa and 1kDa pore size were taken.
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56 4.4.8 *Netherlands soil waters (Jansen et al.)*

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58 Jansen et al. (2001) dialysed soil solutions, obtained by aqueous
59 extraction of a Dutch surface soil horizon, centrifugation and filtration at
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4 0.451Jm, using membranes of 1kDa nominal cut-off and a background
5 ionic strength of 0.02M. Four soil solutions were used, the pH values of
6 which were adjusted to 4.0, 4.1, 7.0 and 7.1 prior to dialysis. The ionic
7 strength of each solution was adjusted to 0.01M using KNO₃; this was also
8 done for the initial inside bag solutions. Fe, Al and DOC were measured
9 on the inside bag solutions after 400 hours equilibration at 20°C.
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12 13 14 15 16 4.4.9 France groundwaters (Pourret *eta/.*) 17

18 Pourret et al. (2007) sampled four groundwaters (pH 6.2-7.1) from two
19 wetlands located in the Kervidy-Naizin and Petit-Hermitage catchments,
20 France. Samples were filtrated (0.21Jm) and ultrafiltered at pore size cut-
21 offs of 30kDa, 10kDa and 5kDa. Concentrations of Na, Mg, K, Ca, Cl, NO₃,
22 SO₄, alkalinity and pH were measured in filtrates. Concentrations of Al, Fe
23 and DOC were measured in ultrafiltrates.
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29 30 4.5 Statistical analysis 31

32 Regression parameters and standard errors were computed in MINITAB
33 Release 14 (Minitab Inc., PA, U.S.A.). Pairwise comparisons of regression
34 model fits were done in Microsoft Excel (Microsoft Inc., WA, U.S.A.) using
35 likelihood ratio testing.
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40 5 Results and Discussion 41

42 43 44 5.1 Water chemistry 45

46 The samples exhibited a wide range of pH, alkalinity and concentrations of
47 calcium and magnesium (Table 2 and Data 1). There are no apparent
48 trends in these variables with location; local geological conditions probably
49 exert a significant influence. Concentrations of DOC showed influences of
50 soil type and flow conditions. At the five sites sampled under both low and
51 high flow conditions, DOC was higher under high flow. The highest
52 concentrations of DOC were seen in the Roudsea Wood stream which
53 drains a lowland peat bog. The influence of flow on chemistry may be
54 seen at some sites; for example, the River Hodder under high flow
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4 (November 2003) exhibited significantly lower pH and higher DOC than
5 under low flow (January 2004). The two larger lowland rivers (the Lune
6 and Ribble) showed similar chemical characteristics under both high and
7 low flow.
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11 Total and filtered (GF/F) concentrations of Fe varied by approximately one
12 order of magnitude across the samples. Fe concentrations tended to be
13 higher at lower pH, although this was not a pronounced trend. There was
14 also a tendency for higher filtered Fe to be associated with higher DOC,
15 although this was not general; the Roudsea Wood stream showed
16 relatively low Fe:DOC ratios on both sampling dates.
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23 **5.2 Dialysate compositions**

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25 Sample pH values measured after dialysis for one week mainly showed
26 increases in pH, of up to 1.2 units, due to CO₂ degassing. Measurements
27 of Fe, Al and DOC in the dialysates are given in Data 2, Data 3 and Data
28 4. Dialysis equilibrium with respect to major ions was achieved, with
29 excellent agreement between the conductivity of inside and outside bag
30 solutions after one week (Pearson correlation = 1.000, $p < 0.001$). In
31 contrast, dialysate DOC concentrations were found to be lower than
32 filterable concentrations, with the exception of a small number of samples
33 where the DOC in the raw sample was low (<2 mg dm⁻³(Figure 1).
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36 Dialysate DOC as a percentage of filtered DOC averaged 37% for
37 dialysates of 3.5kDa and 50% for dialysates of 10kDa. Dialysis at 15kDa,
38 which was not done on all samples, produced DOC concentrations
39 averaging 97% of those obtained by dialysis at 10kDa. Why this apparent
40 lack of equilibrium with respect to DOC occurs is not clear. Possible
41 reasons include slow diffusion of larger organic molecules (Buffle et al.
42 1993), retention of NOM on larger particles due to adsorption and/or
43 aggregation, or the formation of micellar DOM units too large to pass the
44 membrane (Kerner et al. 2003). It is plausible that some DOM is simply of
45 too large a size to efficiently pass the dialysis membrane; in this context, it
46 is noteworthy that in studies using ultrafiltration to isolate low molecular
47 weight fractions of freshwaters, passage of DOM through ultrafiltration
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4 membranes is by no means complete. For example, in the study of
5 Babiarz et al. (2001) (DOM 1.6-94.6 mg l⁻¹) between 20% and 73% of
6 DOM did not pass a 10kDa pore size cutoff ultrafiltration membrane. It is
7 important to realise, however, that ultimately the proportion of the filterable
8 DOM that is dialyzable is not important for this work: it is more important to
9 obtain a sample from which HFO has been removed in order to calculate
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11 **8Fe3+**
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16 17 5.3 Fe³⁺ activities 18

19 Activities of Fe³⁺ in the dialysates (Table 3) were calculated using
20 WHAM/Model VI. The relationship between log aFeJ+ and dialysate pH was
21 modelled by linear regression. Where dialysates of multiple pore sizes
22 were obtained from a single sample, calculated log aFeJ+ values were
23 weighted so that the results from each individual sample were emphasised
24 equally in the regression. With bootstrapping, 10000 estimates of the
25 regression parameters (slope and intercept) were obtained; the means
26 and standard deviations of these estimates were taken as the parameters
27 and their standard errors respectively. Activities showed a strong linear
28 dependence upon pH, which could be described by the equation
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$$38 \quad \log 8\text{Fe}3+ = 2.93(\pm 0.40) - 2.70(\pm 0.06) \cdot \text{pH}; p < 0.001, \text{SEpred} = 0.58 \quad (2)$$

39
40 where SEpred is the standard error of prediction and the bracketed terms
41 are the standard errors of the regression parameters. Addition of a
42 quadratic term in pH produced no significant improvement in the fit. This
43 contrasts with the solubility trend for log aAlJ+ computed by Tipping (2005),
44 where a quadratic term was required to adequately fit the data. The linear
45 trend in log aFeJ+ with pH is consistent with control of Fe³⁺ activities by an
46 HFO type phase. However, the slope of the line differs significantly from
47 the value expected according from the theoretical solubility equilibrium of
48 HFO (Equation 1): none of the 10000 slope values calculated by
49 bootstrapping were below the value of -3.0 predicted.
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58 Fig 2 shows the dependence of log aFeJ+ on pH and compares modelled
59 Fe³⁺ activities with predictions made assuming conventional solubility
60 products. Lines are plotted for standard log solubility products for HFO of
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4 10^{25} and 10^{50} , considered by Tipping et al. (2002) to represent a
5 reasonable range of solubilities for this material based on the literature.
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7 The enthalpy value of Liu and Millero (1999) ($-100.4 \text{ kJ mol}^{-1}$) was used to
8 correct standard solubility products to 283K. It can be seen that at higher
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10 pH (> 6.0), mean Fe(III) solubility is characteristic of the upper end of the
11 literature range while at lower pH it tends towards the lower end of the
12 range. Thus the solubilities that we calculate from our observations
13 correspond well with the literature range. This finding also supports our
14 hypothesis that Fe(III)-organic complexation can be reasonably modelled
15 as a function of bulk DOC concentration rather than by invoking specific
16 organic ligands.
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19 The pH dependence of $\log a_{\text{Fe}^{3+}}$ in Equation (2) is worthy of note, since it
20 can affect the prediction of activities appreciably in comparison with the
21 standard solubility product approach. Slope values significantly below -3.0
22 for the $\log a_{\text{Fe}^{3+}}$ -pH relationship have been found in laboratory studies of
23 Fe(III) solubility. Of particular interest are the studies of Byrne and Luo
24 (2000) and Byrne et al. (2005), where direct potentiometric measurement
25 of Fe^{3+} concentration variation with pH resulted in slope values of
26 $-2.86(\pm 0.01)$ and $-2.73(\pm 0.01)$, respectively, for the solubility of freshly
27 precipitated (15-60 minutes) HFO. Fox (1988) calculated a slope value of
28 -2.35 based on speciation modelling of dialysed synthetic solutions, and
29 considered the slope value to result from the substitution of anionic
30 counterions (e.g. Cr^{3+} , NO_3^-) for OH^- in the solid phase, while Byrne and Luo
31 (2000) proposed as an alternative explanation a pH-dependent variation
32 in the activity of the solid phase, possibly via a particle size effect. Such a
33 correspondence between Equation (2) and such studies is thus intriguing
34 and hints at the possibility of a common effect on the magnitude of the
35 slope term. It is worth noting that the slope found is unlikely to be due to
36 measurement error: if WHAM/Model VI is used to predict the total Fe(III) in
37 the dialysates assuming control by HFO with a standard solubility product
38 of 10^{50} , then in the five dialysates with $\text{pH} < 5.0$ the predicted Fe(III)
39 concentration exceeds that observed by a factor of at least eight.
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41 Conversely, if a standard solubility product of 10^{25} were to be assumed,
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4 dialysate Fe(III) ought to be undetectable ($<2 \text{ IJg l}^{-1}$) at circumneutral pH.
5 Thus, the identified trend in Fe^{3+} -activity appears robust.
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8 Fig 3 compares Fe^{3+} -activities, calculated using Equation (2) and corrected
9 to 298K using the enthalpy change of Liu and Millero (1999), with values
10 calculated from the solubility equations presented by Byrne et al. (2005)
11 and Byrne and Luo (2000) for the concentration of Fe^{3+} in 0.7M NaCl and
12 0.7M NaClO_4 , respectively. Measured Fe^{3+} -concentrations in Byrne et al.
13 (2005) and Byrne and Luo (2000) were corrected for activity effects using
14 Specific Ion Interaction Theory (Grenthe et al. 1997), using species
15 interaction coefficients of 0.56 and 0.38 for $\text{Fe}^{3+}\text{-ClO}_4$ and $\text{Fe}^{3+}\text{-Cl}^-$
16 interactions respectively. Activities predicted after Byrne et al. (2005) are
17 consistently higher than those predicted by us, by 0.9-1.1 log units in the
18 pH range 3 to 9. Within the same pH range the activities predicted after
19 Byrne and Luo (1999) are within 0.6 log units of our predictions, being
20 slightly higher below pH 5 and slightly lower above this pH. As can be
21 seen in Fig 3, the solubility line of Byrne and Luo (2000) is entirely within
22 the confidence intervals of our regression line within the pH range 3-9.
23 The solubility line of Byrne et al. (2005) is within the confidence intervals
24 above pH6, but is outside below this pH.
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Byrne and co-workers measured Fe(III) solubility very shortly after the
onset of precipitation (within one hour). In natural systems HFO is likely to
be somewhat older than this, which may alter its solubility. For further
comparison, we calculated Fe^{3+} -activities from the experiments of Liu and
Millero (1999) in which Fe(III) solubility was estimated between 3 hours
and 21 days after HFO precipitation. The hydrolysis equilibrium constants
calculated by these authors in the same experiments were used in our
calculations. There was excellent agreement (identical to one decimal
place) between the predictions of Liu and Millero (1999) and Byrne et al
(2005) for the solubility of freshly precipitated HFO in NaCl, at pH 4 and
pH 6, although at pH 8 the predicted Fe^{3+} -activities differed by 1.4 log
units. Following 21 days of precipitation the Fe^{3+} -activities were between
0.5 and 0.7 log units lower than those observed for freshly precipitated
material. At pH 4 and pH 6 the predicted activities were closer to the

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4 solubility predicted from our data, and at all pH values the activities were
5 within the confidence intervals on our regression line. Thus, there is
6 encouraging agreement between the results of laboratory studies and the
7 field data presented here, notwithstanding the differences between the
8 results of the laboratory studies. However, given that natural oxides and
9 hydroxides of Fe(III) are chemically and morphologically diverse (e.g.
10 Davison and De Vitre 1993) it would be premature to assert a common
11 mechanism of solubility control between laboratory and field. It must also
12 be borne in mind that our data are subject to greater uncertainty both in
13 measurement (due to the large number of input variables to the model)
14 and modelling, than well-controlled laboratory studies. Further work on
15 iron activity controls in freshwaters is required to investigate this
16 phenomenon further.
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27 **5.4 Modelling of literature data**

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29 The literature studies did not involve the quantification of Fe(II) in
30 ultrafiltrates or dialysates, with the exception of Jansen et al. (2001) where
31 the absence of Fe(II) was established by colorimetry. Thus it was not
32 considered appropriate to combine the literature data with the data
33 generated in this study when parameterising Equation (2). Instead we
34 used Equation (2) to calculate values of $a_{\text{Fe}^{3+}}$ in the literature samples,
35 which were then input to WHAM/Model VI along with the major ion, pH
36 and DOM concentrations to predict the total dialyzable or ultrafiltrable
37 Fe(III). The results (Fig 4a and 4c) indicate a good correlation between
38 observed and calculated values, however the latter are on average
39 overestimated: on average the predicted $a_{\text{Fe}^{3+}}$ was 3.8 times greater than
40 the observed value. Clearly this bias cannot be due to the presence of
41 Fe(II) since if so we would expect to calculate smaller Fe(III)
42 concentrations than the observed totals, on average. A more likely
43 explanation is the expected effect of temperature on Fe^{3+} - activities if the
44 latter are controlled by HFO solubility. Since the dissolution of HFO
45 (Equation 1) is exothermic, we would expect its solubility to decrease with
46 increasing temperature. Thus we would expect the concentration of free
47 ionic and complexed Fe(III) in equilibrium with HFO to decrease also.
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4 Since the mean temperature of the literature samples was 293K, we would
5 expect that on average Equation (2) would overestimate the Fe³⁺-solubility
6 in the literature samples. While it would be possible to extend Equation (2)
7 to empirically account for temperature effects by fitting to the literature
8 data, we have chosen not to do so, as this would discount the possibility of
9 Fe(II) as a confounding factor in the observations. Instead, we *a priori*
10 adjusted the Fe³⁺-activities calculated with Equation (2) assuming HFO
11 solubility control:
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$$19 \quad \log a_{\text{Fe}^{3+}} = \log a_{\text{Fe}^{3+}}^{293\text{K}} + \frac{\Delta H^\circ}{2.3R} \left(\frac{1}{293} - \frac{1}{T} \right) \quad (3)$$

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21
22 where ΔH° is the standard enthalpy change for Equation (1) (after Liu and
23 Millero (1999)). The resulting predicted Fe(III) concentrations show
24 appreciably better agreement with the observations (Figs 4b and 4d), with
25 65 of the 90 predictions falling within a factor of three of the corresponding
26 observation, compared with 53 prior to temperature adjustment. The root
27 mean squared difference (RMSD) in log concentrations dropped from 0.53
28 to 0.44. The dataset of Babiarz et al. (2001), which contained the largest
29 number of samples and a wide range of sample temperatures (273K to
30 303K), showed a decrease in RMSD from 0.44 to 0.27 and improved
31 prediction of total Fe(III) in 17 of the 23 samples.
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40 Following temperature correction, the predicted Fe(III) was on average 1.8
41 times the observed Fe. This is the inverse of the effect that would result
42 from the presence of Fe(II) but does not preclude the possibility that Fe(II)
43 is important in some samples. For example, the discrepancy between
44 observations and calculations in the dataset of Eyrolle et al (1996) could
45 be due to Fe(II).
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52 **5.5 Calculating Fe(III) solubility for speciation modelling**

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54 It is desirable to incorporate the solubility of Fe(III) into speciation models
55 in order to simulate Fe(III) chemistry and thus account for such effects as
56 the competition between Fe(III) and trace metals for binding to humic
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substances (Tipping et al. 2002). This could be done in one of two ways.

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Equations (2) and (3) can be combined to give a temperature-independent expression for log aFe₃₊:

$$\log a_{\text{Fe}^{3+},T} = 2.93 - 2.70\text{pH} + \frac{t \cdot H_R}{2 \cdot 3} \left(\frac{1}{283} - \frac{1}{T} \right) \quad (4)$$

which simplifies further if the enthalpy change of Liu and Millero (1999) is assumed:

$$\log a_{\text{Fe}^{3+},T} = -15.63 - 2.70\text{pH} + \frac{5253}{T} \quad (5)$$

This expression is suitable for the direct calculation of Fe³⁺ activities if the pH is fixed for the speciation calculation. For calculations where the pH is also to be calculated, it is necessary to specify the solubility parameters in the form of a solid phase. If the solid is assumed to have the enthalpy change given by Liu and Millero (1999), then from Equation (2), the putative standard solubility product has the form

$$K_{\text{so}} = \{\text{Fe}^{3+}\}\{\text{H}^+\}^{-2.70} \text{ or } \log K_{\text{so}} = \log a_{\text{Fe}^{3+},T} + 2.70\text{pH} \quad (6)$$

and after Equation (5):

$$\log K_{\text{so}} = -15.63 + \frac{5253}{T} \quad (7)$$

At 298K K_{so} is 10⁻²⁰⁰, from Equation (7).

5.6 Fe:DOM ratios in UK samples

In natural systems, Fe(III) binds relatively strongly to DOM (Tipping et al. 2002) and the major competing species (other than H⁺) for binding is Al. Tipping (2005) has shown that the variability of Al³⁺ activity in surface waters can be reasonably described using a single function of pH. Assuming control of Fe³⁺ activity according to Equation (2) then allows a generic prediction of the ratio of truly dissolved Fe(III) to DOM to be made using WHAM/Model VI, for a temperature of 283K. This is a useful quantity to predict since it can be compared with measured Fe:DOM ratios: if the measured ratio exceeds that calculated, this indicates the presence of

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4 colloidal Fe, or Fe(II). In Fig 4a, such a prediction is compared to the
5 observed Fe(III):DOM ratios for the sample filtrates and dialysates
6 obtained in this study. Observed ratios in the filtrates were almost all in the
7 range 10^{-3} - 10^{-4} mol g⁻¹ and showed no variability with pH. Observed ratios
8 in the dialysates overlapped to a small extent with those in the filtrates, but
9 were generally lower, in the range 10^{36} - 10^{-52} . The ratios also showed a
10 downward trend with pH; below pH 5.0, ratios were similar in the filtrates
11 and dialysates. Values of the predicted Fe(III):DOM ratio are given for pH
12 3.0-9.0 in Data 5.
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20 If a water sample contains Fe(III) not in the form of truly dissolved Fe(III),
21 then we would expect its Fe(III):DOM ratio to exceed that calculated by
22 taking Equation (2) as a starting point. This can be seen in Fig 4a for the
23 filtrates of our samples. In Fig 4b, a set of observed Fe(III):DOM ratios is
24 shown for long term monthly monitoring data from Pool X and Pool Y, two
25 of the sites sampled in this study. The generic prediction of Fe(III):DOM is
26 shown for reference. In line with our theory, the observed ratios are
27 consistently greater than the predicted Fe(III):DOM, with the exception of a
28 small number of outliers. Given the number of samples taken it is not
29 surprising to find outliers with ratios below the predicted Fe(III):DOM,
30 particularly since the prediction relates to a single temperature taken as a
31 typical annual mean for UK waters. Of note is the observation that the
32 increase in Fe(III):DOM with decreasing pH is reflected in the observed
33 Fe(III):DOM ratios, particularly in the dataset from Pool X (pH 3.9-6.3).
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44 Observed Fe:DOM ratios are shown in Fig 5 for circumneutral to alkaline
45 surface waters, comprising data for four rivers monitored under the UK
46 Land Ocean Interaction Study (LOIS) in 1994-96 (Neal and Robson,
47 2000). Here no separate measurements of Fe(II) were made. The
48 predicted Fe:DOM ratios were corrected by assuming Fe(II) in the dialysed
49 fraction to be 32% of the Fe(III), following the observations in the
50 dialysates obtained in this study. This raised the predicted Fe:DOM by
51 0.12 log units (a factor of 1.3). Observed Fe:DOM ratios again largely
52 exceeded the generic Fe:DOM. The exception was the River Trent, where
53 an appreciable number of observed Fe:DOM ratios clustered around the
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4 predicted Fe:DOM. This can be taken as an indication of relatively low
5 concentrations of colloidal Fe(III) in this system. The correction of the
6 predicted Fe:DOM for the presence of Fe(II) does not greatly affect the
7 outcome, since the variability in observed ratio at a given pH is much
8 larger than the amount by which the correction increases Fe:DOM.
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12 13 14 **5.7 The chemistry of Fe(III) in freshwaters**

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16 The generic solubility equation can be used to investigate and predict the
17 effects of changing solution conditions upon Fe(III) speciation. For
18 example, the truly dissolved Fe(III):DOM ratio is predicted to decrease
19 substantially with increasing pH. In the UK, acidic discharges are largely
20 associated with upland areas where buffering of precipitation acidity is low
21 due to either slow weathering of the underlying rock and/or the presence
22 of highly organic acid soils, particularly peats and rankers. Such waters
23 are represented in our dataset by Pool X, and by the River Hodder sample
24 of 13 November 2003 (see Data1 for the full chemical composition). We
25 carried out a series of calculations in order to investigate the predicted
26 effect on Fe(III) speciation of the progressive mixing of an acid water with
27 a circumneutral Ca-rich water more typical of large UK rivers. This was
28 done by taking the composition of the 3.5kDa dialysates of the River
29 Hodder (pH 4.35; dialyzable DOC 3.9 mg l⁻¹; Ca 0.06 mmol l⁻¹) and making
30 a series of calculations by progressively increasing the Ca concentration
31 and allowing WHAM to calculate the pH by charge balance, at a
32 temperature of 283K. The speciation of Fe(III) was considered by
33 calculating the activity of Fe³⁺ from Equation (2). The speciation of Al was
34 calculated by first allowing Al to precipitate as Al(OH)_{3(s)} and secondly by
35 preventing precipitation from occurring. The results (Fig 6) show the
36 predicted decrease in the truly dissolved Fe(III) concentration as pH
37 increases. Between the initial pH and pH 6.0 approximately four-fifths of
38 the truly dissolved Fe(III) is predicted to be lost. Above pH 6.0 the loss of
39 Fe(III) from the truly dissolved pool slows as pH increases further, partly
40 because Al precipitation reduces competition and allows Fe(III) to remain
41 bound to DOM. At pH 8.5 only 7% of the truly dissolved Fe(III) present at
42 the initial pH remains in this form. In the field, losses of Fe(III) from the
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4 truly dissolved pool on neutralisation of acidic waters would occur through
5 precipitation of HFO.
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8 9 **6 Conclusions**

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12 Dialysis is a simple and effective way of separating a sample of 'truly
13 dissolved' Fe from colloidal-sized material. Using this technique, we have
14 been able to compute Fe^{3-} activities for a number of UK surface waters
15 and to show that the trend in log activities with pH is linear. The solubility
16 of Fe^{3-} is close to that predicted by assuming equilibrium with a 'hydrous
17 ferric oxide' type phase. The slope of the relationship between $\log a_{\text{Fe}^{3+}}$
18 and pH is lower than that predicted by the theoretical stoichiometry of the
19 solid phase, a finding previously observed in some laboratory studies of
20 Fe(III) solubility. By the use of a bootstrap method to account for the
21 possible variability in DOM binding 'activity', we have shown that this
22 finding is robust to such variability, and thus the assumption of a mean
23 DOM binding 'activity' is reasonable. These findings strongly support the
24 hypothesis that organic complexation of Fe(III) in freshwaters can be
25 modelled as a function of DOC concentration without the need to invoke
26 distinct organic ligands. The linear relationship between $\log a_{\text{Fe}^{3+}}$ and pH
27 can be used to predict the total Fe in dialysates and ultrafiltrates sampled
28 from a wide variety of surface and soil/ground waters. The prediction is
29 significantly improved if it is assumed that solubility has a temperature
30 dependence predicted by the temperature dependence of HFO solubility,
31 which provides strong support for the contention that HFO controls Fe^{3-}
32 activities in the field. Using the Fe^{3-} activity equation it is possible to make
33 a generic prediction of the Fe(III):DOM ratio expected at a given pH due to
34 inorganic and organic complexation. Higher 'dissolved' Fe:DOM ratios in
35 natural waters may be indicative of the presence of Fe in other forms,
36 particularly colloidal Fe(III) and dissolved or complexed Fe(II).
37 Comparison of the computed Fe(III):DOM ratio with observed Fe:DOM
38 ratios in UK surface waters indicated that in most cases excess Fe, most
39 likely mainly colloidal Fe(III), was indeed present.
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4 A notable aspect of the literature data used in this study is the almost
5 complete absence of Fe(II) measurements. Our data indicate that although
6 Fe(II) might only comprise a small portion of the total 'dissolved' Fe, it is
7 likely to be a more important component of the 'truly dissolved' Fe (an
8 average of 24% in our samples). Clearly, when considering Fe speciation
9 in natural waters the measurement of Fe(II) should have a higher priority.
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14 There is currently a growing interest in quantifying the fluxes of riverine Fe
15 to the oceans (e.g. Krachler et al. 2005), given the important role of Fe in
16 controlling oceanic phytoplankton productivity. Knowledge of Fe(III)
17 speciation is likely to offer considerable insight into the processes
18 controlling such fluxes. While a significant proportion of Fe is lost on
19 mixing of riverine and estuarine waters (e.g. Sholkovitz et al. 1978),
20 evidence exists that truly dissolved Fe comprises a quasi-conservative Fe
21 pool with respect to fluxes through the mixing zone (e.g. Dai and Martin
22 1996). Thus, predicting the truly dissolved Fe(III) at the tidal limit using our
23 solubility equation may allow better estimation of Fe fluxes through
24 estuaries to the ocean.
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35 Acknowledgements We thank David Abel and Sarah Thacker for help with sampling,
36 and Sarah Thacker, Colin Vincent, David Wilson, Gillian Ainsworth and Alan Lawlor for
37 chemical analysis. This work was funded by the Natural Environment Research Council
38 (Grant reference NER/B/S/2002/00513). We thank an anonymous reviewer for comments
39 that led to the improvement of this paper.
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Table 1 Parameters for the considered solution complexation reactions of Fe(III)

Reaction	logK'	$\Delta H'$ (kJ mol ⁻¹)	Reference
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+$	-2.19	43.4	Nordstrom et al. 1990
$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	-5.67	71.4	Nordstrom et al. 1990
$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+$	-12.56	103.5	Nordstrom et al. 1990
$\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_4^- + 4\text{H}^+$	-21.6	133.2	Nordstrom et al. 1990
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_4^{2+} + 2\text{H}^+$	-2.85	57.7	Smith et al. 2004
$3\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3(\text{OH})_6 + 4\text{H}^+$	-6.29	65.4	Smith et al. 2004
$\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{2+}$	1.48	23.5	Nordstrom et al. 1990
$2\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{Fe}_2\text{Cl}^{5+}$	2.13		Nordstrom et al. 1990
$\text{Fe}^{3+} + \text{F}^- \rightleftharpoons \text{FeF}^{2+}$	6.2	11.3	Nordstrom et al. 1990
$\text{Fe}^{3+} + 2\text{F}^- \rightleftharpoons \text{FeF}_2^+$	10.8	20.1	Nordstrom et al. 1990
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4^+$	4.04	16.4	Nordstrom et al. 1990

Table 2 Ranges of chemical determinands in sampled waters

Determinand	Range
pH _{field}	4.16-8.14
pH _{mal}	4.28-8.02
DOC (mg dm ⁻¹)	1.7-40.3
I:(Na, Mg, K, Ca) (mol,dm ⁻³)	235-8122
I:(Cl, NO ₃ , SO ₄) (mol,dm ⁻³)	118-6032
Alkalinity (eq,dm ⁻¹)	0-2668
Total Fe (nM)	1199-16848
Filtered Fe (nM)	859-12337
Total Fe(II) (nM)	<36-340
Filtered Fe(II) (nM)	<36-573
Total monomeric Al (nM)	148-15826
Total acid-reactive Al (nM)	556-15159

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1 Table 3 Fe³⁺ activities for samples in this study and literature datasets, calculated using WHAM/Model VI (subscript 'model') and calculated by multiple linear
2 regression on pH and temperature (subscript 'regression').

Sample name	Pore size cutoff (kDa)	pH	log $a_{\text{Fe}^{3+}, \text{model}}$ (M)	SD log $a_{\text{Fe}^{3+}, \text{model}}$	log $a_{\text{Fe}^{3+}, \text{regression}}$ (M)
Pool Y	3.5	6.9	-16.1	0.7	-15.4
Roudsea Wood	3.5	7.4	-16.8	0.6	-16.7
Whitray Beck tributary	3.5	6.2	-13.2	0.4	-13.6
River Hodder	3.5	4.6	-9.5	0.3	-9.4
Gais Gill	3.5	7.2	-17.0	0.6	-16.1
River Eden	3.5	7.6	-16.9	0.5	-17.2
Pool X (2)	3.5	4.6	-9.7	0.4	-9.2
Whitray Beck tributary (2)	3.5	7.4	-15.8	0.2	-16.6
River Ribble (2)	3.5	8.0	-18.2	0.4	-18.2
Roudsea Wood (2)	3.5	7.4	-16.1	0.4	-16.7
Wad Hazel Sike (2)	3.5	7.8	-17.1	0.3	-17.6
Pool X	10	4.3	-8.1	0.2	-8.5
Pool Y	10	6.9	-16.7	0.8	-15.4
Roudsea Wood	10	7.4	-16.9	0.7	-16.8
Whitray Beck tributary	10	6.4	-13.3	0.4	-14.0
River Hodder	10	4.6	-9.3	0.4	-9.3
River Lune	10	7.6	-16.8	0.3	-17.2
River Ribble	10	7.7	-17.2	0.4	-17.4
Gais Gill	10	7.3	-16.9	0.7	-16.5
River Eden	10	7.6	-16.8	0.5	-17.1
Pool X (2)	10	4.5	-9.4	0.5	-9.0
Pool Y (2)	10	7.3	-16.4	0.6	-16.5
Whitray Beck tributary (2)	10	7.4	-16.4	0.4	-18.3
River Lune (2)	10	8.0	-18.7	0.3	-16.6
River Ribble (2) Roudsea	10	8.0	-18.8	0.4	-18.2
Wood (2) Whitray Beck	10	7.4	-16.8	0.6	-16.7
tributary (2) River Lune	15	7.4	-18.7	0.4	-18.3
(2)	15	8.0	-16.9	0.5	-16.6
Roudsea Wood (2)	15	7.4	-15.1	0.4	-15.1
Wad Hazel Sike (2)	15	7.8	-16.9	0.6	-16.7

Figure captions

- Fig 1** Comparison of filtered (0.7 m) concentrations of organic carbon and concentrations obtained following dialysis for one week. Closed circles: dialysis at 3.5kDa; open circles: 10kDa; closed triangles: 15kDa. The solid line is the 1:1 relationship.
- Fig 2** Activities of Fe^{3+} in dialysates calculated using WHAM/Model VI plotted against pH. Closed circles: 3.5kDa pore size; open circles, 10kDa pore size; closed squares: 15kDa pore size. The solid black line is the best fit regression (Equation (1)). The error bars represent ± 1 standard deviation in $\log a_{\text{Fe}^{3+}}$ due to uncertainty in the 'active' proportion of DOM. The dashed lines show the trends in activities predicted using standard solubility products of 10^{50} (upper) and 10^{25} (lower).
- Fig 3** Comparison of predicted Fe^{3+} activities in this study with literature solubility studies. The shaded area encompasses the 95% confidence interval on the prediction of Fe^{3+} activity variation with pH, at 298K, according to Equations (2) and (4). Solid line: prediction of Fe^{3+} activity variation with pH in the experiments of Byrne et al. (2005), aging time 15-60 minutes: $a_{\text{Fe}^{3+}} = 3.19(\pm 0.06) - 2.73(\pm 0.01)\text{pH}$. Dashed line: prediction of Fe^{3+} activity variation with pH in the experiments of Byrne and Luo (2000), aging time 15-60 minutes: $a_{\text{Fe}^{3+}} = 2.97(\pm 0.06) - 2.86(\pm 0.01)\text{pH}$. Confidence intervals for these two lines are omitted for clarity. Symbols: prediction of Fe^{3+} activity in the experiments of Liu and Millero (1999), aging time 3 hours (squares) and 21 days (circles).
- Fig 4** Concentrations of Fe in ultrafiltrates and dialysates of literature studies (Section 4.4) compared with Fe(III) in truly dissolved form, calculated using Equation (2) and WHAM/Model VI. **a: surface waters, not correcting $a_{\text{Fe}^{3+}}$ for temperature. b: surface waters, correcting $a_{\text{Fe}^{3+}}$ for temperature. c: soil/ground waters, not correcting $a_{\text{Fe}^{3+}}$ for temperature. d: soil/ground waters, correcting $a_{\text{Fe}^{3+}}$ for temperature. Error bars represent ± 1 standard deviation in predicted log [truly dissolved Fe(III)] due to uncertainty in the 'active' proportion of DOM. The 1:1 correspondence is indicated by a solid line. The dashed lines enclose the region corresponding to a factor of three or lower discrepancy between observation and prediction.**
- Fig 5** Top (a): observed Fe(III):DOM ratios in filtrates (0.7 m, open symbols) and dialysates (closed symbols) of UK waters. Error bars represent ± 1 standard deviation of dialysate Fe(III):DOM ratios calculated as the mean of multiple experiments. The solid line is a generic WHAM/Model VI prediction of the Fe(III):DOM ratio based on predictions of $a_{\text{Fe}^{3+}}$ calculated using Equation (1). Bottom (b): observed total Fe(III):DOM ratios in filtrates (0.7 m) of samples taken during long term monitoring of Pool X (closed squares) and Pool Y (open squares) from 1993-2001.
- Fig 6** Filterable (0.45 m) Fe:DOM ratios in surface water samples collected as part of the LOIS project a: River Trent; b: River Derwent; c: River Calder; d: River Ouse. The solid line is the predicted Fe:DOM ratio, including Fe(II).

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1 Fig 7 The predicted effect of neutralisation of an Fe(III) and DOM-rich water on the
2 concentration of 'truly dissolved' Fe(III). Speciation of a water having the composition of the
3 River Hodder of 13 November 2003, at a temperature of 283K, as the pH is increased by
4 increasing the total Ca concentration.

Figure 1

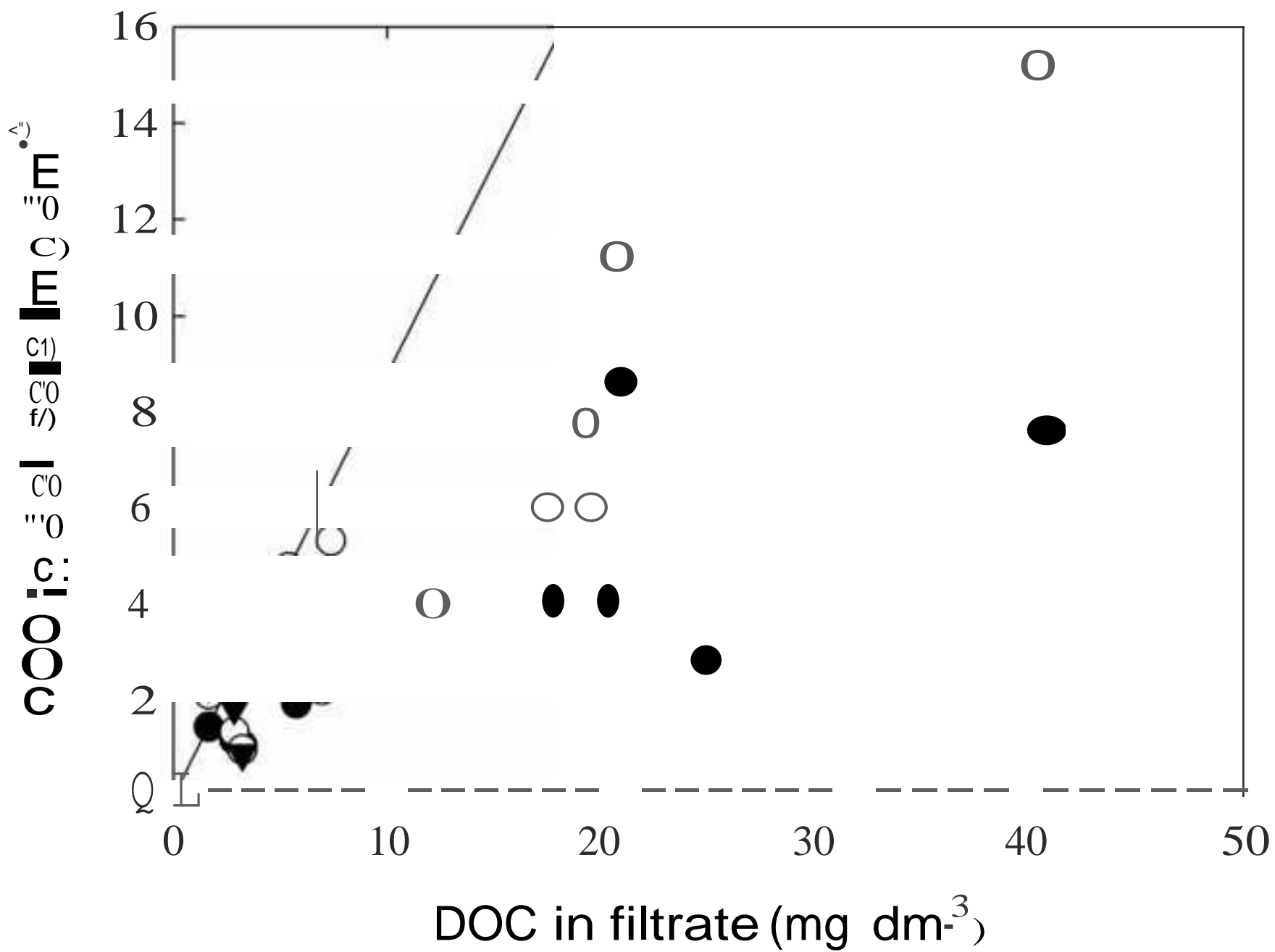


Figure 2

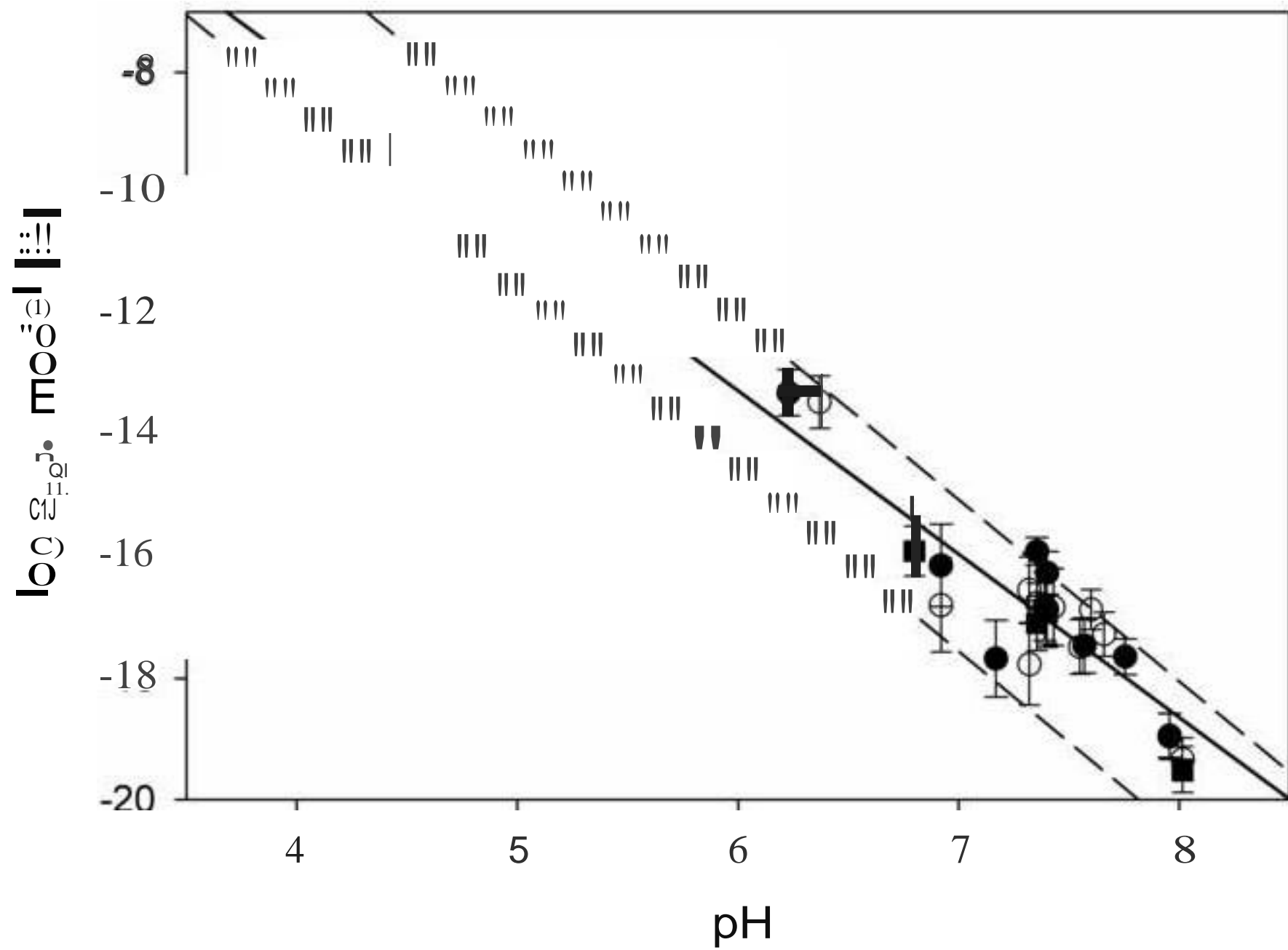


Figure 3

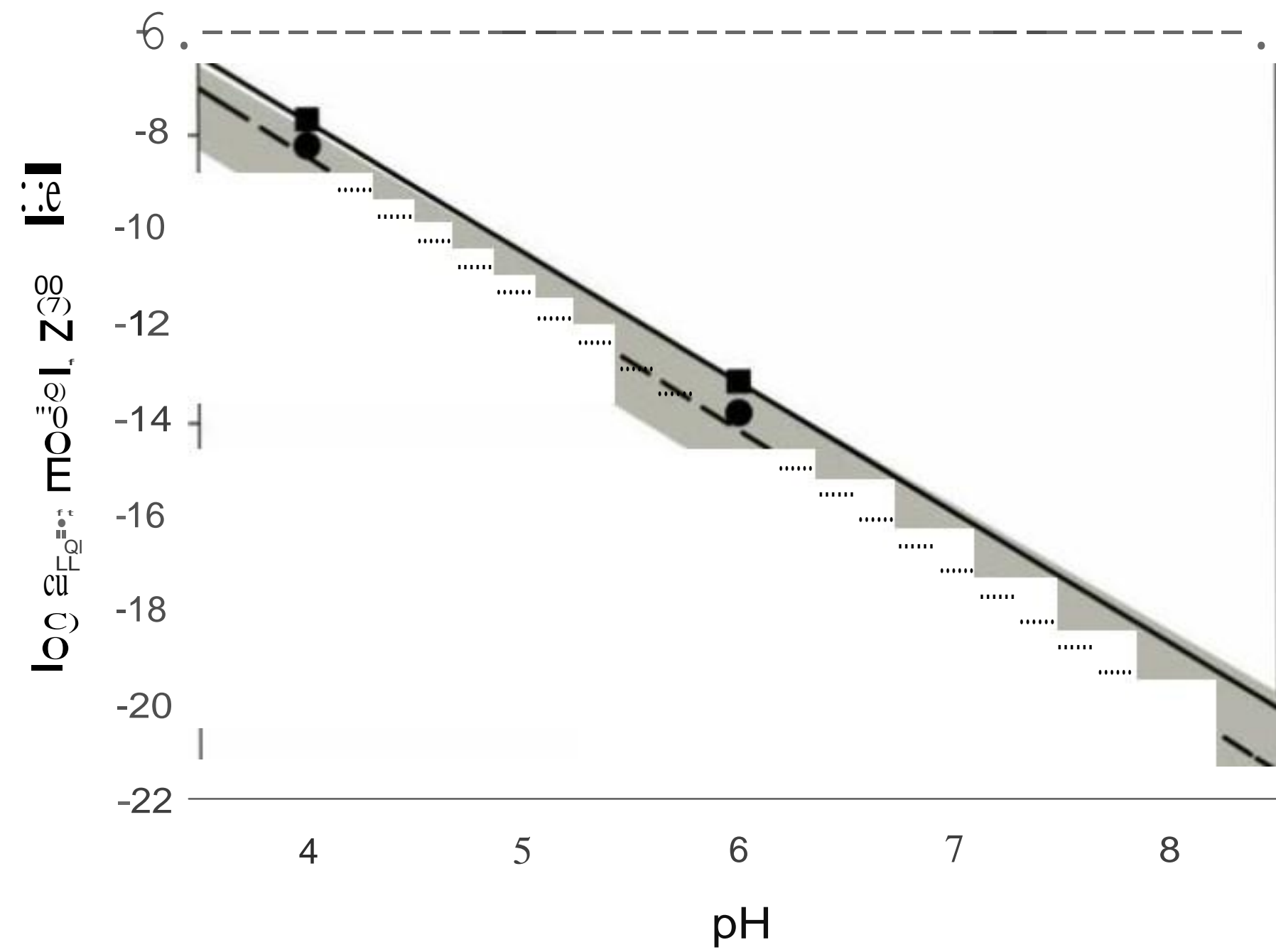


Figure 4

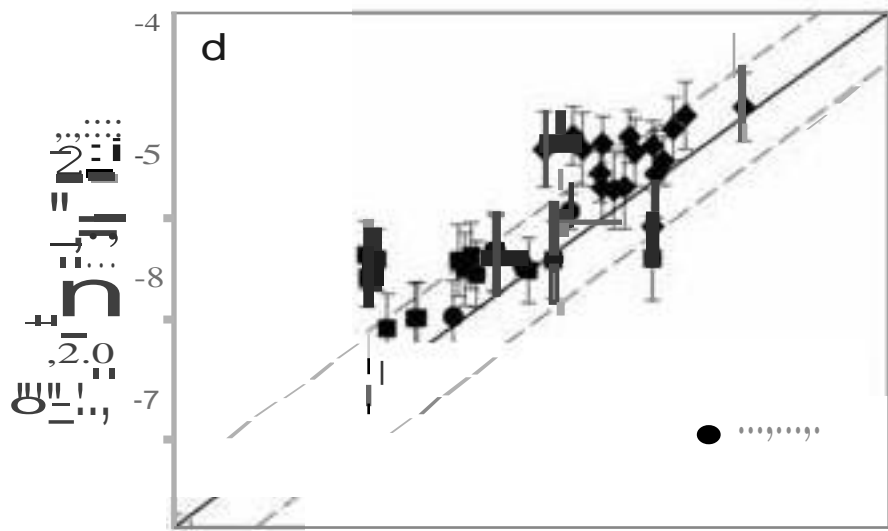
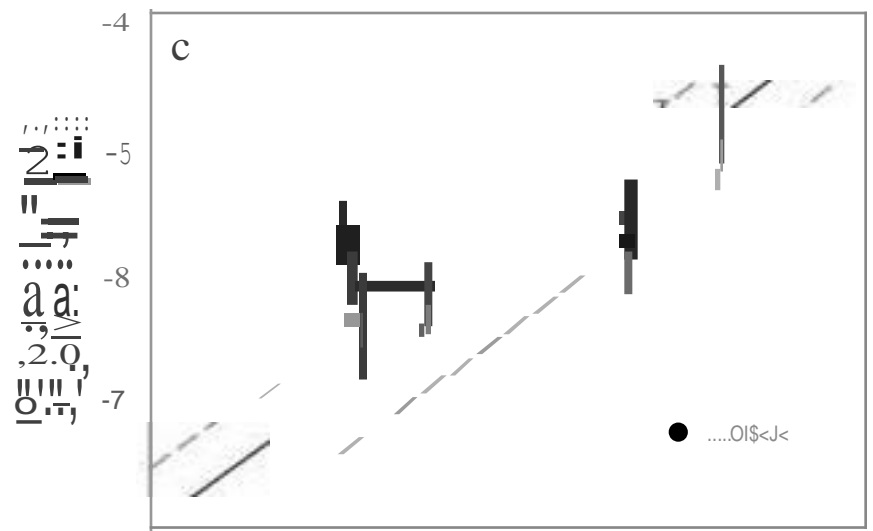
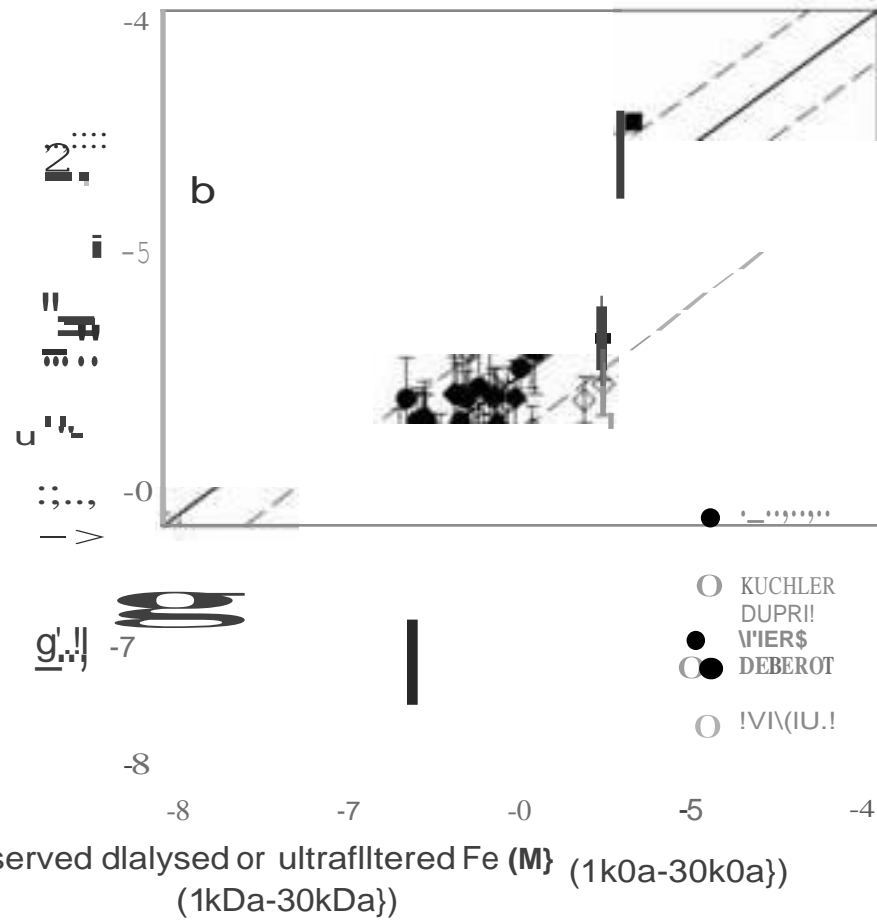
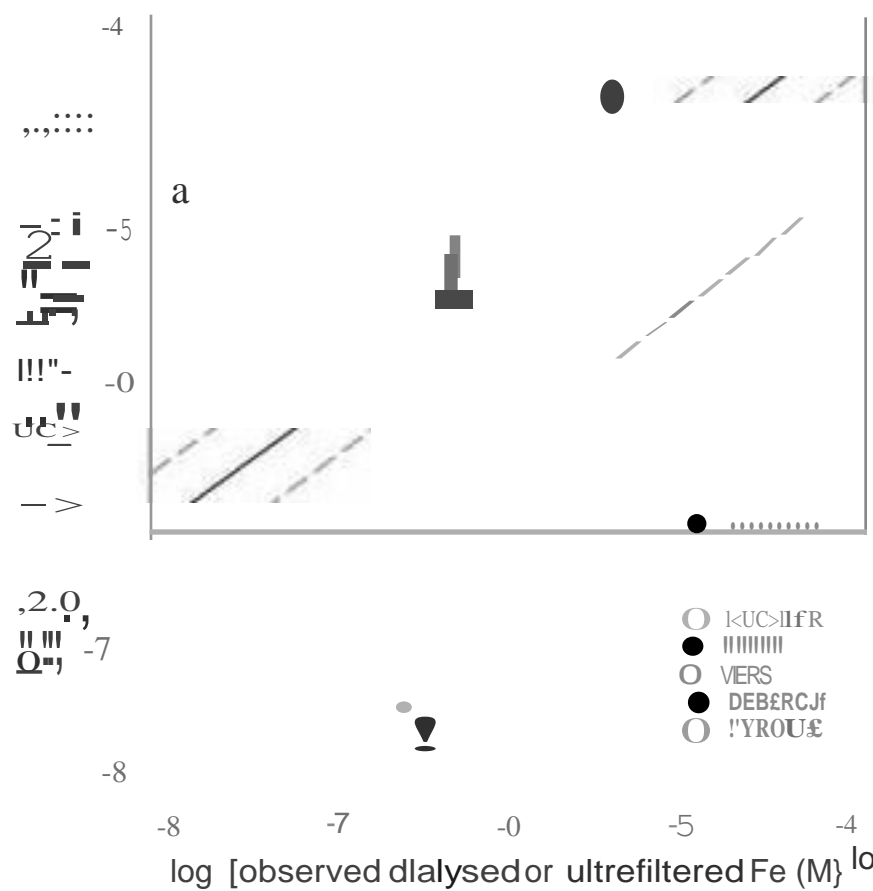


Figure4

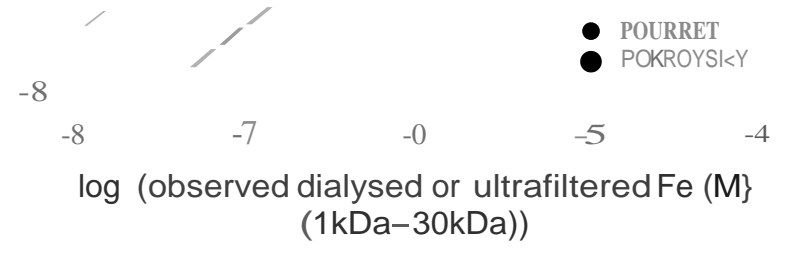
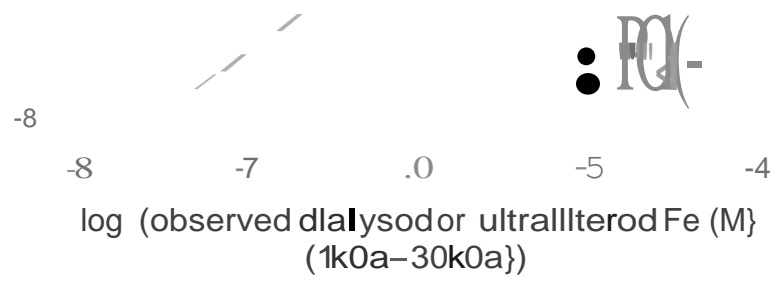
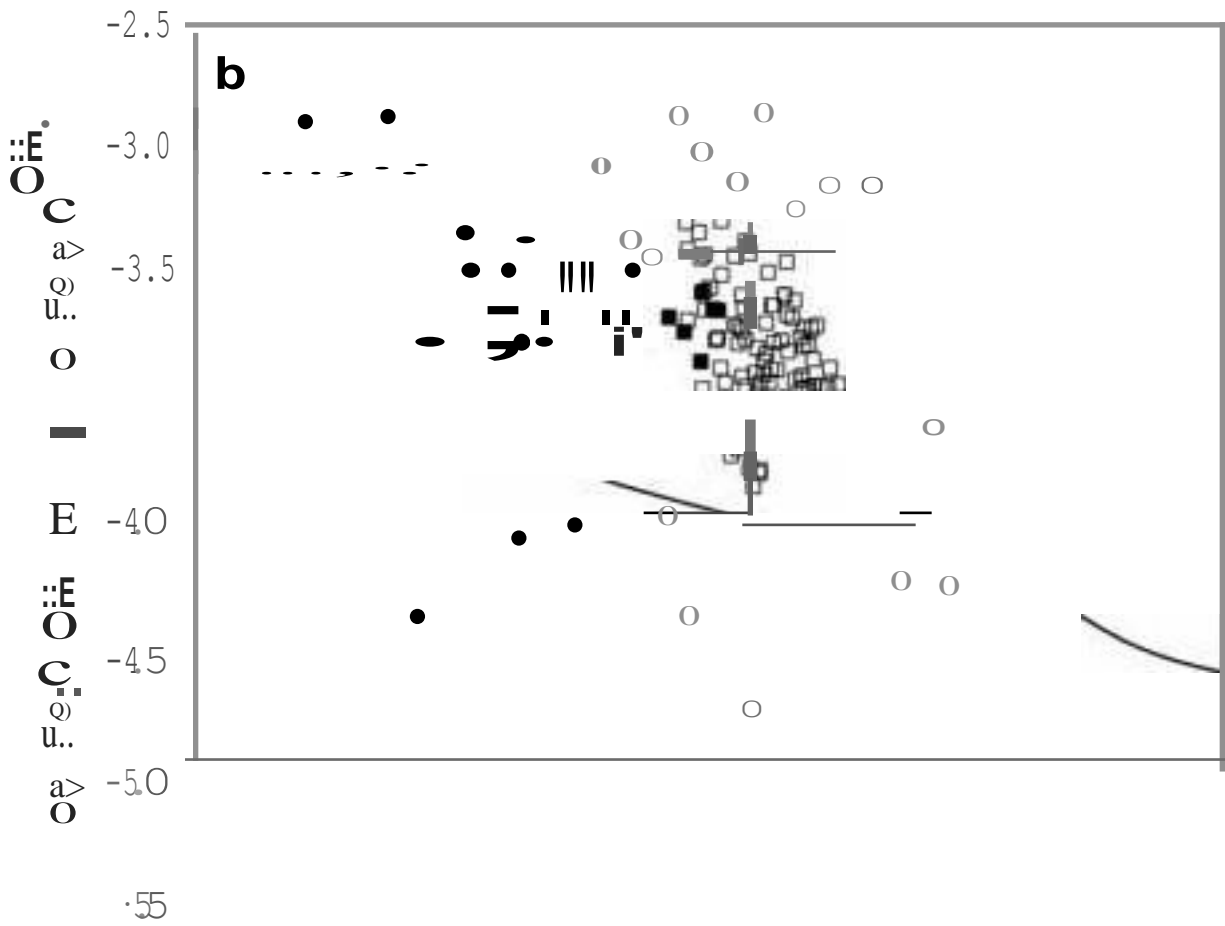
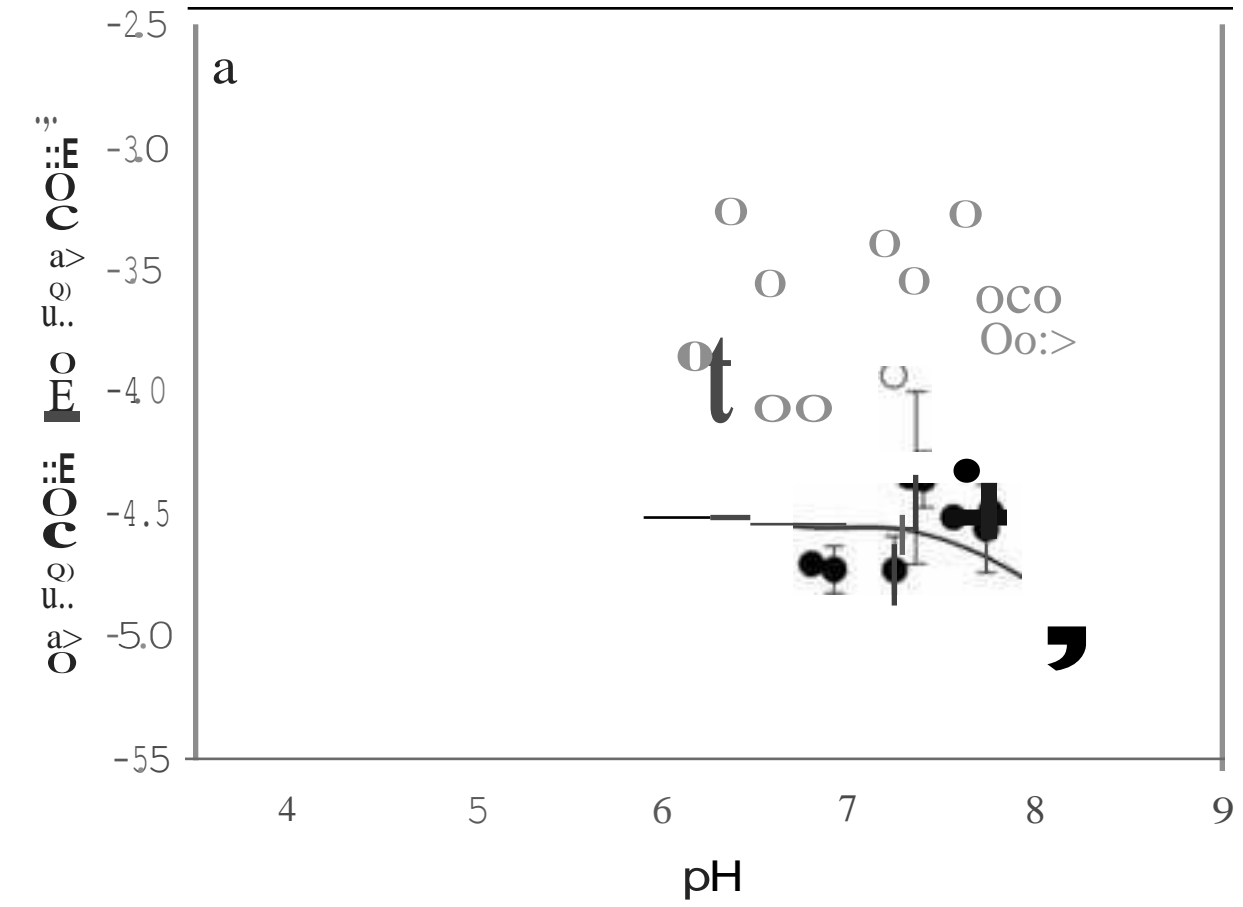


Figure 5



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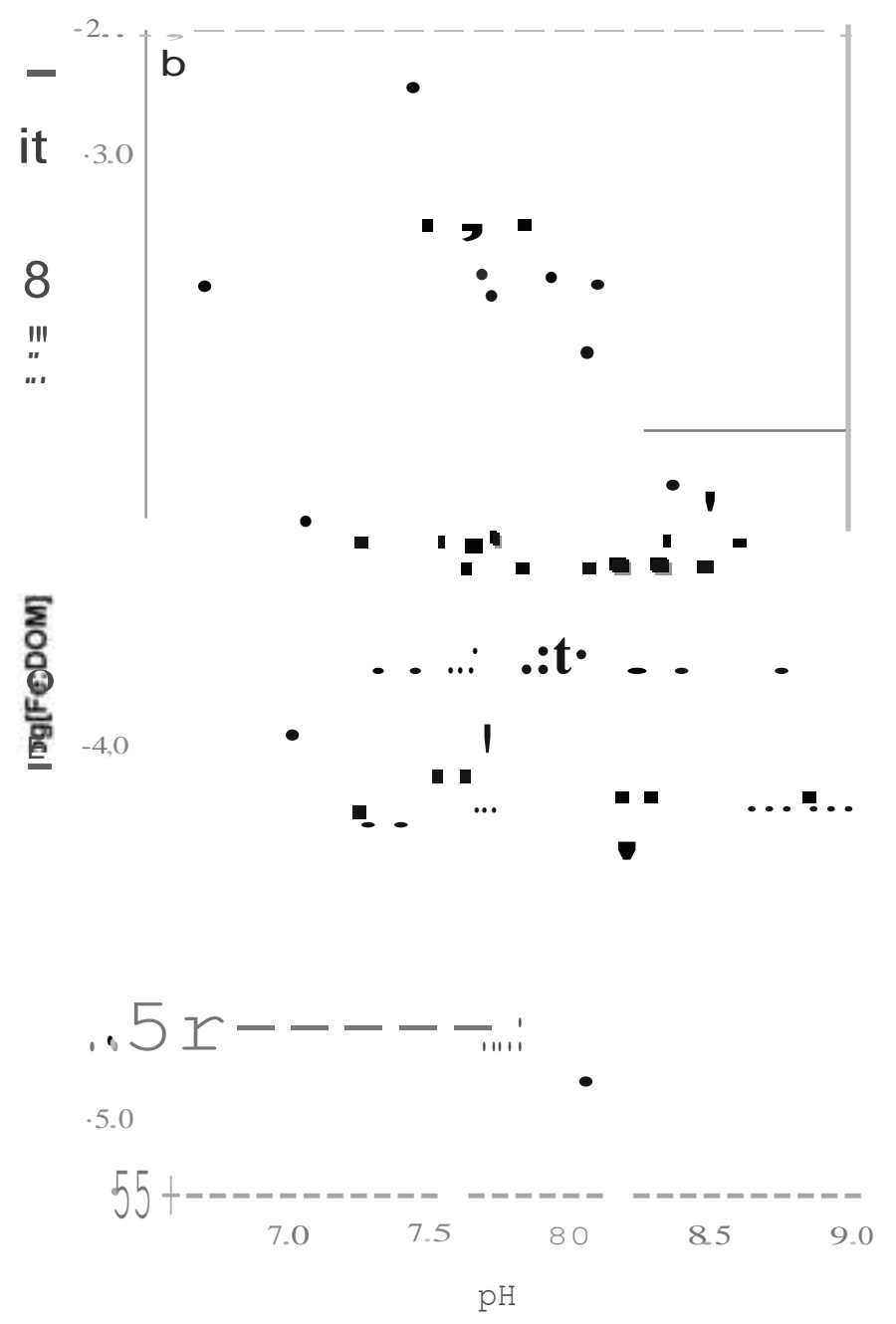
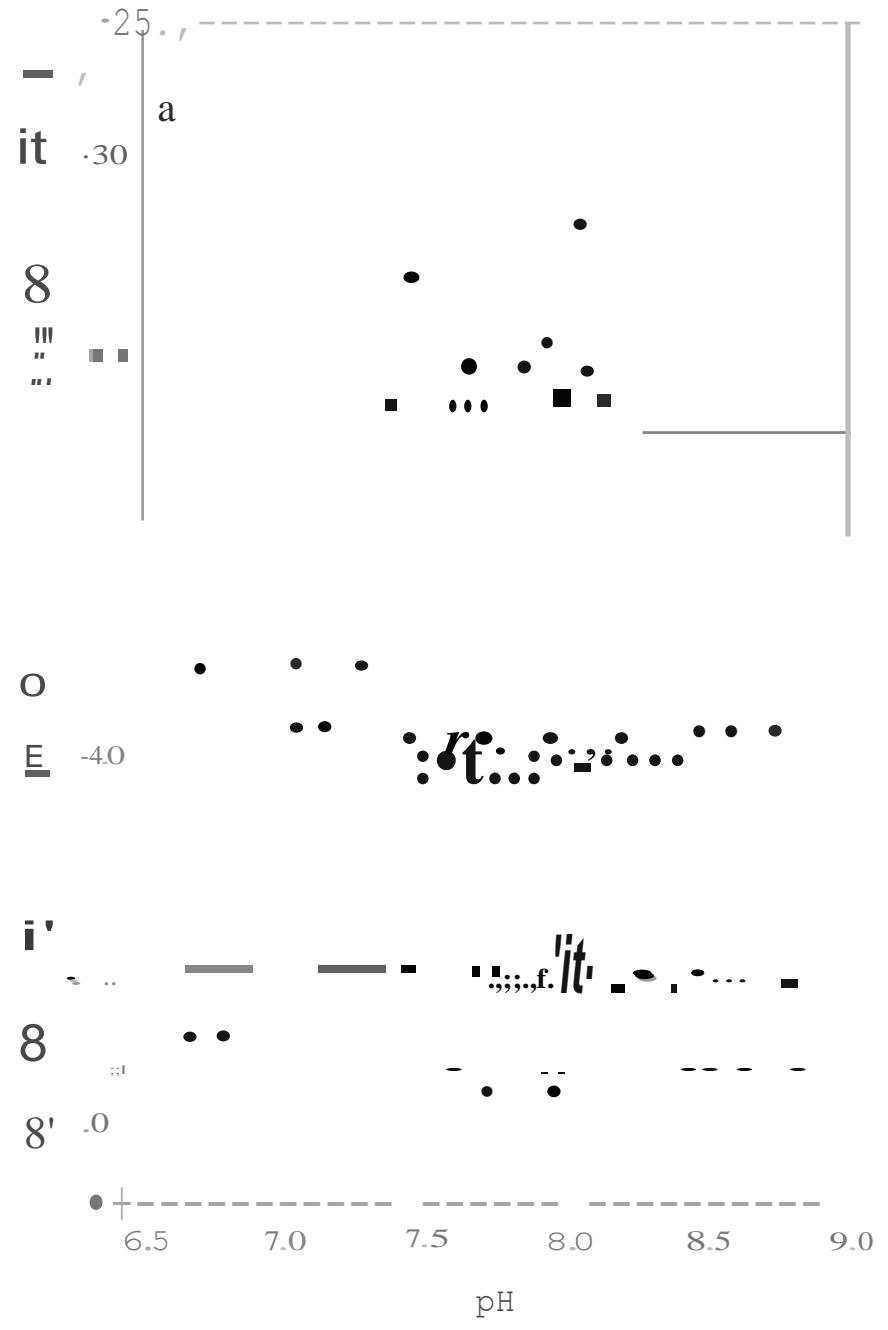
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FigureS



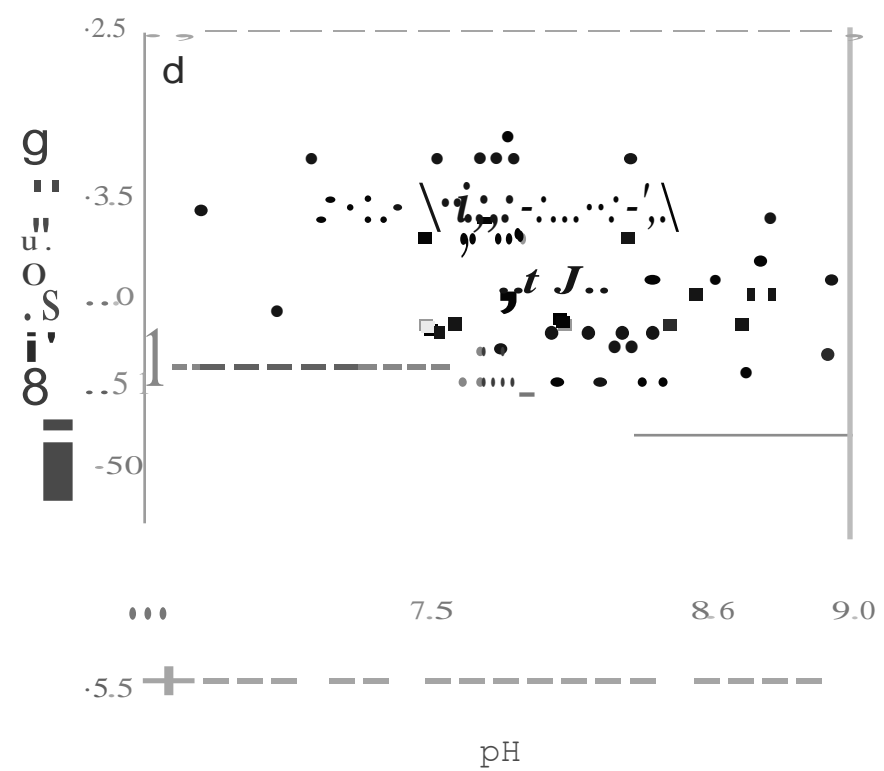
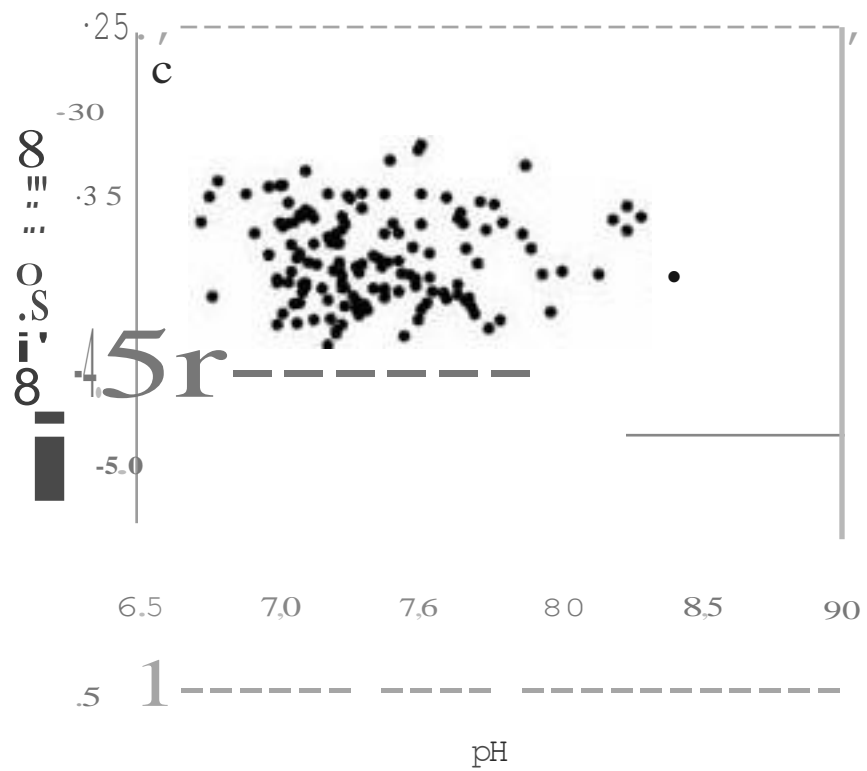
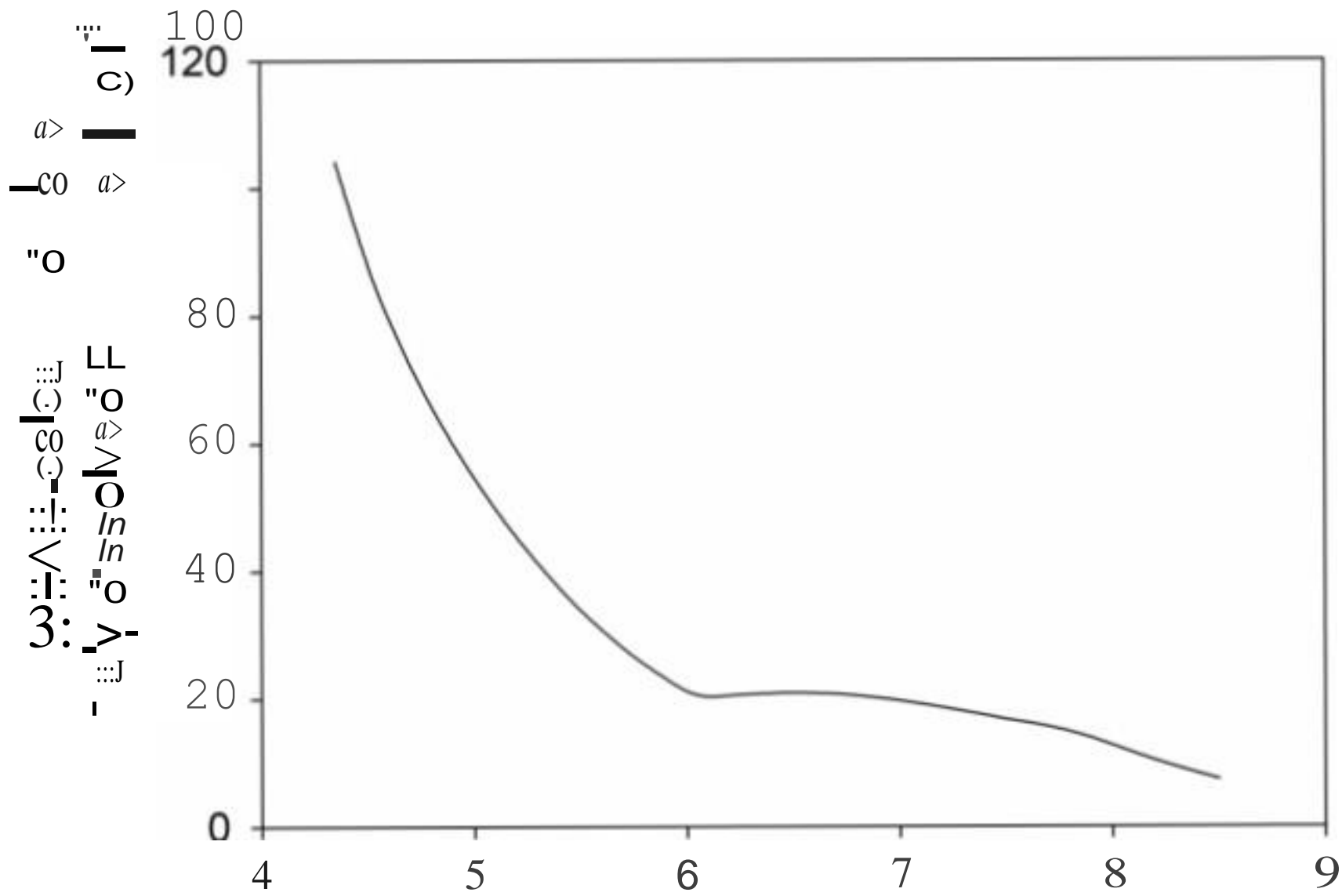


Figure 7



pH

Concentrations of Fe, organic C and Al in 3.5kDa dialysates

Concentrations of Fe, organic C and Al in 3.5kDa dialysates

Sample site	Latitude/Longitude	Sample date (dd/mm/yy)	Fe (ug dm-3)	Fe(II) (ug dm-3)
Black Burn (BB)	54°47'11"N 2°27'20"W	2/26/2004	<2	2
Gais Gill (GG)	54°24'17"N 2°26'15"W	1/8/2004	19	9
Pool X (PX)	54°39'45"N 2°27'43"W	9/25/2003	174	not measured
Pool X (PX)	54°39'45"N 2°27'43"W	1/22/2004	49	10
Pool Y (PY)	54°39'45"N 2°27'43"W	9/25/2003	12	not measured
River Eden (RE)	54°23'13"N 2°20'14"W	1/8/2004	15	6
River Hodder (RH)	54° 1'34"N 2°27'12"W	11/17/2003	72	<2
River Hodder (RH)	54° 1'34"N 2°27'12"W	1/29/2004	5	5
River Lune (RL)	54° 4'34"N 2°43'50"W	1/29/2004	not measured	not measured
River Ribble (RR)	53°45'56"N 2°38'25"W	11/24/2003	11	<2
River Ribble (RR)	53°45'56"N 2°38'25"W	1/29/2004	9	5
River Tees (RT)	54°39' 2"N 2°10'36"W	2/26/2004	3	3
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	11/14/2003	39	<2
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	2/18/2004	40	<2
Wad Hazel Sike (WHS)	54°42'38"N 2°19'11"W	2/26/2004	13	6
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	11/17/2003	17	2
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	1/29/2004	20	<2

DOC (mg dm-3)	monomeric Al (ug dm-3)
2.12	19
3.65	3
8.61	354
4.1	50
4.55	13
2.64	15
3.93	60
1.07	8
1.45	13
4.32	10
3.67	16
2.06	15
7.61	9
2.29	11
1.93	18
1.19	9
2.83	12

Concentrations of Fe, organic C and Al in 10kDa dialysates

Concentrations of Fe, organic C and Al in 10kDa dialysates

Sample site	Latitude/Longitude	Sample date (dd/mm/yy)	Fe (ug dm-3)	Fe(II) (ug dm-3)
Black Burn (BB)	54°47'11"N 2°27'20"W	2/26/2004	2	6
Gais Gill (GG)	54°24'17"N 2°26'15"W	1/8/2004	9	5
Pool X (PX)	54°39'45"N 2°27'43"W	9/25/2003	299	<2
Pool X (PX)	54°39'45"N 2°27'43"W	1/22/2004	107	32
Pool Y (PY)	54°39'45"N 2°27'43"W	9/25/2003	15	<2
Pool Y (PY)	54°39'45"N 2°27'43"W	1/22/2004	21	<2
River Eden (RE)	54°23'13"N 2°20'14"W	1/8/2004	16	8
River Hodder (RH)	54° 1'34"N 2°27'12"W	11/17/2003	128	13
River Hodder (RH)	54° 1'34"N 2°27'12"W	1/29/2004	4	4
River Lune (RL)	54° 4'34"N 2°43'50"W	11/24/2003	18	<2
River Lune (RL)	54° 4'34"N 2°43'50"W	1/29/2004	4	2
River Ribble (RR)	53°45'56"N 2°38'25"W	11/24/2003	23	<2
River Ribble (RR)	53°45'56"N 2°38'25"W	1/29/2004	6	<2
River Tees (RT)	54°39' 2"N 2°10'36"W	2/26/2004	6	9
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	11/14/2003	81	<2
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	2/18/2004	26	<2
Wad Hazel Sike (WHS)	54°42'38"N 2°19'11"W	2/26/2004	7	7
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	11/17/2003	34	<2
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	1/29/2004	8	3

DOC (mg dm-3)	monomeric Al (ug dm-3)
2.93	20
2.21	5
11.24	381
6.06	69
7.77	22
4.02	13
2.55	10
5.97	90
0.98	8
3.14	12
2.12	11
5.32	14
4.77	18
2.94	17
15.2	10
5.78	11
2.91	20
3.25	34
1.35	11

Concentrations of Fe, organic C and Al in 15kDa dialysates

Concentrations of Fe, organic C and Al in 15kDa dialysates

Sample site	Latitude/Longitude	Sample date (dd/mm/yy)	Fe (ug dm-3)	Fe(II) (ug dm-3)
Black Burn (BB)	54°47'11"N 2°27'20"W	2/26/2004	4	7
Gais Gill (GG)	54°24'17"N 2°26'15"W	1/8/2004	not measured	not measured
Pool X (PX)	54°39'45"N 2°27'43"W	9/25/2003	not measured	not measured
Pool X (PX)	54°39'45"N 2°27'43"W	1/22/2004	not measured	not measured
Pool Y (PY)	54°39'45"N 2°27'43"W	9/25/2003	not measured	not measured
Pool Y (PY)	54°39'45"N 2°27'43"W	1/22/2004	not measured	not measured
River Eden (RE)	54°23'13"N 2°20'14"W	1/8/2004	not measured	not measured
River Hodder (RH)	54° 1'34"N 2°27'12"W	11/17/2003	not measured	not measured
River Hodder (RH)	54° 1'34"N 2°27'12"W	1/29/2004	5	3
River Lune (RL)	54° 4'34"N 2°43'50"W	11/24/2003	not measured	not measured
River Lune (RL)	54° 4'34"N 2°43'50"W	1/29/2004	5	3
River Ribble (RR)	53°45'56"N 2°38'25"W	11/24/2003	not measured	not measured
River Ribble (RR)	53°45'56"N 2°38'25"W	1/29/2004	no sample	no sample
River Tees (RT)	54°39' 2"N 2°10'36"W	2/26/2004	2	8
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	11/14/2003	not measured	not measured
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	2/18/2004	26	<2
Wad Hazel Sike (WHS)	54°42'38"N 2°19'11"W	2/26/2004	4	6
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	11/17/2003	not measured	not measured
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	1/29/2004	6	<2

DOC (mg dm-3)	monomeric Al (ug dm-3)
2.77	18
not measured	not measured
not measured	not measured
not measured	not measured
not measured	not measured
not measured	not measured
not measured	not measured
0.9	9
not measured	not measured
2.32	4
not measured	not measured
no sample	no sample
2.8	17
not measured	not measured
6.01	11
2.92	25
not measured	not measured
1.85	11

Captions for Electronic Supplementary Information

Data1. Major water chemistry parameters at sampling sites.

Data2. Concentrations of Fe, organic C and Al in 3.5kDa dialysates.

Data3. Concentrations of Fe, organic C and Al in 10Da dialysates.

Data4. Concentrations of Fe, organic C and Al in 15kDa dialysates.

Data5. Generic predicted ratios of Fe(III):Dom for pH 3.0 to 9.0.

Major water chemistry parameters at sampling sites

Major water chemistry parameters at sampling sites

Sample site	Latitude/Longitude	Sample date (dd/mm/yy)	pHfield
Black Burn (BB)	54°47'11"N 2°27'20"W	2/26/2004	7.94
Gais Gill (GG)	54°24'17"N 2°26'15"W	1/8/2004	7.24
Pool X (PX)	54°39'45"N 2°27'43"W	9/25/2003	4.16
Pool X (PX)	54°39'45"N 2°27'43"W	1/22/2004	4.33
Pool Y (PY)	54°39'45"N 2°27'43"W	9/25/2003	5.82
Pool Y (PY)	54°39'45"N 2°27'43"W	1/22/2004	6.16
River Eden (RE)	54°23'13"N 2°20'14"W	1/8/2004	7.34
River Hodder (RH)	54° 1'34"N 2°27'12"W	11/17/2003	4.35
River Hodder (RH)	54° 1'34"N 2°27'12"W	1/29/2004	6.57
River Lune (RL)	54° 4'34"N 2°43'50"W	11/24/2003	7.79
River Lune (RL)	54° 4'34"N 2°43'50"W	1/29/2004	7.76
River Ribble (RR)	53°45'56"N 2°38'25"W	11/24/2003	8.14
River Ribble (RR)	53°45'56"N 2°38'25"W	1/29/2004	8.03
River Tees (RT)	54°39' 2"N 2°10'36"W	2/26/2004	8.05
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	11/14/2003	6.57
Roudsea Wood (RW)	51°31' 6"N 4°24'30"W	2/18/2004	6.82
Wad Hazel Sike (WHS)	54°42'38"N 2°19'11"W	2/26/2004	7.61
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	11/17/2003	6.37
Whitray Beck tributary (WB)	54° 3'11"N 2°29'36"W	1/29/2004	7.18

pH final	DOC (mg dm-3)	Na (ueq dm-3)	Mg (ueq dm-3)	Ca (ueq dm-3)	Cl (ueq dm-3)	NO3 (ueq dm-3)	SO4 (ueq dm-3)
8.03	5.8	173	91	590	177	14	73
7.25	6.9	130	52	97	118	2	33
4.28	20.6	202	42	148	158	<1	258
4.51	17.2	105	8	23	99	<1	19
6.92	19.4	153	24	241	154	<1	137
7.32	12	119	15	177	101	6	38
7.56	10.2	145	32	202	127	11	31
4.62	19.4	188	44	31	197	17	53
6.8	3.2	208	65	54	189	28	68
7.6	3.9	322	128	848	338	106	115
8.02	1.7	700	140	900	676	151	115
7.74	7.4	943	193	1395	592	197	292
7.96	5.4	3304	279	1440	3099	265	not measured
8.03	5.8	176	75	558	192	18	57
7.41	40.3	1226	172	538	1380	14	135
7.4	24.6	535	82	440	451	10	58
7.76	5.8	114	31	348	118	8	32
6.3	10.9	217	63	59	231	4	54
7.36	2.8	230	96	91	200	11	58

alklinity (ueq dm-3)	total Fe (ug dm-3)	total Fe(II) (ug dm-3)	filtered Fe (ug dm-3)	filtered Fe(II) (ug dm-3)
1090	191	5	182	30
203	108	9	91	<2
0	642	<2	not measured	not measured
0	441	4	365	6
148	941	4	not measured	not measured
230	314	5	188	<2
334	389	19	325	<2
0	818	<2	596	31
78	116	<2	102	<2
1565	83	<2	73	<2
1599	67	<2	48	<2
2503	195	<2	128	<2
2668	199	<2	94	<2
1024	186	4	173	32
732	387	5	376	13
790	298	<2	247	5
594	435	8	372	26
61	697	<2	689	21
240	157	<2	129	<2

total monomeric Al (ug dm-3)	total acid-reactive Al (ug dm-3)
16	40
5	26
427	409
160	132
60	181
55	113
24	52
63	257
33	76
15	17
4	15
27	27
13	31
14	24
82	28
84	110
5	56
39	115
11	36

Generic predicted ratios of Fe(III) to DOM for pH 3.0 to 9.0

Generic predicted ratios of Fe(III):Dom for pH 3.0 to 9.0

pH	Fe(III):DOM (mol Fe(III) [g DOM] ⁻¹)	Fe(III):DOM (μg Fe(III) [mg DOM] ⁻¹)
3.0	8.96E-03	1001
3.1	5.61E-03	627
3.2	3.61E-03	403
3.3	2.39E-03	267
3.4	1.62E-03	181
3.5	1.13E-03	126
3.6	8.15E-04	91.1
3.7	6.06E-04	67.7
3.8	4.63E-04	51.7
3.9	3.62E-04	40.4
4.0	2.90E-04	32.4
4.1	2.37E-04	26.4
4.2	1.97E-04	22.0
4.3	1.66E-04	18.5
4.4	1.42E-04	15.8
4.5	1.23E-04	13.7
4.6	1.07E-04	12.0
4.7	9.45E-05	10.6
4.8	8.42E-05	9.4
4.9	7.59E-05	8.5
5.0	6.91E-05	7.7
5.1	6.36E-05	7.1
5.2	5.88E-05	6.6
5.3	5.49E-05	6.1
5.4	5.15E-05	5.7
5.5	4.84E-05	5.4
5.6	4.58E-05	5.1
5.7	4.33E-05	4.8
5.8	4.10E-05	4.6
5.9	3.90E-05	4.4
6.0	3.71E-05	4.1
6.1	3.54E-05	4.0
6.2	3.38E-05	3.8
6.3	3.23E-05	3.6
6.4	3.10E-05	3.5
6.5	2.98E-05	3.3
6.6	2.90E-05	3.2
6.7	2.83E-05	3.2
6.8	2.81E-05	3.1
6.9	2.81E-05	3.1
7.0	2.81E-05	3.1
7.1	2.82E-05	3.1
7.2	2.79E-05	3.1
7.3	2.73E-05	3.0
7.4	2.62E-05	2.9
7.5	2.49E-05	2.8
7.6	2.33E-05	2.6
7.7	2.15E-05	2.4
7.8	1.97E-05	2.2
7.9	1.77E-05	2.0
8.0	1.59E-05	1.8
8.1	1.42E-05	1.6
8.2	1.26E-05	1.4
8.3	1.13E-05	1.3
8.4	1.02E-05	1.1
8.5	9.36E-06	1.0
8.6	8.68E-06	1.0
8.7	8.15E-06	0.91
8.8	7.75E-06	0.87
8.9	7.41E-06	0.83

9.0

7.12E-06

0.80