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Abstract: Dialysis and chemical speciation modelling have been used to calculate activities of Fe^{3+} for a range of UK surface waters of varying chemistry (pH 4.3-8.0; dissolved organic carbon 1.7-40.3 mg l^{-1}) at 283K. The resulting activities were regressed against pH to give the empirical model:
$\log a_{Fe^{3+}} = 2.93(\pm 0.40) - 2.70(\pm 0.06) \cdot pH$
Predicted Fe^{3+} activities are consistent with a solid-solution equilibrium with hydrous ferric oxide, consistent with some previous studies on Fe(III) solubility in the laboratory. However, as has also sometimes been observed in the laboratory, the slope of the solubility equation is lower than the theoretical value of three. The empirical model was used to predict concentrations of Fe in dialysates and ultrafiltrates of globally distributed surface and soil/ground waters. The predictions were improved greatly by the incorporation of a temperature correction for $a_{Fe^{3+}}$, consistent with the temperature-dependence of previously reported hydrous ferric oxide solubility. The empirical model, incorporating temperature effects, may be used to make generic predictions of the ratio of free and complexed Fe(III) to dissolved organic matter in freshwaters. Comparison of such ratios with observed Fe : dissolved organic matter ratios allows an assessment to be made of the

amounts of Fe present as Fe(II) or colloidal Fe(III), where no separate measurements have been made.

Response to Reviewers: Reviewer #1: Review of AQUA116, "The chemical speciation of Fe(III) in freshwaters", by Stephen Lofts, Edward Tipping and John Hamilton-Taylor.

General response to reviewer #1:
We are very gratified to read this reviewers' very positive comments. We are happy to amend the paper as suggested and agree that further comparison of our results with previous laboratory work is appropriate. Responses to specific comments are listed below beneath each comment in turn.

The authors of this manuscript have used observations of truly dissolved Fe concentrations in freshwaters (obtained via dialysis procedures in UK surface waters) in conjunction with chemical speciation modeling to determine the activity of Fe(III) as a function of pH over a range of dissolved organic carbon concentrations and pH. The results were summarized with a simple empirical model. The empirical model was then used to predict Fe concentrations in dialysates and ultrafiltrates reported for globally distributed surface and soil/ground waters. The authors' model is consistent with previous observations of Fe(III) solubility obtained in the laboratory, and the observed correspondence between observed and predicted Fe(III), using a global dataset, is consistent with laboratory observations of the influence of temperature on the solubility of hydrous ferric oxide. A key element of the authors' work is their focus on description of truly-dissolved Fe concentrations as opposed to operationally defined concentrations.

This manuscript is uncommonly well written, and is one of the more interesting manuscripts I have encountered in a number of years. I think that this work is destined to be much-cited. It will likely serve as a keystone for further quantitative advances toward an understanding of iron biogeochemistry. In their conclusions section the authors indicate that dissolved Fe(II) comprises a substantial fraction of the truly-dissolved Fe pool. Their associated conclusion - that Fe(II) measurements in the environment should be given a higher priority - is compelling and important.

While I am happy to recommend publication of this manuscript, I think that it would be significantly improved through additional comparisons with prior work. The authors compare the slope of equation (2) with the slopes obtained by Byrne and Luo (2000) and Byrne et al. (2005), but have not compared their solubility product (intercept) with the results obtained in either of those works. I recommend that the authors make such comparisons by (a) estimating the activity coefficients of ferric ions and hydrogen ions in the previous analyses that were conducted at 0.7 molal ionic strength and (b) considering the effects of ageing on hydrous ferric oxide documented by Liu and Millero (1999). Ageing effects will reduce the solubility products that were determined by Byrne and Luo (2000) and Byrne et al. (2005) on relatively short time scales.

Response: We have inserted additional text and a new figure discussing the issue. This is an interesting issue that we feel is worth including in the paper, particularly as we had already partly discussed some of the studies concerned.

Infelicities and errata

Comparison of the authors' abstract and the discussion of ferric ion activities on page 15 suggests that the final draft of the authors' manuscript inadvertently contains some elements of earlier versions. The equation highlighted in the abstract should presumably agree with equation 2.

Response: This has been corrected.

On page 5, fourth line of section 2, for many readers it might be useful to have "rankers" defined.

Response: A definition has been inserted.

On page 7 the first sentence (beginning "Total Fe and Fe(II).") is awkward.

Response: The sentence has been simplified.

On page 10, section 4.4.1, I suggest reordering the structure of a sentence as follows - "Stream water temperatures were estimated from the available data by.".

Response: Amended.

On page 19, six lines from bottom of page, "103 - 104" should be given as "10-3 - 10-4".

Response: Amended.

For the final sentence before the Conclusions section I suggest the following - ".would presumably occur through precipitation of HFO."

Response: Amended.

The conclusions section is very well written. However, in the final sentence the meaning of ".so riverine endmember compositions must reflect 'real' conditions and not simply waters having high Fe concentrations." is somewhat enigmatic.

Response: On reflection we have elected to remove the final two sentences of the Conclusions since they detract somewhat from the previous sentence, which itself forms a suitable final point.

In Table 1 the stoichiometry of the next-to-last reaction (formation of FeF2+) is incorrect.

Response: Amended.

Reviewer #2

General response to reviewer #2:
This reviewer feels that there are some difficulties with our experimental methods and results. Their main concerns appear to be the prediction of truly dissolved Fe in the field data, where they consider that "the model predicted result do not appear to match literature measurement values very well". We would take issue with this on two counts: firstly, it is difficult to respond constructively to such a vaguely worded statement in a truly meaningful way, and secondly, we would (and indeed already have) argued that considering the inherent uncertainties in model and measurements, the results are in fact reasonably good. The reviewer considers that the 'poor' predictions may result from the fact that our modelling approach does not considering specific binding ligands for Fe. We have considered this point in the paper, but not explicitly. In the light of these comments, we have inserted additional text to contrast our and other modelling approaches.

The reviewer also considers that there may be difficulties in measuring the truly dissolved Fe in our samples due to our analysis methods. We did in fact take a number of steps to ensure the high quality of our results (detailed in the response to point 2a) below). We would also point out that in freshwater systems the use of clean techniques for Fe analysis is not necessarily appropriate as the metal is usually present at above trace amounts (cf. the oceans where Fe is present in trace amounts).

We have responded to the specific points made by this reviewer below. In each case, we have refuted the criticism, and overall we do not consider it warranted to amend the manuscript on the basis of this review.

Specific points

This manuscript presents an empirical relationship between Fe3+ activity and the solution pH and temperature based on fitting the "WHAM/Model VI model" to the dialysis experiments results for field samples. The experiments appear to have some problems and the model predicted result do not appear to match literature measurement values very well. These may result mainly from the lack of accurate knowledge of Fe-binding constants of dissolved organic matter (and its variation due to the influence by ionic strength, pH and temperature) and the difficulties in accurate determining Fe, especially truly dissolved Fe in the sample. My detailed questions are listed below:

1. Using DOC concentration in the model would not be appropriate if the relationship between DOC concentration and the concentration of organic ligands that bind Fe in the water is not known.

Response: We think that the reviewer is comparing our modelling approach with that used to quantify metal-organic binding in seawater. A central hypothesis of our approach is that we consider the portion of DOC that binds metals to be the humic substances (humic acid and fulvic acid) present in the water. Since humics typically comprise the majority of freshwater DOC in fluvial systems, we then assume that for modelling purposes their concentration can be estimated from a bulk measurement of DOC. In this approach there is no need to quantify concentrations of specific organic ligands binding the metal.

This approach and its uncertainties are discussed in Section 4.3. In response to the reviewers comment we have inserted additional text explaining the approach in the Introduction and Discussion sections.

2. The dialysis results may be questionable because of the lack of considering several factors that may influence the concentration of Fe and DOC in the dialysis bag after prolonged incubation:

a) Trace metal clean techniques are not used in Fe analysis and there is a need to consider influence by Fe contamination;

Response: In addition to the measures outlined in the manuscript (i.e. acid washing of sampling vessels), preparation, insertion and removal of dialysis bags was done under clean conditions and the colorimetric analysis of Fe was rigorously quality-controlled using standards kept in clean conditions.

b) Fe^{3+} and its hydrolysis species may absorb onto the wall of dialysis bag;
c) Fe^{2+} may diffuse through the dialysis bag and then converted to Fe^{3+} during the course of the experiments.
e) During 7 days incubation, Fe^{3+} and DOC may absorb on the wall of the container and the dialysis bag;

Response: These all may indeed occur during the incubation experiments. However, in the presence of hydrous ferric oxide, the Fe^{3+} activity is controlled and thus buffered. Therefore, these phenomena should not affect the Fe^{3+} activity.

d) The portion of DOC that did not diffuse through the dialysis bag may also bind Fe^{3+} and thus lowering Fe^{3+} activity;

Response: The non-dialysable DOC unquestionably will bind Fe^{3+}. However, whether a portion of the DOC is dialyzable or not will not affect the Fe^{3+} activity since at equilibrium this will be the same throughout the system (i.e. inside and outside the bag) as the Fe^{3+} ion and other small ionic species of Fe can equilibrate across the dialysis membrane.

f) Since pH changed during dialysis incubation, it is not clear if the resulting speciation modeling would be valid for natural sample pH.

Response: The objective of our incubation experiments was to generate data on the speciation of Fe under conditions as close to natural as possible (particularly with respect to the presence of natural dissolved organic carbon). This is in practice not possible for reasons including pH shifts as we have pointed out in the paper. Our experimental design took account of possible changes in chemistry by explicit analysis of the samples after incubation. These data were then used for speciation modelling to generate an FeIII solubility expression which was used to predict speciation in other natural waters. Using the chemical composition at the end of incubation in model calibration accounts for any changes that occur during incubation. It was not a part of the work to apply the speciation modelling results obtained from our incubated samples directly back to the natural conditions in those samples.

g) Bacteria may influence DOC content and composition in 7 day period.

Response: This is a plausible hypothesis – but it should be borne in mind that bacteria exert such an influence on DOC under natural conditions anyway. It would have been useful if the reviewer had provided examples in the literature of such an occurrence - we know of no evidence that freshwater DOC composition is significantly altered by bacterial action under similar experimental conditions to ours.

3. What is the explanation for the statement that "There was a tendency for Fe concentrations to be higher at lower pH, although this trend was not especially pronounced. There was also a tendency for higher filtered Fe to be associated with higher DOC, although this was not general"?

Response: This is simply a descriptive statement of trends in Fe concentrations observed in our data, which we provide as (hopefully) useful background information for the reader. To attempt to explain such trends, if possible, would likely require a separate manuscript.

4. "It is important to realize, however, that ultimately the proportion of the filterable DOM that is dialyzable is not important for this work", why?

Response: At equilibrium in the incubated system, the activity of Fe3+ will be the same inside and outside the bag, because it can easily pass through the dialysis membrane. Since the activity of Fe3+ is controlled by a solid oxide phase its activity is independent of the concentration of DOM, or by the distribution of DOM inside and outside the dialysis bag.

5. The model results do not seem to fit the field data in Figure 3 well and the data points have a large deviation from the 1:1 line.

Response: We feel that this is a somewhat inaccurate comment – particularly so since the model describes some of the field data very well. As we point out in the text, after adjustment for temperature most of the predictions fall within a factor of three of the observations, which we would consider very reasonable, given the levels of uncertainty inherent in making predictions of the chemical speciation of field waters. We have attempted to account for at least some of the uncertainty in the model predictions, but we should point out that there will also be measurement uncertainty in the observations. This is a particularly pertinent point as all the data have been gathered using relatively complex methods (e.g. ultrafiltration or dialysis). We would also point out that the observations cover at least two orders of magnitude in truly dissolved Fe and that the model is reasonably successful in reproducing this variability.

6. Should Fe solubility increase instead of "decrease as pH decreases" as stated in the abstract?

Response: It is the apparent solubility product of the hydrous ferric oxide that decreases as pH decreases. We have reworded this part of the abstract to discuss the slope of the solubility equation, since it is this equation on which we focus in the main text.

The chemical speciation of Fe(III) in freshwaters

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Abstract

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

$$\log a_{Fe3+} = 2.93(\pm 0.40) - 2.70(\pm 0.06)\cdot pH$$

Predicted Fe^{3+} activities are consistent with a solid–solution equilibrium with hydrous ferric oxide, consistent with some previous studies on Fe(III) solubility in the laboratory. However, as has also sometimes been observed in the laboratory, the slope of the solubility equation is lower than the theoretical value of three. The empirical model was used to predict concentrations of Fe in dialysates and ultrafiltrates of globally distributed surface and soil/ground waters. The predictions were improved greatly by the incorporation of a temperature correction for a_{Fe3+}, consistent with the temperature–dependence of previously reported hydrous ferric oxide solubility. The empirical model, incorporating temperature effects, may be used to make generic predictions of the ratio of free and complexed Fe(III) to dissolved organic matter in freshwaters. Comparison of such ratios with observed Fe : dissolved organic matter ratios allows an assessment to be made of the amounts of Fe present as Fe(II) or colloidal Fe(III), where no separate measurements have been made.

Iron; speciation; solubility; freshwater; dialysis; ultrafiltration

1 Introduction

Iron is one of the most abundant elements on Earth, and is considered essential for living organisms. It is highly reactive in the freshwater environment, has an oxidation–reduction chemistry that is an important aspect of its aquatic cycling behaviour, and has been shown to have a number of significant roles in the cycling and bioavailability of other elements. In oxic freshwaters the +3 oxidation state is the thermodynamically stable form (Davison, 1993). Iron(III) influences the speciation and bioavailability of phosphorus in lakes (Jones et al., 1993), promotes the decomposition of dissolved organic carbon in surface waters by photochemical means (Stumm and Morgan, 1996), and forms particulate oxides and hydroxides (hereafter collectively referred to as hydrous ferric oxide, HFO) capable of sorbing and transporting trace metals and anionic species (Dzombak and Morel, 1990) and dissolved organic matter (DOM) (Tipping, 1981). More recently, the importance of iron in limiting phytoplankton growth in the oceans has increased interest in riverine fluxes to the oceans (Turner et al., 2001). Additionally, iron influences the aquatic speciation and bioavailability of trace metals by competing for common ligands such as natural organic matter (Tipping et al., 2002). Clearly, knowledge of the speciation of Fe(III) is key in developing a quantitative understanding of these processes.

Our knowledge of inorganic Fe(III) chemistry indicates that in the range of pH (6–9) of the majority of surface waters, the concentration of free and complexed dissolved Fe(III) concentration should be very low due to extensive hydrolysis and precipitation to form HFO. In practice, measured concentrations of dissolved (i.e. filtered) Fe in such waters tend to be larger, sometimes by several orders of magnitude, than concentrations predicted by assuming equilibrium of Fe(III) with an HFO phase. The presence of this additional dissolved Fe has been variously attributed to dissolved organic complexes of Fe(III) (e.g. Perdue et al., 1976; Koenings, 1976) or to the presence of small particles of HFO, perhaps stabilised by surface coatings of natural organic matter (e.g. Shapiro, 1966; Cameron & Liss, 1984; Laxen and Chandler, 1983), but evidence for the relative importance of these forms is somewhat lacking. Recent work on the speciation of iron in natural waters (e.g. Rose et al., 1998; Olivié–Lauquet et al., 1999; Benedetti et al., 2003; Allard et al., 2004) suggests that iron in colloidal phases (variously defined with a lower nominal cutoff in the range 5–30 kDa) can exist both as organic complexes and small hydroxide particles. Lyvén et al. (2003) used flow field–flow fractionation to demonstrate the presence of two distinct iron forms in a surface water – a small fraction (largely below a nominal molecular weight of 30kDa) associated with organic C, and a larger fraction rich in Fe itself. These results are strongly suggestive of the presence of Fe(III) as a mixture of organic complexes and an HFO phase, and also indicate that a reliable size separation method can differentiate the two forms. Sophisticated methods such as flow field–flow fractionation can provide invaluable fine scale information on physical speciation, but are complex and not amenable to high sample throughput. A simpler separation technique, amenable to use on large numbers of samples, is needed to investigate spatial and temporal trends in Fe(III) speciation in surface waters. Ultrafiltration is reasonably well–established yet issues remain regarding artefacts, such as the blockage of filter pores by suspended material, and the formation of 'gel' layers at the filter surface. Dialysis, on the other hand, is relatively simple and non–invasive, and has previously been used to isolate small size fractions of metals (e.g. Beneš and Steinnes, 1974; Jansen et al., 2001).

The ability to quantitatively separate the Fe in the size range below that in which HFO is encountered would be highly useful in the study of whether and how HFO controls the combined concentrations of free and complexed Fe(III) (hereafter referred to as truly dissolved Fe(III)). Laboratory studies on synthetic forms of HFO indicate that for the solubility equilibrium

$$Fe(OH)_{3\,(s)} + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O \qquad (1)$$

values for the standard solubility product K_{SO} are in the range $10^{2.5}$–$10^{5.0}$. Allard et al. (2004) showed that the concentrations of colloidal organically–complexed Fe(III) in waters from the Amazon region were consistent with an equilibrium between the Fe^{3+} ion and an HFO with a single solubility product within this range. However there has been no extension of this work to other environments, particularly to temperate regions and to soil/ground waters. Chemical speciation of a small size fraction from which HFO has been removed would allow the Fe^{3+} activity to be estimated and thus allow controls on Fe(III) solubility to be assessed. This would in principle enable a general model of Fe(III) chemistry in freshwaters to be constructed.

The modelling of the binding of a metal such as Fe(III) to aquatic dissolved organic matter (DOM) is complex, and a clear conceptual picture of the binding properties of the DOM is required. Some workers consider the binding to be to specific organic ligands, while others consider the binding to be controlled by binding sites on the bulk of the organic matter, in competition with protons and other trace metals. In the second hypothesis the degree of binding may in principle be related to the total concentration of DOM whereas in the first hypothesis the concentrations of specific ligands are not necessarily related to the total DOM concentration. In previous work, Tipping et al. (2002) characterised the binding of Fe(III) to isolated humic and fulvic acids using the WHAM/Model VI model and used the paameterised model to simulate Fe(III) speciation in a limited number of field samples, under the assumption that Fe(III) binding to DOC could be related to its binding to fulvic acid.The model was able to describe speciation in the data, if some reasonable variability in model parameters among samples was allowed. There is, however, a pressing need to further assess model performance against field data.

In the work reported here, we have sampled and dialysed natural waters, giving a dialysate excluding fine particulates in which the Fe(III) should be present only in truly dissolved form. We have used WHAM/Model VI to calculate Fe^{3+} activities in these samples, and used the results to produce an empirical expression for the variation in Fe^{3+} activity with pH and temperature. We have compared this expression with predictions of Fe^{3+} activity derived from laboratory studies of Fe(III) solubility, and we have shown how our results may be incorporated into speciation models either empirically or by assuming equilibrium with an HFO–type phase. We then make predictions of truly dissolved Fe(III) in dialysates and ultrafiltrates of surface and soil/ground waters, reported in the literature. We have also investigated the use of the Fe:DOM ratio in the truly dissolved fraction as a means of assessing Fe speciation, and illustrated this using an extensive dataset on UK surface waters.

2 Study sites

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

3 Experimental

Deionised water (conforming to the ASTM Type 1 standard) was used for all dilutions and washings. Sample vessels of 5L or 10L volume were used. All sampling vessels were soaked in 1% v/v nitric acid (BDH 'Aristar' grade) for 24 hours, followed by deionised water for 24 hours. On return to the laboratory, bags of dialysis membrane (SpectraPor 7 regenerated cellulose, Spectrum Laboratories Inc., 3.5kDa, 10kDa and 15kDa molecular weight cutoff) containing deionised water were suspended directly into the solution. All dialysis membranes were thoroughly rinsed with deionised water prior to use. The solution volume within each set of dialysis bags was 2% of the sample volume. Samples containing dialysis bags were stirred at 10^{o}C in the dark for seven days. The dialysis bags were removed, rinsed thoroughly with deionised water and the dialysate solutions removed. A portion was acidified with 5M hydrochloric acid (BDH 'Spectrosol' grade; 200ml per 10ml sample) for colorimetric analysis of total Fe and Fe(II). The remaining dialysate was stored unaltered for analysis of dissolved organic carbon (DOC) and monomeric aluminium. A portion of the outer sample solution was retained for analysis of pH and conductivity. All solutions were stored in the dark at 4^{o}C until analysis.

Field samples for the analysis of water chemistry were obtained at the same time as experimental samples. Samples for the measurement of pH were collected in thoroughly rinsed airtight glass vessels and analysed within 24 hours. Samples for the analysis of major ions, alkalinity, DOC, monomeric aluminium and acid–reactive aluminium were taken in single–use polyethylene terephthalate (PETE) bottles. Unfiltered samples were analysed for alkalinity, monomeric aluminium and acid–reactive aluminium. On return to the laboratory a portion of sample was filtered (GF/F filters, Whatman Inc.) for the analysis of major ions, monomeric aluminium and acid–reactive aluminium. Samples for the analysis of total Fe and Fe(II) were taken in PETE bottles previously soaked in 1% (v/v) nitric acid (BDH 'AnalaR' grade) and rinsed thoroughly with deionised water. The samples were filtered (0.45μm cut–off filters, Whatman Inc.) immediately on return to the laboratory and acidified with 5M hydrochloric acid (BDH 'Spectrosol' grade; 200ml per 10ml sample) prior to storage for analysis of total Fe and Fe(II). All samples were stored in the dark at 4^{o}C prior to analysis.

Total Fe and Fe(II) were analysed colorimetrically using Ferrozine® (Sigma-Aldrich Chemie GmbH) Gibbs (1979) in an acetic acid/sodium acetate buffer at a wavelength of 562nm. Calibration was done using solutions prepared from stock iron(III) nitrate standards (BDH 'Aristar' grade). For the analysis of total iron, a reducing agent (hydroxylammonium chloride) was added to standards and samples to reduce Fe(III) to Fe(II), and a contact time of 10 minutes was allowed prior to analysis. For the analysis of Fe(II), reducing agent was not added and a contact time of 30s was allowed. Prior to analysis, the recovery of Fe(II) from mixed Fe(II)/Fe(III) solutions (1:1 w/w) was analysed; the mean recovery of 50μg dm^{-3} (895nM) and 250μg dm^{-3} (4476nM) Fe(II) from mixed solutions was 105.0%. Quality standards were prepared from an independent iron(III) nitrate stock solution (BDH 'Aristar' grade). The detection limit of the method (calculated as twice the standard deviation of control samples), for both Fe(II) and total Fe, was 2μg dm^{-3} (36nM) for a cell path length of 4cm (Hitachi U-2000 spectrophotometer). All determinations were performed within three days of sampling.

Monomeric and acid–reactive Al were determined by the method of Seip et al. (1984). Measurements of pH were made following the procedures recommended by Davison (1990) using a GK2401C combination electrode

(Radiometer Inc.). Major cations (sodium, magnesium, potassium and calcium) were measured by ICP–OES (Perkin Elmer Optima 4300 DV) on filtered samples after acidification. Major anions (chloride, nitrate, sulphate) were measured by ion chromatography (DX 100, Dionex Corp.). Alkalinity was measured by Gran titration, using a 702 SM Titrino (Metrohm AG). Dissolved organic carbon was measured by flame combustion (TOC-V CPH/CPN analyser, Shimadzu Corp.).

4 Speciation modelling

4.1 Nomenclature

In presenting and discussing the modelling, we will use the term ‘truly dissolved’ Fe(III) to refer to the modelled sum of the free ion, inorganic and organic complexes, and ‘colloidal’ to refer to filterable Fe(III) that is predicted to be precipitated as HFO or to be complexed to organic matter that is not ultrafiltered or dialysed. Where reference is made to modelling in equilibrium with the atmosphere, this refers to the use of a carbon dioxide partial pressure of 3.65×10^{-4} atm for the purpose of simulating the carbonate system.

4.2 WHAM/Model VI

Speciation modelling was done using WHAM/Model VI (Tipping, 1994; Tipping, 1998; Tipping et al., 2003). For the purposes of this work the model can be considered as combining a standard model of thermodynamic equilibria among solution ions, with a model for the equilibrium complexation of ions with fulvic acid (Model VI). Model VI considers complexation of cations to fulvic acid by complexation at discrete sites and by electrostatic accumulation. The model contains 80 specific binding site types. The formulation of binding strengths is structured such that the binding of each metal is described by two metal–specific parameters: K_{MA}, which describes binding to relatively weak, abundant sites, and ΔLK_2, a modifying parameter which accounts for binding to relatively strong, scarce sites. It is assumed that only the free metal ion and its first hydrolysis product can bind, with the same parameter values, and the model has been parameterised on this basis. Tipping (1998) calculated a value of 2.4 for $\log K_{MA}$ for Fe(III) by linear regression of calculated $\log K_{MA}$ values for fulvic acid against those for humic acid. Tipping et al. (2002) calculated a $\log K_{MA}$ of 2.8 for the binding data of Langford and Khan (1975) and proposed a new default $\log K_{MA}$ of 2.6 for fulvic acid binding, which we shall use here.

Thermodynamic parameters for Fe(III) solution species are shown in Table 1. The formation reactions for the Fe(III) dimer $Fe_2(OH)_2^{4+}$ and trimer $Fe_3(OH)_4^{5+}$ were included to test for the possible importance of these species in the samples studied. In practice calculated concentrations of these species were found to be negligible.

4.3 Model inputs

Dissolved organic matter (DOM) comprises a wide range of classes of compound, of which the most important from the metal binding point of view are the humic substances (humic and fulvic acids). WHAM/Model VI has previously been shown to provide adequate descriptions of metal binding to uncharacterised DOM samples, by adjustment of the proportion of dissolved DOM considered to be chemically ‘active’ with respect to binding (e.g. Bryan et al., 2002; Tipping et al, 2002). Thus, within ranges of pH, DOM concentrations and metal concentrations previously studied, the use of humic substances as a surrogate for bulk dissolved NOM has been shown to be reasonable for the simulation of metal binding. NOM was assumed throughout to comprise 50% C. It was also assumed throughout that DOM was 65% chemically ‘active’, i.e. that it behaved as though composed of 65% fulvic acid and 35% inert material with no binding properties, after Bryan et al. (2002). Thus, we make the assumption that binding properties of DOM do not vary among samples. We argue that the assumptions are further justified if it can be shown that the resulting chemical modelling successfully provides a coherent picture of Fe(III) speciation across a broad range of water types.

In order to assess the effect that variability in DOM 'activity' might have upon model outcomes, model calculations were done using bootstrapping. For each sample 10000 speciation calculations were done each with a different 'activity', calculated at random assuming the 'activity' to have a standard deviation of 15%, to give 10000 estimates of the output variable of interest (either log a_{Fe3+} or total Fe(III)). The standard deviation is based on the range of DOM 'activities' found by Bryan (2001), based on copper binding to UK freshwaters. The 10000 estimates of the output variable of interest were used to calculate its standard deviation.

4.4 Literature data

4.4.1 USA surface waters (Babiarz et al.)

Babiarz et al. (2001) filtered 23 surface water samples from the northern and southern U.S.A. using conventional filtration (0.4μm) and tangential–flow ultrafiltration (10kDa cutoff), and measured organic C, Fe and Al in both filtrates. Ultrafiltration was done at ambient temperature. The conductivity and pH of bulk samples were also measured. pH ranged from 3.8 to 8.2 and DOC from 0.2 to 26.5 mg dm^{-3}. Concentrations of major ions (Na, Mg, K, Ca, Cl, NO_3, SO_4, F, and HCO_3) were estimated for 20 of the sites from the United States Geological Survey (USGS) via the National Water Information System (2008) to derive relationships between each major ion and conductivity, from time series samples for the sites closest to those sampled by Babiarz et al. (2001). Stream water temperatures were estimated from the available data by taking the mean of all measured temperatures for the sampling month. For two samples taken in the Florida Everglades, pH, concentrations of DOC, Na, Mg, K, Ca, Cl, SO_4 and alkalinity were taken from the United States Geological Survey South Florida Information Access Service (2008). Major ions at two further Everglades sites were estimated by scaling the available concentrations to the conductivity measurements made at these sites by Babiarz et al. (2001). Surface water temperatures at these four sites were estimated from the mean temperature for the sampling month at the closest site on National Water Information System (2008).

4.4.2 Amazon surface waters (Küchler et al.)

Küchler et al. (1994) filtered samples of two Amazon waters (Rio Negro and Rio Solimões) at 1µm 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 10kDa and 3kDa ultrafiltrates were given. Water temperatures were not given; values of 303K were assumed, based on the mean monitored temperature for the River Solimões 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 Küchler et al. (1994), which was used here. The pH at six locations on the River Solimões was given, ranging from 7.02 to 7.44; the mean of 7.25 was used. Equilibrium with atmospheric CO_2 was assumed for modelling. Both 10kDa and 3kDa filtrates were modelled.

4.4.3 River Awout, Cameroon (Dupré et al.)

Dupré et al. (1999) sampled the Awout River (Cameroon) (pH 4.7) and performed sequential tangential filtration (0.2µm) and ultrafiltration (300kDa and 5kDa nominal cutoff). A subsample of the 0.2µm 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 SO_4 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 0.2µm frontal filtrate; this value was used for both ultrafiltrates. Equilibrium with atmospheric CO_2 was assumed for modelling.

4.4.4 Cameroon surface and ground waters (Viers et al.)

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 0.22µm, 0.025µm or 300kDa, and 5kDa. Concentrations of Na, Mg, Al, K, Ca, Fe, Cl, NO_3, SO_4, alkalinity and DOC were measured in 5kDa filtrates. The pH was measured in 0.22μm filtrates only. Two of the groundwater samples had DOC concentrations below the detection limit so were not used.

4.4.5 Brazil surface waters (Eyrolle et al.)

Eyrolle et al. (1996) sampled surface waters from three locations in Brazil (pH 4.1–7.1). Samples were filtered successively at 0.2μm, 100kDa, 20kDa and 5kDa. Samples taken from the Paraná system were not modelled due to the low recoveries of Fe obtained, which the authors attributed to the use of old ultrafiltration membranes. Speciation was modelled in the 20kDa and 5kDa fractions. Concentrations of Mg, Al, Ca, Fe and DOC were measured in the 20kDa and 5kDa size fractions. Measurements of pH and alkalinity were done on unfiltered samples.

4.4.6 Brazil, Venezuela and Cameroon surface waters (Deberdt et al.)

Deberdt et al. (2002) sampled surface waters from locations in Brazil, Venezuela and Cameroon (pH 5.6–7.7). Samples were filtered successively at 0.2μm, 300kDa, 100kDa, 10kDa and 5kDa. Measurements of pH, alkalinity and temperature were done in the field. Measurements of Fe, Al, Na, Mg, K, Ca, Cl, NO_3, SO_4 and DOC were done on ultrafiltrates. Both 10kDa and 5kDa filtrates were modelled.

4.4.7 Russia soil waters (Pokrovsky et al.)

Pokrovsky et al. (2005) performed filtrations and ultrafiltrations of soil solutions from four locations near Moscow, Russia. The solutions were acidic (pH 3.9–4.7) and high in DOC (39–58 mg dm^{-3} in 0.22μm filtrates). pH, DOC and major ions including Na, Mg, Al, K, Ca, Fe, Cl, NO_3 and SO_4 were measured. Data for filtrates of 0.22μm filter pore size, and for ultrafiltrates of 10kDa and 1kDa pore size were taken.

4.4.8 Netherlands soil waters (Jansen et al.)

Jansen et al. (2001) dialysed soil solutions, obtained by aqueous extraction of a Dutch surface soil horizon, centrifugation and filtration at

0.45µm, using membranes of 1kDa nominal cut–off and a background ionic strength of 0.02M. Four soil solutions were used, the pH values of which were adjusted to 4.0, 4.1, 7.0 and 7.1 prior to dialysis. The ionic strength of each solution was adjusted to 0.01M using KNO_3; this was also done for the initial inside bag solutions. Fe, Al and DOC were measured on the inside bag solutions after 400 hours equilibration at 20°C.

4.4.9 *France groundwaters (Pourret et al.)*

Pourret et al. (2007) sampled four groundwaters (pH 6.2–7.1) from two wetlands located in the Kervidy-Naizin and Petit-Hermitage catchments, France. Samples were filtrated (0.2µm) and ultrafiltered at pore size cut–offs of 30kDa, 10kDa and 5kDa. Concentrations of Na, Mg, K, Ca, Cl, NO_3, SO_4, alkalinity and pH were measured in filtrates. Concentrations of Al, Fe and DOC were measured in ultrafiltrates.

4.5 Statistical analysis

Regression parameters and standard errors were computed in MINITAB Release 14 (Minitab Inc., PA, U.S.A.). Pairwise comparisons of regression model fits were done in Microsoft Excel (Microsoft Inc., WA, U.S.A.) using likelihood ratio testing.

5 Results and Discussion

5.1 Water chemistry

The samples exhibited a wide range of pH, alkalinity and concentrations of calcium and magnesium (Table 2 and Data 1). There are no apparent trends in these variables with location; local geological conditions probably exert a significant influence. Concentrations of DOC showed influences of soil type and flow conditions. At the five sites sampled under both low and high flow conditions, DOC was higher under high flow. The highest concentrations of DOC were seen in the Roudsea Wood stream which drains a lowland peat bog. The influence of flow on chemistry may be seen at some sites; for example, the River Hodder under high flow

(November 2003) exhibited significantly lower pH and higher DOC than under low flow (January 2004). The two larger lowland rivers (the Lune and Ribble) showed similar chemical characteristics under both high and low flow.

Total and filtered (GF/F) concentrations of Fe varied by approximately one order of magnitude across the samples. Fe concentrations tended to be higher at lower pH, although this was not a pronounced trend. There was also a tendency for higher filtered Fe to be associated with higher DOC, although this was not general; the Roudsea Wood stream showed relatively low Fe:DOC ratios on both sampling dates.

5.2 Dialysate compositions

Sample pH values measured after dialysis for one week mainly showed increases in pH, of up to 1.2 units, due to CO_2 degassing. Measurements of Fe, Al and DOC in the dialysates are given in Data 2, Data 3 and Data 4. Dialysis equilibrium with respect to major ions was achieved, with excellent agreement between the conductivity of inside and outside bag solutions after one week (Pearson correlation = 1.000, $p < 0.001$). In contrast, dialysate DOC concentrations were found to be lower than filterable concentrations, with the exception of a small number of samples where the DOC in the raw sample was low (<2 mg dm^{-3}) (Figure 1). Dialysate DOC as a percentage of filtered DOC averaged 37% for dialysates of 3.5kDa and 50% for dialysates of 10kDa. Dialysis at 15kDa, which was not done on all samples, produced DOC concentrations averaging 97% of those obtained by dialysis at 10kDa. Why this apparent lack of equilibrium with respect to DOC occurs is not clear. Possible reasons include slow diffusion of larger organic molecules (Buffle et al. 1993), retention of NOM on larger particles due to adsorption and/or aggregation, or the formation of micellar DOM units too large to pass the membrane (Kerner et al. 2003). It is plausible that some DOM is simply of too large a size to efficiently pass the dialysis membrane; in this context, it is noteworthy that in studies using ultrafiltration to isolate low molecular weight fractions of freshwaters, passage of DOM through ultrafiltration membranes is by no means complete. For example, in the study of Babiarz et al. (2001) (DOM 1.6–94.6 mg l^{-1}) between 20% and 73% of DOM did not pass a 10kDa pore size cutoff ultrafiltration membrane. It is important to realise, however, that ultimately the proportion of the filterable DOM that is dialyzable is not important for this work: it is more important to obtain a sample from which HFO has been removed in order to calculate a_{Fe3+}.

5.3 Fe^{3+} activities

Activities of Fe^{3+} in the dialysates (Table 3) were calculated using WHAM/Model VI. The relationship between log a_{Fe3+} and dialysate pH was modelled by linear regression. Where dialysates of multiple pore sizes were obtained from a single sample, calculated log a_{Fe3+} values were weighted so that the results from each individual sample were emphasised equally in the regression. With bootstrapping, 10000 estimates of the regression parameters (slope and intercept) were obtained; the means and standard deviations of these estimates were taken as the parameters and their standard errors respectively. Activities showed a strong linear dependence upon pH, which could be described by the equation

$$\log a_{Fe3+} = 2.93(\pm 0.40) - 2.70(\pm 0.06)\cdot \mathrm{pH};\ p < 0.001,\ SE_{pred} = 0.58 \quad (2)$$

where SE_{pred} is the standard error of prediction and the bracketed terms are the standard errors of the regression parameters. Addition of a quadratic term in pH produced no significant improvement in the fit. This contrasts with the solubility trend for log a_{Al3+} computed by Tipping (2005), where a quadratic term was required to adequately fit the data. The linear trend in log a_{Fe3+} with pH is consistent with control of Fe^{3+} activities by an HFO type phase. However, the slope of the line differs significantly from the value expected according from the theoretical solubility equilibrium of HFO (Equation 1): none of the 10000 slope values calculated by bootstrapping were below the value of -3.0 predicted.

Fig 2 shows the dependence of log a_{Fe3+} on pH and compares modelled Fe^{3+} activities with predictions made assuming conventional solubility products. Lines are plotted for standard log solubility products for HFO of

$10^{2.5}$ and $10^{5.0}$, considered by Tipping et al. (2002) to represent a reasonable range of solubilities for this material based on the literature. The enthalpy value of Liu and Millero (1999) (-100.4 kJ mol^{-1}) was used to correct standard solubility products to 283K. It can be seen that at higher pH (> 6.0), mean Fe(III) solubility is characteristic of the upper end of the literature range while at lower pH it tends towards the lower end of the range. Thus the solubilities that we calculate from our observations correspond well with the literature range. This finding also supports our hypothesis that Fe(III)–organic complexation can be reasonably modelled as a function of bulk DOC concentration rather than by invoking specific organic ligands.

The pH dependence of log a_{Fe3+} in Equation (2) is worthy of note, since it can affect the prediction of activities appreciably in comparison with the standard solubility product approach. Slope values significantly below -3.0 for the log a_{Fe3+}-pH relationship have been found in laboratory studies of Fe(III) solubility. Of particular interest are the studies of Byrne and Luo (2000) and Byrne et al. (2005), where direct potentiometric measurement of Fe^{3+} concentration variation with pH resulted in slope values of -2.86(±0.01) and -2.73(±0.01), respectively, for the solubility of freshly precipitated (15–60 minutes) HFO. Fox (1988) calculated a slope value of -2.35 based on speciation modelling of dialysed synthetic solutions, and considered the slope value to result from the substitution of anionic counterions (e.g. Cl^-, NO_3^-) for OH^- in the solid phase, while Byrne and Luo (2000) proposed as an alternative explanation a pH–dependent variation in the activity of the solid phase, possibly via a particle size effect. Such a correspondence between Equation (2) and such studies is thus intriguing and hints at the possibility of a common effect on the magnitude of the slope term. It is worth noting that the slope found is unlikely to be due to measurement error: if WHAM/Model VI is used to predict the total Fe(III) in the dialysates assuming control by HFO with a standard solubility product of $10^{5.0}$, then in the five dialysates with pH < 5.0 the predicted Fe(III) concentration exceeds that observed by a factor of at least eight. Conversely, if a standard solubility product of $10^{2.5}$ were to be assumed, dialysate Fe(III) ought to be undetectable (<2 µg l^{-1}) at circumneutral pH. Thus, the identified trend in Fe^{3+} activity appears robust.

Fig 3 compares Fe^{3+} activities, calculated using Equation (2) and corrected to 298K using the enthalpy change of Liu and Millero (1999), with values calculated from the solubility equations presented by Byrne et al. (2005) and Byrne and Luo (2000) for the concentration of Fe^{3+} in 0.7M NaCl and 0.7M $NaClO_4$, respectively. Measured Fe^{3+} concentrations in Byrne et al. (2005) and Byrne and Luo (2000) were corrected for activity effects using Specific Ion Interaction Theory (Grenthe et al. 1997), using species interaction coefficients of 0.56 and 0.38 for Fe^{3+}–ClO_4^- and Fe^{3+}–Cl^- interactions respectively. Activities predicted after Byrne et al. (2005) are consistently higher than those predicted by us, by 0.9–1.1 log units in the pH range 3 to 9. Within the same pH range the activities predicted after Byrne and Luo (1999) are within 0.6 log units of our predictions, being slightly higher below pH 5 and slightly lower above this pH. As can be seen in Fig 3, the solubility line of Byrne and Luo (2000) is entirely within the confidence intervals of our regression line within the pH range 3–9. The solubility line of Byrne et al. (2005) is within the confidence intervals above pH6, but is outside below this pH.

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

5.4 Modelling of literature data

The literature studies did not involve the quantification of Fe(II) in ultrafiltrates or dialysates, with the exception of Jansen et al. (2001) where the absence of Fe(II) was established by colorimetry. Thus it was not considered appropriate to combine the literature data with the data generated in this study when parameterising Equation (2). Instead we used Equation (2) to calculate values of $a_{\mathrm{Fe3+}}$ in the literature samples, which were then input to WHAM/Model VI along with the major ion, pH and DOM concentrations to predict the total dialyzable or ultrafiltrable Fe(III). The results (Fig 4a and 4c) indicate a good correlation between observed and calculated values, however the latter are on average overestimated: on average the predicted $a_{\mathrm{Fe3+}}$ was 3.8 times greater than the observed value. Clearly this bias cannot be due to the presence of Fe(II) since if so we would expect to calculate smaller Fe(III) concentrations than the observed totals, on average. A more likely explanation is the expected effect of temperature on Fe^{3+} activities if the latter are controlled by HFO solubility. Since the dissolution of HFO (Equation 1) is exothermic, we would expect its solubility to decrease with increasing temperature. Thus we would expect the concentration of free ionic and complexed Fe(III) in equilibrium with HFO to decrease also.

Since the mean temperature of the literature samples was 293K, we would expect that on average Equation (2) would overestimate the Fe^{3+} solubility in the literature samples. While it would be possible to extend Equation (2) to empirically account for temperature effects by fitting to the literature data, we have chosen not to do so, as this would discount the possibility of Fe(II) as a confounding factor in the observations. Instead, we *a priori* adjusted the Fe^{3+} activities calculated with Equation (2) assuming HFO solubility control:

$$\log a_{\mathrm{Fe3+,T}} = \log a_{\mathrm{Fe3+,283K}} + \frac{\Delta \mathrm{H}^{\mathrm{o}}}{2.3R}\left(\frac{1}{283} - \frac{1}{T}\right) \tag{3}$$

where ΔH^{o} is the standard enthalpy change for Equation (1) (after Liu and Millero (1999)). The resulting predicted Fe(III) concentrations show appreciably better agreement with the observations (Figs 4b and 4d), with 65 of the 90 predictions falling within a factor of three of the corresponding observation, compared with 53 prior to temperature adjustment. The root mean squared difference (RMSD) in log concentrations dropped from 0.53 to 0.44. The dataset of Babiarz et al. (2001), which contained the largest number of samples and a wide range of sample temperatures (273K to 303K), showed a decrease in RMSD from 0.44 to 0.27 and improved prediction of total Fe(III) in 17 of the 23 samples.

Following temperature correction, the predicted Fe(III) was on average 1.8 times the observed Fe. This is the inverse of the effect that would result from the presence of Fe(II) but does not preclude the possibility that Fe(II) is important in some samples. For example, the discrepancy between observations and calculations in the dataset of Eyrolle et al (1996) could be due to Fe(II).

5.5 Calculating Fe(III) solubility for speciation modelling

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

Equations (2) and (3) can be combined to give a temperature–independent expression for log $a_{\mathrm{Fe3+}}$:

$$\log a_{\mathrm{Fe3+,T}} = 2.93 - 2.70\mathrm{pH} + \frac{\Delta \mathrm{H}^{\circ}}{2.3R}\left(\frac{1}{283} - \frac{1}{T}\right) \tag{4}$$

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

$$\log a_{\mathrm{Fe3+,T}} = -15.63 - 2.70\mathrm{pH} + \frac{5253}{T} \tag{5}$$

This expression is suitable for the direct calculation of Fe^{3+} 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

$$K_{\mathrm{so}} = \{\mathrm{Fe}^{3+}\}\{\mathrm{H}^{+}\}^{-2.70} \text{ or } \log K_{so} = \log a_{\mathrm{Fe3+,T}} + 2.70\mathrm{pH} \tag{6}$$

and after Equation (5):

$$\log K_{so} = -15.63 + \frac{5253}{\mathrm{T}} \tag{7}$$

At 298K K_{so} is $10^{2.00}$, 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 Al^{3+} activity in surface waters can be reasonably described using a single function of pH. Assuming control of Fe^{3+} 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 colloidal Fe, or Fe(II). In Fig 4a, such a prediction is compared to the observed Fe(III):DOM ratios for the sample filtrates and dialysates obtained in this study. Observed ratios in the filtrates were almost all in the range 10^{-3}–10^{-4} mol g^{-1} and showed no variability with pH. Observed ratios in the dialysates overlapped to a small extent with those in the filtrates, but were generally lower, in the range $10^{-3.6}$–$10^{-5.2}$. The ratios also showed a downward trend with pH; below pH 5.0, ratios were similar in the filtrates and dialysates. Values of the predicted Fe(III):DOM ratio are given for pH 3.0–9.0 in Data 5.

If a water sample contains Fe(III) not in the form of truly dissolved Fe(III), then we would expect its Fe(III):DOM ratio to exceed that calculated by taking Equation (2) as a starting point. This can be seen in Fig 4a for the filtrates of our samples. In Fig 4b, a set of observed Fe(III):DOM ratios is shown for long term monthly monitoring data from Pool X and Pool Y, two of the sites sampled in this study. The generic prediction of Fe(III):DOM is shown for reference. In line with our theory, the observed ratios are consistently greater than the predicted Fe(III):DOM, with the exception of a small number of outliers. Given the number of samples taken it is not surprising to find outliers with ratios below the predicted Fe(III):DOM, particularly since the prediction relates to a single temperature taken as a typical annual mean for UK waters. Of note is the observation that the increase in Fe(III):DOM with decreasing pH is reflected in the observed Fe(III):DOM ratios, particularly in the dataset from Pool X (pH 3.9–6.3).

Observed Fe:DOM ratios are shown in Fig 5 for circumneutral to alkaline surface waters, comprising data for four rivers monitored under the UK Land Ocean Interaction Study (LOIS) in 1994-96 (Neal and Robson, 2000). Here no separate measurements of Fe(II) were made. The predicted Fe:DOM ratios were corrected by assuming Fe(II) in the dialysed fraction to be 32% of the Fe(III), following the observations in the dialysates obtained in this study. This raised the predicted Fe:DOM by 0.12 log units (a factor of 1.3). Observed Fe:DOM ratios again largely exceeded the generic Fe:DOM. The exception was the River Trent, where an appreciable number of observed Fe:DOM ratios clustered around the predicted Fe:DOM. This can be taken as an indication of relatively low concentrations of colloidal Fe(III) in this system. The correction of the predicted Fe:DOM for the presence of Fe(II) does not greatly affect the outcome, since the variability in observed ratio at a given pH is much larger than the amount by which the correction increases Fe:DOM.

5.7 The chemistry of Fe(III) in freshwaters

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

6 Conclusions

Dialysis is a simple and effective way of separating a sample of 'truly dissolved' Fe from colloidal–sized material. Using this technique, we have been able to compute Fe^{3+} activities for a number of UK surface waters and to show that the trend in log activities with pH is linear. The solubility of Fe^{3+} is close to that predicted by assuming equilibrium with a 'hydrous ferric oxide' type phase. The slope of the relationship between log a_{Fe3+} and pH is lower than that predicted by the theoretical stoichiometry of the solid phase, a finding previously observed in some laboratory studies of Fe(III) solubility. By the use of a bootstrap method to account for the possible variability in DOM binding 'activity', we have shown that this finding is robust to such variability, and thus the assumption of a mean DOM binding 'activity' is reasonable. These findings strongly support the hypothesis that organic complexation of Fe(III) in freshwaters can be modelled as a function of DOC concentration without the need to invoke distinct organic ligands. The linear relationship between log a_{Fe3+} and pH can be used to predict the total Fe in dialysates and ultrafiltrates sampled from a wide variety of surface and soil/ground waters. The prediction is significantly improved if it is assumed that solubility has a temperature dependence predicted by the temperature dependence of HFO solubility, which provides strong support for the contention that HFO controls Fe^{3+} activities in the field. Using the Fe^{3+} activity equation it is possible to make a generic prediction of the Fe(III):DOM ratio expected at a given pH due to inorganic and organic complexation. Higher 'dissolved' Fe:DOM ratios in natural waters may be indicative of the presence of Fe in other forms, particularly colloidal Fe(III) and dissolved or complexed Fe(II). Comparison of the computed Fe(III):DOM ratio with observed Fe:DOM ratios in UK surface waters indicated that in most cases excess Fe, most likely mainly colloidal Fe(III), was indeed present.

A notable aspect of the literature data used in this study is the almost complete absence of Fe(II) measurements. Our data indicate that although Fe(II) might only comprise a small portion of the total 'dissolved' Fe, it is likely to be a more important component of the 'truly dissolved' Fe (an average of 24% in our samples). Clearly, when considering Fe speciation in natural waters the measurement of Fe(II) should have a higher priority.

There is currently a growing interest in quantifying the fluxes of riverine Fe to the oceans (e.g. Krachler et al. 2005), given the important role of Fe in controlling oceanic phytoplankton productivity. Knowledge of Fe(III) speciation is likely to offer considerable insight into the processes controlling such fluxes. While a significant proportion of Fe is lost on mixing of riverine and estuarine waters (e.g. Sholkovitz et al. 1978), evidence exists that truly dissolved Fe comprises a quasi–conservative Fe pool with respect to fluxes through the mixing zone (e.g. Dai and Martin 1996). Thus, predicting the truly dissolved Fe(III) at the tidal limit using our solubility equation may allow better estimation of Fe fluxes through estuaries to the ocean.

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Table 1 Parameters for the considered solution complexation reactions of Fe(III)

Reaction	log K^o	ΔH^o (kJ mol^{-1})	Reference
$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$	-2.19	43.4	Nordstrom et al. 1990
$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$	-5.67	71.4	Nordstrom et al. 1990
$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3\ (aq)} + 3H^+$	-12.56	103.5	Nordstrom et al. 1990
$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4^- + 4H^+$	-21.6	133.2	Nordstrom et al. 1990
$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	-2.85	57.7	Smith et al. 2004
$3Fe^{3+} + 4H_2O \leftrightarrow Fe_3(OH)_4^{5+} + 4H^+$	-6.29	65.4	Smith et al. 2004
$Fe^{3+} + Cl^- \leftrightarrow FeCl^{2+}$	1.48	23.5	Nordstrom et al. 1990
$2Fe^{3+} + Cl^- \leftrightarrow FeCl_2^+$	2.13	–	Nordstrom et al. 1990
$Fe^{3+} + F^- \leftrightarrow FeF^{2+}$	6.2	11.3	Nordstrom et al. 1990
$Fe^{3+} + 2F^- \leftrightarrow FeF_2^+$	10.8	20.1	Nordstrom et al. 1990
$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+$	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_{final}	4.28–8.02
DOC (mg dm^{-3})	1.7–40.3
Σ(Na, Mg, K, Ca) (μmol_c dm^{-3})	235–8122
Σ(Cl, NO_3, SO_4) (μmol_c dm^{-3})	118–6032
Alkalinity (μeq_c dm^{-3})	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

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

Sample name	Pore size cutoff (kDa)	pH	log $a_{Fe3+, model}$ (M)	SD log $a_{Fe3+, model}$	log $a_{Fe3+, regression}$ (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)	10	8.0	-18.8	0.4	-18.2
Roudsea Wood (2)	10	7.4	-16.8	0.6	-16.7
Whitray Beck tributary (2)	15	7.4	-18.7	0.4	-18.3
River Lune (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 µm) 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_{Fe3+} due to uncertainty in the 'active' proportion of DOM. The dashed lines show the trends in activities predicted using standard solubility products of $10^{5.0}$ (upper) and $10^{2.5}$ (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: $a_{Fe3+} = 3.19(\pm0.06) - 2.73(\pm0.01)\cdot pH$. Dashed line: prediction of Fe^{3+} activity variation with pH in the experiments of Byrne and Luo (2000), aging time 15–60 minutes: $a_{Fe3+} = 2.97(\pm0.06) - 2.86(\pm0.01)\cdot pH$. 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_{Fe3+} for temperature. b: surface waters, correcting a_{Fe3+} for temperature. c: soil/ground waters, not correcting a_{Fe3+} for temperature. d: soil/ground waters, correcting a_{Fe3+} 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 (0.7µm, 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_{Fe3+} calculated using Equation (1). Bottom (b): observed total Fe(III):DOM ratios in filtrates (0.7µm) of samples taken during long term monitoring of Pool X (closed squares) and Pool Y (open squares) from 1993–2001.

Fig 6 Filterable (0.45µm) 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).

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

Figure 1

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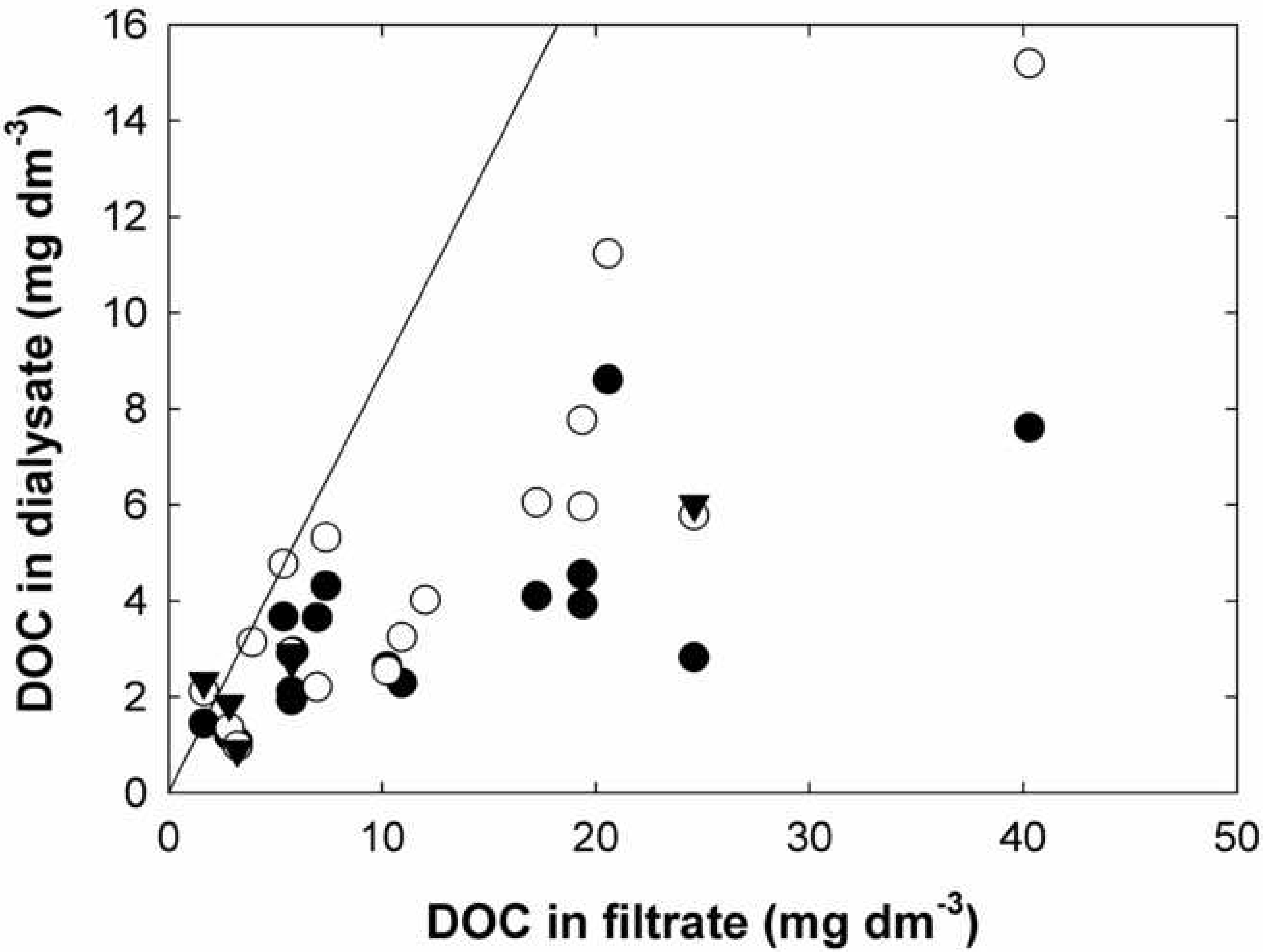

Figure 2

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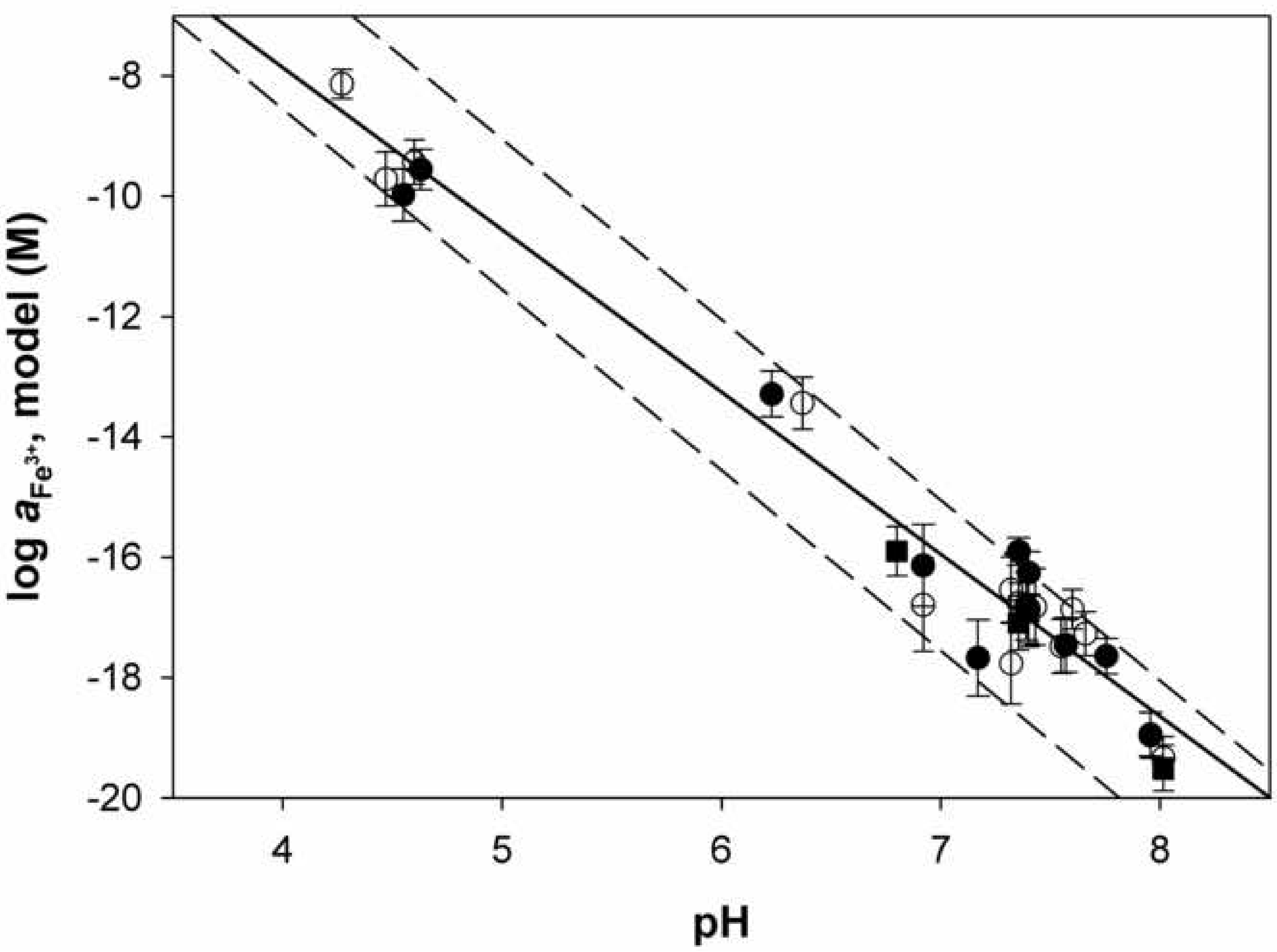

Figure 3

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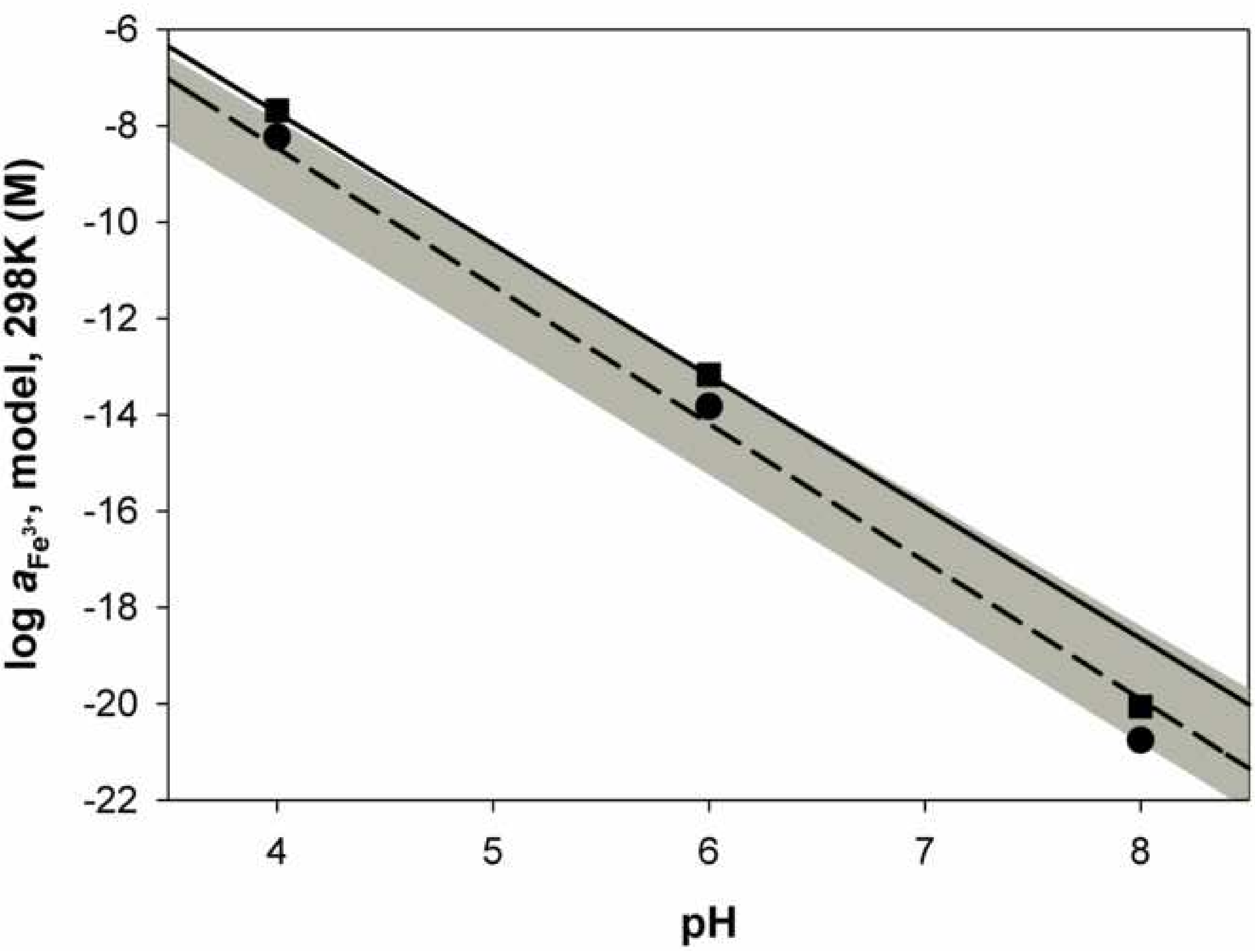

Figure 4

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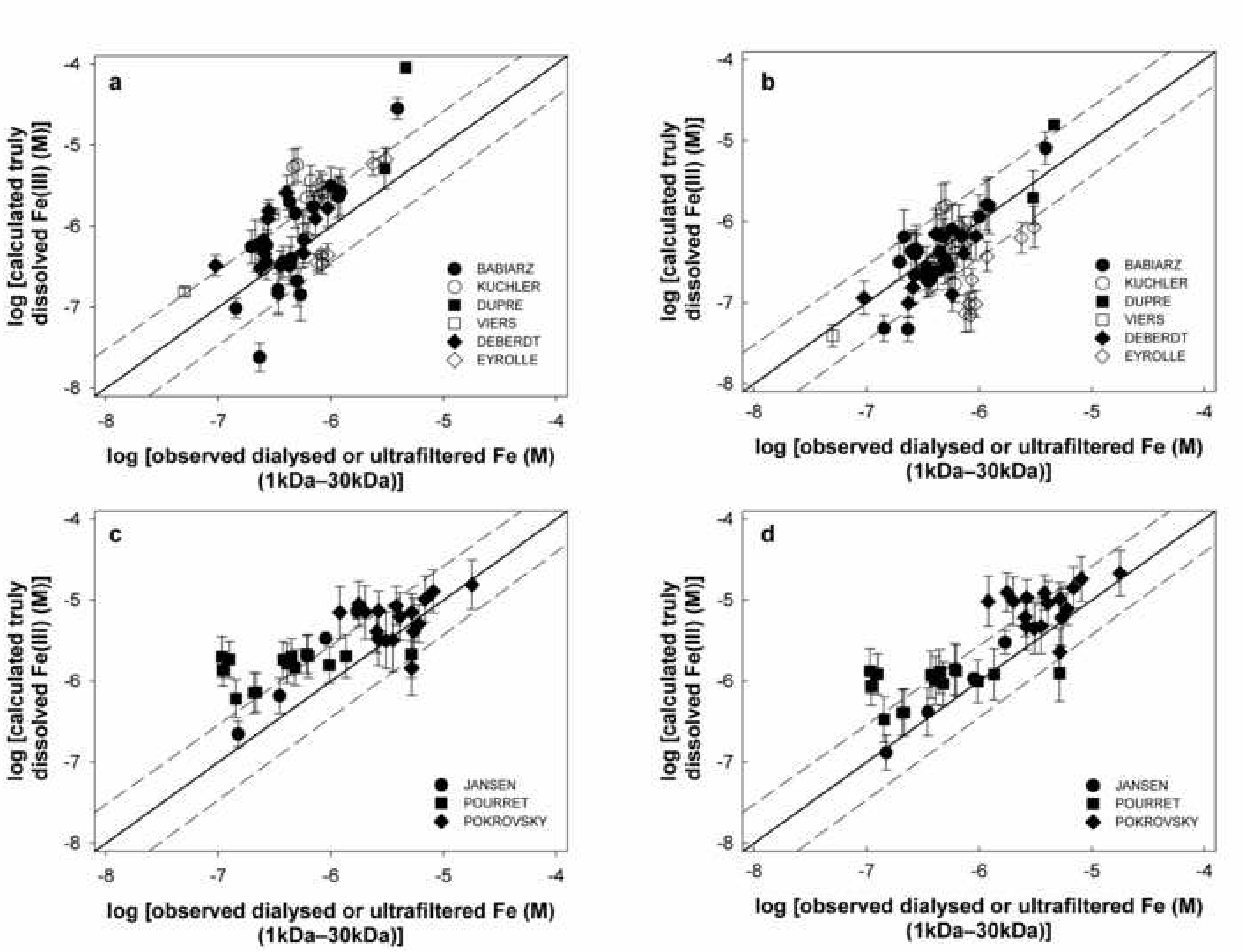

Figure 5

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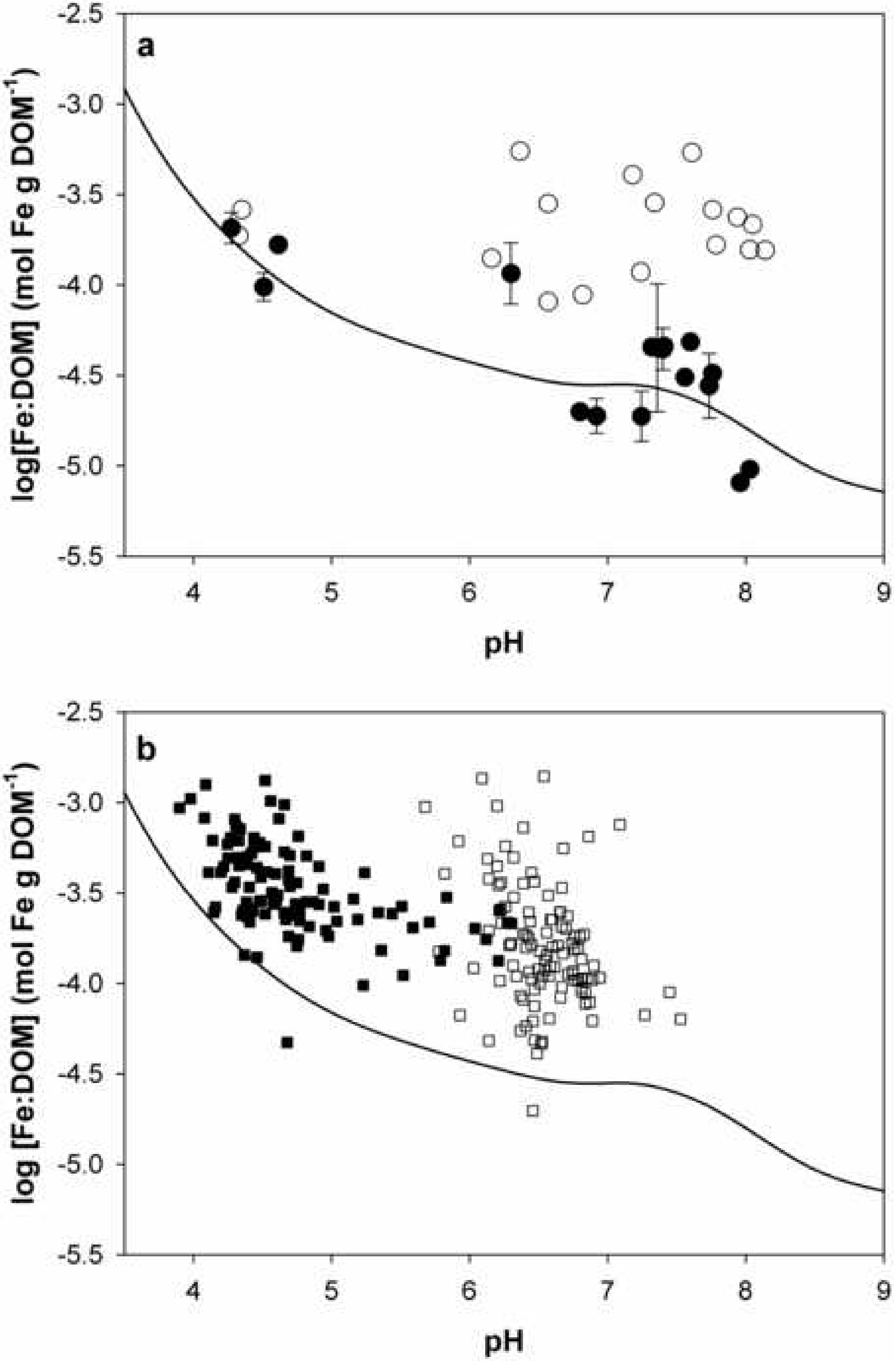


Figure 6

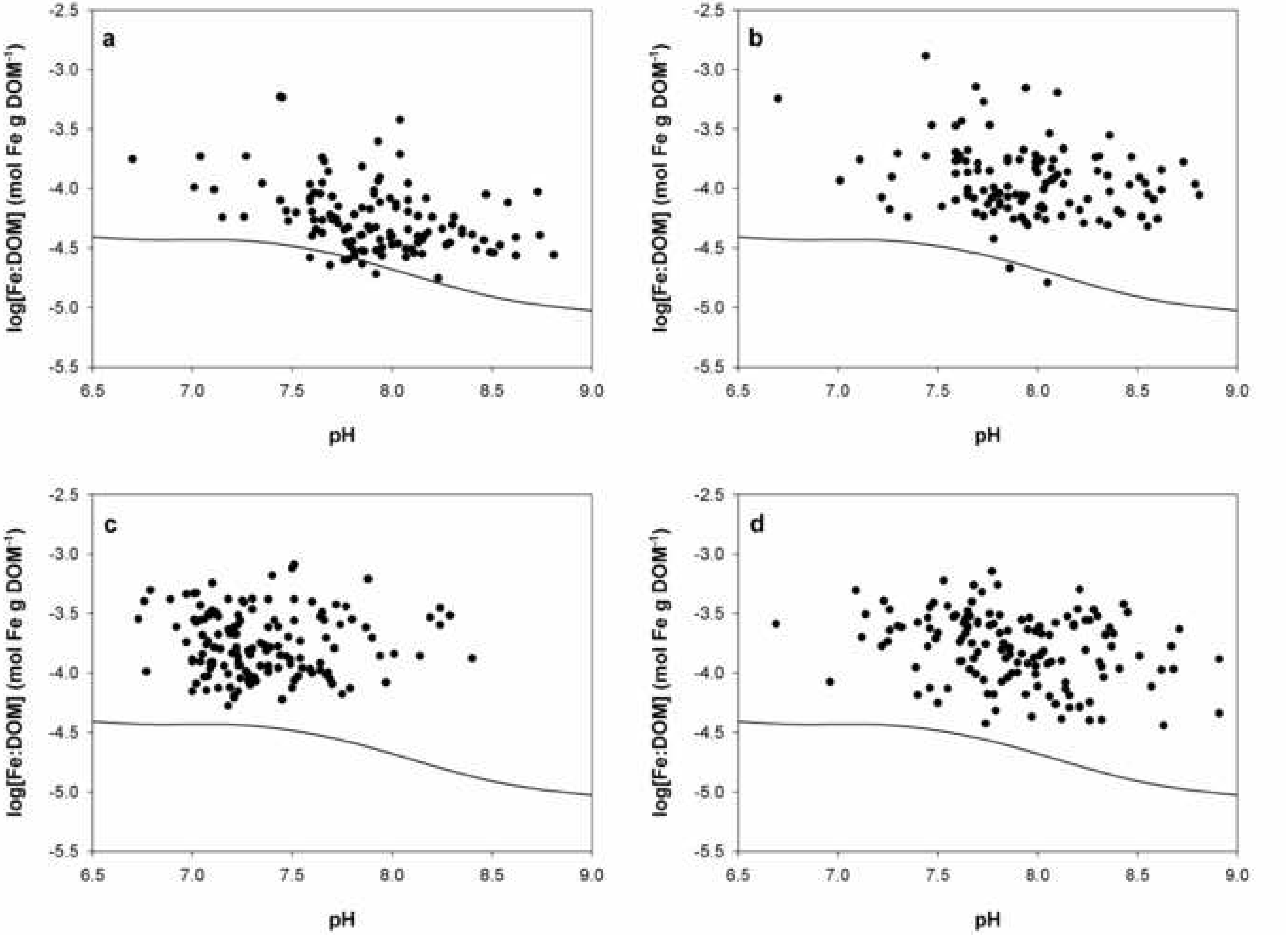
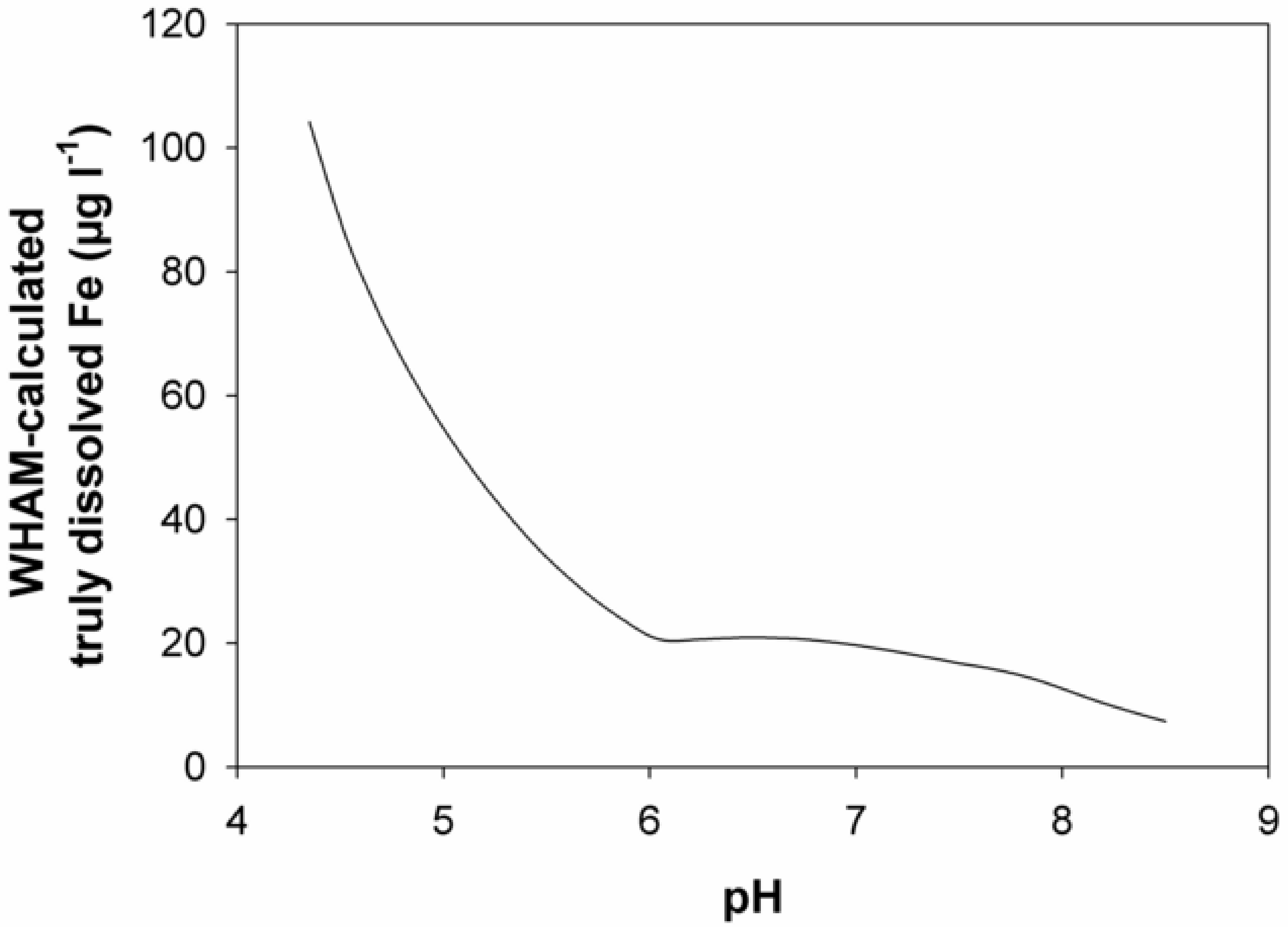

a
b
c
d
log[Fe:DOM] (mol Fe g DOM^{-1})
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
6.5
7.0
7.5
8.0
8.5
9.0
pH

Figure 7


WHAM-calculated
truly dissolved Fe (µg l^{-1})
120
100
80
60
40
20
0
4
5
6
7
8
9
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)	54º47'11"N 2º27'20"W	2/26/2004	<2	2
Gais Gill (GG)	54º24'17"N 2º26'15"W	1/8/2004	19	9
Pool X (PX)	54º39'45"N 2º27'43"W	9/25/2003	174	not measured
Pool X (PX)	54º39'45"N 2º27'43"W	1/22/2004	49	10
Pool Y (PY)	54º39'45"N 2º27'43"W	9/25/2003	12	not measured
River Eden (RE)	54º23'13"N 2º20'14"W	1/8/2004	15	6
River Hodder (RH)	54º 1'34"N 2º27'12"W	11/17/2003	72	<2
River Hodder (RH)	54º 1'34"N 2º27'12"W	1/29/2004	5	5
River Lune (RL)	54º 4'34"N 2º43'50"W	1/29/2004	not measured	not measured
River Ribble (RR)	53º45'56"N 2º38'25"W	11/24/2003	11	<2
River Ribble (RR)	53º45'56"N 2º38'25"W	1/29/2004	9	5
River Tees (RT)	54º39' 2"N 2º10'36"W	2/26/2004	3	3
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	11/14/2003	39	<2
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	2/18/2004	40	<2
Wad Hazel Sike (WHS)	54º42'38"N 2º19'11"W	2/26/2004	13	6
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"W	11/17/2003	17	2
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"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

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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)	54º47'11"N 2º27'20"W	2/26/2004	2	6
Gais Gill (GG)	54º24'17"N 2º26'15"W	1/8/2004	9	5
Pool X (PX)	54º39'45"N 2º27'43"W	9/25/2003	299	<2
Pool X (PX)	54º39'45"N 2º27'43"W	1/22/2004	107	32
Pool Y (PY)	54º39'45"N 2º27'43"W	9/25/2003	15	<2
Pool Y (PY)	54º39'45"N 2º27'43"W	1/22/2004	21	<2
River Eden (RE)	54º23'13"N 2º20'14"W	1/8/2004	16	8
River Hodder (RH)	54º 1'34"N 2º27'12"W	11/17/2003	128	13
River Hodder (RH)	54º 1'34"N 2º27'12"W	1/29/2004	4	4
River Lune (RL)	54º 4'34"N 2º43'50"W	11/24/2003	18	<2
River Lune (RL)	54º 4'34"N 2º43'50"W	1/29/2004	4	2
River Ribble (RR)	53º45'56"N 2º38'25"W	11/24/2003	23	<2
River Ribble (RR)	53º45'56"N 2º38'25"W	1/29/2004	6	<2
River Tees (RT)	54º39' 2"N 2º10'36"W	2/26/2004	6	9
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	11/14/2003	81	<2
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	2/18/2004	26	<2
Wad Hazel Sike (WHS)	54º42'38"N 2º19'11"W	2/26/2004	7	7
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"W	11/17/2003	34	<2
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"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

Click here to download table: Data 4.xls

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)	54º47'11"N 2º27'20"W	2/26/2004	4	7
Gais Gill (GG)	54º24'17"N 2º26'15"W	1/8/2004	not measured	not measured
Pool X (PX)	54º39'45"N 2º27'43"W	9/25/2003	not measured	not measured
Pool X (PX)	54º39'45"N 2º27'43"W	1/22/2004	not measured	not measured
Pool Y (PY)	54º39'45"N 2º27'43"W	9/25/2003	not measured	not measured
Pool Y (PY)	54º39'45"N 2º27'43"W	1/22/2004	not measured	not measured
River Eden (RE)	54º23'13"N 2º20'14"W	1/8/2004	not measured	not measured
River Hodder (RH)	54º 1'34"N 2º27'12"W	11/17/2003	not measured	not measured
River Hodder (RH)	54º 1'34"N 2º27'12"W	1/29/2004	5	3
River Lune (RL)	54º 4'34"N 2º43'50"W	11/24/2003	not measured	not measured
River Lune (RL)	54º 4'34"N 2º43'50"W	1/29/2004	5	3
River Ribble (RR)	53º45'56"N 2º38'25"W	11/24/2003	not measured	not measured
River Ribble (RR)	53º45'56"N 2º38'25"W	1/29/2004	no sample	no sample
River Tees (RT)	54º39' 2"N 2º10'36"W	2/26/2004	2	8
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	11/14/2003	not measured	not measured
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	2/18/2004	26	<2
Wad Hazel Sike (WHS)	54º42'38"N 2º19'11"W	2/26/2004	4	6
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"W	11/17/2003	not measured	not measured
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"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
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)	54º47'11"N 2º27'20"W	2/26/2004	7.94
Gais Gill (GG)	54º24'17"N 2º26'15"W	1/8/2004	7.24
Pool X (PX)	54º39'45"N 2º27'43"W	9/25/2003	4.16
Pool X (PX)	54º39'45"N 2º27'43"W	1/22/2004	4.33
Pool Y (PY)	54º39'45"N 2º27'43"W	9/25/2003	5.82
Pool Y (PY)	54º39'45"N 2º27'43"W	1/22/2004	6.16
River Eden (RE)	54º23'13"N 2º20'14"W	1/8/2004	7.34
River Hodder (RH)	54º 1'34"N 2º27'12"W	11/17/2003	4.35
River Hodder (RH)	54º 1'34"N 2º27'12"W	1/29/2004	6.57
River Lune (RL)	54º 4'34"N 2º43'50"W	11/24/2003	7.79
River Lune (RL)	54º 4'34"N 2º43'50"W	1/29/2004	7.76
River Ribble (RR)	53º45'56"N 2º38'25"W	11/24/2003	8.14
River Ribble (RR)	53º45'56"N 2º38'25"W	1/29/2004	8.03
River Tees (RT)	54º39' 2"N 2º10'36"W	2/26/2004	8.05
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	11/14/2003	6.57
Roudsea Wood (RW)	51º31' 6"N 4º24'30"W	2/18/2004	6.82
Wad Hazel Sike (WHS)	54º42'38"N 2º19'11"W	2/26/2004	7.61
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"W	11/17/2003	6.37
Whitray Beck tributary (WB)	54º 3'11"N 2º29'36"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