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The effect of pH, dissolved humic substances, and ionic composition on the transfer of iron and phosphate to particulate size fractions in epilimnetic lake water

Abstract—Transformations of dissolved iron and phosphate to particulate material (>0.2 μm) were investigated by adding $^{55}FeCl_3$ and $^{32}PO_4^{3-}$ to pH adjusted epilimnetic lake water samples of contrasting ionic strengths and dissolved humic substances (DHS) concentrations. The distributions of these tracers between particulate size fractions in samples without appreciable DHS after 24 h of dark incubation varied markedly over the pH range 4–8. The effect of pH on the movement of ^{55}Fe and ^{32}P to particulate size fractions in clear-water samples depended on the ionic strength. Over the same pH range, the presence of DHS suppressed the movement of ^{55}Fe and ^{32}P to particulate size fractions. There was little difference between low and high ionic strength DHS-rich samples. The capability of DHS to maintain added ^{55}Fe and ^{32}P in solution (<0.2 μm) was confirmed by simultaneous measurements of precipitation losses.

The presence of appreciable quantities of dissolved organic C (DOC) appears to be an important factor in determining responses of lacustrine ecosystems to inputs of inorganic acids from anthropogenic sources. Recent investigations have shown that DOC is an important energy source and system regulator in surface lake waters (Salonen et al. 1992). Dissolved humic substances (DHS) are a significant component of the DOC pool in lakes. The influence of DHS on biotic and abiotic interactions in lake water can be modified by changes in pH and other environmental factors, such as UV irradiation and trophic status (De Haan 1992). Differences between the ecological responses of clear-water and humic lakes to acidification may thus be due in part to the influence of pH-sensitive abiotic processes involving DHS.

It has been suggested that the presence of DHS in lakes modifies the speciation and subsequent bioavailability of key nutrients (Francko and Heath 1979; De Haan et al. 1990). There is substantial evidence for an association of phosphate and iron with DHS, and the quantities of iron and phosphate apparently associated with DHS in lake waters also vary with pH (Shaw et al. 1992; Jones et al. 1993). The association is reversible, and the release of bound phosphate can be stimulated by exposure to light (Francko and Health 1979, 1982; Jones et al. 1988).

Investigations of abiotic transformations involving iron and phosphate in epilimnetic waters to date have been largely concerned with interactions in the dissolved or colloidal phase (<0.2 μm). Fewer studies of iron and phosphate interactions involving particulate size fractions >0.2 μm have been conducted. Tipping et al. (1982) showed that particulate iron exists in natural surface waters but largely as centrifugable particles of submicron size. Phosphorus and humic substances were also identified as important constituents of these particles. Buffle et al. (1989) reported that the size of most particulate iron at the oxic–anoxic boundary of a eutrophic lake was <0.2 μm and found a correlation between the iron and phosphorus contents of the particles.

Experimental studies have also highlighted the significance of interactions between dissolved colloidal and particulate material in natural surface waters. For example, Carpenter and Smith (1984) demonstrated that when phosphate was added to suspensions of different composition, the fraction of phosphate retained by filters of 0.2-μm pore size depended on salinity, pH, and the presence of amorphous iron hydroxide. Tipping (1981) showed that adsorption of DHS by submicron hydrous iron oxide particles (goethite and hematite) depended on pH and the ionic composition of the electrolyte. Interactions between ferric iron and humic substances are capable of maintaining iron in "dissolved" form (<0.45 μm) in oxygenated water (Cameron and Liss 1984).

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Particles containing iron, phosphate, and humic substances may thus be present in epilimnetic lake waters and may interact with dissolved, colloidal, and particulate components. The aim of this study is to assess, using double-isotope-labeling techniques combined with membrane filtration through a broad range of membrane pore sizes, the extent to which interactions involving iron and phosphate may result in the formation of particulate size fractions. The movement of iron and phosphate to material of particulate size at different pH was examined in epilimnetic waters of contrasting ionic composition and DHS content, prefiltered to exclude direct transfer to material of particulate size.

Natural epilimnetic water samples were passed through 0.2-μm pore-size Anodisc inorganic membrane filters (not prerinsed) to remove particulate material. NaN_3 was added to a final concentration of 0.02% to ensure sterile conditions (*see* De Haan et al. 1990). The addition of NaN_3 increased the ionic strength of the samples by 3 mM. The samples were filtered and sterilized as soon as possible after sampling (hours to days) and stored in darkness at 4°C. Prior to NaN_3 addition, subsamples were taken for ionic composition analysis (anion analysis by Dionex ion chromatography; cation analysis by AAS; bicarbonate analysis by the method of Mackereth et al. 1989). The ionic compositions, locations, sampling months, and basic physicochemical parameters of the samples are shown in Table 1. Concentration or chemical fractionation procedures were avoided to minimize potential effects of experimental handling on the properties of the DHS in the brown-water samples (Hayes 1985).

Table 1. Ionic compositions and basic physicochemical parameters for the samples investigated after passing through 0.2-μm pore size filters (E_{254} is absorbance at 254 nm, 10-mm light path; I is ionic strength in mM; all concentrations in mM; $[Fe_{tot}]$ and $[P_{tot}]$ are total concentrations; nd—not detected; na—not analyzed).

	Tjeukemeer (N. Netherlands)	Mekkojärvi (S. Finland)	Seathwaite (English Lake District)	Malham (N. England)
	December 1990		January 1991	
E_{254}	0.80	0.5	0.02	0.08
pH	8.0	5.0	5.1	8.2
I	8.49	0.43	0.45	4.17
$[Ca^{2+}]$	1.29	0.03	0.01	1.18
$[Mg^{2+}]$	0.53	0.45	0.03	0.10
$[Na^{+}]$	1.70	0.09	0.21	0.15
$[K^{+}]$	0.29	0.32	0.01	0.02
$[Cl^{-}]$	2.44	0.04	0.41	0.12
$[HCO_3^{-}]$	1.84	0.23	0	2.34
$[SO_4^{2-}]$	0.86	0.05	0.02	0.015
$[Fe_{tot}]$	0.0097	0.0106	0.0014	na
$[P_{tot}]$	0.0013	na	na	na
$[PO_4^{3-}]$	0.0011	nd	nd	nd

The pH range of 4–8 was chosen because it includes the pH values likely to be encountered in many northern temperate lakes. The pH was adjusted by adding 0.05 M H_2SO_4 as required. Aliquots of 50 ml were spiked first with 355 kBq $^{55}FeCl_3$ (sp act 59.7 MBq mg^{-1} Fe; Amersham Int.) and then with 64 kBq $H_3{}^{32}PO_4$ (carrier-free, sp act 314.5–337.5 TBq mol^{-1}; DuPont) and incubated in the dark for 24 h at room temperature (~20°C). Concentrations of ^{55}Fe and $^{32}PO_4^{3-}$ in the spiked samples were 2.2 μM and 3.9 nM. The pH of each spiked sample was measured before and after incubation. Sample pH drifted during incubation but not by >0.36 pH units and generally by <0.1 pH units. The movement of the radioisotopes to particulate material was determined by passing 1-ml aliquots through 25-mm-diameter Isopore track-etched polycarbonate membrane filters (Millipore) of pore sizes 0.2, 0.4, 0.8, 1.2, 3.0. 5.0, and 10.0 μm. The filters were then washed with 2 ml of Milli-Q water (pH ~5.5). Five replicates were made for each sample and each filter size.

Losses of the added radioisotopes from solution during incubation were assessed by comparing the activity concentrations in the spiked samples before and after incubation. Five replicate 1-ml aliquots were taken from the spiked samples before and after incubation. Reductions in the concentrations of spike activities during incubation were presumably due to the sedimentation of added ^{55}Fe and ^{32}P associated with large particles.

All ^{55}Fe and ^{32}P activities were determined with a Packard scintillation counter after addition of Milli-Q water to a final volume of 5 and 10 ml of Ecoscint A scintillation fluor (Packard). The presence of the filter membrane in samples prepared for scintillation counting did not result in significant changes in scintillation counting efficiency.

The potential contribution of methodological artifacts to the particulate size distributions of added ^{55}Fe and ^{32}P was assessed as follows. Sections of the filter material were placed in solutions of Milli-Q water spiked with ^{55}Fe or $^{32}PO_4^{3-}$ at different pH for periods of 1, 3, or 10 min. ^{55}Fe and ^{32}P activities associated with the filter sections were larger than could be explained by the absorption of water but did not show a consistent pattern with variation of pH and exposure time. However, the ^{32}P activity of the filter sections tended to increase with exposure time. The material of the filters was therefore not inert with respect to iron and phosphate. In all tests conducted, $<3\%$ of the total ^{55}Fe or $^{32}PO_4^{3-}$ in spiked solutions became adsorbed to the filter material during contact times of up to 10 min, which is longer than the maximum duration of filtration in the experiments.

The absorption of water and the filtration rates of filters of different pore size were also investigated. Filtration times for 3-ml aliquots of Milli-Q water were varied for filters of the same pore size as a result of the variable pore density of these filters and were significantly longer for 0.2-μm pore-size filters than for the others. The volume of water absorbed by filters ranged between 0.2 and 1.5 μl for 3-ml aliquots of Milli-Q water.

Absorption of water and interactions of ^{55}Fe or $^{32}PO_4^{3-}$ with the filter material may have contributed to the measured retention of radioisotopes. However, it was estimated that retention of radioisotopes would be increased at the most by 4–5% of the activities in the solutions that were filtered. Evaluation of the retention of ^{55}Fe and ^{32}P as a function of vacuum differential was not practical, as only a water vacuum pump was available in the radioisotope laboratory used. Coagulation of colloidal and particulate material at the membrane surface due to concentration polarization may have also led to filtration artifacts (Buffle et al. 1992). However, in view of the rapid filtration of 1-ml sample aliquots (<70 s), coagulation at the filter surface would have to be extremely rapid to result in appreciable artifacts.

The proportions of ^{32}P and ^{55}Fe remaining in the spiked solutions after incubation are shown in Fig. 1. Differences in the responses to pH of ^{55}Fe precipitation losses were found between the clear waters tested. Precipitation losses of ^{55}Fe from the Seathwaite sample and the Milli-Q water increased as pH decreased (Fig. 1a,b). Conversely, precipitation losses of ^{55}Fe from the Malham sample increased with increasing pH (Fig. 1c). Precipitation losses accounted for $<3\%$ of the ^{32}P added to Milli-Q water (Fig. 1a). For the Seathwaite sample, appreciable precipitation of ^{32}P was observed only at pH 3.72 (Fig. 1b). In contrast to the Seathwaite sample, precipitation losses of ^{32}P from the Malham sample were only significant at the intermediate pH tested (Fig. 1c).

Precipitation losses of added ^{55}Fe and ^{32}P from the brown-water samples generally accounted for $<6\%$ of initial activities (Figs. 1d,e). However, some 14% of added ^{55}Fe precipitated from the spiked Tjeukemeer sample during incubation at the intermediate pH (Fig. 1e).

The proportions of the ^{55}Fe and ^{32}P activities retained by membrane filters of different pore size are shown in Figs. 2–6. Filter-retained activities are expressed as percentages of the activities in the 1-ml aliquots of the incubated spiked samples run through the filters.

Experiments with spiked Milli-Q water (Fig. 2) demonstrated a clear response of particulate size distributions of ^{55}Fe and ^{32}P to pH. The distributions of ^{55}Fe and ^{32}P retained by filters followed similar patterns of response to pH, and fractions of ^{32}P retained were of lower magnitude. At the low and intermediate pH, filter retention of both added radioisotopes varied little between filters of pore sizes of 0.2–1.2 μm but decreased markedly with increasing pore size for filters of 3.0–10.0 μm. This finding indicated that most of the particulate ^{55}Fe and ^{32}P was of size 1.2–3.0 μm at these pH values. Fractions of ^{55}Fe and ^{32}P retained were higher at the intermediate pH than at the lowest. At the highest pH, the particulate distributions of ^{55}Fe and ^{32}P were rather different in that filter retention diminished rapidly with increasing filter pore size. Most of the particulate ^{55}Fe and ^{32}P was 0.2–0.4 μm in size at this pH.

A clear response to pH of particulate size distributions of ^{55}Fe and ^{32}P activities was also demonstrated in experiments with the Seathwaite Tarn water sample (Fig. 3). At the intermediate and highest pH values, the fractions of ^{55}Fe and ^{32}P retained by filters of pore size ≤ 31.2 μm tended to be substantially higher than for filters of pore size ≥ 3.0 μm. More than 50% of the filtered ^{55}Fe was retained by

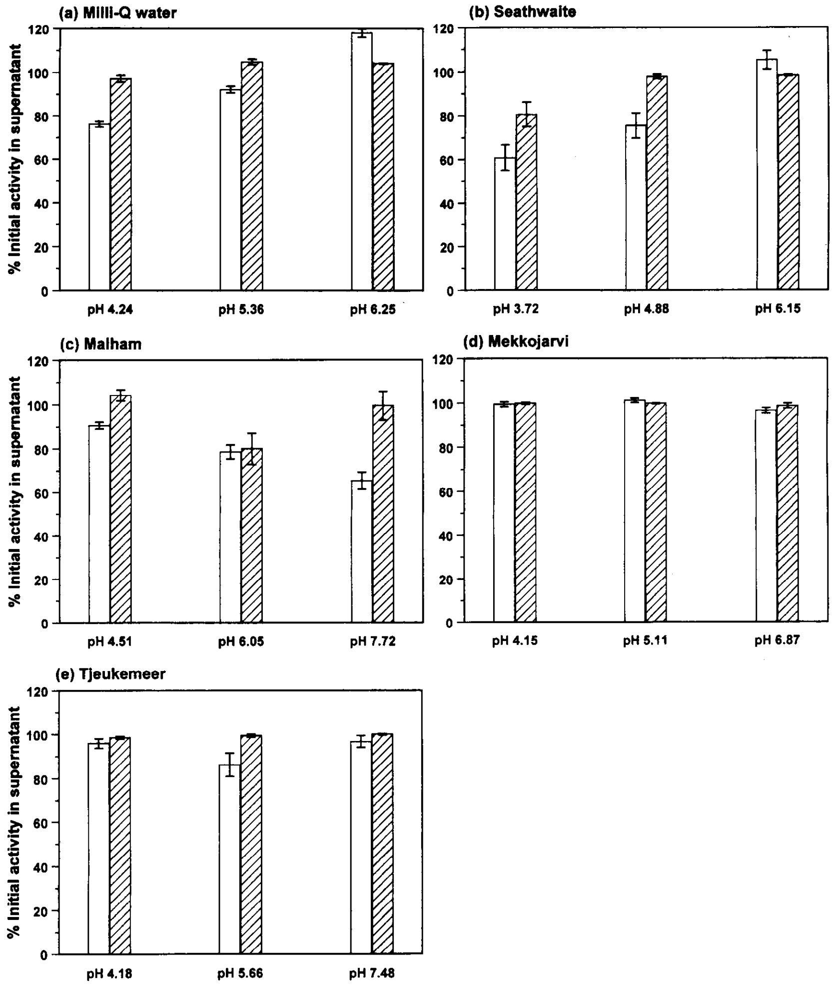

Fig. 1. Percentages of added ^{55}Fe (open) and ^{32}P activities (hatched) remaining in the supernatant after 24 h of incubation with pH-adjusted Milli-Q water and samples (0.2-μm filtered) from four lakes. Vertical bars show standard error.

filters of 0.2–1.2-μm pore size at these pH values (Fig. 3a), and most of the particulate ^{55}Fe and ^{32}P was 1.2–3.0 μm in size. At the highest pH, filter-retained ^{55}Fe activities were similar for filters of 0.2–1.2-μm pore size. At intermediate pH, retained ^{55}Fe activity decreased more gradually with increasing filter pore size. Proportions of ^{55}Fe retained by 0.2–1.2-μm filters at the lowest pH were significantly lower than at the higher pH (Fig. 3a). As for the Milli-Q water sample, the distributions of ^{32}P were qualitatively similar to those of ^{55}Fe but tended to be of lower magnitude.

In experiments with the Malham Tarn sample (Fig. 4), the proportions of ^{55}Fe retained by filters of <3.0 μm at the highest pH were substantially greater than proportions retained by filters of the same pore size at lower pH and decreased with increasing filter pore size. Less than 5% of filtered ^{55}Fe and ^{32}P activities were retained by filters of all pore sizes at the intermediate and lowest pH and by filters of >1.2-μm pore size at the highest pH. The filter retention of ^{32}P in Malham water was qualitatively similar to that of ^{55}Fe but was of lower magnitude at all pH values tested, particularly the highest (Fig. 4b).

For the brown-water samples, the propor-

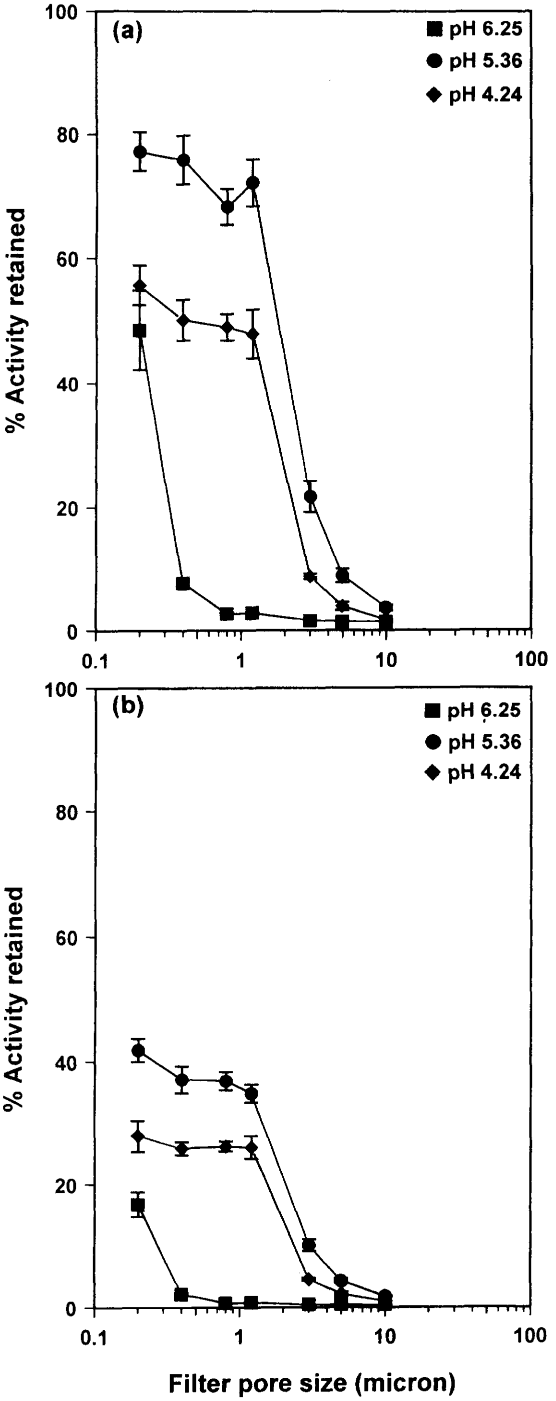

Fig. 2. Retention of (a) ^{55}Fe and (b) $^{32}PO_4^{3-}$ by filters of increasing pore size 24 h after addition to Milli-Q water. Vertical bars show standard error.

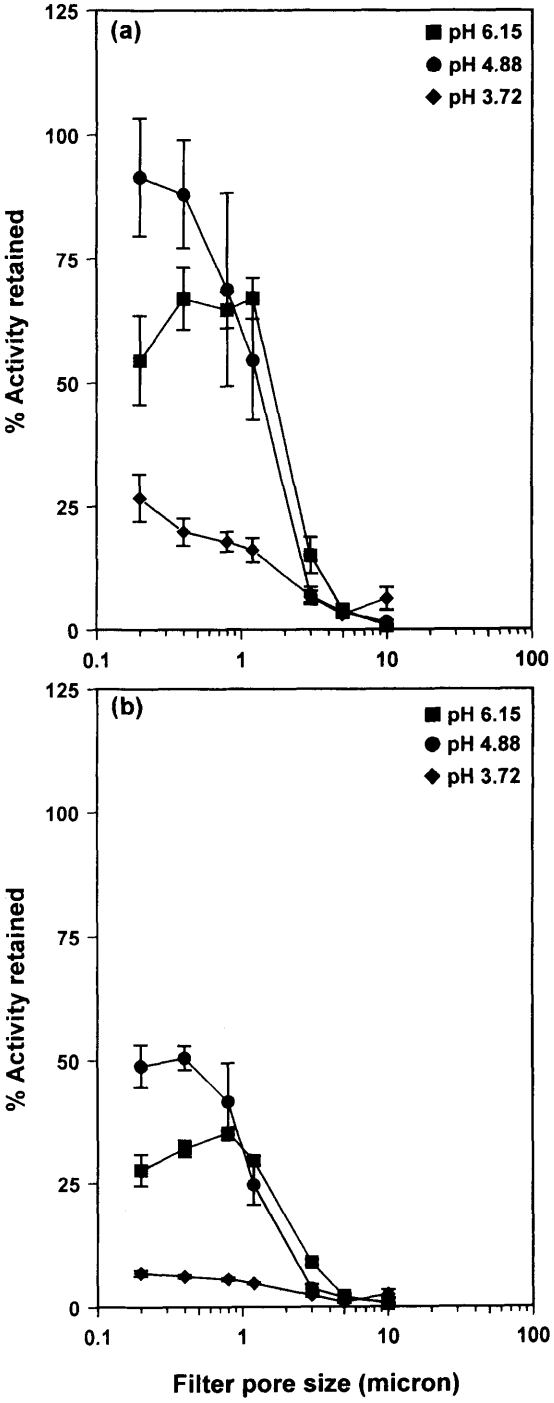

Fig. 3. Retention of (a) ^{55}Fe and (b) $^{32}PO_4^{3-}$ by filters of increasing pore size 24 h after addition to 0.2-μm-filtered Seathwaite Tarn water. Vertical bars show standard error.

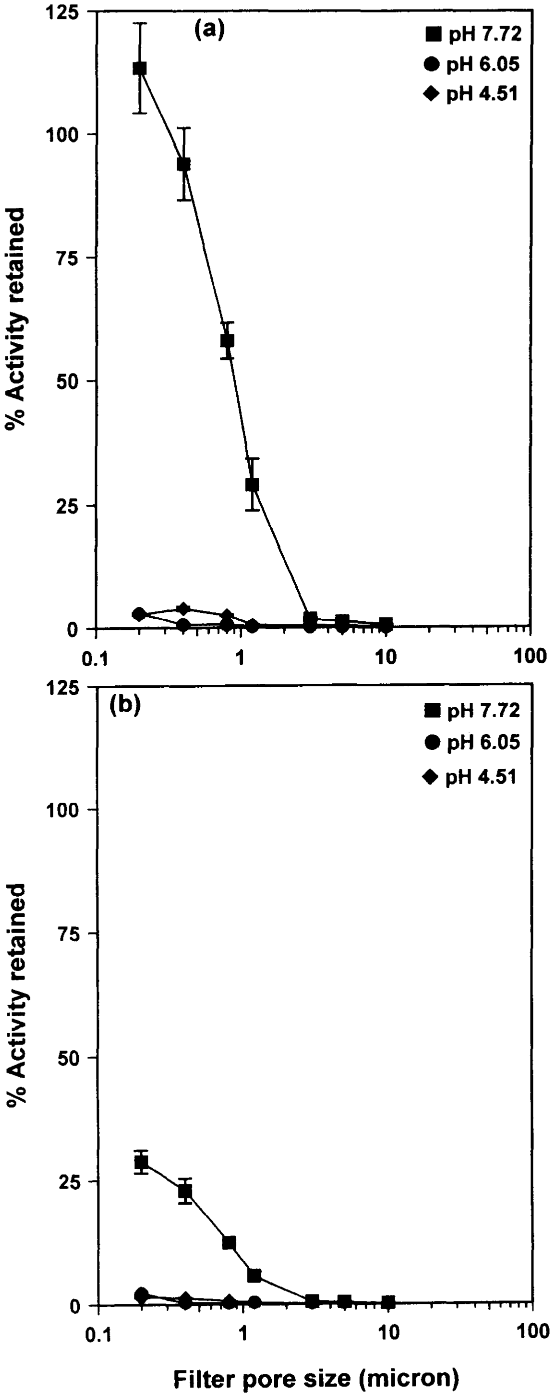

Fig. 4. As Fig. 3, but for Malham Tarn water.

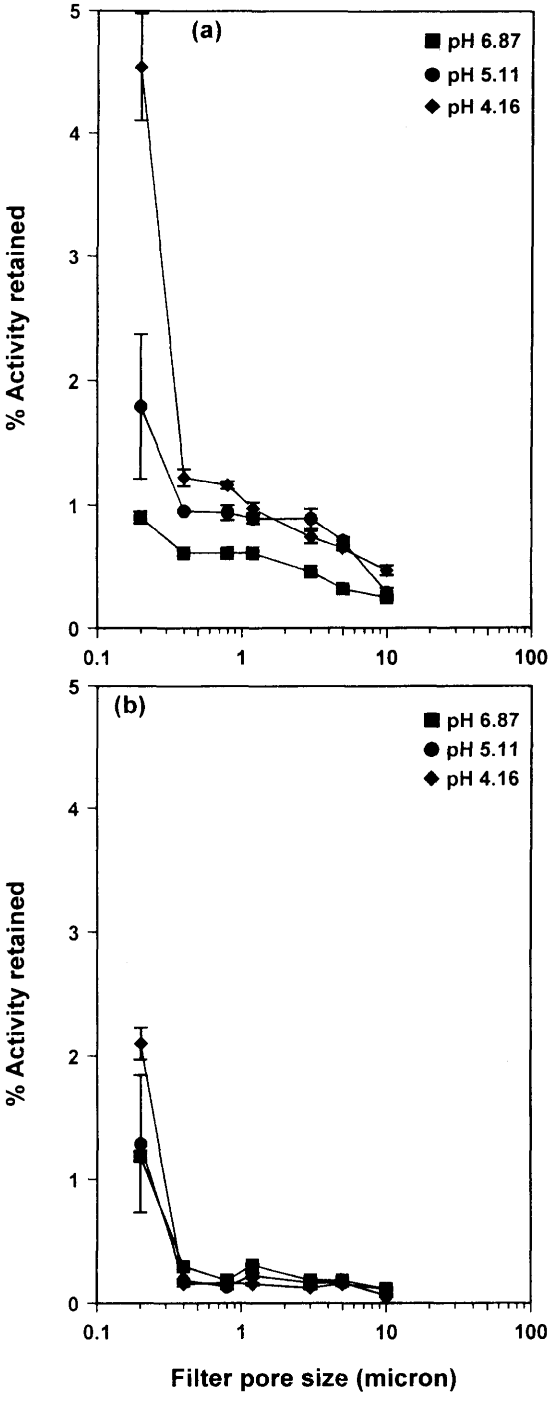

Fig. 5. As Fig. 3, but for Mekkojärvi water. Note change in vertical scale.

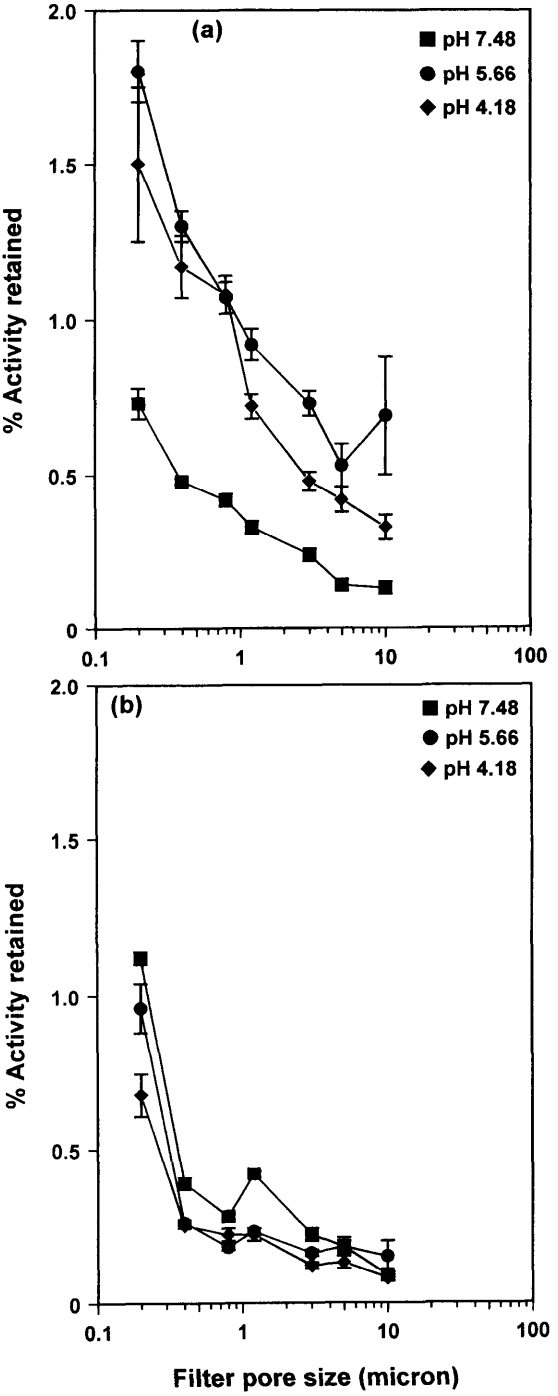

Fig. 6. As Fig 3, but for Tjeukemeer water. Note change in vertical scale.

tion of activities retained by the filters was appreciably smaller than for the clear-water samples and varied less in response to pH. In experiments with Mekkojärvi water, the proportions of ^{55}Fe retained by filters of 0.2-μm pore size decreased with increasing pH (Fig. 5a). Proportions of ^{55}Fe retained by filters of larger pore size varied little in response to variation of pH. The filter retention of ^{32}P was qualitatively similar to that of ^{55}Fe but did not vary significantly with changing pH (Fig. 5b). More of the particulate ^{55}Fe and ^{32}P was in the size range 0.2–0.4 μm than in larger size classes. In experiments with the Tjeukemeer sample, the retention of ^{55}Fe by filters decreased gradually with increasing filter pore size (Fig. 6a). The proportions of ^{55}Fe retained by filters of all pore sizes were lowest at the highest pH. The filter retention of ^{32}P was qualitatively similar to that of ^{55}Fe but did not vary significantly in response to variation of pH (Fig. 6b). More ^{32}P was observed in the 0.2–0.4-μm size range than in larger size ranges. The fractions of ^{55}Fe and ^{32}P activities retained did not exceed 5% of the filtered activities in any of the experiments with brown-water samples.

The results of this study demonstrated that more of the added iron and phosphate remained in "dissolved" or subparticulate form (<0.2 μm) in lake waters with DHS than in clear waters of comparable ionic strength. Subtracting precipitation losses and the proportions of ^{55}Fe and ^{32}P >0.2 μm from the inital spike concentrations to give the fractions remaining in dissolved form clearly illustrates the influence of DHS in maintaining dissolved forms of Fe and P (Fig. 7). This comparison also demonstrates almost identical behavior for the samples containing DHS and the dependence of the quantity of the dissolved ^{55}Fe and ^{32}P fractions in the clear-water samples on pH and ionic composition. It should be noted that the present study concerns only results for a limited number of lake-water samples and generalizations should not be made.

Maintenance of an operationally defined dissolved (<0.2 μm) pool of iron in the presence of humic substances and other agents have been reported previously. Cameron and Liss (1984) found that both humic acid and phosphate were capable of holding iron in dissolved form at concentrations higher than would be predicted on the basis of simple inorganic solution chemistry. Carpenter and Smith (1984) found that the presence of humic substances (HS) maintained iron in a form filterable through a 0.2-μm membrane. It has been suggested that the solubilization of iron may be due to the stabilization of fine colloidal particles (<0.45 or 0.2 μm) against flocculation by the adsorption of inorganic or organic aquatic species (Cameron and Liss 1984; Carpenter and Smith 1984). Evidence for the adsorption of HS onto subparticulate iron species (goethite and hematite), as shown by microelectrophoresis, has been given by Tipping (1981). Abiotic interactions between iron, phosphate, and DHS have also been demonstrated by investigations of the transfer of iron and phosphate to material of subparticulate size by gel filtration chromatography (e.g. Shaw et al. 1992; Jones et al. 1993).

Studies have also shown that the adsorption of phosphate onto amorphous iron hydroxides (Lijklema 1980), amorphous iron oxides, and iron-HS complexes (Gerke and Hermann 1992) is pH-dependent. Adsorption isotherms for different values of pH demonstrated that adsorption of phosphate to iron oxides decreased as pH increased (Lijklema 1980), while Gerke and Hermann (1992) found that phosphate adsorption to Fe-HS complexes increased with pH was raised from 5.2 to 6.2. Addition of Ca^{2+} ions increased adsorption of phosphate to Fe-HS complexes at pH 6.2 but not at pH 5.2, probably due to electrostatic effects (Gerke and Hermann 1992). Results of this study do not correspond to the findings of Gerke and Hermann in that transformations of phosphate and iron to material of particulate size were smaller at higher pH and were larger for the humic water sample containing the smaller Ca^{2+} concentration. Results of experiments examining clear-water samples were not consistent with the findings of Lijklema (1980) in that responses of filter retained ^{55}Fe and ^{32}P to pH were not coherent. The formation of particles containing iron in samples examined in this study was therefore unlikely to be attributable to the pH-dependent adsorption of phosphate onto iron hydroxide particles by the ligand exchange mechanism described by Lijklema or to the adsorption of phosphate onto Fe-HS complexes described by Gerke and Hermann (1992).

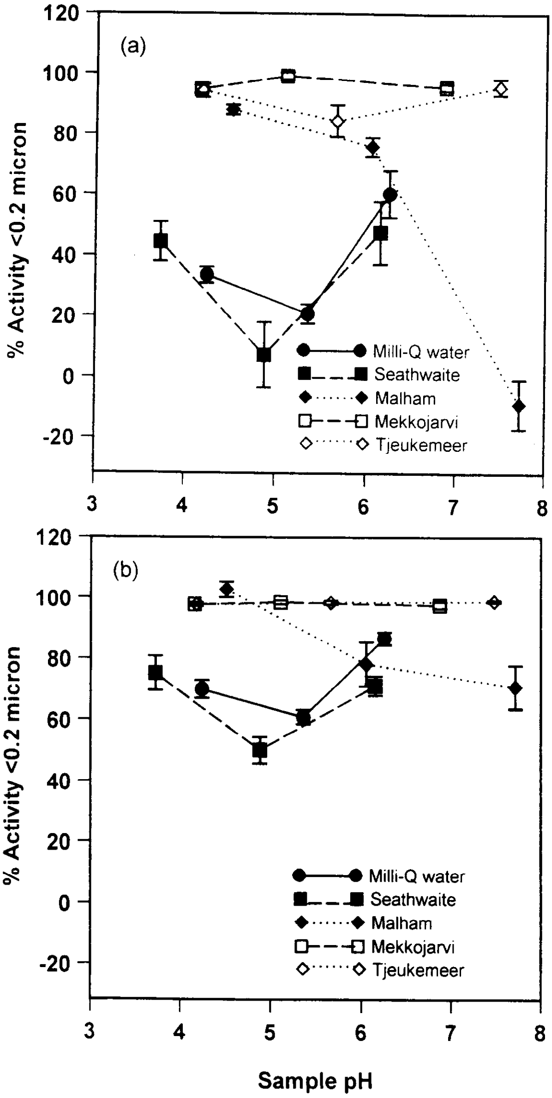

Fig. 7. Percentages of added ^{55}Fe (a) and $^{32}PO_4^{3-}$ (b) filterable through 0.2-μm pore-size filters after 24 h of incubation with pH-adjusted Milli-Q water and samples (0.2-μm filtered) from four lakes. Vertical bars show standard error.

Further analysis of the experimental data showed that for the samples containing DHS, variation of particulate ^{55}Fe was not reflected by variation of ^{32}P. In contrast, particulate ^{55}Fe and ^{32}P formed in the clear-water samples followed the same pattern. Analysis of filter-retained activities (Figs. 4–6) revealed that ratios of $^{55}Fe : {}^{32}P$ (in terms of the percentages of supernatant activities retained by filters of different pore size) were consistent for each sample at each pH. However, molar ratios of ^{55}Fe : ^{32}P for the retained activities were in the 500–1,400 range, were not significantly different for the different samples, and did not respond coherently to pH. These ratios are in contrast to the Fe : P ratios found in iron-containing particles at the oxic–anoxic interface of a eutrophic lake studied by Buffle et al. (1989), which were found to be more consistent and two orders of magnitude smaller. In view of the lack of data concerning the quantities and size of the Fe and P in the original samples (Table 1), a more detailed interpretation of the nature of the ^{55}Fe and ^{32}P retained by the filters will not be undertaken.

Variation of pH and differences in the ionic strengths of the two brown-water samples had only minor effects on filter retained proportions of ^{55}Fe and $^{32}PO_4^{3-}$. Gel filtration chromatography studies of abiotic interactions between iron and phosphate in water samples of different composition indicated that the presence of DHS fosters the movement of both iron and phosphate to material of large molecular size ("colloidal") while enabling the bulk of the added phosphate to remain in an apparently unchanged inorganic form (Shaw et al. 1992; Jones et al. 1993). In the absence of DHS, iron and phosphate did not transfer to colloidal material (Jones et. al. 1993). These studies have also shown that movement of Fe and PO_4^{3-} to large molecular size fractions diminishes with decreasing pH. Results from this study show that in the presence of DHS, the formation of particulate ^{55}Fe is suppressed at higher pH. It is known that pH influences both the protonation of DHS functional groups (Schnitzer and Khan 1972) and the conformation of DHS molecules (Ghassemi and Christman 1968). Thus, the "stretched" conformation and low protonation of DHS at higher pH appear to favor colloidal and truly dissolved forms of Fe and PO_4^{3-}, and this preference may be due to the formation of stabilized Fe(III) oxide colliods (Stumm and Morgan 1981). At lower pH, the greater extent of protonation and more closed conformation of DHS molecules appear to result in an increase in the quantity of particulate Fe. The increased protonation of DHS molecules at lower pH also increases their hydrophobicity and may lead to aggregation by hydrophobic bonding (Stumm and Morgan 1981).

The presence of a high Ca^{2+} concentration in the Tjeukemeer sample had little effect on the precipitation and particulate quantities of ^{55}Fe and ^{32}P. Formation of colloidal or particulate forms of ^{55}Fe and ^{32}P via interactions with $CaCO_3$ and DHS may have occurred, but the similarity of results from experiments with Mekkojärvi and Tjeukemeer water indicates that the influence of Ca^{2+} is of minor consequence in determining quantities of particulate ^{55}Fe and ^{32}P. Significant differences in the results of experiments with clear-water samples of low and high $[Ca^{2+}]$/ionic strength indicate a stronger dependence of precipitation and quantities of particulate ^{55}Fe and ^{32}P on ionic composition. These differences may be due to competitive interaction between iron and calcium that results in the inhibition of inorganic Fe-PO_4^{3-} particle formation. At higher pH, this inhibition did not occur, possibly due to effects of pH-dependent changes in iron speciation. It should be noted that deviation of sample pH away from the natural pH value resulted in an increase in proportion of ^{55}Fe and ^{32}P remaining in dissolved form for the two clear waters (Fig. 7, Table 1).

The effects of DHS on particulate transformations and subsequent precipitation of iron and phosphate are of significance in terms of the cycling and bioavailability of these key nutrients in lake-water ecosystems. The size dependence of particle sedimentation rates is well known. The residence time of material associated with smaller particles in the water column would be expected to be rather longer than that of material associated with larger particles undergoing more rapid sedimentation. Furthermore, Honeymen and Santschi (1991) have proposed that the transfer of dissolved species to large aggregates via colloidal intermediates—colloidal pumping—may result in slow sorption kinetics of trace elements. The association of nutrients with colloidal material may reduce the quantity of immediately available nutrients while maintaining a "dissolved" pool potentially available for biological uptake in the longer term. This hypothesis has yet to be substantiated.

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