

Variations in the chemical lability of iron in estuarine, coastal and shelf waters and its implications for phytoplankton

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ABSTRACT

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The relationship between total and chemically labile Fe has been studied in estuarine, coastal and shelf waters of the Gulf of Maine, U.S.A. Measurements of the labile fraction of total Fe, defined by complexation with 8-hydroxyquinoline in 1 h, correlate with the availability of Fe to marine phytoplankton and therefore can be used to estimate Fe availability in seawater. The results show that the relative lability (= labile/total) of Fe in seawater varied both spatially and temporally from near-zero to 100%. Although particulate Fe (>0.45 μm) was generally less labile than dissolved Fe (<0.45 μm), the particulate fraction often contributed substantially to labile Fe concentrations overall. Conversely, as much as 75% of 'dissolved' Fe was non-labile, and therefore was probably not available to phytoplankton. In seawater/river-water mixing experiments, aggregation diminished the relative lability of Fe by ~30%, even though much of it remained in the 'dissolved' fraction. Considering phytoplankton nutrition, these results demonstrate that equating dissolved Fe concentrations with 'available' metal can be misleading. Furthermore, the large variability observed in the labile proportion of total Fe in seawater indicates that Fe availability to phytoplankton cannot be estimated by applying fixed lability-ratios to total Fe concentrations.

INTRODUCTION

Iron has been long recognized as an essential micronutrient for phytoplankton (Gran, 1933; Harvey, 1937; Menzel and Ryther, 1960), and its availability may be limiting phytoplankton growth in waters where major nutrients (NO_3 , PO_4 and SiO_4) are never depleted (e.g. subarctic Pacific and Antarctic oceans) (Martin and Gordon, 1988; Martin and Fitzwater, 1988; Martin et al., 1989, 1990). There also is evidence that phytoplankton are experiencing

Fe limitation in waters traditionally considered to be nitrogen limited (e.g. the Sargasso Sea) (Entsch et al., 1983; Subba Rao and Yeats, 1984) and that Fe availability influences the rate of N_2 fixation by cyanophytes (Rueter, 1988). At present, quantification of the effects of Fe limitation on primary production is based on the low concentrations of total dissolved ($< 0.4 \mu\text{m}$) Fe. However, because Fe availability is more a function of its chemistry than of its total concentration, the proportion of total Fe in seawater that is available to phytoplankton is unknown.

Because of its insolubility in seawater, most Fe exists in various colloidal and particulate oxyhydroxides and oxides (Murray, 1979; Mill, 1980). For Fe uptake by phytoplankton to occur, these solid substrates must dissolve to replenish the dissolved Fe pool (Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$) which is drawn upon directly by phytoplankton (Anderson and Morel, 1982; Morel and Hudson, 1985, Hudson and Morel, 1990). Even slight crystallinity of the colloidal phase can reduce severely the supply of Fe to phytoplankton (Wells et al., 1983; Wells et al., 1991). However, because of analytical limitations, definitions of biologically available Fe in seawater have been necessarily oversimplified. Most commonly, available Fe has been equated with 'soluble' Fe ($< 0.45 \mu\text{m}$) as a first approximation (e.g. Huntsman and Sunda, 1980). However, the validity of this approach remains untested for natural waters.

We have developed a chemical technique for estimating biologically available Fe in seawater. The technique, described elsewhere in detail (Wells et al., 1991), employs the complexing agent 8-hydroxyquinoline (oxine) to bind free ionic Fe in solution. By reacting with free ionic Fe, and the rapidly equilibrating dissolved hydroxy species, oxine becomes, in a broad sense, a chemical analog to phytoplankton. Adding oxine in great excess coarsely simulates a high biological demand for Fe, causing dissolution of colloidal and particulate Fe phases. Subsequent isolation and determination of the oxine-labile Fe concentrations provides some measure of the Fe potentially available for phytoplankton uptake. A strong positive relationship has been demonstrated between measurements of oxine-labile Fe and phytoplankton growth in experiments using colloidal substrates that have differing availabilities (Wells et al., 1991). Although this relationship differs among algae because of dissimilar uptake efficiencies and metabolic requirements for Fe (Brand et al., 1983; Murphy et al., 1984), the oxine technique provides a relative measure of Fe availability in seawater.

The objective of this investigation was to use the oxine technique to study the distribution of Fe in estuarine, coastal, and shelf waters. The relative availability of Fe in these waters was estimated using ratios of oxine-labile Fe to total Fe concentrations. The Fe lability ratio was determined in both dissolved ($< 0.45 \mu\text{m}$) and particulate ($> 0.45 \mu\text{m}$) fractions to test the validity of past assumptions which equate dissolved Fe with available Fe concentrations. Seasonal as well as spatial differences were determined, to characterize

the variability of this lability ratio, and thereby evaluate the advisability of extrapolating fixed values to untested waters.

MATERIALS AND METHODS

Concentrations of total and oxine-labile Fe were measured in waters of the Sheepscot and Saco River estuaries, and in coastal and shelf waters of the Gulf of Maine (Fig. 1). Estuarine transects were made in June, 1988 (Sheepscot, Saco), and again in March, 1989 (Saco). Saco river water was collected in February, 1989 and April, 1989 for detailed characterization. Coastal surface waters near Boothbay Harbor, Maine (Fig. 1) were sampled (5 m) at six stations from mid-April to October, 1988. Shelf surface waters were collected (10 m) at six stations along a transect extending from Boothbay Harbor to Georges Bank in July, 1988 (Fig. 1). Water samples were collected using a MERCOS (Hydrobios), all-Teflon sampler designed for trace metal studies in open-ocean environments (Freimann et al., 1983). The MERCOS sampler was hand-operated off the bow of the research vessel using a nylon line equipped with a plastic-coated weight and messenger. The exception was the 1989 Saco River survey, which was sampled from shore by hand using polypropylene bottles. Samples from the estuarine and Gulf of Maine transects were filtered ($0.4 \mu\text{m}$) directly from the Teflon collection bottles by inert gas (N_2) pressure; the filters and filtrates were retained for dissolved ($<0.4 \mu\text{m}$) and particulate ($>0.4 \mu\text{m}$) Fe determinations. Coastal water samples were analyzed without filtration.

Trace metal clean techniques were employed during sampling and analysis. Sample collection bottles and filter-holders were soaked before use in 10% HCl for a minimum of 24 h and rinsed thoroughly with deionized water (Barnstead Nanopure®). They were then resoaked with deionized water acidified to pH 1.5 with sub-boiled distilled 6 N HCl for a minimum of 12 h, and, finally, rinsed with copious amounts of deionized water. Bottles were stored in large Ziploc® bags both before and after sample collection. Filtrations were done using Millipore 25-mm polypropylene filter-holders and Nuclepore polycarbonate filters ($0.4 \mu\text{m}$). Filters were soaked in 10% sub-boiled distilled HCl and rinsed with deionized water before use. The filtrates were stored and analyzed in cleaned (as above) polypropylene bottles; the filters were placed in well-leached, cleaned (as above) linear polyethylene bottles containing 25 ml of deionized water.

Oxine-labile Fe (OFe) concentrations were determined by a method described in detail elsewhere (Wells et al., 1991). Briefly, oxine (1 ml of 6.15 mM stock) was added to samples (50–100 ml) buffered to pH 6 with 1 M sodium phosphate (monobasic). After 1 h of incubation at room temperature, during which oxine complexed the labile (or reactive) Fe fraction most available to phytoplankton (Wells et al., 1991), the samples were drawn by

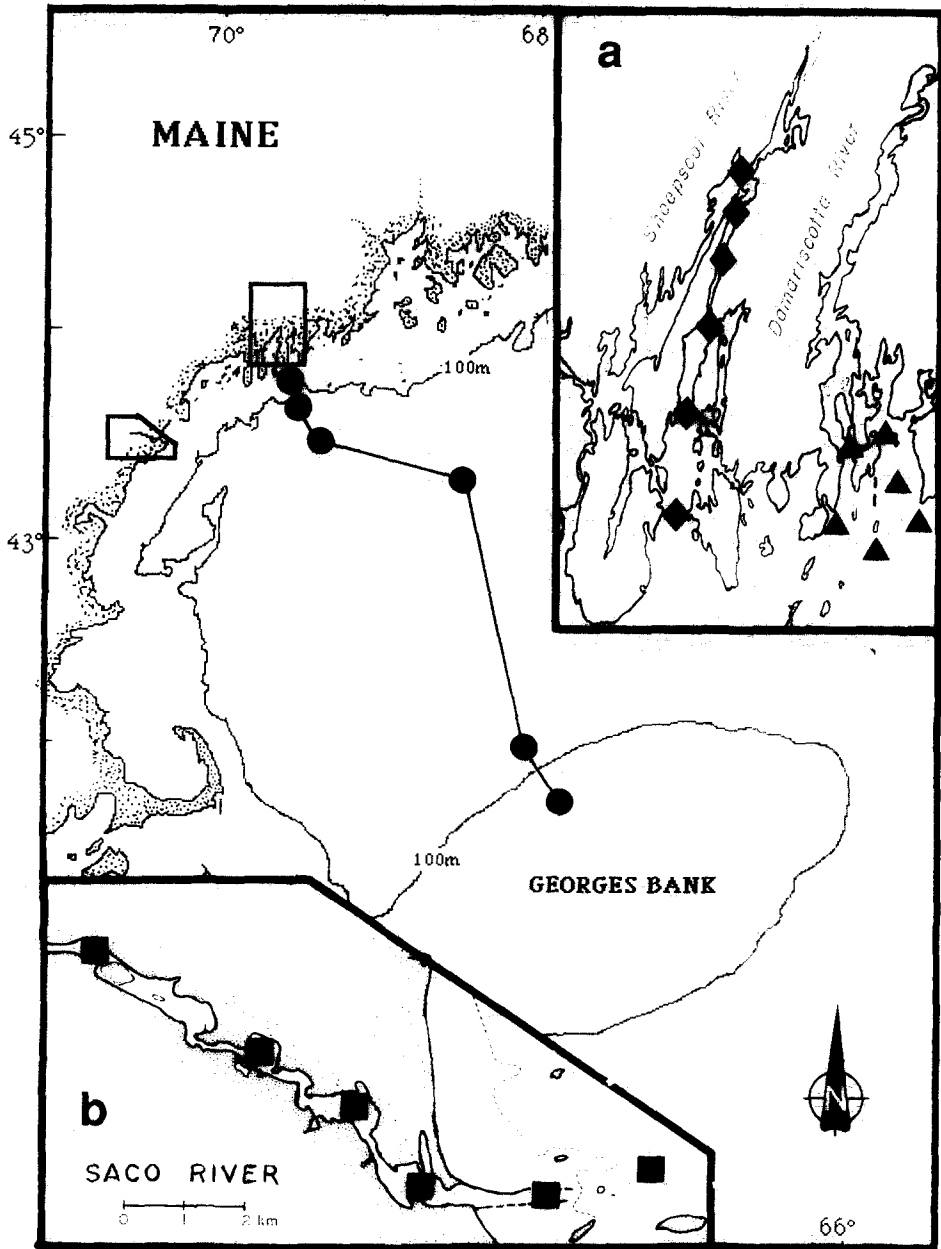


Fig. 1. The study area. Samples were collected from the coastal waters off the Damariscotta River (\blacktriangle), from the adjacent Sheepscot River estuary (\blacklozenge), and from the Saco River estuary (\blacksquare) (see insets a and b). Gulf of Maine surface waters were sampled (\bullet) along a transect from Boothbay Harbor to Georges Bank.

vacuum through Sep-Pak[®] C₁₈ columns which retained the OFe complexes. The columns were then eluted with 2 ml of glass-distilled methanol and the Fe in the eluates was analyzed by graphite furnace atomic absorption (GFAA); concentrations were determined by comparison with standards prepared in methanol (equimolar in oxine). The oxine and buffer reagents were purified before use to reduce Fe contamination — oxine by vacuum sublimation at 120°C onto a cold finger (Honjo et al., 1978) and the buffer by repeated extraction with the purified oxine. The C₁₈ columns also required cleaning. They were subjected to repeated (> 3) sequential passes of the oxine–buffer mixture and methanol. The methanol eluates of the last oxine–buffer pass were retained and used as the combined reagent–column blank. To reduce contamination further, column cleaning and sample processing were done under a filtered-air bench (Class 100). Recoveries of acidified Fe spikes from seawater were 100% ± 10% (1 s.d.) and the detection limit for 100 ml samples was ~ 1 nM Fe. Seawater samples and dense algal suspensions processed without oxine added yielded Fe values that were < 10% of that determined with oxine, demonstrating that the technique was specific for the oxine-labile Fe phase.

Total Fe (ToFe) concentrations were determined by three different procedures over the course of sampling: (1) direct injection GFAA, (2) GFAA after preconcentration of ToFe with oxine, and (3) the standard Ferrozine technique (Mayer, 1982b). In the first two methods, the samples were digested before analysis by acidification to pH 1.6 with 6 N sub-boiled distilled HCl and either aging at room temperature for a minimum of 2 weeks, or heating to 60°C for 2.5 days (Fletcher et al., 1983). The high-temperature treatment was adopted after the results of the two methods were shown to be comparable. Oxine was preconcentrated onto C₁₈ after neutralizing the sample with sub-boiled distilled NH₄OH. Detection limits (2 × blank) for ToFe analyses ranged from 1 to 100 nM depending on the technique employed.

The size distribution of OFe and ToFe in the Saco River was examined by filtering river water through decreasing pore-sized filters and determining the Fe concentrations in each filtrate. Filtration was done by N₂ positive pressure (18 psi) using 0.45-, 0.1- and 0.025- μ m nitrocellulose filters (Schleicher & Schuell) and 100 000 MW membranes (Amicon). Concentrations of ToFe and OFe in the filtrates and unfiltered river water were measured using the methods described above. Because of the high Fe concentrations encountered in the Saco River, ultraclean techniques were not employed; bottles and the filtration assembly were soaked with only 10% reagent grade HCl and rinsed with deionized water before use. Filters were used without acid-washing, the first 50 ml of filtrate being instead discarded.

The effect of increasing salinity on the relative lability of 'dissolved' Fe (< 0.45 μ m) was determined in a series of mixing experiments with Saco River water and seawater. Room-temperature solutions of filtered (0.45 μ m)

Saco River water and Sargasso seawater were mixed to give a salinity of 14. After 1 h at room temperature, sub-samples of the mixture were refiltered ($0.45 \mu\text{m}$) and OFe and ToFe concentrations in the particulate and dissolved fractions were measured using the methods described above.

RESULTS

An examination of the various analytical techniques for measuring total Fe showed decreasing recoveries — in the order acid-digestion/direct injection, Ferrozine colorimetry, acid-digestion/oxine preconcentration — with values averaging in a relative ratio of 1.0:0.90:0.72. The last technique was employed for most samples in this study, in spite of relatively poor recoveries, because the greater sensitivity achieved with preconcentration was needed in many of the environments examined. Digestion/preconcentration methods also are the techniques most commonly used for determining total Fe in seawater (e.g. Sturgeon et al., 1980, 1981; Danielsson et al., 1985; Landing and Bruland, 1987). Seawater analyses by direct injection GFAA suffer from relatively poor reproducibility, and this method shares with the Ferrozine method rather poor sensitivity. Because imperfect recoveries would underestimate total Fe concentrations, most of the oxine-labile Fe: total Fe (OFe: ToFe) ratios reported here should be regarded as maximum values. Nevertheless, these recoveries are not sufficiently poor or variable to obviate the data trends to be discussed in this paper.

The OFe concentrations at the six coastal stations were between 5 and 50 nM, whereas ToFe concentrations were more variable, ranging from 32 to 2500 nM Fe over the same time period. Three of the six sampling stations generally had perceptible, often strong, tidal currents, as indicated by boat drift. Stations were therefore grouped according to the relative influence of tidal currents (high — visually apparent; low — not visually apparent; Fig. 2a and b). OFe concentrations were consistently higher at those stations most affected by currents ($p < 0.05$, paired *t*-test). However, spatial differences were superseded by temporal oscillations in OFe concentrations that had time-scales on the order of weeks. These temporal changes were not related significantly to water temperature, clarity (Secchi depth), or salinity ($p < 0.05$, paired *t*-test), nor with the state of tide. ToFe concentrations were also higher at those stations affected more by tidal currents, although the temporal oscillations were not as apparent as for OFe values (Fig. 2a and b). OFe:ToFe ratios ranged from 0.02 to 0.31, with the highest values occurring during summer months and uniformly low values in the autumn (Fig. 2c).

The dissolved ($< 0.4 \mu\text{m}$) and particulate ($> 0.4 \mu\text{m}$) OFe and ToFe concentrations in the upper salinity range (27–31‰) of the Sheepscot River estuary are shown in Fig. 3a and b. Although particulate ToFe concentrations were much greater than dissolved values, OFe concentrations were similar in

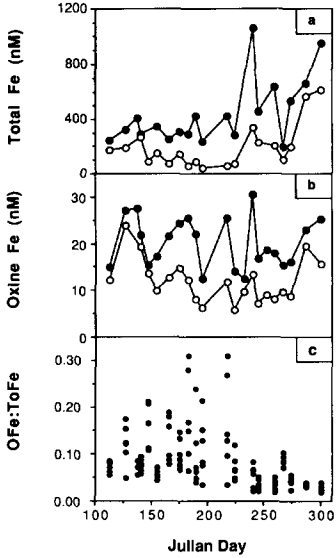


Fig. 2. Concentrations of total (a) and oxine Fe (b) in unfiltered coastal surface waters vs. time in Julian days. Station locations are those shown in Fig. 1a. Values are each the mean of three stations, grouped according to the relative influence of tidal currents (see text). (●) High, (○) low. (c) The ratios of OFe: ToFe at all six stations.

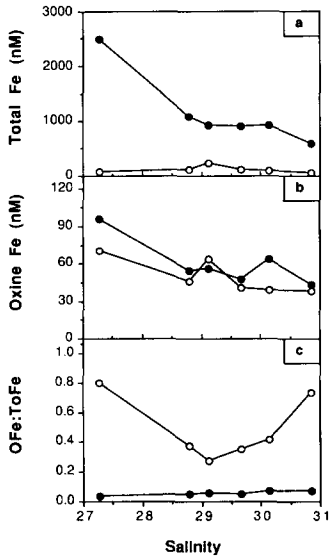


Fig. 3. Dissolved (○) and particulate (●) Fe in the Sheepscot River estuary, June, 1988. (a) total Fe; (b) oxine Fe; (c) OFe: ToFe.

the two fractions. As a result, dissolved OFe: ToFe values (0.35–0.80) greatly exceeded those in the particulate fraction (0.04–0.07) (Fig. 3c). Combining the respective OFe and ToFe concentrations in the two fractions gave ‘unfiltered’ OFe: ToFe values of 0.06–0.13, which is within the range found in the adjacent coastal waters (Fig. 2c). The narrow salinity range of these data prevents meaningful discussion of the Fe/salinity variations observed in the estuary.

The Saco system was studied to determine the estuarine mixing behavior of riverine iron. Aggregation of riverine iron in this estuary has been characterized previously (Mayer, 1982a, b). The riverine end-member was studied in detail using filtration/ultrafiltration separates collected in winter (February, 1989) and during the spring flood (April, 1989). Results typically showed low OFe: ToFe ratios in the particulate fractions and higher ratios, from 0.54 to ~ 1 , in the various colloidal size ranges (Fig. 4). An especially low ratio of 0.11 was found for the particulates in the muddy spring flood sampling.

In the estuary, the dissolved OFe showed a similar negative, nonconservative behavior (Fig. 5) to that found for total dissolved iron in this and many other estuarine systems (Boyle et al., 1977; Sholkovitz et al., 1978; Moore et al., 1979; Mayer, 1982a). The intensity of removal from the dissolved pool, defined as the per cent deviation from the conservative mixing line between the riverine and seaward end-member samples, was often slightly higher for OFe than for ToFe. Particulate OFe and ToFe showed slightly positive, non-conservative behavior, with the exception of the winter particulate ToFe which was roughly uniform across the salinity range.

The OFe: ToFe ratios of the dissolved and particulate phases in the Saco

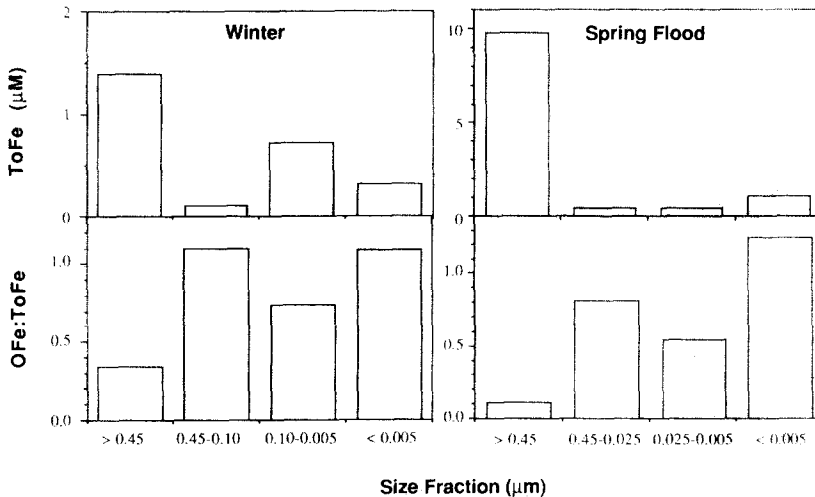


Fig. 4. The size distribution of total Fe (upper) and OFe: ToFe (lower) in Saco River water in winter (February) and during the spring flood (April) 1989.

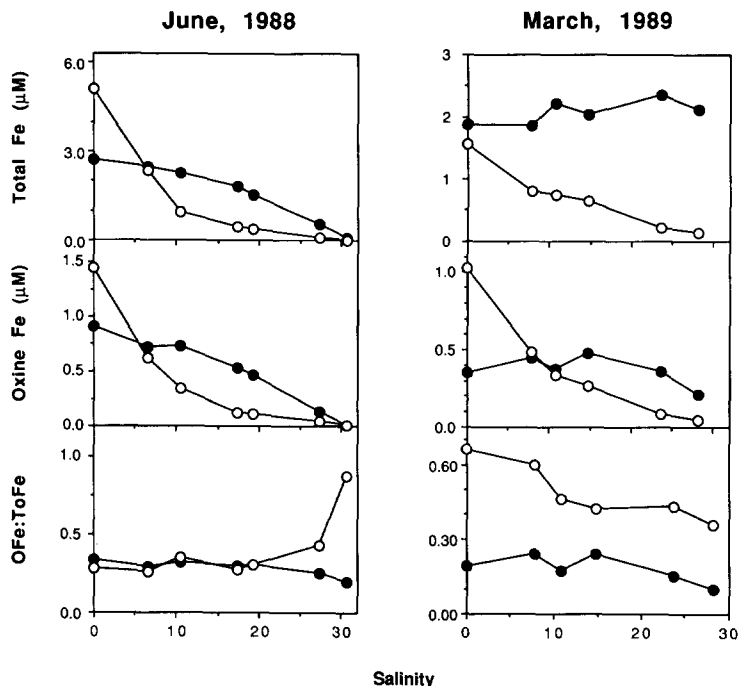


Fig. 5. Dissolved (○) and particulate (●) Fe in the Saco River estuary in June 1988 and March 1989; total Fe (upper); oxine Fe (middle); OFe: ToFe (lower).

TABLE 1

Results of mixing^a experiments

Date	Sample	ToFe (µM)	OFe (µM)	OFe: ToFe
March 8, 1989	Expected ^b	0.94	0.62	0.66
	Unfiltered	1.00	0.43	0.43
	1 h (> 0.45 µm)	0.25	0.07	0.28
	1 h (< 0.45 µm)	0.66	0.35	0.53
April 4, 1989	Expected	1.17	1.15	0.98
	Unfiltered	1.22	0.92	0.75
	1 h (> 0.45 µm)	0.39	0.06	0.15
	1 h (< 0.45 µm)	0.89	0.80	0.90

^aFiltered (0.45-µm) Saco River water was mixed with filtered (0.45-µm) Sargasso seawater to give a salinity of 14. The solution was filtered after 1 h at room temperature, and Fe concentrations were determined.

^bCalculated from dilution of Saco River water.

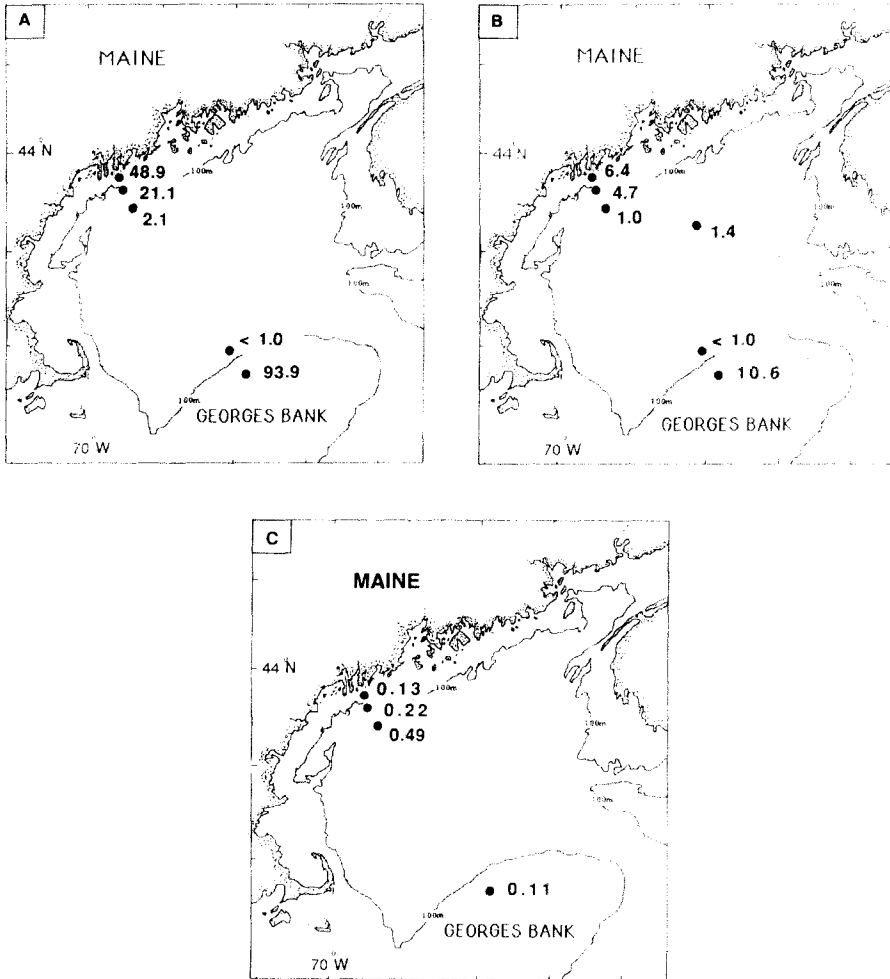


Fig. 6. Concentrations of total Fe (A), oxine Fe (B) and OFe:ToFe (C) at 10-m depth in the Gulf of Maine, July 1988.

River were seasonally variable (Fig. 5). During winter (March, 1989), the OFe:ToFe values in the particulate fractions were lower than in the dissolved fractions. However, in late spring (June, 1988) both fractions had similar OFe:ToFe values in the lower-salinity range, with a higher value for the dissolved fraction appearing at the marine end-member.

Mixing experiments with 0.45- μm -prefiltered river water and seawater showed a reduction in OFe:ToFe of both the resultant mixture and of its filtrable and non-filtrable components (Table 1). This reduction, compared with expected values calculated from simple dilution of river waters, was particularly marked for the aggregates retained on the filters, but also occurred to a

small extent in the filtrates. The decrease in OFe:ToFe of the control (a subsample of the unfiltered mixture) demonstrated that losses in OFe:ToFe were not an artefact of analyzing flocs caught on a filter.

The shelf waters of the Gulf of Maine were studied in a transect from Boothbay Harbor to Georges Bank in July, 1988. OFe and ToFe concentrations decreased rapidly with increasing distance from shore, with values diminishing to near or below detection (1 nM) within 50 km (Fig. 6a and b). OFe:ToFe ratios increased from 0.13 to 0.49 across this range (Fig. 6c). The increase in OFe:ToFe was attributable to both higher dissolved OFe:ToFe ratios and decreased particulate ToFe concentrations (data not shown). Calculation of OFe:ToFe ratios for the central Gulf of Maine was not possible because values were either at or below analytical detection. Over Georges Bank, concentrations of OFe and ToFe were considerably higher than in Gulf of Maine basin waters, and even exceeded those measured in nearshore waters.

DISCUSSION

Early attempts to quantify biologically available Fe in seawater relied on the criterion of size separation, with Fe in $<0.45\text{-}\mu\text{m}$ fractions being considered 'soluble' and therefore probably available to phytoplankton (Huntsman and Sunda, 1980). We know now that 'dissolved' Fe in seawater probably consists largely of colloidal substrates, perhaps differing little in composition from that in 'particulate' phases (Murray, 1979). We would therefore not expect size to be an appropriate parameter in the definition of available Fe. In the strictest sense, 'available Fe' is that which is directly transported across the cell membrane (Fe^{3+} and to a lesser extent Fe^{2+} ; Anderson and Morel (1982)). However, because the concentrations of Fe^{3+} in seawater are extremely low (Stumm and Morgan, 1981), far below that needed to sustain phytoplankton growth, this narrow definition of available Fe has little, if any, relevance from an ecological perspective. Instead, a more useful definition would encompass those substrates (solids and organic-metal complexes) that have dissolution (or dissociation) kinetics which operate on the same time-scale as phytoplankton generation times, such that biologically sequestered Fe is replenished rapidly in response to uptake. According to this view, Fe availability would hinge upon its chemical lability. We developed the oxine technique to measure Fe lability in seawater and have found a strong empirical relationship between measurements of oxine-labile Fe and the nutritional quality of colloidal Fe phases (Wells et al., 1991). Here, we have applied this biologically calibrated technique to study the relative lability of Fe (OFe:ToFe) in estuarine, coastal and shelf waters.

There was a considerable range in OFe:ToFe values among the various waters and size fractions studied, extending from near-zero to 100%. OFe:ToFe ratios in unfiltered coastal waters had a low central tendency near

0.08, although values as high as 0.3 occurred during summer months when concentrations of ToFe decreased. Similarly, the sharp decrease in ToFe in surface waters with increasing distance from shore was accompanied by a factor of four increase in OFe:ToFe (Fig. 6c), which invites speculation that biological processes may exert some influence on the nutritional state of Fe retained in surface waters. The low OFe:ToFe ratio at Georges Bank (0.11) was similar to that measured in estuarine and coastal waters. This similarity may have been due to the shallow depth (30 m) and isothermal conditions at this offshore station, which would have favored resuspension of bottom sediments (largely non-labile, crystalline materials). It is worth noting that the OFe:ToFe values reported here are maximum estimates; the ToFe method intercalibrations in our laboratory indicate that the acid-digestion/preconcentration method may have underestimated ToFe by up to 28%.

The mixing experiments with Saco River water demonstrated that the OFe:ToFe of riverine colloidal Fe is diminished by aggregation. The reduction in OFe:ToFe during the aggregation process (Table 1) is consistent with our observations of low particulate OFe:ToFe relative to the dissolved fraction in the estuary, although other sources of particulate Fe (e.g. resuspension) may also have been responsible for this trend. The reduction in OFe:ToFe upon aggregation of the riverine colloids may be due to occlusion of colloidal Fe in a more organic-rich floc during mixing with seawater. Mayer (1982b) showed that Fe and organic matter appeared to show different aggregation kinetics during flocculation, with organic carbon flocculating preferentially in the early phase of the reaction. The organic carbon:Fe ratios of these early-phase flocs were fairly high — typically 14–80 after a few minutes of reaction. Occlusion of this sort could reduce the kinetics of dissolution of Fe from the flocs and hence the rate of Fe complexation by oxine or phytoplankton. It is conceivable that this reduction in OFe:ToFe is reversible under estuarine (or coastal) conditions if either disaggregation or heterotrophic processes cause re-exposure of the occluded iron colloids to the solution phase.

The OFe:ToFe ratios in the dissolved fractions of estuarine and marine waters (0.26–0.88) provide strong evidence that definitions of available Fe based on size fractionation are wrong by perhaps a factor of three or more. The low OFe:ToFe ratios of 'dissolved' Fe were probably caused by a high degree of order within colloidal matrices (Wells et al., 1983, 1991) or by strong organic complexes which kinetically were relatively inert (e.g. Finden et al., 1984). Of particular interest was the spatial and temporal variability in dissolved OFe:ToFe, which indicated changes in the composition of 'dissolved' Fe. This variability cautions against extrapolating fixed Fe lability ratios to other waters, or even to the same waters at different times.

With few exceptions, the OFe:ToFe ratios in dissolved fractions (0.26–0.88) were greater than those in particulate fractions (0.04–0.34) in both estuarine and offshore waters. Changes in the distribution of Fe between these

phases may have been a principal cause of variation of OFe:ToFe in the unfiltered coastal waters (Fig. 2c). However, the low OFe:ToFe ratios found in the particulate phases do not preclude this fraction from having a substantial, if not major, contribution to the overall OFe concentrations. This situation is well illustrated in the Saco data (Fig. 5), where OFe concentrations in the particulate phases exceeded those in the dissolved fraction by as much as a factor of four. The dominance of particulate OFe was most evident in the lower part of the estuary, where relatively intense resuspension of particulates (Mayer, 1982a) coincided with low dissolved Fe because of river water dilution. The significance of particulates is also apparent in the Sheepscot and Georges Bank data, where approximately half of the OFe was derived from the particulate phase. These findings underscore suggestions that eolian particulates may play an important role in the Fe economy of phytoplankton in the open ocean (e.g. Moore et al., 1984; Martin and Gordon, 1988).

This conjecture about the importance of particulate Fe phases for phytoplankton nutrition assumes a uniform relationship between OFe and Fe availability in both colloidal and particulate-sized matter. Because particulate Fe is more poorly disseminated in solution, differences in the degree of dispersion of oxine and phytoplankton may be more important than with the colloidal-sized Fe materials used to calibrate the technique (Wells et al., 1991). At $\sim 10^{19}$ molecules l^{-1} , oxine is dispersed in solution to a much greater extent than is phytoplankton (maximum abundances on the order of 10^8 – 10^9 cells l^{-1}) or particulate matter. Hence, the diffusional limitations for Fe complexation (uptake) rates from particulates would be less for oxine than for phytoplankton, leading to non-uniform characterization of Fe lability in particulate and dissolved fractions. Thus, although the survey data indicate that particulate fractions may be a major source of biologically available Fe, the more homogeneously dispersed 'dissolved' Fe phases may be better suited for phytoplankton utilization because of smaller diffusional restrictions. Such arguments obviously would not apply where particulates are adsorbed to phytoplankton surfaces (Harvey, 1937; Goldberg, 1952; Lewin and Guillard, 1963; M.L. Wells, unpublished results, 1980).

Other factors that potentially influence the bioavailability of Fe are not addressed in this paper. We have found, for example, that photoreduction of colloidal Fe oxides in seawater can raise the OFe:ToFe ratio, whereas aging processes of amorphous Fe oxyhydroxides lower it (Wells and Mayer, unpublished data, 1989). Complexation of Fe with extremely strong ligands can reduce its bioavailability (Finden et al., 1984), presumably because of slow dissociation kinetics. Finally, the efficiency and capacity of metal uptake systems can be affected by both the nutritional status of the organism and by other dissolved constituents (Huntsman and Sunda, 1980; Harrison and Morel, 1983). Thus, because Fe availability may be a dynamic parameter, per-

haps changing on a time-scale of hours, some caution is necessary when interpreting single-point, static measurements of relative Fe lability.

Acknowledging these potential limitations, the data presented here have several implications for phytoplankton assemblages in the Gulf of Maine. Clearly, OFe concentrations (and by association, Fe availability) were highest in the nearshore environment but diminished rapidly offshore, with concentrations in Gulf of Maine basin waters being similar to that of open ocean environments. This rapid transition in nearshore waters (0–50 km from shore) correlates with changes in phytoplankton abundance, cell volume and species composition across this zone (Marshall, 1984a, b). Over Georges Bank, waters are richer in labile Fe than in the nearshore environment, which may partly explain the high productivity of this region. Whether or not Fe is limiting primary production in the Gulf of Maine basin cannot be deduced from these data; oxine-labile Fe is not quantitatively equivalent to available Fe concentrations and the Fe requirements of organisms in basin waters are not known. However, the very low OFe concentrations in the basin waters suggest that Fe availability may be an important constraint to phytoplankton growth. It was Gran (1933) who wrote of the Gulf of Maine that soluble Fe compounds, washed out from the shores, may give the explanation of the relatively high productivity of coastal waters in comparison with the open ocean. The data presented here are consistent with his early hypothesis.

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