Effects of phytoplankton blooms on the cycling of manganese and iron in coastal waters

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Abstract

The development of intense plankton blooms during spring controls the concentrations of dissolved Mn and Fe in eutrophic shallow coastal waters of the North Sea. Proliferation of diatoms, Phaeocystis colonies, and Noctiluca was accompanied by changes of particulate and dissolved Mn and Fe in the water column. The latter parameters were measured simultaneously with relevant physical, chemical, and biological variables at two sites in the coastal waters of the Southern North Sea, in 1993 at one site and in 1994 at both sites. Removal of dissolved Fe and particulate Fe, Mn, and Al occurred during the inception of the spring bloom. This could be due to biological uptake, adsorption of abiotic particles onto settling phytoplankton cells, or ingestion of abiotic particles by zooplankton during grazing, with subsequent settling of fecal pellets. We also observed a seasonal increase of dissolved Mn and Fe and progressive changes in the composition of the particulate Mn and Fe in the water column after peaks in spring diatom and Phaeocystis blooms. This can be explained by the following sequence of events. The organic matter produced during the spring phytoplankton blooms is degraded by the heterotrophic organisms in the water column and the sediment. This leads to anoxic conditions near the surficial layer in the shallow coastal sediments. First, Mn oxides and then Fe oxides are used as oxidants for the degradation of organic matter, resulting in the reduction and dissolution of Mn and Fe. Dissolved Mn and Fe diffuse to the oxic overlying water and are partly adsorbed or precipitated on the suspended particulate matter. The other part remains in solution longer because of a decrease in the oxidation rate. This decrease results from a lowering of both the pH from 8.6 to 8.1 and the oxygen concentrations from 378 to 204 µM in the water column due to the activity of heterotrophs in the water column and sediment. Noctiluca could also be responsible for the reduction of Mn and Fe associated with bacteria and phytoplankton. Overall, the seasonal evolution of dissolved and particulate Mn and Fe is consistent with the successive autotrophic and heterotrophic activities.

Studies of the impact of phytoplankton blooms on the biogeochemical cycling of Mn and Fe in coastal waters are limited. Mn and Fe are two essential elements for phytoplankton growth (Sunda 1988/1989). Uptake of dissolved Mn and Fe by phytoplankton is enhanced in coastal eutrophic waters, where primary productivity and associated Mn and Fe cellular requirements are particularly high. (Brand et al. 1983; Sunda et al. 1991; Sunda and Huntsman 1995). In general, the wax and wane of a phytoplankton bloom is accompanied by first an increase and then a decrease of pH and oxygen. This is due to photosynthetic and heterotrophic activities, whether in the ambient seawater or within a microenvironment. Microenvironments of high pH (>9) can exist around either large phytoplankton cells and aggregates >20 µm (Richardson et al. 1988; Richardson and Stolzenbach 1995) or within large colonies of algae, notably Phaeocystis sp. (Lubbers et al. 1990). Subsequent accumulation of precipitated Mn has been observed on cultured Phaeocystis sp. collected from the Southern Ocean (Davidson and Marchant 1987) and the North Sea (Lubbers et al. 1990). The high pH sustained in and near the actively photosynthesizing colonies is thought to also be favorable for precipitation of Fe (Lancelot and Rousseau 1994), although it has not yet been investigated.

Phaeocystis sp. is a cosmopolitan species with a unique life cycle in which the ecological function of the colonial stage is subject of vigorous debate (Lancelot and Rousseau 1994; Rousseau et al. 1994; Lancelot 1995; Riegman and Van Boekel 1996). Nowadays, Phaeocystis sp. produces
massive blooms of large (100–8,000 µm) gelatinous colonies. During spring, it dominates the phytoplankton community in the eutrophic coastal waters of the North Sea (Bätje and Michaelis 1986; Cadée and Hegeman 1986; Lancelot et al. 1987; Lancelot 1995; Cadée 1996). It is also a major bloom-forming species in polar waters, where it may account for part of the oceanic carbon uptake (Wassmann et al. 1990; Smith et al. 1991, 1996). The brownish color of colonies observed in Antarctic (Davidson and Marchant 1987) and North Sea waters (Bätje and Michaelis 1986) was thought to be due to the Mn precipitates either at the surface or within the colony. It is therefore hypothesized that Phaeocystis may play a key role as a vector for Mn and Fe transport in the coastal waters of the North Sea, where it constitutes the major component of the spring phytoplankton community (Lubbers et al. 1990; Lancelot and Rousseau 1994; Riegman and Van Boekel 1996; this study).

Phytoplankton can affect the Mn and Fe concentrations in the water column, not only via metal uptake. Increase of dissolved Mn and Fe in the water column may indirectly originate from the decline of phytoplankton blooms. Large amounts of organic matter produced in the euphotic zone may deposit. The degradation of this phytoplankton-derived material may lead to anoxic conditions in the sediments. In this case, bacteria use Mn(IV) and Fe(III) solid phases as oxidants. If Fe and Mn are reduced near the sediment–water interface, Mn(II) and Fe(II) will diffuse from the anoxic interstitial waters to the overlying water (Sundby et al. 1981; Kremling 1983; Sundby et al. 1986; Slomp et al. 1997).

Phytoplankton blooms may thus affect the biogeochemical cycles of Mn and Fe in several ways because of: (1) adsorption on the cells as well as intracellular uptake of dissolved Mn and Fe; (2) precipitation and accumulation of Mn and Fe at the surface or within phytoplankton-oxidizing microenvironments, i.e., large diatoms, aggregates, and Phaeocystis colonies; and (3) decomposition of sedimented, phytoplankton-derived materials with resultant release of dissolved Mn and Fe due to both cell remineralization and reduction of Mn and Fe oxides in reducing surficial sediments.

The aim of this work was to study the impact of phytoplankton dynamics on the cycling of Mn and Fe in coastal waters dominated by Phaeocystis sp. blooms. In this context, we measured concentrations of particulate and dissolved Mn and Fe during seasonal cycles simultaneously with relevant physical, chemical, and biological variables at two shallow coastal stations in the North Sea, where blooms of Phaeocystis globosa are recurrent spring events.

Materials and methods

Study sites and sample collection—Surface samples were collected at two stations in the Southern Bight of the North Sea (Fig. 1). This coastal region is dominated by strong tidal currents and wind mixing. The combination of strong tidal currents, which maintain a highly turbulent regime, with shallow water depths in the Southern Bight of the North Sea ensures general vertical mixing throughout the year (Otto et al. 1990; Charnock et al. 1994). Sampling at one depth was consequently considered representative for the whole water column for substances in solution and, in general, also for suspended particles (Chen 1995). Local waters of the North Sea are of Atlantic origin with a net northeastward transport from the Dover Strait along the Belgian–Dutch coasts.

Sta. 330 (51°26'05''N, 02°48'50''E) is about 40 km off the coast and is influenced by river Scheldt. It has served as the Phaeocystis reference station in the Belgian coastal zone for >10 yr. The depth versus mean sea level is about 22 m. The Marsdiep Station (53°02'00''N, 04°58'00''E) is located at the NIOZ (Netherlands Institute for Sea Research) jetty at 7-m local water depth along the deeper Marsdiep channel of the Dutch Wadden Sea. The station has been monitored as reference station for phytoplankton distribution in the Dutch coastal area since 1973 (Cadée and Hegeman 1986). It is influenced by the outflows of the river Rhine. The Marsdiep tidal channel has greatest depths of about 40 m due to intense tidal exchange of North Sea waters. To sample North Sea water at the Marsdiep Station, sampling was carried out at high tide. This strategy and the general net northeasterward transport of waters along the Dutch coast ensure that the samples represent the North Sea region some 10–20 km to the southwest of the station.

At Sta. 330, sampling was done in general once to twice a week from the RV Belgica in 1993 and 1994. At the Marsdiep Station, samples were taken once to three times a week from March to August 1994. Samples were collected using an acid-cleaned polyethylene (HDPE) bucket attached to a kevlar cable. The bucket had a wide lip to avoid disruption of fragile Phaeocystis colonies during sample pouring. Samples were taken from the upwind and upstream sides of ei-
ther ship or jetty and directly carefully transferred to a clean 10-liter HDPE bottle. This method was compared with the GoFlo bottle sampling method and was shown not to contaminate.

Manganese, iron, and aluminum—Laboratory materials used for trace metal analysis were made of Teflon, polycarbonate, or high density polyethylene. They were previously washed in 7 N HNO₃ (48 h), except for the less resistant polycarbonate containers and filters, which were soaked in 1 N HCl (24 h). After acid washing, all material, including filters, was thoroughly rinsed with ultra pure water (Barnstead Nanopure system). All procedures were carried out in a Class 100 laminar flow bench.

Samples for trace metal analyses were filtered in polycarbonate devices (Sartorius) refitted with Teflon O-rings. The samples were successively filtered over 10-, 0.8-, and 0.1-µm Nuclepore polycarbonate membrane filters of 47-mm diameter without storage between the different filtrations. Filtration volumes were adjusted according to the filter porosity and the concentration of the suspended matter, to avoid clogging of the filter. About 150–1,600 ml was filtered over 10- and 0.8-µm membranes and 100–400 ml over 0.1 µm. No vacuum was applied during the filtration over 10 µm to avoid squeezing and disruption of the Phaeocystis colonies. Vacuum pressure applied to the second filtration was kept lower than 0.3 atm to keep phytoplankton cells intact as much as possible (Goldman and Dennett 1985).

The fraction >10 µm is assumed to contain the large phytoplankton, including Phaeocystis colonies and large diatoms. The fraction retained on the 0.8-µm filter included small-sized phytoplankton such as the Phaeocystis single cells. However, no correlation was found between the phytoplankton size and the fractionation for trace metal, so particular Mn, Fe, and Al on 0.8 and 10 µm are shown together as the total particulate fraction (e.g., Mnₚ). Since particulate Mn, Fe, and Al concentrations on the 0.1-µm filter were either below detection limit or <5% of the total particulate concentration, this fraction was not taken into account. The filtrate passing 0.1 µm was considered to contain dissolved Mn and Fe. Concentrations of Mn and Fe were similar in filtrates below either 0.8 or 0.1 µm (r = 0.99, P < 0.0001, n = 26, and slope = 1.02 for Mn and r = 0.97, P < 0.0001, n = 10, and slope = 0.93 for Fe). Therefore, we defined the total metal concentration in the sample (total; e.g., Mnₜ) as the sum of the metal concentrations retained on the 10- and 0.8-µm membranes (total particulate; e.g., Mnₚ) together with the fraction below 0.1 µm (dissolved; e.g., Mnₜ). Filtered water samples were acidified to pH < 2 with three times quartz distilled (3Q) 14 N HNO₃, and stored in Teflon bottles at 4°C until analysis. Filters were stored in polycarbonate petri dishes at -18°C until further treatment.

Particulate Mn, Fe, and Al collected on the 10-µm filters in 1994 were subjected to a three-step extraction method (Lewis and Landing 1991). During the first step, filters were submerged in 25% (4.5 M) acetic acid (3Q-HAc) at room temperature to extract the most reactive fraction (HAc). Filters were drained and transferred to be soaked in dilute aqua regia solution, containing 2 M 3Q-HCl and 1 M 3Q-HNO₃, also at room temperature (AR). Finally, the most refractory fraction (REF) and the filters were hydrolyzed with 750 µl 12 N 3Q-HCl, 250 µl 14 N 3Q-HNO₃, and 250 µl 40% HCl (Merck Suprapur) in Teflon bombs at 100–120°C. This final step of the digestion procedure was directly applied to the 10-µm filters collected in 1993, as well as to all of the 0.8- and 0.1-µm filters, to measure the total particulate Mn, Fe, and Al retained on these filters. These extractions were also applied to a marine reference sediment material for trace metals analysis (BCSS-1, available from the National Research Council of Canada) to verify the accuracy of the methods. Results of the three-step extraction (summing results obtained for each step) and results of the total digestion alone were within the range of values certified by the National Research Council of Canada. Blank values were below 5% of the measured sample signals.

Dissolved and extracted Mn, Fe, and Al were measured by Flame Atomic Absorption Spectrophotometry (Perkin Elmer 2380) for high concentrations (>50 µg liter⁻¹ for Mn and Fe and >500 µg liter⁻¹ for Al). Samples with lower concentrations were analyzed by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS, Perkin Elmer Zeeman 5100 PC) using calibration by standard addition. Multiple injection of the sample was applied for Mn and Fe concentrations below 20 nM. Accuracy of the analytical method for seawater samples was verified by measuring CASS-3 (for Mn and Fe) and NASS-4 (Mn only, below detection limit for Fe) seawater reference material for trace metals (National Research Council of Canada). The relative standard deviation of the method was better than 5%. A detection limit of three times the standard deviation of the lowest measured seawater concentration for the direct measurements (without dilution) of dissolved concentrations in seawater was found to be 3 nM for Fe and 2 nM for Mn.

Physical, chemical, and biological parameters—Salinity was determined by conductivity using a Beckman salinometer. Total suspended matter was analyzed in 1994 by weighing 0.8-µm porosity preweighed Nuclepore polycarbonate membrane filters after the filtration of 200–1,000 ml of water sample and drying at 55°C for 48 h. Alkalinity was determined by acid titration in a closed vessel, upon which the titration curve was fitted with a modified Gran plot (Stoll et al. 1993). Total inorganic carbon (TIC) was measured on an automated coulometer modified after Johnson et al. (1987) according to the method described in DOE (1991). The pH and aqueous carbon dioxide concentrations ([CO₂]ₚ) were calculated from alkalinity and TIC, using the dissociation constants given by Goyet and Poisson (1989). Dissolved oxygen was measured according to the Winkler method, and oxygen saturation percentages were calculated taking into account water temperature and salinity. Nutrients were determined in a 0.45-µm membrane (Sartorius cellulose-ace-tate) filtered seawater according to the methods described in Grasshoff et al. (1983). Chlorophyll a (Chl a) was quantified spectrophotometrically following Lorenzen (1967) after 90% v:v acetone extraction (12 h) in the dark at 4°C of the particulate material retained on glass-fiber filters (Whatman GF/C).

Phytoplankton samples were fixed with a 1% lugol-glu-
Fig. 2. Temporal evolution of salinity (\(\bullet\)), temperature (\(\circ\)), and particulate suspended matter (\(\bullet\)) in 1993 and in 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl \(a\) maximum, and the maximum concentration in dissolved Mn.

taraldehyde solution. The species composition, cell density, and biovolumes of diatoms and Phaeocystis colonies were determined under an inverted microscope (Leitz Fluovert) after a 12-h sedimentation of 5–10-ml samples in Utermöhl chambers (Hasle 1978). A carbon content of 0.11 pg C \(\mu \text{m}^{-3}\) of plasmavolume (Edler 1979) was used to convert the diatom biovolumes measured on a cell population during their bloom period. Phaeocystis colony sizes were converted into carbon biomass using the equations established by Rousseau et al. (1990). Biomass of the giant heterotrophic dinoflagellate, Noctiluca miliaris, was determined by counting the cells under a darkfield illuminated stereomicroscope directly after sampling and using a factor of 0.2 \(\mu \text{g C cell}^{-1}\) (Uhlig and Sahling 1990).

Results

Physical, chemical, and biological observations—At both stations, the temperature increased from about 5\(^{\circ}\)C in early March to about 20\(^{\circ}\)C in early July (Fig. 2a–c). The salinity varied between 31.8 and 34.9 at Sta. 330, and between 23.7 and 30.5 at the Marsdiep Station (Fig. 2a–c). At the end of March in 1993 and late February–early March of 1994, salinities decreased sharply at Sta. 330 (Fig. 2a,b). Between March and July, no regular trend was observed at Sta. 330 in 1994 (Fig. 2b), while salinities tended to increase at the Marsdiep Station between March and July (Fig. 2c). Suspended particulate matter was about fourfold smaller at Sta. 330 compared with that at Marsdiep Station (Fig. 2d,e). It increased at the peak of the bloom and was at minimum in early June (Fig. 2d,e).

Average winter levels of nutrients (Fig. 3) as well as peak plankton concentrations (Fig. 4) were higher at the Marsdiep Station than at Sta. 330. Nutrient concentrations increased in late March 1993 and late February 1994 (Fig. 3). They decreased in February–March and increased again in May–June. At Sta. 330, Chl \(a\) concentrations (Fig. 4a,b) exhibited similar maxima (45 mg m \(^{-3}\)) in early May 1993 and late April 1994. At the Marsdiep Station, the phytoplankton blooms showed three Chl \(a\) maxima of 75, 45, and 40 mg m \(^{-3}\) from late April to early July (Fig. 4c). Diatoms bloomed from March to the end of May (Fig. 4d–f). P. globosa blooms started later in April and also ended at the end of May (Fig. 4d–f). Phaeocystis dominated the spring phytoplankton biomass in 1993 at Sta. 330 (Fig. 3d; note the difference of scale for diatoms and Phaeocystis), whereas diatoms were dominant in 1994 at both stations (Fig. 4e,f). In late May early June, biomass of the heterotrophic dinoflagellate, N. miliaris, was highest at both stations (Fig. 4g–i). These organisms suddenly disappeared in late June–early July.

During diatom blooms at the Marsdiep Station, oxygen concentrations increased from 328 to 378 \(\mu \text{M}\), meaning that oxygen saturation increased from 100 to 125% (Fig. 5a). Undersaturations were reached in late May, with a minimum value of 75% corresponding to an oxygen concentration of 204 \(\mu \text{M}\) in early June when the Noctiluca peaked (Fig. 4i). Aqueous carbon dioxide concentrations \([\text{CO}_2]_{aq}\) decreased...
Mn and Fe cycling

![Temporal evolution of silicate (+), phosphate (o), ammonium (●), and nitrate (○) in 1993 and in 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl a maximum, and the maximum concentration in dissolved Mn.](image)

from 27 µM to 6 µM, and the pH increased from 8.1 to 8.6 during the bloom of the diatoms and the beginning of the bloom of Phaeocystis (Figs. 4f, 5b). From late May to late June, when diatoms and Phaeocystis disappeared from the water column and Noctiluca developed, dissolved carbon dioxide concentrations were again higher ([CO2]aq ~ 13 µM), with a pH of about 8.2.

Manganese, iron, and aluminum concentrations—At Sta. 330, the dissolved Mn is quite low at about 25–50 nM throughout 1993, except for a distinct increase to 80 nM in the May–June period following the spring bloom (Fig. 6d). This increase was confirmed in the 1994 record (Fig. 6e). At the more near-shore Marsdiep site, the dissolved Mn values tended to be higher, but the same trend toward a maximum at early June after the spring blooms was observed (Fig. 6f). This postbloom dissolved maximum is consistent with a maximum of total Mn (dissolved + particulate; Fig. 6a–c), suggesting a net input into the water column in May–June. In the spring period, most of the Mn is in the dissolved state at Sta. 330 (Fig. 6d,e). At the Marsdiep Station, this is the case only in early June (Fig. 6f). In contrast, the strong maxima of total Mn in winter at Sta. 330 (Fig. 6a: February–March 1993, November 1993) are due to resuspension of sediment particles by winter storms, as shown by the dominance of the particulate form of Mn at that time and the consistent maxima of particulate Mn and Fe as well as Al in those months (Figs. 6d, 7a,d).

Dissolved Fe tended to show a more (Fig. 7a) or less (Fig. 7b) distinct decrease of about 40 nM at the onset of the spring plankton bloom at Sta. 330 (we did not consider the exceptionally high concentration of dissolved Fe at the end of March 1993, which seems to correspond to a river discharge pulse). Unfortunately, at the Marsdiep Station, there are no Fe data at the onset of the bloom. Particulate Mn, Fe, and Al were decreasing at the same time, suggesting a strong coincidence of removal of terrigenous particles with the onset of the spring bloom. The particulate Mn, Fe, and Al were at minimum in late May–early June (Figs. 6d,e, 7a,b,d,e).

Only at the Marsdiep site does one find a distinct increase of dissolved Fe in May–June (Fig. 7c). This Fe maximum is consistent with, but slightly lagging behind, the increase of dissolved Mn. At the more offshore site 330, an input of Fe is not discernible in May–June (Fig. 7a,b).

Composition of the particulate suspended matter—The composition of the suspended particulate matter is reported only for the largest fraction (>10 µm), as this was the only fraction subjected to sequential chemical extractions. Some 93 ± 3% of the particulate Al was found in the refractory portion; the remaining 3 ± 2% were in the AR- and HAc-leachable portions. Thus, particulate Al, whether overall (HAc + AC + REF) or refractory (REF), is deemed an excellent indicator of nonreactive terrigenous material. Both from the above dissolved distributions and the particulate fractions, it is clear that Mn is very reactive and dynamic in this coastal environment. Some 76 ± 9% of the particulate Mn is in the most reactive HAc-leachable
Fig. 4. Temporal evolution of Chl a (●), diatom biomass (●), P. globosa biomass (○), and N. miliaris biomass (▲) in 1993 and in 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl a maximum, and the maximum concentration in dissolved Mn.

fraction; some 8 ± 4% is found in the intermediate AR fraction, and the remaining 16 ± 7% is in the refractory portion. The Fe behaves intermediately between Al and Mn. Some 13 ± 6% of particulate Fe is in the easily leachable HAc fraction; 8–24% is in the AR fraction; and finally, 68 ± 9% resides in the refractory portion.

The elemental ratios in the suspended particulate matter changed progressively from May to the end of July at the Marsdiep Station (Fig. 8f–j). The molar ratios of total amounts of (HAc + AR + REF) Mn and Fe over REF Al were stable in March–April and close to the average soil ratio (Fig. 8f; Mn/Al = 0.0069 and Fe/Al = 0.27) as calculated from the average content of Mn, Fe, and Al in soils (Chester 1990). From May to the end of July, a distinct increase of (HAc + AR + REF) Mn and Fe compared to REF Al was found (Fig. 8f). This increase is consistent with significant increasing trends over time of HAc, AR, and REF portions of both Mn and Fe versus refractory particulate Al (Fig. 8g–i). At that time, the HAc-leachable Mn and Fe also increased relative to the diluted aqua regia and the refractory fraction (AR + REF; Fig. 8j). Fe enrichment in the suspended matter was observed mostly in the refractory portion (Fig. 8i), contrary to Mn, which occurred mainly in the easiest leachable portion (Fig. 8g). Similar trends, although obscured by general scatter, were recorded at the more offshore station for total amounts of Mn and HAc versus refractory Al, as well as for HAc Mn relative to the diluted aqua regia and the refractory fraction (Fig. 8a,b,e). No apparent temporal trend of these ratios was observed for Fe at Sta. 330 (Fig. 8a–e).

Discussion

Seasonal succession of plankton, Mn, and Fe—Seasonal succession of plankton and trace metals Mn and Fe is characterized by three major biological and chemical events: the onset of the spring phytoplankton bloom, the maximum Chl a, and the maximum dissolved Mn. These events are indicated as vertical lines in the figures and distinctly mark in time the exponential growth phase of the bloom, the stationary phase and decline, and the postbloom situation characterized by heterotrophic activity.

At the onset of the spring diatom bloom at Sta. 330, dissolved Fe decreased by 40 nM when corrected for salinity effects. During the same period in 1994, primary production amounted to 24.4 μM of C (Becquevort et al. 1998), corresponding to an uptake of 4.9 nM of Fe considering an Fe:C ratio of 200 μmol Fe mol⁻¹ C for coastal diatoms (Sunda and Huntsman 1997). As this is only 12% of the total decrease, it demonstrates the overwhelming effect of adsorp-
Fig. 5. Temporal evolution of dissolved oxygen saturation (•), dissolved oxygen concentrations (○), pH (◇), and dissolved CO₂ (◇) in 1993 and 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl a maximum, and the maximum concentration in dissolved Mn.

Fig. 6. Temporal evolution of total Mn (Mn_{tot} = Mn_{p} + Mn_{d}; ●), dissolved Mn (Mn_{d}; ▲), and particulate Mn (Mn_{p}; ○) in 1993 and 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl a maximum, and the maximum concentration in dissolved Mn.

Throughout the maximum abundance of Chl a, the total Mn/Al and total Fe/Al ratios remained fairly stable at the Marsdiep Station (Fig. 8f). This suggests that the total Mn and Fe of the suspended matter remained dominated by the presence of terrigenous materials, despite the absolute amount of biogenic matter having increased. Similarly, the Mn/Al ratio remained fairly uniform around the Chl a maximum at Sta. 330 in 1994.

Several authors have proposed that Phaeocystis colonies could play an important role in the cycling of Mn and Fe by producing, oxidizing and accumulating microenvironments for these trace metals (Davidson and Marchant 1987; Lubbers et al. 1990; Rieglman and Van Boekel 1996). Morris (1971, 1974) attributed observed variations in the
dissolved and particulate Mn in the Menai Straits to a concomitant bloom of *Phaeocystis*. Our results show no direct effect of only *Phaeocystis* blooms on Mn and Fe concentrations at the studied stations. In 1993, *Phaeocystis* dominated the total phytoplankton cell number and biomass, as is usually the case in the coastal waters of the Southern North Sea (Cadée and Hegeman 1993). In 1994, the *Phaeocystis* bloom in spring was exceptionally low (Cadée 1996) and diatoms dominated the spring phytoplankton community instead. Even so, particulate Mn and Fe were similar during the spring phytoplankton blooms of 1993 and 1994 at Sta. 330. There was no significant accumulation of Mn and Fe in the suspended particulate matter relative to crustal abundances.

At the decline of the spring phytoplankton bloom, the dissolved and total Mn increased at both stations. They reached their maxima when Chl *a* concentrations were at minimum. At the same time, the heterotrophic dinoflagellates *Noctiluca* were growing exponentially. Maxima in dissolved Mn coincided, or slightly lagged behind, maxima in *Noctiluca* biomass, which in turn corresponded to sharp increases in ammonia, a good indicator for heterotrophic activity. At the Marsdiep Station, the oxygen had now shifted to undersaturation at its lowest (Fig. 5a). The oxygen depletion, the pH minimum, as well as the dissolved CO$_2$maxima all show the dominance of heterotrophic activity over autotrophic activity at this time (May–June). Dissolved Fe also increased at the Marsdiep Station but was at maximum a few days after dissolved Mn was at its maximum.

The concentrations of total and dissolved Mn started to increase directly after the maximum of Chl *a* concentrations and peaked later when Chl *a* concentrations were minimal. This increase of total Mn shows the presence of a source of Mn to the water column, which appears to be linked to the decline of the phytoplankton blooms. The progressive enrichment in HAc-leachable Mn in the particulate matter also occurred at the same time. This is likely due to a transfer of the imported dissolved Mn to the suspended particles, which would also explain the enrichment in total Mn relative to Al in the particulate suspended matter. The similar changes observed for Fe in the composition of the particulate suspended matter could be due to the same process. Fe is much more rapidly oxidized than Mn (Murray and Brewer 1977). Therefore, Fe is more rapidly transformed into more refractory material. As a result, the Fe enrichment in the suspended matter was observed mostly in the refractory portion.

The mobilization of Mn (at both stations) and Fe (at the Marsdiep Station only) and the resulting increases of dissolved Mn and Fe during the postbloom situation may be due to a combination of processes, for which the relative importance will be discussed below.

**Regeneration of Fe and Mn**—Recycling and regeneration of dissolved Mn and Fe occur during the remineralization of the phytoplankton (Hutchins and Bruland 1994). In other words, the observed increases might be ascribed solely to the logical extension of the classical Redfield ratio with essential trace elements Mn and Fe. However, above, it was shown that the initial cellular removal of dissolved Fe during the onset of the bloom can only account for at most some

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**Fig. 7.** Temporal evolution of dissolved Fe (Fe$^+$; •), particulate Fe (Fe$^-$; ○), and particulate Al (Al$^-$; ○) in 1993 and 1994 at Sta. 330 and in 1994 at the Marsdiep Station. The vertical lines indicate, respectively, the initiation of the spring bloom, the spring Chl *a* maximum, and the maximum concentration in dissolved Mn.
12% of the observed decrease of dissolved Fe. Therefore, any decomposition of such algal matter would in itself only bring a negligible amount of Fe back into solution.

For dissolved Mn, similar calculations can be made. At Sta. 330 in late May–early June 1993 and 1994 (during and following the decline of the spring phytoplankton blooms), we observed an increase of dissolved Mn of about 4 nM d\(^{-1}\) in the surface waters for a period of 10–15 d. If we consider the spring diatom production of 112 g C m\(^{-2}\) and the spring *Phaeocystis* production of 110 g C m\(^{-2}\) as calculated by Becquevort et al. (1998) for Sta. 330 in 1994, an average depth of 22 m and a range for the Mn: C ratio of 20–32 µmol Mn mol \(^{-1}\) C for diatoms (Sunda 1988/1989; Sunda and Huntsman 1996) as well as a range for the Mn: C ratio of 20–30 µmol Mn mol \(^{-1}\) C for *Phaeocystis* (V. Schoemann unpubl. data) from coastal areas with the same range of metal concentrations as in the present study, the phytoplankton could only have accumulated about 11–26 nM during the whole spring bloom. Another estimate of regenerated intracellular Mn could be obtained from the observed increase in ammonia (13 µM) and phosphate (≈0.8 µM) during May and June of 1994. Using the Redfield C:N of 6.6 and C:P of 106, the estimated regenerated C would be 0.085 mM, and the associated intracellular Mn released would be 0.5–2.7 nM, or only 1–4% of the observed decrease of Mn. Both estimations show that the regeneration of dissolved Mn from the phytoplankton could therefore only account for a small part of the release of dissolved Mn observed after the spring phytoplankton bloom. However, if the phytoplankton has oxidatively scavenged Mn, then redissolution of these oxides in the reducing conditions of surface sediments would result in additional inputs of dissolved Mn.

**Role of aggregates**—Both diatoms and *P. globosa* have been shown to produce aggregates toward the end of blooms (Riebesell 1991, 1993; Lancelot 1995). These aggregates may scavenge other microorganisms and inorganic particles such as clays (Avnimelech et al. 1982; Lancelot 1995) and would also tend to oxidize Mn on their surfaces. Such aggregates were observed mid-May at Sta. 330 (Becquevort et al. 1998) and at the beginning of June at the Marsdiep Station (V. Schoemann pers. comm.). The scavenged mineral materials of these aggregates increase the density of the phytoplankton debris and may enhance their exportation to the sediments (Avnimelech et al. 1982; Wassmann 1994). Aggregation during the decline of the diatoms and *Phaeocystis* blooms could thus contribute to the rapid removal of both organic and inorganic materials from the water column and to their export to the sediments. This mechanism could explain the observations in late May–early June in the water column, where a decrease of Chl \(a\) is accompanied by minima of particulate Al, particulate Mn, and particulate Fe. It could decrease the amount of suspended particles in the water column and hence decrease the amount of adsorptive sites for Mn and Fe and of surface catalytic sites for the oxidation of Mn (Kessick and Morgan 1975; Stumm and Morgan 1981; Sung and Morgan 1981; Yeats and Strain 1990; Turner et al. 1992). It would also provide Mn and Fe oxides to the sediments.

**Role of pelagic heterotrophs**—Heterotrophs can favor the dissolution of Mn and Fe not only via the mineralization of the phytoplankton (Hutchins and Bruland 1994) but also by producing reducing microenvironments (Hutchins and Bruland 1994; Wells et al. 1995; Barbeau et al. 1996); by changing chemical conditions like the pH and the dissolved oxygen concentrations in the ambient water; and by “cleaning up” the water column from suspended matter. It has been suggested that the acidic digestive systems of plankton grazers are hydrolytic and reducing microenvironments, which could play a major role in the chemical speciation of Mn and Fe (Hutchins and Bruland 1994; Wells et al. 1995; Barbeau et al. 1996). The enzymatic degradation, combined with low pH, within feeding vacuoles can transform organically bound cellular Mn and Fe as well as ingested Mn and Fe oxides (e.g., those associated with cell surfaces) into inorganic dissolved Mn and Fe (Frey and Small 1979; Hutchins and Bruland 1994; Barbeau et al. 1996).

The pH of *Noctiluca* vacuoles is as low as 4.35 (Taylor 1987). Among heterotrophic microorganisms, *N. militaris* was dominant in biomass (>70%) at Sta. 330 in late May–early June 1993 and 1994 (S. Becquevort pers. comm.). At the same site in 1994, bacterial production and biomass were low from the end of May to late June (Becquevort et al. 1998). *Noctiluca* also developed at the Marsdiep Station at the time we observed increases of dissolved Mn and Fe concentrations. Our results suggest that *Noctiluca* could have played a role in the dissolution of Mn and Fe. *Noctiluca* activity can be very intense (Weisse et al. 1994). They are large omnivorous dinoflagellates feeding on phytoplankton, like *Phaeocystis* cells, microprotozoa, and bacteria (Weisse and Scheffel-Müser 1990; Weisse et al. 1994). They could therefore dissolve the Mn and Fe associated with these organisms. The very high net production of ammonia observed simultaneously with their bloom could be due to their intense regenerating activity, together with the decline of the autotrophs that no longer consumed nitrogen. *Noctiluca* could also be mainly responsible for the strong decrease in dissolved oxygen concentrations to undersaturated values, coupled with the increase in carbon dioxide concentrations and decrease in pH. Bätje and Michaelis (1986) found similar results of oxygen saturation, decreasing to 60% as a consequence of disintegrating *Phaeocystis* material in the Frisian coastal waters of the North Sea. At the Marsdiep Station in 1993, Brussaard et al. (1996) measured a comparable decrease of pH from 8.7 at the top of the bloom of *Phaeocystis* to 8.0 when Chl \(a\) concentrations were at minimum and when *Noctiluca* as well as other microzooplankton peaked.

In accordance with the following kinetic equations for the rates of oxidation of dissolved Fe(II) and Mn(II) in seawater,

\[
\frac{d[Fe(II)]}{dt} = k[Fe(II)][OH^-][O_2]
\]

after (Millero et al. 1987) (1)

and

\[
\frac{d[Mn(II)]}{dt} = (k_0 + k[MnO_2^-][O_2][OH^-])[Mn(II)]
\]

after (Stumm and Morgan 1981) (2)
the observed changes in pH (pH = −log[H+] and K_w = [OH−][H+] and Kw = contains a term for suspended particles, which may have a surface coating of (ferro)manganese oxides, hence sometimes referred to as an autocatalytic reaction (Stumm and Morgan 1981). The fact that Noctiluca are opportunist organisms feeding on all kinds of microorganisms will decrease the amount of suspended particles and therefore decrease the transfer of dissolved Mn and Fe to the particles. The apparent rate constant k0 may often be influenced by bacterial mediation, i.e., bacterial activity catalyzing the overall reaction (Mandernack et al. 1995; Johnson et al. 1996). This is consistent with the reported presence of Fe Mn coatings on bacteria in the open-water column (Cowen and Bruland 1985). In 1994 at Sta. 330, bacterial production was at maximum in mid-May and declined to a minimum in late May–early June (Becquevort et al. 1998) at the time of the Noctiluca biomass maximum. The role of bacteria in catalyzing oxidation of dissolved Mn and Fe could therefore have become negligible at that time.

Role of the sediments—The observed increase of total Mn (Fig. 6a–c) as discussed above shows the existence of an external source of Mn to the water column. This can either be from surficial sediments or an advective contribution from elsewhere, for example, by river input. The settling of organic debris to the sediments, along with less vigorous turbulence later in the season, is well known to lead to more reducing conditions within the upper sediment layers, both in the Marsdiep (Kieskamp et al. 1991) and at more offshore sites (Lohse et al. 1993). As a result, the metals Mn and Fe are becoming remobilized and diffuse into the overlying water column (Epping et al. 1998).

Our results confirmed, with a high time resolution, that seasonal variations occur in the concentrations of dissolved Mn and Fe in the North Sea, with maxima often occurring in late spring and early summer compared to lower values in winter (Burton et al. 1993; Tappin et al. 1993, 1995). Consistent with those of Burton et al. (1993), our results of Mn and Fe in the suspended particulate matter showed enrichments earlier in the season than those reported by Dehairs et al. (1989). The latter observed higher values of particulate Mn/Al and Fe/Al only in late summer and autumn. These authors attributed these variations to inputs of Mn and Fe by benthic recycling. Diagenetic benthic fluxes of dissolved Mn and Fe are indeed a potential source of dissolved Mn and Fe to the water column in organic-rich shallow coastal areas (Sundby et al. 1981; Kremling 1983; Sundby et al. 1986). Dissolved Mn and Fe are produced when aerobic biological remineralization of freshly sedimented organic matter depletes oxygen in the sediments. Oxides of Mn and Fe are then used as secondary oxidants for further degradation of the organic matter and become reduced and solubilized. When this is happening at, or close to, the sediment–water interface, dissolved Mn and Fe may escape by diffusion to the water column because of the formation of a steep concentration gradient between pore waters and the overlying water column (Sundby et al. 1981; Slomp et al. 1997). This process may provide dissolved Mn and Fe to the water column during the decline of spring blooms, when high quantities of phytoplankton-derived material are transported to the sediment.

Fluxes of dissolved Mn and Fe were estimated from sandy sediment cores collected at the end of July 1994 at an intertidal shallow station close to and contributing to the Marsdiep Station (Epping et al. 1998). In the absence of photosynthetic activity by benthic diatoms, an average flux of 0.79 mmol m−2 d−1 was calculated for dissolved Mn, while for Fe, a high variability was recorded, likely due to the high removal rate of Fe by adsorption and oxidation. The average Fe flux was 0.59 mmol m−2 d−1. Assuming an average water depth of the Dutch coastal zone of 18 m and a well-mixed water column, these fluxes could supply 44 µmol m−3 d−1 Mn and 33 µmol m−3 d−1 Fe to the water column. These findings show the existence of fluxes high enough to explain the observed late spring net increases of 17 µmol m−3 d−1 for Mn and 27 µmol m−3 d−1 for Fe.

Seasonal changes in the benthic fluxes of dissolved Mn and Fe, with higher values in spring and summer, have been observed in estuarine and coastal waters (Aller and Benninger 1981; Aller 1994) as well as in mesocosm experiments (Hunt 1983). These variations were attributed to several factors. Hunt (1983) showed the dependence of these fluxes on temperature and on the rates of primary production in the water column. The quantity but also the quality of the organic matter accumulating in the sediments, as well as the magnitude of the benthic heterotrophic activity, will determine the oxygen and nitrate penetration depth. This is the depth below which Mn and Fe will become reduced in the sediments and determines the possibility for dissolved Mn and Fe to escape from the sediment to the water column (Chester 1990 and references therein; Slomp et al. 1997).

The higher increases in dissolved Mn and Fe at the Marsdiep Station than at Sta. 330 could be partially explained by the differences between the two stations in primary production rates and inputs in particulate Mn and Fe oxides to the sediments. Because of higher nutrient inputs from the Rhine compared to the Scheldt, higher primary production can be sustained in the Dutch than in the Belgian coastal area of the North Sea (Fig. 3, Cadée and Hegeman 1986; Veldhuis et al. 1986; Lancelot 1995). As shown by the data of Chl a and phytoplankton biomass, the phytoplankton bloom was...

Fig. 8. Temporal evolution of particulate molar ratios on 10-µm filters at Sta. 330 and at the Marsdiep Station in 1994 of: total (HAc + AR + REF) Mn (●) and Fe (○) over refractory Al (REF Al; a,f); Mn (▲), and Fe (△) dissolved in, respectively, 25% acetic acid (HAc; b,g), diluted aqua regia (AR; c,h) and concentrated HCl, HNO3, and HF (REF; d,i) over REF Al; HAc Mn (▲) and HAc Fe (○) over particulate Mn and Fe hydrolyzed in the second and third steps (AR + REF; e,j) of the sequential extraction. The vertical lines indicate, respectively: the initiation of the spring bloom, the spring Chl a maximum, and the maximum concentration in dissolved Mn.
higher at the Marsdiep Station than at Sta. 330 (Fig. 4). Hence, more phytoplankton-derived material could have reached the sediment in the Marsdiep area and induced higher benthic fluxes of dissolved Mn and Fe.

Even if in 1993 and 1994 the phytoplankton biomass differed at Sta. 330, we still observed similar increases in dissolved Mn. In 1993, *Phaeocystis* colonies dominated, whereas in 1994, it was the diatoms. Due to specific biodegradability and fate of these two types of algae at the end of their development, a similar quantity of easily biodegradable phytoplanktonic material could have reached the sediments in 1993 and 1994.

Slomp et al. (1997) showed that most of the North Sea sediments are relatively poor in Mn and Fe oxides. The quantity of Mn and Fe oxides already present in the sediments and imported during the deposition of the phytoplankton-derived material, in particular with the aggregates, could also influence the benthic fluxes. It would explain, on the one hand, the difference in maxima of dissolved Mn between the two stations and, on the other hand, the similarity in the maxima of dissolved Mn at Sta. 330 in both 1993 and 1994.

**Contribution of Mn and Fe by rivers**—At Sta. 330, sharp maxima in nutrients at the end of March 1993 and late February-early March 1994 coincide with sharp depressions in salinity. This indicates increased inputs of freshwater from rivers and associated nutrients just before the onset of blooms. Dissolved Mn and Fe may also be delivered by rivers to coastal waters (Duinker and Nolting 1976, 1978; Duinker et al. 1979; Turner et al. 1991). However, the here-reported increase in dissolved Mn or Fe was much later in the season and not at all accompanied by a decrease in salinity. In fact, at the Marsdiep Station, we observed gradually higher salinities, reflecting the lower discharge of the river Rhine from April to July (Van Dcr Gicsscn et al. 1990; Visser et al. 1991). Thus, the maxima of dissolved Mn and Fe in May/June cannot be ascribed directly by variations in river run-off.

Indirectly, the increased river input of nutrients over the past decades (Van Bennecom et al. 1975) must have had a major influence on the mobilization of metals Mn and Fe. The nutrient increases have been accompanied by major enhancements of blooms in general, and *Phaeocystis* blooming in particular (Cadée and Hegeman 1986). This eutrophication would also have led to much more active dissolution and precipitation cycles of Mn and Fe over the past decades, such cycles having been monitored here in unprecedented detail for years 1993 and 1994 only.

**Other processes**—Several other processes may play a role, but the lack of observational data on these processes does not allow us to estimate their relative contribution to the variations of Mn and Fe. Notably, Mn oxides can be directly photoreduced to soluble Mn (II) by organic compounds such as phenols or humic materials (Stone and Morgan 1984; Sunda and Huntsman 1994). The dissolution of colloidal iron oxides is also enhanced by organic compounds and sunlight (Waite and Morel 1984). A reduction in resuspension coupled with increased penetration of light resulted in an increase of the photic zone from 1.3 to 10 m, as calculated from Secchi disk measurements of about 0.5 m at the peak of the bloom and 2.2 m in early June at the Marsdiep Station (G. Cadée pers. comm.). Above, we mentioned the disappearance of suspended particulate Al, indicative of the lower turbidity, coinciding with increases in dissolved Mn (Figs. 6, 7). The lower turbidity and stronger insolation may have led to increased photoreduction of suspended Mn in early June, helping to keep Mn and Fe (Marsdiep Station only) in solution.

**Conclusions**

The observed increase of dissolved Mn and Fe at the end of spring would be the consequence of sedimentation favored by aggregation processes of large amounts of phytoplankton-derived material. The deposit of fresh organic matter would have stimulated benthic microbial activity, depleting oxygen at or close to the surface of the sediments. Bacterial degradation of organic matter in suboxic condition is then accompanied by reduction and dissolution of Mn and Fe. Dissolved Mn and to a lesser extent Fe (due to its rapid oxidation rate) are released in the water column by diffusion from the pore water. Part of this dissolved Mn and Fe is adsorbed or precipitated on suspended particles and will enrich the particulate matter in Mn and Fe compared to Al. The rest remains longer in solution because of the heterotrophic activity, in particular of *Noctiluca* and due to the lowered amount of particles. The biogeochemical cycles of Mn and Fe are driven by the eutrophication-dependent magnitude of phytoplankton blooms, the heterotrophic activity that follows the spring bloom, and the quality of phytoplankton-derived material reaching the sediment.

Similar sequences of plankton bloom and biogeochemical cycling of Mn and Fe are likely to be significant all over the world in those shallow coastal waters experiencing seasonality. Of course, in such other regions, different plankton species may prevail, while the intensity also depends on supply of nutrients and local light regime.

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