

Aluminum
Manganese
North Atlantic Ocean
Removal mechanisms
Manganese oxidation

Aluminium
Manganèse
Atlantique Nord
Extraction
Oxydation

A comparison of dissolved and particulate Mn and Al distributions in the Western North Atlantic

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ABSTRACT

The dissolved Mn distribution on an oceanographic section along 50°W in the western North Atlantic shows decreasing concentrations in the offshore direction in the surface layer and with depth at the deep water stations. Leachable particulate Mn concentrations are low in the open ocean surface waters and elevated at intermediate depths. Dissolved Al concentrations in the surface layer are higher in the open ocean than on the shelf and the vertical distributions are characterized by surface maxima, a subsurface minimum at ≈1 000 m and increasing concentrations in the deep waters. Leachable particulate Al concentrations are elevated on the shelf and in open ocean surface waters compared to the intermediate and deep waters. The Deep Western Boundary Current has high levels of dissolved Al and leachable particulate Mn and Al, and low levels of dissolved Mn.

The distribution of dissolved Al is controlled primarily by inputs from atmospheric dust and removal onto biogenic particles. Both fluvial and atmospheric inputs affect dissolved Mn levels with removal occurring primarily by oxidation of Mn²⁺. The Al distribution is characterized by short residence times in shelf and surface waters and relatively constant distribution coefficients. The Mn distribution is characterized by longer surface water residence times, shorter deep water residence times, and more widely varying distribution coefficients than Al. Removal of Al by a surface adsorption mechanism and Mn by slower oxidation of Mn²⁺ are consistent with these observations. A model of Mn oxidation kinetics accurately predicts the intermediate depth leachable particulate Mn maximum.

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RÉSUMÉ

Comparaison des répartitions de Mn et Al dissous et particulaires dans le nord-ouest de l'Atlantique

La répartition du Mn dissous le long du méridien 50°W dans le nord-ouest de l'Atlantique montre des concentrations qui décroissent de la côte vers le large dans la couche superficielle et qui, aux stations profondes, décroissent de la surface vers le fond. Les concentrations en Mn particulaire sont faibles dans les eaux superficielles du large et élevées aux profondeurs intermédiaires. Les concentrations en Al dissous dans la couche superficielle sont plus élevées au large que sur

le plateau continental et les profils verticaux sont caractérisés par des maxima superficiels, par un minimum de subsurface vers 1 000 m et par des concentrations croissantes dans les eaux profondes. Les concentrations en Al particulaire sont élevées sur le plateau continental et dans les eaux superficielles du large, en comparaison avec les eaux intermédiaires et profondes. Le courant profond à la limite occidentale présente des taux élevés de Al dissous et de Mn et Al particulaires, et de faibles taux de Mn dissous.

La répartition de Al dissous est essentiellement régie par les apports de poussière atmosphérique et par l'extraction de Al par adsorption sur des particules d'origine biologique. Les apports fluviaux et atmosphériques de Mn influent sur les taux de Mn dissous, l'élimination de cet élément intervenant principalement par oxydation de Mn^{2+} . La répartition de Al est caractérisée par des temps de résidence courts dans les eaux du plateau continental et les eaux de surface, et par des coefficients de distribution relativement constants. La répartition du Mn est caractérisée par des temps de résidence plus longs dans l'eau superficielle et plus courts dans l'eau profonde comparativement à Al, et par des coefficients de distribution variant dans une gamme plus large. L'extraction de Al par un mécanisme relativement rapide d'adsorption superficielle et celui de Mn par une oxydation plus lente de Mn^{2+} concordent avec ces observations. Un modèle cinétique de l'oxydation de Mn permet de calculer avec précision le taux maximal de Mn particulaire dans l'eau intermédiaire.

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INTRODUCTION

Manganese and aluminum are particle reactive elements with short residence times in the oceans (≈ 100 years). They typically exhibit vertical distributions characterized by surface water maxima, mid-depth minima and increasing concentrations in the deep water. Despite these first order similarities, several recent studies indicate that certain features of the oceanographic distributions of Mn and Al differ significantly. In the western North Atlantic (Moore and Millward, 1984; Measures *et al.*, 1984; 1986) and eastern North Pacific (Orlans and Bruland, 1986), dissolved Al levels are depleted in continental shelf waters relative to open ocean surface waters. In contrast, dissolved Mn concentrations in these regions decrease with distance from the shelf (Bruland and Franks, 1983; Landing and Bruland, 1987; Yeats, 1988). In western North Atlantic deep waters, dissolved Al concentrations are significantly higher than at intermediate depths (Hydes, 1979; Measures *et al.*, 1986; Moran and Moore, 1991), whereas Mn concentrations increase only slightly in the near-bottom waters (Yeats and Bowers, 1985; Statham and Burton, 1986).

Differences in the oceanographic distributions of Al and Mn should reflect differences in input and removal functions and their marine chemistries. At the pH of seawater, dissolved Al exists predominantly as particle-reactive hydrolysis products, $Al(OH)_3^0$ and $Al(OH)_4^-$, whereas dissolved Mn exists mainly as Mn^{2+} and $MnCl^+$ (Bruland, 1983) and is slowly oxidized to insoluble Mn IV oxides. This reaction has been shown to be autocatalytic in the laboratory (Morgan, 1967). In the marine environment bacteria can influence both the oxidation of Mn^{2+} and the reduction of MnO_2 (Sunda and Huntsman, 1988).

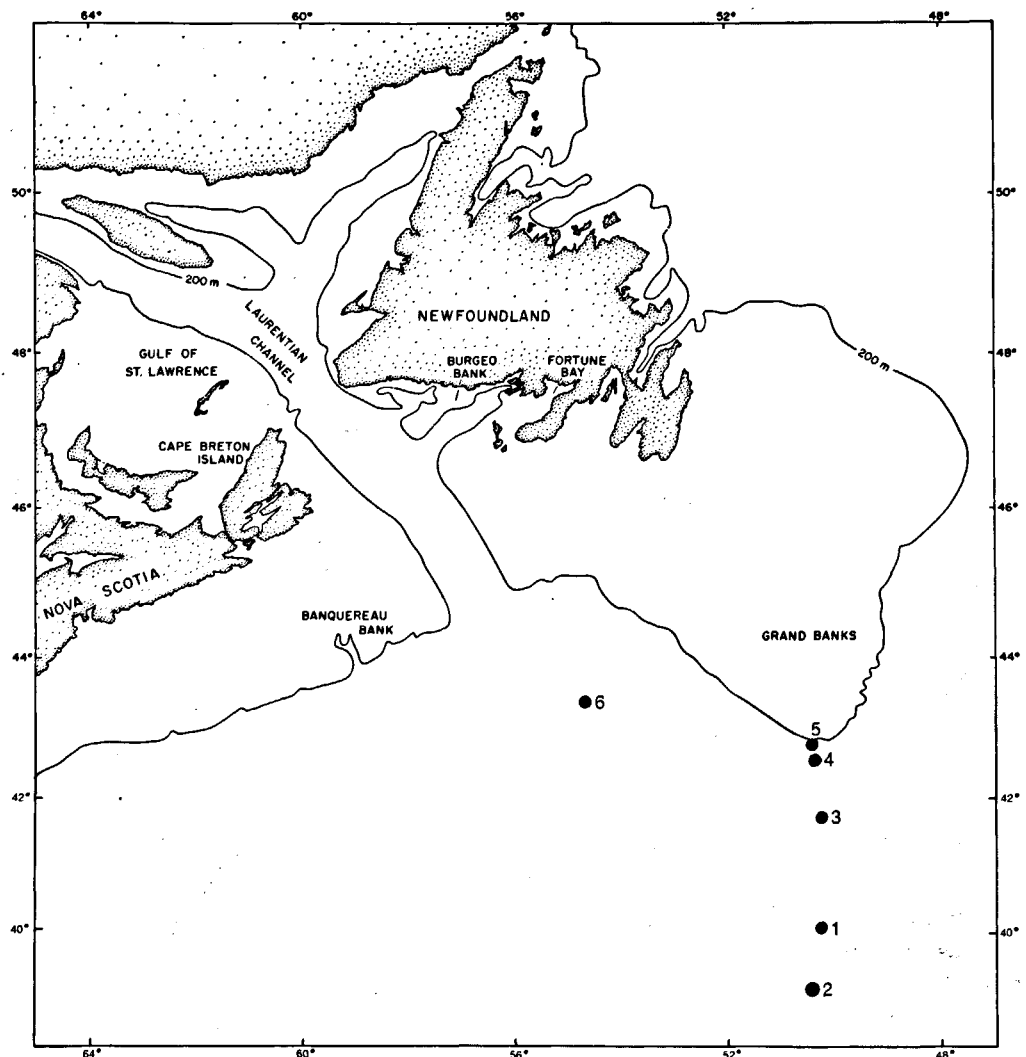
In this paper we present new dissolved and particulate Al and Mn data for shelf, slope and open ocean waters of the western North Atlantic. The open ocean dissolved and particulate Al data were recently used to examine the potential source of dissolved Al from suspended sediments to the North Atlantic Deep Water (Moran and Moore, 1991); here we focus on differences and similarities in the Mn and Al distributions and discuss the importance of Mn^{2+} oxidation in controlling deep water dissolved and particulate Mn levels in the western North Atlantic.

METHODS

Seawater samples were collected for dissolved and leachable particulate Mn and Al analyses at six stations southeast of Newfoundland in the western North Atlantic during cruise 88-001 of the CSS Hudson (Fig. 1). Samples were collected using clean 12 l teflon coated Go-Flo bottles fitted with silicon o-rings and teflon stopcocks and mounted on a stainless steel hydrowire. Samples were pressure (N_2) filtered from the Go-Flo through clean, tared, Nuclepore membrane filters (47 mm diameter, 0.4 μm pore size) held on clean Sartorius polycarbonate filter holders. Because of limited wire time on this cruise, particulate samples from adjacent depths were combined to increase the loading on the filters. Filtered subsamples for dissolved Mn analysis were stored acidified at pH 1.5 (5 ml Seastar HCl in 2 l sample) in clean 2 l polyethylene bottles. Filtered subsamples for dissolved Al analysis were stored frozen in clean 125 ml polyethylene bottles. Filters were washed of residual salt with Milli-Q water, dried and stored in clean petri dishes. The filters were weighed to determine the suspended particulate matter (SPM) concentration in a clean room laboratory.

Figure 1

Locations of stations occupied during cruise 88-001.



Dissolved Mn was determined by extraction of the filtered samples with 8-hydroxyquinoline into 4-methyl 2-pentanone (methyl isobutyl ketone) at pH 9. Extracts were analysed for Mn by graphite furnace atomic absorption spectrophotometry using a Perkin-Elmer HGA 500/5000 system equipped with Zeeman background correction and an AS40 autosampler. Replicate analyses of NASS-1 seawater reference material had a precision of 7 % and relative accuracy of 9 %. Dissolved Al was determined on 0.4 μm filtered samples using the lumogallion fluorimetric method (Hydes and Liss, 1976) modified for small sample volumes (Moran and Moore, 1991). The precision was 5 % for a 20 nM sample with a blank of 2.5 nM. Filters were leached with 4.5 M Seastar acetic acid at room temperature for two hours (Chester and Hughes, 1967) and the leachates analysed for Mn (HAc Mn) and Al (HAc Al) by graphite furnace atomic absorption spectrophotometry and fluorescence, respectively. The acetic acid leach dissolves carbonates and amorphous Mn oxides and mobilizes surface bound, exchangeable particulate Mn and Al (Chester and Hughes, 1967; Bolger *et al.*, 1978). A complete listing of the analytical results is given in Table 1.

RESULTS AND DISCUSSION

Hydrography

The surface waters along the 50°W section change from cold, fresh Labrador Current waters at station 5 to a warm, salty mixture of Slope and Gulf Stream water on stations 1 and 2. Mixing in these surface waters results in the interleaving of these warm salty upper waters with cold, fresher water of Labrador Sea origin. Deeper cold, fresh features at $\approx 700\text{--}800$ m have T-S characteristics very similar to the Labrador Sea Water (LSW) component of the North Atlantic Deep Water [NADW (Lee and Ellett, 1967)]. Dissolved Al concentrations in these cold fresh features (*e.g.* 250 m on station 1 and 250, 500 and 1250 m on station 3) are all lower than for those above and below these depths but dissolved Mn concentrations seem to be unaffected by these T-S features.

Measures *et al.* (1986) showed that the minimum in dissolved Al at $\approx 1\ 000$ m is associated with water having T-S characteristics indicative of mixing between LSW, Antarctic Intermediate Water and Mediterranean Water.

Table 1

Salinity, silicate, aluminum manganese and SPM data and distribution coefficients for cruise 88-001.

Depth (m)	Salinity	Si (μM)	Al (nM)	Mn (nM)	HAc Al (nM)	HAc Mn (nM)	SPM ($\mu\text{g/l}$)	K_d	
								Al ($\times 10^6 \text{ ml/g}$)	Mn
STATION 1, 40°15'N, 50°05'W, BOTTOM DEPTH 4 288 M									
25	36.319	1.40	35.6	1.35	5.6	0.055	72.9	2.2	0.56
100	36.252	2.33	36.7	1.40	2.8	0.057	43.0	1.8	0.95
250	36.281	1.67	30.1	1.06	5.4	0.018	85.0	2.1	0.20
500	35.832	5.09	34.6	0.53	3.2	0.291	38.0	2.4	1.40
800	35.256	13.35	16.9,14.2	0.22	2.2	0.255	18.0	7.9	52
1 100	35.061	14.67	15.2,15.2	0.33					
1 400	35.303	12.26	16.2,17.2	0.18	2.5	0.228	24.3	6.2	55
1 583	34.957	13.79	20.6,21.1	0.29					
1 700	34.982	11.98	14.3,16.4	0.25	0.9	0.256	27.3	2.3	29
2 083	35.089	13.13	14.4	0.40					
2 583	35.074	13.31	17.5,19.4	0.29	1.2	0.237	17.3	3.6	34
3 083	34.933	16.40	19.3,19.6	0.40					
3563	34.993	17.46	19.8	0.44	1.4	0.219	17.3	4.0	34
3 583	34.970	16.31	21.2	0.31					
3973	34.889	27.47	27.8,28.1	0.24	0.9	0.233	24.6	1.5	40
3 983	34.889	28.38	17.4	0.24					
4 083	34.901	21.66	24.4	0.31					
STATION 2, 39°42'N, 50°15'W, BOTTOM DEPTH 5 215 M									
50	36.502	1.82	44.6	0.93	1.6	0.042	44.7	0.8	1.01
250	36.487	1.85	26.8	0.93	4.8	0.037	50.0	3.6	0.80
500	36.193	3.56	21.8	-	0.9	0.285	18.2	3.8	45
750	35.524	9.93	13.2	0.35					
1 000	34.972	13.40	9.6	0.61	2.1	0.258	28.5	5.1	21
1 690	34.959	11.84	17.4,16.7	0.27					
2 690	-	17.74	11.9	0.24	1.3	0.220	16.2	6.8	53
3 690	34.920	13.70	11.8	0.27					
4 190	34.900	23.60	14.4	0.29	0.5	0.163	16.7	1.6	36
4 690	34.902	30.04	22.4	0.25					
STATION 3, 41°48'N, 50°09'W, BOTTOM DEPTH 3 650 M									
25	35.222	2.79	7.3	1.49	1.2	0.025	96.5	1.7	0.17
100	35.476	4.22	14.4	1.00	2.3	0.164	54.5	2.9	3.0
250	35.239	8.10	10.5	0.67	1.9	0.345	35.0	5.1	15
500	34.802	12.35	10.6	0.62					
750	34.895	10.61	11.3	0.53	1.9	0.318	41.3	4.7	14
1 000	34.967	11.27	8.3	0.53					
1 250	34.899	10.43	7.7	0.35	1.5	0.214	18.3	8.1	36
1 500	34.948	11.58	12.4	0.29					
1 900	34.955	13.25	14.7	0.20	2.8	0.121	20.0	9.5	30
2 300	34.945	14.37	18.1	0.16	1.4	0.227	19.2	4.6	55
2 800	34.936	11.22	13.4	0.27					

Table 1 (continued)

Depth (m)	Salinity	Si (μM)	Al (nM)	Mn (nM)	HAc Al (nM)	HAc Mn (nM)	SPM ($\mu\text{g/l}$)	K_d	
								Al ($\times 10^6 \text{ ml/g}$)	Mn
STATION 3 (continued)									
3 480	34.933	16.39	18.1	0.42	1.9	0.449	35.6	2.9	50
3 500	34.933	15.95	-	0.25					
3 580	34.908	18.45	25.2	0.13	4.3	0.875	43.9	3.2	153
3 600	34.905	18.96	36.2	0.13					
STATION 4, 42°35'N, 50°20'W, BOTTOM DEPTH 1 725 M									
20	34.039	1.98	2.1	1.93	2.1	0.066	134	7.4	0.26
100	34.826	5.19	8.7,11.6	1.27	2.8	0.282	102	2.7	2.2
500	35.100	12.77	13.7	0.69	2.5	0.224	22.2	8.2	15
900	34.943	11.34	10.0	0.53	0.9	0.220	17.6	5.1	24
1 200	34.945	11.39	11.6	-	1.1	0.257	22.6	4.9	30
1 400	34.937	11.24	8.3	0.38					
1 600	34.908	11.30	11.5,10.4	0.42	1.7	0.198	29.7	5.4	17
1 700	34.917	11.92	10.1	0.38					
STATION 5, 42°50'N, 50°15'W, BOTTOM DEPTH 205 M									
20	33.001	4.04	6.3	2.80	14.7	0.104	667	3.5	0.06
20	-	-	-	-	16.2	0.106	730	3.5	0.05
40	33.347	5.09	2.9	2.15	3.2	0.230	323	3.4	0.33
70	34.069	4.12	3.2	1.69	6.0	0.110	211	8.9	0.31
100	34.262	5.02	10.1,11.7	1.53	2.2	0.130	74.3	2.7	1.9
150	34.126	7.49	4.1	1.67	2.0	0.276	87.7	5.6	1.9
180	34.127	7.57	3.8	1.60	1.6	0.331	84.0	5.0	2.5
STATION 6, 43°22'N, 54°38'W, BOTTOM DEPTH 3 930 M									
500	34.857	11.13	7.7	0.58	1.3	0.216	36.4	3.1	12
1 000	34.947	11.35	15.0	0.48					
1 500	34.925	11.65	10.3	0.42	1.7	0.141	18.1	8.5	24
2 000	34.955	13.76	11.1	0.24					
2 500	34.945	14.62	15.8	0.24	1.9	0.437	24.7	3.0	114
2 900	34.930	17.75	18.5	0.18					
3 420	34.906	20.25	25.0	0.11	2.6	0.775	57.0	1.9	54
3 720	34.901	22.88	25.9	0.20					
3 900	34.899	22.72	24.7	0.25					

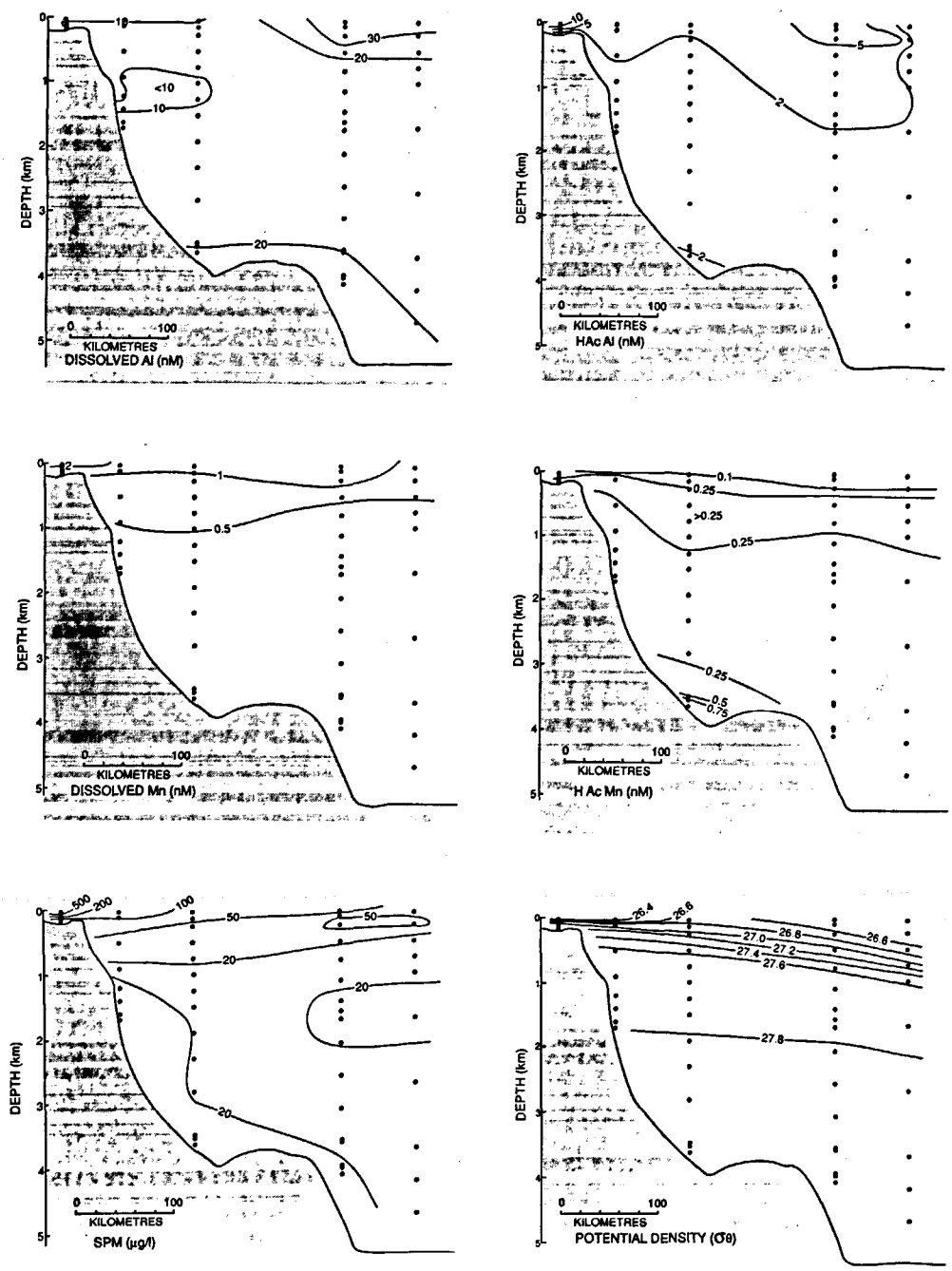
Dissolved Mn concentrations are slightly elevated (≈ 0.5 nM) at 1 000 m relative to the deep waters and, in the depth range of LSW (700-1 700 m), Mn and Al are negatively correlated ($n = 16, r = 0.70$). If an important determinant of the Al minimum in this region is advection of low Al LSW, then this water mass, whose origin is near surface in the Labrador Sea, would be expected to have high dissolved Mn concentrations.

From ≈ 1 000 m to the bottom, T-S characteristics decrease gradually from $5^\circ, 35.0$ to $1.8^\circ, 34.89$ with slightly lower

salinity in the 1 000-2 000 m depth range associated with the LSW. The high-energy Deep Western Boundary Current (DWBC) is located between 3 500 and 4 500 m near the continental slope. Silicate concentrations and, to a lesser extent, salinity provide a means for distinguishing between the DWBC and the adjacent deep waters. The silicate and salinity values below approximately 3 500 m on stations 3 and 6 and the deepest sample from station 1 are indicative of the northern source waters associated with the DWBC (Tab. 2). In addition to the silicate and salinity

Figure 2

Distribution of dissolved Al, HAc Al, dissolved Mn, and HAc Mn on the 50°W section.



signatures, SPM concentrations are elevated in the more energetic DWBC relative to the open ocean bottom waters. Mn and Al concentrations in the NADW are generally low and uniform (Fig. 2) and similar to those previously reported for the western North Atlantic (Moore and Millward, 1984; Yeats and Bowers, 1985; Measures *et al.*, 1986; Statham and Burton, 1986), although Al is lower than the earlier measurements of Hydes (1979). In the DWBC, both dissolved and particulate Al and particulate Mn concentrations are higher than in the NADW or the adjacent bottom waters (Tab. 2) while dissolved Mn concentrations are lower.

Surface waters

Dissolved and leachable particulate Mn concentrations in the surface waters decrease with distance from the shelf to

Table 2

Comparison of concentrations in the Deep Western Boundary Current with those from similar depths on stations 1 and 2.

	Sal	Si (µM)	Al (nM)	Mn (nM)	HAc Al (nM)	HAc Mn (nM)	SPM (µg/l)
DWBC x	34.909	20.12	26.9	0.19	2.7	0.634	40.3
σ	0.011	2.53	4.6	0.07	1.1	0.224	13.6
Stations							
1 and 2 x	34.919	24.22	19.1	0.30	1.0	0.209	18.7
3 500- 4 200 m σ	0.034	4.95	5.2	0.07	0.4	0.031	4.0

the open ocean (Fig. 2). In contrast, dissolved and leachable particulate Al concentrations show a general inverse relationship, with dissolved Al levels increasing toward the open ocean. Similar Mn and Al distributions have been reported for the surface waters of the eastern North Pacific (Orlans and Bruland, 1986; Landing and Bruland, 1987). These offshore gradients in Mn and Al are also reflected in the relationships with salinity (Fig. 3 a). The curved rela-

tionship between dissolved Mn and salinity is interesting as other western North Atlantic transects have been described by linear relationships with somewhat steeper slopes (Bruland and Franks, 1983; Yeats, 1988).

The SPM-salinity plot for the surface layer (Fig. 3 b) shows a marked decrease in SPM between the shelf edge and the first slope station (#4), followed by a gradual decrease farther offshore. The plot for leachable Al (Fig. 3 c) follows the SPM trend to salinity 35.2, then displays a noticeable increase at higher salinity (stations 1 and 2). The linear regression of HAC Al against SPM for all shelf and surface layer samples from stations 3 to 5 ($n = 11$, $r = 0.96$) indicates a leachable particulate Al content of the SPM of 0.057 %, comparable to previous measurements of Al in Pacific Ocean marine phytoplankton (0.004-0.044 %; Martin and Knauer, 1973; Collier and Edmond, 1984). For the station 1 and 2 surface layer, the Al content of the SPM is higher, ≈ 0.16 %. Leachable particulate Mn concentrations in the surface samples decrease more gradually between shelf and slope than do Al or SPM but the increase on stations 1 and 2 is still visible. The leachable Mn content of the surface water SPM increases from 8 $\mu\text{g/g}$ on station 5 to 50 $\mu\text{g/g}$ on station 2. The offshore concentrations are higher than those reported for Pacific Ocean phytoplankton (5-11 $\mu\text{g/g}$; Martin and Knauer, 1973; Collier and Edmond, 1984), perhaps reflecting the impact of atmospheric dust particles on the leachable particulate Mn concentrations.

The low levels of dissolved Al and high levels of leachable particulate Al in the surface waters of station 5 are consistent with enhanced scavenging of Al within the productive, biogenic particle-rich waters over the Grand Bank combined with an atmospheric source. Recent studies provide evidence in support of a passive removal mechanism involving sorption of Al onto the surfaces of living (Moran and Moore, 1988) and dead (Moran and Moore, 1992) diatoms in seawater. For the open ocean stations, the marked increase in dissolved Al at high salinity suggests that a potentially important source of dissolved Al is advection of Al-enriched surface waters within the Gulf Stream. Long-range transport of dust via the easterly trade wind belt results in the highest deposition of dust between 20°N and 40°N (Prospero, 1981; Prospero *et al.*, 1987). For dissolved and leachable particulate Mn, the surface water distributions indicate a significant fluvial source and less efficient net removal of Mn than Al within coastal waters. Removal of Mn from seawater by sorption on particles has been observed (Martin and Knauer, 1980; 1983), however, an additional removal mechanism via oxidation of Mn^{2+} to manganese oxides is also important (Morgan, 1967). Photoreduction of MnO_2 that can occur in surface waters (Sunda *et al.*, 1983) will tend to counteract these removal mechanisms and contribute to the dissolved Mn maximum. The importance of the photoreduction reaction is indicated by the very low levels of leachable particulate Mn observed in open ocean surface waters.

The levels of dissolved and leachable particulate Mn and the leachable particulate to dissolved Mn ratios observed for open ocean surface waters in this study are similar to those reported for the Central Pacific by Landing and Bruland (1987). For Al, the ratio of leachable particulate to

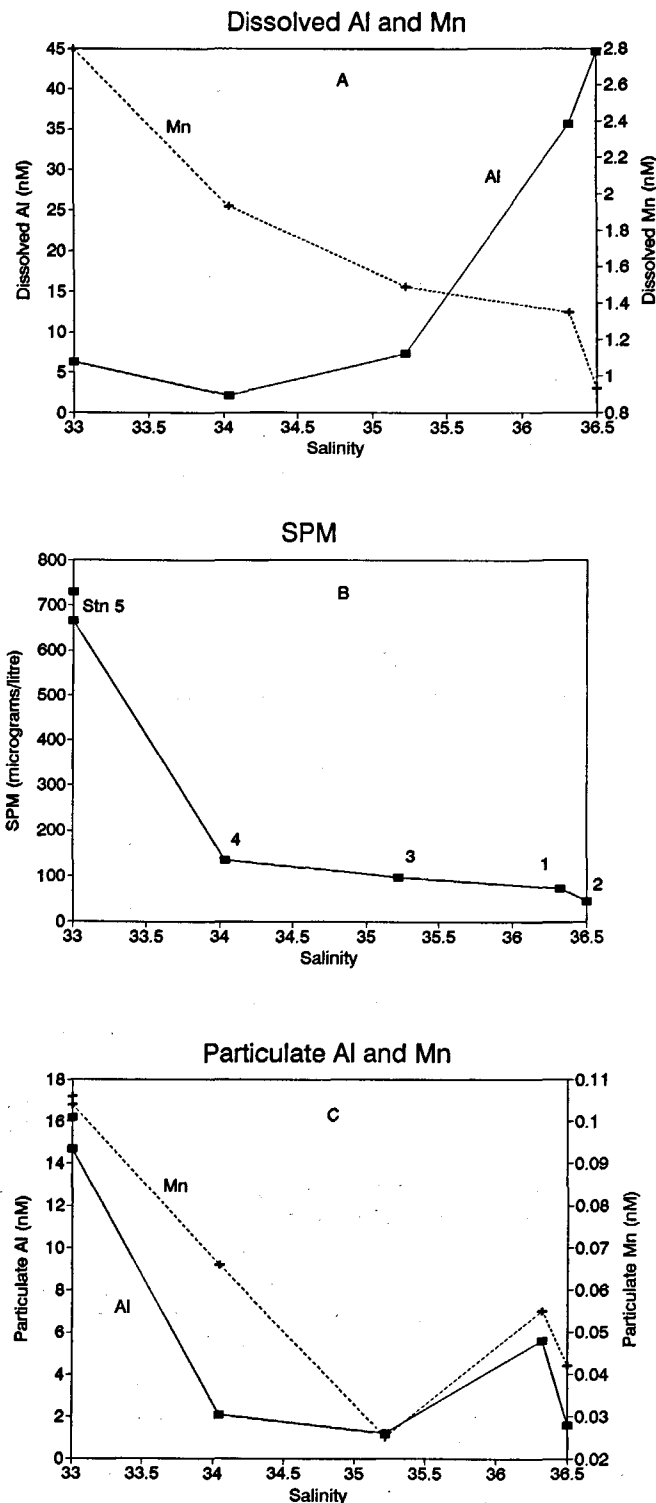


Figure 3

Plots of (a) dissolved Al and Mn, (b) SPM, and (c) HAC Al and Mn versus salinity for surface waters along the 50°W section.

dissolved is similar to that found in the Pacific (Orians and Bruland, 1986), however, the absolute concentrations of dissolved and leachable particulate Al are about 10 to 50 times greater in the surface waters of the western North Atlantic than in the central Pacific. Higher concentrations of dissolved and particulate Al reported in this study may reflect a greater atmospheric flux of Al to the North Atlantic (≈ 370 nmol Al/cm²/yr) relative to the central Pacific (≈ 55 nmol/cm²/yr; Orians and Bruland, 1986).

Coefficients (K_d) for the distribution of aluminum between particles and water, defined, for SPM in $\mu\text{g/l}$, as

$$K_d = \frac{\text{HAc Al}}{\text{Al}_d} \cdot \frac{10^9}{\text{SPM}} \text{ (ml/g)},$$

decrease slightly from $4.6 \pm 2.1 \times 10^6$ ml/g on station 5 to $2.1 \pm 1.2 \times 10^6$ on stations 1 and 2. The relative invariance of K_d values for Al is consistent with a reversible sorption mechanism for removal of dissolved Al. In contrast, the distribution coefficients for Mn increase markedly from 5×10^4 ml/g in the surface waters at station 5 to 1×10^6 ml/g at station 2. The varying distribution coefficients for Mn suggest that Mn removal is not controlled by reversible adsorption onto particles. The increase in K_d from the shelf to the open ocean could reflect the relative importance of fluvial inputs and estuarine and nearshore remobilization processes (station 5) versus atmospheric inputs (station 2) on the surface Mn distributions.

Residence times for Al and Mn in the surface layer can be estimated using data presented here and atmospheric fluxes (Chester, 1982; Buat-Ménard, 1983; Statham and Chester, 1988), allowing for partial dissolution of atmospheric particulates (Maring and Duce, 1987, Statham and Chester, 1988). The fluvial input of dissolved Al is not considered in these calculations as several studies (Measures *et al.*, 1984; 1986; Orians and Bruland, 1986; Moran, 1990; Hydes, 1991) have indicated that the fluvial flux of Al to open ocean surface waters is small compared with the atmospheric flux. Fluvial dissolved Mn inputs are more important and a value of 5×10^8 moles/yr (Yeats, 1991) has been used for the input to the North Atlantic. The residence times calculated with these values for dissolved Al (4-6 years), HAc Al (1-4 weeks), dissolved Mn (7-15 years) and HAc Mn (16-20 weeks) are comparable to surface water residence times calculated for the Pacific (Orians and Bruland, 1986; Landing and Bruland, 1987). Longer residence times for Mn are consistent with the less efficient removal of Mn than Al from surface waters.

Intermediate and deep waters

Several explanations have been proposed to explain the elevated dissolved Al levels in the deep relative to the intermediate waters of the western North Atlantic (Moore and Millward, 1984; Measures *et al.*, 1986; Moran and Moore, 1991). It is important to note that marked increases in dissolved Mn are not observed in this region. A pressure dependence on Al solubility (Moore and Millward, 1984) is specific for aluminum and would not require increases in

dissolved Mn but is inconsistent with the dissolved Al distributions in the deep waters of the eastern North Atlantic. If an advective input of fluvial Al from the northern European shelf (Measures *et al.*, 1986) is important, this process would be expected to also generate high levels of dissolved Mn in the deep waters. The oxidation of Mn^{2+} will remove dissolved Mn during the transit time [less than a decade (Measures *et al.*, 1986)] from the European shelf to the NADW. Because the oxidation rate is dependent on a number of factors including dissolved and particulate Mn concentrations, it is difficult to estimate the extent of removal of dissolved Mn by oxidation, but it is unlikely to have reduced levels to ≈ 0.2 nM in < 10 years. This reaction, however, would tend to decrease gradients in deep water dissolved Mn concentrations since the particulate concentrations, and thus the oxidation rate, are higher in the deepest waters. A third explanation for the increases in dissolved Al with depth in the western North Atlantic is based on reversible desorption of Al from resuspended sediments associated with bottom nepheloid layers (Moran and Moore, 1991). Because removal of Mn by oxidation is non-reversible in oxic waters (except for photo-oxidation in the surface layer), this explanation would not require parallel increases in dissolved Mn.

The most concentrated flow of the southward moving deep water of Arctic origin is the DWBC. The deepest samples from stations 1, 3 and 6 have been identified as having the greatest DWBC character (Tab. 2). These samples show high concentrations of dissolved Al and leachable Al and Mn but not dissolved Mn. Dissolved Al concentrations are 5-10 nM in the formation regions for these deep waters (van Beusekom, 1983). Dissolved Mn measurements have not been reported, but surface layer dissolved Mn concentrations in the Arctic Ocean are 1-2 nM (Yeats, 1988; Yeats and Westerlund, 1991), similar to levels in North Atlantic surface waters. Between the source region and our study area, dissolved Al concentrations appear to have increased by a factor of 2-4 while those of Mn may have decreased by a factor of 5-10.

Differences in dissolved and leachable particulate Mn concentrations between the surface waters and the DWBC result in dramatic changes in the manganese distribution coefficients. The K_d 's increase from $0.5-1 \times 10^6$ ml/g at the surface to $50-150 \times 10^6$ ml/g in the DWBC and $\approx 40 \times 10^6$ ml/g in the rest of the deep waters, a factor of ≈ 100 . These differences reflect the non-equilibrium nature of Mn chemistry in these waters. In surface waters the distribution is displaced from equilibrium by the photo-reduction of particulate Mn while in the deep waters an oxidation reaction occurs with a pseudo-first-order rate constant of ≈ 0.02 year⁻¹ for deep ocean conditions (Yeats and Strain, 1990). The reaction rate is increased by high concentrations of particulate Mn, as found in the deep boundary current, resulting in the DWBC having the lowest levels of dissolved Mn. Distribution coefficients for Al are more nearly constant. For the surface waters, DWBC, and the rest of the deep water, K_d values for Al are indistinguishable at an average of $3.1 \pm 1.7 \times 10^6$ ml/g. Between 500 and 2 000 m, where minimum dissolved Al concentrations are found, K_d 's are slightly higher, $\approx 6 \times 10^6$ ml/g. These results sug-

gest a much closer approach to sorption/desorption equilibrium for Al than Mn.

Greater reactivity for Mn than Al in the deep waters is indicated by these results. This is in contrast to the surface waters where shorter residence times and hence greater reactivity of Al is observed. Deep-water residence times that should reflect this reactivity can be calculated using the deep water dissolved and particulate metal data and a residence time for suspended particles (Bacon and Anderson, 1982). The residence time for Al is 200 years, and for Mn, 25 years, assuming a particle residence time of 15 years for the deep western North Atlantic (Spencer, 1984). Both estimates are consistent with previous estimates of deep water residence times for Al and Mn (Weiss, 1977; Yeats and Bowers, 1985; Orians and Bruland, 1986). A prominent feature in the leachable particulate Mn distribution (Fig. 2) is the concentration maximum found between 800 and 1 000 m depth. This feature may be related to the hydrography and/or the oxidation of dissolved Mn. The maximum occurs at depths similar to the dissolved Al minimum already discussed (Hydrography), but is displaced to shallower depths on most stations. If the maximum is associated with LSW it would be expected to originate with low leachable particulate Mn and high dissolved Mn. If the leachable particulate Mn concentrations at the bottom at station 5 are indicative of deep shelf water concentrations further north, the particulate Mn concentrations may be augmented to the extent that deep shelf waters contribute to this feature.

Manganese oxidation

Leachable particulate Mn can be produced by the oxidation of Mn²⁺ to MnO₂. This process can produce a maximum in particulate manganese concentrations as shown by the following model of the oxidation reaction. In this model, dissolved and particulate Mn concentrations are calculated as a function of time using the oxidation rate equation of Yeats and Strain (1990):

$$-d[Mn_d]/dt = k[Mn_d][Mn_p][O_2]f_t$$

Table 3

Manganese oxidation model results.

RUN	INITIAL CONDITIONS			MODEL RESULTS		
	Mn _d (nM)	Mn _p (nM)	Settling rate (%/yr)	Mn _{p,max} (nM)	Mn _d (@ Mn _{p,max}) (nM)	t (@ Mn _{p,max}) (yr)
1	1.5	0.04	30 → 10	0.34	0.44	12.5
2	1.5	0.04	30 → 5	0.34	0.44	12.5
3	1.5	0.06	30 → 10	0.33	0.44	10.5
4	2.0	0.04	30 → 10	0.61	0.36	11
5	1.5	0.04	25 → 10	0.43	0.40	10.5
6	1.5	0.04	25 → 5	0.43	0.40	10.5
7	1.5	0.06	25 → 10	0.44	0.40	9
8	1.0	0.04	25 → 10	0.19	0.32	18.5
9	2.0	0.04	25 → 10	0.73	0.36	8.5
10	1.5	0.04	20 → 10	0.53	0.37	9.5

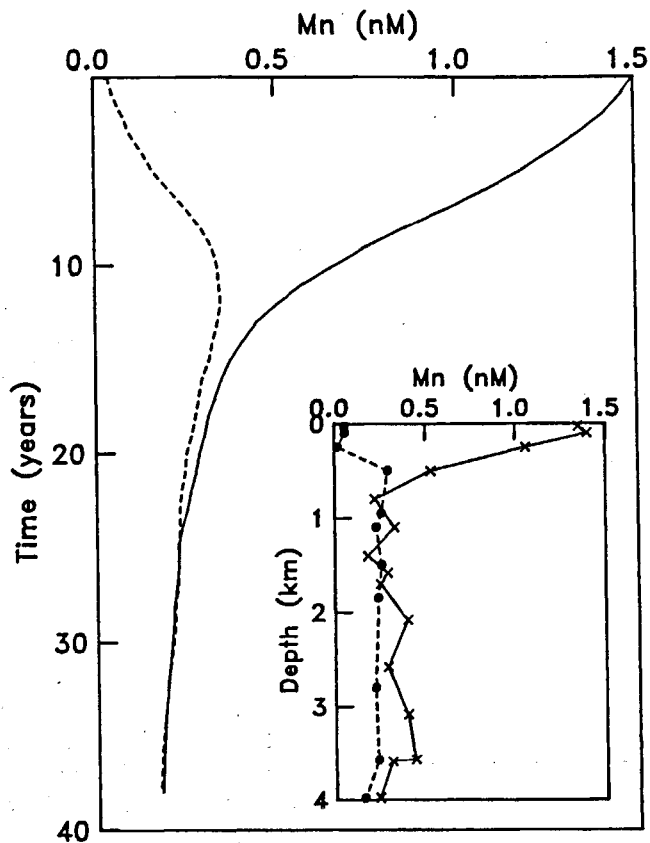


Figure 4

Plot of calculated dissolved (solid line) and particulate (dashed line) Mn concentrations against time for the oxidation of Mn²⁺ using a surface water removal rate of 30 %/yr decreasing to 5 %/yr in the deep water. Inset shows vertical profiles of dissolved Mn (x) and HAc Mn (●) at station 1.

where the rate constant, $k = 3.6 \times 10^{-5} \mu M^{-2} d^{-1}$, is derived from oceanographic field measurements, and f_t accounts for the effect of temperature on the reaction rate. Dissolved (Mn_d) and particulate (Mn_p) Mn concentrations were calculated for yearly intervals assuming various initial conditions for Mn concentrations and settling rates for particles: dissolved Mn concentrations of 1-2 nM; particulate Mn concentrations of 0.04-0.06 nM; and particle removal rates of 20-30 %/yr for surface waters (based on estimates of new production; Platt *et al.*, 1989), decreasing to 5-10 %/yr for deeper waters (based on deep water particle settling rates; Lal, 1980). Results for a range of conditions are listed in Table 3 with one example shown in Figure 4. Initial conditions were chosen to reflect anticipated conditions at the base of the euphotic zone in off-shore waters.

For the various conditions described above, a particulate Mn maximum ranging from 0.32-0.73 nM is calculated for 9-13 years with dissolved Mn concentrations ranging from 0.36-0.44 nM at the particulate Mn maximum. Results for the run using initial Mn_d=1.0 nM have been excluded since 1.0 nM represents surface waters in central gyres rather than in ventilation regions. The model is most sensitive to changes in dissolved Mn concentrations, with greatest variability in model results appearing in particulate manganese concentrations. The particulate Mn maximum at 9-13 years corresponds to the observed maximum (Fig. 4, inset) at 500-800 m. The ventilation age for this depth range in

this part of the North Atlantic is in the range of 9-17 years (Austin and Green, 1985; Li *et al.*, 1984), in good agreement with the predicted value of 9-13 years. The observed maximum leachable Mn concentration of 0.29-0.35 nM and dissolved Mn of 0.35-0.62 nM at the particulate Mn maximum are also in good agreement with the predicted Mn concentrations for water of age 9-13 years. Concentrations of dissolved and particulate Mn calculated for $t > 30-40$ years are within the range of Mn levels observed in western North Atlantic deep waters. While a more exact treatment would be desirable, these calculations do show that Mn^{2+} oxidation could produce the particulate Mn maximum that is observed at intermediate depth in these waters.

CONCLUSIONS

Atmospheric dust inputs give rise to dissolved Al maxima in open ocean surface waters, whereas enhanced scavenging in productive shelf waters with high biogenic particle concentrations results in low dissolved Al concentrations. Increasing surface water dissolved Al concentrations offshore appear to be a consistently observed feature in the North Pacific and Atlantic Oceans, suggesting little net fluvial input of dissolved Al into open ocean surface waters. The observations indicate that oceanic distributions of dissolved Al are primarily controlled by inputs from atmospheric particles and passive removal onto biogenic particles.

Dissolution of atmospheric dust also provides a surface water source of dissolved Mn, however, in the western North Atlantic this input is apparently less important than for Al. Coastal (fluvial and/or sediment) inputs coupled with slow, oxidative removal result in elevated dissolved Mn concentrations in shelf waters and a general decrease in the surface waters toward the open ocean. Low dissolved Mn concentrations in the western North Atlantic interme-

diated and deep waters may be attributed primarily to the slow oxidation of Mn^{2+} . This suggestion is consistent with calculations of the oxidation of Mn^{2+} which show good agreement with observed dissolved and particulate Mn concentrations.

Despite the fact that Al and Mn are both particle-reactive elements influenced by similar inputs (atmospheric, fluvial, sediment), significant differences are evident in their oceanic distributions, reactivities and residence times. These differences can be explained largely in terms of the removal mechanisms for these elements in the oceans. The removal of dissolved Al is consistent with a surface-adsorption mechanism which occurs at a rate proportional to the concentration of predominantly biogenic particles. The relatively narrow range of K_d values for Al ($4.5 \pm 2.7 \times 10^6$ ml/g) in shelf, slope and open ocean waters suggests a relatively rapid approach to surface adsorption-desorption equilibrium. In contrast, dissolved Mn shows relatively longer residence times in shelf and surface waters, yet shorter residence times in deep ocean waters compared with dissolved Al. These observations reflect the importance of slow oxidative removal of dissolved Mn. That the removal of dissolved Mn in the oceans is controlled primarily by the oxidation of Mn^{2+} is consistent with the wide variation in K_d values, which ranged in this study from 6×10^4 ml/g in shelf waters to 1×10^8 ml/g in the DWBC region.

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