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Biogeochemical behavior and mass balance of dissolved aluminum in the western Mediterranean Sea

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Abstract—The biogeochemical cycle of dissolved aluminum in the western Mediterranean has been thoroughly investigated during the EROS 2000 program. Measurements of the concentration of this element were carried out for 5 years both in the water column and in the pore waters of the sediment. Special attention was paid to the distribution of dissolved Al in the river plumes of the Rhone and Ebro. The vertical profiles of this element in the vicinity of the straits of Gibraltar and Sicily also were determined in order to quantify the exchange fluxes of Al at these two boundaries. Budget calculations indicate that the mass balance of the input and output fluxes is fairly well constrained. They also show that atmospheric dust of Saharan origin is by far the most important external source of dissolved Al for the western Mediterranean and thus is responsible for the anomalously high concentrations of this element observed in the water column. Data obtained in this study strongly support the hypothesis that the unusual nutrient-like vertical distribution is controlled mainly by biological activity. Calculations of renewal times of dissolved Al imply that its concentration and distribution can be affected significantly at time scales of a few decades if the atmospheric input is modified. Presently the net input flux of dissolved Al to the western Mediterranean is entirely exported to the Atlantic. © 1997 Elsevier Science Ltd.

INTRODUCTION

Although aluminum is one of the most abundant elements on earth, its biogeochemical behavior in natural waters is not well understood. Early investigations of the distribution of dissolved Al in the Mediterranean (Mackenzie *et al.*, 1978; Caschetto and Wollast, 1979a) indicated that this semi-enclosed sea is characterized by relatively high concentrations of this element in the water column and a nutrient-like vertical profile, unusual for an oceanic system. These authors found a good correlation between dissolved Al and Si and concluded that biological processes were the principal controls of the vertical distribution of dissolved Al. There have been various vertical profiles of dissolved Al reported more recently for open oceans (Hydes, 1983; Moore and Millward, 1984; Orians and Bruland, 1985, 1986; Measures *et al.*, 1984, 1986; Measures and Edmond, 1990, 1992), indicating a surface maximum, a mid-depth minimum and concentrations increasing with depth below 1000 m. This distribution suggests the control of this element by eolian input at the surface, scavenging at mid-depths and enrichment through re-dissolution at depth. Another established finding is that concentrations of dissolved Al in the open ocean are much lower than those of the Mediterranean Sea.

Later investigations confirmed the anomalous characteristics of dissolved Al in the

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Mediterranean Sea: its high concentration and nutrient-like distribution (Hydes *et al.*, 1988; Measures and Edmond, 1988). Dissolved Al anomalies have been used to trace and identify the plume of the Mediterranean in the deep waters of the North Atlantic Ocean (Hydes, 1983; Measures and Edmond, 1988).

The origin of the high concentrations has not yet been clearly identified. Three main potential sources of dissolved Al for marine systems may be considered:

(1) *River input*: The concentration of dissolved Al is much higher in river water than in seawater.

(2) *Atmospheric input*: Recent measurements of the solubility of Al in rain water and on marine eolian dust suggest that 5–10% of Al present in the aluminosilicates could be released in the surface water and the water column during settling (Maring and Duce, 1987; Prospero *et al.*, 1987; Losno *et al.*, 1993; Lim *et al.*, 1994).

(3) *Sediment–water interface*: There are only limited data available on the concentration of dissolved Al in pore waters (Caschetto and Wollast, 1979b; Stoffyn-Egli, 1982; Mackin and Aller, 1984; Hydes *et al.*, 1988). The concentration gradient near the interface suggests that pore waters could be either a source or a sink for dissolved Al for the overlying water. Hydrothermal vents also could act as a potential source for this element.

It has been suggested by several authors that eolian dust is the primary source of dissolved Al in the open ocean (Hydes, 1979, 1983; Orians and Bruland, 1985, 1986; Measures *et al.*, 1984, 1986; Prospero *et al.*, 1987; Measures and Edmond, 1990). The atmospheric input is of particular importance in the Mediterranean Sea due to Saharan dust deposition, especially during dust storm events (Ganor and Mamane, 1982; Loye-Pilot *et al.*, 1986; Hydes *et al.*, 1988; Guerzoni *et al.*, 1991; Guieu *et al.*, 1993). However, there is no quantification of the relative importance of this process.

The nutrient-like distribution of dissolved Al in the Mediterranean was first attributed to control by biological activity because of the observed good correlation of this element with dissolved Si (Mackenzie *et al.*, 1978). Stoffyn (1979) obtained later experimental evidence that dissolved Al was incorporated into the opal skeleton of diatoms. This author found that these organisms were able to remove efficiently dissolved Al at concentration levels encountered in the Mediterranean, but that the presence of this element had no noticeable effect on its productivity. Some evidence also was established from mesocosm studies that marine plankton could take up a significant amount of aluminum probably by a surface adsorption mechanism or active incorporation into cell tissue (Moran and Moore, 1988). van Beusekom (1988b) demonstrated with laboratory experiments on batch cultures that (i) dissolved Al was taken up by diatoms and (ii) the amount of uptake depended on the ambient Al/P ratio. The low dissolved Al concentrations and its close correlation with dissolved Si in the North Sea allowed the same author to conclude that the dissolved Al distribution in early summer was strongly influenced by the phytoplankton bloom. Hydes (1989) showed that dissolved Al concentrations in the English Channel varied with the seasonal cycle in dissolved nutrients. A continued decrease in dissolved Al after diatom production has ceased suggested that Al removal might be generally linked to primary production.

Hydes *et al.* (1988) were the first to provide a general coherent picture of various processes affecting the biogeochemical cycle of dissolved Al in the Mediterranean Sea. Their estimations indicate that the dissolved Al concentrations are probably produced by Al dissolution of eolian dust and advective mixing of Al-rich deep waters into the surface layer, balanced by biologically associated removal processes. The Al removed from the surface layer redissolves during settling in the deep water to raise Al concentrations at high levels. However, these authors were unable to quantify the magnitude of these processes due to insufficient data available.

During the EROS 2000 program, the biogeochemical behavior of dissolved Al in the western Mediterranean Sea was investigated thoroughly. The objective of the study was first to investigate the possibility to use this element as a tracer of water masses both in the river plume and in the vicinity of the Strait of Gibraltar. This element is also of particular interest for the evaluation of the relative importance of the atmospheric input to a marine system. Furthermore, the Mediterranean Sea is an unique marine environment where the importance of biological processes on the removal of dissolved Al can be easily investigated. Attempts also were made during this program to evaluate the role of fluxes at the benthic boundary in the possible recycling of dissolved Al in sediments.

The final objective of this study was to construct a budget for dissolved Al from the data obtained at the boundaries of the western Mediterranean (rivers, atmosphere, sediment–water interface and exchanges at the Straits of Gibraltar and Sicily). The aim of this modelling effort was to gain a quantitative understanding of the apparent anomalous distribution of dissolved Al in this marine environment and to identify the processes controlling the input and removal of this element to and from the water column. Due to the large differences in the concentration of dissolved Al between the Mediterranean Sea and the North Atlantic Ocean, this budget calculation also provided a good opportunity to test the validity of water fluxes at the Strait of Gibraltar.

MATERIAL AND METHODS

Sampling and sample treatment

Rivers. Samples in the Rhone River and Ebro River plumes were collected in an area covering a wide range of salinities from a rubber boat in polyethylene bottles previously cleaned with 10% HCl. Water samples were transported within a few hours to a shore-based station or to a nearby ship, filtered with pre-acid cleaned 0.4 μm Nuclepore or 0.45 μm Millipore filters, acidified with Merck suprapure HCl (50 μl/100 ml), and analyzed for dissolved Al and Si.

Water column. Five major cruises for water column biogeochemical studies were conducted during the EROS 2000 program: *Discovery* (December 1988), *Bannock* (July 1989), *Marion Dufresne* (April 1990), *Valdivia* (February 1992) and *Discovery* (July 1993). The sampling locations are shown in Fig. 1. Water samples were collected with Teflon-lined Go-Flo bottles provided by the University of Southampton and filtered under nitrogen atmosphere with pre-acid cleaned 0.4 μm Nuclepore filters. The filtrates were acidified with Merck suprapure HCl (50 μl/100 ml) and kept at 4°C, and were analyzed for dissolved Al and Si in the laboratory on land. During the first *Discovery* cruise (December 1988) duplicate samples were collected at certain stations and analyzed onboard. Shipboard and laboratory analyses showed comparable results within analytical error.

Pore water. Sediment cores were taken during the second leg of the *Marion Dufresne*

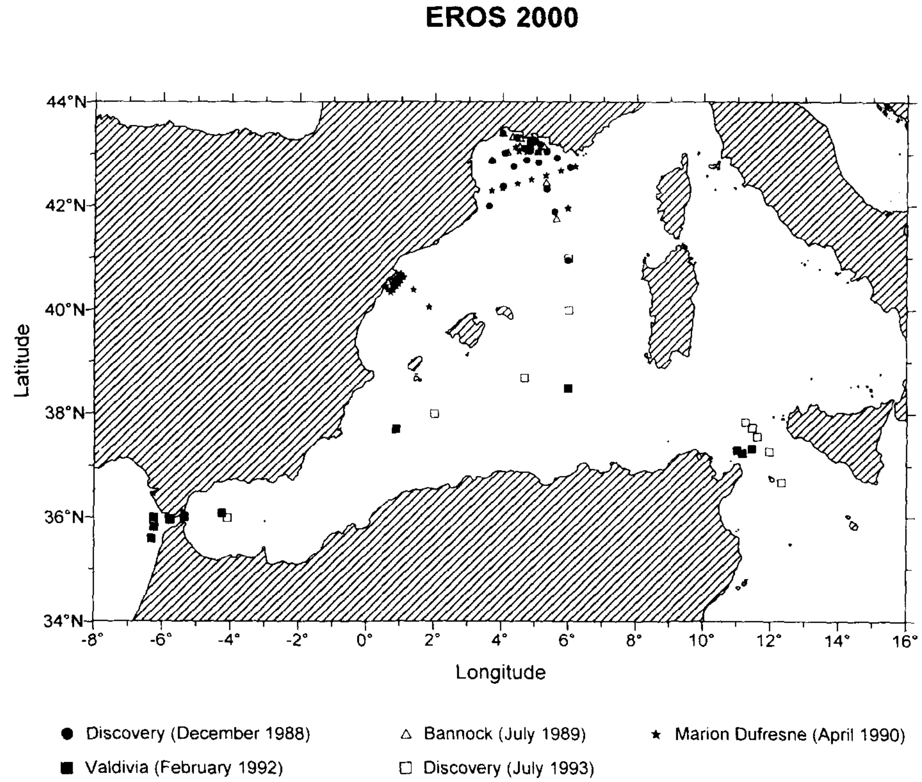


Fig. 1. Sampling positions for water column studies during the EROS cruises.

cruise (May 1990) using a box corer from NIOZ (Netherlands Institute for Sea Research). Positions of the coring stations are shown in Table 1. Core samples were sliced onboard the ship in sections of 2-cm intervals. Interstitial waters were obtained by either squeezing the sliced sediments under a nitrogen atmosphere through 0.45 μm Sartorius filters or by centrifuging them at 3000 r.p.m. followed by subsequent filtration of the supernatant through 0.45 μm Sartorius filters. Pore water samples were kept at 4°C and analyzed in the laboratory on land. The squeezing method produced erratic results. Therefore, only pore water profiles obtained from the centrifugation method will be reported here.

Analytical

Dissolved Al was determined fluorimetrically using Lumogallion as complexing reagent, according to the method described in Hydes and Liss (1976). The procedure was slightly modified for rapid analysis of small-volume samples. Treated samples were either incubated in an oven at 80°C for 2 h or left at room temperature overnight to allow full development of the aluminum–lumogallion complex. The fluorescence was measured at 555 nm with a Perkin-Elmer model 2000 fluorometer with a 471 nm filtered excitation light. To avoid interference from other elements and organic matter present in seawater and especially in pore waters, the standard addition method was used in all measurements. Preliminary measurements performed onboard the ship demonstrated that the acidification has no

Table 1. Sampling positions of the EROS cruises. Only stations for which the vertical profiles are shown in this paper are listed. Stations BC are locations where box cores were taken. Others are stations for water column studies

Station	Latitude	Longitude	Station	Latitude	Longitude
	Discovery (12/88)			*Marion Dufresne* (4/90)	
MA1	40°57'N	5°59'E	ROUSTAN	43°15'N	4°54'E
MA2	41°53'N	5°33'E	EBRO	40°42'N	0°52'E
MA3	42°20'N	5°19'E	RC1	42°45'N	6°10'E
MA4	42°50'N	5°05'E	RC2	42°40'N	5°44'E
MA5	43°04'N	4°50'E	RC3	42°35'N	5°18'E
MA6	43°17'N	4°51'E	RC4	42°30'N	4°52'E
MA7	43°13'N	4°50'E	RC5	42°25'N	4°27'E
MA8	43°08'N	4°49'E	RC6	42°20'N	4°00'E
MC1	41°60'N	3°37'E	RC7	42°17'N	3°41'E
MC2	42°23'N	4°02'E	EBB4	40°03'N	1°51'E
MC3	42°45'N	4°20'E	EBB7	40°23'N	1°23'E
MC4	43°06'N	4°39'E		*Marion Dufresne* (5/90)	
MF1	42°44'N	6°01'E	BC4	43°09'N	4°40'E
MF2	42°55'N	5°38'E	BC5	42°19'N	3°41'E
MF3	43°03'N	5°20'E	BC6	42°51'N	3°25'E
MF4	43°11'N	5°07'E	BC7	40°46'N	0°53'E
	Bannock (7/89)		BC9	40°53'N	1°01'E
25	42°27'N	5°19'E	BC10	40°58'N	2°09'E
			BC12	40°03'N	1°51'E
			BC13	40°20'N	0°28'E
			BC15	41°57'N	5°56'E
			BC17	43°03'N	4°45'E
			BC18	42°45'N	6°10'E
				Discovery (7/93)	
			D14	36°41'N	12°19'E

detectable influence on the analysis. Ten determinations of a solution close to blank level gave a standard deviation of 0.5 nM.

Dissolved Si was analyzed colorimetrically with the Molybdate Blue method as outlined in Grasshoff *et al.* (1983), modified for automated analysis using a Technicon AutoAnalyzer. The absorbance was measured through a 880 nm cut-off filter. Ten determinations of a solution close to blank level gave a standard deviation of 20 nM.

RESULTS AND DISCUSSION

River plumes

Rhone. The behavior of dissolved Al in the mixing zone of the Rhone River plume was examined during December 1988, July 1989 and April 1990. Because of the very limited tidal amplitude of the Mediterranean, there is no strong salt intrusion in the Rhone River, which can be classified as an outer estuary. At the mouth of the Rhone, the salinity in the surface water was usually around 5, and most of the mixing of fresh water with seawater occurred in the adjacent coastal zone. This salinity depends strongly on the mistral wind condition, which also affects the geographic extent of the Rhone plume.

Figures 2a, 2b and 2c show the concentrations of dissolved Al and Si as a function of salinity for the three cruises. They indicate clearly that the concentrations of dissolved Al and Si decrease linearly with increasing salinity, suggesting a simple dilution of the river components by seawater, without any significant removal or production of these elements during the mixing process. This is what one would expect because the residence time of water in the mixing zone is only of the order of a few days. The concentration of dissolved Al of the riverine end member varied from 400 nM to 600 nM with a mean value of 500 nM. It should be pointed out that there may be a removal of dissolved Al in the fresh water part of the estuaries (salinity < 1) as observed in other cases (Morris *et al.*, 1986; Chou and Wollast, 1993). The concentration of dissolved Si of the riverine end member varied significantly from 20 to 80 μM with low values found in the spring and summer. This variation is probably related to fresh water diatoms, which consume dissolved Si and likely some dissolved Al in the upstream part of the river.

Hydrodynamical model output indicates that the maximum thickness of the plume is at the mouth of the Rhone where it is of the order of 2 m (Buckley and O'Kane, 1992). This

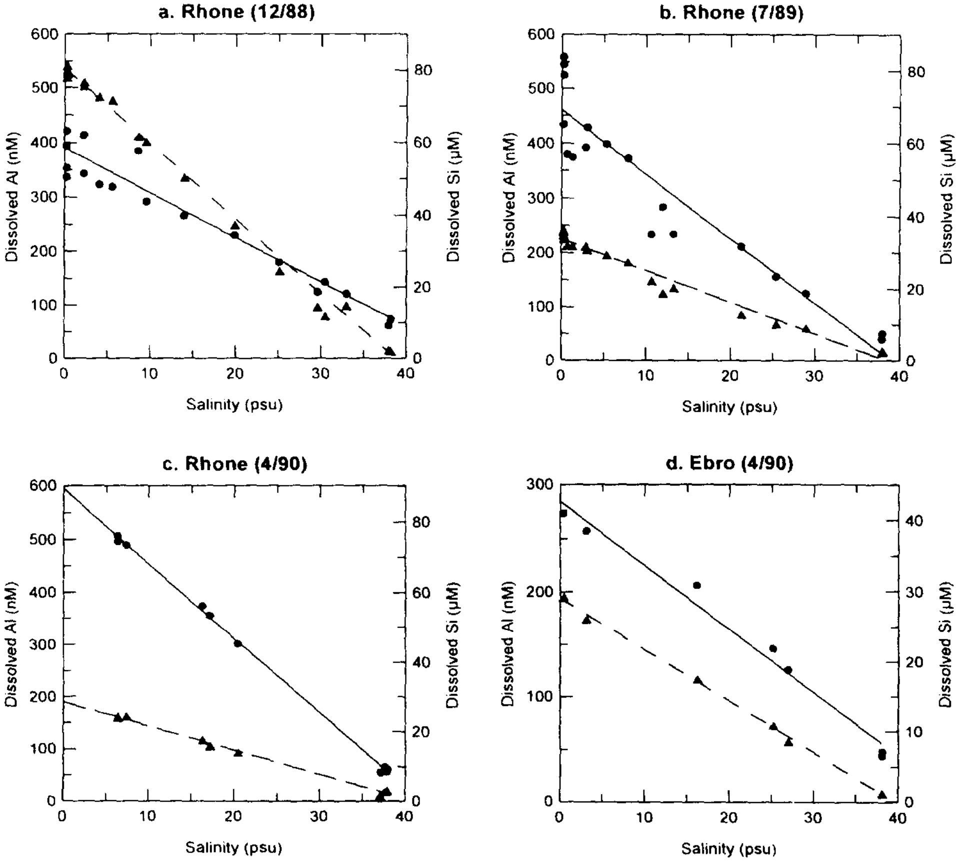


Fig. 2. Concentrations of dissolved Al (●) and Si (▲) as a function of salinity in the Rhone (a)–(c) and Ebro (d) plumes.

thickness rapidly diminishes by an order of magnitude over a distance of 1–2 km. Vertical profiles of dissolved Al and Si determined in April 1990 at Station Roustan, situated about 12 km from the mouth of the Rhone River, demonstrate the still pronounced influence of the plume at the surface where the salinity is about 20 (Fig. 3a).

Ebro. The longitudinal distribution of dissolved Al and Si in the Ebro plume was investigated in April 1990. The results are shown in Fig. 2d. They also show a negative correlation of the concentrations of these two elements with salinity, reflecting once more their conservative behavior during the mixing of fresh river water with seawater. Figure 2d also shows that the Ebro fresh water end member has a much lower dissolved Al content than the Rhone. The difference in concentration may be attributed to the lithology of the drainage basin, the residence time of the water and anthropogenic activities. However, the mechanism controlling the dissolved Al concentrations in fresh waters is still unknown. Dissolved Si concentrations are similar in both rivers for the same period. The effect of the Ebro plume was still observed at a station located about 7 km from the river mouth (Fig. 3b).

Western Mediterranean

Vertical distribution. The water column in the western Mediterranean is basically three-layered (Wüst, 1961; Lacombe and Tchernia, 1972). The surface layer is characterized by the warmer and less saline water of Atlantic origin, which is separated from the weakly stratified deep layer of Western Mediterranean Deep Water (WMDW) by an intermediate salinity-maximum layer, the Levantine Intermediate Water (LIW) at about 200–500 m depth. The near-surface flow is cyclonic, with the Liguro-Provenal Currents flowing westward along the Cote d'Azur, supplied in the east by the east and west Corsican currents and turning into the Catalan current, which partially continues southward along the Spanish coast and partially recirculates eastward along the southern rim of the Gulf of Lions (Font *et al.*, 1988; Astraldi and Gasparini, 1992; Millot, 1991; Schott *et al.*, 1994).

A typical CTD profile taken at Station MA1 onboard the *Discovery* in December 1988 (Fig. 4) indicates clearly the three-layer structure as described in the literature. A subsurface

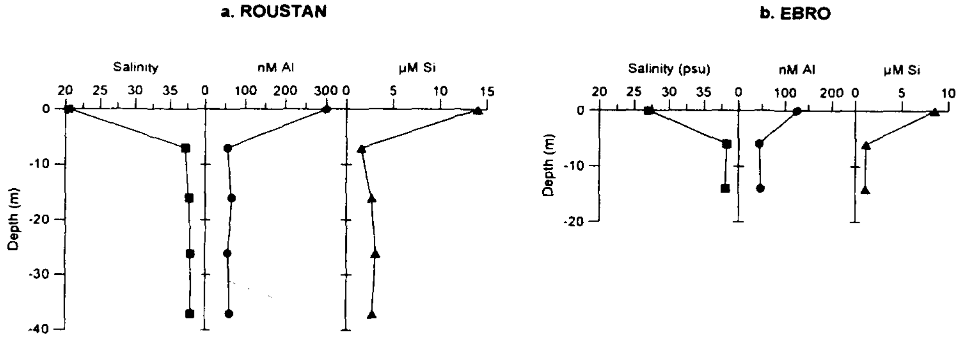


Fig. 3. Vertical profiles of salinity, dissolved Al and Si at stations visited in April 1990 near the mouths of the Rhone (a) and Ebro (b).

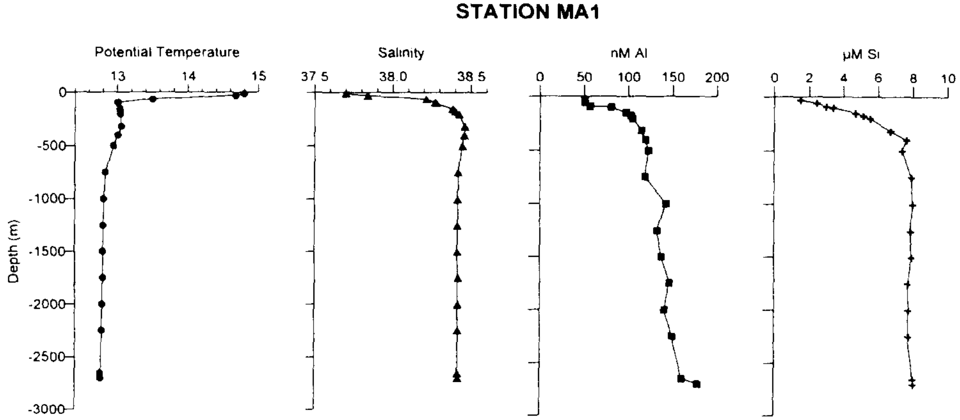


Fig. 4. Vertical profiles of potential temperature, salinity, and dissolved Al and Si at Station MA1 (*Discovery* 12/88). See Table 1 for the sampling position.

temperature and salinity maximum was observed at about 400 m, which is characteristic of the LIW. The dissolved Al profile mimics that of dissolved Si at MA1 (Fig. 4).

Vertical distributions of dissolved Al for transects MA, MF and MC conducted during the *Discovery* cruise (December 1988) are shown in Fig. 5. The depletion of dissolved Al in surface waters is well demonstrated in the deep-sea profiles, with a concentration as low as 50 nM. The concentration increases rapidly to about 110 nM at a depth of 300 m, and then continues to increase more slowly with depth reaching a value close to 140 nM at 2400 m. The dissolved Al content in the LIW was found to be near 120 nM. Our results are in good agreement with the earlier data of Hydes *et al.* (1988).

The top surface layer (upper 100 m) at Station MA3 has a higher dissolved Al content. This is possibly due to the vertical mixing resulting from the development of deep convection during the winter period, which will be discussed later. The influence of the Rhone River can be seen clearly at Station MA6, which is situated close to the river mouth. The presence of a fresh water layer at the surface is indicated by the high value of the dissolved Al concentration. Similar distributions were observed for transects RC and EBB surveyed during the *Marion Dufresne* cruise in April 1990 (Fig. 6).

Several deep stations (MA1, MA2, MA3 and RC1) show an increase in dissolved Al concentration close to the sea bottom (Figs 5 and 6). This could be explained by an input of this element from the pore waters at the sediment–water interface. This particular aspect will be discussed in a later section.

Dissolved Al exhibits a nutrient-like profile in the Mediterranean that has not been observed for any other open ocean. The close relationship between dissolved Al and Si in the upper 1000 m (Fig. 7) indicates clearly that these two elements covary. It has been reported that diatoms are the most abundant species in the northwest Mediterranean (Velasquez and Cruzado, 1990). Therefore, distributions of dissolved Al and Si could be closely associated with diatom production. Incorporation of dissolved Al into Si-shells during the growth of diatoms has been demonstrated experimentally by Stoffyn (1979), Moran and Moore (1988) and van Beusekom (1988b). Close correlation between dissolved Al, Si and other nutrients also has been observed in the North Sea and in the English Channel. Phytoplankton bloom was attributed to control the distribution of dissolved Al in the North Sea in early summer

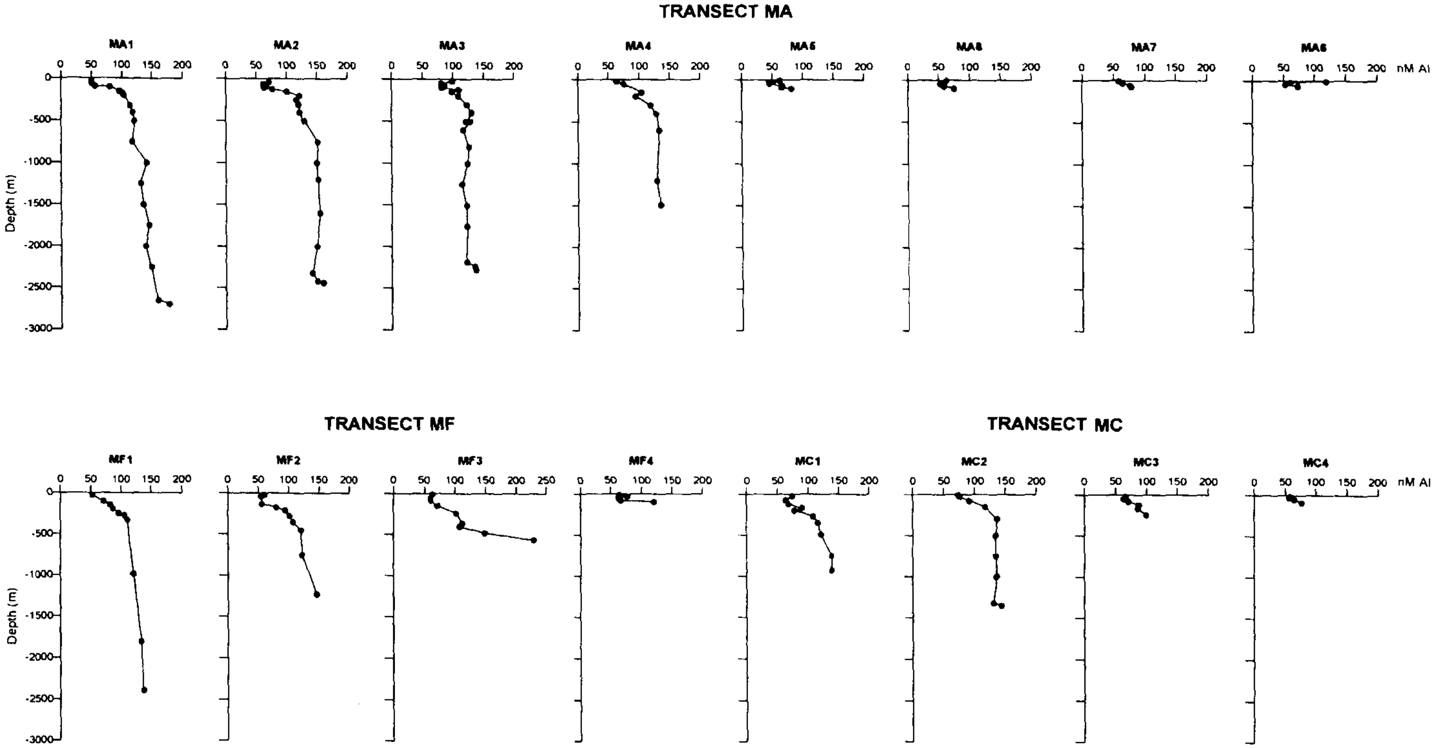


Fig. 5. Vertical profiles of dissolved Al for selected transects conducted during the *Discovery* 12/88 cruise. See Table 1 for positions of the stations

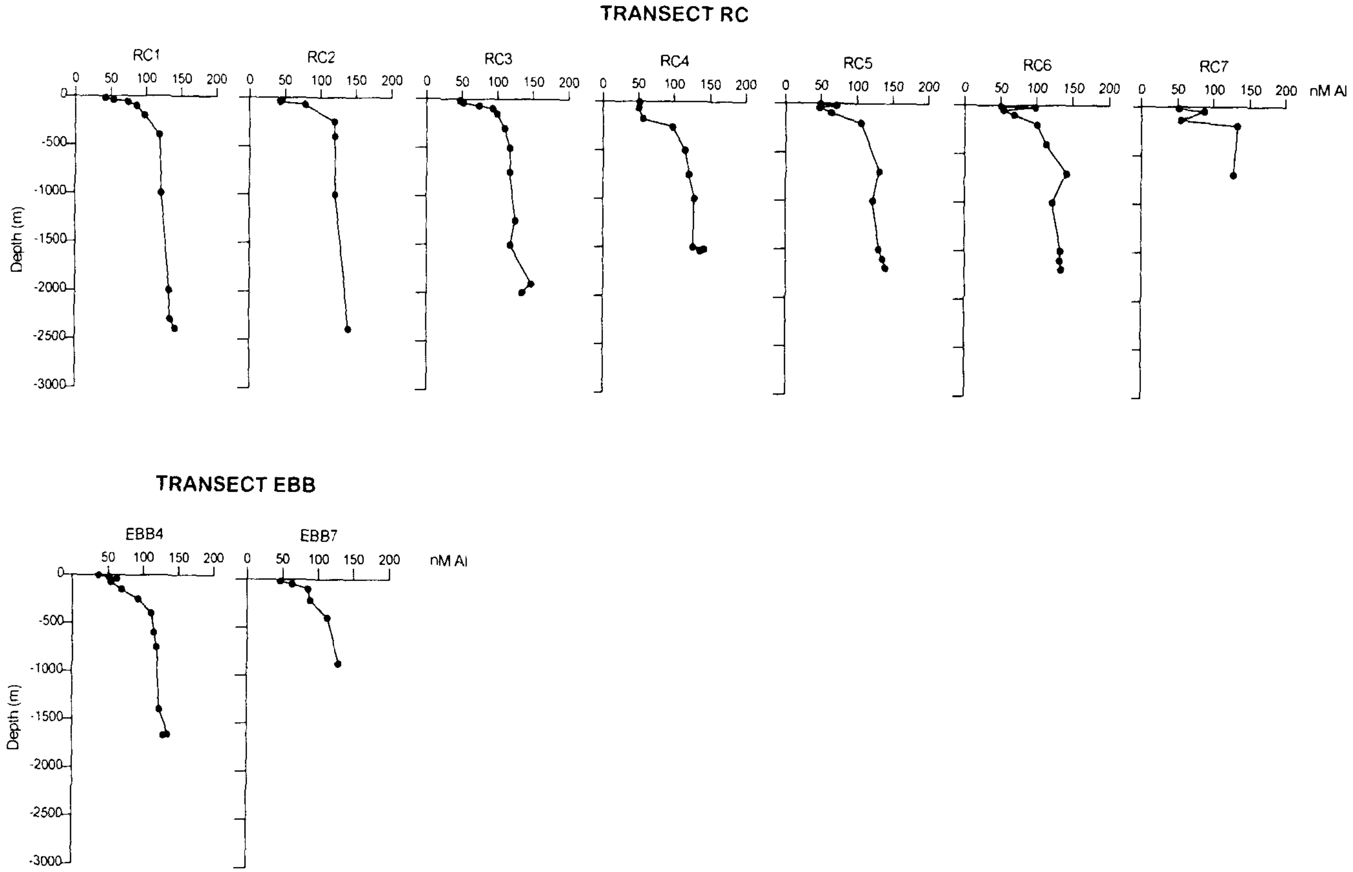


Fig. 6. Vertical profiles of dissolved Al for selected transects conducted during the *Marion Dufresne* 4/90 cruise. See Table 1 for positions of the stations.

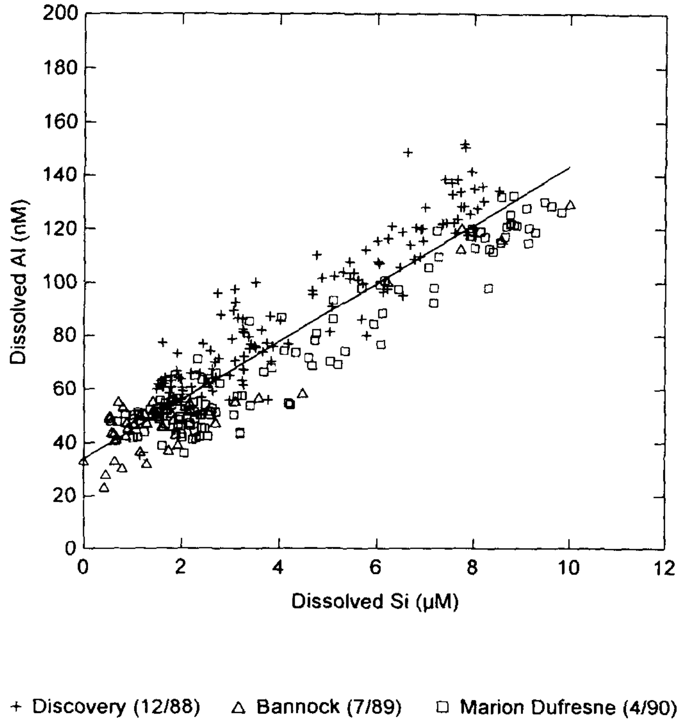


Fig. 7. Dissolved Al as a function of dissolved Si for data obtained during three various cruises (*Discovery* 12/88, *Bannock* 7/89 and *Marion Dufresne* 4/90) in the upper 1000 m of the water column. The straight line depicts the linear regression. The linear regression line corresponds to nM Al = 34.1 + 10.9 × μM Si. The number of data points plotted is 300 and the linear correlation coefficient is 0.93.

(van Beusekom, 1988b). Hydes (1989) found that after the end of the spring diatom bloom in the English channel, dissolved Al continued to decrease together with phosphate and nitrate concentrations. Accordingly, these authors suggested that the removal of dissolved Al may be more generally associated with biological production than specifically with diatom production. It is interesting to note that the slope of the regression line in Fig. 7 corresponds to an Al/Si ratio of 0.011, which falls in the range of what have been observed in diatom skeletons (Martin and Knauer, 1973; van Bennekom and van der Gaast, 1976). This further demonstrates the role of biologically related processes in the control of the vertical distribution of both dissolved Al and Si in the Mediterranean.

Comparison of concentrations of dissolved Al obtained during the *Discovery* (12/88) and *Bannock* (7/89) cruises shows seasonal fluctuations. Surface waters contain less dissolved Al in the summer compared to winter (Table 2). One station was visited during the *Discovery* (12/88), *Bannock* (7/89) and *Marion Dufresne* (4/90) cruises. The vertical profiles obtained provide an opportunity to examine the distribution of dissolved Al during three different seasons: winter, spring and fall. Figure 8 indicates that in the Gulf of Lions there is a progressive consumption of dissolved Al and Si in the surface waters (upper 70 m) through the spring and summer. At greater depths, the observed profiles are similar.

The gradual displacement with season of the vertical profiles of dissolved Al and Si in the

*Table 2. Concentrations of dissolved Al and Si at station MA3 (*Discovery 12/88*), station 25 (*Bannock 7/89*) and station RC3 (*Marion Dufresne 4/90*)*

Depth (m)	nM Al	µM Si	Depth (m)	nM Al	µM Si
Discovery 12/88 Station MA3			*Bannock* 7/89 Station 25		
−24	100	3.51	0	46	1.60
−51	82	3.26	−5	52	1.43
−76	87	3.16	−10	56	1.41
−101	82	3.64	−25	37	1.15
−125	110	4.76	−35	31	0.79
−149	98	6.21	−50	40	1.93
−199	109	6.77	−75	57	3.58
−301	123	7.58	−100	59	4.47
−399	131	8.20	−150	100	6.22
−500	121		−300	113	7.73
−502	128	8.07	−480	116	8.58
−599	117	8.03	*Marion Dufresne* 4/90 Station RC3		
−800	126	7.92	−20	47	2.18
−1000	124	7.66	−40	52	2.16
−1250	115	7.90	−70	74	4.34
−1500	122	7.76	−100	93	5.10
−1750	123	7.46	−150	99	6.05
−2183	122	7.39	−300	110	7.27
−2235	135	7.75	−500	117	7.92
−2277	137	7.53	−750	117	8.65
			−1250	125	9.45
			−1500	118	9.21
			−1900	147	9.45
			−1990	135	9.04

very top layer of the surface water column reflects a balance between the rates of supply of this element and those of removal. Our results suggest that the rate of supply has not kept up with that of removal, resulting in a decrease of dissolved Al and Si in surface waters when one proceeds from the winter to spring and summer. Furthermore, it is interesting to note that a subsurface minimum of both dissolved Al and Si was observed at the same depth for the *Bannock* station (Fig. 8), where dissolved oxygen was at its maximum (Chou and Wollast, 1990).

Surface distribution. The hydrodynamics of the Mediterranean is controlled by meteorological conditions. In the winter, the water circulation in the western basin is driven by the wind (Lacombe and Tchernia, 1972). It has been established that three combined factors make the Gulf of Lions a preferred site for deep convection. Stratification, circulation and wind combine over the early parts of winter, November to January, in the so-called preconditioning phase to prepare the water column for subsequent deep convection (Schott *et al.*, 1994).

The cyclonic circulation leads to a shoaling of the isotherms, isohalines and isopycnals in an elongated dome. In the center of the dome, the LIW salinity maximum is brought into shallow enough depths to be exposed to mixed-layer entrainment. The center of the isopycnal dome, situated near 42°N and 5°E, lies right in the path of the strong mistral winds

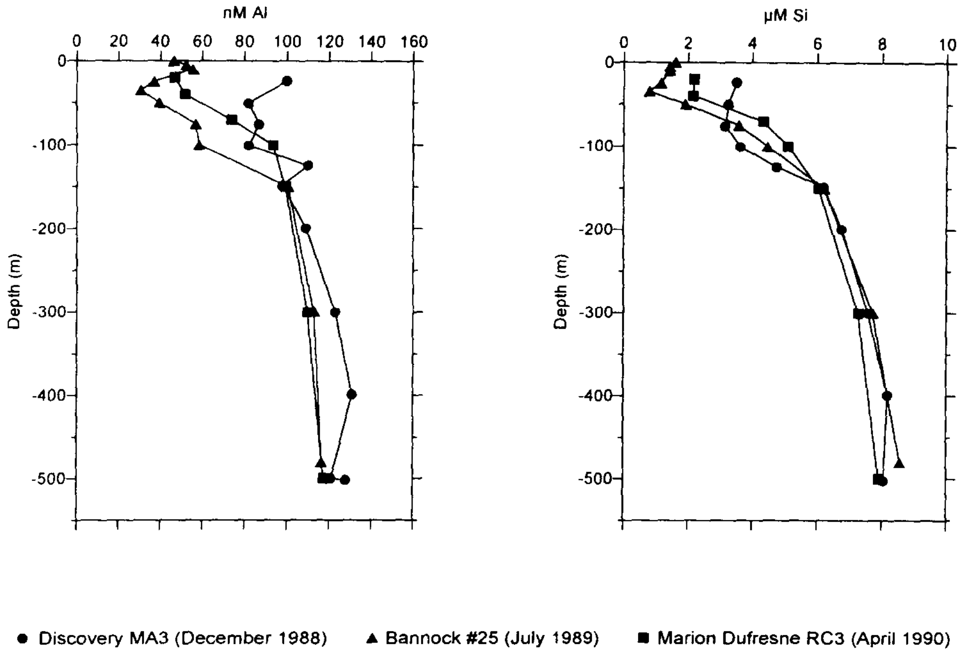


Fig. 8. Distribution of dissolved Al and Si in the Gulf of Lions for winter, spring and summer situations.

occurring in the winter, favoring the formation of deep convection (Schott *et al.*, 1994). Before the December 1988 *Discovery* cruise took place, there had been a persistent mistral wind blowing down the Rhone valley. The much colder wind results in heat transfer from the sea surface to the atmosphere and enhances the evaporation of surface water, forming dense water (Fig. 9). A temperature minimum was observed in the region described by Schott *et al.* (1994) for the preconditioning of deep convection in the Gulf of Lions. This suggests that vertical mixing was already occurring in December due to the onset of the deep convection during the winter period.

Surface distribution of dissolved Al in December 1988 (Fig. 9) shows that a maximum concentration was observed where there was a temperature minimum described earlier. This confirms the occurrence of vertical mixing of surface water containing low dissolved Al with deeper water of high dissolved Al content. The influence of the Rhone can be demonstrated again by the increasing dissolved Al concentrations approaching the river mouth. In the western part of the Gulf of Lions, surface waters seem to contain a higher amount of dissolved Al, suggesting a local source for this element during the period investigated.

Pore waters

Shelf stations. Pore water profiles of dissolved Al and Si for cores taken in shallow waters of the Gulf of Lions are shown in Fig. 10a. For cores BC4 and BC6, dissolved Al concentrations increase sharply in the first few centimeters and then decrease rapidly

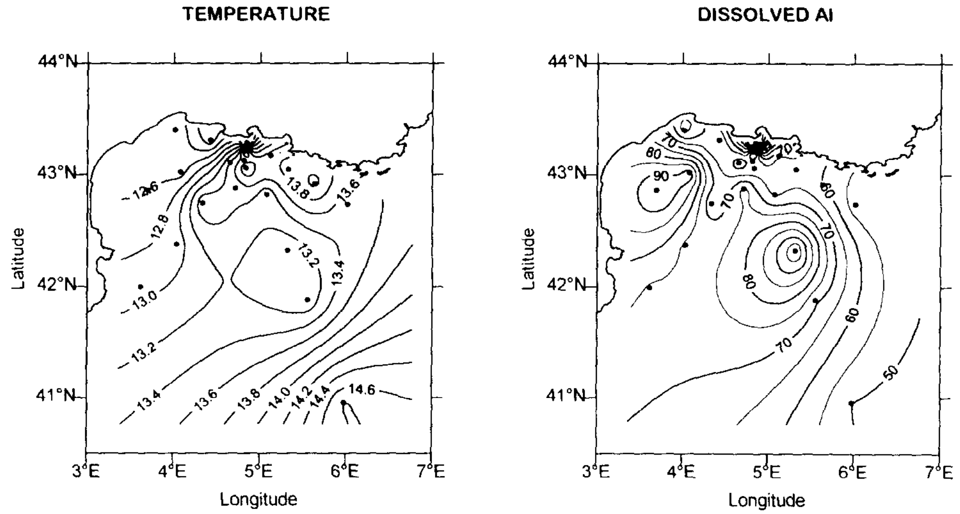


Fig. 9. Surface distribution of temperature and dissolved Al in the Gulf of Lions (*Discovery* 12/88). Sampling stations are indicated by solid circles.

reaching a more or less constant value. For core BC17, the dissolved Al concentration increases again from 9 to 11 cm and then decreases. Dissolved Si in these three cores increases rapidly with depth from the sediment–water interface to a depth of about 4–5 cm reaching a maximum and then decreases again reaching a constant value. The dissolved Si gradient below the depth where the maximum Si concentration is observed varies from one core to another.

Three cores were sampled in the shallow waters near the Ebro area. Pore water profiles of dissolved Al and Si for these stations also are shown in Fig. 10a. A general trend is observed for dissolved Al for cores BC7 and BC9, showing a sharp increase in the first centimeter and then decrease with depth. No consistent pattern is observed, however, for core BC13. Dissolved Si either increases continuously with depth or reaches a subsurface maximum at about 1 cm. It is interesting to point out that core BC7 where dissolved Si increases continuously with depth was collected right at the mouth of the Ebro River.

Deep stations. Pore water profiles of dissolved Al and Si for cores collected in deep waters of the northwest Mediterranean (Fig. 10b) show similar distributions for dissolved Al. It increases rapidly reaching a maximum in the first few centimeters and then decreases slowly with depth reaching concentration values close to those found at the sediment–water interface. For dissolved Si, three trends were observed. Its concentration increasing rapidly in the first centimeter, and then (1) increasing more slowly and continuously with depth for core BC15, (2) increasing slowly and reaches constant values for cores BC5, BC18 and BC12, or (3) increasing more slowly reaching a maximum and then decreasing slowly with depth for core BC10.

Early diagenesis. In all pore water profiles analyzed, both dissolved Al and Si concentrations show an increase for the first few centimeters. It is thus reasonable to conclude that it was the biogenic silica, which was subjected to the dissolution process

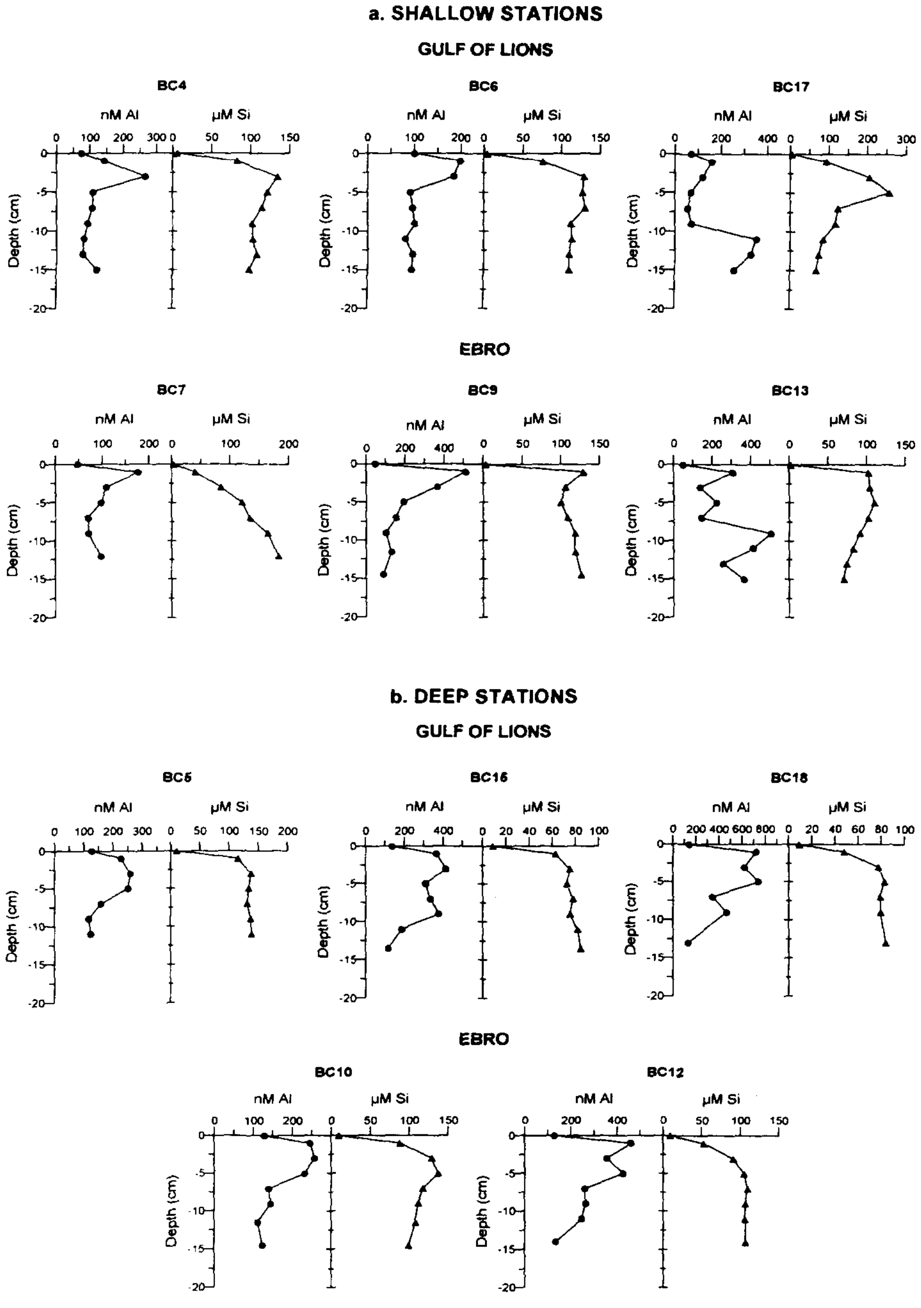


Fig. 10. Pore water profiles of dissolved Al and Si (a) at shallow stations in the Gulf of Lions and near the mouth of the Ebro, and (b) at deep stations in the northwest Mediterranean. See Table 1 for positions of the coring stations.

during early diagenesis that supplied Al and Si to the pore waters. Our results show that the amount of dissolved Al and Si released in the first 2 cm of the sediments has a mean Al/Si ratio of 2.8×10^{-3} with a standard deviation of 2.0×10^{-3}, excluding an abnormal value of 14.8×10^{-3} at station BC18. This ratio agrees with the values reported in the literature for the skeletons of diatoms which contained 1–10 mg Al/g SiO_2 (Martin and Knauer, 1973; van Bennekom and van der Gaast, 1976). It also falls well within the range of values observed for diatom growth during the laboratory culture and mesocosm studies by Stoffyn (1979), Moran and Moore (1988) and van Beusekom (1988b), who found an Al/Si removal ratio of 2.5×10^{-3}, 8.5×10^{-3} and $1\text{–}2 \times 10^{-3}$, respectively. This further supports that aluminum is released together with silica during early burial when dissolution of biogenic silica occurs.

In most pore water profiles obtained in this study, dissolved Al concentrations decrease with depth after the initial increase, indicating removal of this element in the deeper part of the sediments. It has been suggested that reactions between seawater and silicate minerals (reverse weathering) play a significant role in controlling the chemical composition of seawater (Sillén, 1961; Mackenzie and Garrels, 1966; Wollast and Mackenzie, 1983). Our dissolved Si profiles show that in most cases a steady-state Si concentration is reached at depth, suggesting that the addition of this element in the upper layer of the sediments is balanced by its removal. The removal process may involve the formation of authigenic clays (Hurd, 1973; Wollast, 1974; van Bennekom and van der Gaast, 1976; Marchig and Gundlach, 1981; Mackenzie *et al.*, 1981; Mackin and Aller, 1984, 1989).

The role of sediments as a source or a sink for dissolved Al is a subject of controversy mainly due to the few pore water studies existing in the literature. Orians and Bruland (1986) observed an increase of dissolved Al concentration in the water column of the Pacific above the sediment–water interface. They have considered pore water as one candidate among others being responsible for the enrichment of dissolved Al in the near-bottom waters, based on the measurements obtained by Stoffyn-Egli (1982) in the North Atlantic. On the contrary, Measures and Edmond (1992) concluded that the increase of dissolved Al concentration with depth that they observed in the Greenland Sea was due to the mixing of various water masses. They excluded pore water as a possible source for this element to the overlying water, based on the results of Mackin and Aller (1984) who found an uptake of dissolved Al from pore water profiles and during incubation experiments for sediments taken from the East China Sea shelf. van Beusekom (1988a), on the other hand, has shown that sediments in the German Bight of the North Sea can act as both a source and a sink for dissolved Al depending on the seasonal and regional conditions. It seems thus unreasonable to draw conclusions concerning the role of sediments in the recycling of Al in a given marine environment without interstitial water measurements.

Straits of Gibraltar and Sicily

In order to construct a budget for dissolved Al in the western Mediterranean, it is important to investigate the fluxes of this element at the southern boundaries. The transect from the Strait of Gibraltar to that of Sicily was conducted during two cruises: *Valdivia* (February 1992) and *Discovery* (July 1993), during which vertical profiles of dissolved Al were determined at the two straits and in the southwestern Mediterranean.

At the Strait of Gibraltar, North Atlantic Water flows into the Mediterranean at the surface. The outflowing Mediterranean water is principally modified Levantine

Intermediate Water (LIW). Vertical distributions in the upper 1500 m of salinity and dissolved Al for the transect Gibraltar–Sicily conducted during the *Discovery* cruise in summer 1993 (Fig. 11) indicate clearly that the surface water in the southern section of the western Mediterranean is mainly of North Atlantic origin with low salinity and dissolved Al content.

There exist very few data concerning dissolved Al near the Strait of Gibraltar. Measures and Edmond (1988) reported two vertical profiles: one in the Alboran Sea and one in the Gulf of Cadiz. The dissolved Al concentrations in the Alboran Sea determined in this study are comparable to those of Measures and Edmond (1988) who found 12 nM in the North Atlantic Surface Water (NASW) and 112 nM in the WMDW (Table 3 and Fig. 11). Hydes (1983) also reported dissolved Al concentrations ranging from 16 to 33 nM for North Atlantic surface waters entering the Mediterranean Sea.

As the inflowing North Atlantic Water passes through the western Mediterranean towards the eastern basin, its dissolved Al concentration continues to increase as a result of mixing with the Mediterranean water. This modified surface water mass also mixes vertically with the underlying LIW which flows westwards from the eastern basin into the western Mediterranean. Station D14 is situated more in the eastern basin, where at the depths below the LIW core layer, vertical mixing of LIW and EMDW (Eastern Mediterranean Deep Water) takes place. CTD data indicated a salinity maximum (38.768 psu) at approximately 400 m indicative of the LIW containing 125 nM of dissolved Al (Fig. 12). This is in agreement with Wüst (1961) who reported the core layer of the LIW located at a depth of 400 m, in the vicinity of the Strait of Sicily during the summer having a salinity of about 38.7 psu. The dissolved Al content in the EMDW at this station is about 150 nM. EMDW in the eastern basin may contain dissolved Al as high as 170 nM (Hydes *et al.*, 1988). In all cases, Mediterranean surface waters are strongly depleted in dissolved Al compared to deep waters.

FLUXES AT THE BOUNDARIES

In order to make budget calculations for dissolved Al in the western Mediterranean, we need to identify and quantify the various sources of input and output of this element that are required to perform the calculations.

River input

In the Gulf of Lions, the Rhone is the largest river entering the Mediterranean, with a mean annual discharge of 54 km^3 $year^{-1}$ (Milliman *et al.*, 1995). It was demonstrated earlier that dissolved Al behaved conservatively during estuarine mixing. Therefore, the fresh water end member concentration of this element, which was found to be 500 nM, can be used to evaluate the input of dissolved Al from the Rhone to the Mediterranean. This gives an input of 27×10^6 mol Al $year^{-1}$, or 729 t Al $year^{-1}$. Ebro, on the other hand, has a smaller water discharge of 17 km^3 $year^{-1}$ (Milliman *et al.*, 1995) and a lower dissolved Al content of about 300 nM, resulting in an input of 5.1×10^6 mol Al $year^{-1}$, or 138 t Al $year^{-1}$. Therefore, the total input from these two rivers is 867 t Al $year^{-1}$. The river discharge from other rivers to the western Mediterranean is estimated to be 29 km^3 $year^{-1}$ (Milliman *et al.*, 1995). Since no data on dissolved Al concentration in other rivers are available, we have roughly estimated the input of this element from these

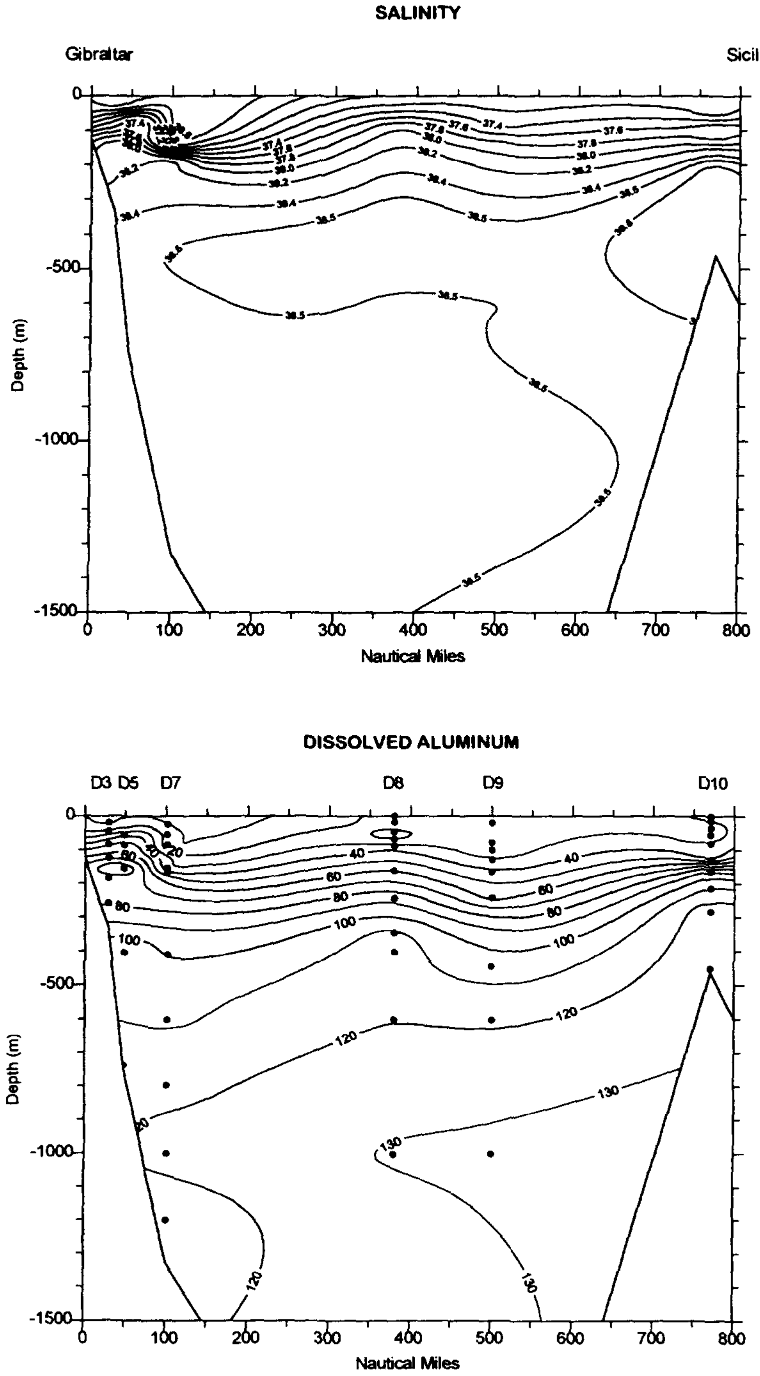


Fig. 11. Cross-sections of salinity and dissolved Al for the Gibraltar–Sicily transect (*Discovery* 7/93).

Table 3. *Summary of boundary flux calculations for dissolved Al at the straits*

	Parameters				Fluxes 10^9 mol Al year^{-1} (10^3 t Al year^{-1})	
	In		Out			
	(10^3 km^3 year^{-1}) Water flux	(nM) Dissolved Al	(10^3 km^{3}year^{-1}) Water flux	(nM) Dissolved Al	In	Out
Gibraltar	53	15	50.5	90	0.80 (21.6)	4.55 (123)
Sicily	38	105	39.8	35	3.99 (108)	1.39 (37.5)

rivers by taking the value found in the Rhone, which gives 391 t Al year^{-1}. The total river input of dissolved Al to the western Mediterranean is thus 1258 t year^{-1}.

Atmospheric input

Atmospheric input of dissolved trace metals to the Mediterranean is of particular importance due to Saharan dust storm events. Its evaluation is, however, not an easy task because of the sporadic nature of the storm events and the difficulties involved in the wide geographic and seasonal coverage. Guerzoni *et al.* (1992) estimated the dust flux related to Saharan transport as a function of latitude. According to these authors, this flux can fluctuate from 100 t km^{-2} year^{-1} near the African coast to 1 t km^{-2} year^{-1} in the northern part, with a geometric mean of 10 t km^{-2} year^{-1}. Buat-Ménard *et al.* (1989) found a mean atmospheric flux of 2 mg Al m^{-2} day^{-1} (0.73 t Al km^{-2} year^{-1}) for the particulate Al to the northwest Mediterranean in sediment traps deployed at 200 m depth near Corsica.

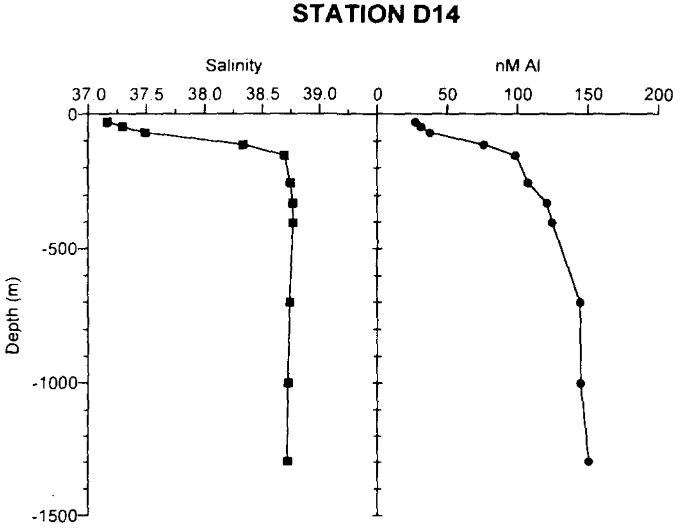


Fig. 12. Vertical profile of salinity and dissolved Al at station D14, situated in the Strait of Sicily (*Discovery* 7/93). See Table 1 for sampling position.

Assuming that Al represents on average 7% by weight of the atmospheric dust (Martin and Whitfield, 1983), this gives a particulate flux of 10 t km^{-2} year^{-1}, which is in good agreement with that estimated from Guerzoni *et al.* (1992). This value also corresponds well to that calculated by Bergametti (1987) who found a total atmospheric depositional flux of 970 mg Al m^{-2} year^{-1} (0.97 t Al km^{-2} year^{-1}) in the northwestern Mediterranean. For the same area, the atmospheric group of the EROS 2000 suggested a range for the total Al deposition from 0.14 to 0.95 t Al km^{-2} year^{-1} (Guieu *et al.*, 1997).

Most of the atmospheric flux of Al to the ocean is in the particulate form. Recent data collected on the concentrations of dissolved and particulate Al in precipitation over the western Mediterranean have shown that the solubility of this element is on average 9% (Lim *et al.*, 1994). Guieu *et al.* (1997) also found a solubility of Al ranging from 7 to 11% for atmospheric deposition in the Mediterranean environment. The solubility of Al in seawater reported in the literature varies significantly, ranging from 0.6 to 10% (Hodge *et al.*, 1978; Maring and Duce, 1987). It should be pointed out that one would expect a higher solubility of Al in rain water compared to that in seawater due to the corrosive nature of the former.

If we adopt a value of 10 t km^{-2} year^{-1} for atmospheric dust input to the western Mediterranean with a surface area of 840 000 km^2 and 5% mean solubility of aluminum as suggested by Duce *et al.* (1991), we find an input of 29 × 10^3 t year^{-1} for the dissolved Al. This value is well within the range reported by Guieu *et al.* (1997) for the dissolved Al flux from the atmosphere (8.4–84 × 10^3 t Al year^{-1}). Note that this mineral aerosol flux is about 10 times the mean deposition rate evaluated for the global ocean by Duce *et al.* (1991). The dissolved fraction represents about 20 times the river input, underlining the importance of atmospheric input in the western Mediterranean Sea.

Pore water input

Our interstitial water profiles show that concentration gradients of dissolved Al near the benthic boundary range from 0.44×10^{-10} to 5.8×10^{-10} mol Al cm^{-4}, with a mean value of 2.2×10^{-10} mol Al cm^{-4} and a standard deviation of 1.7×10^{-10} mol Al cm^{-4}. There is no significant trend for pore water dissolved Al gradients between the near-shore environment and deep basin. If we take 2×10^{-10} mol Al cm^{-4} for the gradient and 1×10^{-5} cm^{2}s^{-1} the molecular diffusion coefficient, we obtain a diffusive flux of 630 mol Al km^{-2} year^{-1}, or 17×10^{-3} t Al km^{-2} year^{-1}. An annual flux of dissolved Al of 14 × 10^3 t Al year^{-1} from the sediments to the overlying seawater can be estimated for the total surface area of the western Mediterranean. This flux is about one-half that for the atmospheric input and 10 times that of the fresh river water input. It should be pointed out, however, that the value estimated here represents the minimum because we have not taken into consideration bioturbation which tends to increase the diffusion coefficient of dissolved species in pore waters.

Exchange at the Straits

For the western Mediterranean, exchanges at the Straits of Gibraltar and Sicily are very important for budget calculations of dissolved Al due to the large water fluxes involved at these two boundaries and the differences in dissolved Al concentration in the North Atlantic inflow water and in the outgoing Mediterranean water.

The two coherent evaluations of the water fluxes at both the Gibraltar and Sicily straits

(Bethoux, 1980; Lacombe and Richez, 1982) are based on heat and salt balances and differ slightly due to the values chosen for seawater end members. Copin-Montégut (1993) has shown that the fluxes suggested by Bethoux (1980) allow a better mass balance for alkalinity in the Mediterranean, and they have thus been selected here for the evaluation of dissolved Al fluxes.

The mean water flux and averaged dissolved Al concentration for the inflowing and outflowing waters at the two straits used to calculate the exchange fluxes are summarized in Table 3. Our mass balance calculation shows that the western Mediterranean exports 101×10^3 t Al year^{-1} to the Atlantic at the Strait of Gibraltar. Using the approach of Boyle *et al.* (1985), Measures and Edmond (1988) estimated an export of 76×10^3 t Al year^{-1}. It is interesting to point out that according to our calculations, an amount of 70×10^3 t Al year^{-1} is being imported into the western Mediterranean from the eastern basin though the Strait of Sicily.

BIOGEOCHEMICAL CYCLE OF DISSOLVED ALUMINUM IN THE WESTERN MEDITERRANEAN SEA

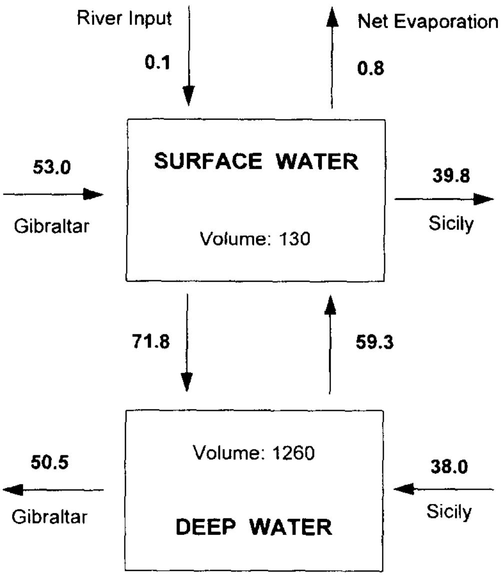
Water budget

The fluxes evaluated above are used in this section to describe the biogeochemical cycle of dissolved Al in the western Mediterranean. An understanding of this cycle can be obtained if we distinguish two vertical boxes in the water column. On one hand, this approach allows a more rational description of the circulation of the water masses in the western basin. On the other hand, one may take into account the vertical fluxes of elements related to biological activity in the water column. We have divided the water column into a surface layer of 150 m based on both the thickness where the Atlantic surface water prevails and where photosynthesis takes place. This approach, however, requires knowledge of vertical water fluxes in the system. In his study of horizontal fluxes and salinity variations in the Mediterranean, Bethoux (1980) estimated the upward water flux to be 59.3×10^3 km^3 year^{-1} for the western Basin. This value was confirmed by the same author (Bethoux, 1989) from estimations of new production and the phosphorus budget in the western Mediterranean, which gave a vertical flux of 63×10^3 km^3 year^{-1}. The estimates of the water budget selected for the following mass balance calculations and chosen according to the fluxes suggested by Bethoux (1980) and Bethoux (1989) are represented in Fig. 13.

There are several interesting characteristics of importance for the discussion of the Al cycle that can be derived from the water circulation (Fig. 13). The mean renewal time of western Mediterranean water by the Atlantic inflow water is 26 years, and by deep eastern Mediterranean water 37 years. Due to vertical exchange the renewal times of surface and deep water are, respectively, 2.2 and 18 years. The residence time of the water masses is short compared to the renewal time of dissolved Al in the world ocean, which is of the order of 100 years (Martin and Whitfield, 1983).

Tentative mass balance of dissolved aluminum

Taking into account the fluxes of dissolved Al at the boundaries of the western Mediterranean estimated above, we have presented the tentative mass balance of dissolved Al in the western Mediterranean in Fig. 14. The total inputs amount to



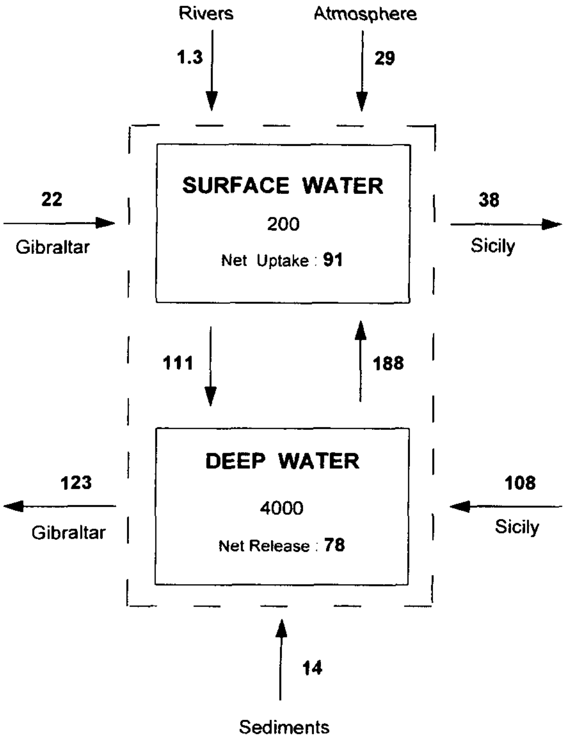
Numbers in **bold** are fluxes in 10^3 km^3 y^{-1}. Voume is in 10^3 km^3

Fig. 13. Water budget for the western Mediterranean.

174×10^3 t Al year^{-1} and the output 161×10^3 t year^{-1}. These two fluxes are remarkably well balanced, which lends some confidence in the boundary fluxes estimated here.

A more detailed budget can be established by considering a two-layer model and the water budget proposed by Bethoux (1980). From the mean concentrations of dissolved Al in deep and surface waters obtained in this study, as well as the upwelling and downwelling water fluxes of Bethoux (1989), we have calculated the rate of vertical transfer of dissolved Al. As shown in Fig. 14, there is a net input of 77×10^3 t Al year^{-1} to the surface waters due to the much higher dissolved Al content in the deep waters. A mass balance for the surface layer indicates an excess input of 91×10^3 t Al year^{-1}. We have shown in previous sections that this excess dissolved Al could be consumed due to biological activity and mainly by diatoms. The biological uptake also can be estimated from the difference between the integrated vertical profile of dissolved Al during winter and summer (see Fig. 8). Assuming that the water column is well mixed in the upper 150 m, the summer profile indicates that about 5 mmol Al m^{-2} year^{-1} are consumed in the surface water of the northwestern Mediterranean Sea. If we extrapolate this value to the entire western Mediterranean, we obtain a net biological uptake flux of 110×10^3 t Al year^{-1} which is close to the value obtained from the mass balance applied to the surface waters. The higher value obtained here is probably due to the fact that the vertical profiles were taken in an area where intensive vertical mixing occurs relative to the deep water formation. This biogenic aluminum is exported to the deep waters as particulate material by settling of the biological debris.

For the deep water, similar calculations indicate that the total input is 233×10^3 t Al year^{-1} and the total output 311×10^3 t Al year^{-1}. The difference of



Numbers in **bold** are fluxes in 10^3 ton Al y^{-1}. Mass is in 10^3 ton Al.

Fig. 14. Mass balance of dissolved Al in the western Mediterranean.

78×10^3 t Al year^{-1} can be easily attributed to the dissolution of biogenic siliceous skeletons, which occurs rapidly in the water column (Wollast, 1974). This means that 85% of the biogenic material containing Al is dissolved in the deep water column during settling. The flux of the particulate biogenic Al reaching the sea floor is thus only 13×10^3 t year^{-1}. This value is similar to the diffusive pore water fluxes of dissolved Al estimated above, indicating that the sediment is not a sink for dissolved Al. It should be pointed out, however, that the calculated rate of deposition of biogenic Al results from the differences between larger numbers and indicates only the order of magnitude of this flux.

There are two important inputs of dissolved Al to the western Mediterranean, one from the atmosphere and one from the eastern Mediterranean (Fig. 14). If we make a mass balance for the eastern Mediterranean, we need a total input of 70×10^3 t Al year^{-1} in order to sustain the export of this element to the western Mediterranean. It is likely that this input is mainly supplied by the atmosphere, considering the fact that the surface area of the eastern Mediterranean is almost twice that of the western Mediterranean and assuming similar atmospheric deposition rate.

We have assumed in the mass balance presented above that the system is at steady-state. It is possible to use this mass balance to construct a predictive model describing the response of the system to changing conditions. This model describes fluxes between the three reservoirs that are considered homogeneous (see Fig. 15). All the advective terms are simple first-order relations between the concentration of dissolved Al and water flux. The only exception is the part of the cycle linked to biological activity. As a first approximation, one can nevertheless assume that the uptake of Al by the phytoplankton is simply proportional to the concentration of dissolved Al. For the deep water box, we have not distinguished the dissolution of biogenic Al occurring in the water column during settling from that dissolved after deposition and diffused back to the water column. In other words, we have considered that the amount of dissolved Al consumed in the photic zone is released by the dissolution of the biological debris in the deep water reservoir. The model is then reduced to three equations expressing the mass balance of each reservoir.

One interesting application of the constructed first-order model is that it allows us to test the relative importance of the atmospheric input in the distribution of dissolved Al. A simple calculation indicates that the dissolved Al concentrations are reduced by a factor of 2.0 for the surface water of the western Mediterranean, by 2.2 for the deep water and by 2.5 for the eastern Mediterranean, if the atmospheric input to the entire Mediterranean is decreased by a factor of three with respect to the present-day flux. This confirms that the high concentration of dissolved Al observed in the Mediterranean can be attributed to higher atmospheric input compared to the mean value found for the world ocean.

CONCLUSIONS

It is not surprising that the most important dissolved Al fluxes are associated with the general water circulation in the western Mediterranean. This is due to (1) the huge water fluxes at the straits and those related to vertical exchange, and (2) the large differences in

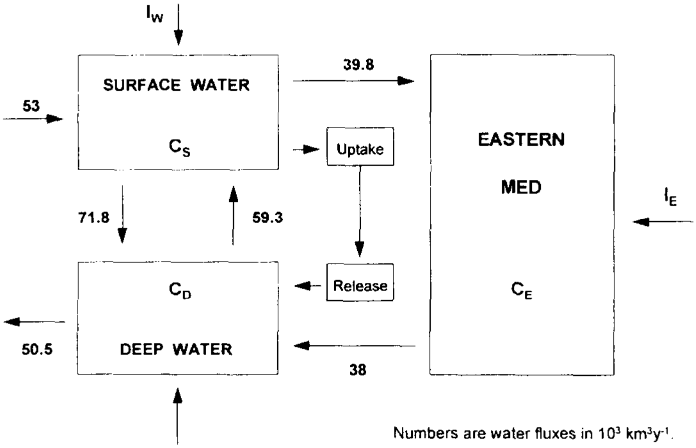


Fig. 15. First-order box model of dissolved Al in the western Mediterranean. C_S and C_D represent, respectively, the concentrations of dissolved Al of surface and deep waters in the western Mediterranean. C_E denotes the concentration of dissolved Al in the eastern Mediterranean. I_W and I_E are the fresh water inputs (atmospheric plus river) of dissolved Al to the western and eastern Mediterranean, respectively. Concentrations are in mg m^{-3} and inputs in 10^3 t year^{-1} (see text).

dissolved Al concentrations between the surface and deep waters of the western Mediterranean and between the Atlantic inflow water and the deep Mediterranean outflow water. The budget of dissolved Al in the western Mediterranean (Fig. 14), based on the water budget of Bethoux (1980) and Bethoux (1989), is well balanced and gives some confidence in the conclusions that can be drawn from the fluxes involved.

The fluxes at the straits of Gibraltar and Sicily are indeed relatively large compared to those at the interfaces. The western Mediterranean imports a net flux of 70×10^3 t Al year^{-1} from the eastern Mediterranean and exports a net flux of 101×10^3 t Al year^{-1} to the Atlantic. In order for the eastern Mediterranean to sustain the export of 70×10^3 t Al year^{-1} to the western Mediterranean, it requires a net equivalent input of dissolved Al, which is most likely of atmospheric origin.

There is an intensive vertical circulation linked to the formation of cold dense water masses in the northwestern Mediterranean in the winter. A net flux of 77×10^3 t Al year^{-1} is upwelled from the deep water, which helps to maintain the relatively high concentration observed in the surface water of the western Mediterranean.

One can calculate a theoretical renewal time of dissolved Al in the western Mediterranean by considering the total Al content (4200×10^3 t) in the system and the input fluxes due to external sources (river and atmosphere: 30×10^3 t Al year^{-1}). This renewal time, 140 years, is four times longer than the residence time of the water masses in the system, indicating the large influence of the water circulation at the straits on the Al budget.

If we consider the sources of dissolved Al at the boundaries of the marine system, it is clear that the atmosphere constitutes by far the largest external source, as suggested by several authors (Hydes, 1979, 1983; Measures *et al.*, 1984, 1986; Orians and Bruland, 1985, 1986; Prospero *et al.*, 1987; Hydes *et al.*, 1988). The contribution of river input represents only 3.5% of the atmospheric input. At the sediment–water interface, there is a small input from the pore waters, but this dissolved flux is compensated almost exactly by an output of particulate Al present in biological debris. This reactive particulate Al originates from the uptake of dissolved Al by phytoplankton in the photic zone. Therefore, the sediment in the western Mediterranean is neither a source nor a sink for dissolved Al.

There are other convincing arguments obtained in this study in favor of biological control to explain the high reactivity of Al in surface waters of the western Mediterranean. The very good correlation between dissolved Al and Si (see Fig. 7) suggests that the uptake of Al is due to the incorporation of this element in the siliceous skelets of diatoms. The seasonal pattern, indicating a progressive depletion of dissolved Al in the photic zone from winter to summer, also supports this hypothesis (see Fig. 8). One can calculate as above the renewal time of Al in the surface water due to biological activity, which is only 2.2 years. Similarly, it would take 51 years to renew dissolved Al in the deep water by dissolution of the organic debris. These values confirm the high reactivity of dissolved Al in the marine system.

In summary, the present study provides consistent explanations for the anomalous biogeochemical behavior of dissolved Al in the western Mediterranean. The high concentrations of this element can be explained by the large atmospheric input related to Saharan dust storm events. Renewal times of dissolved Al in the water column indicate that perturbations of the fluxes at the boundaries may significantly modify the distribution and dissolved concentration of this element in the whole system within time scales of a few decades. At present, the net dissolved Al input to the western and eastern Mediterranean is exported to the Atlantic Ocean.

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