

Distribution and origin of dissolved aluminium in the English Channel

English Channel
North Sea
Dissolved Al
Dispersion
Seine

Manche
Mer du Nord
Al dissous
Dispersion
Seine

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ABSTRACT

The distribution of dissolved Al in the Channel along the English coast shows the existence of a strong gradient of this element extending over a distance of several hundred nautical miles. These profiles suggest that wind-driven export from the North Sea to the Channel is seasonally important. These findings confirm the predictions of the recent circulation models of Salomon and Breton (1991). A gross mass balance of dissolved Al in the Channel indicates that the input of the river Seine is insignificant and that the contribution of other minor fresh water sources cannot account for the observed values. The input of dissolved Al from the North Sea seems thus to be the most likely largest source of this element in the Channel. This could also be the case for other trace metals exhibiting similar gradients across the Dover Strait.

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RÉSUMÉ

Distribution et origine de l'aluminium dissous dans la Manche

La distribution de l'aluminium dissous le long de la côte anglaise de la Manche montre l'existence d'un fort gradient de cet élément qui s'étend sur une distance de plusieurs centaines de milles marins. Ces profils suggèrent qu'il existe une exportation d'eau de la Mer du Nord vers la Manche engendrée par le vent, qui peut être saisonnièrement importante. Ces résultats sont en accord avec les prédictions des modèles de circulation récents de Salomon et Breton (1991). Un bilan de matière approximatif de l'aluminium dissous dans la Manche indique que l'apport de la Seine est négligeable et que les autres sources d'eau douce, qui sont mineures, ne permettent pas d'expliquer les concentrations observées. L'apport d'aluminium par la Mer du Nord semble être la source principale de cet élément dans la Manche. Ceci pourrait aussi être le cas pour d'autres éléments en traces qui manifestent un gradient de concentration similaire au travers du Pas de Calais.

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INTRODUCTION

Exchanges through the Dover Strait constitute a major source of nutrients and trace elements for the southern bight of the North Sea. It has been generally accepted that there is a net flux of dissolved constituents from the Channel to the North Sea, corresponding to the direction of

the residual flow of water. Fluxes of dissolved elements through the Channel are usually calculated by multiplying the net annual water flux by their mean concentrations found at the Dover Strait (Statham, 1993). However, the circulation pattern in the area of the Strait is rather complex and is strongly dependent on meteorological conditions. A more careful approach is thus required in order to better evaluate the fluxes between the Channel and the North Sea.

Physical models and measurements indicate that the mean annual flux of water from the Channel to the North Sea is of the order of $130,000 \text{ m}^3/\text{s}$ (Salomon and Breton, 1991; Prandle, 1993; Salomon *et al.*, 1993). The tidal component of this flux ranges from $27,000$ to $40,000 \text{ m}^3/\text{s}$, indicating that the principal flux is mainly a result of the mean wind stress (Pingree and Griffiths, 1980; Pingree and Maddock, 1985; Salomon and Breton, 1991). Using a mathematical model describing the transport and dispersion of radionuclides in the Channel, Salomon *et al.* (1991) have calculated that, for a permanent and average wind-tide situation, the total flux at the Dover Strait is $119,000 \text{ m}^3/\text{s}$. Starting from this steady-state condition, the flux is reduced to $27,000 \text{ m}^3/\text{s}$ if no wind stress is applied for two months. Starting again from the equilibrium state, the flux at the Strait was further reduced to $10,000 \text{ m}^3/\text{s}$ if the same wind stress, but from the east, is applied during one month. Using a similar approach, Salomon *et al.* (1993) examined real monthly wind-tide situations over a period of nine years (1983-1991) and found an average annual flow of $114,000 \text{ m}^3/\text{s}$ with a high monthly variability.

Detailed tide-related trajectories indicate that there is a net residual current from the North Sea to the Channel along the English coast all the way to the Isle of Wight (Salomon and Breton, 1991). Salomon and Breton (1993) used a two-dimensional mathematical model to calculate the long term trajectories and velocities of water masses in the Channel under various tide and wind directions. Their results show that the flow direction in the Channel can be from the east to the west if the wind is blowing from the north, north-east or north-west. Many dissolved trace elements exhibit much higher concentrations in the southern bight of the North Sea than in the Channel, due to riverine and coastal inputs (Kremling, 1985). Therefore, even if the water fluxes from the North Sea to the Channel are small, the corresponding metal fluxes may be significant, especially along the English coast. Furthermore, tidal circulation induces a strong longitudinal dispersion along the axis of the Channel across the Strait. Due to the high concentration gradient, an important diffusive flux of some dissolved metals may thus be additionally transferred from the North Sea to the Channel.

Dissolved Al is known to be a good tracer of water masses of different origin. For example, Measures and Edmond (1988) have successfully used dissolved Al concentration in combination with the salinity data to identify the Levantine Intermediate Water enriched in dissolved Al at the outflow of the Mediterranean into the North Atlantic through the Strait of Gibraltar.

Atlantic waters of the upper 1000 m contain concentrations of dissolved Al from 3 to 40 nM (Hydes, 1983; Kremling, 1985; Chou, unpublished). In the southern bight of the North Sea, concentrations of dissolved Al are found to comprise from 10 to 210 nM (Kremling, 1985; van Beusekom, 1988; Hydes and Kremling, 1992; this study). Rivers entering the southern bight of the North Sea have dissolved Al concentrations of 1150 nM using the data of Kremling (1985) extrapolated to zero salinity, 1300 nM for the Rhine (Hydes and Kremling, 1992), and 200 nM for the

Scheldt (Chou, unpublished). This indicates that dissolved Al in various aquatic environments exhibits significantly different concentrations.

In this study, we have investigated the distribution of dissolved Al in the Channel in order to explore the "unconventional" thinking of a possible transfer of certain dissolved trace metals from the North Sea to the Channel through the Dover Strait. We have concentrated our sampling stations along the English coast where the influence of the North Sea inputs is more likely to be the greatest.

MATERIAL AND METHODS

Surface waters of the Channel were collected at - 3 to - 5 m on board the *R/V Belgica* using Go-Flo bottles (General Oceanic) mounted on stainless steel hydrowire. Sampling locations are shown in Figures 1 a-c for cruises conducted in July 1990, June-July 1991 and June 1992 respectively. Samples were filtered through pre-acid washed $0.45 \mu\text{m}$

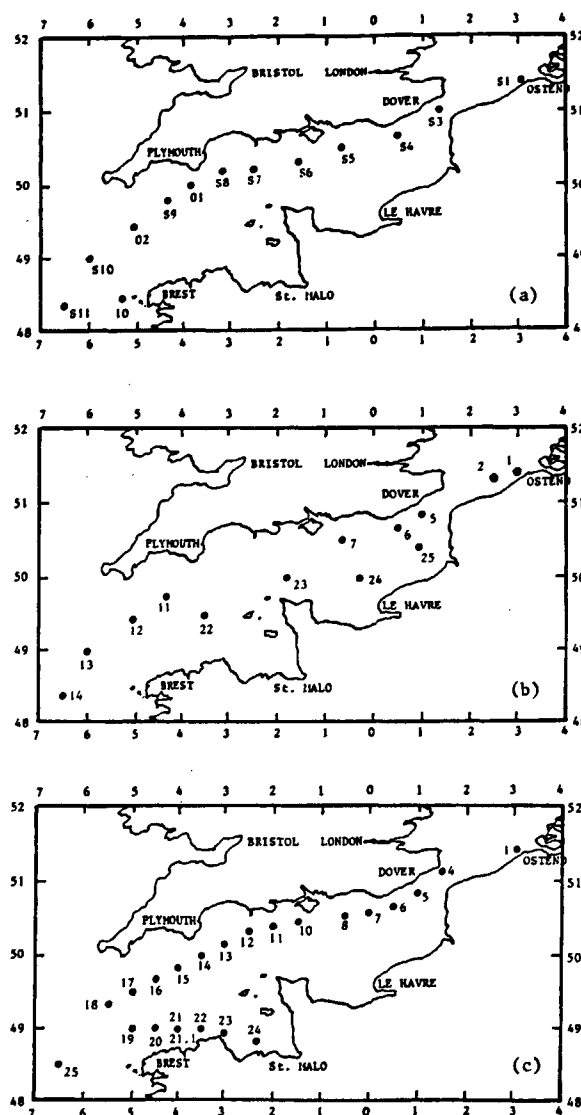


Figure 1

Sampling locations for the July 1990, June-July 1991 and June 1992 cruises conducted in the English Channel.

Millipore filters or 0.4 μm Nuclepore filters. Filtrates were collected for dissolved Al and Si analysis in the laboratory and acidified with Merck suprapure concentrated HCl (50 $\mu\text{l}/100\text{ ml}$) to avoid adsorption on to the container walls. Preliminary measurements performed on board demonstrated that the acidification has no detectable influence on the analysis. Tests conducted on board on samples filtered with both 0.45 and 0.1 μm Millipore filters also showed no significant affect on the results of dissolved Al concentration.

Dissolved Al was determined by the fluorimetric method described in Hydes and Liss (1976). Standard additions were made to avoid interferences due to fluoride and other organic complexing agents present in sea water. Dissolved Si was analyzed colorimetrically following the method described in Grasshoff *et al.* (1983). Salinity and temperature data were collected with a CTD rosette (Sea-Bird Electronics).

RESULTS

Results of salinity, temperature, dissolved Al and Si are summarized in Table 1 for the three cruises conducted in this study. Figures 2 *a* and *b* show the vertical distributions of salinity along the transects on the English side of the Channel for July 1990 and June 1992 respectively, indicating that the penetration of Atlantic water into the Channel was much less extensive in July 1990 due to the prevailing NE wind. At the same time, the intrusion of low-salinity water from the North Sea into the Channel along the English coast is much more pronounced in July 1990. It is worth noting that there is little variation in the vertical distribution of salinity, indicating a good vertical mixing inside the Channel.

Figures 3 *a* and *b* show as an example the longitudinal distributions of dissolved Al and Si along the English coast from Dover to the mouth of the Channel for June 1992. The very high values for dissolved Al and the strong concentration gradient observed near the Dover Strait clearly point to an input of North Sea water where the concentration of dissolved Al reached 268 nM for a salinity of 32.47. The high concentration observed at Station 10 suggests a local fresh water input rich in dissolved Al, probably originating in the Solent or from a local waste water discharge. At station 16, a slight increase in dissolved Al is also observed. Since fresh water input in this region is negligible, this could be explained by the occurrence of fronts originating in the deeper part of the Atlantic, enriched in dissolved Al. As may be seen in Table 1, similar situations were observed in 1990 and 1991, although the concentrations of dissolved Al in the North Sea end member were lower in these two years. The distribution of dissolved silica observed in 1992 (Fig. 3 *b*) is completely different. Low concentrations are found near the Dover Strait, reflecting the fact that silica is strongly depleted in the southern bight of the North Sea due to the spring blooms of diatoms. Higher concentrations observed at stations 10 and 11 confirm a local fresh water input enriched in dissolved Si. At station 16, an increase in dissolved Si is also pronounced, probably also due to the front arriv-

Table 1

Summary of results obtained for surface sea water samples collected during the July 1990, June-July 1991 and June 1992 cruises conducted in the English Channel.

Station	Temperature ($^{\circ}\text{C}$)	Salinity	nM Al	μM Si
JULY 1990				
S1	16.40	34.960	53.3	0.41
S3	15.04	35.035	32.2	0.38
S4	14.95	35.072	37.0	0.36
S5	15.22	34.988	43.3	0.54
S6	14.13	35.228	29.6	0.46
S7	13.98	35.197	21.5	1.55
S8	13.95	35.227	18.1	1.06
01	13.87	35.293	12.2	0.30
S9	13.88	35.336	11.1	0.26
02	13.17	35.412	9.6	0.37
S10	14.46	35.259	7.8	0.67
S11	15.08	35.400	7.8	0.51
10	15.26	35.450	5.9	0.43
03	15.39	35.610	3.0	0.41
JUNE-JULY 1991				
1	14.45	34.090	181.9	0.91
2	13.23	34.860	47.4	0.28
5	11.90	35.200	19.8	0.47
6	11.85	35.200	19.3	0.42
7	13.21	35.080	23.9	0.46
11	13.23	35.320	5.3	0.41
12	13.53	35.320	6.6	0.91
13	13.76	35.390	9.6	0.39
14	14.16	35.490	7.3	0.39
22	12.83	35.100	7.5	2.92
23	13.06	35.200	13.7	0.97
24	13.12	34.830	23.1	0.67
25	13.93	35.150	13.6	0.48
JUNE 1992				
1	17.47	32.470	268.0	1.74
4	14.97	34.980	101.3	0.59
5	13.86	35.240	76.5	0.38
6	13.44	35.290	64.1	0.41
7	12.80	35.280	48.5	0.38
8	13.29	35.280	44.1	0.27
10	15.08	35.050	88.9	0.88
11	13.77	35.340	50.8	1.15
12	13.96	35.300	40.1	0.80
13	12.95	35.440	20.5	0.19
14	12.87	35.370	19.3	0.79
15	13.55	35.520	14.1	1.24
16	14.40	35.520	20.8	1.70
17	13.82	35.530	15.8	1.03
18	13.21	35.530	6.0	0.69
19	12.70	35.530	8.1	0.85
20	13.12	35.510	19.7	1.36
21	13.01	35.490	14.0	1.31
22	13.25	35.460	19.4	1.09
22.1	13.69	35.420	27.5	1.41
23	14.89	35.340	36.4	1.30
24	14.80	35.340	23.9	1.34
25	14.28	35.580	2.6	0.08

ing from the deeper part of the Atlantic, containing higher concentrations of dissolved Si. The dissolved nitrate data confirms this hypothesis (M. Elskens, personal communication). The conclusion to be drawn is that dissolved silica is a less suitable tracer for inputs from the North Sea.

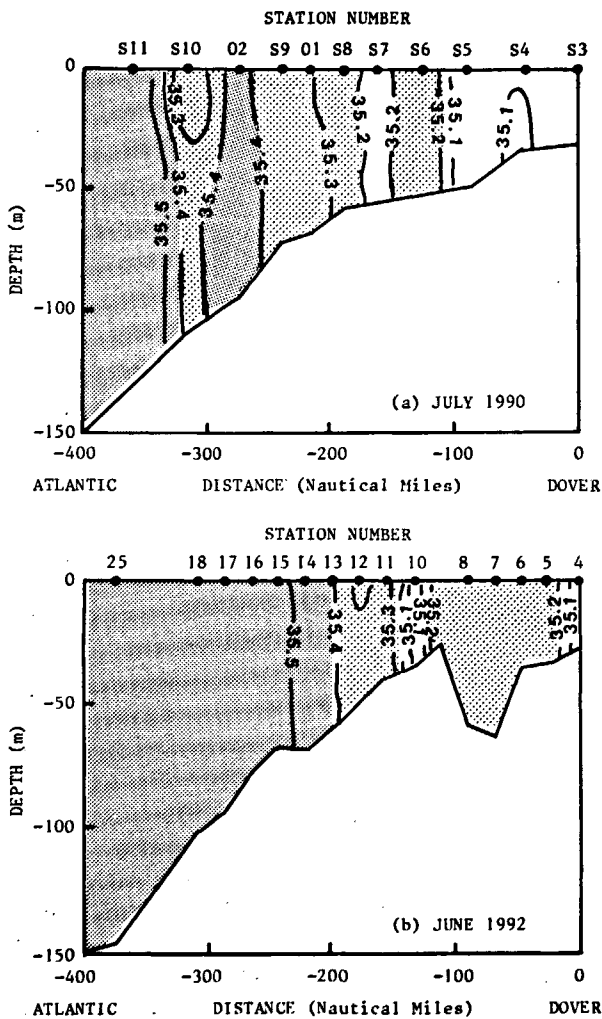


Figure 2

Vertical distribution of salinity along the transects in the English part of the Channel for the July 1990 (a), and June 1992 cruises (b). The more densely dotted area represents water of salinity > 35.4, the less densely dotted area water of salinity between 35.2 and 35.4, the undotted area water of salinity < 35.2.

Table 2

Summary of results obtained for samples collected in November 1992 in the Seine estuary.

Sample N°	Salinity	nM Al	µM Si	Distance to the mouth*(km)
Poses-1	0.0	630	154	175
10	0.22	554	161	42
11	0.22	183	150	34
12	0.5	105	140	32
19	2.87	130	138	15
21	8.98	103	107	14
23	19.8	82	69.1	2
16	22.27	106	47.4	49°26'01 N 0°06'01 E
17	26.14	96	45.5	49°27'53 N 0°01'08 E
14	34.76	42	3.8	49°36'44 N 0°21'12 W

*Distance to the mouth along the river Seine is taken with respect to the mouth of the estuary which is situated in front of Le Havre.

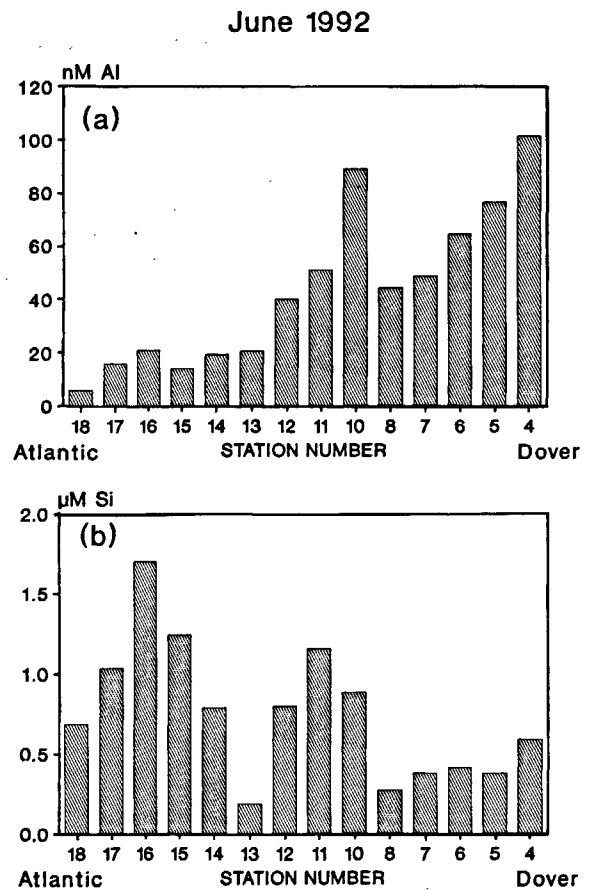


Figure 3

Longitudinal distribution of dissolved Al (a) and Si (b) in the English part of the Channel for the June 1992 cruise.

The English Channel can be described, to a certain extent, as an estuary subject to strong tidal influence (Salomon and Breton, 1991). In such a system, the mixing of dissolved elements can be examined by their distribution in relation to salinity, which may indicate their conservative or non-conservative behaviour. Figure 4 shows the concentration of dissolved Al as a function of salinity for the three cruises. In all cases, the relationship between dissolved Al and salinity along the English coast deviates from a straight line and is better described by an exponential decay function. This behaviour will be discussed later.

In 1991 and 1992, a few points were sampled along the French coast of the Channel. In the western part, corresponding to the high salinity range, the concentrations are similar on the English and French sides, which is in agreement with the circulation model by Salomon and Breton (1991). However, in the Baie de Seine, station 24 (1991) with low salinity (34.83) exhibits a concentration of dissolved Al of only 23 nM. This station is situated in the gyre that captures waters discharged by the river Seine. It is interesting to point out that Kremling and Hydes (1988) obtained for dissolved Al in the Western Channel and the Baie de Seine values similar to those observed in this study for the 1990 and 1991 cruises.

In order to investigate the origin of this low value, we performed measurements of the concentration of dissolved Al

and Si in the Seine estuary, covering the entire range of salinity. The results are shown in Table 2 and Figure 5. The concentration of dissolved Al in the fresh water reaches 600 nM, which is in the usual range observed in rivers. It drops to around 100 nM as soon as the salinity exceeds 1 and then behaves almost conservatively at higher salinities. Dissolved Si shows a similar profile. It exhibits a sharp drop in the fresh water part and then decreases almost linearly with increasing salinity from 140 μM upstream to 4 μM at the mouth of the Seine. The conservative mixing

Seine Estuary November 1992

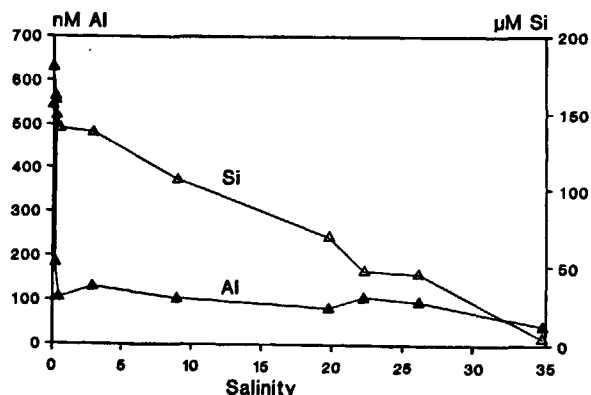


Figure 5

Dissolved Al and Si as a function of salinity for the Seine estuary.

behaviour is what one would usually expect in an estuary during periods of low diatom productivity.

A similar situation has been observed in the Tamar estuary (Morris *et al.*, 1986). Removal of dissolved Al is initiated at the up-estuarine extremity of the turbidity maximum which coincides also with the limit of salt intrusion. Further seaward, dissolved Al concentrations decrease regularly towards the lower concentrations prevalent near the marine boundary. The decrease of dissolved Al at low salinities has been attributed by these authors to sorption of this element by suspended matter, which is especially important in the pronounced turbidity maximum that occurs in the Tamar estuary. Despite the major input of fresh water by the river Seine, its influence on dissolved Al in the Channel remains limited because of the low values of the concentration of this element observed in the estuarine region, due to its removal in the fresh water part of the river.

DISCUSSION

The longitudinal profile of dissolved Al observed in the Channel along the English coast is characterized by a marked gradient starting from the Dover Strait. This gradient can only be the result of an input from the Southern Bight of the North Sea. Longitudinal dispersion due to tidal action is insufficient to explain the intrusion of dissolved Al over the distances observed. For a longitudinal dispersion coefficient of the order of 1000 m^2/s and a residual velocity of about 0.02 m/s (Salomon and Breton, 1991), the distance over which this gradient would be observed could not exceed 50 km (30 nautical miles). On the other hand, the longitudinal distribution of dissolved Al along the English coast can be explained by the existence of residual currents oriented westward along that coast, which may be especially important during northeasterly wind events.

It is possible to evaluate roughly this exchange by considering a mass balance budget of dissolved Al for the Channel. If we take a mean concentration of dissolved Al at the Strait of the order of 50 nM and a mean flux of water of 130,000 m^3/s , this represents a flux equal to 6.5 moles

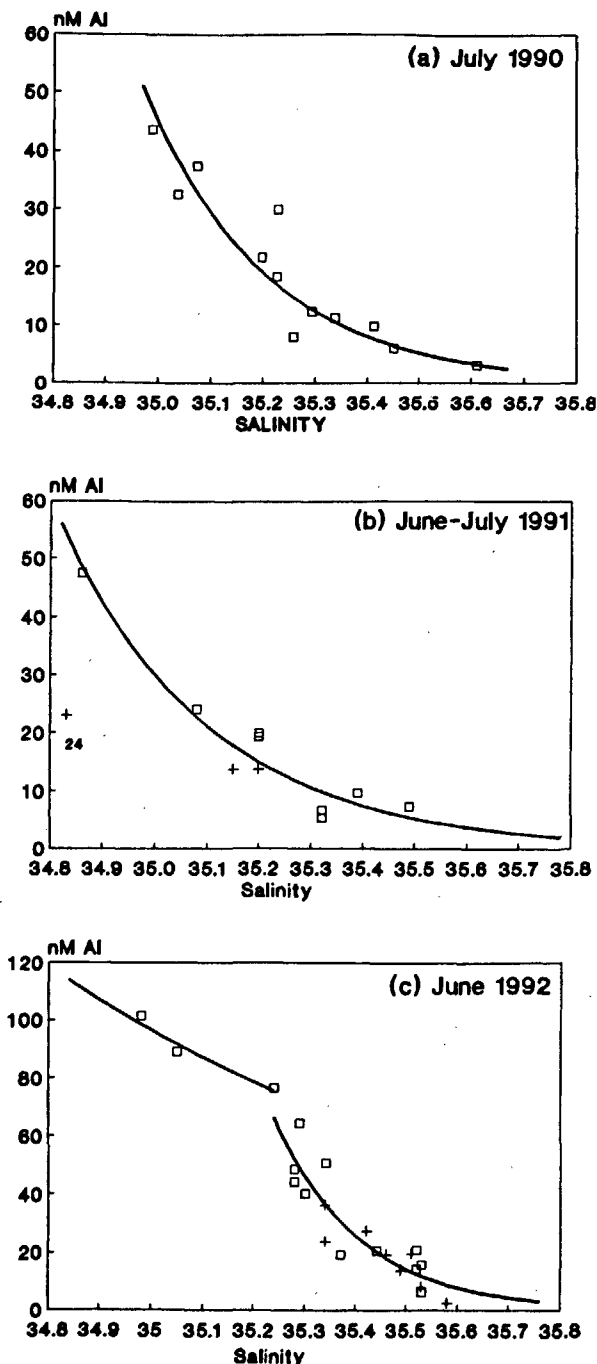


Figure 4

Dissolved Al as a function of salinity for the July 1990 (a), June-July 1991 (b), and June 1992 (c) cruises. Data obtained for samples from the English coast are represented by symbol \square and from the French coast by $+$. Curves indicated in the figures depict the best fit of the data points with exponential functions.

Al/s. The input flux of Al from the Atlantic may be estimated to be 1 mole/s, if a mean concentration of 7 nM for the Atlantic water is used. The total input of fresh water in the Channel from the continent has been carefully evaluated by Taylor *et al.* (1981) and a value of around 900 m³/s was found. If all the missing Al (5.5 moles/s) is coming from the fresh water input, then its concentration should be equal to 6 µmoles/l which is very excessive. We have seen that the major riverine water input of dissolved Al to the Channel from the river Seine, which accounts for approximately 50 % of the freshwater input, is very small. It may be estimated to be 0.045 moles Al/s for a concentration of 100 nM (Tab. 2) and a mean river discharge of 450 m³/s. Even if all the other sources are far more concentrated, it is not possible to explain the observed fluxes at the Dover Strait without evoking another external source. Thus, a missing flux of 5 moles Al/s at the Dover Strait seems to be a reasonable lower estimate. Assuming a concentration of 100 nM Al in the water of the southern bight of the North Sea which is exported to the Channel, this requires a flux of water of the order of 50,000 m³/s. This value is of the same order of magnitude as for the fluctuations of water fluxes when the wind direction shifts from the west to the east, which is about 100,000 m³/s according to the model calculations of Salomon *et al.* (1991).

We have shown in Figure 4 that the evolution of the concentration of dissolved Al as a function of salinity is not linear and is better described by an exponential decrease. One possible explanation for this observation is the non-conservative behaviour of dissolved Al during mixing of North Sea water with North Atlantic water.

In addition to physico-chemical reactions affecting dissolved Al, as observed in the Tamar and Seine estuaries, this element can also be actively involved in biological processes (Mackenzie *et al.*, 1978; Caschetto and Wollast 1979; van Beusekom, 1988; Chou and Wollast 1990; 1991 and 1992), which results in a non-conservative behaviour. The lack of correlation of dissolved Al and Si (Fig. 3) does not, however, favour this hypothesis.

An alternative explanation is the mixing of several water masses in the Channel representing different end members. One can easily identify, for example, intermediate or surface water of the North Atlantic flowing in the middle of the Channel, water of the Baie de Seine strongly influenced by fresh water input with low dissolved Al content, water from the Solent with much less fresh water influence but with a high Al content and finally North Sea water.

Lateral gradients of composition between English and French coasts can result in mixing. The lateral dispersion coefficients are, however, generally small but can nevertheless give rise to departure from an ideal mixing curve, since

more than two end members are involved. The results obtained in our study do not allow us, however, to distinguish at present between the various mechanisms. It should be pointed out that if dissolved Al does not behave conservatively during mixing and is removed due to physico-chemical or biological processes in the Channel, then the missing input flux of this element would be even greater than what was calculated above (5 moles Al/s).

CONCLUSIONS

One of the objectives of this study was to investigate the possibility of using trace elements as characteristic parameters to identify and to quantify water masses. Dissolved Al has been demonstrated as an interesting tracer for this purpose. Mass balance calculations of this element indicate that the main source of dissolved Al in the Channel is the input from the North Sea. If we consider the distribution of the concentration of other trace elements (Kremling, 1985), several metals show also high concentration gradients across the Dover Strait and all the way to the mouth of the Channel. This suggests that there can also be a significant input of these metals from the North Sea.

In order to obtain more reliable estimates of fluxes between the North Sea and the Channel and to verify existing physical models, it is necessary to investigate further the conservative or non-conservative behaviour of dissolved Al. More detailed scrutiny of the vertical and horizontal distributions of dissolved Al in the vicinity of the Dover Strait and the southern bight of the North Sea would provide further information on the exchange between the southern bight of the North Sea and the Channel.

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