

Fluxes of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn through the Strait of Dover into the southern North Sea

Dissolved trace metals
Particulate trace metals
Seawater
Fluxes
Strait of Dover

Métaux-traces dissous
Métaux-traces particulaires
Eau de mer
Flux
Détroit du Pas-de-Calais

Peter J. STATHAM^a, Yves AUGER^b, J. Dennis BURTON^a, Pascale CHOISY^b,
Jean-Claude FISCHER^b, Rachael H. JAMES^a, Nicholas H. MORLEY^a,
Baghdad OUDDANE^b, Émile PUSKARIC^b and Michel WARTEL^b

^a Department of Oceanography, University of Southampton, Southampton SO9 5NH, U.K.

^b Université des Sciences et Techniques de Lille-Flandres Artois, Laboratoire de Chimie Analytique et Marine, Bâtiment C8, 59655 Villeneuve d'Ascq Cedex, France.

ABSTRACT

Measurements of dissolved and particulate Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn have been made on a regular basis over a fifteen month period at stations across the Strait of Dover, as a part of the *Fluxmanche* programme. These measurements have been integrated with data on fluxes of water and suspended particulate matter also obtained within the *Fluxmanche* programme to provide estimates of fluxes of these elements into the southern North Sea. For Fe, Mn, and Pb, particulate fluxes are greater than dissolved fluxes, whilst the reverse is true for Cd, Cu and Ni. Significant daily changes in magnitude of the modelled fluxes of water through the Strait when combined with averaged metal concentrations over longer timescales, result in large changes of fluxes of metals on a day to day basis. However, relatively small changes are evident for integrated autumn fluxes of metals for consecutive years using the available database. The annual fluxes of dissolved plus leachable particulate metals through the Strait of Dover relative to the most recent estimates of riverine and atmospheric inputs to the North Sea were in the order Cu (44 %) > Cd (39 %) > Zn (16 %) > Pb (11 %).

Oceanologica Acta, 1993. 16, 5-6, 541-552.

RÉSUMÉ

Flux de Cd, Co, Cu, Fe, Mn, Ni, Pb et Zn du détroit du Pas-de-Calais vers la Mer du Nord

Les teneurs en Cd, Co, Cu, Fe, Mn, Ni, Pb et Zn (phases dissoute et particulaire) ont été déterminées chaque mois, de septembre 1990 à novembre 1991, en six sites dans le détroit du Pas-de-Calais. Les flux de ces éléments vers la Mer du Nord ont été déduits des flux d'eaux et de matières en suspension estimés dans le cadre du programme *Fluxmanche*. Pour Fe, Mn, et Pb, les flux particuliers sont supérieurs aux flux des métaux dissous, contrairement à Cd, Cu et Ni. Si des variations importantes de ces flux peuvent être observées d'une campagne à l'autre, elles deviennent faibles entre deux périodes automnales consécutives. Les rapports des flux des métaux (dissous + mobilisables) dans le détroit du Pas-de-Calais aux flux des métaux provenant de l'atmosphère et des rivières sont de l'ordre de 44 % pour Cu, 39 % pour Cd, 16 % pour Zn et 11 % pour Pb.

Oceanologica Acta, 1993. 16, 5-6, 541-552.

INTRODUCTION

Water flow through the Strait of Dover represents a major input of water and suspended particulate matter (SPM) into the southern part of the North Sea. Estimates vary (Postma, 1990), but this input from the Channel represents about 10 % of the total water input to the whole of the North Sea (ICES, 1983). For the southern part of the North Sea alone the advective input of water through the Strait of Dover is estimated to be even more important, as it is about five times that from the northern North Sea (ICES, 1983). Once introduced into the North Sea this water mixes predominantly with waters to the east, as indicated by radio-tracer studies (Salomon *et al.*, 1993) and as predicted from the generally accepted circulation in the North Sea (ICES, 1983). This substantial water flow through the Strait of Dover transports a range of chemical substances in both dissolved and particulate forms, and to these inputs in the southern region of the North Sea are added riverine and atmospheric contributions of metals and other chemicals from the adjacent land masses. The Strait of Dover input is thus potentially of importance in the geochemical budget for these elements in the southern North Sea. In particular how significant are they in relation to the anthropogenic and natural inputs from riverine and atmospheric sources to this area? Do these Strait of Dover inputs dilute concentrations of these materials already present, and are these components important in the overall geochemical budgets of these chemical substances?

The work reported here focuses on a range of trace metals, and provides estimates of fluxes into the southern North Sea. This research is part of the *Fluxmanche* programme, which has taken a multidisciplinary view of fluxes of water, SPM, and associated chemicals, through the Strait of Dover (SOD). Data on dissolved and particulate metals in samples collected at stations across the SOD has been combined with information on SPM and water fluxes from other parts of the *Fluxmanche* programme to generate estimates of the

fluxes of these elements into the North Sea. These data also provide an opportunity for studying the intra and inter-annual variability in fluxes, the relative importance of dissolved and particulate phases in the transport of metals, and the significance of these metal inputs in relation to other inputs into the southern North Sea.

SAMPLE COLLECTION

Sampling for dissolved and particulate trace metals was carried out on a monthly basis over a fifteen-month period from September 1990 to November 1991. Two depths were sampled at each of the six stations in the Strait of Dover (Fig. 1), and there were very few occasions when, because of bad weather, all samples were not taken. The sampling work alternated between the French and UK groups, except when inter-calibration work was undertaken.

Trace metal clean procedures originally developed for open ocean work were used throughout the sample collection and processing. Either an all-PTFE bellows pump connected to a weighted 12.5 mm internal diameter polyethylene tube, or 10 l Teflon lined Go-Flo sampling bottles were used for sample collection. The sampling bottles were deployed from a rosette on RRS *Challenger* or a Kevlar non-metallic line on *Pluteus*.

Due to its small size (19 m) no onboard sample processing was possible on *Pluteus*. Full containerised clean sample handling facilities were available for the other two vessels, supplied either by NERC (described in Morley *et al.*, 1988) or by IFREMER. On *Pluteus*, samples were taken into pre-cleaned 4.5 l low density polyethylene bottles and returned to shore for immediate subsequent filtration; during transport samples were stored in low-light and cool conditions. On *Noroit*, samples were taken into 4.5 l bottles and filtered on board immediately after completion of sampling. On board *Challenger*, samples were filtered directly from the Go-Flo

bottles, with no intermediate sample storage. In all cases samples were filtered under about 1 bar pressure, using either the Go-Flos or storage bottles as pressure vessels, through acid cleaned 142 mm diameter, 0.4 μm pore size Nuclepore filters, mounted in polypropylene holders. The gas used to provide pressure was either filtered nitrogen, or compressed air which had undergone extensive filtration and cleaning prior to use. In all cases the first litre of filtrate was discarded in order to thoroughly rinse the filtration system, prior to taking samples for dissolved trace metal analysis. Samples for dissolved trace metals were acidified by addition of 1 ml of sub-boiling distilled HNO_3 per litre of seawater, and stored in acid-cleaned (Morley *et al.*, 1988) low density polyethylene bottles. Used filters were rinsed with about 50 ml of Milli-Q water, in order to remove traces of salt, and then stored frozen in petri dishes. Seawater samples of between 3 and 10 l were filtered, which gave total particulate masses in the range 20 to 100 mg. Total suspended particulate matter (SPM) masses were determined by weighing air dried filters before and after sample filtration using a five figure balance; filters were

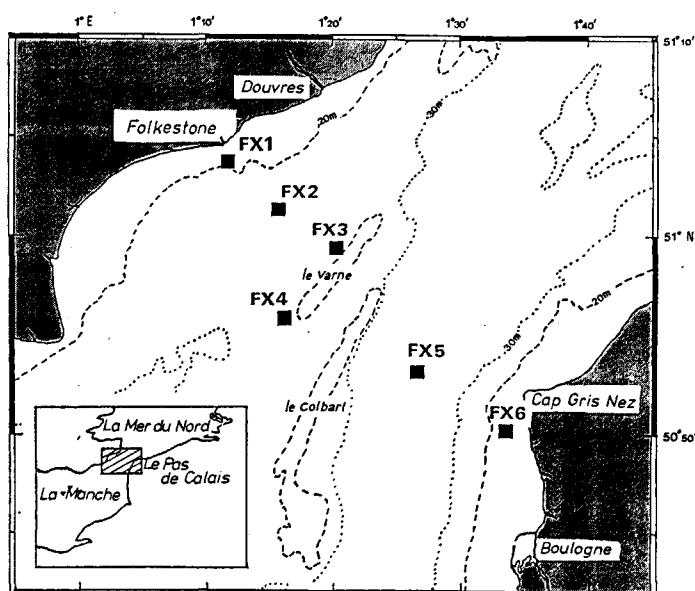


Figure 1

Location of Fluxmanche stations across the Strait of Dover.

equilibrated in a known humidity environment (over saturated ammonium nitrate solution; 63 % relative humidity at 20°C) prior to weighing.

ANALYSIS

Each laboratory analyzed the samples collected by them, as well as the inter-calibration samples.

Dissolved metals

Southampton

Analysis was carried out ashore under clean room conditions using the solvent extraction/graphite furnace atomic absorption spectrophotometry (GFAAS) of Danielsson *et al.* (1978) as modified by Statham (1985) and Tappin (1988). In this method the metals are complexed, at near neutral pH, with a mixed ammonium pyrrolidine dithiocarbamate / diethylammonium diethyldithiocarbamate (APDC/DDDC) reagent (0.2 % of each complexant) and extracted into 1,1,2-trichloro-1,2,2-trifluoroethane followed by back extraction into a final dilute nitric acid solution prior to determination of the metals by graphite furnace atomic absorption spectrometry. A relatively high complexant concentration is required in order to extract Mn quantitatively. The accuracies of the determinations are indicated by the general oceanographic consistency of the data obtained for open ocean samples, by satisfactory results obtained in inter-laboratory comparisons *e.g.* ICES (Berman and Boyko, 1987) and EROS-2000 (Elbaz-Poulichet *et al.*, 1989), and by results of analyses of reference samples (NASS-2 and CASS-2; NRCC Marine Analytical Chemistry Programme).

Lille

Dissolved Cd, Cu, Pb and Zn were determined in filtered samples by differential pulse anodic stripping voltammetry (DPASV) after acidification and addition of hydrogen peroxide (5 µl/ml) and ultra-violet irradiation (550W medium pressure lamp for 12 hours) in silica vials. A mercury coated rotating glassy carbon electrode and associated polarography unit (Rotel-2 EG&G) was used for the determination of Cd, Cu and Pb, whilst a PAR model 303 dropping mercury electrode in combination with a PAR 384 polarography unit was used for the determination of Zn. The Zn determination was done at a pH of 1 with additions of acetate buffer to prevent hydrogen wave interference. The technique is described in detail in Ouddane (1990).

Dissolved manganese was determined by direct graphite furnace atomic absorption spectrometry using a Pt matrix modifier (Skiker *et al.* 1988). Standard reference materials (NRCC marine analytical chemistry NASS-2 and CASS-2) were used to validate the method. Detection limit and precision estimates for dissolved trace metal measurements made at Southampton and Lille are given in Table 1.

Table 1

Detection and precision estimates for the analytical methods used for dissolved trace metals. ^a Three times the standard deviation of the blank.

Metal	SOUTHAMPTON (Althaus, 1992)		LILLE	
	Relative standard deviation (%)	Detection limit ^a (nmol/l)	Relative standard deviation (%)	Detection limit (nmol/l)
Cadmium	8	0.03	5-15	0.01
Cobalt	15	0.16		
Copper	8	1.1	5-15	0.40
Iron	15	1.8		
Manganese	5	0.8	10-15	0.9
Nickel	12	1.0		
Lead	11	0.04	5-8	0.04
Zinc	8	1.5	5-10	0.3

Inter-calibration for dissolved metals

In this type of study in which two laboratories are providing data which will be used together, it is crucial that the two data sets are accurate and comparable. As well as the use of standard seawater solutions and other procedures as described above, inter-calibration exercise for those elements determined by both laboratories were undertaken on replicate sub-samples of seawaters collected during the field work.

The agreement between Southampton and Lille for the elements determined by both groups (Cd, Cu, Pb, and Zn) is satisfactory as shown in Table 2, except for manganese in some cases. Whilst the pattern of concentrations of

Table 2

Inter-comparison of analytical methods used by the two laboratories (all concentrations in nmol/l; Lille data are means of triplicate determinations).

	Cd	Cu	Mn	Pb	Zn
Sample collected in July 1991 at Fluxmanche Station 4					
SUDO	0.14, 0.15	5.24, 5.55	9.67, 9.37	0.30	11.07, 11.32
LILLE	0.19±0.03	5.20±0.50	2.0±0.3	0.37±0.05	10.3±0.6
inter-calibration between SUDO and Lille (Skiker 1989)					
SUDO			28.4		
LILLE			25.8 ± 1		
inter-calibration for Manganese only, March 1992					
SUDO	36.2	110	4.1	14.0	70.5
LILLE	38.2±3.6	94.7±3.6	<1.8	5.8±0.91	47.3±3.6

manganese in samples are the same for both laboratories, in some cases in the inter-calibration there was variability, the cause of which is not clear. Because of the slightly better detection limit for the SUDO method for manganese, this provides the data base used here for flux calculations. This approach means a more uniform analytical technique has been applied, and circumvents problems of averaging values containing concentrations below the detection limit of the method, which occurred for some samples with the Lille method.

Particulate metals

Trace metals present in marine particulate and sedimentary materials are present in a variety of forms ranging from association with lattice sites in silicates or refractory minerals, to being weakly adsorbed at surfaces (Chester, 1990). The trace metals locked away in lattice sites and more refractory phases may be released into solution, where they can become involved in interactions in the milieu, on geological time scales. Of much greater importance from the point of view of environmental quality and shorter time-scale geochemical cycling are the trace metals present in the more labile phases. Once those trace metals present as adsorbed or weakly complexed material, or associated with carbonates, easily reduced iron and manganese oxides and other relatively reactive phases, are released into solution, they are then free to interact with biota and other components of the environment.

In this work therefore, a chemical leaching technique using 25 % acetic acid has been used to provide an empirical estimate of these environmentally available trace metals. This is the procedure recommended for non-total measurements in a recent ICES publication (Loring and Rantala, 1990). Filters were totally immersed in 5 ml of 25 % glacial acetic acid (quartz sub-boiling distilled) in 13 ml polyethylene centrifuge tubes. After 15 hours the samples were centrifuged and the supernatant transferred to 6 ml polypropylene tubes. It is important to maintain consistent analytical conditions (time, temperature, *etc.*) because of the non-total nature of the procedure. The residues were retained for future total digestion and analysis.

Determination of the metals brought into solution was by GFAAS, using the method of standard additions with palladium matrix modification (Bowell and Morley, personal communication) for Cd, Co, Cu, Ni and Pb, and by flame AAS, using a micro sampling technique in order to conserve sample, for Fe, Mn and Zn. Whilst standards exist for total metals in SPM, no such certified values exist for this partial leach method.

The total trace metal content of the SPM was also determined for most of the months. This determination was felt useful in providing an unequivocal estimate of the flux of metals (*i. e.* total), as well as providing an important comparator for the available metal measurements in a geochemical context. In the Southampton laboratory samples were brought into solution by a nitric-hydrochloric-hydrofluoric acid mixture using perfluoroalkoxy digestion vessels in a microwave digestion system. Metals in solution were measured by

flame or flameless AAS after addition of boric acid to ensure no precipitation of fluoride salts. At Lille samples were decomposed using a nitric/hydrochloric/hydrofluoric acid mixture in PFA bombs in a microwave oven. The excess acid was evaporated, and the residue was brought into solution by an acid leach prior to determination of Al, Fe, and Ca by inductively coupled plasma-atomic emission spectrometry, and Mn, Zn, Pb, Cd, and Cu by GFAAS. The accuracy of the measurements has been demonstrated by good agreement with certified values for Standard Reference materials (MESS-1 and BCSS-1).

DESCRIPTION OF THE DATABASE

Dissolved and particulate metals

The dissolved and particulate database is given in the Appendix. The database has been screened for any obvious outliers or other spurious data. Where there is no obvious reason to exclude an outlier (*i. e.* no noted problems in sampling or analysis), the point has been flagged. The concentrations reported here are of similar magnitude to other recent high quality metal data for the North Sea area (*e. g.* Tappin, 1988; Kremling and Hydes, 1988; *see* Tab. 3), although they are greater than the averaged values given in this other work. This feature in the data given here probably reflects the greater number of samples collected in the nearshore zone where higher concentrations are experienced, relative to this other work. Unless specifically noted to the contrary, discussion of the particulate phase work below refers to the leachable "available" fraction of the metals present.

Other data

Available salinity data are given in the Appendix. Data on nutrients obtained from samples collected at the same time

Table 3

Comparison of dissolved trace metal data from this work with other recent data from the region.

	Metal concentration (nmol/l)		
	Strait of Dover (this work)	Central southern North Sea (Burton <i>et al.</i> , 1993)	North Sea (Kremling and Hydes, 1988)
Cd	0.20±0.09	0.17±0.07	0.14±0.04
Co	0.32±0.21	0.16±0.10	0.12±0.12
Cu	5.4±2.4	2.8±2.0	3.6±1.5
Fe	17±16	3.4±2.5	
Mn	11±13.8	6.2±7.0	8.2±5.6
Ni	6.7±2.8	4.3±2.5	3.4±0.8
Pb	0.33±0.38	0.11±0.06	
Zn	9.4±5.1	3.7±2.0	

Table 4

Division of the Strait of Dover into ten cells for the calculation of water fluxes.

Latitude (° N)	Longitude (° E)	Station from which metal data used	Cell No.	Distance from English Coast (m)	Cell width (m)
51.0598	1.1894	1	1	2,550	4,589
51.0431	1.2411	1	2	6,628	4,081
51.0264	1.2929	2	3	10,711	3,288
51.0097	1.3188	2	4	13,203	2,361
50.9763	1.3188	3	5	15,434	3,713
50.9429	1.3706	average of stations 3 and 4	6	20,629	3,897
50.9262	1.3965	average of stations 3 and 4	7	23,228	3,898
50.8928	1.4483	5	8	28,425	5,196
50.8594	1.5000	5	9	33,619	5,196
50.8260	1.55518	6	10	38,818	7,848
Totals				44,067	44,067

as the metal samples are provided in Bentley *et al.* (1993). Water and suspended particle fluxes have been obtained from work undertaken by colleagues in the *Fluxmanche* programme, and which is reported in this volume (Salomon *et al.*, 1993; Lafite *et al.*, 1993).

CALCULATION OF METAL FLUXES

Many of the limitations and problems associated with calculating fluxes are evident when the general forms of the flux equations for a chemical in dissolved or particulate form passing through the Strait of Dover are considered. The fluxes (F) over a period of time, of a material of dissolved concentration D and particulate concentration P, with S being the SPM concentration and U the instantaneous velocity (depth z, horizontal distance across the strait x and time t) are given by:

$$F_{dissolved} = \int_t \int_x \int_z U_{(x,z,t)} * D_{(x,z,t)} dx dz dt$$

and

$$F_{particulate} = \int_t \int_x \int_z U_{(x,z,t)} * S_{(x,z,t)} P_{(x,z,t)} dx dz dt$$

In the case of *Fluxmanche* we have effectively a simplification of this situation, as we do not have continuous records of SPM and water fluxes, or metal concentrations. The division of the strait into a series of cells and the temporal interpolation procedure used are described below.

Spatial division of the Channel cross section

For the calculation of metal fluxes the transect has followed the division used in the water mass movement and suspended particulate matter flux calculations. There are thus ten boxes, the

dimensions and locations of which are given in Table 4. Each box extends from the surface to the sea floor. The *Fluxmanche* station metal data used for each cell is given in the table. *Fluxmanche* station 4 is not used separately, as it essentially duplicates, as regards water flow, station 3. Cell 10 uses data from station 6 only as it is believed that the position of the front near the French coastline is unlikely to extend beyond the boundary defining this cell.

Temporal interpolation of data

Water fluxes used to generate the dissolved trace metal fluxes have been generated on a daily basis commencing on 15 August 1990 (day 1) and terminating on 31 December 1991 (day 504); see Salomon *et al.* (1993) for details of the method used. Suspended particulate matter fluxes, derived from these water fluxes and SPM data, which are used in the calculation of particulate trace metal fluxes, commence on 21 August 1990 (day 7) and finish on 21 November 1991 (day 464).

Dissolved and particulate metal data have been extrapolated to cover the periods on either side of the actual sampling day as indicated in Table 5 below. For those dissolved metals, and particulate metals, where only Southampton data are available, the longer interpolation times are also shown in Table 5.

Calculation of metal fluxes

The metal fluxes for the dissolved phase are calculated on a per day basis by multiplying the appropriate interpolated dissolved metal concentrations by the daily

Table 5

Interpolation periods for metal data used in flux calculations.
 a Southampton University, Department of Oceanography.

SAMPLING DATE	DAY	LABORATORY	INTERPOLATION PERIOD:	
			Cd, Cu, Mn, Pb, Zn Lille + SUDO ^a	Co, Fe, Ni SUDO
23/9/90	40	SUDO ^a	1-46	1-56
5/10/90	52	LILLE	47-69	
8/11/90	86	LILLE	70-99	
4/12/90	112	SUDO	100-132	57-152
12/1/91	151	LILLE	133-171	
21/2/91	191	SUDO	172-206	153-218
22/3/91	220	LILLE	207-232	
15/4/91	244	SUDO	233-259	219-277
14/5/91	273	LILLE	260-291	
19/6/91	309	SUDO	292-321	278-358
12/7/91	332	LILLE	322-342	
31/7/91	351	LILLE	343-379	
24/9/91	406	SUDO	380-421	359-421
24/10/91	436	SUDO	422-450	422-461
21/11/91	464	LILLE	451-504	

Table 6

Estimates of dissolved and particulate ["environmentally available", and total (environmentally available plus refractory)] metal fluxes through the Strait of Dover in the period August 1990 to November 1991.

ELEMENT FLUX (tonnes/ indicated time)										
DISSOLVED	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	Al	Ca
Autumn 1 (21/8/90 to 19/11/90)	15.7	14.7	211.5	639	210	340	49.2	481		
Autumn 2 (20/8/91 to 21/11/91)	17.7	13.3	285	499	248	339	37.5	651		
Annual (21/8/90 to 19/8/91)	61.7	41.7	894	1660	1280	1040	168	1680		
"AVAILABLE" PARTICULATE	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	Al	Ca
Autumn 1 (21/8/90 to 19/11/90)	0.74	17.7	19.2	20400	1200	26.3	113	160		
Autumn 2 (20/8/91 to 18/11/91)	2.1	22.3	64.9	26900	1880	51.3	145	322		
Annual (21/8/90 to 19/8/91)	11.6	56.7	125	68600	5590	103	506	733		
TOTAL PARTICULATE	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	Al	Ca
Autumn 1 (21/8/90 to 19/11/90)	2.21		61.3	121000	4730		159	2880	127000	276000
Autumn 2 (20/8/91 to 18/11/91)	2.42		131	200000	3400		318	1090	256000	514000
Annual (21/8/90 to 19/8/91)	12.1		422	624000	12600		1000	5770	728000	2010000
12 MONTH TOTALS	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	Al	Ca
OVERALL DISSOLVED + AVAILABLE PARTICULATE	73.3	98.4	1020	70300	6870	1140	674	2420		
OVERALL DISSOLVED + TOTAL PARTICULATE	73.8		1320	626000	13900		1170	7450		

water flux; the daily fluxes are then summed over the appropriate longer period. Particulate metal fluxes were calculated by multiplying the SPM fluxes (Lafite *et al.*, 1993) by the appropriate solid phase concentration of the metals, and summing over the chosen longer period; both available and total particulate fluxes are given.

Uncertainties in the estimates of fluxes of metals arise from the errors associated with the estimated water and suspended particle fluxes, from the assumptions made in the interpolation procedures, and from analytical error. Evaluation of the errors on the estimates of bulk phase transport is outside the remit of this paper, and there are insufficient observations to test the assumptions involved in the interpolation of data. The overall error in flux estimates arising from analytical causes is considerably reduced relative to the analytical precision values given in Table 1, because of the large number of measurements which contribute to the final estimate. Errors can be calculated using the analytical precision estimates and the average flux calculated from daily estimates for only those days on which concentrations were actually measured. For example, for dissolved manganese, the metal showing the lowest analytical standard deviation (relative standard deviation of $\pm 5\%$), the uncertainty in the flux calculated from this restricted data set is $\pm 0.7\%$ when the above approach is taken. Error limits derived solely from analytical precision are, however, misleading since they neglect the other factors mentioned above, and thus no ranges have been given here.

The resulting estimates of metal fluxes are given in Table 6 on an annual basis, and for the three-month autumn period for which there is an inter-annual overlap.

RELATIVE IMPORTANCE OF FLUXES OF TRACE METALS IN DISSOLVED AND PARTICULATE PHASES

The relative importance of dissolved and particulate fluxes of metals through the Strait of Dover into the southern North Sea is shown in Figure 2. The metal concentrations are estimates of the "environmentally available" fraction in the particulate phase, and thus the total metal fluxes including refractory phases will be higher. The metals fall into two major classes with Fe, Mn, and Pb being transported primarily in the particulate phase, and Cd, Ni, and Cu mainly in the dissolved phase. The fluxes of Co and Zn are

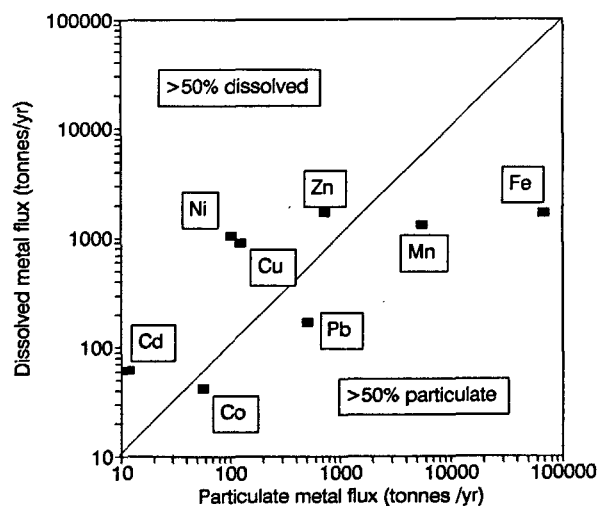


Figure 2

The relative importance of dissolved and particulate trace metal transport through the Strait of Dover. The fluxes are annual sums for the first twelve-month period of the Fluxmanche programme. The particulate fluxes are for environmentally available metals.

of similar magnitude in each phase. This partitioning reflects the relative abundance of the elements in SPM and their marine geochemistry (see e.g. Chester, 1990). Iron and manganese are abundant components in marine SPM due to oxidative scavenging onto particles, and the presence of oxy-hydroxide phases in particles introduced into the coastal marine environment. Lead is very particle reactive, and removal onto SPM in coastal and estuarine regions is well documented (Elbaz-Poulichet *et al.*, 1989; Balls, 1989).

The relative importance of particulate metals from resuspension and riverine sources in the Strait of Dover is difficult to assess, although the former process is expected to dominate [see Lafite *et al.* (1993), for a discussion of particulate material in this region, and its origins]. Resuspension may also introduce dissolved metals into the water column, although the magnitude of this process is uncertain.

The fate of dissolved and particulate metals, having passed the Strait of Dover, will be expected to be different. Metals in solution, particularly if conservative in behaviour, can potentially be transported long distances. The fate of the particle borne metals is less clear, and will reflect the transport pathways and depositional environments of the SPM. If reducing sediments are encountered, dissolution of the Fe and Mn oxy-hydroxide phases will lead to release of associated metals through diffusion or sediment re-suspension events, into the overlying water column (Kersten *et al.*, 1988). Organisms can also play a role in the uptake and re-cycling of metals in sediments and SPM (Aller, 1980). Whatever the long term fate of the suspended and dissolved metals, it is clear from this data that the particulate metal flux through the Strait of Dover is a very important component for several elements.

INTRA- AND INTER-ANNUAL VARIABILITY IN METAL FLUXES

As fluxes have been calculated on a daily basis, it is possible to see the short term variability. As an example the

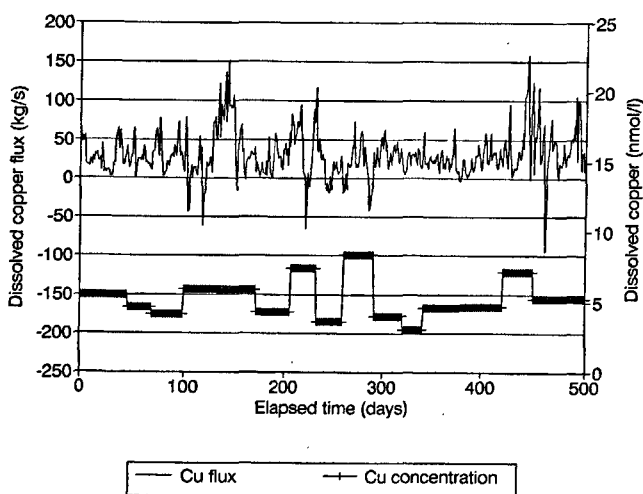


Figure 3 Short-term variability in fluxes of dissolved copper through the Strait of Dover. The averaged dissolved copper concentrations for the cell concentrations across the strait for the appropriate periods are also shown.

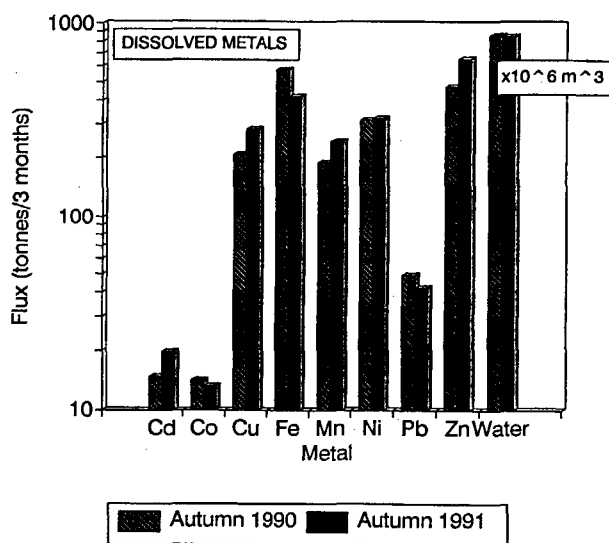


Figure 4 Comparison of dissolved metal fluxes through the Strait of Dover in autumn 1990 and autumn 1991. Note different scale for water flux.

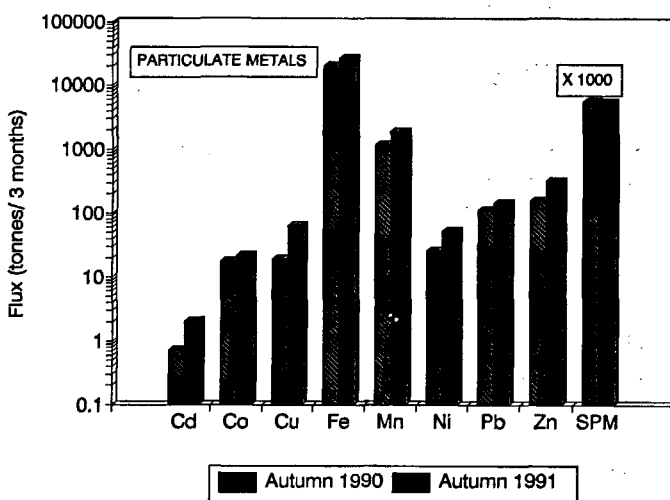


Figure 5 Comparison of particulate metal fluxes through the Strait of Dover in autumn 1990 and autumn 1991. Note different scale for particle flux.

dissolved fluxes of Cu are shown in Figure 3. The negative fluxes result from winds from northerly directions pushing water back into the Channel. The general variability in fluxes is primarily driven by changes in wind strength and direction, although changes in metal concentrations will also influence the magnitude of the flux. The data show the caution needed in trying to extrapolate short term flux measurements to longer time scales, and in this system the dominant effect of the water fluxes.

The fifteen-month data set also provides an opportunity to compare inter-annual variability for the autumn periods in 1990 and 1991. The respective dissolved and particulate fluxes are shown in Figures 4 and 5. For both the water and suspended particulate matter there is very little difference in fluxes between the two years. There is a general trend of increase in fluxes of particulate metals between the two years. There are a variety of processes which could lead to changes particulate metal

concentrations, including variations in riverine discharges, recycling and uptake processes, and atmospheric inputs. The detailed examination of the factors leading to variations will require further studies of processes, and improved estimates of fluxes will require a much larger data base which will be provided by a new generation of analytical tools, such as chemical sensors mounted on buoy systems.

COMPARISON OF STRAIT OF DOVER FLUXES TO OTHER INPUTS FOR THE NORTH SEA

The principal inputs of trace metals into the North Sea are from riverine and atmospheric sources (Liss, 1990), and by exchange at the boundaries, *i. e.* the Northern boundary, through the Dover Strait, and to a lesser extent, with the Baltic. Additional biogeochemical processes including cycling through biota and uptake and release from suspended and sedimentary particles, will influence the distribution within the North Sea.

There is relatively little data on estimates of fluxes of metals into the North Sea. Recent data on riverine and atmospheric inputs have been critically assessed and summarised by Liss (1990). Table 7 compares the Dover Strait input flux with estimates of riverine and atmospheric inputs to the North Sea given for Cd, Cu, Pb and Zn. It is clear from Table 7 that the Dover Strait input is very important relative to other inputs for cadmium and copper, and is also significant for Pb and Zn. The degree of importance indicated depends on the accuracy of the estimates of atmospheric and riverine inputs previously reported. Also, if it is assumed that the literature input estimates in Table 7 are total values (*i. e.* dissolved plus total particulate), then for comparability the total particulate metal data for the Strait of Dover from this study should be used, and the inputs estimated here then become even more important. The relative low importance of the Dover Strait input for lead is not unexpected given the dominant atmospheric input for this element.

In terms of the overall mass balance of metals in the North Sea, the flux from the Channel is obviously important. However, the inputs given in Table 7 do not include inputs across the northern boundary. Water exchange is high here (ICES, 1983), and thus even the low concentrations of metals anticipated in these waters will give significant transfers of metals. A first order estimate of fluxes based on trace metal concentrations in a cross shelf transect, and estimates of water fluxes, is provided by Hydes and Kreming (1993), and it is clear that with the large volumes of water involved, these northern exchanges can be very important for the trace metal budgets for the whole of the North Sea. On the more local scale of the southern North Sea, the Dover Strait inputs are of more significance. The area is shallower than further north, and is subjected to stronger inputs from rivers. In terms of

Table 7

Comparison of dissolved plus leachable particulate metal fluxes through the Strait of Dover (estimates from this work) with other estimated inputs to the North Sea (based on a Table in Liss, 1990).

Metal	Data from Report of The Scientific and Technical Working Group on the North Sea, Anonymous (1987) [10^6 kg/yr]				Dover Strait Flux as % of Total
	GROSS RIVER	ATMOSPHERE	TOTAL	Dover Strait input (this work)	
Cd	0.049	0.14	0.189	0.073	39
Cu	1.3	1.0	2.3	1.02	44
Pb	0.9	5.0	5.9	0.67	11
Zn	7.6	8.0	15.6	2.42	16

concentrations of metals the central Channel waters entering through the Strait of Dover appear to be a diluent of the higher concentration nearshore waters influenced by riverine discharges; evidence of this concentration gradient can be seen in data from the NERC North Sea project (*see* for example Burton *et al.* 1993), and other studies in this area (Duinker and Nolting, 1978).

CONCLUSIONS

Dissolved plus "available" particulate fluxes of Cd and Cu are important (39 and 44 % respectively), and Pb and Zn significant (11 and 16 % respectively), relative to other identified inputs to the North Sea. If total particulate metals rather than the available fraction alone are considered, then these estimates are raised. Fluxes of "environmentally available" particulate Fe, Mn, and Pb are dominant over dissolved fluxes of these elements. The long term transport and thus fate of this material after passing through the Strait of Dover may be very different to the dissolved phase metals. Fluxes of total particulate metals are greater than available metals alone, and thus the significance of dissolved metal fluxes is reduced when they are included in the flux calculations. However, these metals are unlikely to be involved in biogeochemical processes on less than geological timescales, and their fluxes mainly reflect their transfer from one sink region to another. Fluxes of Cd, Cu, and Ni are predominantly in the dissolved phase, with the relative importance of dissolved flux relative to the total (dissolved plus leachable) fluxes reported here being in the order Ni > Cu > Cd. When successive autumn periods are compared, inter-annual variations in fluxes of metals are generally small. Where differences are seen, they are not simply due to a change in SPM loading or water flow, but appear to reflect changes in concentrations in dissolved and particulate phases.

Acknowledgements

This work is the product of the interaction with, and the combined efforts of many colleagues within the *Fluxmanche* programme, and particularly those who provided data on water and SPM fluxes. Without the skills and good humour of the officers and crews of *Pluteus*, *Noroit*, *Suroit*, RRS *Challenger*, the work at sea, often done under difficult circumstances could not have been done. The use of the Wimereux Station facilities was greatly appreciated for the processing of collected

samples. The one individual we do wish to identify for particular note is Professeur Louis Cabioch, who throughout the programme from earliest concepts to these fruitful stages we are now in has been a tireless, patient and essential force in keeping the programme on track. The French laboratory research was undertaken within the framework of the European Communities MAST (Marine Science and Technology) programme (MAST 0053-C), and the Southampton component was funded under contract PECD 7/8/183 to the UK Department of the Environment as part of its coordinated programme of research on the North Sea.

REFERENCES

- Aller R.C. (1980). Diagenetic processes near the sediment-water interface of Long Island Sound. II: Fe and Mn. *Adv. Geophys.*, **22**, 351-415.
- Althaus M. (1992). Dissolved trace metals in the estuarine plumes of the Humber, Thames and Rhine rivers. *Ph.D. Thesis, University of Southampton, UK*, 329 pp.
- Anonymous (1987). Quality Status of the North Sea. A report by the scientific and technical working group. International North Sea Conference, Department of the Environment, London, UK, 88 pp.
- Balls P.W. (1989). The partition of trace metals between dissolved and particulate phases in European coastal waters: A compilation of field data and comparison with laboratory studies. *Neth. J. Sea Res.*, **23**, 7-14.
- Bentley D., R. Lafite, N.H. Morley, R. James, P.J. Statham and J.-C. Guary (1993). Flux de nutriments entre la Manche et la Mer du Nord. Situation actuelle et évolution depuis dix ans. *Oceanologica Acta*, **16**, 5-6, 599-606.
- Berman S.S. and V.J. Boyko (1987). ICES sixth round inter-calibration for trace metals in estuarine water. *JMG 6/TM/SW*, Preliminary report, 50 pp.
- Burton J.D., M. Althaus, G.E. Millward, A.W. Morris, P.J. Statham, A.D. Tappin and A. Turner (1993). Processes influencing the fate of trace metals in the North Sea. *Phil. Trans. R. Soc. A*, **343**, 557-568.
- Chester R. (1990). *Marine Geochemistry*. Unwin Human, London, UK, 698 pp.
- Danielsson L.-G., B. Magnusson and S. Westerlund (1978). An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrometry with electrothermal atomisation. *Analytica chim. Acta*, **98**, 47-57.
- Duinker J.C. and R.F. Nolting (1978). Mixing removal and mobilisation of trace metals in the Rhine Estuary. *Neth. J. Sea Res.*, **12**, 205-223.
- Elbaz-Poulichet F., D.M. Guam, P. Seyler, J.-M. Martin, N.H. Morley, P.J. Statham, J.D. Burton, L. Mart and P. Klahre (1989). Dissolved trace metals and metalloids in the Rhône river/estuarine system. *Water Pollut. Res. Rpt.*, **13**, 395-422.
- Hydes D.J. and K. Kremling (1993). Patchiness in dissolved metals (Al, Cd, Co, Cu, Mn, Ni) in North Sea surface waters: seasonal differences and influence of suspended sediment. *Continental Shelf Res.*, **13**, 1083-1101.
- ICES (1983). Flushing times of the North Sea. ICES Cooperative Research Report No. 123, 159 pp.
- Kersten M., M. Dicke, M. Kriews, K. Naumann, D. Schmidt, M. Schulz, M. Schwikowski and M. Steiger (1988). Distribution and fate of heavy metals in the North Sea, in: *Pollution of the North Sea. An assessment*, W. Salomons et al., editors. Springer Verlag, 301-347.
- Kremling K. and D.J. Hydes (1988). Summer distribution of dissolved Al, Cd, Co, Cu, Mn and Ni in surface waters around the British Isles. *Continental Shelf Res.*, **8**, 89-105.
- Lafite R., Shimwell S., Grochowski N., Dupont J.-P., Nash L., Salomon J.-C. and Collins M.B. (1993). Suspended particulate matter fluxes through the Strait of Dover. submitted to *Oceanologica Acta*.
- Liss P.S. (1990). Land-to-ocean transport of contaminants: comparison of river and atmospheric fluxes, in: Technical Annexes to the report on the state of the marine environment. UNEP Regional Seas Reports and Studies No. 114/2, Annex IX, 417-446.
- Loring D.H. and R.T.T. Rantala (1990). *Sediments and suspended particulate matter: total and partial methods of digestion*. Techniques in Marine Environmental Sciences, 9, ICES, Copenhagen, Denmark, 14.
- Morley N.H., C.W. Fay and P.J. Statham (1988). Design and use of a clean shipboard handling system for seawater samples. *Advances in Underwater Technology, Ocean Science and Offshore Engineering*, **16**, *Oceanology '88*, 283-289.
- Ouddane B. (1990). Comportement des éléments majeurs et mineurs dans un milieu soumis à des gradients physico-chimiques marqués: cas de l'estuaire de la Seine. *Thèse, Université de Lille, France*, 272 pp.
- Postma H. (1990). *Facets of modern biogeochemistry*, V. Ittekkot et al., editors. Springer-Verlag, Berlin, Germany, 147-154.
- Salomon J.-C., Breton M. and P. Guéguéniat (1993). Flux d'eau calculé à travers le détroit du Pas-de-Calais. *Oceanologica Acta*, **16**, 5-6, 449-455.
- Skiker M. (1989). Comportement du manganèse dans les eaux marines du détroit du Pas-de-Calais. *Ph. D. Thesis, Université des Sciences et Techniques de Lille-Flandres-Artois, France*, 161 pp.
- Skiker M., E. Puskaric, M. Hoenig and M. Wartel (1988). Le manganèse dans l'eau de mer: dosage et étude de sa dispersion dans le détroit du Pas-de-Calais. *Oceanis*, **14**, 453 - 460.
- Statham P.J. (1985). The determination of dissolved manganese and cadmium in sea waters at low nmol l⁻¹ concentrations by chelation and extraction followed by electrothermal atomic absorption spectrophotometry. *Analytica chim. Acta*, **169**, 149-159.
- Tappin A.D. (1988). Studies of trace metals in shelf waters of the British Isles. *Ph.D. Thesis, University of Southampton, UK*, 279 pp.

APPENDIX

Dissolved, available (main body of the appendix) and total particulate (summary table at the end of the appendix) trace metal data for the Fluxmanche stations. Suspended particulate matter (SPM) concentrations are in mg/l.

DEPTH	SALINITY	DISSOLVED METALS				METALS				AVAILABLE PARTICULATE METAL								
		Cd pM	Co nM	Cu nM	Fe nM	Mn nM	Ni nM	Pb nM	Zn nM	SPM mg/l	Cd nmol/g	Co nmol/g	Cu nmol/g	Fe micromol/g	Mn micromol/g	Ni nmol/g	Pb nmol/g	Zn nmol/g
SEPTEMBER 1990																		
SURF																		
1	35.08	280	0.47	8.7	8.3	6.8	9.2	0.13	10	16.4	0.86	41	52	60	4.1	78	84	380
2	35.08	210	0.26	6.8	24.0	3.4	7.5	0.1	8.8	7.2	0.67	65	54	80	5.5	77	109	480
3	35.12	220	0.23	4.7	6.8	2.5	5	0.06	5.8	5.8	1.03	59	68	81	4.5	175	105	510
4	35.12	225	0.25	4.4	14.0	2.8	5	0.06	11	3.4	1.48	50	53	44	2.7	47	77	375
5	35.11	160	0.72	3.3	5.5	1.3	5.8		7.1	5.5	1.31	34	40	49	3.4	56	115	370
6	34.68	180	0.52	4.0	17.0	6.4	5.4	0.14	7.1	15.4	5.70	42	104	56	7.4	91	130	745
DEEP																		
1	35.08	300	0.7	8.6	12.0	16	9.4	0.26	12	18.1	1.04	37	44	68	4.4	60	86	408
2	35.08	170	0.47	5.7	31.0	4.7	7.3	0.06	4.9	9.8	0.93	28	31	65	4.2	101	101	440
3	35.12	160	0.37	4.1	6.8	1.8	4.8	0.05	3.2	7.5	1.16	57	59	72	4.5	159	159	460
4	35.12	160	0.32	4.1	5.8	3.6	4.7	0.06	6.6	4.3	0.59	40	34	46	3.5	66	112	315
5	35.11	160	0.2	4.5	9.0	2.2	5.8	0.06	2.8	5.2	0.86	49	63	48	3.4	72	105	350
6	34.66	155	0.51	5.1	15.0	6.2	5.2	0.1	6.3	19.7	2.88	18	24	26	3.9	51	69	415
OCTOBER 1990																		
SURF																		
1	35.17	180		5.8					0.71	13.0								12.8
2	35.16	220		8.6					0.8	9.0								10.3
3	35.17	180		3.5					0.7	15.0								4.5
4	35.19	130		2.4					0.83	8.1								5.6
5	35.18	160		2.1					0.47	5.7								2.8
6	34.73	280		4.2					0.77	6.8								13.4
NOVEMBER 1990																		
SURF																		
1	35.01	250		6.8					0.34	5.4								11.1
2	35.13	220		3.0					0.24	5.4								10.2
3	35.32	190		2.6					0.24	1.4								5.8
4	35.33	200		4.2					0.24	1.7								3.7
5	35.16	130		2.4					0.25	2.8								5.6
6	34.92	210		5.4					0.32	6.7								13.2
DEEP																		
1	35.24	280		6.4					0.32	6.3								12.6
2	35.32	140		3.2					0.16	6.7								11.2
3	35.2	190		4.7					0.2	4.1								6.4
4	35.12	230		3.8					0.24	1.4								5.2
5	34.94	150		3.1					0.14	8.4								5.8
6	34.92	570		5.3					0.4	4.9								16.2
DECEMBER 1990																		
SURF																		
1	34.85	130	0.31	6.7	47.0	5	9.9	0.14	10.8	15.1	0.95	79	80	103	5.5	123	94	570
2	35.1	130	0.2	6.7	14.0	3.4	8	0.05	8.5	13.2	1.49	99	66	106	5.9	188	126	640
3	35.2	370	0.24	6.2	16.0	3	8	0.12	12.3	8.8	0.67	49	48	74	3.7	81	86	400
4	35.26	170	0.15	4.2	2.5		6.6	0.06	5.9	6.8	1.12	76	96	116	5.6	72	136	600
5	35.26	105	0.4	4.8	42.0	6	8.3	0.22	10.6	2.8	1.10	43	51	47	2.5	33	67	410
6	34.26	200	0.32	5.8	22.0	9.8	7.4	0.11	20.3	20.0	10.20	36	75	50	6.3	63	141	590
DEEP																		
1	35.08	130	0.3	7.7	37.0	5.3	8.4	0.05	7.4	26.1	1.04	87	71	101	4.9	108	99	540
2	35.11	175	0.23	7.1	26.0	3.3	8.1	0.14	12.7	24.3	0.70	62	55	79	4.9	118	109	460
3	35.2	170	0.25	5.5	24.0	9.1	7.1	0.09	6.9	13.4	0.64	70	51	83	4.1	64	101	470
4	35.26	110	0.29	4.8	32.0	5.3	5.4	0.13	7	12.0	1.17	60	71	80	3.7	83	111	510
5	35.27	90	0.24	4.8	16.0	3.8	5.1	0.12	10.5	8.7	0.38	48	37	41	2.2	41	73	310
6	34.41	220	0.22	5.7	18.0		7.5	0.15	20.9	36.0	5.80	35	46	48	6.0	54	138	650
JANUARY 1991																		
SURF																		
1	35.13	180		6.0					0.24	14.2								
2	35.3	190		4.4					0.16	5.2								
3	35.39	200		5.0					0.15	2.45								
4	35.36	180		2.3					0.22	6.42								
5	35.32	290		4.5					0.12	3.82								
6	32.46	240		6.8					0.17	9.64								
DEEP																		
1	35.16	280		7.7					0.39	3.21								10.4
2	35.21	230		7.2					0.22	5.05								8.5
3	35.26	200		11.3					0.24	4.13								6.8
4	35.41	220		7.5					0.38	3.67								7.5
5	35.36	300		8.0					0.14	5.2								5.1
6	33.93	300		5.7					0.25	10.3								57.3
FEBRUARY 1991																		
SURF																		
1	35.46	115	0.38	5.8	12.1	8.1	6.8	0.20	25.47	7.7	3.24	33	116	69	3.4	82	95	531
2	35.54																	
3	35.53	135	0.10	3.4	9.7	2.4	4.9	0.25	19.2	5.9	3.16	41	173	54	3.6	141	96	577
4	35.5																	
5	35.32																	
6	35.52	470	0.26	5.1	10.2	52.2	6.7	0.09	22.2	16.7	4.22	22	80	32	5.7		105	847
DEEP																		
1	35.44	80	0.33	5.2		8.5	6.2	0.23	16.6	7.8	0.94	35	39	64	3.4	60	70	477
2	35.54	110	0.13	3.9	29.0	3.3	4.8	0.19	8.9	5.8	5.88	49	159	88	5.0	118	118	732
3	35.53	115	0.09	3.2	23.0	2.3	4.3	0.08	19.2	6.0	2.04	37	96	43	2.7	101	74	444
4	35.5	140	0.17	3.5	27.0	3.3	5.9	0.10	21.9	8.5	1.48	38	105	53	4.2	92	85	451
5	35.32	195	0.06	4.5	43.0	4.3	4.8	0.16	8.6	3.2	2.16	25	165	36	3.6	144	97	818
6	35.52	285	0.30	5.6	32.2	57.1	8.7	0.19	22.4	17.7	3.94	24	59	36	5.8	84	116	847

FLUXES OF TRACE METALS THROUGH THE DOVER STRAIT

DEPTH	SALINITY	DISSOLVED METALS				AVAILABLE PARTICULATE METAL												
		Cd pM	Co nM	Cu nM	Fe nM	Mn nM	Ni nM	Pb nM	Zn nM	SPM mg/l	Cd nmol/g	Co nmol/g	Cu nmol/g	Fe micromol/g	Mn micromol/g	Ni nmol/g	Pb nmol/g	Zn nmol/g
MARCH 1991																		
SURF																		
1	35.11	140		5.7				1.01	17	16.3								
2	35.23	150		6.5				0.48	17.4	8.2								
3	35.29	120		8.5				0.47	7.95	10.3								
4	35.33	90		3.5				0.30	14.7	11.0								
5	35.33	180		9.7				0.61	5.35	3.5								
6	34.39	250		15.6				0.29	9.94	9.6								
DEEP																		
1	35.11	150		8.6				1.08	17	24.2								
2	35.23	160		6.5				0.46	18.2	8.9								
3	35.33	120		3.4				0.39	7.8	9.9								
4	35.34	90		3.5				0.39	9.02	10.7								
5	35.34	180		8.5				0.70	12.1	3.3								
6	34.47	230		10.8				0.26	10.6	13.5								
APRIL 1991																		
SURF																		
1	35.15	110	1.03	4.5	10.8	12.6	8.4	0.21	11.2	10.0	2.24	40	57	70	3.8	70	97	757
2	35.25	145	0.46	4.6	32.0	7.2	7.3	0.06	9.7	3.4	1.63	48	66	53	4.1	63	85	654
3	35.41	95	0.09	2.7	11.0	3.6	4.0	0.05	7.9	1.4	1.81	48	71	48	4.1	43	100	1531
4	35.42	140	0.18	3.6	27.0	5.3	4.9	0.11	11	3.4	3.39	75	93	71	5.0	53	112	856
5	35.34	115	0.04	2.4	44.0	4.4	3.7	0.05	5.8	0.9	7.09	45	2	41	3.2	37	107	333
6	34.33	225	0.42	5.5	13.9	34.6	5.2	0.53	29.17	1.8	8.34	135	223	61	9.0	67	199	1534
DEEP																		
1	35.15	185	1.09	4.1	5.4	14.5	7.6	0.22	7.6	16.5	1.66	39	29	46	3.3	59	105	360
2	35.25	85	0.31	4.5	4.2	5.2	5.6	0.05	9.2	3.7	1.80	50	128	57	4.1	75	98	484
3	35.41	110	0.06	3.0	4.8	3.4	4.2	0.22	9.4	1.39	55	61	47	4.2	55	92	825	
4	35.42	155	0.27	3.6	3.0	5.9	6.4	0.06	10.5	3.6	1.36	34	164	33	3.1	24	40	377
5	35.34	100	0.06	2.2	4.7	6.6	4.4	0.11	6.4	1.3	2.05	46	86	40	3.6	40	100	420
6	34.72	165	0.45	3.7	39.1	32.2	6.5	0.06	10.7	3.3	7.56	19	85	64	4.9	1	97	828
MAY 1991																		
SURF																		
1	34.52	160		8.9				2.46	18.8	37.4								
2	34.77	210		16.9				0.58	14.7	16.3								
3	34.89	160		6.7				1.14	8.57	35.2								
4	35.01	160		9.4				1.16	17.4	17.6								
5	35.06	230		6.3				0.7	13.6	1.7								
6	34.57	270		7.8				1.14	14.4	30.8								
DEEP																		
1	34.55	280		12.5				3.31	14.4	38.6								
2	34.78	200		10.4				0.67	19.7	24.4								
3	34.91	150		7.1				1.3	11	11.9								
4	35	170		7.7				0.87	17.1	14.0								
5	35.06	330		6.1				0.8	18.1	9.8								
6	34.58	300		5.7				1.61	14.8	21.5								
JUNE 1991																		
SURF																		
1	35.1	170	0.59	6.6	26.5	23.0	6.6	0.08	10.8	11.3	1.98	46	32	163	6.3	127	108	440
2	35.3	150	0.66	4.1	32.3	30.8	8.3	0.12	2.88	1.5	8.90	41	428	41	4.5	156	86	425
3	35.55	100	0.17	3.1	25.4	14.1	3.3	0.05	2.8	0.7	63.16	25	787	72	30.9	652	1071	
4	35.6	240	0.12	3.0	34.7	14.0	2.8	0.04	2.49	2.3	7.30	56	32	8	0.0	48	190	24
5	35.5	150	0.45	4.6	4.7	9.9	4.5	0.06	4.03	1.7	9.75	49	626	14	2.3	102	29	
6	34.5	140	0.39	5.5	81.6	70.5	6.8	0.23	5.07	8.4	6.73	29	100	49	11.5	56	110	730
DEEP																		
1	35.1	130	0.65	5.7	3.9	24.0	6.6	0.06	3.88	10.2	1.87	54	117	71	7.2	50	97	885
2	35.3	90	0.6	3.1	5.0	24.1	3.7	0.07	2.74	2.6	15.00	57	152	39	4.4	111	447	
3	35.55	100	0.21	1.8	2.2	15.1	3.4	0.06	2.11	1.8								
4	35.6	120	0.19	2.6	4.3	13.7	3.4	0.07	2.44	2.0	8.88	37	128	19	1.5	368	75	41
5	35.5	200	0.04	3.4	2.5	8.3	3.1	0.13	10.1	1.1	11.56	16	360	20	2.5	185	1991	
6	35.5	120	0.48	4.3	77.9	66.2	5.7	0.14	5.07	13.5	8.07	24	36	53	10.6	65	119	743
JULY 1991																		
surf																		
1		300		5.2				0.42	6.73	18.4								
2		350		1.8				0.47	9.02	11.6								
3		180		1.8				0.2	8.42	5.1								
4		170		2.1				0.27	6.42	2.0								
5		150		4.7				0.34	6.88	4.0								
6		380		4.9				0.38	8.26	9.1								
deep																		
1		300		3.8				0.35	7.89	23.1								
2		180						0.33	5.05	16.0								
3		280		2.5				0.28	9.48	5.1								
4		190		2.2				0.47	8.41	6.2								
5		140		3.2				0.38	11.2	4.0								
6		340		2.3				0.65	4.89	9.1								
AUGUST 1991																		
SURF																		
1		140		4.9				0.32	6.57	6.2								
2		330		5.4				0.54	10.6	4.3								
3		180		3.4				0.22	6.88	2.0								
4		200		4.5				0.22	5.35	1.5								
5		200		2.6				0.24	4.13	1.5								
6		740		6.9				0.26	7.19	2.0								
DEEP																		
1		180		5.7				0.46	10.6	8.5								
2		280		5.9				0.46	10.1	4.7								
3		190		4.3				0.27	10.6	2.2								
4		130		3.5				0.17	4.44	2.7								
5		180		3.3				0.23	5.86	1.8								
6		270		5.6				0.23	4.74	2.0								

DEPTH	SALINITY	DISSOLVED METALS				AVAILABLE PARTICULATE METAL													
		Cd pM	Co nM	Cu nM	Fe nM	Mn nM	Ni nM	Pb nM	Zn nM	SPM mg/l	Cd nmol/g	Co nmol/g	Cu nmol/g	Fe micromol/g	Mn micromol/g	Ni nmol/g	Pb nmol/g	Zn nmol/g	
SEPTEMBER 1991																			
SURF																			
1	34.92	250	0.78	6.1	1.5	7.9	9.6	0.32		29.9	1.56		96	112	5.7		140	1116	
2	34.95	220	0.43	4.2	0.7	8.8	8.4	0.19	16.4	4.9	1.83		159	72	5.9	124	105	784	
3	35.02	180	0.47	4.1	0.4	12.2	5.5	0.11	5.85	3.6	4.94	47	212	59	0.5	156	82	716	
4	35.02	150	0.17	3.1	0.1	3.2	6.0	0.12	6.72	1.7	4.94	11	147	13	1.6	49	24	176	
5	34.94	180	0.16	4.1	0.3	4.0	5.1	0.2	10.5	1.4	7.62	16	495	16	6.5	184	118	614	
6	34.45	220	0.36	3.5	0.6	7.1	7.0	0.15	21.5	4.1	12.87	65	312	49	27.3	189	260	2173	
DEEP																			
1		340	0.81	8.0		21.1	11.5	0.62		53.237	1.62	69	121	139	7.0		136	951	
2	34.96	190	0.32	5.1	0.5	6.4	8.7	0.14	15.1	6.9	4.78	117	262	116	8.8	228	178	1255	
3	35.02	160	0.31	4.4	0.3	4.8	6.0	0.22	7.44	3.3	4.90	31	234	42	3.2	221		1159	
4	35.03	160	0.47	4.7	0.3	4.1	5.2	0.1	7.2	3.5	9.37	22	135	14	2.0	84	68	559	
5	34.95	180	0.17	3.5	0.3	5.1	5.4	0.12	17.6	1.5	11.99	12	582	31	7.8	271	222	654	
6	34.38	170	0.34	3.3	0.7	9.8	7.9	0.12	6.76	5.9	8.00	33	259	44	20.1	160	205	1171	
OCTOBER 1991																			
SURF																			
1	34.9	310	0.27	11.4	23.5	5.8	8.5	0.26	24.5	13.2	2.66	91	190	129	6.7		192	979	
2	34.95	270	0.26	8.7	6.9	4.2	8.2	0.19		32.27	15.9	2.52	78	158	96	6.0	155	136	1064
3	35.05	180	0.4	6.4	20.9	5.7	7.8	0.27	12.5	6.4	7.87	130	319	155	11.3	273	282	1770	
4	35	180	0.22	8.0	5.9	3.8	8.4	0.14	10	8.1	2.24	63	165	75	5.1	222	129	779	
5	35.1	140	0.15	9.8	18.4	3.5	8.1	0.16	6.05	2.1	2.11	58	144	46	5.0	124		559	
6	34.4	130	0.29	5.2	19.1	9.5	5.6	0.16	7.53	6.3	5.00	32	82	66	11.0	73	133	928	
DEEP																			
1	34.9	230	0.28	10.6	1377	11.4	11.0	0.34	18.9	30.2	1.28	81	128	108	6.3	82	153	740	
2	34.95	200	0.16	8.2	41.0	5.3	8.7	0.15	6.69	24.2	1.86	103	142	131	6.9		134	864	
3	35.05	160	0.18	5.4	16.8	4.1	5.7	0.18	10.5	6.6	2.00	86	201	89	6.7	160		903	
4	35	160	0.23	6.8	13.8	4.9	7.2	0.42	9.42	7.1	3.23	83	275	100	6.8	212	193	1286	
5	35.1	140	0.26	4.3	3.3	3.9	25.4	0.19	3.74	2.4	3.19	40	128	30	4.8	225	80	513	
6	34.4	150	0.37	5.2	15.2	8.4	6.8	0.16	7.76	11.1	5.76	43		75	11.6	80	146	1024	
NOVEMBER 1991																			
SURF																			
1	34.22	270		6.2					0.54	9.02								14.0	
2	35.05	240		4.6					0.26	5.66								12.3	
3	35.06	270		6.1					0.32	8.11								9.8	
4	35.07	230		2.8					0.29	5.2								15.8	
5	34.93	220		5.4					0.27	4.44								2.5	
6	34.26	300		4.1					0.23	12.2								13.0	
DEEP																			
1	34.95	310		5.2					0.41	22.6								24.0	
2	35.05	250		4.2					0.28	10.9								26.5	
3	35.06	420		5.5					0.41	8.11								17.8	
4	35.07	250		3.4					0.59	8.72								4.6	
5	34.94	250		5.9					0.23	7.8								4.5	
6	34.19	380		8.1					0.68	13.3								139.7	

MEAN AND STANDARD DEVIATION (SD) OF TOTAL PARTICULATE METALS IN THE STRAIT OF DOVER.
Mn, Zn, Ca, Mg, Fe, and Al in microgrammes/l; all other elements in nanogrammes/l.

	Al	Ca	Cd	Cu	Fe	Mn	Pb	Zn
23 September 1990								
mean	331	370	4.57	141	200	4.89	263	
SD	157	196	2.88	54	86	1.58	78	
5 October 1990								
mean	117	80	0.98	44	83	2.32	202	2.2
SD	105	70	0.56	40	73	1.42	271	2.68
8 November 1990								
mean	96	426	1.37	50	93	1.1	136	1.14
SD	47	287	0.6	30	46	0.45	75	0.32
12 January 1991								
mean	431	1275	6.13	229	252	4.6	727	1.58
SD	189	1260	4.03	140	136	1.68	579	0.66
22 March 1991								
mean	423	672	2.44	121	214	3.78	500	1.43
SD	165	234	1.28	34	83	1.34	234	0.42
14 May 1991								
mean	250	1960	4.27	142	249	3.3	226	0.54
SD	358	1340	1.69	68	227	1.88	236	0.13
12 July 1991								
mean	341	542		169	200	3.76	412	1.2
SD	278	432		111	179	2.03	297	0.59
31 July 1991								
mean	207	434	2.13	112	122	2.34	225	1.27
SD	142	253	0.59	71	89	1.27	91	0.51
21 November 1991								
mean	443	853	4.13	173	300	5.57	423	1.19
SD	256	404	2.89	80	238	2.32	168	0.41