

# Aspects of the geochemistry of dissolved and particulate Cd, Cu, Ni, Co, and Pb in the Dover Strait

*FluxManche*  
Trace metals  
Geochemistry  
Shelf seas  
Temporal variation

*FluxManche*  
Métaux traces  
Géochimie  
Mers bordières  
Variation temporelle

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## ABSTRACT

Water column samples have been collected at six stations across the Dover Strait within the framework of the *FluxManche* programme every month for fifteen months and analyzed for particulate and dissolved trace metals. Important seasonal variations in trace metal distributions have been identified. Dissolved Cu and Ni exhibit similar behaviour in the Strait; while seasonal variation in their distribution may be determined by changes in freshwater input, additional processes including biological uptake and regeneration and benthic input probably perturb water column inventories. Consistently with the suggestion of other authors, Co and Mn in both the dissolved and particulate phase exhibit some degree of covariance; substantial increases in the concentration of dissolved Mn in the summer (9.0-69.0 nM as opposed to 3.3-9.6 nM in the winter) across the entire Channel are to some extent supported by increases in dissolved Co concentrations. Summer maxima are accompanied by a reduction in the acetic acid leachable particulate Mn, possibly implying release from this phase in the summer or increased uptake during the winter. Data for particulate cadmium are consistent with the metal being largely associated with biogenic material; biological activity is inferred to generate a spring depletion in dissolved Cd concentrations. In contrast to deep ocean environments, there is no obvious correspondence between dissolved Cd and the classical nutrient elements in this environment. Dissolved Pb concentrations appear to be strongly influenced by seasonal variation in freshwater input and shorter time scale variation in atmospheric input. There is some evidence that biological activity perturbs the water column inventory. This is supported by observations from the particulate phase where atmospheric or fluvially derived particles appear largely to determine the total particulate Pb concentration in winter but other phases become important in its regulation in summer.

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## RÉSUMÉ

Aspects de la géochimie du Cd, Cu, Ni, Co et Pb dissous et particulaires dans le détroit du Pas-de-Calais

Des échantillons ont été prélevés mensuellement pendant quinze mois en six stations dans le détroit du Pas-de-Calais, dans le cadre du programme *FluxManche*, afin de déterminer les concentrations en métaux traces dissous et particulaires. Cette série de données, échantillonnée à haute fréquence, révèle des fluctuations

saisonniers importantes dans la distribution des différents métaux traces. Le Cu et le Ni dissous montrent des comportements similaires dans le détroit et, bien que les fluctuations saisonnières dans leurs distributions soient déterminées principalement par des variations dans les apports d'eau douce, d'autres voies, dont l'assimilation biologique, la régénération et l'apport benthique, peuvent perturber leurs concentrations dans la colonne d'eau. Comme suggéré par d'autres auteurs, le Co et le Mn particulaires et dissous montrent une corrélation : une augmentation substantielle du Mn dissous en été (9.0-69.0 nM par rapport à 3.3-9.6 nM en hiver) dans toute la Manche est accompagnée par une augmentation du Co dissous. Les maxima estivaux sont accompagnés par une diminution du Mn particulaire mobilisé par un traitement à l'acide acétique, impliquant probablement une libération de cette phase en été, ou une sorption accrue en hiver. L'analyse de la phase particulaire met en évidence que le Cd est, dans une large mesure, biogénique et que l'activité biologique implique un appauvrissement en Cd dissous au printemps. Contrairement à ce qui se passe en milieu océanique, il n'y a pas de relation évidente entre le Cd dissous et les nutriments dans cet environnement. La distribution du Pb dissous paraît être fortement influencée par les variations saisonnières dans l'apport d'eau douce et par les variations, à plus court terme, des apports atmosphériques. Il y a des signes que l'activité biologique perturbe le contenu en métaux de la colonne d'eau. Cette idée est soutenue par la composition en Pb de la phase particulaire, qui est largement conditionnée par les apports en hiver. En été, d'autres facteurs interviennent dans le contrôle de la distribution du Pb.

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## INTRODUCTION

As part of the *FluxManche* programme, clean trace metal techniques have been employed to collect water samples at six stations across the Dover Strait at two depths every month for fifteen months (Fig. 1). Hence sampling encompassed a full seasonal cycle and a three month overlap period which allows a study of inter-annual variability. Across the Channel both coastally influenced and deeper central Channel waters which are predominantly of open Atlantic origin, were sampled. We believe the *FluxManche* data set represents one of the most intensive data sets, on both a temporal and spatial scale, currently available in a shelf sea environment.

The data set (given in the "Appendix") provides important information regarding the input of trace metals, some of which are potential contaminants, from the English Channel into the North Sea, and contributes to the assessment of the "state of health" of the North Sea for the next Quality Status Report (QSR) (Statham *et al.*, 1993). However such a data set also allows an insight into the biogeochemical behaviour of trace metals in shelf sea environments which is currently not well understood (Kremling and Hydes, 1988).

The concentrations of the more conservative dissolved trace metal species in coastal waters are likely to be significantly influenced by mixing between outer shelf waters of low concentration and higher concentration river waters. This phenomena would generate a simple covariance of concentration with salinity for conservative metals, with high concentrations found in association with waters of low salinity and *vice versa*. A weaker correlation may reflect variability of

freshwater inputs, or suggest other processes are in operation leading to perturbation of trace metal distributions. Such processes include additional input from sediments or the atmosphere or removal effected by sedimentation and biological uptake. In addition, the partitioning of a metal between the dissolved and particulate forms may vary according to biological activity and particle exchange processes.

This paper reports new results for Cu, Ni, Mn, Co, Cd and Pb in dissolved and particulate phases in the Dover Strait,

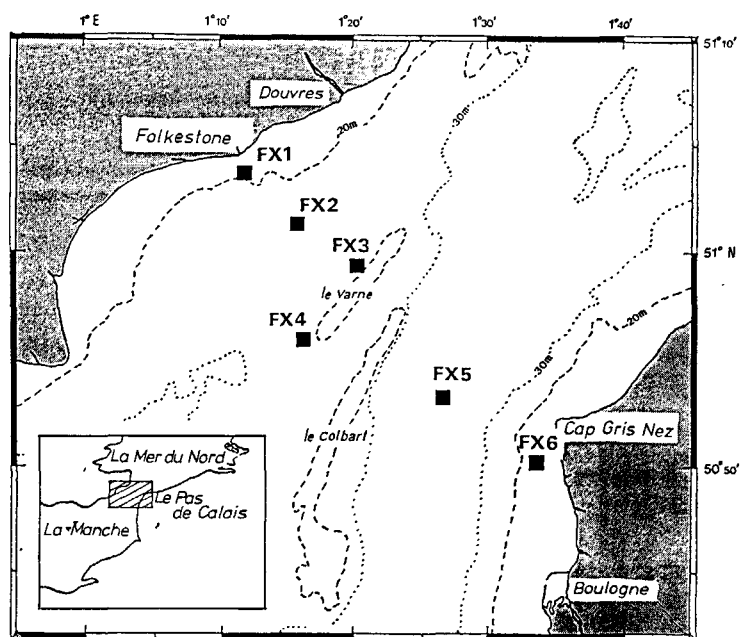


Figure 1

Location of the FluxManche sampling stations.

and discusses known and likely processes controlling their concentration and phase association on both a temporal and spatial basis.

## MATERIALS AND METHODS

The basic trace metal data set is given in "Appendix 1". Sampling was divided between the authors laboratory and co-workers at Université de Lille, described in Statham *et al.* (1993). Figure 1 depicts the sampling stations. In outline, either an all-PTFE/plastic pumping system or 10l Teflon lined Go-Flo sampling bottles were used for seawater collection and samples were filtered through acid cleaned 142mm diameter, 0.4  $\mu\text{m}$  pore size Nuclepore filters. These were supported on a porous polyethylene frit mounted on a filter holder constructed of polypropylene and sealed using an FEP encapsulated Si "O" ring. Samples were acidified by addition of 1ml sub-boiling distilled  $\text{HNO}_3$  per litre of seawater, and stored in acid cleaned (Morley *et al.*, 1988) low density polyethylene bottles. Analysis was divided between groups in the same manner, with inter-calibration assessments to ensure data compatibility in September 1990 and July 1991. Samples at Southampton were analyzed for dissolved phase Pb, Co, Cu, Mn, Fe, Cd, and Ni using the solvent extraction/graphite furnace atomic absorption spectrophotometry (GFAAS) technique of Danielsson *et al.* (1978) as modified by Statham (1985) and Tappin (1988). Particulate trace metals (those listed above plus Al) were extracted in 25 % acetic acid; the residue of selected samples was subsequently totally digested in  $\text{HNO}_3/\text{HCl}/\text{HClO}_4$  according to the method of Loring and Rantala (1992). Samples at Lille were analyzed by differential pulse anodic stripping voltammetry using techniques described in Statham *et al.* (1993). Detection limits and analytical precision are denoted in the Table.

## RESULTS AND DISCUSSION

The complete data set is presented in the Appendix. A vertically well mixed water column throughout the year (L.

Table

Detection and precision estimates for the analytical methods used for dissolved trace metals.

| Metal     | SUDO<br>(Althaus, 1992)         |                                       | LILLE                           |                          |
|-----------|---------------------------------|---------------------------------------|---------------------------------|--------------------------|
|           | Relative standard deviation (%) | Detection limit <sup>a</sup> (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                     |
| MANGANESE | 5                               | 0.8                                   | 10-15                           | 0.9                      |
| NICKEL    | 12                              | 1.0                                   |                                 |                          |
| LEAD      | 11                              | 0.04                                  | 5-8                             | 0.04                     |

<sup>a</sup> Three times the standard deviation of the blank.

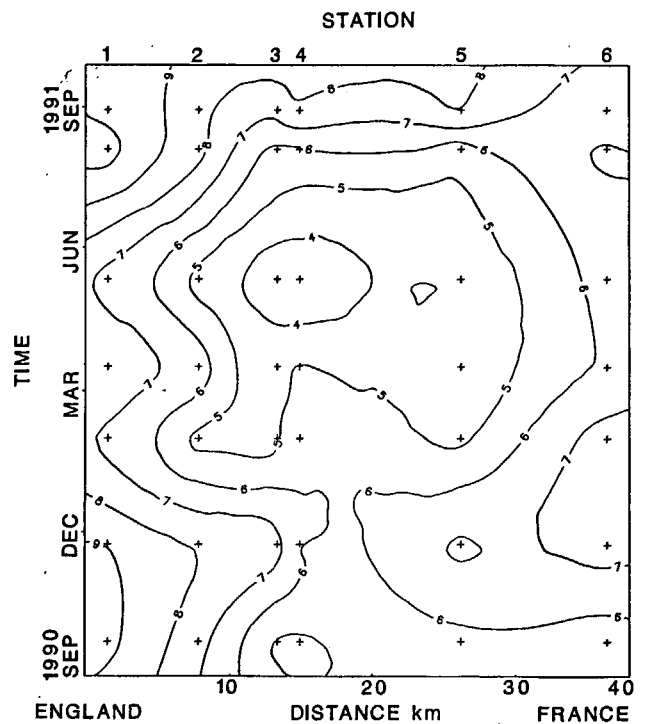


Figure 2

Temporal and spatial distribution of dissolved Ni. Contours represent dissolved Ni concentration in nM; crosses represent sampling sites and occasions.

Nash, personal communication) ensures that results obtained for surface and deep waters ( $\sim 20\text{m}$ ) are, except where marked in the script, within standard error; thus generally no distinction has been made between the data for different depths.

### Copper and nickel

The temporal and spatial distributions of Cu and Ni in both the dissolved and particulate phase show distinct similarities and therefore are discussed in parallel.

Figure 2 indicates that lowest dissolved Ni concentrations (3.7-6.1 nM) are always obtained for central Channel waters most distant from fluvial input, with values increasing towards the coastlines (7.3-9.8 nM at FX1; 6.1-7.6 nM at FX6). The increase is consistently greater at FX1 than FX6. A similar distribution is observed for copper (Cu vs Ni,  $r = +0.76$ ,  $n = 102$ ), with central Channel concentrations (3.0-4.4 nM) similar to those measured in western Atlantic shelf waters (4 nM; Bruland and Franks, 1983). While values obtained at those stations adjacent to FX1 and FX6 are slightly higher than those found in the central Channel suggesting a degree of lateral mixing, it appears that between stations FX5 and FX6 in particular, the decline in concentrations recorded away from the coast is rapid. This suggests that the coastal front observed in this region (Brylinski, 1986; Brylinski *et al.*, 1988) impedes the diffusion of dissolved species. It is also evident from Figure 2 that dissolved Ni concentrations fall by some 10 % at the coastal stations, rising to 30 % in the mid-Channel, during the summer months. This feature is less obvious for Cu where an enhanced temporal coverage revealed the exist-

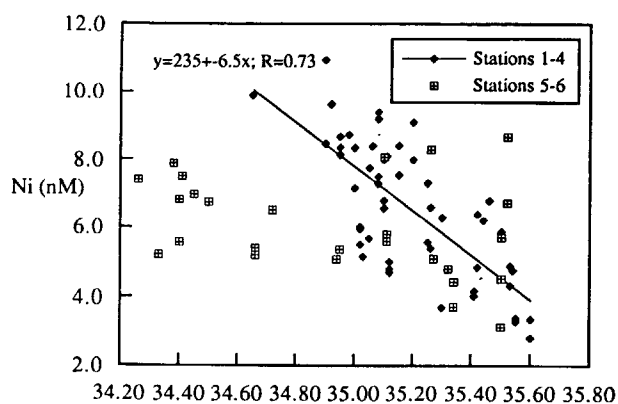


Figure 3

Relationship between dissolved Ni and salinity in the Strait of Dover. A similar relationship is observed for Cu. Numbers relate to sampling positions.

tence of unusually fresh waters (34.52-35.06) throughout the Channel (but most notably at the English coastline) in May associated with markedly higher dissolved trace metal (5.7-16.9 nM) and suspended particulate matter (SPM) concentrations (Lafite *et al.*, 1993). The presence of this feature is associated with an extended period of north-easterly winds (dominant wind direction is south-westerly) preceding sampling which brings water from the southern North Sea into the Dover Strait (L. Nash, personal communication). Slightly elevated dissolved Cu concentrations (no Ni data is available) in October 1991 may also be linked to this phenomenon.

Cu and Ni are amongst the most conservative trace metals during estuarine mixing (Althaus, 1992). Figure 3 suggests that the relationship between metal concentration and salinity for Channel waters is clearly complicated by differing English and French freshwater endmembers. While it is difficult to establish a line of best fit incorporating the French coastal stations an attempt is made to fit the English coastal station and central Channel waters ( $r = 0.73$ ;  $n = 54$ ). From this it is apparent that data from FX5 and FX6 fall below this line; this is consistent with a French freshwater end-member of lower dissolved Ni and Cu concentration relative to that at the English coast. It is suggested that the temporal distribution of dissolved Cu and Ni is strongly determined by salinity, although other processes are significant.

Seasonal removal of Ni in shelf sea environments by plankton has been observed by Noriki *et al.* (1985), and Kremling and Pohl (1989) provide data showing seasonal depletion in the Channel. In addition, Cu is widely regarded to exhibit "nutrient"-type behaviour often modified by some scavenging in open ocean waters (Spivack *et al.* 1983). This, however, contrasts with findings for this shallow coastal environment where correlation between Cu and the nutrient elements P and N as phosphate and nitrate (Bentley *et al.*, 1993) is poor. For Ni the relationship is improved (Ni vs P,  $r = +0.55$ ,  $n = 102$ ), although this may be due to dissolved phosphate concentrations being driven by riverine input. Tappin (1988) calculates that up to 8% of the winter water column inventory of Ni may be removed during a bloom, and the seasonal variation observed in this data set described

above is clearly in excess of this figure. Hence it appears that the distribution of dissolved Cu and Ni is perturbed by biological activity, but it remains difficult to quantify any relationship with the classical nutrient elements or to resolve the percentage of the winter water column inventory that may be removed under bloom conditions.

In the particulate phase brought into solution by acetic acid Ni and Cu maintain a strong correlation ( $r = +0.7$ ,  $n = 102$ ) which would be consistent with their suggested association with iron and manganese oxyhydroxide phases (Mn vs Cu,  $r = +0.5$ ,  $n = 102$ ; Mn vs Ni,  $r = +0.7$ ,  $n = 102$ ). While for both elements there is a degree of correlation between the mass of SPM and its metal content on a weight per volume of seawater basis (Ni,  $r = +0.6$ ,  $n = 102$ ; Cu,  $r = +0.4$ ,  $n = 102$ ) scatter exists which must therefore relate to differences in the metal content of the SPM on a mass/mass basis.

At all stations, Ni concentrations in the particulate phase (77-222 nmol/g) are observed to increase throughout the autumn into winter, with average concentrations of  $107 \pm 44$  at FX1,  $130 \pm 61$  at FX2-5 and  $94 \pm 46$  nmol/g at FX6 ( $\pm \sigma$ ). In April, minimum concentrations are recorded at all stations, falling to 65,  $49 \pm 12$  and  $34$  nmol/g for the stations described above. This reduction becomes progressively more marked towards the French coast. The Cu content of the SPM exhibits less variability, with mean concentrations of  $84 \pm 50$ ,  $162 \pm 100$  and  $114 \pm 87$  nmol/g at FX1, FX2-5 and FX6 respectively. In the residual phase, higher concentrations of Cu are found in association with the more crystalline fraction in June than December by some 30% in central Channel waters falling to 10% at the coast.

Figure 4 shows the "classical" relationship between the Cu content of the SPM (a similar plot is obtained for Ni) and the concentration of SPM in the water column (described in Lafite *et al.*, 1993), with highest trace metal concentrations found in the least turbid waters. A similar relationship has been noted by Duinker *et al.* (1979) in the Dutch Wadden Sea for Cd, Pb, Cu and Zn, and by Jones and Jefferies (1983) in the Irish and southern North Sea for Cu, Pb and Zn. They suggest that proportionally more metal is associated with the finer fractions of the SPM (where surface area is greater), and in less turbulent water there is a

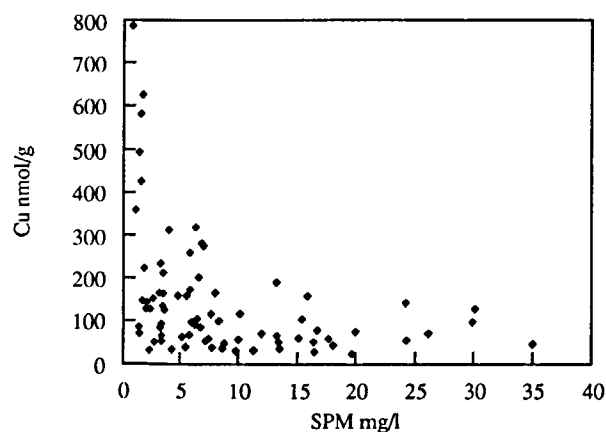


Figure 4

Mass of Cu in the SPM compared with the mass of SPM per litre of seawater.

greater proportion of this finely divided, permanently suspended material. It therefore appears that particle size is probably an important variable in determining trace metal concentration in the SPM in the strait.

Hydrous iron and manganese oxides are ubiquitous in the marine environment; as partial coatings on other minerals, or as discrete oxide particles. Such surfaces have an extremely high adsorption capacity for trace metals (Drever, 1988) and dissolution of such phases under mildly reducing conditions is likely to lead to concomitant release of any associated trace metal. The relationships described above between manganese and Cu or Ni suggest that both elements are indeed adsorbed by such phases (as correlation between Mn and organic carbon is poor) and seasonal variation in Cu and Ni content of the SPM may to some extent reflect changes in the scavenging of these elements. It is interesting to note from Figure 5 that in December, total (acetic acid reducible + residual) particulate Cu concentrations correlate positively with corresponding Al concentrations, suggesting a simple relationship between Cu and the terrigenous derived component of the SPM, while a clear positive deviation from this relationship is observed in June, implying that Cu is no longer dominantly associated with these fractions of the SPM. It is suggested therefore that Cu shows an affinity for organic material, which being more ubiquitous during periods of intense biological activity leads to an enhancement in the Cu content of the SPM in the summer.

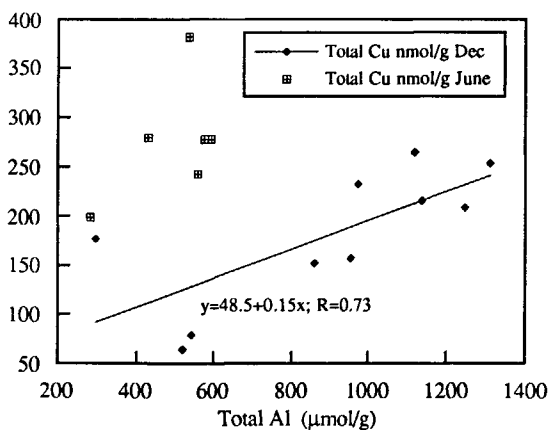


Figure 5

Total Cu and Al in the SPM in summer and winter.

### Manganese and cobalt

A detailed description of the Mn data acquired during the *FluxManche* programme is presented elsewhere in this edition (Domez *et al.*, 1993); this paper focuses on complementing this data with that obtained for cobalt. Several authors (Kremling *et al.*, 1987; Tappin, 1988; Kremling and Hydes, 1988) have reported a strong covariance between dissolved Mn and Co distributions which they suggest may indicate a similar geochemical pathway for these two elements.

The temporal and spatial variation in dissolved Mn is depicted in Figure 6 to provide background for the discus-

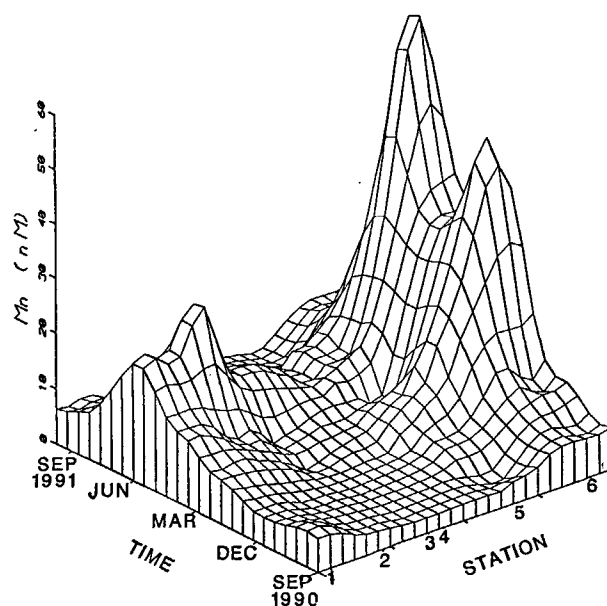


Figure 6

Temporal and spatial distribution of dissolved Mn.

sion of Co. A three dimensional plot is used to facilitate identification in the distribution.

Three distinct features are identified:

- 1) concentrations increase quite substantially in the summer months (range = 69.0-9.0 nM as opposed to 9.6-3.3 nM in the autumn and winter);
- 2) concentrations recorded at FX6 are generally higher than those recorded at FX1.
- 3) no clear relationship between dissolved Mn and salinity is evident.

Mean dissolved Co concentrations calculated as a yearly average over the entire sampling period are markedly uniform for the central stations ( $0.23 \pm 0.12$  nM). At the English coast concentrations increase to  $0.57 \pm 0.27$  nM, and it is assumed that lateral advection and mixing generates a slightly higher mean concentration at the adjacent station relative to other central stations ( $0.34 \pm 0.16$  nM). At FX6 results are higher than those in the central Channel, but lower than those for the English coast ( $0.38 \pm 0.09$  nM). These results are similar to those observed for Cu and Ni, but clearly contrast with those obtained for Mn at FX6. On a temporal basis, the central Channel stations show maximum Co concentrations in the autumn, while those water masses most coastally influenced (FX1, 2 and 6) appear to exhibit maximum concentrations in the summer. Throughout the sampling period, concentrations exhibit poor correlations with salinity.

Hence it is evident that large dissolved Mn concentrations at FX6 do not have corresponding increases in Co concentrations, suggesting a different source for Mn at this station. Figure 7 shows all data with station FX6 omitted. There is some covariance between dissolved Co and Mn with a correlation coefficient of  $r = +0.6$ ,  $n = 102$ . This suggests that high dissolved Mn concentrations in summer are accompanied by increases in dissolved Co concentrations. Heggie and Lewis (1984) suggest that a large fraction of the solid

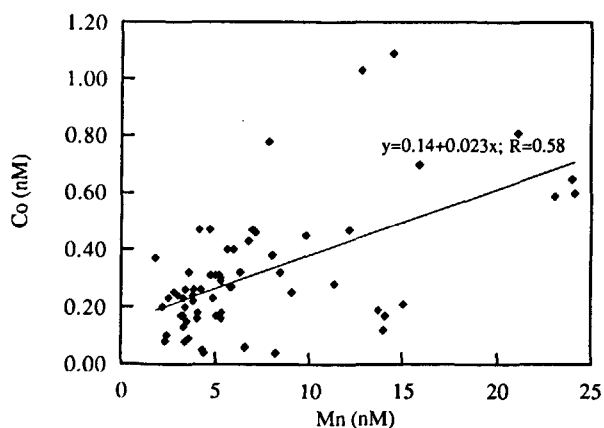


Figure 7

Relationship between dissolved Co and dissolved Mn across the Strait of Dover (omitting data from the French coast).

phase Co and Mn that settles into the remobilization zone of sedimentary material is recycled through porewaters upon reduction of solid manganous oxide phases and can be released to the water column. Concurrent increases in dissolved Co and Mn concentrations are therefore consistent with a benthic source for these two elements, with the average molar ratio of the released elements being 25:1 (Mn:Co). The ratio of Mn:Co in porewaters is however not clearly established (Shaw *et al.*, 1990) and the overall importance of this process in determining water column budgets of these trace metals needs further investigation for this environment.

In the particulate phases dissolved by acetic acid, Mn displays some correlation with the SPM distribution on a mass/volume of seawater basis ( $r = +0.74$ ,  $n = 102$ ) although scatter exists, most notably at FX6. This scatter is a function of changes in the Mn content of the particle population. Throughout the year the concentration of Mn in the SPM is lowest in the central Channel (2.4–4.5  $\mu\text{mol/g}$ ) increasing slightly at FX1 (3.6–6.8  $\mu\text{mol/g}$ ) and more notably at FX6 (7–10.5  $\mu\text{mol/g}$ ). Minimum values at FX4 and 5 are recorded in June, while the remaining stations show minimum values in April, representing a reduction of some 30% over concentrations recorded for the winter water column inventory. The amount of Mn in the residual fraction remains fairly constant during this period, suggesting either release from the acetic acid soluble phase in the summer or increased uptake in the winter leads to the overall change in Mn content of the SPM. Correlation between dissolved Mn and acetic acid soluble particulate Mn is however complicated by the large range of summer dissolved Mn concentrations.

Corresponding concentrations of particulate Co also linearly correlate with the SPM concentration with  $r = +0.6$ ,  $n = 102$ , on a mass per volume of seawater basis. Maximum concentrations of Co in the SPM are in the autumn and winter periods at all stations. Mean concentrations for this period are  $63 \pm 25$ ,  $55 \pm 23$  and  $35 \pm 13$  nmol/g for FX1, FX2–5 and FX6 respectively; in the spring and early summer values generally exhibit a slight reduction ( $45 \pm 8$ ,  $45 \pm 12$  and  $29 \pm 5$  nmol/g, stations as above). Concentrations

of Co in the SPM tend to be lower at FX6 than FX1 in contrast to findings for Mn. Eliminating data for FX6, a reasonable positive correlation is obtained ( $r = +0.7$ ,  $n = 102$ ). A similar correlation coefficient is produced if Co data from all stations is plotted against the Fe content of the SPM ( $r = +0.7$ ,  $n = 102$ ). The correlation coefficients described above therefore suggest that Fe and Mn oxyhydroxide phases are important in regulating the Co content of particulate matter. The relationship between Co and Mn at FX6 is clearly complicated by anomalously large concentrations of Mn in the SPM at this station.

## Cadmium

In accordance with observations for other trace metals studied, dissolved Cd concentrations are lowest in central Channel waters at all times of the year, with some evidence of limited lateral advection and mixing between the coastal and adjacent stations. During autumn, the value recorded at FX1 ( $0.27 \pm 0.04$  nM) is greater than that found for the corresponding period at FX6 ( $0.20 \pm 0.06$  nM) while throughout the remainder of the year concentrations at FX6 (winter  $0.29 \pm 0.09$ , spring  $0.24 \pm 0.04$  and summer  $0.25 \pm 0.10$ ) are elevated compared to those at FX1 (winter  $0.15 \pm 0.06$ , spring  $0.17 \pm 0.05$  and summer  $0.20 \pm 0.07$ ). Over an annual cycle it is apparent that highest dissolved Cd concentrations are recorded during the winter at stations 3–6. Some depletion of concentrations recorded in spring is evident, particularly at the central Channel stations, although this diminution may be partly masked by enhanced Cd values recorded in May (as for Cu) due to advection of water from the southern North Sea. If spring values are assessed on the basis of data for March and April only, then mean concentrations for UK, central Channel, and French waters respectively are  $0.15 \pm 0.03$ ,  $0.12 \pm 0.02$  and  $0.22 \pm 0.03$  nM, representing a decrease by some 20% at the coast rising to 30% in the central Channel over the winter water column inventory. In summer, concentrations at all stations are approaching those recorded in autumn.

In contrast with Cu and Ni, dissolved Cd shows a relatively weak relationship with salinity. Concentrations of the metal were slightly lower in the spring than in winter, possibly reflecting its involvement with the biological cycling of material. The concentrations of dissolved Cd and those of nitrate and phosphate were, however, poorly correlated (for nitrate,  $r = 0.2$ ,  $n = 144$ ; for phosphate  $r = 0.01$ ,  $n = 144$ ). Close relationships between concentrations of dissolved Cd and nutrient elements have been widely observed in the open ocean following the early investigations of these relationships by Boyle *et al.* (1976) and Bruland (1980). The extent to which changes in dissolved concentrations of Cd in shelf waters are associated with nutrient cycling is, however, less apparent. Valenta *et al.* (1986) attributed a decrease in dissolved Cd concentrations in the eastern Scheldt estuary during summer months to specific binding of the metal to living phytoplankton, and it has been suggested (Kremling and Hydes, 1988) that differences between concentrations found for dissolved Cd (and also Cu, Ni and Zn) in the western Baltic Sea in later summer 1982 and winter 1984 may have resulted from biological uptake.

Danielsson *et al.* (1985) found, however, that following major depletion of nutrients by phytoplankton production in the North Sea concentrations of trace metals, including Cd, remained relatively high; this is consistent with the results of Kremling *et al.* (1987). In a study of Channel waters, covering periods with high and low nutrient concentrations, Tappin (1988) found no significant correlation between dissolved Cd and nutrients. The present data appear to accord with low removal of metals in association with nutrient utilisation.

Whilst the relatively low distribution coefficient ( $K_D$ ) calculated for Cd reflects the importance of the dissolved phase in the water column budget ( $\log K_D \sim 3.8$  in winter;  $\log K_D \sim 4.7$  in summer), temporal and spatial variations in the Cd content of the SPM may be sufficient to influence these values. The relationship between particulate Pb, Cu and Ni and the water column particle loading reflects changes in metal composition with particles of different size, but for Cd a different metal composition/particle size relationship is evident. Figure 8 reveals two distinct features in the temporal and spatial distribution of Cd in the SPM in the Dover Strait:

- an increase in Cd content in the summer months which is most pronounced in the central Channel;
- enhanced levels of Cd in the SPM at FX6 throughout the year.

These trends are also reflected in the residual (organic and crystalline) particulate fraction, with values of 1.3, 0.8, 4.3, 5.5, 4.4 and 6.2 nmol/g for FX1-6 in December, as opposed to values of 5.2, 12.6, 21.7, 22.6 and 2.8 nmol/g for FX1, 2, 4, 5 and 6 respectively in June.

Consistent with the observation of Collier and Edmond (1984) on marine biogenic particles, it is suggested that in the Dover Strait, particulate Cd is to a large extent bound in biogenic fractions; the correlation observed between residually associated Cd (which will include organic fractions) and the organic content of the SPM is strongly positive ( $r = +0.9$ ,  $n = 24$ ). At all times of the year, total particulate Cd concentrations are poorly related to total particulate Al concentrations, again inferring that organic, as opposed to refractory crystalline phases are the important carrier phases for particulate Cd.

This relationship is, however, insufficient to describe temporal and spatial trends observed in the acetic acid soluble fraction. Correlation between Cd and Mn or Fe concentrations in the SPM is poor, implying that Fe and Mn oxyhydroxides are not important carrier phases of Cd. The incorporation of Cd in foraminiferal  $\text{CaCO}_3$  shells during their formation has been used by some authors (Deurer *et al.*, 1978; Prohic and Kniewald, 1987) to explain the presence of Cd in the carbonate fraction of sedimentary material. However covariance between the concentrations of Ca and Cd in the SPM samples considered here is small and indicates that carbonate phases do not extensively control the concentration of Cd in the acetic acid reducible particulate phase.

The concentration of Cd in the SPM decreases with increasing SPM concentration as observed for Cu and Ni. This phenomena has also been observed for Cd by Duinker *et*

*al.* (1979) in the Dutch Wadden Sea. Although this relationship holds for the particle population at FX6, data collected at this station tends to plot consistently above that for the remaining stations and these particles appear to have a different Cd signature, which may be related to dumped dredge spoil from Boulogne harbour.

## Lead

The dissolved Pb distribution is dominated by significantly enhanced values at all stations in May 1991 (0.58-3.31 nM), a feature related to the ingress of water from the southern North Sea), and to a lesser extent in March 1991 (0.30-1.06 nM) and October 1990 (0.47-0.77 nM), both periods for which a significant fraction of winds were observed to be north-easterly. Throughout the remainder of the year concentrations of  $0.29 \pm 0.14$ ,  $0.19 \pm 0.11$  and  $0.23 \pm 0.14$  nM are recorded at FX1, FX2-5 and FX6 respectively. There are increased values at the coastlines, with concentrations recorded at FX1 generally greater than those at FX6. Lowest values are consistently detected in the central Channel waters.

A weak relationship between dissolved Pb and salinity exists, although it is apparent that data for FX6 falls somewhat below the line of fit generated for the remaining stations. If results from FX6 are removed, then a correlation coefficient of  $r = -0.5$  ( $n = 85$ ) is obtained, slightly stronger than that reported by Tappin (1988) for a winter cruise in the Channel to the west of the present study area ( $r = -0.29$ ). The same author also found a positive correlation between salinity and dissolved Pb during a later spring

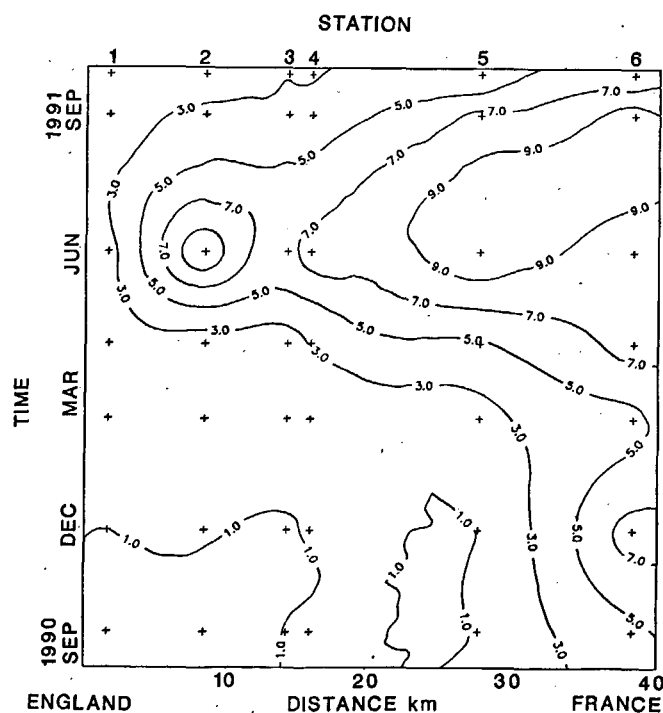


Figure 8

Temporal and spatial distribution of acetic acid soluble particulate Cd. Contours represent particulate Cd concentration in nmol/g; crosses represent sampling sites and occasions.

cruise, while Balls (1985) found no correlation with salinity for a transect off the Humber estuary into the North Sea. While enhanced dissolved Pb values recorded in May may be largely described in terms of a fresher water mass present throughout the Channel during the sampling period, coherently high results obtained in October 1990 and March 1991 are not readily related to the salinity distribution. These enhanced values are accompanied to some extent by increased Zn concentrations, and occasionally by increased dissolved Cu concentrations. It was suggested by Tappin *et al.* (1993) that atmospheric fluxes of Pb and Zn may be as important to the mass balance of the English Channel as fluxes estimated for the river Seine by Boust (1981). While no measurements of atmospheric aerosols were performed during the course of this study, atmospheric inputs to this area are suggested as important for Pb and Zn (Otten *et al.*, 1989). It is therefore reasonable to suggest that high dissolved Pb levels for these months may reflect sporadic atmospheric input, which can account for the lack of correlation with salinity and explain the similar increase in concentration over the entire Channel.

If data collected during March and May is discounted on account of its unusual behaviour (accompanied by a suite of changes to other water column parameters not experienced on any other sampling occasions), then dissolved Pb concentrations decrease in the spring. This reduction may be up to 50 % of the dissolved Pb winter water column inventory in central Channel waters, although this percentage falls towards the coastlines where additional inputs of dissolved Pb may mask seasonal signatures. Removal of lead as a result of biological uptake has been previously reported (Boyle *et al.*, 1986), and in Channel waters, Tappin (1988) used a simple calculation to suggest that up to 30 % of the winter water column inventory may be removed as a result of such activity. Correlation of Pb and traditional indicators of diatom activity (Si and Al) is however poor and clearly complicated in coastal waters. Tappin *et al.* (1993) suggest that a decrease in input from the river Seine of 50 % would result in a reduction of dissolved Pb concentration in the Channel of *ca.* 14 %, and changes in riverine input may therefore also be important in perturbing apparent dissolved Pb distributions.

The total water column Pb budget is however dominated by its association with the particulate phase (*see* Statham *et al.*, 1993). Distribution coefficients exhibit little variation throughout the year ( $K_D = 6.0 \pm 0.2$ ), reflecting only nominal changes in the temporal particulate Pb distribution. Average concentrations of Pb in the acetic acid soluble fraction are  $113 \pm 36$ ,  $106 \pm 33$  and  $136 \pm 47$  nmol/g for FX1, FX2-5 and FX6 respectively.  $K_D$  values generated for the coastal stations are fractionally ( $\sim 0.2$ ) smaller than those given for central waters, reflecting higher dissolved Pb concentrations in this region. On a weight for volume basis, the particulate Pb distribution is clearly controlled by the quantity of SPM in the water column ( $r = + 0.8$ ,  $n = 102$ ). Some scatter is however evident, particularly at the coastlines, reflecting variations in the Pb content of the particle population.

The correlation between the concentration of Pb and Mn or Fe in the SPM ( $r = + 0.9$ ,  $n = 102$ ) is consistent with the fact that Mn/Fe oxyhydroxide surfaces are highly efficient scavengers of Pb and thus markedly influence its solid phase distribution. Lead is known to be rapidly adsorbed onto particulate phases following input from riverine systems (Elbaz-Poulichet *et al.*, 1984) and data presented here suggest that Fe/Mn hydrous oxide coatings on particles are responsible for this. Correlation of Pb released under both mildly and strongly acidic conditions with the organic component of the SPM is weak, advocating that the biogenic phase is not a major carrying phase of Pb. Total particulate Pb concentrations correlate well ( $r = 0.7$ ;  $n = 11$ ) with total particulate Al concentrations in December implying that the winter particulate Pb content is strongly determined by fluvially and atmospherically derived particles which can be enhanced in Pb, whilst in June scatter about this line is evident, suggesting that Pb concentrations are influenced by further processes within the water column.

## SUMMARY AND CONCLUSION

This spatially and temporally intensive data set allows identification of a series of important features in the geochemical cycling of the trace metals studied.

### Cu and Ni

- 1) Dissolved Cu and Ni concentrations co-vary strongly in the English Channel and appear to be dominantly determined by freshwater input.
- 2) Endmember concentrations at the English and French coast are distinctly different and complicate overall Channel relationships with salinity.
- 3) There is limited evidence that additional processes such as biological uptake and regeneration and benthic input can perturb dissolved concentrations, although it is difficult to resolve the extent these processes.
- 4) The size characteristics of the particle population may be reflected by the trace metal content of the particles. As observed in other coastal and estuarine environments, smaller particles have higher Ni and Cu concentrations.
- 5) The data are consistent with an association of Ni, and to a lesser extent Cu, with Fe/Mn oxyhydroxide phases; and an association of Cu also with the organic fraction.

### Mn and Co

- 1) Large summer increases in dissolved Mn concentrations are to some extent accompanied by an increase in dissolved Co concentrations, invoking a common source for these two elements. A benthic source is consistent with this covariance.
- 2) A reduction in acetic acid soluble particulate Mn and Co is observed during the summer, possibly implying release from this phase during the summer or increased uptake in the winter.



3) These relationships are clearly more complex at FX6. Unusually high concentrations of Mn in both the dissolved and particulate phase (probably attributable to local inputs) are not accompanied by increases in respective Co concentrations.

#### Cd

1) There is only a very weak relationship between dissolved Cd and salinity, demonstrating minimal fluvial influence for Cd.

2) Biological activity is inferred to generate a spring decrease in dissolved Cd concentrations, although there is no strong dissolved Cd:phosphate relationship as seen in the open ocean.

3) Evidence from the particulate phase suggests that particulate Cd is to a large extent biogenic.

4) Cd concentrations in both the dissolved and particulate phase are elevated at FX6.

#### Pb

1) Dissolved Pb concentrations in the Dover Strait appear to be sensitive to variations in freshwater and atmospheric inputs, and in addition may be perturbed to some degree by

biological activity.

2) The concentration of Pb in the acetic acid reducible phase is highly correlated to Fe and Mn inferring its incorporation into/onto Fe/Mn oxyhydroxide phases.

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## APPENDIX

*The FluxManche data set.*

| DEPTH  | SALINITY | DISSOLVED TRACE METALS |          |          |          |          |          |
|--------|----------|------------------------|----------|----------|----------|----------|----------|
|        |          | Cd<br>pM               | Co<br>nM | Cu<br>nM | Mn<br>nM | Ni<br>nM | Pb<br>nM |
| 2      | 35.3     | 190                    |          | 4.4      |          |          | 0.16     |
| 3      | 35.39    | 200                    |          | 5        |          |          | 0.15     |
| 4      | 35.36    | 180                    |          | 2.3      |          |          | 0.22     |
| 5      | 35.32    | 280                    |          | 4.5      |          |          | 0.12     |
| 6      | 32.46    | 240                    |          | 6.8      |          |          | 0.17     |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.16    | 260                    |          | 7.7      |          |          | 0.39     |
| 2      | 35.21    | 230                    |          | 7.2      |          |          | 0.22     |
| 3      | 35.28    | 200                    |          | 11.3     |          |          | 0.24     |
| 4      | 35.41    | 220                    |          | 7.5      |          |          | 0.38     |
| 5      | 35.36    | 300                    |          | 8        |          |          | 0.14     |
| 6      | 33.93    | 300                    |          | 5.7      |          |          | 0.25     |
| Feb-91 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.46    | 113                    | 0.381    | 5.77     | 8.07     | 6.8      | 0.199    |
| 2      | 35.54    |                        |          |          |          |          |          |
| 3      | 35.53    | 133                    | 0.095    | 3.36     | 2.42     | 4.89     | 0.252    |
| 4      | 35.5     |                        |          |          |          |          |          |
| 5      | 35.52    |                        |          |          |          |          |          |
| 6      | 35.52    | 472                    | 0.256    | 5.07     | 52.19    | 6.73     | 0.092    |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.44    | 78                     | 0.325    | 5.2      | 8.48     | 6.22     | 0.228    |
| 2      | 35.54    | 109                    | 0.126    | 3.89     | 3.32     | 4.76     | 0.186    |
| 3      | 35.53    | 116                    | 0.085    | 3.15     | 2.34     | 4.33     | 0.077    |
| 4      | 35.5     | 137                    | 0.167    | 3.47     | 3.29     | 5.88     | 0.104    |
| 5      | 35.32    | 195                    | 0.05     | 4.5      | 4.33     | 4.81     | 0.159    |
| 6      | 35.52    | 287                    | 0.304    | 5.55     | 57.11    | 8.67     | 0.191    |
| Mar-91 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.11    | 140                    |          | 5.7      |          |          | 1.01     |
| 2      | 35.23    | 150                    |          | 6.5      |          |          | 0.48     |
| 3      | 35.29    | 120                    |          | 8.5      |          |          | 0.47     |
| 4      | 35.33    | 90                     |          | 3.5      |          |          | 0.3      |
| 5      | 35.33    | 160                    |          | 9.7      |          |          | 0.61     |
| 6      | 34.39    | 250                    |          | 15.6     |          |          | 0.29     |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.11    | 150                    |          | 8.6      |          |          | 1.06     |
| 2      | 35.23    | 160                    |          | 6.5      |          |          | 0.46     |
| 3      | 35.33    | 120                    |          | 3.4      |          |          | 0.39     |
| 4      | 35.34    | 90                     |          | 3.5      |          |          | 0.39     |
| 5      | 35.34    | 180                    |          | 8.5      |          |          | 0.7      |
| 6      | 34.47    | 230                    |          | 10.8     |          |          | 0.26     |
| Apr-91 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.15    | 110                    | 1.03     | 4.47     | 12.8     | 8.41     | 0.213    |
| 2      | 35.25    | 144                    | 0.46     | 4.57     | 7.17     | 7.32     | 0.081    |
| 3      | 35.41    | 94                     | 0.09     | 2.72     | 3.59     | 4.02     | 0.051    |
| 4      | 35.42    | 140                    | 0.18     | 3.58     | 5.34     | 4.86     | 0.11     |
| 5      | 35.34    | 115                    | 0.04     | 2.43     | 4.41     | 3.71     | 0.053    |
| 6      | 34.33    | 223                    | 0.42     | 5.54     | 34.61    | 5.2      | 0.528    |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.15    | 185                    | 1.09     | 4.14     | 14.49    | 7.55     | 0.217    |
| 2      | 35.25    | 84                     | 0.31     | 4.51     | 5.21     | 5.58     | 0.045    |
| 3      | 35.41    | 110                    | 0.08     | 2.99     | 3.4      | 4.17     | 0.219    |
| 4      | 35.42    | 113                    | 0.27     | 3.55     | 5.89     | 6.4      | 0.062    |
| 5      | 35.34    | 101                    | 0.06     | 2.21     | 6.63     | 4.43     | 0.108    |
| 6      | 34.72    | 167                    | 0.45     | 3.67     | 32.15    | 6.52     | 0.061    |
| Sep-90 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.08    | 278                    | 0.47     | 8.7      | 6.8      | 9.2      | 0.13     |
| 2      | 35.08    | 210                    | 0.26     | 6.8      | 3.4      | 7.5      | 0.1      |
| 3      | 35.12    | 220                    | 0.23     | 4.7      | 2.5      | 5        | 0.06     |
| 4      | 35.12    | 225                    | 0.25     | 4.4      | 2.8      | 5        | 0.08     |
| 5      | 35.11    |                        | 0.72     | 3.3      | 1.3      | 5.6      |          |
| 6      | 34.66    | 160                    | 0.52     | 4        | 6.4      | 5.4      | 0.14     |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.08    | 300                    | 0.7      | 8.6      | 15.9     | 9.4      | 0.26     |
| 2      | 35.08    | 170                    | 0.47     | 5.7      | 4.7      | 7.3      | 0.06     |
| 3      | 35.12    | 160                    | 0.37     | 4.1      | 1.8      | 4.8      | 0.05     |
| 4      | 35.12    | 160                    | 0.32     | 4.1      | 3.6      | 4.7      | 0.08     |
| 5      | 35.11    | 160                    | 0.2      | 4.5      | 2.2      | 5.8      | 0.08     |
| 6      | 34.66    | 155                    | 0.51     | 5.1      | 6.2      | 5.2      | 0.1      |
| Oct-90 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.17    | 180                    |          | 5.8      |          |          | 0.71     |
| 2      | 35.16    | 220                    |          | 8.6      |          |          | 0.6      |
| 3      | 35.17    | 180                    |          | 3.5      |          |          | 0.7      |
| 4      | 35.19    | 130                    |          | 2.4      |          |          | 0.53     |
| 5      | 35.18    | 160                    |          | 2.1      |          |          | 0.47     |
| 6      | 34.73    | 280                    |          | 4.2      |          |          | 0.77     |
| Nov-90 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 35.01    | 250                    |          | 6.8      |          |          | 0.34     |
| 2      | 35.13    | 220                    |          | 3        |          |          | 0.24     |
| 3      | 35.32    | 190                    |          | 2.6      |          |          | 0.24     |
| 4      | 35.33    | 200                    |          | 4.2      |          |          | 0.24     |
| 5      | 35.16    | 130                    |          | 2.4      |          |          | 0.25     |
| 6      | 34.92    | 210                    |          | 5.4      |          |          | 0.32     |
| DEEP   |          |                        |          |          |          |          |          |
| 1      | 35.24    | 280                    |          | 6.4      |          |          | 0.32     |
| 2      | 35.32    | 140                    |          | 3.2      |          |          | 0.16     |
| 3      | 35.2     | 190                    |          | 4.7      |          |          | 0.2      |
| 4      | 35.12    | 230                    |          | 3.8      |          |          | 0.24     |
| 5      | 34.94    | 150                    |          | 3.1      |          |          | 0.14     |
| 6      | 34.92    | 570                    |          | 5.3      |          |          | 0.4      |
| Dec-90 |          |                        |          |          |          |          |          |
| SURF   |          |                        |          |          |          |          |          |
| 1      | 34.65    | 128                    | 0.31     | 6.7      | 5        | 9.9      | 0.14     |
| 2      | 35.1     | 127                    | 0.2      | 6.7      | 3.4      | 8        | 0.05     |
| 3      | 35.2     | 371                    | 0.24     | 6.2      | 3        | 8        | 0.12     |
| 4      | 35.26    | 171                    | 0.15     | 4.2      |          | 6.6      | 0.06     |
| 5      | 35.26    | 106                    | 0.4      | 4.6      | 6        | 8.3      | 0.22     |
| 6      | 34.26    | 197                    | 0.32     | 5.8      | 9.8      | 7.4      | 0.11     |



| Mar-91 |       |       |     |     |      |     |     |    |  |
|--------|-------|-------|-----|-----|------|-----|-----|----|--|
| SURF   |       |       |     |     |      |     |     |    |  |
| 1      | 16.30 |       |     |     |      |     |     |    |  |
| 2      | 8.20  |       |     |     |      |     |     |    |  |
| 3      | 10.30 |       |     |     |      |     |     |    |  |
| 4      | 11.00 |       |     |     |      |     |     |    |  |
| 5      | 3.50  |       |     |     |      |     |     |    |  |
| 6      | 9.60  |       |     |     |      |     |     |    |  |
| DEEP   |       |       |     |     |      |     |     |    |  |
| 1      | 24.20 |       |     |     |      |     |     |    |  |
| 2      | 8.90  |       |     |     |      |     |     |    |  |
| 3      | 9.90  |       |     |     |      |     |     |    |  |
| 4      | 10.70 |       |     |     |      |     |     |    |  |
| 5      | 3.30  |       |     |     |      |     |     |    |  |
| 6      | 13.50 |       |     |     |      |     |     |    |  |
| Apr-91 |       |       |     |     |      |     |     |    |  |
| SURF   |       |       |     |     |      |     |     |    |  |
| 1      | 10.02 | 2.24  | 40  | 57  | 3.8  | 70  | 97  | 17 |  |
| 2      | 3.39  | 1.63  | 48  | 66  | 4.1  | 63  | 85  | 27 |  |
| 3      | 1.39  | 1.81  | 48  | 71  | 4.1  | 43  | 100 | 37 |  |
| 4      | 3.36  | 3.39  | 75  | 93  | 5.0  | 53  | 112 | 48 |  |
| 5      | 0.94  | 7.09  | 45  | 2   | 3.2  | 37  | 107 | 36 |  |
| 6      | 1.82  | 8.34  | 135 | 223 | 9.0  | 67  | 199 | 34 |  |
| DEEP   |       |       |     |     |      |     |     |    |  |
| 1      | 16.47 | 1.66  | 39  | 29  | 3.3  | 59  | 105 | 8  |  |
| 2      | 3.66  | 1.80  | 50  | 126 | 4.1  | 75  | 98  | 30 |  |
| 3      |       | 1.39  | 55  | 61  | 4.2  | 55  | 92  | 34 |  |
| 4      | 3.55  | 1.36  | 34  | 164 | 3.1  | 24  | 40  | 24 |  |
| 5      | 1.34  | 2.05  | 46  | 86  | 3.6  | 40  | 100 | 46 |  |
| 6      | 3.29  | 7.56  | 19  | 85  | 4.9  | 1   | 97  | 31 |  |
| May-91 |       |       |     |     |      |     |     |    |  |
| SURF   |       |       |     |     |      |     |     |    |  |
| 1      | 37.35 |       |     |     |      |     |     |    |  |
| 2      | 16.25 |       |     |     |      |     |     |    |  |
| 3      | 35.20 |       |     |     |      |     |     |    |  |
| 4      | 17.57 |       |     |     |      |     |     |    |  |
| 5      | 1.66  |       |     |     |      |     |     |    |  |
| 6      | 30.75 |       |     |     |      |     |     |    |  |
| DEEP   |       |       |     |     |      |     |     |    |  |
| 1      | 38.57 |       |     |     |      |     |     |    |  |
| 2      | 24.38 |       |     |     |      |     |     |    |  |
| 3      | 11.89 |       |     |     |      |     |     |    |  |
| 4      | 14.03 |       |     |     |      |     |     |    |  |
| 5      | 9.79  |       |     |     |      |     |     |    |  |
| 6      | 21.45 |       |     |     |      |     |     |    |  |
| Jun-91 |       |       |     |     |      |     |     |    |  |
| SURF   |       |       |     |     |      |     |     |    |  |
| 1      | 11.28 | 1.98  | 46  | 32  | 6.3  | 127 | 108 | 42 |  |
| 2      | 1.53  | 8.90  | 41  | 426 | 4.5  | 156 | 86  | 36 |  |
| 3      | 0.74  | 63.16 | 25  | 787 | 30.9 |     | 652 | 43 |  |
| 4      | 2.32  | 7.30  | 56  | 32  | 0.0  | 48  | 190 |    |  |
| 5      | 1.67  | 9.75  | 49  | 626 | 2.3  |     | 102 | 42 |  |
| 6      | 8.37  | 6.73  | 29  | 100 | 11.5 | 56  | 110 | 36 |  |
| DEEP   |       |       |     |     |      |     |     |    |  |
| 1      | 10.15 | 1.87  | 54  | 117 | 7.2  | 50  | 97  | 43 |  |
| 2      | 2.64  | 15.00 | 57  | 152 | 4.4  |     | 111 | 35 |  |
| 3      | 1.83  |       |     |     |      |     |     |    |  |
| 4      | 1.99  | 8.88  | 37  | 128 | 1.5  | 368 | 75  |    |  |
| 5      | 1.06  | 11.58 | 16  | 360 | 2.5  |     | 185 | 30 |  |
| 6      | 13.48 | 8.07  | 24  | 36  | 10.6 | 65  | 119 | 36 |  |
| Jul-91 |       |       |     |     |      |     |     |    |  |
| surf   |       |       |     |     |      |     |     |    |  |
| 1      | 18.36 |       |     |     |      |     |     |    |  |
| 2      | 11.57 |       |     |     |      |     |     |    |  |
| 3      | 5.06  |       |     |     |      |     |     |    |  |
| 4      | 1.99  |       |     |     |      |     |     |    |  |
| 5      | 3.97  |       |     |     |      |     |     |    |  |
| 6      | 9.10  |       |     |     |      |     |     |    |  |
| deep   |       |       |     |     |      |     |     |    |  |
| 1      | 23.10 |       |     |     |      |     |     |    |  |
| 2      | 16.00 |       |     |     |      |     |     |    |  |
| 3      | 5.12  |       |     |     |      |     |     |    |  |
| 4      | 6.15  |       |     |     |      |     |     |    |  |
| 5      | 3.97  |       |     |     |      |     |     |    |  |
| 6      | 9.10  |       |     |     |      |     |     |    |  |
| Aug-91 |       |       |     |     |      |     |     |    |  |
| SURF   |       |       |     |     |      |     |     |    |  |
| 1      | 6.20  |       |     |     |      |     |     |    |  |
| 2      | 4.30  |       |     |     |      |     |     |    |  |
| 3      | 2.00  |       |     |     |      |     |     |    |  |
| 4      | 1.50  |       |     |     |      |     |     |    |  |
| 5      | 1.50  |       |     |     |      |     |     |    |  |
| 6      | 2.00  |       |     |     |      |     |     |    |  |
| DEEP   |       |       |     |     |      |     |     |    |  |
| 1      | 8.50  |       |     |     |      |     |     |    |  |
| 2      | 4.70  |       |     |     |      |     |     |    |  |
| 3      | 2.20  |       |     |     |      |     |     |    |  |

| Sep-91 |        |       |     |  |     |      |     |     |    |
|--------|--------|-------|-----|--|-----|------|-----|-----|----|
| SURF   |        |       |     |  |     |      |     |     |    |
| 1      | 29.93  | 1.56  |     |  | 98  | 5.7  |     | 140 | 48 |
| 2      | 4.85   | 1.83  |     |  | 159 | 5.9  | 124 | 105 | 65 |
| 3      | 3.55   | 4.94  | 47  |  | 212 | 0.5  | 156 | 92  | 32 |
| 4      | 1.65   | 4.94  | 11  |  | 147 | 1.6  | 49  | 24  |    |
| 5      | 1.39   | 7.62  | 16  |  | 495 | 6.5  | 184 | 118 | 37 |
| 6      | 4.05   | 12.87 | 65  |  | 312 | 27.3 | 189 | 260 | 23 |
| DEEP   |        |       |     |  |     |      |     |     |    |
| 1      |        | 1.62  | 69  |  | 121 | 7.0  |     | 136 | 63 |
| 2      | 6.87   | 4.76  | 117 |  | 282 | 8.8  | 228 | 178 | 83 |
| 3      | 3.32   | 4.90  | 31  |  | 234 | 3.2  | 221 |     | 41 |
| 4      | 3.50   | 9.37  | 22  |  | 135 | 2.0  | 84  | 68  |    |
| 5      | 1.53   | 11.99 | 12  |  | 582 | 7.8  | 271 | 222 |    |
| 6      | 5.87   | 8.00  | 33  |  | 259 | 20.1 | 160 | 205 | 45 |
| Oct-91 |        |       |     |  |     |      |     |     |    |
| SURF   |        |       |     |  |     |      |     |     |    |
| 1      | 13.21  | 2.66  | 91  |  | 190 | 6.7  |     | 192 | 67 |
| 2      | 15.87  | 2.52  | 78  |  | 158 | 6.0  | 155 | 138 | 58 |
| 3      | 6.36   | 7.87  | 130 |  | 319 | 11.3 | 273 | 282 | 85 |
| 4      | 8.06   | 2.24  | 63  |  | 165 | 5.1  | 222 | 129 | 45 |
| 5      | 2.07   | 2.11  | 58  |  | 144 | 5.0  | 124 |     | 57 |
| 6      | 6.30   | 5.00  | 32  |  | 92  | 11.0 | 73  | 133 | 51 |
| DEEP   |        |       |     |  |     |      |     |     |    |
| 1      | 30.15  | 1.28  | 81  |  | 128 | 6.3  | 82  | 153 | 49 |
| 2      | 24.20  | 1.96  | 103 |  | 142 | 6.9  |     | 134 | 69 |
| 3      | 6.63   | 2.00  | 86  |  | 201 | 6.7  | 160 |     | 63 |
| 4      | 7.07   | 3.23  | 83  |  | 275 | 6.6  | 212 | 193 | 70 |
| 5      | 2.38   | 3.19  | 40  |  | 128 | 4.6  | 225 | 60  |    |
| 6      | 11.08  | 5.76  | 43  |  |     | 11.6 | 80  | 146 | 44 |
| Nov-91 |        |       |     |  |     |      |     |     |    |
| SURF   |        |       |     |  |     |      |     |     |    |
| 1      | 14.00  |       |     |  |     |      |     |     |    |
| 2      | 12.30  |       |     |  |     |      |     |     |    |
| 3      | 9.80   |       |     |  |     |      |     |     |    |
| 4      | 15.80  |       |     |  |     |      |     |     |    |
| 5      | 2.50   |       |     |  |     |      |     |     |    |
| 6      | 13.00  |       |     |  |     |      |     |     |    |
| DEEP   |        |       |     |  |     |      |     |     |    |
| 1      | 24.00  |       |     |  |     |      |     |     |    |
| 2      | 26.50  |       |     |  |     |      |     |     |    |
| 3      | 17.80  |       |     |  |     |      |     |     |    |
| 4      | 4.60   |       |     |  |     |      |     |     |    |
| 5      | 4.50   |       |     |  |     |      |     |     |    |
| 6      | 139.70 |       |     |  |     |      |     |     |    |

TOTAL PARTICULATE TRACE METAL RESULTS

|        | Mn<br>uM/g | Cd<br>nM/g | Cu<br>nM/g | Pb<br>nM/g | Al<br>uM/g |
|--------|------------|------------|------------|------------|------------|
|        |            |            |            |            |            |
| SURF   |            |            |            |            |            |
| 1      | 8.3        | 2.2        | 254        | 205        | 1311       |
| 2      | 8.7        | 2.3        | 265        | 220        | 1120       |
| 3      | 5.8        | 7.3        | 152        | 132        | 860        |
| 4      | 8.3        | 5.1        | 208        | 243        | 1248       |
| 5      | 4          | 6.4        |            | 80         | 358        |
| 6      | 8.5        | 12         | 177        | 203        | 296        |
| DEEP   |            |            |            |            |            |
| 1      | 7.6        |            | 216        | 180        | 1138       |
| 2      | 7.2        | 1.4        | 232        | 181        | 974        |
| 3      | 5.3        | 2.6        | 64         | 115        | 519        |
| 4      | 5.5        | 8.6        | 157        | 151        | 955        |
| 5      | 3.6        | 3.4        | 79         | 117        | 542        |
| 6      | 8          | 17         | 89         | 213        |            |
| Jun-91 |            |            |            |            |            |
| SURF   |            |            |            |            |            |
| 1      | 7.9        |            | 243        | 114        | 558        |
| 2      | 8.2        | 17         | 280        | 314        | 429        |
| 3      |            |            |            |            | 870        |
| 4      | 3.7        | 23         |            | 301        | 826        |
| 5      | 5.3        | 29         |            | 320        | 519        |
| 6      | 15.6       | 8.4        | 278        |            | 595        |
| DEEP   |            |            |            |            |            |
| 1      | 9          | 7.1        | 278        | 137        | 576        |
| 2      | 6.1        | 32         | 382        | 139        | 535        |
| 3      |            |            |            |            |            |
| 4      | 7.8        | 38         |            |            | 782        |
| 5      | 4.6        | 37         |            | 234        | 540        |
| 6      | 16.6       | 12         | 199        | 230        | 282        |