

Trace metal fronts in waters of the Celtic Sea

Trace metals
Celtic Sea
Frontal zone
Continental margin

Métaux traces
Mer Celtique
Zone frontale
Marge continentale

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Received 24/06/93, in revised form 16/12/93, accepted 8/02/94

ABSTRACT

Two transects across the Celtic Sea and adjacent continental slope in August 1985 and August 1988 illustrate the importance of dynamic physical processes on dissolved trace metal distributions (Cd, Ni, Cu, Pb, Co, Fe, Mn). The influence of a coastal frontal zone can be seen in the 1985 transect, while an intrusion of open ocean waters into the shelf environment is the main factor influencing the horizontal distribution of trace metals in 1988. A third transect across the continental slope bordering the Porcupine Seabight (May 1984) reveals marked horizontal fronts in the concentrations of Fe, Mn and Cu at the shelf edge (over a 21 km distance, concentrations fall from 3 to 1 nM for Fe, from 2 to 0.5 nM for Mn, from 2 to 1 nM for Cu) which are unaccompanied by any coincident hydrographic features.

In transects 85 & 88, variations of metal concentrations versus salinity can be represented as two linear segments intersecting within the coastal frontal zone and at the leading edge of the oceanic intrusion, respectively. We propose that benthic inputs of metals to these waters are less important than previously assumed. By contrast, the remobilization of Fe, Mn and Cu from shelf edge sediments does provide the most plausible explanation for the presence of some unusual metal fronts observed at the Celtic shelf edge in 1984. The 1984 transect indicates not only a common benthic source of Fe, Mn and Cu in that particular area but also similarities in their cycling through the water column. These similarities are interpreted in terms of the photoreductive dissolution of oxidized forms of Fe and Mn, coinciding with the enhanced organic complexation of Cu.

None of the elements investigated shows any large scale perturbation of concentration by biological activity, even though nutrient concentrations are low where σ_θ is less than 27.00, *i.e.* in surface waters as well as landward of the isohaline coastal fronts. However, the 1985 transect suggests that some oxidative removal of Mn is probably taking place throughout the Celtic Sea and that dissolved Co and Pb are removed in places by uptake onto suspended solids.

RÉSUMÉ

Répartition et comportement des métaux dissous dans la Mer Celtique

Les concentrations en métaux dissous (Mn, Fe, Co, Ni, Cu, Cd et Pb) ont été mesurées le long de trois radiales s'étendant du plateau continental nord-européen à la proche plaine abyssale. Tandis que ces concentrations – à l'exception du nickel et du plomb – augmentent toutes en direction du continent, les variations horizontales les plus importantes sont enregistrées en divers emplacements de la plate-forme continentale selon les phénomènes mis en jeu. Un premier type

de discontinuité, observé en août 1985, est lié à la présence d'un front côtier saisonnier (température et salinité) séparant les eaux stratifiées de la Mer Celtique de celles bien brassées de la zone côtière du Pays de Galles. En août 1988, le gradient de salinité contrôle également la répartition de surface de ces métaux dans la zone de transition entre la Manche et la Mer Celtique : ainsi les variations observées en août 1988 résultent-elles d'une rencontre, au milieu de la plateforme continentale, entre l'eau de surface Nord-Atlantique et les eaux dessalées en provenance du continent. L'examen des profils verticaux du fer, manganèse et cuivre établis au travers du talus continental qui borde le Porcupine Seabight suggère un troisième mode de formation possible de gradients métalliques côtière. Dans ce dernier cas de figure, les données hydrologiques (T , S , σ_t) ne montrent aucun gradient et par conséquent ne permettent pas d'expliquer l'écart entre les valeurs relevées au-dessus de l'isobathe 600 m ($Fe = 1,1 \pm 0,3$ nM; $Mn = 0,5 \pm 0,1$ nM; $Cu = 1,3 \pm 0,1$ nM) et celles observées à la même immersion en bordure du talus continental ($Fe = 2,7 \pm 1,0$ nM; $Mn = 1,9 \pm 0,2$ nM; $Cu = 1,9 \pm 0,2$ nM). Un relargage de ces éléments par les sédiments de la plateforme continentale, suivant l'hypothèse de Kremling (1983), doit être invoqué pour expliquer ces derniers résultats.

Aucune des trois études ne permet de déceler une influence de l'activité du phytoplancton sur la répartition des métaux traces. Les répartitions obtenues en août 1985 pour le manganèse, le cobalt et le plomb sont néanmoins compatibles avec l'hypothèse générale selon laquelle les mers épicontinentales font fonction de filtre vis-à-vis des apports continentaux à l'océan (Martin et Windom, 1991).

Oceanologica Acta, 1994. 17, 4, 383-396.

INTRODUCTION

Some of the major controls on the open ocean distributions of trace metals have been established from the interpretation of vertical profiles of the dissolved and/or particulate phase of these metals. This is because such profiles are generally produced by a steady-state balance between transport terms and particle-water reaction terms at any one depth. Hence the major sources and sinks can be inferred, and the trace elements can be classified according to an oceanographic – as opposed to purely chemical – basis (Whitfield and Turner, 1987). A first-order classification scheme would group Cd and Zn together as nutrient-like elements, because their vertical distributions parallel those of PO_4 , NO_3 , or Si; Fe, Co, Mn and Pb would belong to a second group of elements whose vertical distributions reflect their sources at oceanic boundaries and their rapid incorporation into solid phases.

In continental shelf regions, a method of interpretation based on inference and correlation is unlikely to help elucidate the processes controlling metal distributions. In particular, the temporal and spatial variability in river inputs, the short term variability of the wind-driven circulation and the effect of resuspension events will all be superimposed on any biological or geochemical interdependencies. This variability is illustrated by the frontal structure prevailing on the Hebrides Shelf in August 1981 (Kremling, 1983) and May 1983 (Balls, 1985 *a*), but which did not appear in July 1984 (Kremling and Hydes, 1988). It also raises a question, addressed in this paper, about the degree of interdependency between hydrographic features such as salinity or temperature fronts, and areas of marked horizontal trace metal gradients. The limited results from previous studies certainly imply a close association between the two (Kremling, 1983; Balls, 1985 *a*; Riso *et al.*, 1988).

We present here results from three transects across the continental shelf bordering the Celtic Sea, which in turn, illustrate as many combinations between the physical and chemical structure of the water.

The variable and non-uniform characteristics of shelf environments mean that the distributions obtained during oceanographic surveys may correspond to unique situations that cannot be reproduced. For this reason, Martin and Windom (1991) performed global mass balance calculations as a means of quantifying how much of the trace element input is retained on continental shelves worldwide. Their estimates are in the range 90-95%, and take into account the removal of elements of oceanic origin. A more direct approach to the estimation of fluxes across continental shelves is nevertheless required, particularly in the context of global environmental changes such as the greater intensity and frequency of algal blooms due to increased inputs of nutrients. Recent information regarding cross-shelf vertical distributions of trace metals is largely derived from studies of the North American shelf (Symes and Kester, 1985; Heggie *et al.*, 1987; Sañudo and Flegal, 1991). An important feature of the first two studies is the occurrence of a frontal boundary separating the colder and fresher shelf water from the waters of the slope region. Such fronts do not seem to occur at the northwestern European shelf edge (Simpson *et al.*, 1978; Bowden, 1981); in fact, on-shelf advection of oceanic water appears to be a common occurrence at the Celtic Sea shelf edge (Pingree and Maddell, 1981; Pingree and Le Cann, 1990). The observations reported in this paper were made to see if the trace metal distributions reflected these differences. We show that the water circulation characteristics of the Celtic Sea tend to inhibit the mixing of coastal water with more saline outer shelf water, as well as the direct spilling of shelf waters to

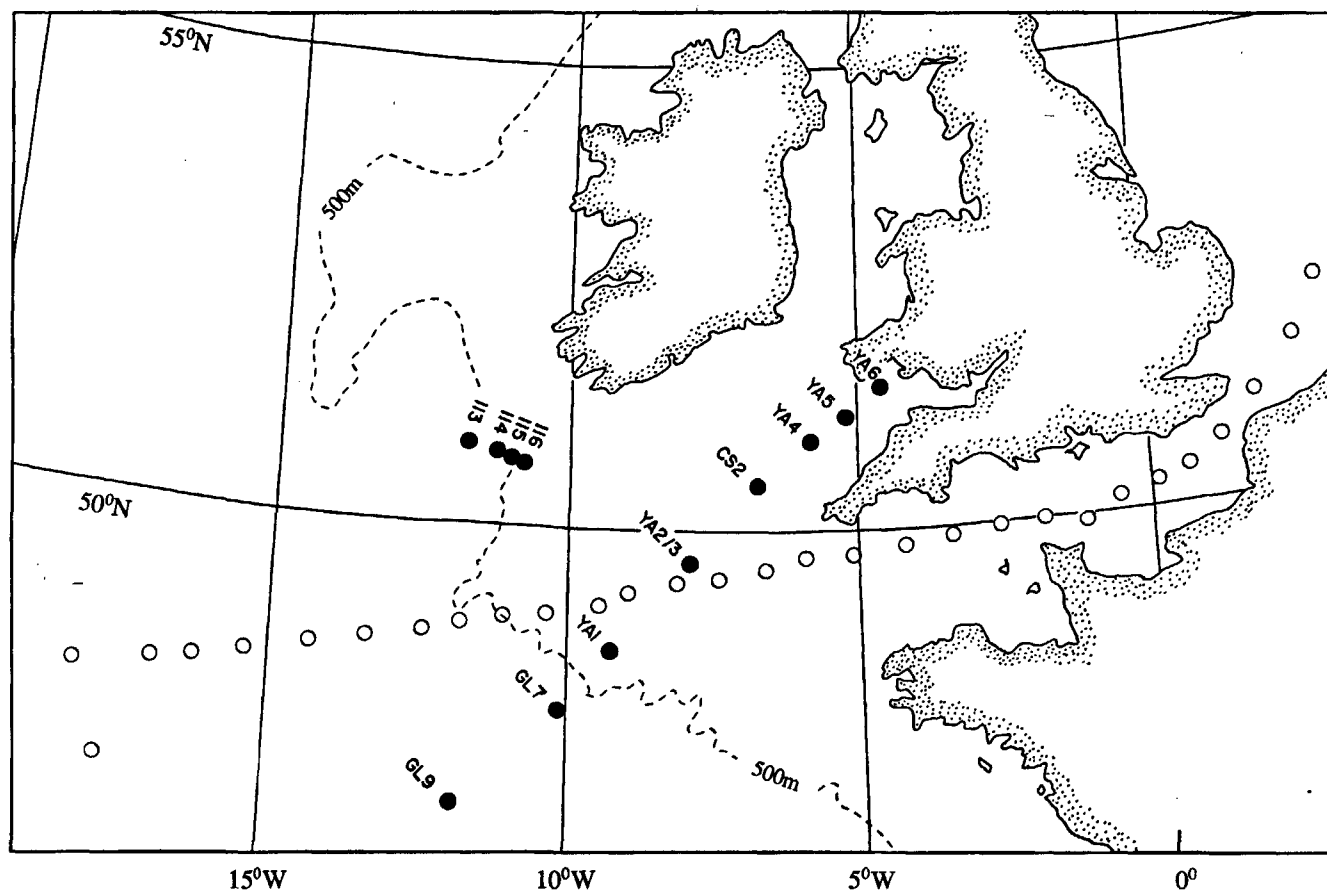


Figure 1

Positions of sampling stations on the northwestern European shelf and in the adjacent northeast Atlantic. Vertical profiles were examined at all labelled stations. The unlabelled sampling positions (open circles) are for the surface transect sampled in August 1988.

Carte des stations d'échantillonnage Discovery 147 (mai 1984), Darwin CD 2/85 (août 1985) et Poseidon 149 (août 1988). Tous les points numérotés représentent un échantillonnage complet de la colonne d'eau. Les autres (points blancs) sont les points de prélèvement de surface de la campagne d'août 1988.

the open ocean. These conditions imply that the northwestern European shelf acts as a filter for the continental fluxes of trace metals, in line with the global predictions of Martin and Windom (1991).

METHODS OF SAMPLING AND ANALYSIS

Vertical sampling of the water column took place during RRS *Discovery* cruise 147, April-May 1984, and RRS *Darwin* cruise CD 2/85, July-August 1985. The four *Discovery* stations provided a transect across the shelf edge at 51°N, near the Porcupine Seabight, and are designated as "transect 84" thereafter (Fig. 1). The outward leg of the *Darwin* cruise ran southwestward from the outer Bristol Channel, across the Celtic Shelf and into the Bay of Biscay. It consisted of eight vertical stations, referred to collectively as "transect 85" (Fig. 1). During both cruises samples were taken using Teflon-lined 2.5 litre GO-Flo bottles, modified and rigorously cleaned to reduce the

contamination potential for trace metals, deployed on a rosette multisampler. Unfiltered samples were taken for shipboard determination of oxygen, salinity, chlorophyll *a* and micronutrients nitrate, phosphate and silicon. Samples for dissolved metal analysis were pressure-filtered directly from the GO-Flo bottles through in-line 0.4 µm Nuclepore filters within an area of the laboratory which was isolated to provide as clean an environment as possible. Filtered samples were acidified to pH 2 and stored for subsequent analysis of the total dissolved trace elements. Critical handling stages (acidification and filter loading) were carried out in a Class 100 laminar flow hood.

Surface samples were collected during RV *Poseidon* cruise 149 in August 1988. The transect ("transect 88") extended through the English Channel, across the shelf edge and into the open Atlantic Ocean, with a distance of 32 nautical miles between sampling locations. Samples were collected from 7 m depth using an all-Teflon clean pumping system described by Kremling and Petersen (1984). Initial sample processing and handling were similar to those described above.

	Cd	Pb	Mn	Fe	Cu	Ni	Co
Detection limit (nM)	0.03	0.014	0.17	1.7	0.16	0.49	0.033
Precision (%)	8	12	9	10	6	6	6

Table 1

Mean values of the detection limits and precision estimates for the analysis of dissolved trace metals. The detection limit was calculated as three times the standard deviation of the blank. The precision was calculated from the standard error on the slope of a calibration line generated by spiking a composite sea water sample at analyte concentrations spanning those found in the samples. The results of five extraction batches were averaged to produce these numbers.

Limites de détection et précisions moyennes relatives au mode opératoire extraction + analyse des métaux traces. La limite de détection est définie comme trois fois l'écart-type des blancs. La précision des résultats est reliée à celle de pente de la droite d'étalonnage, laquelle est définie par six ajouts standards à une solution constituée du mélange de deux ou trois échantillons déjà utilisés.

Trace metals were separated from the seawater matrix and concentrated by chelation with a mixed dithiocarbamate reagent (ammonium pyrrolidine dithiocarbamate / diethylammonium diethyldithiocarbamate) and solvent extraction with 1,1,2-trichloro-1,2,2-trifluoroethane, followed by back extraction into sub-boiled nitric acid; the acid extract was then diluted with sub-boiled distilled water to obtain a medium suitable for injection into the graphite furnace of a Model 1100B atomic absorption spectrometer (Perkin Elmer). The extraction procedures followed the method of Danielsson *et al.*, (1978) modified by Statham (1985) and Tappin (1988), and reappraised by Muller *et al.*, (1991). Detection limits and precisions are given in Table 1. Accuracy was tested by measurement of NASS-1 reference seawater (National Research Council Canada).

RESULTS AND DISCUSSION

Copies of the complete data set, *i.e.* 158 samples × 15 variables, are available on request from the authors.

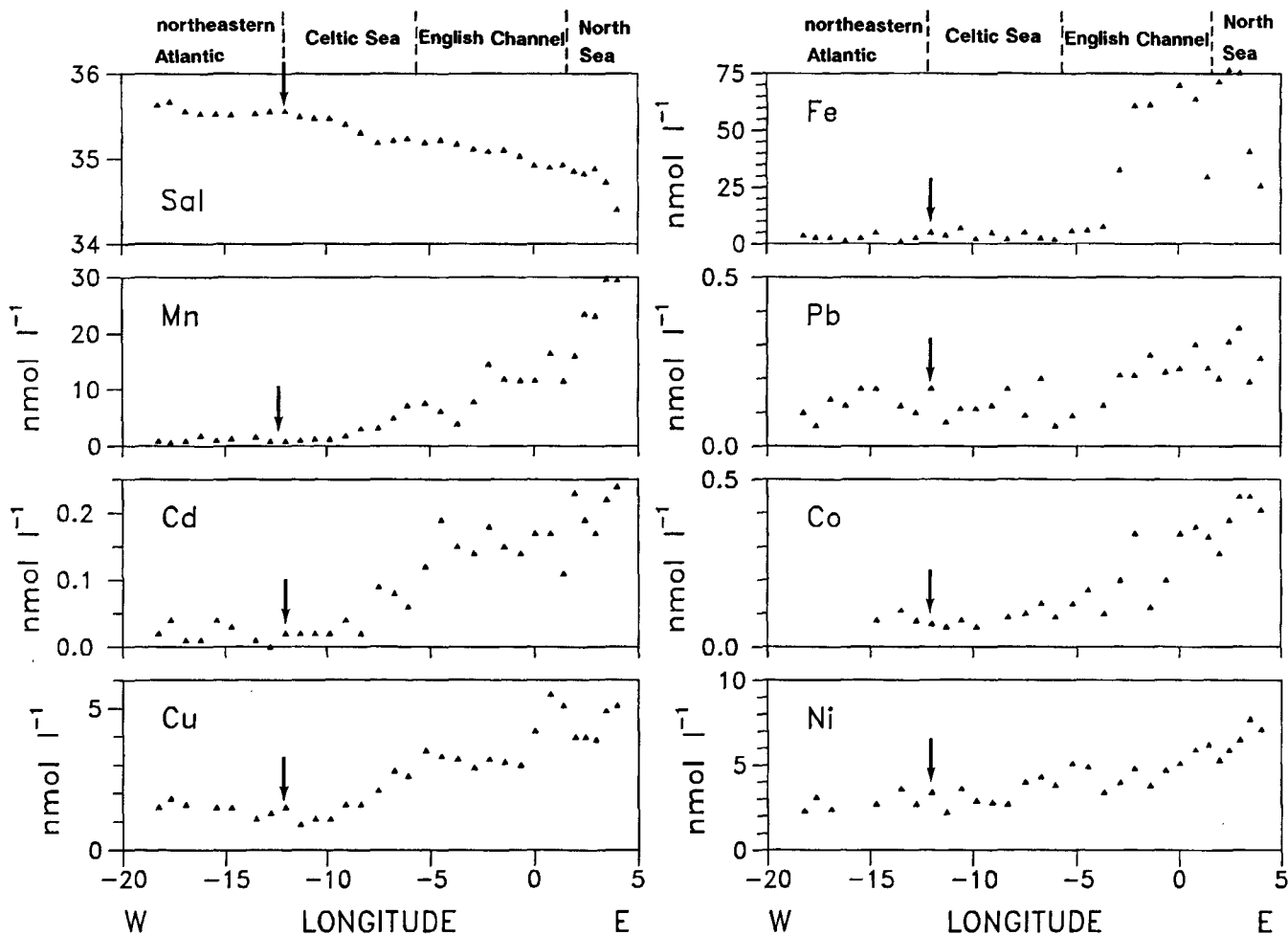


Figure 2.

Salinity and trace metal data from transect 88, plotted as a function of longitude. The data points refer to the cruise track represented by open circles in Figure 1. A vertical arrow marks the position of the 500 m isobath.

Représentation à une dimension de la salinité et des métaux dissous en fonction de la longitude, août 1988. La localisation exacte des points de prélèvement est donnée par la figure 1 (points blancs). Flèche verticale: emplacement de l'isobathe 500 m.

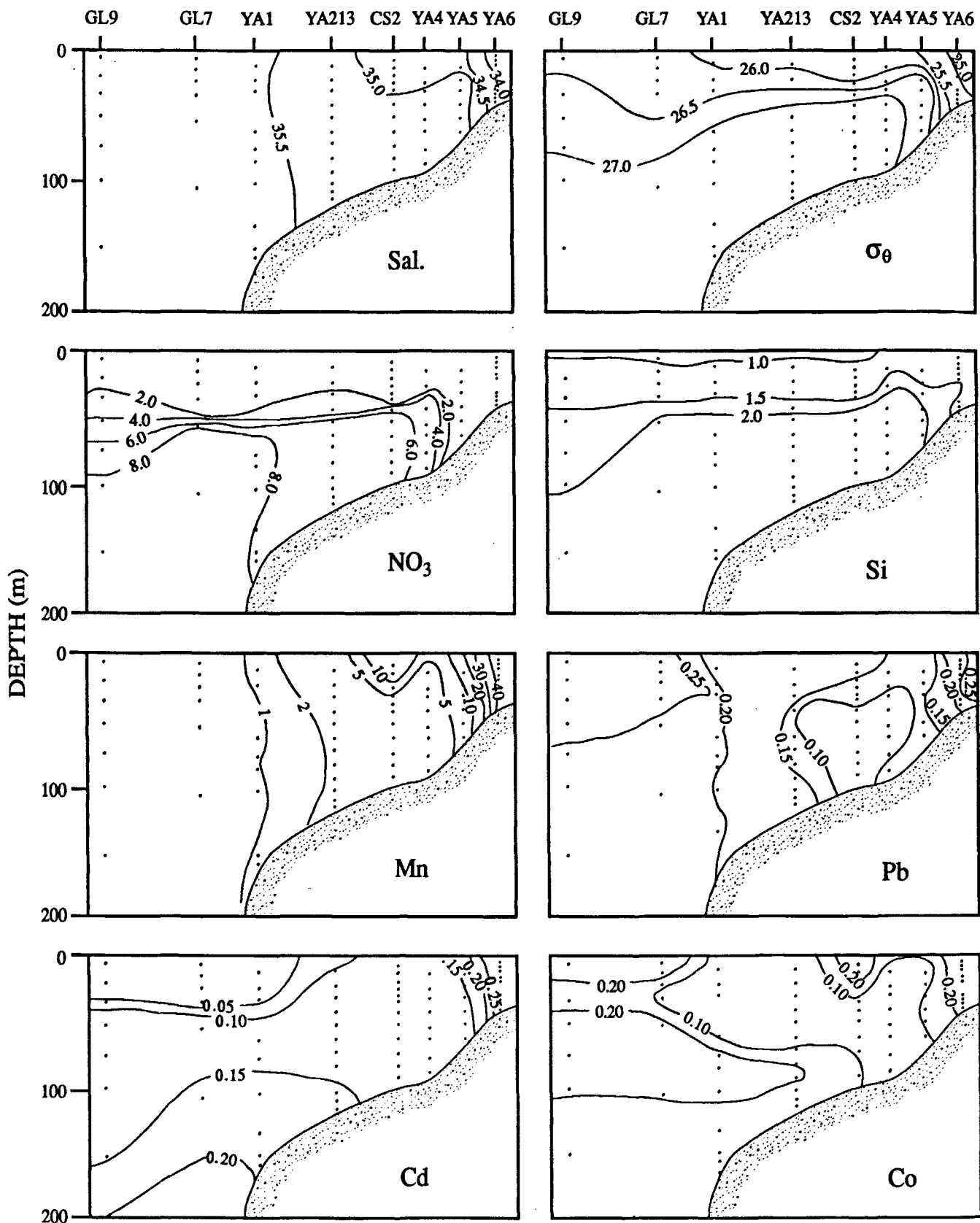


Figure 3

Hydrographic section of the Celtic shelf (transect 85) showing, (a) S psu, (b) σ_{θ} , (c) NO_3 μM , (d) Si μM , (e) Mn nM, (f) Pb nM, (g) Cd nM, (h) Co nM. Station numbers correspond to those given in Figure 1.

Section perpendiculaire à la côte (août 1985) représentant: (a) S psu, (b) σ_{θ} , (c) NO_3 μM , (d) Si μM , (e) Mn nM, (f) Pb nM, (g) Cd nM, (h) Co nM.

Hydrography

In each of the three transects, salinity increases from east to west as fresh water inputs from northwestern European rivers mix with high salinity North Atlantic waters. Salinity distributions from transect 88 (Fig. 2) and transect 85 (Fig. 3) are consistent with the existence of summer frontal structures observed in these seas (Simpson *et al.*, 1978; James, 1981; Pingree and Mardell, 1981; Riso *et al.*, 1988; Matthews *et al.*, 1993; Morin *et al.*, 1993). Fig. 3 shows that the position of the 1985 front can also be described according to $\sigma_\theta = 25.6$, which highlights the separation between tidally mixed coastal water and stratified shelf water. A second indication of these frontal structures is the observation of a minimum in sea surface temperature (not

shown) upon crossing the front; in both cases this minimum temperature lies about 0.6° C below that of inshore and offshore waters. Such a minimum is indicative of upwelling along the front (Simpson *et al.*, 1978; Pingree and Mardell, 1981).

The infrared image of Figure 4 shows a clear discontinuity between the cooler, well-mixed inshore waters (in blue) and the warmer stratified offshore waters (in green to orange) during transect 85. Such a discontinuity did not appear along transect 88 where it might have been anticipated, *i.e.* intersecting the cruise track at 49°20'N, 09°05'W. It is likely that the horizontal chemical gradients observed at that location do not materialize a thermal front, but simply the leading edge of an oceanic water intrusion into equally warm and stratified – but lower salinity – shelf waters. Despite their different origins, both features are described here as “trace metal fronts”.

Consistent with previous work on the slope region of the Celtic Sea (Pingree and Mardell, 1981; Pingree and Le Cann, 1989), we find no evidence of a hydrographic boundary centred over the slope in any of the three transects (Fig. 2, 3 and 5). Indeed, the net onshore advection of oceanic water over this region (Pingree and Mardell, 1981; Pingree and Le Cann, 1989) helps maintain a uniformly high salinity on either side of the slope, and the surface chemical signature of this circulation has been noted by Kremling and Pohl (1989). A deepening of the thermocline and pycnocline over the slope is another feature of the shelf edge transects (Fig. 3 and 5). It is thought to indicate enhanced mixing caused by water motions of several origins. Density driven currents flowing poleward along the slope (Bowden, 1981; Pingree and Le Cann, 1989), high-frequency internal waves impinging on the slope (Pingree and Mardell, 1981; Dickson and McCave, 1986) and internal tides (Pingree and New, 1989) are all possibilities.

Nutrients and chlorophyll *a*

The waters of the Celtic Sea and English Channel support phytoplankton blooms dominated by diatoms during the spring and other planktonic species throughout the summer (Pingree *et al.*, 1977; Sournia *et al.*, 1987), resulting in the phosphate, nitrate and silicon concentrations along transect 88 generally falling below their detection limits of 0.02, 0.2 and 0.2 $\mu\text{mol l}^{-1}$ (μM) respectively.

The vertical distributions of nitrate and silicon along the shallower part of transect 85 are shown in Figure 3. They

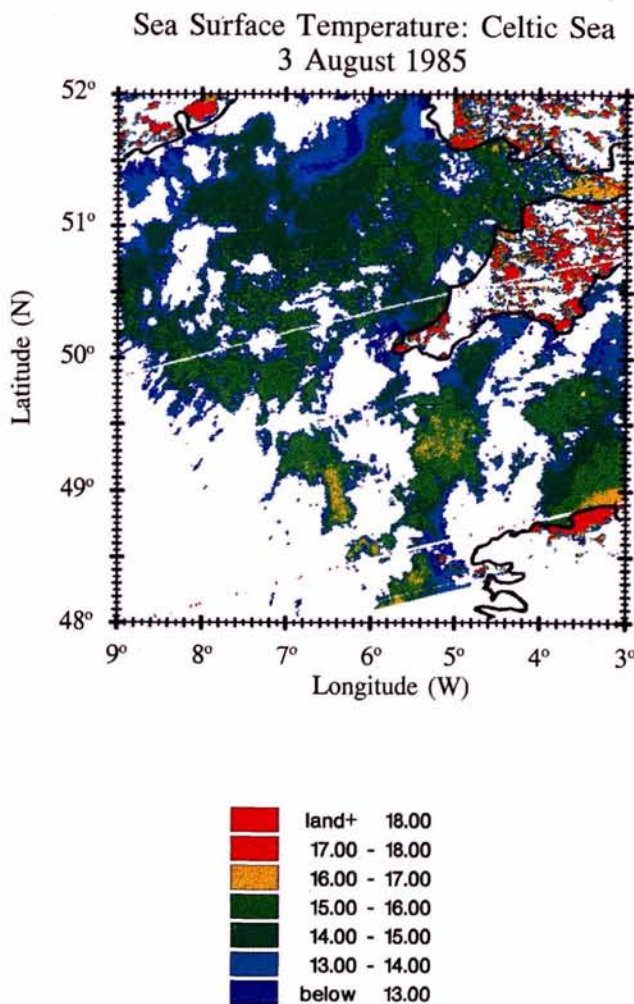


Figure 4

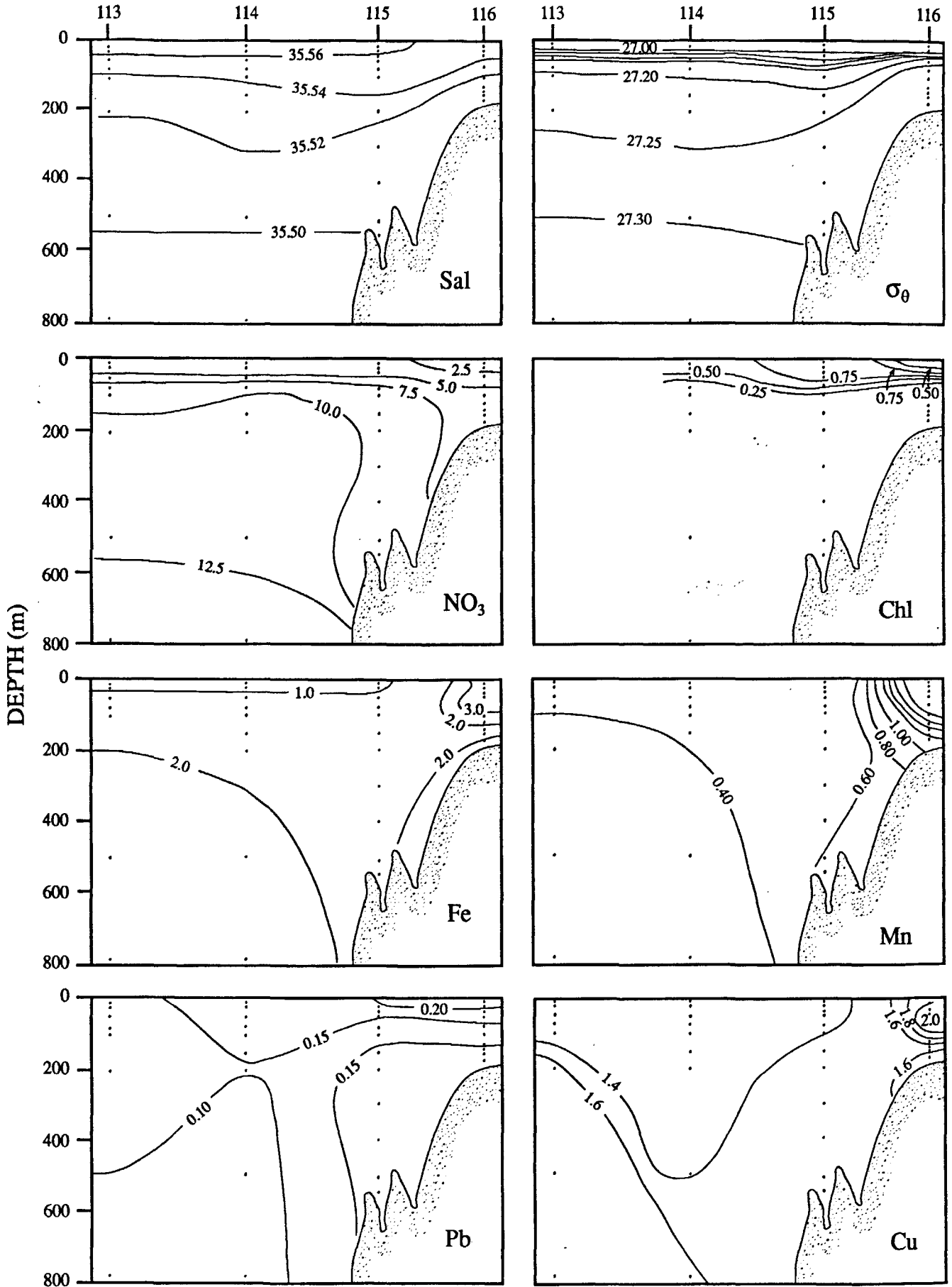
Remotely-sensed sea surface temperature of the Celtic Sea at the time when transect 85 was sampled. Prominent in this picture are, from north to south along the same line, the Celtic front (between the southwestern tip of Wales and Ireland), the Scilly Isles front and the Ushant front.

Distribution de la température de surface en Mer Celtique pendant la période d'échantillonnage d'août 1985. Les systèmes frontaux côtiers sont clairement délimités par les transitions entre bleu (ou vert-bleu) et vert clair. Les zones blanches correspondent aux nuages.

Figure 5

Hydrographic section of the continental slope region (transect 84) showing, (a) S psu, (b) σ_θ , (c) NO_3 μM , (d) Chl $\mu\text{g l}^{-1}$, (e) Fe nM, (f) Mn nM, (g) Pb nM, (h) Cu nM. Station numbers correspond to those given in Figure 1.

Coupe verticale du talus continental (mai 1984) montrant, (a) S psu, (b) σ_θ , (c) NO_3 μM , (d) Chl $\mu\text{g l}^{-1}$, (e) Fe nM, (f) Mn nM, (g) Pb nM, (h) Cu nM.



show a marked correspondence with the σ_θ contours; even the broadening of the surface layer over the continental slope is clearly visible. One main feature is the general depletion of nutrients from surface waters, as well as from the relatively well mixed waters inshore of the coastal front. This type of distribution is consistent with biological removal of nutrients and remineralization in the underlying waters and sediments. Previous studies in the western English Channel have reported the regeneration and entrapment of nutrients below the thermocline in the summer months (Holligan and Harbour, 1977; Pingree *et al.*, 1977; Tappin *et al.*, 1993).

The situation in transect 84 differs from that found during transect 85. For example, the distribution of nitrate near the

shelf edge (Fig. 5) does not mirror the stratification of the water column in terms of either salinity or density. Instead, nitrate concentrations decrease towards the shelf along a given salinity or σ_θ horizon, and this gradient is particularly pronounced below the thermocline. Given that the net transport of water is onto the shelf, such a distribution would suggest increased biological uptake of nitrate over the shelf. However, the chlorophyll *a* data does not provide any evidence in support of this hypothesis (Fig. 5).

Dissolved metals: transects 88 and 85

Transect 88, which extends from the southern North Sea to the open Atlantic Ocean, is characterized by the following

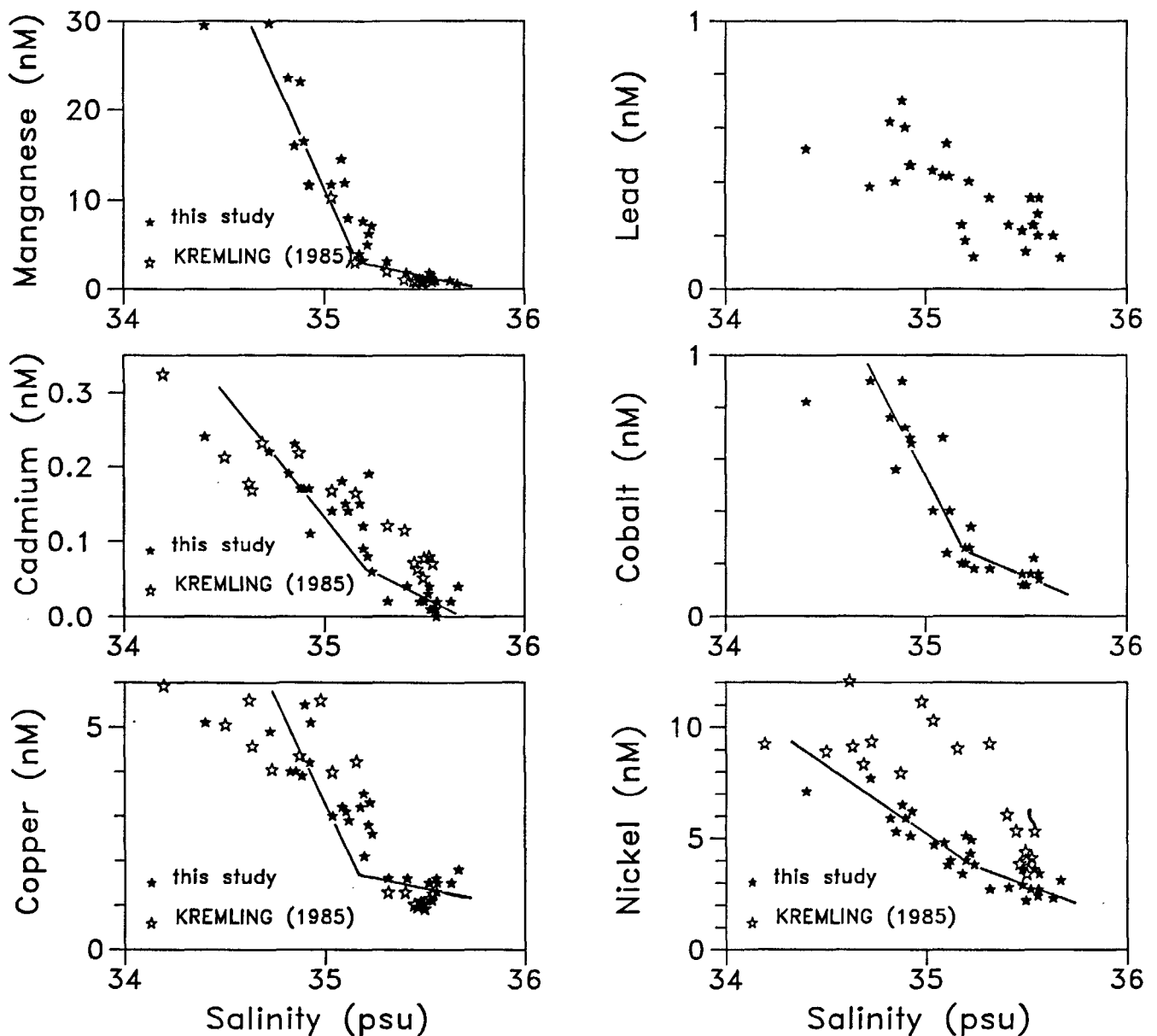


Figure 6.

Relationships between the concentrations of some trace metals and salinity in samples from transect 88. Data from the survey of Kremling (1985) which was based on a closely similar transect have been plotted on the same axes for comparison, but have not been included in the linear regressions.

Relations métaux-salinité pour les échantillons de surface prélevés en août 1988. Les données de Kremling (1985) sont également représentées à titre de comparaison mais ne font pas partie de la régression linéaire.

features: (1) salinity and dissolved metal concentrations show little variation from the outermost station to a station situated 160 km inshore of the shelf edge (Fig. 2); (2) all metals except iron and lead show an increase through the transition zone between high salinity Atlantic water and lower salinity shelf water, as well as further stepwise increases as one proceeds eastward through the English Channel (Fig. 2) (3) metal-salinity relationships inshore of the transition zone ($S < 35.2$ psu) are essentially linear, and distinct from the relationships tentatively defined at higher salinities ($35.2 < S$ (psu) < 35.7) (Fig. 6).

When these observations are compared with other quasi-synoptic surveys in the same area (Kremling, 1985; Kremling and Pohl, 1989), it becomes clear that oceanic surface water unmodified with respect to trace metals has been advected some 160 km shoreward of the shelf edge. No horizontal concentration gradient is therefore observed across the shelf edge, in contrast with earlier observations (Kremling, 1985; Kremling and Pohl, 1989). Although the hydrographic conditions may have been different, the metal-salinity relationships are indistinguishable from those observed by Kremling (1985) for manganese, cadmium and cop-

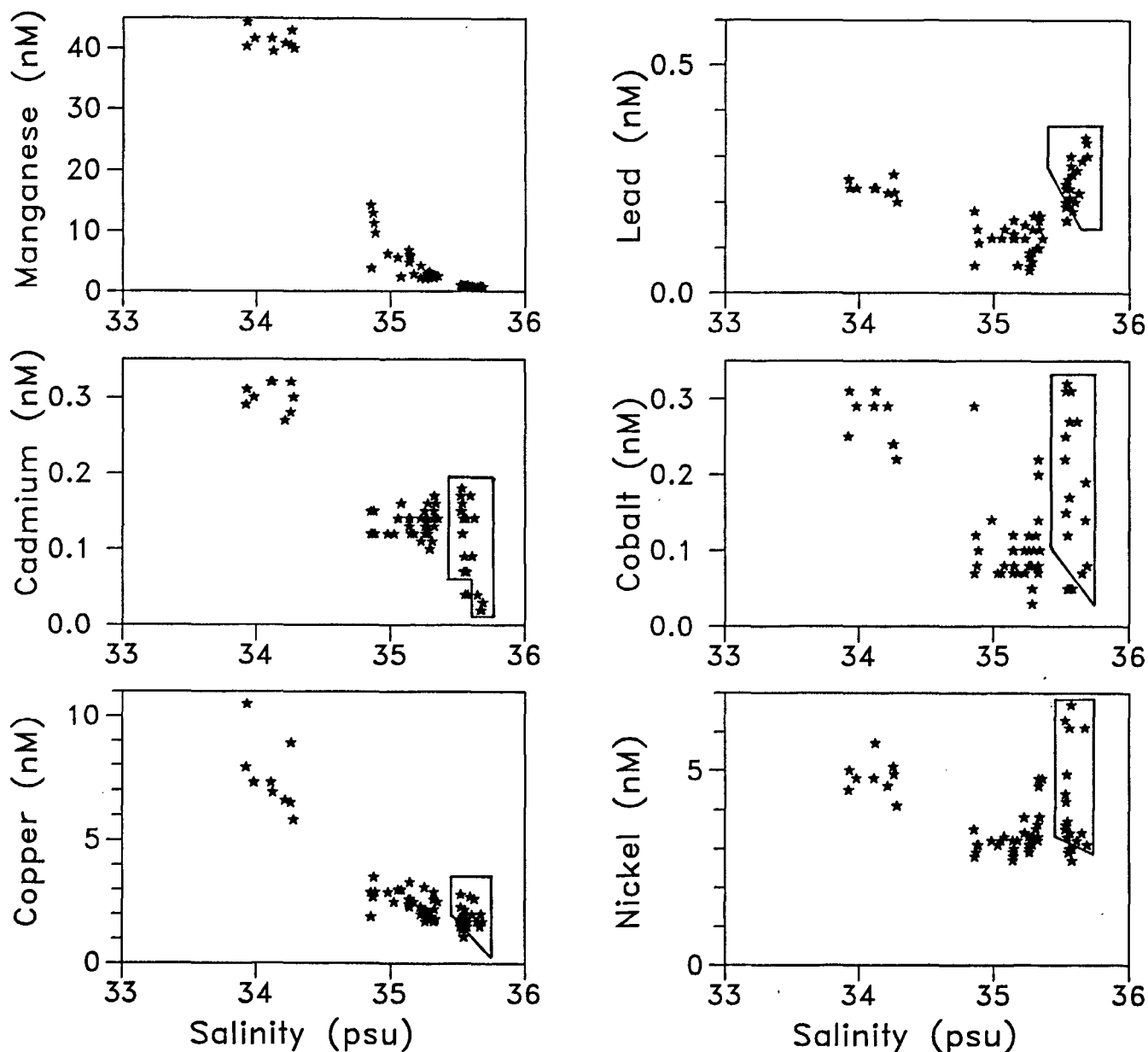


Figure 7

Relationships between the concentrations of some trace metals and salinity in samples from transect 85. With Cd, Pb, Co and Ni, the offshelf data from stations GL9 and GL7 (in boxes) are clearly identifiable as a separate group. As with Fig. 3, samples taken deeper than 200 m have not been included.

Relations métaux-salinité pour les échantillons de la radiale d'août 1985 prélevés entre 0 et 200 m. Les données océaniques (stations GL9 et GL7) constituent clairement à un groupe à part.

per (Fig. 6). Kremling (1985) interpreted those as reflecting binary mixing between higher salinity North Atlantic water and lower salinity coastal waters, but we believe that they can best be represented by two linear segments intersecting at $S = 32.2$ psu (Fig. 6). The first mixing zone corresponds to the southern North Sea and the English Channel. It receives major inputs from rivers Rhine and Seine, which become mixed by tidal action. The metal-salinity relationship in the higher salinity zone is likely to be influenced by freshwater runoff from the west coasts of Britain and France, as well as evaporation and precipitation.

The main processes acting on trace metals in the Celtic Sea at the time of the 1985 survey can be inferred from the vertical sections shown in Figure 3, together with the associated relationships with salinity shown in Figure 7. An inverse relationship with salinity is found for all the measured elements (Fig. 7), which suggests that terrestrial inputs are important in controlling their distribution. It is clear from Figure 3 that manganese in particular has a dominant land-based origin, with values significantly enhanced not only at the innermost station (YA6) but also in the lower salinity surface layer at station CS2. The inverse S shape of the manganese-salinity relationship also suggests additional inputs (*e.g.* sediments or suspended solids) to the waters landward of the coastal front – perhaps coupled with removal over the shelf – relative to simple linear conservative mixing between freshwater and shelf water. Addition of manganese somewhere between the coastline and the front is all the more likely as dissolved manganese concentrations in rivers rarely reach the value obtained by extrapolating the shelf manganese-salinity relationship of Figure 7 to zero salinity. Throughout the central part of the shelf, removal through incorporation in suspended solids would be expected to proceed to an even greater extent for an element of such high particle reactivity as lead. Figures 3 and 7 suggest that this prediction is generally correct, with lead concentrations falling below 0.15 nM over much of the Celtic Shelf despite the higher concentrations at both the inner and outer stations of the shelf. The open ocean stations GL7 and GL9 are clearly influenced by additional inputs to the surface, probably from the atmosphere. Lambert *et al.* (1990) recently argued that the strength of the atmospheric lead source to the northeastern Atlantic decreased away from the shelf. Hence the low concentrations measured inshore of the shelf edge at the time of our survey would indeed require high scavenging rates over the shelf. We also note that both stations GL7 (48°00'N 10°00'W) and GL9 (47°00'N 12°00'W) are close to the Lambert *et al.* (1990) site at 47°20'N 8°30'W. A comparison reveals a 0.03 nM offset between the two data sets below 200 m (our lead values higher) and a further 0.10 nM difference at around 30 m due to the presence of a subsurface maximum in our lead data which is not defined in the Lambert *et al.* (1990) profile. Vertically integrated inventories of lead from our study are accordingly higher (0.56 and 0.48 $\mu\text{g cm}^{-1}$ against 0.45 $\mu\text{g cm}^{-1}$) in the top 100 m of the water column. These inventories, coupled with the ones for transect 84 (see below), reinforce the interpretation given by Lambert *et al.* (1990) of enhanced anthropogenic atmospheric inputs over the northeastern, relative to the northwestern, Atlantic. Perhaps more important is the observation that the two surveys were conducted

within one month of each other, as it emphasizes the transient nature of lead profiles. The cobalt distribution along transect 85 also suggests some degree of removal over the Celtic Shelf (Fig. 3). By contrast, cadmium appears to behave conservatively inshore of station CS2 (*i.e.* its distribution mirrors that of salinity) but shows a recycled behaviour (*i.e.* follows the same trend as nutrients) offshore. Leaving aside the deep water stations GL7 and GL9, cadmium provides one of the best examples of quasi-conservative behaviour among the trace metals (Fig. 7). In addition, the slope of the cadmium-salinity relationship is the same on both sides of the coastal front, as it was in transect 88 (compare Fig. 7 and Fig. 6). Nonetheless, as noted with manganese, extrapolation of the dissolved cadmium concentrations to lower salinities would yield values far in excess of any concentrations measured in estuaries. Thus it is clear that a significant release of dissolved cadmium must take place between the estuarine zone and the coastal front. Burton *et al.* (1993) have noted that the fluxes of some dissolved metals are considerably modified in the estuarine plumes of the North Sea. The longer residence time of fresh, particle-rich water through a plume potentially allows slow desorption reactions to occur to a greater extent than in the estuary. The coupling between estuarine and shelf waters would thus be an important issue to address in the future. Copper and nickel concentrations also appear to be controlled by mixing, but again, provided a limited salinity range (34–35 psu) is considered. Seaward of the frontal zone, their concentrations are rather featureless, and therefore have not been represented in Figure 3.

In summary, the trace metal data of transects 88 and 85 – with the notable exception of lead – reflect the increase in concentrations from the higher salinity open Atlantic waters to the lower salinity river-influenced coastal waters. The outer shelf is characterized by a great horizontal homogeneity of properties, particularly when and where open ocean water is advected onto the shelf (transect 88). The inner shelf provides the scene for the development of coastal frontal zones shoreward of which strong horizontal gradients are observed in both salinity and dissolved metals. Superimposed on this first order distribution, there is an indication that metals of higher particle reactivity such as manganese, lead and cobalt (iron data were not obtained in transect 85) are removed from the waters of the Celtic Shelf by uptake onto suspended particles. The distribution of the latter two elements confirms the role of the shelf as a filter for both continental and oceanic fluxes of dissolved trace elements (Martin and Windom, 1991). Finally, none of the metal investigated exhibits increasing concentrations with depth at any of the shelf stations. Since upper layer motions are partly decoupled from deeper motions seaward of the front (Pingree and Griffiths, 1978; Amiard *et al.*, 1991), this suggests that sedimentary sources are unlikely to have been important, despite the prevalence of muddy sand or sandy mud on the Celtic Shelf bottom (BGS, 1987).

Dissolved metals: transect 84

Plots against salinity are not very useful in interpreting the transect 84 dissolved metal data because salinity variations

are very small and occur for the most part in the deep ocean (stations 113 and 114 on Fig. 1). Salinity distributions across the shelf edge are characterized by horizontal uniformity along any depth or density horizon (Fig. 5). Nutrients and dissolved cadmium also exhibit relative homogeneity upon crossing the shelf edge, at least in the surface layer. In contrast, three of the metals examined (Fe, Mn, Cu) show strong horizontal gradients between stations 115 and 116, *i.e.* in the vicinity of the shelf edge (Fig. 5). These gradients are unaccompanied by any similar hydrographic features and are therefore quite distinct from the trace metal fronts observed previously in northwestern European shelf waters (Balls, 1985 *a, b*; Riso *et al.*, 1988; Amiard *et al.*, 1991) or shelf edge (Kremling, 1983). The unusual nature of the cross-sectional distributions of iron, manganese and copper observed here (51°N) is best illustrated by a comparison with the surface sections obtained by Kremling at 58°N (Kremling, 1983, 1985). For example, the sea surface salinity changes by only 0.03 psu over a distance of 25 km whereas the change over a similar distance is 0.30 psu in the situation documented by Kremling (1985). In addition, the overall salinity range encompassed by our trace metal data is so limited that the data cannot be meaningfully plotted as a function of salinity. By contrast, Kremling's metal-salinity plots for the surface section between the Hebrides shelf edge to the German Bight (Kremling, 1985) clearly suggest that the metals investigated (Mn, Cd, Cu, Ni) reflect the dilution of freshwater with seawater. There is certainly no suggestion from these plots that the slope of the metal-salinity relationships is any greater near the shelf edge, *i.e.* near the site of the hydrographic front; in fact, the opposite is true for manganese and copper. Therefore, we endorse the interpretation of Balls (1985 *a*) that the hypothesis of metal remobilization from the shelf sediments put forward by Kremling (1983) and Kremling and Hydes (1988) is hard to defend on the basis of their data. The nonlinearity in the manganese and cadmium relationships with salinity (Kremling, 1985) points instead to the removal of these elements over the Hebrides shelf, as we have suggested was the case over the Celtic Shelf (transect 85).

The question still remains as to what mechanism might have produced the unexpected frontal patterns for iron, manganese and copper in this transect. Conceptually, the patterns followed by these elements could reflect either their enhanced removal along the continental slope or their addition to the waters overlying the shelf. The first mechanism can be discounted on at least three lines of evidence. Firstly, there is a net on-shelf advection of Atlantic surface water in this region (Dickson and McCave, 1986; Pingree and Le Cann, 1989), and this is corroborated by the salinity distributions observed here. Secondly, a crude calculation of the vertical flux required to balance the hypothetical off-shelf diffusive transport of manganese (Martin and Knauer, 1984) leads us to a scavenging rate constant which is 2-3 orders of magnitude greater than the rate constants reported for mid-depth scavenging in open ocean environments (Martin and Knauer, 1984) and 1-2 orders of magnitude greater than for coastal environments (Yeats and Strain, 1990). It is not at all clear what mechanism could produce such scavenging - as well as equally intense scavenging of

Table 2

Linear regressions ($Cu = a \times Mn + b$) between dissolved manganese and dissolved copper in different data sets; r is the correlation coefficient and n is the number of observations.

Paramètres d'une régression linéaire ($Cu = a \times Mn + b$) entre les concentrations du manganèse et du cuivre dissous, représentés pour plusieurs campagnes; r est le coefficient de corrélation et n le nombre de mesures.

Data	a	b	r ²
UK Continental Shelf surface, $S \geq 34$ (from KREMLING, 1985)	0.13 ± 0.03	2.57 ± 1.20	0.50
Transect 88 surface, $S \geq 34$	0.13 ± 0.01	1.60 ± 0.72	0.73
Transect 85 stations YA 4, YA 5, YA 6	0.14 ± 0.01	1.73 ± 0.80	0.91
Transect 84 station 116 only	0.37 ± 0.04	1.16 ± 0.13	0.81

iron and copper - throughout the entire water column. Thirdly, enhanced removal rates in the vicinity of the Fe/Mn/Cu front through incorporation onto suspended solids should be manifested by a particle-reactive element such as lead, but Figure 5 does not show this. In conclusion, and although an actual increase in concentration towards the sediments is detected only for iron, it seems reasonable to suggest that the Fe/Mn/Cu front is the result of the remobilization of all three elements from the sediments in the vicinity of the shelf edge. Support for the common benthic source hypothesis can be found next in the inter-element relationships observed at station 116.

One general relationship which can be identified among the variables, is that linking manganese and copper concentrations. Table 2 shows that a single relationship seems to apply to the shelf waters of the British Isles in spring and summer. This is consistent with our earlier conclusion that these elements have a continental origin, and further suggests little modification of their fluxes to the ocean in the salinity range of interest. By contrast, the form of the relationship existing between manganese and copper concentrations at station 116 is different, and implies an enrichment of copper relative to manganese. The elemental Cu:Mn ratio is on the order of 0.08 in riverine suspended solids and 0.8 in phytoplankton. The type of signature shown in table 2 could thus be anticipated from a sedimentary source if a significant fraction of the sedimenting solids was derived from phytoplankton.

The nature of the processes affecting the cycling of iron, manganese and copper in the shelf edge environment of station 116 may be inferred from the vertical distributions presented in Figure 8. There is a pronounced chlorophyll *a* maximum at the base of the pycnocline, at around 50 m, while iron concentrations peak at 75 m. On the other hand, copper and manganese show a poorly defined maximum spanning the range of elevated chlorophyll *a* concentrations. O'Sullivan *et al.* (1991) recently measured iron(II) in the surface waters of the equatorial Pacific. They generally

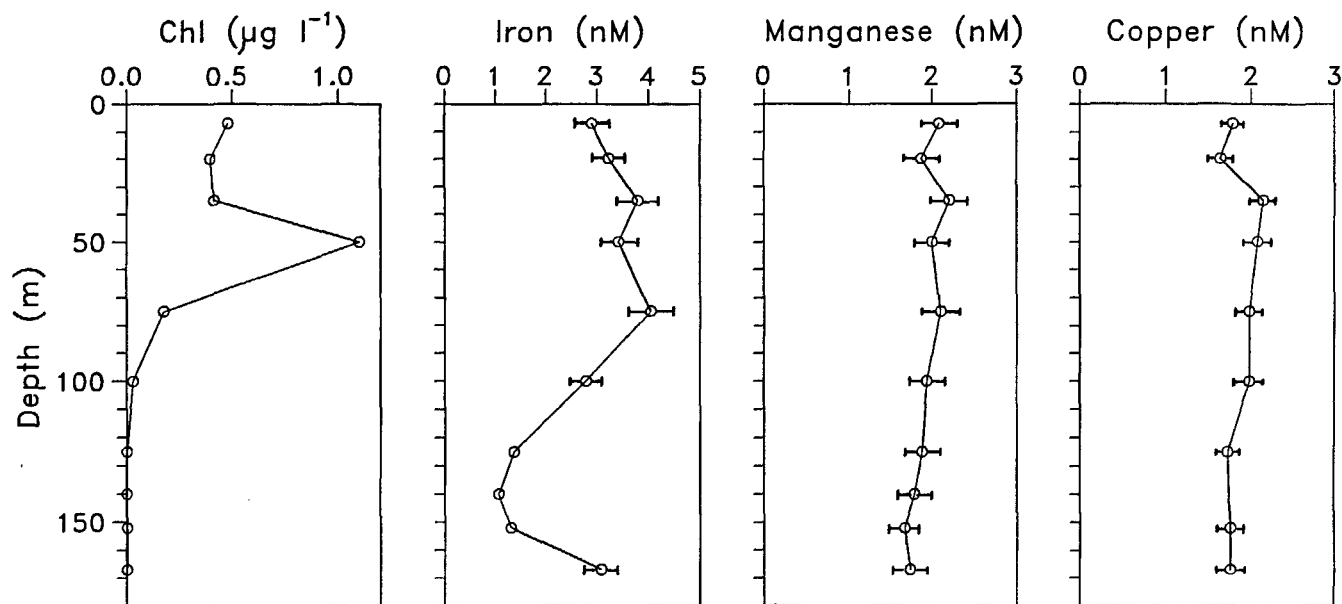


Figure 8

Profiles of concentration of Chl, Fe, Mn and Cu at the shelf edge station, i.e. station 116, of transect 84. Error bars shown reflect the analytical precision.

Profils des concentrations de Chl, Fe, Mn et Cu à la station 116 (mai 1984), située en bordure du talus continental. Intervalle de confiance: $\pm 1\sigma$.

found a maximum at or near the chlorophyll *a* maximum, which turned out to be generated, at least in part, by the photochemical reduction of iron(III). Wells *et al.* (1991) also demonstrated that this mechanism can operate in the upper ocean and lead to increased steady-state concentrations of dissolved iron, although their wavelength-dependent model predicted a maximal rate of photolysis (and hence production of iron(II)) at the very surface of the ocean. There is, however, considerable evidence that some organic compounds can, in the presence of light, promote the reductive dissolution of the oxidized forms of iron and manganese (for a review, see *e.g.* Stone and Morgan, 1987; Stumm and Sulzberger, 1992; Hudson *et al.*, 1992). There is also evidence from laboratory cultures that bacteria and phytoplankton can participate in reductive dissolution reactions by releasing strong reductive and complexing agents (Sunda *et al.*, 1983; Ghiorse, 1986; Sunda and Huntsman, 1988). Although little is known about the release of such metabolites and their influence on trace element speciation, we believe that they may have promoted the apparent interdependency seen in Figure 8 between iron and chlorophyll *a* on the one hand, and manganese and copper on the other. Reductive dissolution by organic compounds produced *in situ* may thus explain the mid-water maximum in iron concentrations. Complexation by the same organic compounds is likely to stabilize copper in solution and thus lead to the mid-water copper maximum seen in Figure 8.

CONCLUSIONS

Several authors have already noted the quasi-conservative behaviour of manganese, cadmium, cobalt, copper and nic-

kel over the range of freshwater-seawater dilution encountered in different regions of the shelf around the British Isles (Kremling, 1985; Balls, 1985 *a*; Kremling and Hydes, 1988; Riso *et al.*, 1988; Tappin *et al.*, 1993). Our first contribution has been to extend this broad picture to the Celtic Sea and to show how the nature of the conservative relationship with salinity can be modified by the presence of frontal zones which occur during the summer. It should be noted that the data presented in this and other studies encompass a limited salinity range – typically 33 to 36 psu – so that caution should be exercised in invoking one specific process or another (Morel *et al.*, 1991). It does seem, however, that mixing is the most important factor contributing to the distributions of the metals measured here. In particular, we found no evidence of cadmium or copper enhancement close to the coastal fronts, such as was observed in estuarine tidal fronts (Sick *et al.*, 1978) as well as during the establishment of the Ushant front, off the coast of Brittany (Riso *et al.*, 1988; Amiard *et al.*, 1991). Nor was there evidence of sedimentary inputs of manganese, cadmium and copper to the water column (such inputs were originally proposed by Kremling (1983) for the northwestern European Shelf, but their relative contribution was later questioned by Balls (1985 *a*)). In fact, it is more likely that removal processes exert the second largest influence after mixing on the shelf water concentrations of manganese, and possibly iron, lead and cobalt (Fig. 7). Indeed, the role of ocean margins as a filter for continental fluxes, inferred by Martin and Windom (1991) from global mass balance calculations, is reflected more clearly by the data from the northwestern European Shelf (Kremling, 1985; Balls, 1985 *a*; Kremling and Hydes, 1988; Riso *et al.*, 1988; Tappin *et al.*, 1993; this study, transects 88 & 85) than by the equivalent data from

North America (Heggie *et al.*, 1987; Shaw *et al.*, 1990). One possible contributory factor to this difference is the persistent occurrence of hydrographic fronts near the shelf edge off the northeast and northwest coast of North America (Flagg and Beardsley, 1978; Houghton *et al.*, 1988; Hansell *et al.*, 1989; Blanton, 1991). Off western Europe, such fronts do not occur at the shelf edge but instead tend to form on the inner part of the shelf (Pingree and Griffiths, 1978; Simpson *et al.*, 1978; Huang *et al.*, 1991; Morin *et al.*, 1993; this study, Fig. 2 & 3). This is generally attributed to one of the following (Bowden, 1981): (a) the persistent northwesterly flow occurring along the Armorican and Celtic shelves – driven in part by prevailing WSW winds and in part by pressure distributions or by non-local wind stress (Pingree and Le Cann, 1989) – is weaker than its North American counterpart; (b) there is a smaller input of freshwater from runoff and a smaller seasonal heat flux on the European side; (c) the shelf is wider on this side.

In the light of the transect 88 and transect 85 data, which show good agreement with the more limited data sets of Kremling (1985) and of Kremling and Hydes (1988), the trace metal front (Fe, Mn, Cu) of transect 84 (Fig. 5) seems very unusual. Given the complete absence of any frontal hydrographic feature, it seems reasonable to conclude that its existence is related to the presence of the shelf edge and/or the nature of the sediments at this important natural boundary. The most likely scenario is that the metals (Fe,

Mn, Cu) were released from the seabed during winter mixing. As the water column began to stratify, *i.e.* at around the time of transect 84, their vertical distribution became influenced by redox (Fe, Mn) and complexation (Cu) reactions promoted by planktonic organisms. Determining the temporal variations in iron(II) concentrations (Hong and Kester, 1986; O'Sullivan *et al.*, 1991), in the complexation parameters of copper (Van den Berg *et al.*, 1987) and in the benthic fluxes of manganese (Heggie *et al.*, 1987; Shaw *et al.*, 1990) would provide the direct evidence needed to support the contention of benthic inputs at this site.

Acknowledgements

We express our thanks to Klaus Kremling (Institut für Meereskunde an der Universität Kiel, Germany) for collecting the 32 samples of transect 88 and supplying us with associated temperature and salinity data. Thanks are also due to RVS support staff, as well as to colleagues from the Plymouth Marine Laboratory for provision of ancillary data relating to CD2/85. Peter Lancaster (this department) generated the infrared image of Fig. 4. This work was supported by NERC Research Grant GR3/6149A to François Muller and by an NERC studentship to Alan Tappin.

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