

# Distribution of some trace metals in well-mixed and stratified areas of the western Brittany coastal waters

Trace metals  
Distribution  
Coastal waters  
Stratified area  
Well-mixed area  
Métaux traces  
Répartition  
Eaux côtières  
Zone stratifiée  
Zone homogène

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## ABSTRACT

The behaviour of three metallic elements (Cu, Pb, Cd) was studied in summer in two different areas (well-mixed and stratified zones) in relation to a number of hydrological and biological factors.

In the well-mixed area, concentrations of Cu, Pb and Cd vary only a little along the water column except at the surface where they are much higher.

In the stratified area, two different cases have to be considered.

In the surface layer (0-30 m), important variations are observed with Cu and Pb, while the concentration of Cd remains relatively constant.

Below the thermocline (30-95 m), the water mass is homogeneous and cooler. Under these conditions there is no significant variation of the levels of the trace elements studied.

Such behaviour could be explained by complexation and/or adsorption phenomena according to a biogeochemical mechanism.

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## RÉSUMÉ

Distribution de quelques éléments traces en zones homogène et stratifiée de la côte ouest de la Bretagne (Atlantique nord-est)

Une étude comparée en zones homogène et stratifiée concernant trois éléments métalliques (Cu, Pb, Cd) à l'état de trace a été développée en relation avec la variation de quelques paramètres hydrologiques et biologiques.

En zone homogène, les concentrations relatives à chaque métal varient peu le long de la colonne d'eau sauf en surface où des valeurs beaucoup plus fortes sont mesurées.

En zone stratifiée des variations significatives des concentrations en cuivre et en plomb sont enregistrées dans la couche de surface (0-30 m) alors que la teneur en cadmium reste relativement constante. Au-dessous de la thermocline (30-95 m) le caractère homogène de la masse d'eau conduit tout naturellement à des faibles variations quelle que soit l'espèce considérée.

Pour rendre compte de ce comportement complexe, nous avons retenu l'intervention de phénomènes de complexation et d'adsorption selon un modèle biogéochimique.

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## INTRODUCTION

A high degree of variation in hydrographic conditions is found in the so-called Iroise Sea, off the west coast of Brittany. The first investigations of the thermal variations of these continental shelf waters (Vincent and Kurc, 1969; Vincent, 1973) have shown significant

differences according to areas and seasons. In winter, there is generally a horizontal gradient decreasing to the coast, where colder waters are observed. In summer, the increase in temperature of the surface waters produces a stratification of the water masses. While such stratification is found in areas characterized by a high depth and weak tidal currents, it does not occur in areas where there is a continual mixing of the water

column. The formation in summer of two well-defined structures (well-mixed and stratified) leads to thermal discontinuities which are called "fronts".

Morin *et al.* (1985) have studied in detail the main hydrographic features of the coastal waters of Brittany in summer. The formation of two clear-cut boundaries is displayed: *a*) the Iroise inner front; and *b*) the Ushant front. If the water mass located between these two fronts is well-mixed, a more or less important thermal stratification is observed on both sides.

In a previous paper we have investigated the effect of the formation of the Iroise inner front on the seasonal variation of cadmium and copper in this particular ecosystem (Riso *et al.*, 1988).

Before the front has formed and after it has disappeared, Cu and Cd concentrations are mainly modified by external inputs such as low salinity waters, the highest levels being measured inshore.

In summer, when the front is established, the highest concentrations are found in adjacent surface and deep water samples.

The latter observation has also been reported by other authors in the cases of an estuary front (Sick *et al.*, 1978) and of a coastal front (Kremling, 1983; Balls, 1985).

The purpose of the present work is to discuss the variations of copper, lead and cadmium concentrations along the water column at two selected stations; the first in a well-mixed area (M) between the two frontal zones, the second (S) is in the stratified area offshore of the Ushant front.

## SAMPLING AND ANALYTICAL PROCEDURE

Sea-water samples were taken up at two stations (Fig. 1) during the "Iroise 86" cruises (July-August

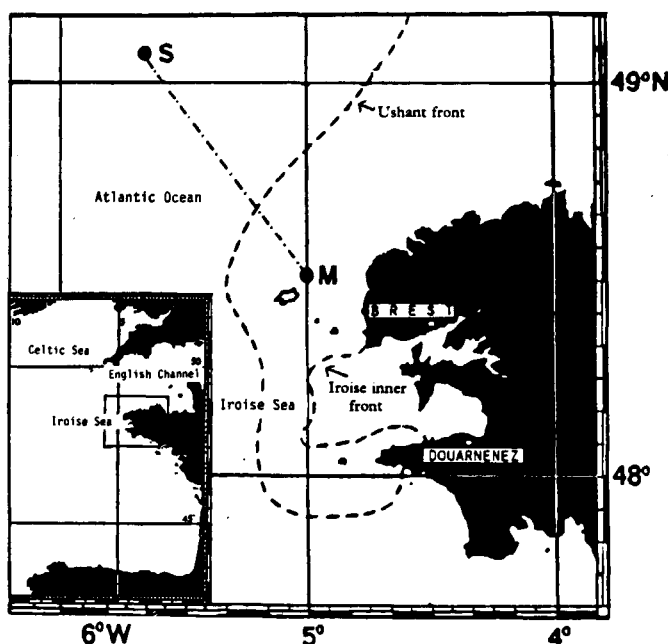


Figure 1  
Study area, location of sampling stations (●)  
Zone d'étude. Localisation des points de prélèvement (●).

1986). Surface and subsurface waters (0-95 m) were collected in modified Niskin samplers (Bewers and Windom, 1982).

The unfiltered samples for heavy metal analyses were stored in polyethylene bottles and preserved by the addition of 1 ml/l of concentrated hydrochloric acid (Merck suprapur). All storage bottles were previously cleaned according to a procedure described by Danielsson *et al.* (1982). Trace metal analyses were done within a week after sampling by differential pulsed anodic stripping voltammetry (DPASV). The detection limits ( $2\sigma$ ) are 0.04 nM, 0.30 nM and 0.03 nM for cadmium, copper and lead respectively.

A Princeton Applied Research polarographic analyser (PAR 364) was used in conjunction with a Tacussel rotating disk electrode. The electrode tip was of glassy carbon (Tokay) with a diameter of 6 mm; a rotation speed of 2 500 rpm was used.

The mercury glassy carbon electrode was prepared *in situ* by depositing mercury from the deoxygenated sample (purified nitrogen) which was made  $5 \times 10^{-5}$  M in  $Hg^{2+}$  by the addition of mercuric nitrate according to a method successfully applied by Florence (1970), Brugman *et al.* (1983), Balls (1985), Nürnberg (1986). The  $Hg(NO_3)_2$  solution was prepared by dissolving Hg in  $HNO_3$ -both Merck suprapur—to a 0.01 M solution. The potentials are measured with respect to a Ag/AgCl ( $Cl^- = 0.7$  M) reference electrode. A platinum wire placed in a special tube separated by a frit from the sample solution served as an auxiliary electrode.

Vertical temperature and salinity profiles were obtained with a CTD system (Guildine 8705), the nominal precision being 0.01°C and 0.015 respectively.

Water samples were also filtered on GF/C Whatman filters which were stored in the darkness at  $-20^\circ C$ . They were subsequently extracted in acetone-water (90-10) for the measurement of chlorophyll-*a* concentration, according to the method of Yentsch and Menzel (1963) and the equations of Lorenzen (1966), using a Turner model 111 fluorometer calibrated beforehand; the analytical precision is about 10%.

Water samples intended for the analyses of inorganic nutrients were passed through a plankton net cloth with a mesh width of 200  $\mu m$  to remove coarser particulate matter into incompletely filled 125 ml polyethylene flasks which were immediately frozen at  $-20^\circ C$  in an upright position. The measurements were made using a Technicon Autoanalyzer II as described by Treguer and Le Corre (1975), with an analytical precision of  $\pm 0.1 \mu M$ . Samples intended for the analyses of the dissolved organic matter (DOC), the strong complexing organic substances (HS) and the particulate organic matter (POC) were filtered on GF/C Whatman filters precombusted beforehand. The filters and the eluates (stored in carefully cleaned glass bottles) were preserved at  $-20^\circ C$ .

The analysis of DOC was carried out according to an automatic method derived from the procedure of Schreurs (1978) based upon an UV oxidation in a persulphate medium (pH ~ 9). POC was measured according to a high-temperature combustion method

in a Perkin-Elmer 240 analyser. The variation of the strong complexing organic substances was done using an electrochemical technique detailed in Quentel *et al.* (1987). Handling of the samples and polarographic procedures were performed on a flow laminar clean bench, US Federal Standard 209 *a*, class 100, ESI. All electrochemical analyses were done in a silica cell with a water jacket thermostated at  $25 \pm 0.5^\circ\text{C}$ . All solutions were prepared with deionised water cleaned by additional ion exchange and filtration through activated carbon (Millipore Milli Q). Samples intended for trace metal analyses were poured into quartz tubes (100 ml), then UV-irradiated at pH 2 (HCl suprapur, Merck) with a 700 W mercury arc lamp during 12 hours.

## RESULTS AND DISCUSSION

### Physicochemical and biological parameters

The temperatures and salinities measured at the stations M and S are reported in table 1 and depicted on figure 2. The vertical profiles of these two parameters show that M and S have different hydrological patterns.

Station M, which is located between the two clear-cut boundaries of the Iroise inner front and the Ushant front, is in a well-mixed area ( $\Delta S \neq 0$ ;  $\Delta T = 0.02^\circ\text{C}$ , differences between surface and bottom).

Station S, which is located offshore of the Ushant front, is in a stratified area. The thermohaline stratification divides the water column into two specific masses, a first layer (0-30 m) where the salinity and temperature values are about 35.30 and  $16^\circ\text{C}$  respectively, and a second one (30-95 m) where the salinity is higher (35.42) and the temperature colder ( $11^\circ\text{C}$ ).

Taking into account the hydrological properties of the water masses at M and S it is not surprising to notice different biological activity at these stations (table 1, figure 2).

At station M, the vertical distribution of nitrates agrees with the well-mixed pattern of the water column, all the concentrations being at a mean level of some  $3 \mu\text{mol}$

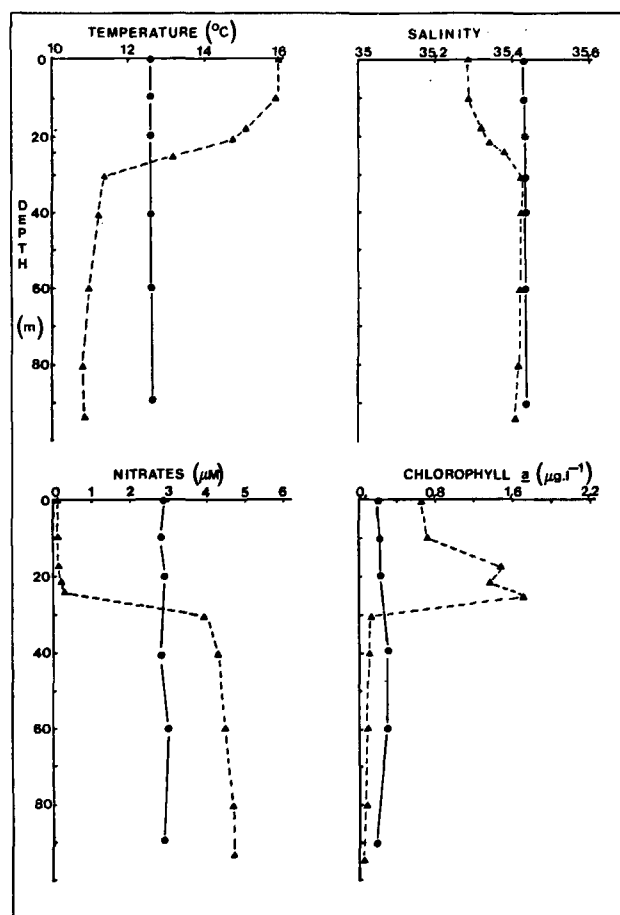


Figure 2

Vertical profiles of salinity, temperature ( $^\circ\text{C}$ ), nitrates ( $\mu\text{M}$ ) and chlorophyll *a* ( $\mu\text{g l}^{-1}$ ) at stations M ( $\bullet$ ) and S ( $\blacktriangle$ ).

Distributions verticales de la salinité, de la température ( $^\circ\text{C}$ ) des nitrates ( $\mu\text{M}$ ) et de la chlorophylle *a* ( $\mu\text{g.l}^{-1}$ ) aux stations M ( $\bullet$ ) et S ( $\blacktriangle$ ).

$\text{l}^{-1}$ . This value is high enough for the season; it still agrees with the chlorophyll-*a* data ( $0.15\text{--}0.35 \mu\text{g l}^{-1}$ ), showing the absence of an important primary production.

At station S, on the other hand, the vertical profiles of nitrates and chlorophyll-*a* show a break at the level of the thermocline boundary. In the surface layer (0-

Table 1

Data from seawater analyses at two stations

Station	Depth. (m)	S	T $^\circ\text{C}$	$\text{NO}_3^-$ ( $\mu\text{M}$ )	Chl <i>a</i> ( $\mu\text{g l}^{-1}$ )	DOC ( $\mu\text{g C l}^{-1}$ )	POC ( $\mu\text{g C l}^{-1}$ )	HS ( $\mu\text{g C l}^{-1}$ )	Cu (nM)	Cd (nM)	Pb (nM)
M	0	35.43	12.56	2.9	0.21	750	105	120	5.3	0.16	0.72
	10	35.43	12.55	2.8	0.23	760	90	115	3.2	0.12	0.52
	20	35.43	12.55	2.9	0.23	780	120	110	2.8	0.12	0.35
	40	35.43	12.55	2.8	0.33	750	100	115	2.9	0.11	0.37
	60	35.43	12.54	3.0	0.29	760	135	110	3.2	0.12	0.27
	90	35.43	12.54	2.9	0.17	740	190	120	3.2	0.11	0.38
S	0	35.29	15.97	0.1	0.65	870	260	135	3.0	0.13	0.22
	10	35.29	15.97	0.1	0.72	860	240	120	—	—	—
	18	35.32	15.03	0.1	1.50	860	335	160	3.7	0.14	0.60
	21	35.34	14.71	0.2	1.37	840	370	155	3.5	0.13	0.51
	24	35.38	13.20	0.2	1.69	810	270	145	—	—	—
	30	35.43	11.31	4.0	0.13	710	110	120	3.5	0.13	0.30
	40	35.43	11.17	4.3	0.10	730	100	105	2.2	0.14	0.36
	60	35.42	10.98	4.5	0.08	730	105	—	—	—	—
	80	35.42	10.81	4.7	0.06	710	75	105	2.0	0.15	0.22
	95	35.41	10.81	4.7	0.05	710	100	105	1.9	0.12	0.29

30 m), where the temperature is about 16°C, we notice an increase of chlorophyll-*a* ( $0.7-1.7\mu\text{g l}^{-1}$ ) leading to a depletion of the nitrates ( $0.1\mu\text{mol l}^{-1}$ ), while in the deeper waters ( $>30\text{ m}$ ) the biological activity is much less intensive ( $0.1\mu\text{g l}^{-1}$  chlorophyll-*a*,  $4.5\mu\text{mol l}^{-1}$  of nitrates).

The vertical distributions of the dissolved organic matter (DOC) and of the complexing organic substances (HS) are depicted in Figure 3.

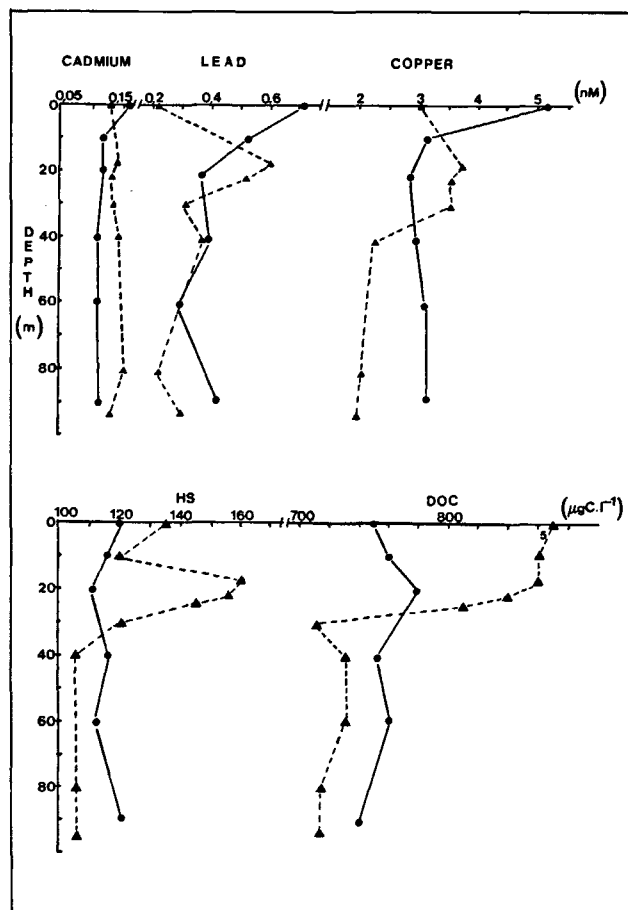


Figure 3  
Vertical profiles of complexing organic substances HS ( $\mu\text{g C l}^{-1}$ ) dissolved organic carbon COD ( $\mu\text{g C l}^{-1}$ ) and trace metals (nM) Cu, Pb, Cd, at stations M (●) and S (▲).

Distributions verticales des substances organiques IIS ( $\mu\text{g C l}^{-1}$ ) à pouvoir complexant élevé, du carbone organique dissous COD ( $\mu\text{g C l}^{-1}$ ) et de quelques éléments traces métalliques (nM): Cu, Pb, Cd, aux stations M (●) et S (▲).

At station M they agree with the well-mixed pattern of the water column. At station S the evolution of DOC is mainly influenced by the origin of the two water masses [ $848\mu\text{g C l}^{-1}$  as a mean level for the surface waters (0-30 m)  $718\mu\text{g C l}^{-1}$  for the deeper waters (30-95 m)], while the concentration of the strong complexing organic substances seems to depend more particularly on the biological activity of the ecosystems. This latter observation agrees with that reported previously by Nouredin (1988), who noticed a high increase of the Cu complexing capacity of the waters of the "rade de Brest" during a phytoplankton bloom. In addition, if the DOC level is relatively constant in the surface layer (0-30 m) of the stratified area, the POC

level (table 1) shows a significant variation, the highest values being measured at a depth where chlorophyll *a* is the highest.

All these physicochemical and biological results will be taken into account in investigating the relationship between the thermohaline stratification and the vertical distribution of three trace metals (Cu, Pb and Cd). The affinity of these elements with the dissolved substances (complexation) and the particulate matter (complexation and/or adsorption) being probably different according to the nature of the ligands, their distribution should be particularly influenced (Mantoura, 1981; Morel, 1983; Florence, 1986).

#### Trace metals

Data of total metal are reported in Table 1. It will be remarked that they are of the same order of magnitude as those previously measured in the same area (Riso *et al.*, 1988) and in neighbouring coastal waters (Balls, 1985; Kremling and Hydes, 1988).

The vertical distributions of Cu, Pb and Cd at stations M and S are depicted in Figure 3. In the well-mixed area (M), the concentrations of the three elements vary only a little along the water column except at the surface, where higher levels than those expected by extrapolation are encountered. The analyses of samples collected at a nearby station give values of the same order of magnitude ( $0.16\text{ nM}$  for Cd;  $0.60\text{ nM}$  for Pb;  $4.70\text{ nM}$  for Cu), which would mean that the high concentrations found are not due to a pollution during sampling and/or storage. The same observation has also been made by other authors (Boyle *et al.*, 1977; Yeats and Campbell, 1983) who have suggested atmospheric inputs to explain the high concentration increase at the surface. In the stratified area, significant variations of Pb and Cu concentrations are observed in the surface layer (0-30 m) while Cd level remains relatively constant. Below the thermocline, the homogeneous character of the water mass gives on the other hand small variations in each case. If the main processes governing the vertical distribution of trace metals have been pointed out in oceanic waters (Bruland, 1983), in coastal areas the mechanisms which take place are more complex (Kremling and Hydes, 1988). Other more important phenomena may superimpose themselves on those encountered in the open ocean: atmospheric inputs are not the only external ones; freshwater inputs have to be taken into account; more intensive internal mechanisms are observed owing to the low depth of the water column and to the particular dynamics of these coastal ecosystems; phytoplankton blooms are also more important. In the well-mixed area, the intensive mixing of waters gives a similar vertical distribution for the three heavy metals, while this is not the case in the stratified zone, specially in the surface layer. Indeed we can notice: the absence of prominent levels at the surface for each trace element; an increase of the copper and lead concentrations above the thermocline. Such behaviour is consistent with that observed for copper by Buckley and Van Den Berg (1986) in a zone close to station S. To explain such a phenomenon Monteiro and Orren (1985) have

proposed a mechanism controlled by three biogeochemical processes: (i) uptake by organisms; (ii) regeneration in the water column through bacterially mediated oxidation; (iii) scavenging of dissolved species by settling particles. The concentration gradient which is observed is a result of the thermocline formation which slows down the settling particles, producing an increase of the total trace metal level near the thermocline boundary. The same mechanism can also be proposed for lead as this metal adsorbs better on particulate matters (Balls, 1985). Conversely, the weak reactivity of cadmium to organic substances in the presence of a high concentration of chloride and its weak capacity to adsorb (Davis, 1984; Florence, 1986) could explain its distribution.

## CONCLUSION

The data reported in the present work show that the behaviour of the heavy trace metals investigated in this particular ecosystem can be affected by physicochemical and biological processes according to their natural

disposition to form organic and inorganic complexes and to adsorb on particles. They show in particular, that lead and copper demonstrate behaviours which are highly dependent on the well-mixed or stratified nature of the water column, while this is not the case where cadmium is concerned.

Nevertheless, in order to obtain more accurate information about the mechanisms which occur, we intend to improve this study by daily sampling in a fixed station over a period of one month, hoping thereby better to understand the variations of copper, lead and cadmium concentrations in relation to the water column evolution (homogeneous-stratified-homogeneous).

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