

# Distribution of particulate trace elements in the Northeastern Atlantic

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## Abstract.

From 1989 to 1992, five cruises were conducted in an area covering the English Channel, the Celtic Sea and the Gulf of Biscay. During these campaigns, suspended matter was collected by different techniques in order to analyze the spatial and vertical distribution of several particulate trace elements in relation to the global biogeochemical cycle of carbon. It appears that horizontal distribution varies strongly from one element to another and is mainly influenced either by anthropogenic and terrigenous inputs or by scavenging processes. On the other hand, the vertical distribution seems mainly linked to the primary production. In parallel to these trace element measurements, experiments were carried out to estimate the transfer rates of these elements from the dissolved to the particulate phase using radioactive tracers. The results clearly indicate that biological activity plays an important role in these transfers.

## 1.- Introduction.

Very little attention has been paid until now to the trace element content of suspended matter in the water column. Trace metals are however known to be enriched in the particulate phase, and their contents in the suspended materials or sediments often reflect the history of surrounding environments with respect to pollution. In the photic zone for example, passive or active sorption processes occur onto the organic matter produced by the organisms, and they are responsible for the transfer of many elements from the dissolved to the particulate phase. As suspended matter is one of the main sources of carbon either for pelagic or for benthic food webs, its elemental composition also directly alters heavy metal concentrations in high trophic levels.



The present paper describes results of trace element measurements performed on suspended matter collected during the Global Change cruises (1989 to 1992) by the Belgian team. One of the objectives of the Global Change programme is to study the processes controlling the transfer of trace elements related to the carbon cycle between both particulate and dissolved phases. The sampling area covers a wide range of zones with different dynamics: (i) the English Channel, characterized by complex hydrological processes due to bottom profile and strong tidal currents, (ii) the Celtic Sea, on both sides of the continental margin, (iii) the center of the Gulf of Biscay, a deep (> 4,000 m) oligotrophic area, and (iv) the Northwestern Spanish coast which is the center of an intense upwelling.

With respect to the goals of the Global Change programme, the mechanisms and rates of transfer of trace metals from the dissolved to the particulate phase in the oceanic system were also investigated. Radioactive trace metals have been used successfully in previous studies in order to evaluate the distribution coefficient and the rate of transfer of trace elements from the dissolved to the particulate phase in sea-water (Balistrieri & Murray, 1983; Li *et al.*, 1984; Nyffeler *et al.*, 1984; Buchholtz *et al.*, 1985; Santschi *et al.*, 1986; Jannasch *et al.*, 1988). Most of these measurements were made during laboratory experiments using artificial suspensions of sediments mixed with sea-water or in mesocosm systems mimicking the natural environment. The results indicate a very fast initial sorption of the radiotracers followed by a much slower uptake. This suggests that there is a rapid adsorption at the surface of the particles followed by a slower transfer process which may be due to physico-chemical or biological processes.

Mouchel & Martin (1990) were the first to propose the use of radiotracer uptake experiments carried out immediately on samples collected in rivers, estuaries and marine systems. The results obtained during these experiments were in fact very similar to those obtained in the laboratory and are characterized by an important and rapid initial transfer. These authors have suggested to use this method to define a fast distribution coefficient ( $K_D$ ), easily evaluated by comparing the radioactivity of the solid collected after an initial stage, usually limited to 24 hours, with the radioactivity remaining in solution. This coefficient is very useful because it allows one to characterize the capacity of the suspended matter to induce scavenging of trace elements in the system considered. These short time measurements may also be used to understand the behaviour of trace metals in rapidly changing environments like estuaries or coastal zones.

Two of us have suggested (Wollast & Loijens, 1991) to improve this method by performing incubation experiments with natural samples spiked with radioactive trace metals similarly to the incubation experiments carried out with  $^{14}\text{C}$  labelled  $\text{HCO}_3^-$  to measure primary production. By comparing the uptake of trace metals incubated under natural or controlled light conditions or in the dark,



with or without inhibitors of the biological activity, it is possible to understand and to evaluate the contribution of the biological activity in the transfer of trace metals from the dissolved to the particulate phase. It is well known that many trace metals act as oligo-elements essential for the metabolic activity of living organisms. They often exhibit a nutrient like behaviour in aquatic systems indicating that the organisms can act as major scavenging agents of trace elements in sea-water.

## 2.- Sampling methods. Intercomparison.

Samples of total suspended matter (TSM) were collected during the following cruises on board the *R/V Belgica*: campaign 89/21 (September 11th to 26th, 1989) and campaign 90/18 (July 2nd to 18th, 1990) in the English Channel, Western Biscay and Northwestern Spanish Shelf areas (• in figure 1); campaign 91/16 (June 24th to July 9th, 1991) in the Channel, Northern Biscay and Celtic Sea areas (■ in figure 1); campaign 92/23 (October 8th to 23rd, 1992) in the Northern Biscay shelf break area (La Chapelle Bank, ▲ in figure 1). The position of the stations and corresponding TSM amounts in surface waters are listed in Table 1.

TSM was sampled using three different techniques, depending on whether horizontal distributions or vertical profiles were investigated. Sample preparation for trace metal determination also differed according to sampling technique. Comparisons of the results obtained by the three following methods will be discussed further.

- (i) For horizontal distribution pattern determination (1991 cruise), TSM was sampled by continuous centrifugation of surface seawater pumped forward at 3 m depth while the ship was making headway; sampling periods ranged from 3 to 8 hours (courses from 45 to 160 km). TSM concentrations measured by this method are listed on Table 1. Samples were stored in petri-dishes and deep frozen. For the analysis of trace metals (Al, Cd, Cr, Cu, Pb, Ti, Zn) suspended matter was mineralized in a mixture (1:1) of 65% nitric acid and 37% hydrochloric acid at about 75°C during 12 hours. Elemental determinations were made by ICP-AES (A.R.L. 3510).
- (ii) Vertical distribution of particulate trace elements was investigated using 30 l Niskin bottles (1990 to 1992 cruises). Immediately after sampling, these bottles were pressurized with filtered air (0.3 bar) and seawater was filtered with Nuclepore membranes (0.45 µm). Niskin bottles were slightly adapted to fit the filterholders onto the lower lid instead of the original outlet, allowing the collection of rapidly settling particles. Membrane samples were air dried and kept at room temperature. For analysis, a preliminary mineralization and dissolution is made using a fusion technique with lithium

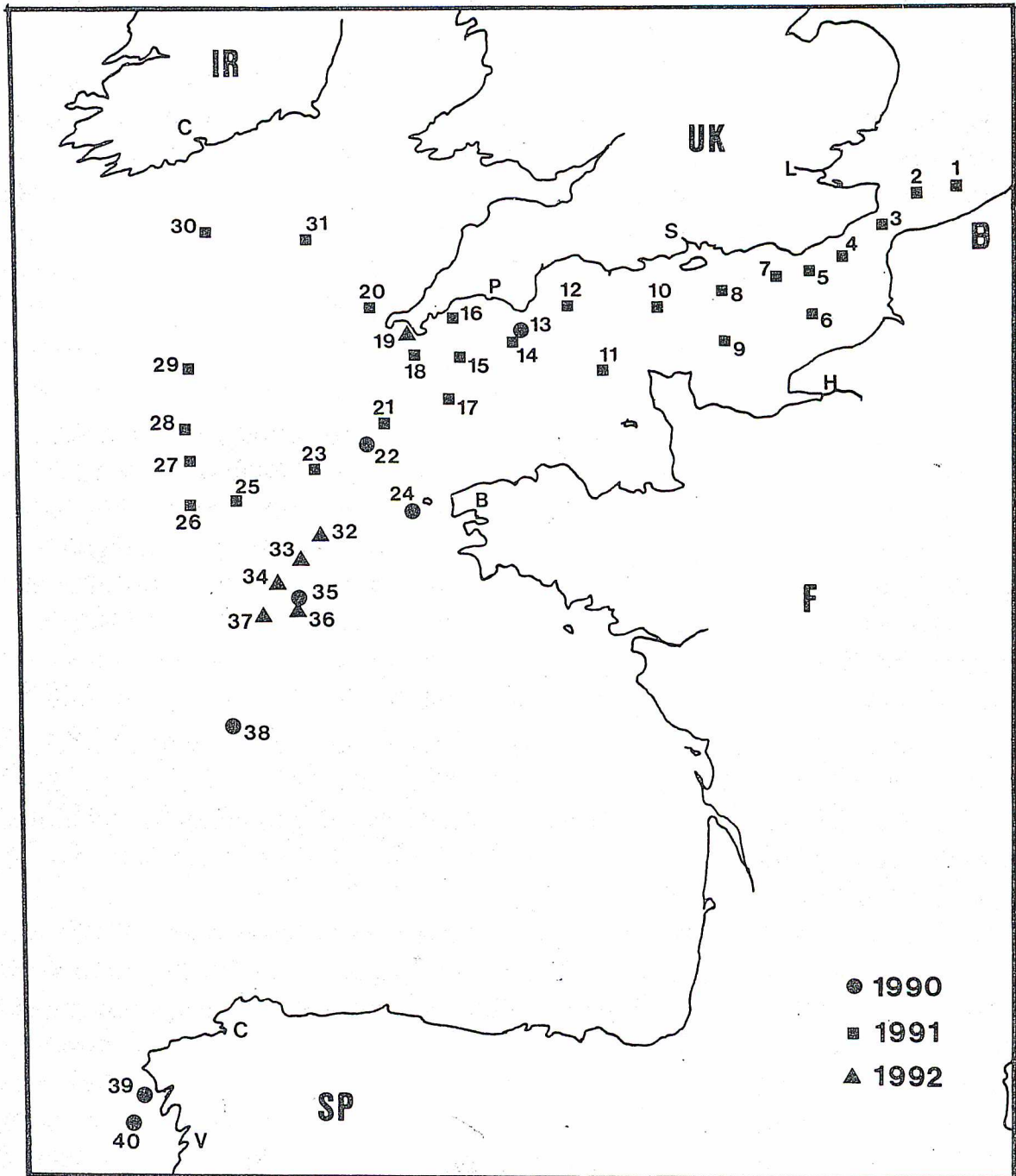


Fig. 1.— Position of the TSM sampling sites for the 1990, 1991 and 1992 cruises

metaborate as the flux. Elemental determinations were also performed with ICP-AES (Jobin-Yvon-48).

- (iii) Collection of larger amounts of TSM along vertical profiles was performed with a Stand Alone Pump (SAP), an *in situ* particle sampler, housed with a polycarbonate 30 cm filter holder fitted with a 1  $\mu\text{m}$  Nuclepore membrane. This device allows the filtration of a large volume of seawater (up to 2,000 l) at great depths (down to 5,000 m), and thus the collection of sufficient



Table 1  
 Sampling dates and locations, bottom depths, and TSM concentrations  
 (sampling by centrifugation)

Station #	Position	Depth (m)	Date	TSM (mg/l)
1	51°23'N-03°00'E > 51°20'N-02°30'E	11	91-Jun	4.10
2	51°20'N-02°30'E > 51°20'N-02°08'E	24	91-Jun	1.97
3	51°20'N-01°50'E > 50°50'N-01°00'E	34	91-Jun	1.92
4	50°50'N-01°00'E > 50°40'N-00°30'E	29	91-Jun	2.78
5	50°41'N-00°30'E	28	91-Jun	2.60
6	50°25'N-00°57'E > 50°01'N-00°04'W	41	91-Jul	3.79
7	50°41'N-00°30'E > 50°30'N-00°39'W	41	91-Jun	1.17
8	50°30'N-00°39'W > 50°20'N-01°35'W	52	91-Jun	1.34
9	50°00'N-00°15'W > 50°02'N-01°40'W	60	91-Jul	0.84
10	50°20'N-01°35'W > 50°15'N-02°30'W	52	91-Jun	1.62
11	50°00'N-01°49'W > 49°30'N-03°30'W	86	91-Jul	1.94
12	50°15'N-02°30'W > 50°05'N-03°30'W	58	91-Jun	1.58
13	50°00'N-03°50'W	72	90-Jul	2.75
14	50°05'N-03°30'W > 49°44'N-04°20'W	66	91-Jun	2.01
15	50°00'N-06°00'W > 49°30'N-03°30'W	101	91-Jul	1.31
16	50°08'N-05°05'W	10	91-Jun	1.62
17	49°44'N-04°22'W > 49°25'N-05°04'W	87	91-Jun	1.70
18	49°25'N-06°30'W > 50°06'N-05°00'W	77	91-Jun	1.77
19	50°03'N-05°19'W	28	92-Oct	1.31
20	50°15'N-05°40'W > 50°00'N-06°00'W	48	91-Jul	1.26
21	49°25'N-05°04'W > 49°05'N-06°10'W	107	91-Jun	1.95
22	49°00'N-06°00'W	120	90-Jul	1.89
23	48°56'N-06°01'W > 48°20'N-06°30'W	127	91-Jun	1.06
24	48°25'N-05°21'W	110	90-Jul	1.13
25	48°20'N-06°30'W > 48°09'N-08°14'W	340	91-Jun	1.38
26	48°09'N-08°20'W	1200	91-Jun	1.74
27	48°09'N-08°29'W > 49°00'N-08°33'W	475	91-Jun	1.10
28	49°00'N-08°22'W	155	91-Jul	0.53
29	49°04'N-08°11'W > 50°30'N-08°30'W	130	91-Jul	0.59
30	50°30'N-08°30'W > 51°45'N-08°20'W	65	91-Jul	0.64
31	51°45'N-08°15'W > 50°15'N-05°40'W	65	91-Jul	1.02
32	48°12'N-06°44'W	160	92-Oct	0.71
33	47°57'N-06°59'W	171	92-Oct	0.69
34	47°42'N-07°11'W	169	92-Oct	0.69
35	47°35'N-07°00'W	205	90-Jul	0.61
36	47°30'N-07°00'W	510	92-Oct	0.70
37	47°25'N-07°16'W	2000	92-Oct	0.72
38	46°25'N-08°00'W	4800	90-Jul	0.32
39	42°43'N-09°19'W	123	90-Jul	4.24
40	42°30'N-09°30'W	1230	90-Jul	4.21

quantities of suspended matter in waters of low particulate load. For each sample collected, metal concentrations (Cd, Cr, Co, Cu, Mn, Ni,

Pb, Zn) were measured using a Varian SpectrAA-400 Zeeman graphite furnace spectrometer. The analytical method involves direct injection of solid samples without the intermediate digestion step, as developed by Hoenig *et al.* (1989). Particulate Si and Al were also measured following the method described in Hoenig *et al.* (1991 a, b).

In order to control the reliability of metal determination, the entire analytical procedure was tested against standard reference sediments supplied by the National Institute of Standards and Technology (NIST), International Atomic Energy Agency (IAEA), Bureau Communautaire de Référence (BRC, EEC) and National Research Council of Canada (NRCC).

Table 2.

Intercomparison of trace element data obtained by the three different sampling and analytical techniques in various geographical areas

Areas (station #)	Elements	<i>In situ</i> pump 1990 data	Centrifugation 1991 data	Niskin 1992 data	
2, 3, 4, 5	Al (mg/g)		5.2	8.3	
5, 7, 8			5.9	6.1	
8, 10			7.8	9.3	
12, 14		5.5	5.4	4.1	
15, 21		1.1	1.1	0.9	
25, 26, 27, 28	Cd ( $\mu\text{g/g}$ )	0.32	0.42	0.41	
13, 14		0.61	0.6		
13, 14		Cr ( $\mu\text{g/g}$ )	20.3	15.3	
13, 14		Cu ( $\mu\text{g/g}$ )	25.3	23.2	
13, 14		Pb ( $\mu\text{g/g}$ )	25.3	17.7	
13, 14		Zn ( $\mu\text{g/g}$ )	47.5	58.3	

As different TSM collection techniques and metal determination methods were used, it is necessary to compare the results for the same water masses, *i.e.* for similar locations during the same sampling period, and ideally at the same depths. Unfortunately, few data are available for such a comparison because of the "weather at sea" which obliged us to use preferentially one sampling technique against another. Despite this drawback, concentrations obtained by different methods and laboratories on TSM collected at same sites and depths during the summer are very similar (Table 2). Intercomparison of these results allows us to control the quality of our data. The trace metal concentrations of TSM obtained in this study, regardless of the sampling and analytical techniques, are furthermore in good agreement with those obtained by Dehairs *et al.* (1985) and Baeyens *et al.* (1987) for similar sampling areas.

For experiments designed to study the transfer rate of trace metals from the dissolved to the particulate phase, the water samples were usually collected in



surface waters at depths corresponding to the maximum of fluorescence or of dissolved oxygen as recorded during the lowering of the CTD rosette. Samples were immediately spiked with the radionuclides and incubated under constant light conditions, at the surface seawater temperature. A few experiments were also carried out under variable light conditions. In order to reduce the perturbations of the natural conditions during the incubation experiment, the concentration of the carrier was kept at a low level. The final concentration obtained after addition of radionuclides is equal to  $10 \text{ nmol l}^{-1}$  for Mn, Co, Zn and  $5 \text{ nmol l}^{-1}$  for Cd. The influence of the amount of spike solution on the uptake of the radionuclide was investigated during a preliminary experiment. After incubation, samples were filtered on Sartorius  $0.4 \mu\text{m}$  membranes and rinsed with pre-filtered seawater. Preliminary tests have shown that absorption of radionuclides onto the Sartorius cellulose filter was negligible. The activities were measured with a HPGE Canberra detector with a relative efficiency of 20% and a multichannel spectrometer serie 20 Model 2802. The activities recorded on the filters after incubation of open-sea water samples are often of the order 0.1 dpm and requires long counting times. The minimum number of counts was fixed at 1,000 to reduce the statistical error related to counting.

### 3.- Results and discussion.

#### 3.1.- Horizontal surface distribution.

##### 3.1.1.- Results from centrifugation (Table 3 and Figure 2).

###### *Aluminium.*

The distribution of the particulate Al concentrations is roughly correlated with that of particulate load. This is not surprising since particulate aluminium is mainly present in the sea as terrigenous aluminosilicates via riverine or atmospheric input. Observed concentrations are very similar all along the English Channel (from  $3$  to  $16 \mu\text{g l}^{-1}$ , from  $2$  to  $7.5 \text{ mg g}^{-1}$  TSM), with, however, higher values near the English coasts; these data are slightly lower than those of Dehairs *et al.* (1985) for the Eastern Channel, and are significantly below values measured in the Southern Bight of the North Sea by Duinker & Nolting (1977) and Dauby *et al.* (1993) who found concentrations up to  $1.2 \text{ mg Al l}^{-1}$ . In the Celtic Sea, concentrations are much lower, averaging  $0.3 \mu\text{g l}^{-1}$  ( $0.4 \text{ mg g}^{-1}$ ), because the TSM in that region is mainly composed of organic matter. In the center of the Gulf of Biscay, concentrations decrease below  $0.2 \mu\text{g l}^{-1}$  but rise sharply (up to  $50 \mu\text{g l}^{-1}$ ) when approaching the Spanish coast.

Table 3  
Particulate metal concentrations in surface seawater ( $\mu\text{g/l}$  or  $\text{mg/l}$ ) and in TSM collected by centrifugation ( $\mu\text{g/g}$  or  $\text{mg/g}$ ) during the June 1991 cruise

Station #	Al		Cd		Cr		Cu		Pb		Ti		Zn	
	( $\mu\text{g/l}$ )	( $\text{mg/g}$ )	( $\text{ng/g}$ )	( $\mu\text{g/l}$ )	( $\text{ng/g}$ )	( $\mu\text{g/l}$ )	( $\text{ng/g}$ )	( $\mu\text{g/l}$ )	( $\text{ng/g}$ )	( $\text{ng/g}$ )	( $\mu\text{g/l}$ )	( $\text{ng/g}$ )	( $\text{ng/g}$ )	( $\mu\text{g/l}$ )
1	27.3	6.7	16.9	4.13	166	40.5	152	37.1	470	114.7	287	70	1549	377.9
2	11.0	5.6	4.3	2.20	51	25.8	67	34.2	79	40.3	159	80	487	247.1
3	8.6	4.5	1.1	0.59	18	9.5	27	14.1	15	7.9	71	37	101	52.7
4	16.0	5.8	3.6	1.30	48	17.2	176	63.2	94	34.0	176	63	272	97.9
5	12.8	4.9	2.9	1.11	39	14.9	102	39.3	80	30.6	90	34	237	91.1
6	8.4	2.2	0.5	0.14	54	14.3	67	17.7	35	9.3	134	35	82	21.8
7	6.2	5.3	1.6	1.37	19	16.1	58	49.6	35	30.2	45	38	103	87.8
8	10.0	7.5	2.2	1.66	28	20.9	134	99.7	52	38.7	63	47	181	135.1
9	3.8	4.5	0.4	0.53	15	18.0	19	22.5	16	18.8	52	61	38	44.9
10	13.0	8.1	0.7	0.44	32	19.6	29	17.8	33	20.3	78	48	92	57.1
11	2.8	1.4	0.6	0.32	21	10.9	36	18.5	25	13.0	42	21	54	28.0
12	7.9	5.0	1.9	1.20	24	15.3	30	18.8	28	17.8	69	43	104	65.8
14	11.4	5.7	1.2	0.60	31	15.3	47	23.2	36	17.7	60	30	117	58.3
15	1.6	1.2	0.7	0.56	21	15.8	31	23.4	13	10.0	26	20	64	48.6
16	8.8	5.5	1.3	0.83	29	17.6	39	24.1	33	20.5	40	25	117	72.1
17	6.5	3.8	1.4	0.84	28	16.4	60	35.5	35	20.6	25	15	135	79.3
18	3.7	2.1	1.5	0.84	36	20.1	37	20.7	17	9.7	24	13	126	71.0
20	2.7	2.1	0.9	0.72	68	54.2	33	26.3	27	21.8	39	31	84	67.0
21	1.7	0.9	2.2	1.10	34	17.3	44	22.8	16	8.0	21	11	141	72.1
23	5.4	5.1	1.5	1.38	46	43.6	89	83.9	70	65.6	61	57	214	201.7
25	1.0	0.8	0.9	0.66	12	9.0	21	15.1	13	9.3	13	10	40	29.3
26	0.9	0.5	1.7	0.97	21	12.3	22	12.4	14	7.8	13	7	53	30.7
27	0.2	0.2	1.8	1.60	19	17.6	23	21.3	11	10.2	2	2	38	34.9
28	0.1	0.2	0.3	0.63	8	14.9	15	28.6	1	0.9	2	3	13	24.2
29	0.4	0.7	0.3	0.52	99	167.6	16	27.3	7	11.6	3	4	27	45.4
30	0.2	0.3	0.3	0.46	14	21.4	12	18.7	1	1.6	2	3	23	36.6
31	0.5	0.5	0.4	0.38	85	83.7	17	16.7	14	13.7	9	9	55	54.3
soils*		71		0.35		70		30		35		5000		90
rivers*		94		(1)		100		100		100		5600		250

\* Data for mean soils and river particulate material from Martin & Meybeck, 1979.



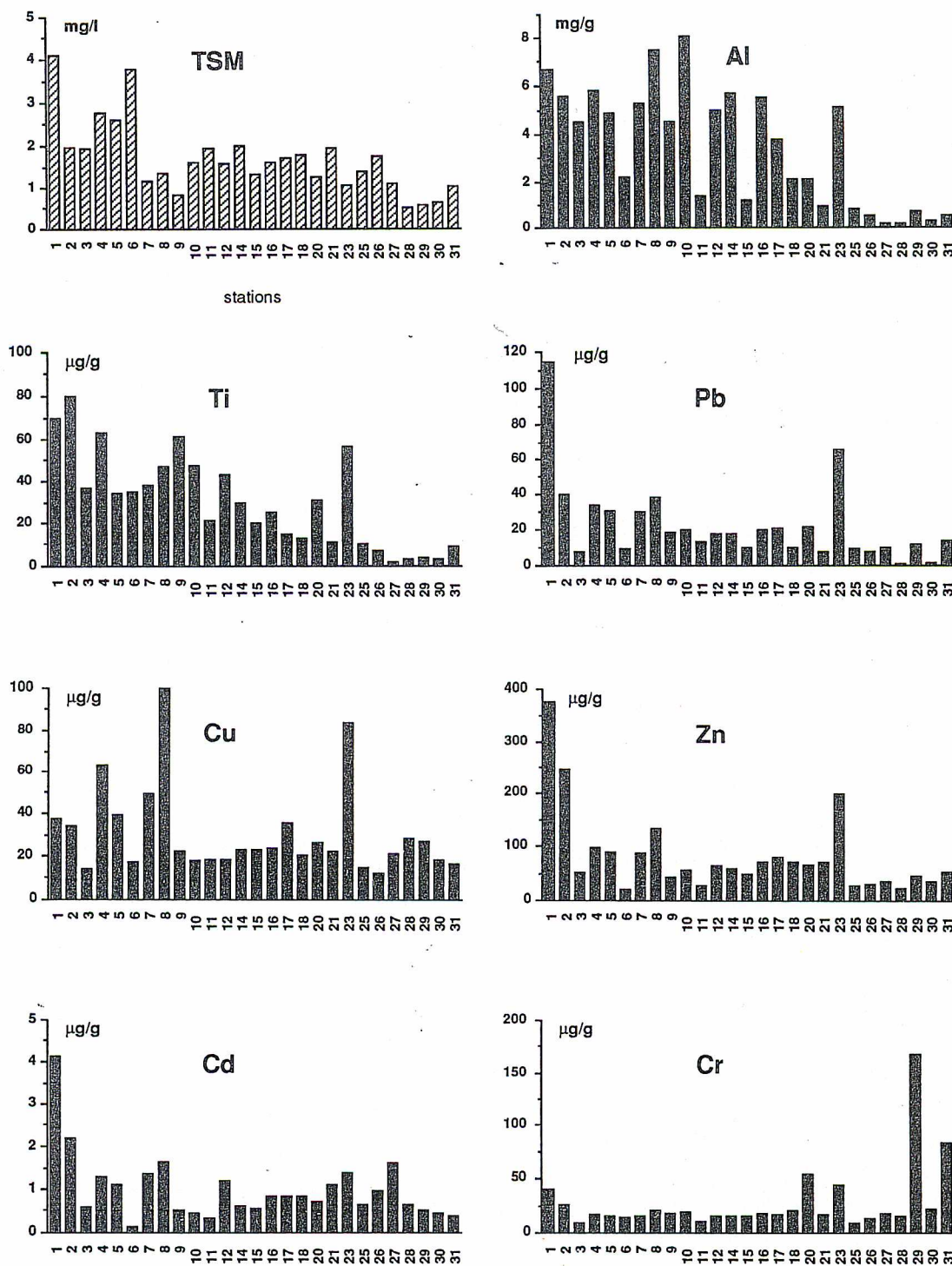


Fig. 2.- TSM concentrations in surface waters sampled by centrifugation during the June 1991 cruise, and heavy metal concentrations in this TSM.

*Titanium.*

The distribution of Ti associated with TSM is similar to that of aluminium, as this element is also a tracer of terrestrial material. The concentrations are nevertheless particularly high ( $\geq 70 \mu\text{g g}^{-1}$ ) in the Southern Bight (where

Nolting & Eisma, 1988, have found up to  $2 \text{ mg Ti g}^{-1}$ ) and the Strait of Dover, and could be attributed to the presence of several recent dumping sites of titanium dioxide production waste; these dumps, if now theoretically stopped, should progressively release this metal and are probably responsible for the observed concentrations.

#### *Copper.*

The measurements of Cu concentration in the TSM show minimum values in the whole Celtic Sea (except for Station 23) and in the Western Channel, about  $25 \text{ } \mu\text{g g}^{-1}$  on the average. In the Eastern Channel, concentrations increase, especially along the English coast, indicating a land source of Cu, likely related to the large industrial complexes of the Southeastern UK. It is also worth noting that there is no correlation between TSM concentration in surface seawater and Cu concentration in TSM, and that thus this metal seems to be associated with particulate matter inputs, either terrigenous or resuspended. The observed concentrations are in good agreement with those obtained by Dehairs *et al.* (1985) in the same area.

#### *Zinc.*

Among the elements analyzed in TSM, zinc is the one (after Al) which presents at all the stations (except the 6th) the highest concentrations, as also previously observed by Dehairs *et al.* (1985) and Baeyens *et al.* (1987). In the Southern Bight, values are peculiarly high, going beyond mean crustal or riverine values; this could be attributed to the drastic influence of Scheldt River and to the resuspension processes related to shallowness and tidal mixing. In the Channel, two relative maxima ( $> 200 \text{ } \mu\text{g g}^{-1}$ ) are observed, on both the western and eastern parts of the English coast, probably related to industrial activities. In the Celtic Sea, values are much lower (between  $30$  and  $55 \text{ } \mu\text{g g}^{-1}$ ), except for Station 23 where high concentrations of copper and lead are also observed; the unexpectedly high metal concentrations observed there could be the result of a recent local sewage release.

#### *Lead.*

The relative distribution of particulate Pb in the area studied is very similar to that of Zn, with a maximum (nearly  $115 \text{ } \mu\text{g g}^{-1}$ ) close to the Belgian coast (input from the Scheldt River) and high values (around  $40 \text{ } \mu\text{g g}^{-1}$ ) on the English coast of the Eastern Channel. As for both the latter metals, no apparent correlation could be found between TSM concentrations in seawater and metal concentrations in TSM, suggesting a passive sorption of metal on suspended matter.



### *Cadmium.*

This metal is relatively peculiarly abundant in the waters off the Belgian coast, near the Scheldt Mouth, as was also described by Baeyens *et al.* (1987), Bouquegneau *et al.* (1992) and Dauby *et al.* (1993); this is not surprising as Belgium is the largest Cd consumer in Western Europe. In the Channel, concentrations range from 0.4 to 1.3  $\mu\text{g g}^{-1}$  along the English coast, with a maximum observed off Southampton. The French side and the Western Channel are less contaminated, with values around 0.3  $\mu\text{g g}^{-1}$ . Concentrations observed in the Celtic Sea waters are low (about 0.3  $\text{ng l}^{-1}$ ), but are relatively high in the corresponding TSM (about 1  $\mu\text{g g}^{-1}$ ), suggesting a process of high metal uptake (see further) by suspended matter in these oligotrophic waters.

### *Chromium.*

Particulate Cr concentrations in the water are nearly constant throughout the whole Channel (about 20  $\mu\text{g g}^{-1}$ ), and present two maxima: one in the Southern Bight, probably related to riverine discharge, and another one of lower importance in the Celtic Sea. This second maximum appears, however, much more important when considering the Cr concentrations in TSM (figure 2) that reach, in that area, 5 to 10 times (up to 167  $\mu\text{g g}^{-1}$ ) the concentrations observed elsewhere. TSM thus seems to have a high affinity for chromium, and this scavenging process is confirmed by the inverse exponential relationship between Cr/TSM ratios and TSM concentrations in seawater.

### **3.1.2.- Results from *in situ* pumping.**

As was also observed for centrifugation samples, the particulate Al concentrations in all the SAP samples are well below 70  $\text{mg g}^{-1}$  which is the value found in soils (Martin & Whitfield, 1983), suggesting that the particulate material collected has a high organic content. Suspended matter sampled in waters close to the coastal area (Stations 13, 24 and 39) contains higher Al, implying continental inputs of terrigenous material. It should be pointed out that Station 39, located right at the Spanish coast in an area where there are many Rias estuaries, has the highest particulate Al contents.

The surface distribution of particulate trace metals are shown in figure 3. It is interesting to point out that particulate Mn shows spatial distribution very similar to that observed for particulate Al. This suggests that these two elements are intimately linked with a correlation coefficient of 0.81 and have the same origin. There is a particularity regarding Station 38 compared to Station 24, both situated in the Gulf of Biscay. Indeed, Station 38 is far from the continent and thus likely receives the least terrestrial inputs as indicated by the lowest Al contents. However, when normalized with respect to Al, the suspended matter



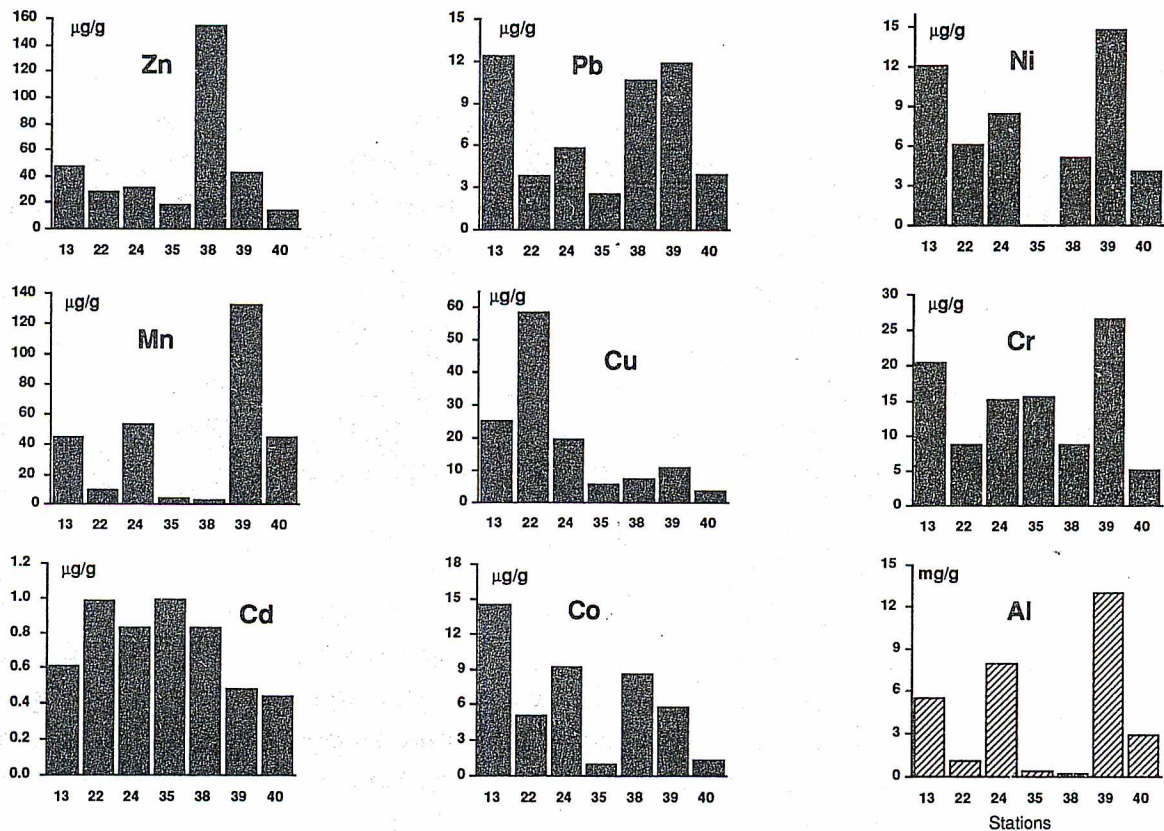


Fig. 3.— Trace element concentrations in surface water TSM sampled by *in situ* pumping during the July 1990 cruise.

collected at Station 38 is enriched in several trace metals, especially Pb, Co, Cu and Zn compared to Station 24. This implies that these metals are enriched mainly in the planktonic phase, and that an active scavenging process likely occurs in these oligotrophic waters, what is confirmed by the data obtained for trace metals in TSM with the centrifugation technique. Furthermore, it has been recognized that phytoplankton generally plays an important role in the biogeochemical cycling of trace elements in the aquatic environment (Morel & Hudson, 1985; Price & Morel, 1990), and that trace metals tend to be scavenged by organic matter due to their strong complexation with organic ligands. Therefore, in areas of high productivity, seasonal variations can be observed and correlated with the annual production cycle (Bacon *et al.*, 1985).

### 3.2.— Vertical distribution.

#### 3.2.1.— Results from *in situ* pumping (Figures 4 to 6).

During the 1992 cruise (▲ in figure 1), TSM was collected in the northern part of the Gulf of Biscay, on both sides of the continental slope, but only the results obtained for Stations 32 and 37 will be presented here. Vertical distribution of particulate trace metal concentrations were determined and the



Table 4

Summary of results on the particulate trace metal concentrations of TSM collected at Stations 32 and 37 by *in situ* pumping during the October 1992 cruise

Depth (m)	Al (mg/g)	Zn ( $\mu\text{g/g}$ )	Ni ( $\mu\text{g/g}$ )	Cr ( $\mu\text{g/g}$ )	Mn ( $\mu\text{g/g}$ )	Cu ( $\mu\text{g/g}$ )	Cd ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Co ( $\mu\text{g/g}$ )	Fe (mg/g)	POC (%)
Station 32											
10	2.4	108.1	19.1	41.8	81.5	20.8	2.46	10.3	0.66	1.3	
40	9.9	184.3	34.9	78.4	185.8	66.7	3.96	15.7	1.09	5.3	
80	23.9	94.6	23.7	52.9	327.7	24.7	0.96	22.8	2.07	11.2	
110	10.1	47.3	14.8	49.9	146.8	14.3	0.93	11.4	0.84	4.5	
Station 37											
20	4.2	120.9	15.0	42.6	192.3	16.3	2.78	11.9	0.84	1.5	9.8
50	5.9	123.0	15.6	29.3	226.2	20.3	1.56	14.0	0.75	3.1	5.0
80	27.5	155.4	75.6	84.8	537.5	38.0	1.35	38.1	2.93	13.2	2.5
140	27.5	122.3	38.4	62.7	690.0	38.1	3.05	23.0	2.85	12.7	1.7
200	10.1	102.1	24.1	40.0	325.4	31.3	0.85	25.5	1.37	4.3	2.1
500	20.1	169.5	53.2	145.7	550.8	54.3	1.68	43.5	2.73	10.7	1.0
600	25.4	167.7	34.9	62.4	543.6	55.1	0.34	43.1	3.55	12.9	0.65
800	13.2	98.1	22.0	38.7	245.5	31.9	0.83	23.9	1.94	5.4	0.67
1000	14.4	153.6	50.3	57.4	240.5	86.2	1.57	42.2	1.44	7.0	0.41

results are summarized in Table 4 where the particulate Al and organic carbon contents are also indicated. Vertical profiles of temperature and salinity are shown in figure 4. The *T/S* diagramme reveals clearly that four different water masses (surface, 200 m, 600 m, bottom) can be identified for Station 37, located on the deepest edge of the slope.

Contaminants such as heavy metals are usually accumulated in the fine fractions of sediments or suspended materials containing elements like Al, Fe and organic matter (ICES, 1988). Normalization of particulate trace metal concentrations has been a subject of discussion (Loring, 1988; Windom *et al.*, 1989). Application of appropriate normalization procedure may help in deciphering the data. Particulate Al is a good indicator of fine terrestrial origin such as clays. Therefore, it can be considered as a suitable candidate to be used for normalization purpose. Figure 5 shows the vertical distribution of Al and organic carbon for Stations 32 and 37. It is worth noticing that particulate organic carbon content of the suspended matter decreases exponentially with depth indicating a very fast remineralization of organic matter during settling. At the same time, the particulate Al content is the lowest in the photic zone suggesting a dilution of this element by biogenic material due to primary production.

The vertical distribution of particulate trace metals (normalized with respect to Al) are shown in figure 6 where the particulate Ba/Al is also indicated. A general trend is observed for most trace metals investigated except for Fe and Ba.

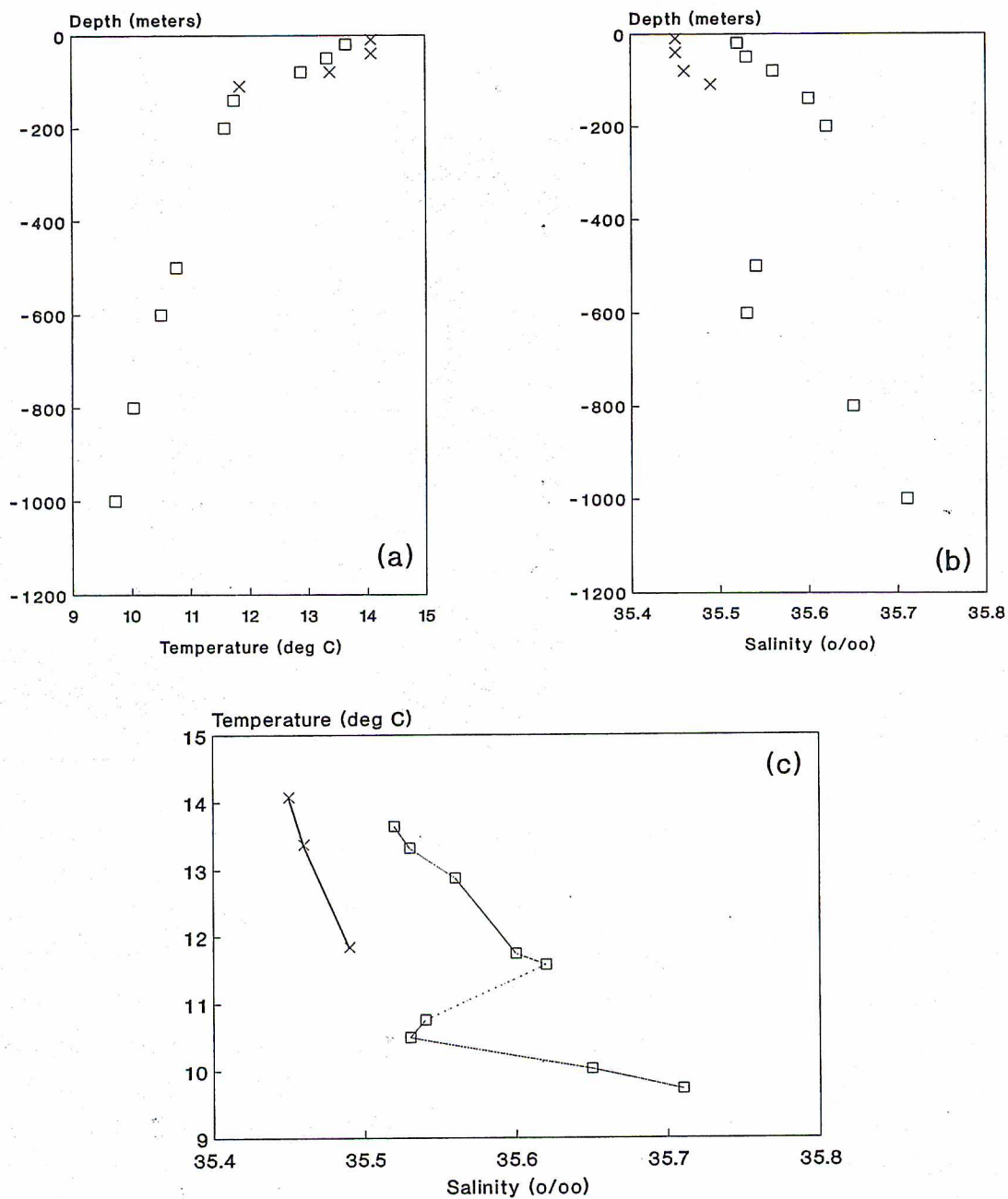


Fig. 4.- Temperature, Salinity, and *T/S* diagramme for Station 32 (x) and Station 37 (□) for October 1992 cruise.

There is an enrichment in the photic zone, especially for Cd. This is probably due to an uptake of trace elements by phytoplankton via biological and/or physico-chemical pathways. The variations in particulate trace metal concentrations with respect to Al below the photic zone seem to be related to different water masses existing that have all different particulate trace metal chemistry. Particulate Ba shows a different vertical profile compared to other metals. Its behaviour strongly influenced by biological activity will be discussed in detail in the following section. It is finally interesting to point out that particulate Fe/Al remains fairly constant



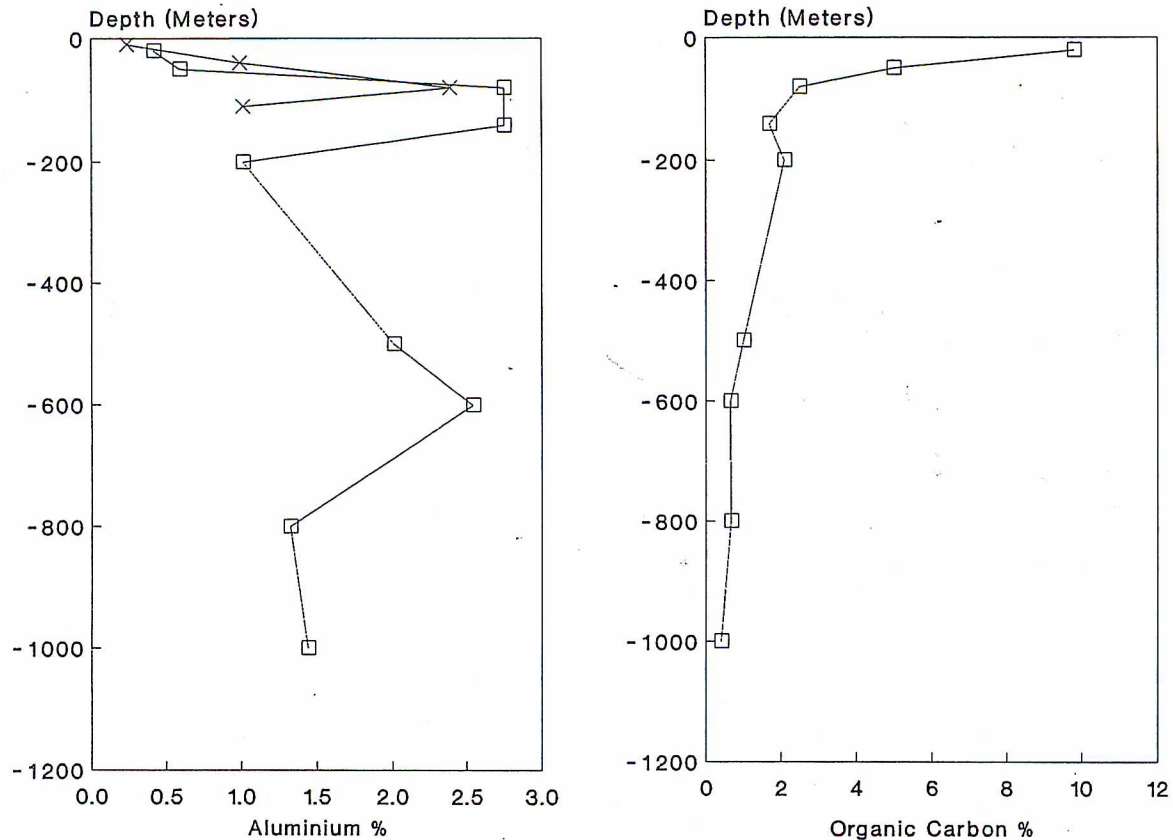


Fig. 5.- Vertical distribution of particulate Al and organic carbon in the TSM collected by *in situ* pumping during the October 1992 cruise for Station 32 (x) and Station 37 (□).

at a ratio close to 0.49 throughout the water column. This ratio is typically found for atmospheric dust over the North Atlantic (Duce *et al.*, 1991).

### 3.2.2.- Results from Niskin sampling – Ba distribution (Figures 6 to 8).

It is known that the main carrier of particulate Ba in suspended matter is Ba-barite (Dehairs *et al.*, 1980). The fraction of the Ba associated with aluminosilicates in suspended matter was calculated using the Ba/Al ratio for mean crust (Al: 82 mg g<sup>-1</sup>; Ba: 500 µg g<sup>-1</sup>; Bowen, 1979) and the Al content of the sample:

$$(\text{Al})_{\text{sample}} * (\text{Ba/Al})_{\text{crust}} = (\text{Ba})_{\text{sample associated with aluminosilicates}}$$

This exercise showed that the highest fraction of Ba in aluminosilicates are usually below 25% of the total Ba concentrations. Such values can occur in surface and bottom waters. Atmospheric deposition and sediment resuspension may be responsible for this observation. For the rest of the water column, the fraction of Ba in aluminosilicates is generally less than 10%. It follows that the vertical distribution of particulate Ba, normalized with respect to Al content, shows a substantial enrichment in Ba especially at depths ranged between 100 and 600 m (figure 6). This points towards another component as the main Ba carrier.

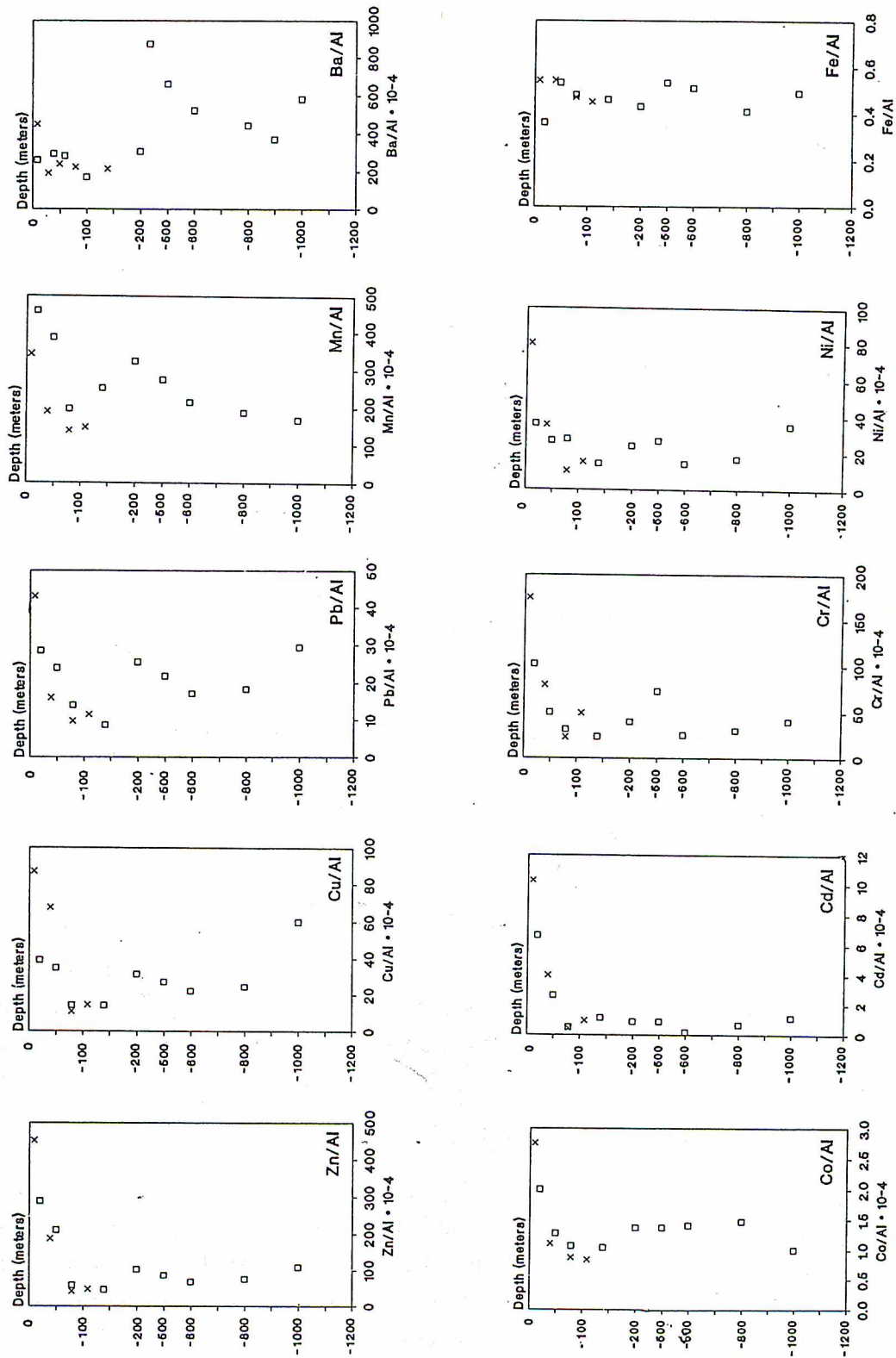


Fig. 6.-- Vertical distribution of particulate trace metals in the TSM collected by *in situ* pumping during the October 1992 cruise for Station 32 (x) and Station 37 (□)



It has been known for some time that particulate Ba-barite in the oceanic water column and the sediments reflects production in the surface layers (Bishop, 1989; Dymond *et al.*, 1992; Dehairs *et al.*, 1980, 1990). These studies have revealed that Ba is incorporated by the biota (it is not known whether this process is active or passive) and precipitates thereafter as  $\text{BaSO}_4$  (barite) within aggregates of biogenic detritus. These aggregates form the suitable micro-environments wherein barite saturation conditions are likely to be fulfilled (Bishop, 1988; Stroobants *et al.*, 1991; Dehairs *et al.*, 1980). Such barite micro-crystals account for the largest fraction of total particulate Ba at mesopelagic depths (Dehairs *et al.*, 1980). Furthermore, investigations in the Southern Ocean indicate that the occurrence of Ba-barite at mesopelagic depths is related to the type of production (*i.e.* new *versus* recycled) in the euphotic layer, with significant mesopelagic barite accumulation reflecting predominance of new, or export production (Dehairs *et al.*, 1992).

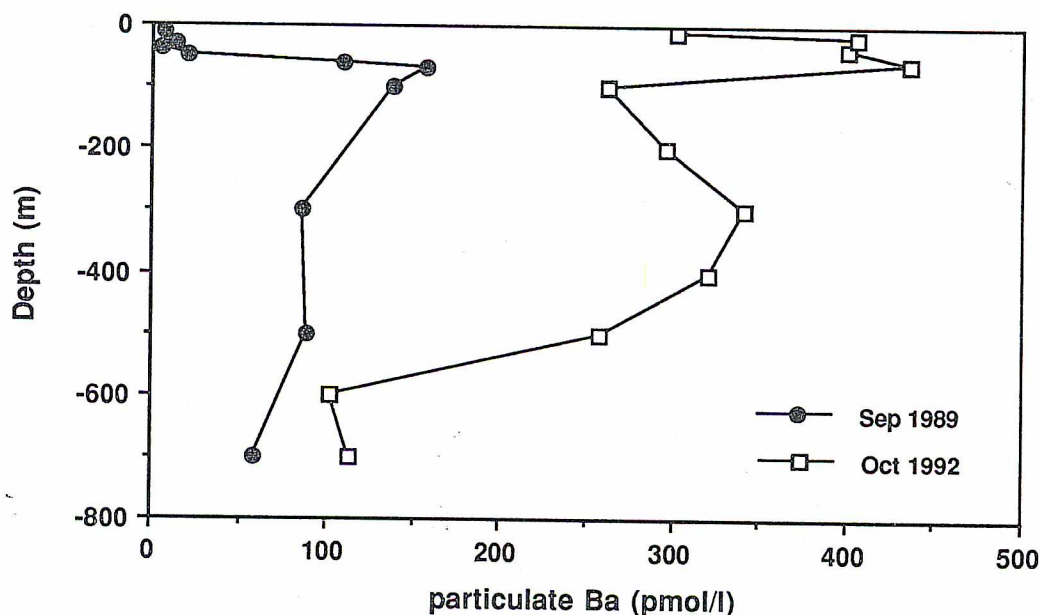


Fig. 7.— Vertical profiles of total particulate barium in the upper 600 m of water column at Station 45°00' N – 8°28' W (September 1989 cruise) and at Station 37 (October 1992 cruise).

To investigate the spatial and temporal variability of new and recycled production in the Gulf of Biscay, the distribution of mesopelagic Ba-barite was systematically studied. During September 1989 and June 1990, generally low mesopelagic Ba-barite concentrations were observed. A typical profile at a station located in the deep basin region (45°00' N, 8°28' W) is shown in figure 7. Despite the relatively low Ba concentrations (maxima are close to 200  $\text{pmol l}^{-1}$ ) the broad Ba maximum in the 100 to 400 m depth range is clearly visible. Such relatively low concentrations were also observed during spring and summer in the marginal ice zone (MIZ) of the Scotia-Weddell Confluence and in the

coastal and continental shelf (CCSZ) area of Prydz Bay (Dehairs *et al.*, 1991, 1992). In these areas the low mesopelagic Ba-barite concentrations coincided with high biomasses and primary productivities. Values of net production vary between 600 and 1400 mg C m<sup>-2</sup> d<sup>-1</sup> (Mathot *et al.*, 1992). However, the primary production was observed to be mainly ammonium sustained (*f*-ratio < 0.5; Goeyens *et al.*, 1991; Dehairs *et al.*, 1992); reflecting predominance of recycling over export. On the contrary, the low barite concentrations in the Gulf of Biscay correspond to low productivities. Primary production in this zone ranges from 47 to 220 mg C m<sup>-2</sup> d<sup>-1</sup> (Elskens *et al.*, this volume). The nitrogen assimilation experiments indicate that, during spring, the ecosystem evolves from a first phase of about 2 months where new production predominates into a second one dominated by regenerated production (*f*-ratio ranging from 0.1 to 0.9). In this case, it is thus possible that both effects (low productivities and limited export production) contribute to the low observed mesopelagic barite.

During June and October 1992 at the ocean margin of the Gulf of Biscay (La Chapelle Bank), the situation was quite different. At these stations, significant concentrations of mesopelagic Ba-barite are observed (maximal Ba concentrations up to 580 pmol l<sup>-1</sup> at 200 m; Station 47°25' N, 7°18' W). Figure 7 shows the profile for October, 1992. Such high concentrations were observed mainly in the ice free open ocean zone (OOZ) of the Antarctic Circumpolar Current (ACC), both in the Atlantic and Indian Ocean sectors (Dehairs *et al.*, 1990, 1991). These latter systems, though generally less productive than the MIZ and CCSZ systems, are characterized by increased relative importance of the new *versus* recycled production (*f*-ratio ≥ 0.5).

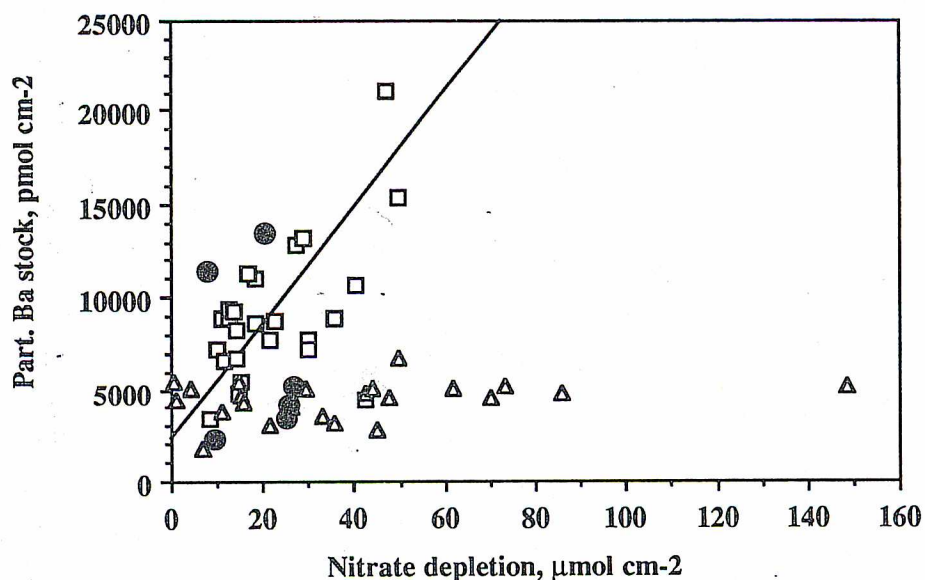


Fig. 8.— Stocks of total particulate Ba (pmol cm<sup>-2</sup>) at mesopelagic depth (*i.e.* between 100 to 500 m depth) *versus* nitrate depletion (11 μmol cm<sup>-2</sup>) for Southern Ocean Oozes (□) and MIZ + CCSZ stations (Δ) as given in Dehairs *et al.* (1992) and Gulf of Biscay (●; this study).



To visualize the difference between the two situations, Ba-barite stocks in the 60 to 500 m depth interval were plotted *versus* nitrate depletion over the season (figure 8). Ba stocks represent the integrated Ba amount, in  $\text{nmol m}^{-2}$ , over the depth interval considered. As previously mentioned in Elskens *et al.* (this volume), nitrate depletion is the integrated difference between the winter nitrate concentration and the observed *in situ* concentration in the mixed layer. It represents a conservative estimate of the nitrate consumed over the season, nitrate being either exported to the deep or recycled to a large degree. In figure 8, the data obtained in the Southern Ocean have also been reproduced. For the Southern Ocean, stations in the MIZ and the CCSZ typically have a wide range of nitrate depletion, but only a narrow range of low Ba-barite stocks. On the other hand, the Ooz of the ACC shows generally much larger Ba-barite stocks for similar nitrate depletions and positive correlation between barite stocks and nitrate depletions is observed (figure 9). The stations sampled during 1989 and 1990 in the Gulf of Biscay fit the MIZ and CCSZ barium-nitrate depletion picture, while the stations of 1992 fit the Ooz situation. This behavior suggests that export during 1992 have been significant while it was not in 1989 and 1990.

What differentiates these years? During 1989, 1990 and 1991, the surface waters (upper 60 m) have generally low stocks of particulate Ca, Sr and Si. Data in Table 5 show maximum stock concentrations of 742, 5.6 and 149  $\text{nmol cm}^{-2}$  for Ca, Sr and Si respectively. During 1992, both in June and October, particulate Ca, Sr and Si stocks in the upper 60 m increased about tenfold, to reach a maximum of 4833, 47.4 and 2100  $\text{nmol cm}^{-2}$ , respectively. This significant increase in Ca, Sr and Si contents during 1992 was not paralleled by a similar increase in POC. In June 1992 the stock concentrations of POC was 82  $\mu\text{mol cm}^{-2}$ , while in October it was 20  $\mu\text{mol cm}^{-2}$ , similar to the values observed during the previous years. The phytoplankton community thus appear to have been quite different in 1992 with predominance of  $\text{CaCO}_3$  secreting species (Coccolithophoridae) and also diatoms. This difference in phytoplankton composition has probably resulted in very large Ba uptake in the euphotic layer (stock concentrations of Ba in surface water during June is up to 28,946  $\text{pmol cm}^{-2}$ !) but also in the build-up of larger mesopelagic Ba-barite stocks (Table 5). Thus increased contribution of skeleton forming groups in the phytoplankton community of 1992 has increased the relative importance of export production, probably as the result of increased particle density.

### 3.3.- Dissolved to particulate transfer experiments.

One of the aim of our study is also to understand the mechanism and to quantify the kinetics of the transfer of dissolved trace metals from the dissolved phase to the particulate phase. The vertical distribution of the concentration



Table 5

Stock concentrations in the upper 60 m of water column for POC, PN, Chlorophyll *a*, particulate Al, Ca, Sr, Si and Ba. Concentrations of Ca, Sr, Si and Ba have been corrected for the fraction carried by the terrigenous aluminosilicate fraction using crustal compositions as given by Bowen, 1979. Stocks represent depth-integrated concentrations of the respective elements over the thickness of the mixed layer. Nitrate depletion over the season were calculated according to Elskens *et al.* (this volume). Mesopelagic Ba stocks are depth-integrated concentrations between 100 and 500 m depth.

Position	St.	Date	POC $\mu\text{mol}/\text{cm}^2$	PN $\mu\text{mol}/\text{cm}^2$	Chl. <i>a</i> $\mu\text{g}/\text{cm}^2$	Al $\text{nmol}/\text{cm}^2$	Ca $\text{nmol}/\text{cm}^2$	Sr $\text{nmol}/\text{cm}^2$	Si $\text{nmol}/\text{cm}^2$	Ba $\text{pmol}/\text{cm}^2$	$\text{NO}_3$ depletion $\mu\text{mol}/\text{cm}^2$	Mesopelagic Ba $\text{pmol}/\text{cm}^2$
47°17'N 8°37'W		Sep-89	14.9	2.4	1.6	13.2	738	5.6	119	65	24.9	3395
46°00'N 8°29'W		Sep-89	18.6	2.5	1.6	6	466	3.4	163	59	25.4	4230
45°00'N 8°28'W		Sep-89	20.4	2.8	1.1	9.6	589	4.3	149	113	26.8	5172
46°25'N 8°00'W	38	Jul-90	30.6	4.4	2.6	15.9	742	4.6	—	67	9.2	2310
47°23'N 7°18'W		Jun-92	82.1	9.2	5.7	200	4833	47.4	1630	28946	20.6	13416
47°25'N 7°15'W	37	Oct-92	19.7	2.5	6.3	46.3	3465	22.1	2100	2378	7.8	11415



of trace elements normalized with respect to Al clearly indicate their relative enrichment in the photic zone suggesting a possible influence of the biological activity during this transfer. This is confirmed by the fact that the vertical distribution of dissolved metals often exhibits a nutrient like profile, where the metals are strongly depleted in the photic zone (Bruland & Franks, 1983). For some metals like for example Zn, Mn or Fe, their metabolic rôle is known and their role as essential oligo-elements well established. Others like Cd have no active role in the metabolism of organisms, but the dissolved species are also strongly depleted in the photic zone and the composition of the particles exhibits a relative enrichment of this metal in the surface ones. One may thus assume that besides the active uptake of trace elements by the plankton, there may be also passive adsorption of some other elements by the solid-liquid interface created during the production of particulate organic matter.

In order to gain a better understanding of the behaviour of the trace metals in the euphotic zone, we have first investigated the influence of the concentration of the metal on its rate of uptake by using radiotracers supported by concentration of the stable isotope slightly higher than the natural concentration. Thus in the following experiments 1 nCi represents between 50 and 100 pmol of the non-radioactive metal.

The influence of the amount of radionuclide added to the sample on its transfer from the dissolved to the particulate phase is shown in figure 9. Since the amount transferred to the solid phase represents no more than 5% and is usually less than 1% of the total radioactivity of the system, one may consider that the activity of the aqueous and thus the concentration of the metal phase remain constant during the experiment. As shown in the figure, the experimental results are well described by a Langmuir type adsorption isotherm where

$$(1) \quad X^* = \frac{S_T x^*}{x^* + \frac{1}{K}}$$

$x^*$  and  $X^*$  are respectively the activities of the aqueous and solid phases,  $S_T$  is the total amount of adsorption sites and  $K$  is the equilibrium constant of the adsorption reaction

$$(2) \quad x^* + S_o = X^*$$

where  $S_o$  is a non-occupied site of the solid phase.

It is however important to note that this equation may also represent the uptake resulting from a biological activity governed by a Menten-Michaelis kinetic process, where the rate equation is given by

$$(3) \quad r = \frac{k_{\max} x^*}{K_m + x^*}$$

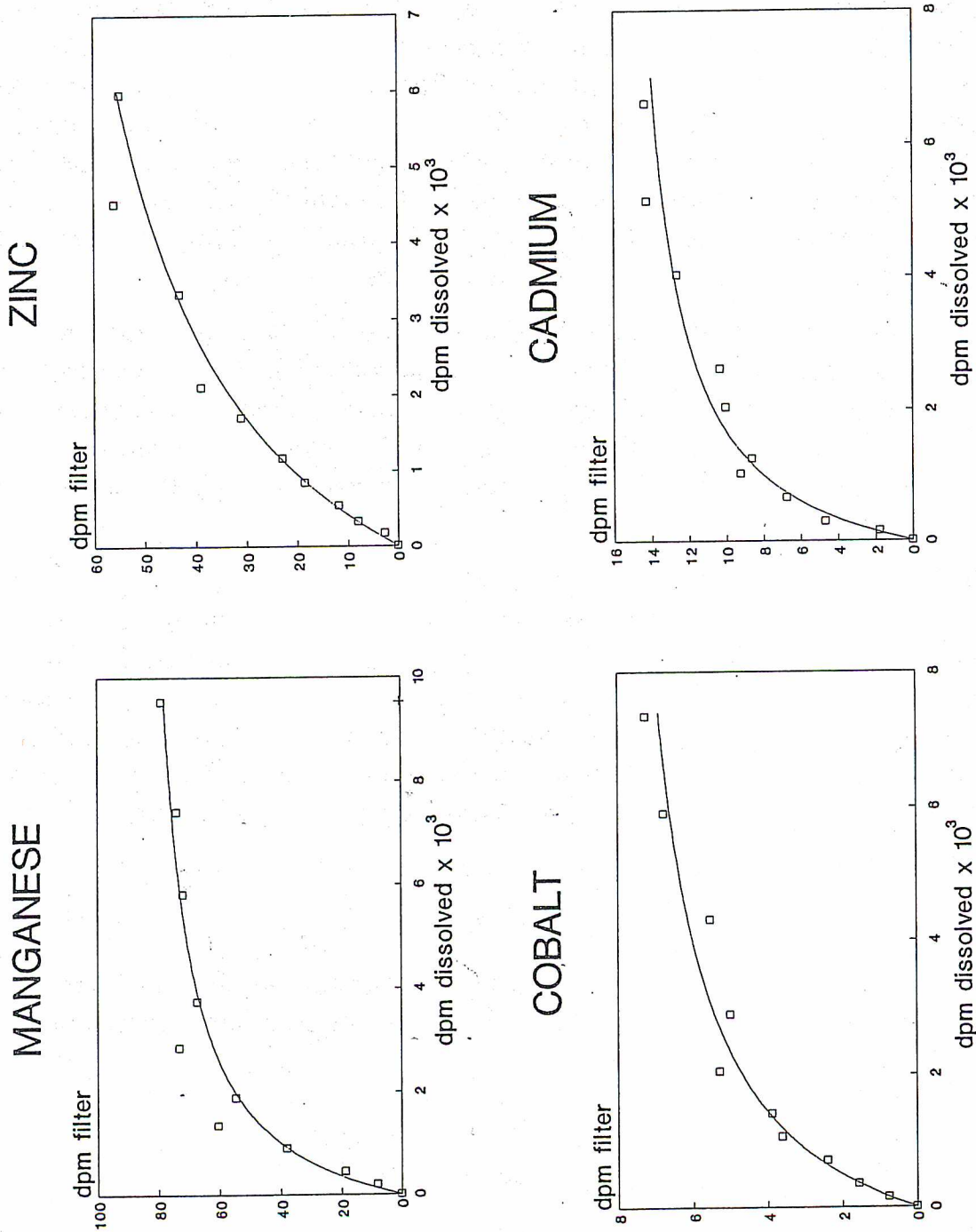


Fig. 9.- Activity of the particles as a function of the remaining activity of the aqueous solution after 24 hours of reaction. Activities corresponding to a sample of 600 ml of seawater taken at Station 21.



where  $k_{\max}$  is the maximum rate of uptake of a substrate and  $K_m$  the Michaelis constant. In fact, equations (1) and (3) are similar expressions and it is impossible to distinguish the two mechanisms by considering the influence of the concentration of the metal in the dissolved phase on its transfer to the solid phase. We have thus performed other experiments in order to better define the role of organisms in this transfer.

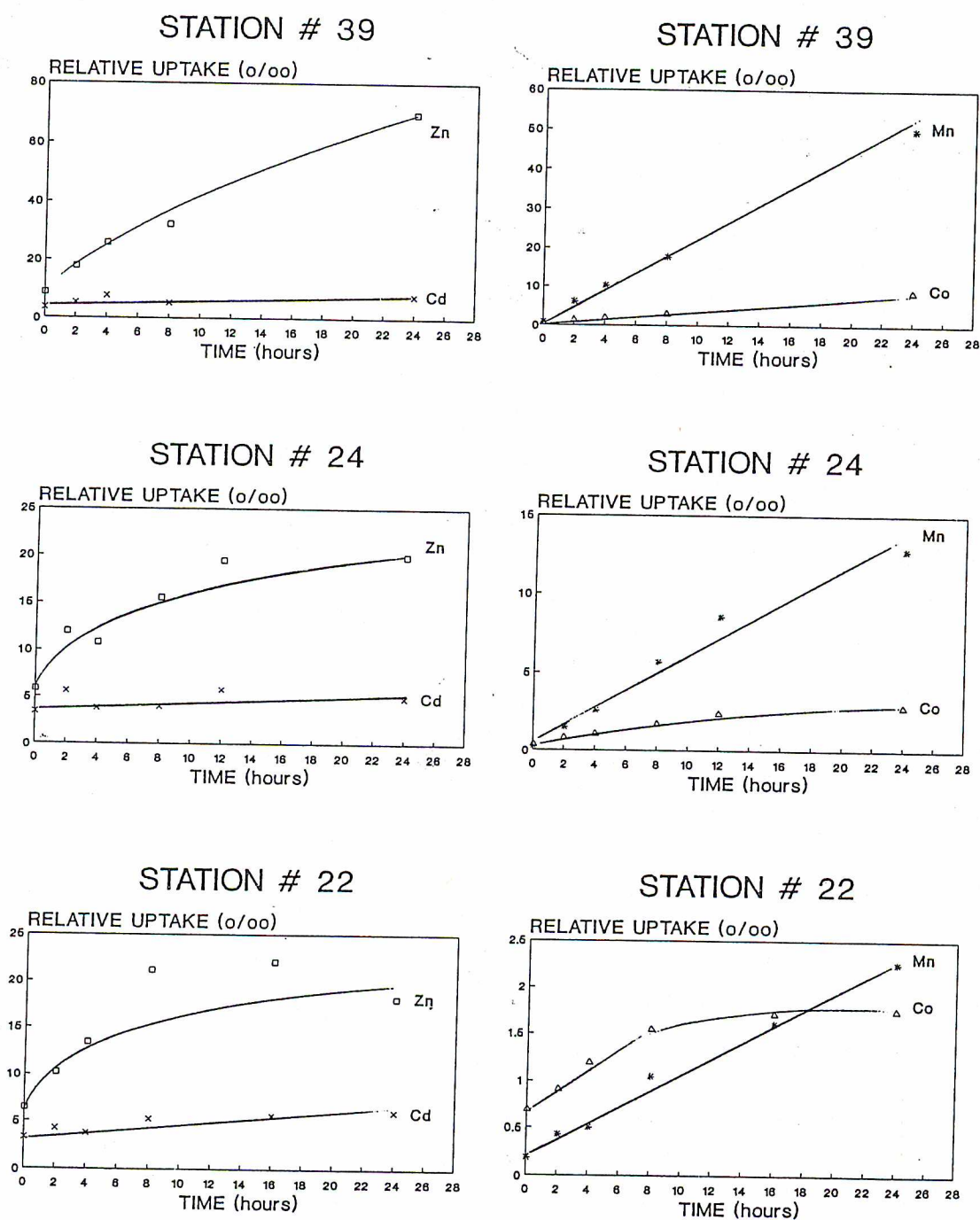


Fig. 10.— Comparison of the kinetics of transfer of radionuclides at three stations corresponding to various primary productions (#22: 457, #24: 900, #39: 2100 mg C m<sup>-2</sup> d<sup>-1</sup>). The results are expressed in terms of activity of the solid phase divided by the total activity of the sample, in %.

In the following kinetic experiments, the spikes have been adjusted in order to obtain an initial radioactivity of the aqueous phase close to 1000 dpm per 100 ml seawater for all the radionuclides. We will first compare rates of uptake of the radionuclides obtained during 24 hours incubation experiments under constant light conditions at three stations with contrasting productivities. At station 22 on the continental shelf the  $^{14}\text{C}$  measured productivity was  $457 \text{ mg C m}^{-2} \text{ d}^{-1}$ . The uptake of radionuclides as a function of time is given in figure 10.

The results are expressed in terms of relative uptake which represents the radioactivity of the solid phase after a given reaction time divided by the total radioactivity of the spiked seawater sample (dissolved + particulate). The kinetic behaviour of the various radionuclides is very similar to what has been observed in the English Channel and the Mediterranean (Wollast & Loijens, 1991). In the case of Zn and Cd, an important instantaneous uptake of radionuclides is observed, followed by a slower transfer. In the case of Zn, the concentration of sorbed element reaches rapidly a maximum and even starts to decrease. Mn and Co on the other hand are only very slightly adsorbed during the initial stage but are transferred at a rate which remains almost constant during the 24 hours of the experiment.

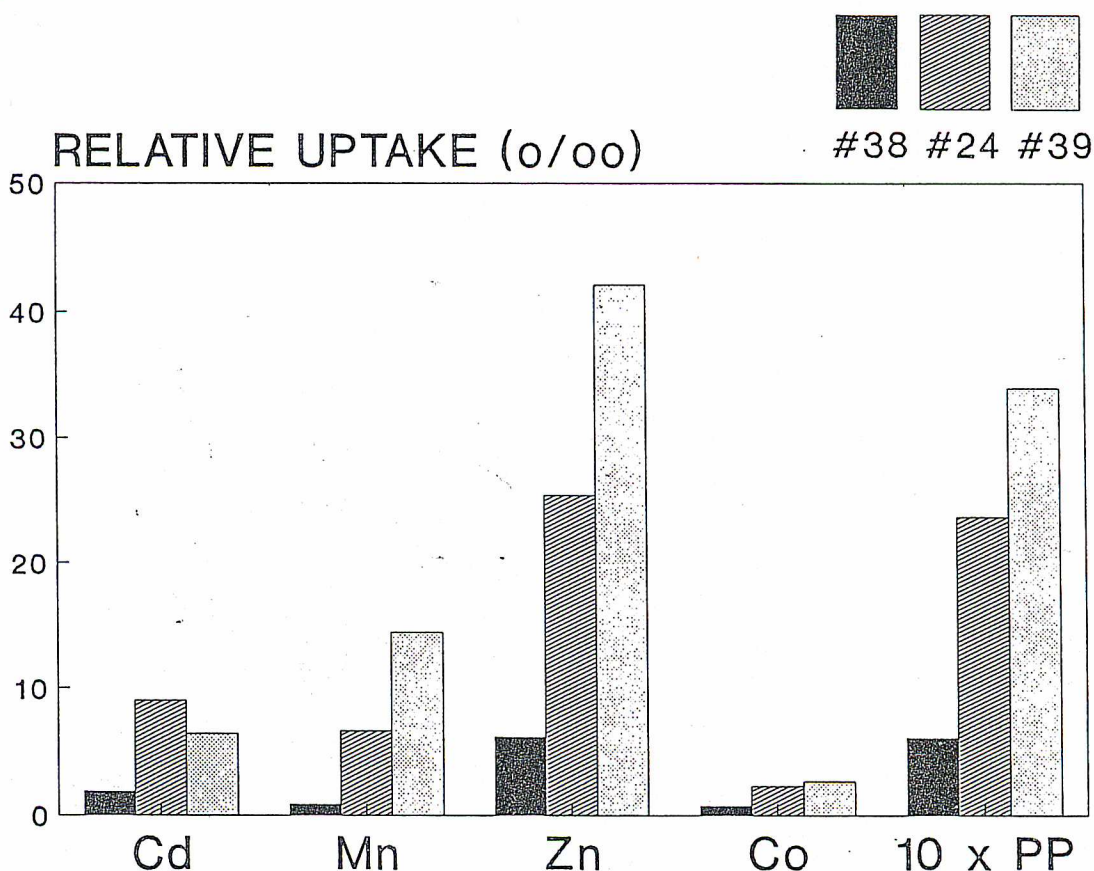


Fig. 11.- Comparison of the uptake of radioactive trace elements and radiocarbon (PP) during incubation experiments of 12 hours under natural light conditions.



The results obtained are rather different at station 39 which is situated in the upwelling region along the Spanish coast. The measured  $^{14}\text{C}$  productivity was  $2100 \text{ mg m}^{-2} \text{ d}^{-1}$ . (Elskens *et al.*, this volume). There is still a rather high initial uptake of Cd and Zn during the incubation experiment (figure 10) but there is also a continuous and linear increase of the amount transferred to the solid phase for all the elements except maybe for Cd. The uptake after 24 hours is also significantly higher for Mn, Zn and Co as compared with the experiment carried out at the previous station. This result suggests that the transfer due to the photosynthetic activity might be predominant in this upwelling area. The role of biological activity is also confirmed by the results obtained at Station 24 for which an intermediate primary production was observed ( $900 \text{ mg C m}^{-2} \text{ d}^{-1}$ ).

The influence of primary production on the transfer of trace metals is also well demonstrated by an incubation experiment under natural light conditions performed at Stations 38, 24 and 39, corresponding to areas of increasing productivity. As shown in figure 11, there is an excellent correlation between the  $\text{C}_{\text{inorg}}$  uptake and the trace metals fixations.

The influence of biological activity on the transfer of trace metals from the dissolved to the particulate phase was also investigated by using different conditions during the incubation experiment. Three spiked seawater samples were incubated respectively under constant light, in the dark and after addition of sodium azide to inhibit biological activity. The results of one of these experiments performed at Stations 38, 24 and 39 are shown on figure 12. The effect of these various conditions on the rate of transfer is the largest for Station 39 which is the station exhibiting the highest productivity. At Station 38 located in the Biscay oligotrophic area with a primary production of  $142 \text{ mg C m}^{-2} \text{ d}^{-1}$ , the uptake of trace elements is limited and the influence of the various conditions on the relative uptake is strongly reduced.

The influence of these conditions is also less pronounced at Station 24, characterized by an intermediate primary production ( $900 \text{ mg C m}^{-2} \text{ d}^{-1}$ ). This station is however under the influence of the French coast and the Channel entry. The solid phase thus probably contains a significant fraction of inorganic detrital particles of continental origin.

Finally a few long term experiments were also performed, where the transfer of trace elements during incubation experiments carried out in the dark were followed for a few months. The results obtained at Station 7 located in the English Channel are shown as an example in figure 13. This station is strongly under the influence of continental input as indicated by its high Al content (see above).

The behaviour of the trace metals shown here is very similar to what has been observed during the laboratory experiments of Li *et al.* (1984) Nyffeler *et al.* (1984), Jannasch *et al.* (1988) or during mesocosm experiments (Santschi *et*



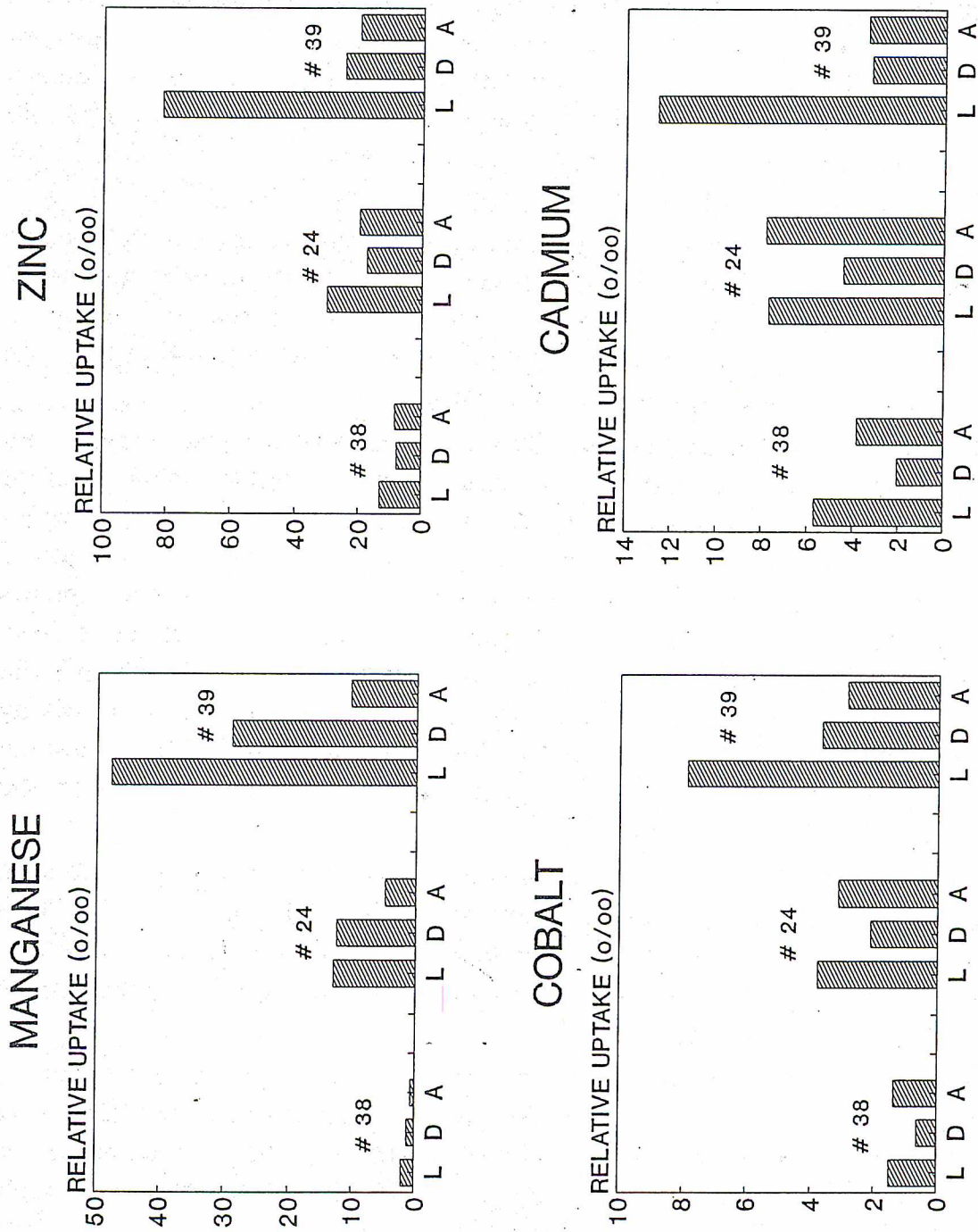


Fig. 12.- Influence of the incubation conditions on the transfer of radionuclides. Incubation during 24 hours under constant light (L), in the dark (D), and with samples inhibited with sodium azide (A). The primary productions are as for figure 11.



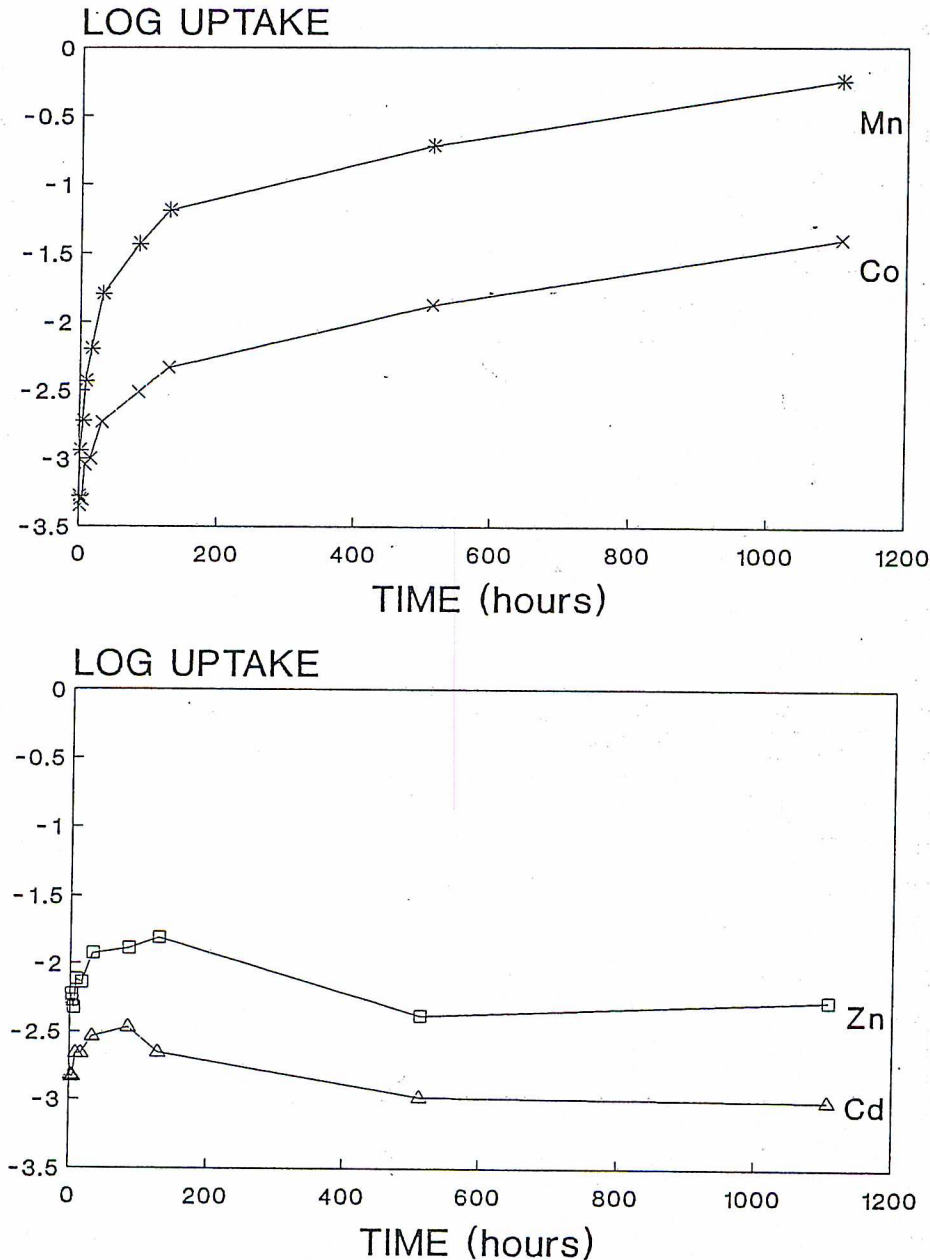


Fig. 13.— Relative uptake of radionuclides during long term experiments performed in the dark at Station 7 which is dominated by the presence of detrital material.

*al.*, 1986). However differences can be distinguished. For Co and Mn, there is a slow and continuous uptake of the dissolved elements which is still going on after two months. A very large fraction of the Mn added to the system has been removed from the aqueous solution after two months (56%). In the case of Cd and Zn, the uptake reaches a maximum after a few days and the radionuclides are then released back to the aqueous solution. The uptake of Zn and Cd after two months represents only 5‰ and 1‰ of the initial spike respectively. In this case it may be assumed that the system is close to equilibrium since the activities of the two metals have reached a steady concentration.

#### 4.- Conclusions.

The distribution of particulate trace metals in the Southern Bight of the North Sea, the English Channel and the Gulf of Biscay reflects well the origin of the suspended matter and allows one to distinguish between the detrital fraction of continental origin and the biogenic material produced in the water column. As one may expect, the relative importance of the biological fraction is gradually increasing from the North Sea to the Gulf of Biscay. Abnormally high values have been detected, which can be attributed to anthropogenic effects.

The vertical distribution of the particulate trace metals in the water column is strongly influenced by the uptake of nutrient like elements in the euphotic zone. Most of the trace elements are strongly enriched in the particles of the surface waters, but seem rapidly released during the remineralization process in the deeper waters.

The use of radiotracers during incubation experiments carried out on natural seawater samples has been proven to be a very successful method to investigate the mechanism and the rate of transfer of trace elements from the dissolved to the particulate phase. The results obtained during the Belgian Global Change Programme indicate that biological activity plays an important role in the transfer of trace metals in the area investigated. The importance of this transfer explains well the enrichment observed for most of the trace metals in the particles present in the euphotic zone. There is however also a rapid chemical sorption process which is especially important for zinc and cadmium. The use of inhibitors of the biological activity indicates that a positive uptake is superposed to active biological process. In the case of manganese, the transfer is largely dominated by the biological uptake and there is furthermore a strong positive influence of light on the transfer.

As shown by several authors, this method can be used successfully to evaluate distribution coefficients of trace metals in the marine environment. One may hope that this method will also provide Redfield ratios for trace elements which will be used to evaluate quantitatively the contribution of biological activity to the scavenging of trace metals in the ocean.

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