

Lead and zinc as indicators for atmospheric and riverine particle transport to sediments in the Gulf of Lions

Lead
Zinc
Concentration
Sediments
Gulf of Lions

Plomb
Zinc
Concentration
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Golfe du Lion

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ABSTRACT

Profiles of 0.1 N HCl leachable Pb and Zn in the sediments of the Gulf of Lions (North West Mediterranean) indicate that the concentrations of these metals are, especially in the vicinity of the Rhône outflow and in the Rhone plume, determined by input from the river. Solid phase Pb and Zn are more than three times higher than their pre-industrial background.

At the offshore, deep (> 2 000 m) stations in the Gulf of Lions, the surface concentration of solid phase Pb and Zn are about twofold enriched compared to background values. The profiles from these deep stations preserve, due to the restricted mobility of Pb and Zn and the lack of bioturbation in the sediment, a historical record of the increased atmospheric deposition of these metals since 1890, similar to results from the North-East Atlantic (Veron *et al.*, 1987).

The decrease of the ratio solid phase Zn/Pb, when going in off-shore direction, indicates that the distribution of Zn is relatively more dependent on riverine input, while that of Pb more on atmospheric deposition.

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RÉSUMÉ

Plomb et zinc traceurs des apports particuliers atmosphériques et fluviaux aux sédiments du Golfe du Lion

Les profils de Pb et de Zn extractibles (HCl 0.1N) dans les sédiments du Golfe du Lion (Méditerranée nord-occidentale) indiquent la concentration de ces métaux au débouché du Rhône et dans la zone d'influence des eaux turbides fluviales en mer. Les concentrations des phases solides du Pb et du Zn sont trois fois plus élevées que pour l'ère pré-industrielle.

Plus au large, dans les stations profondes (> 2 000 m) du Golfe du Lion, les concentrations superficielles de la phase particulaire de ces éléments montrent un enrichissement d'un facteur 2 par rapport aux valeurs du bruit de fond. Les profils dans ces stations profondes, compte tenu de la faible mobilité du Pb et du Zn dans les sédiments, sont l'enregistrement historique de l'augmentation des apports d'origine atmosphérique de ces métaux depuis 1890, similaires aux résultats trouvés dans le nord-est de l'Atlantique (Veron *et al.*, 1987).

La diminution vers le large du rapport Zn/Pb pour la phase solide indique que la distribution du Zn est relativement plus dépendante de l'apport du fleuve que pour le Pb, plus lié aux apports d'origine atmosphérique.

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INTRODUCTION

The global emission of lead into the atmosphere is at present about 200 times higher than during pre-industrial time (Settle and Patterson, 1982). The exhausts from industries as smelters and from burning of leaded gasoline have been indicated as the major anthropogenic sources (Ng and Patterson, 1982). The effects have been recorded in water and sediment of fresh water and marine systems (Bruland *et al.*, 1974; Edginton and Robbins, 1976; Goldberg *et al.*, 1977; Goldberg *et al.*, 1978; Müller *et al.*, 1980; Ng and Patterson, 1982; Nriagu and Rao, 1987). Notably the increases of solid-phase Pb in recent fresh water- and marine sediments have been explained by the increased use of leaded automobile gasoline and this interpretation is strengthened by the observation that the ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ in recent sediments is similar to that of industrial Pb but different from that of natural Pb found in ancient sediments (Ng and Patterson, 1982; Hamilton and Clifton, 1979; Chow *et al.*, 1975). Although most of the evidence comes from fresh water- and coastal marine sediments with relatively high sediment accumulation rates, Veron *et al.* (1987) showed evidence for modern Pb pollution in deep North-East Atlantic sediments. The preservation of the increased Pb signal in the sedimentary record seems to indicate that Pb is hardly affected by diagenetic processes. However, vertical profiles of easily extractable solid phase Pb and the occurrence of dissolved Pb concentrations in porewaters at levels orders of magnitude higher than in the overlying water (Gobeil and Silverberg, 1989), indicate the involvement of Pb in early diagenetic processes, in line with earlier reports (Ridgway and Price, 1987; Westerlund *et al.*, 1986). This process is however not important in the explanation of sedimentary records, taking into account K_d values of more than 10^3 in sediments.

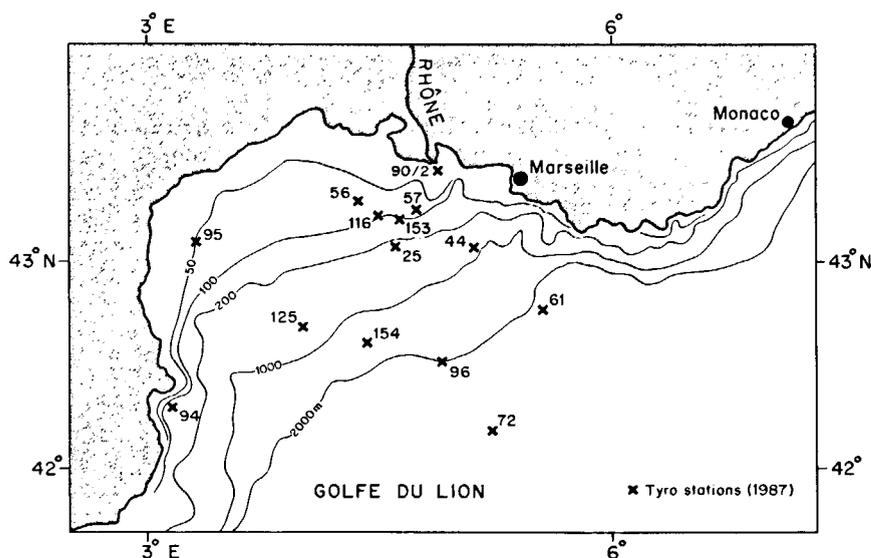


Figure 1

Map with depth contours and station positions.

Carte bathymétrique et position des stations.

In this study we present solid-phase and dissolved Pb and Zn profiles from fourteen locations in the Gulf of Lions, covering the shallow Rhône river plume area as well as stations with waterdepths > 2 000 m. The ratio of solid Zn/Pb at the different stations helped us to be able to discriminate between sediment supply from the Rhone *versus* by atmospheric deposition.

This study was part of the overall European River Ocean Study (EROS 2000; Martin and Barth, 1989).

METHODS

Sampling

Sediment cores were collected by means of a cylindrical box corer (internal diameter 30 cm) at 14 stations shown in Figure 1, in July 1987 with the Dutch R.V. *Tyro*. Data from an additional core (station 90-2; see Fig. 1) taken in april 1990 with the R.V. *Marion Dufresne* were included in this data-set to give better information on sediment deposition in the direct vicinity of the Rhône outflow. The box corer, equipped with a hydraulic dampened closure of the top lid, was specially designed at NIOZ to sample an undisturbed sediment surface and to avoid exchange of enclosed water during the upcast. Once on board the overlying water was carefully siphoned off. Thereafter the core was subsampled by means of three plastic subcores (internal diameter 6 cm), which were closed with rubber stoppers and carefully removed from the box. Directly after subsampling, the cores were transported to a refrigerated container, in which the temperature was kept at *in situ* bottomwater temperature. Sub-cores were sliced in 0.5 cm thick slices down to 2 cm depth, and in slices of 1, 2 or 4 cm deeper down till 14 cm. The sliced sediments were transferred to teflon squeezers (all Teflon and of the type described by Reeburgh, 1967) and under nitrogen gas pressure (1-3.5 bar N_2), the interstitial water was squeezed from the sediment and collected in teflon bottles. All care was taken to avoid oxidation of the sediment by fast handling of the samples (less than 3 minutes). Our experience with this procedure did not indicate significant effects compared to glove box (N_2 atmosphere) handled samples. Squeezing was done over $0.2 \mu\text{m}$ cellulose-acetate filters. Slices of corresponding depth intervals were combined to obtain enough pore water for analyses. The squeezed water was acidified with Supra Pure HCl to pH 2. Squeezed sediment samples were stored in plastic bags in a refrigerator prior to analyses in the

Texel laboratory. All materials used during the whole procedures were carefully cleaned with acid treatments for several days. After these treatments the materials were extensively rinsed with Milli-Q water and stored in plastic bags until use. Additional sub-cores were collected for sedimentation rate determinations by ^{210}Pb (Zuo *et al.*, 1989; 1991).

Porewater analysis

To determine the Pb and Zn concentrations in pore water it was first subjected to a preconcentration procedure. In a 5 ml sub-sample the pH was brought to 4-5 with an ammonium-acetate buffer, then the metals were complexed with a 1 % APDC/DDDC solution and extracted in freon. After phase separation the metal complexes in the freon were destroyed by adding 50 μl concentrated Supra Pure HNO_3 . For back extraction 0.95 ml Milli-Q water was added to the freon and the solution was shaken for two minutes (Danielsson *et al.*, 1978). Thus, the samples were concentrated five times, and sea salts were removed. Lead was determined by graphite furnace atomic absorption with the STPF (Stabilised Temperature PlatForm) technique, on a Perkin Elmer 5100 Zeeman AAS) using standards with the same acid concentration as the samples. Zinc was determined by flame AAS.

Sediment analysis

The sediments were dried at 60°C and homogenized by grinding in a teflon mortar. From the homogenized sediment 100 mg was transferred to a polypropylene 50 ml flask and this was treated with 0.1 N HCl for 18 hours to obtain the exchangeable metal fraction. (Duinker and Nolting, 1976). Lead was determined by graphite furnace AAS with the STPF technique. Zinc, iron and calcium were determined by flame AAS, with the method of standard additions. Blanks were run during the whole procedure and were negligible.

RESULTS

Sediments

Results of profiles of solid phase Pb and Zn distributions with depth are given in Figure 2. In Figure 2 *a* the profiles of stations 90-2, 57 and 56 are shown. These shallow stations (water depths < 70 m; Fig. 1), which are all located in the vicinity of the Rhône outflow have in common that the distribution with depth is uniform both for Pb and Zn. Going from station 90-2 to station 56 the concentrations of Pb as well as of Zn decrease with distance from the river

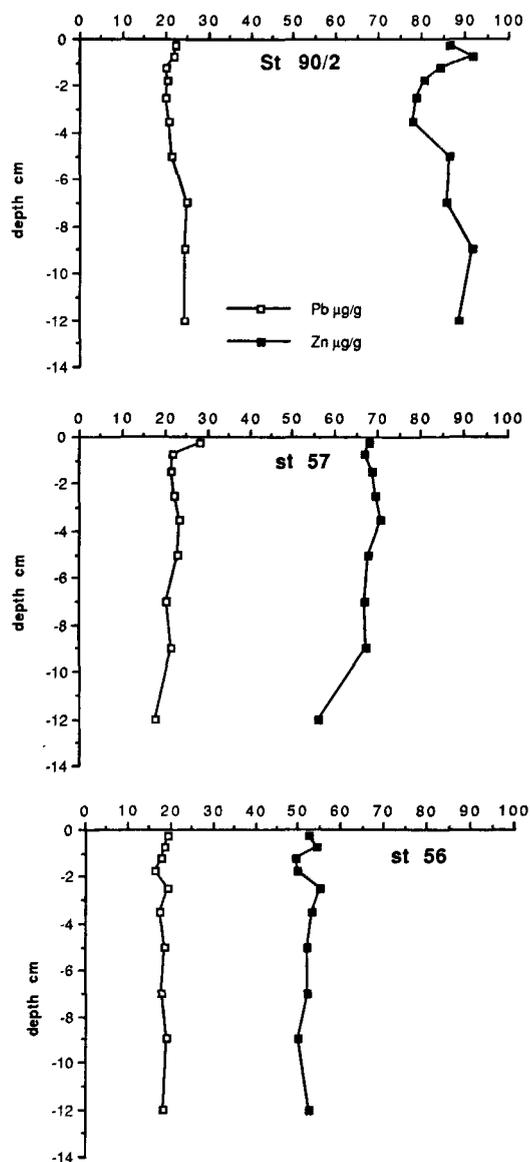


Figure 2 *a*

Depth profiles of Pb and Zn ($\mu\text{g.g}^{-1}$) in sediment cores collected in the Rhône mouth and prodelta. Sedimentation rates $0.14\text{-}0.63\text{ cm.yr}^{-1}$, mixed surface layer 3-15 cm (Zuo *et al.*, 1991.)

Distribution verticale du Pb et du Zn ($\mu\text{g.g}^{-1}$) dans les sédiments prélevés par carottier-boîte à l'embouchure et au niveau du prodelta du Rhône. Taux de sédimentation $0,14\text{-}0,63\text{ cm.a}^{-1}$, épaisseur de la couche de mélange superficielle 3-15 cm (Zuo *et al.*, 1991).

outflow.

Figure 2 *b* summarizes the solid phase concentration profiles of Pb and Zn for stations 44, 116 and 125; all with intermediate waterdepth (70-700 m; Fig. 1). These stations are located outside the Rhône plume area and have sediment accumulation rates of $0.11\text{-}0.15\text{ cm.yr}^{-1}$. In contrast to the stations summarized in Figure 2 *a* solid phase Pb and Zn are more or less at constant levels near the surface, but decrease with depth deeper down to the base of the cores. Pb and Zn profiles at individual stations are remarkably similar in shape.

Figure 2 *c* gives the solid phase Pb and Zn profiles from stations 61, 72 and 96, all at water depths > 2 000 m (Fig.

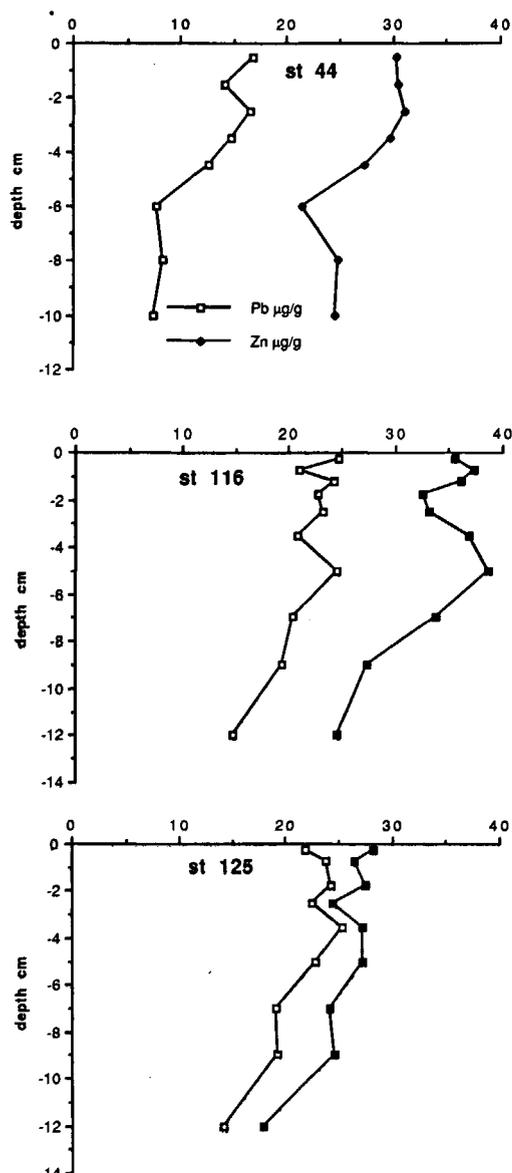


Figure 2 b

Depth profiles of Pb and Zn ($\mu\text{g.g}^{-1}$) in sediment cores collected on the shelf. Note change in concentration axis compared to Figure 2 a. Sedimentation rates $0.11\text{-}0.15\text{ cm.yr}^{-1}$, mixed surface layer 0-3 cm (Zuo et al., 1991).

Distribution verticale du Pb et du Zn ($\mu\text{g.g}^{-1}$) dans les sédiments prélevés sur le plateau continental. Noter le changement des gammes de concentration en comparaison de celles de la figure 2 a. Taux de sédimentation $0,11\text{-}0,15\text{ cm.a}^{-1}$, épaisseur de la couche de mélange superficielle 0-3 cm (Zuo et al., 1991).

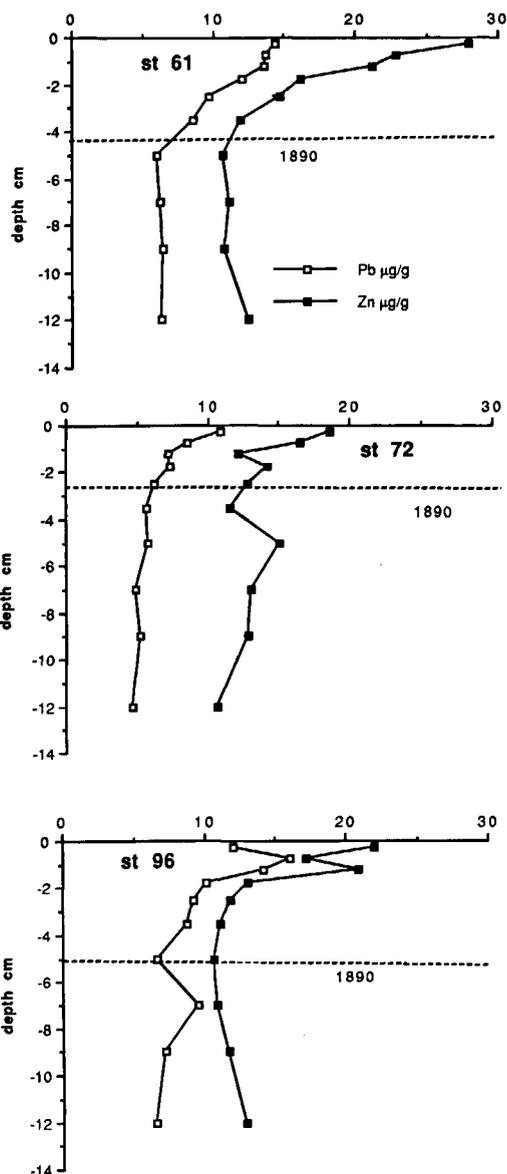


Figure 2 c

Depth profiles of Pb and Zn ($\mu\text{g.g}^{-1}$) in sediment cores collected in the deeper part of the gulf (water depth $> 2\ 000\text{ m}$). Note change in concentration axis compared to Figure 2 a, b. Sedimentation rates $0.02\text{-}0.05\text{ cm.yr}^{-1}$ no mixed layer (Zuo et al., 1991).

Distribution verticale du Pb et du Zn ($\mu\text{g.g}^{-1}$) dans les sédiments prélevés dans le domaine profond du Golfe du Lion (profondeur $> 2\ 000\text{ m}$). Noter le changement des gammes de concentration en comparaison de celles de la figure 2 a, b. Taux de sédimentation $0,02\text{-}0,05\text{ cm.a}^{-1}$, pas de couche de mélange superficielle (Zuo et al., 1991).

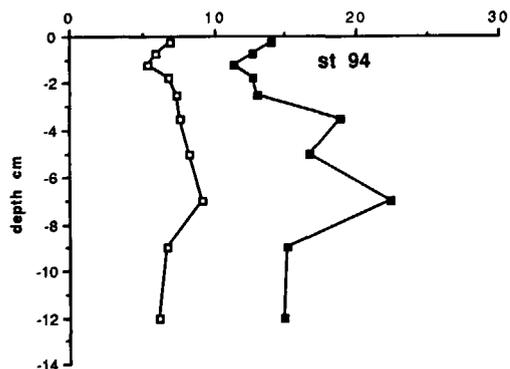


Figure 2 d :

1). They are located far from the Rhône outflow and the sediment accumulation rates are typically $< 0.05\text{ cm.yr}^{-1}$ (Zuo et al., 1991). The Pb and Zn profiles in Figure 2 c have in common that both for Pb and Zn the concentrations are rather constant and at low levels ($5\text{-}7\ \mu\text{g.g}^{-1}$ for Pb and about $12\ \mu\text{g.g}^{-1}$ for Zn) in the deeper part of the profiles, but that significant increases for both metals are observed towards the surface. Based on the sediment accumulation

Depth profiles of Pb and Zn ($\mu\text{g.g}^{-1}$) in a sediment core collected close to the Spanish coast.

Distribution verticale du Pb et du Zn ($\mu\text{g.g}^{-1}$) dans les sédiments prélevés à proximité des côtes espagnoles.

Table 1

Pb and Zn concentrations in sediment cores expressed on a calcium carbonate free basis from all stations (s. surface and s.s subsurface). Ratio of Pb and Zn concentrations in surface sediment divided by the calculated background value (Pb.s surface, Pb.b background value 12 $\mu\text{g}\cdot\text{g}^{-1}$, Zn.s surface, Zn.b background value 23 $\mu\text{g}\cdot\text{g}^{-1}$). Ratio of Zn and Pb in surface and subsurface parts of the cores.

Concentrations du Pb et du Zn dans les sédiments des box-cores, exprimées sur la base du carbonate de calcium libre pour l'ensemble des stations (s. surface et s.s subsurface). Rapport des concentrations de Pb et de Zn dans les sédiments superficiels divisé par la valeur calculée du bruit de fond (Pb.s surface, Pb.b valeur du bruit de fond 12 $\mu\text{g}\cdot\text{g}^{-1}$, Zn.s surface, Zn.b valeur du bruit de fond 23 $\mu\text{g}\cdot\text{g}^{-1}$). Rapport des concentrations de Zn et de Pb dans les sédiments de surface et de subsurface.

Station n°	Pb $\mu\text{g}\cdot\text{g}^{-1}$	Zn $\mu\text{g}\cdot\text{g}^{-1}$	Pb.s/Pb.b	Zn.s/Zn.b	Zn/Pb
90/2 s	30	115	2.5	5.0	3.9
s.s	33	118	2.8	5.1	3.6
57 s	33	97	2.8	4.2	2.9
56 s	28	75	2.3	3.3	2.7
153 s	29	59	2.4	2.6	2.0
25 s	17	45	1.4	2.0	2.6
s.s	18	34	1.5	1.5	1.9
44 s	29	53	2.4	2.3	1.8
s.s	12	38	1.0	1.7	3.2
116 s	38	54	3.2	2.3	1.4
s.s	23	38	1.9	1.7	1.7
125 s	31	39	2.6	1.7	1.3
s.s	22	28	1.8	1.2	1.3
95 s	38	62	3.2	2.7	1.6
s.s	26	49	2.2	2.1	1.9
154 s	31	47	2.6	2.0	1.5
s.s	16	20	1.3	0.9	1.3
61 s	23	45	2.1	2.0	2.0
s.s	11	22	0.9	1.0	2.0
72 s	21	35	2.1	1.5	1.7
s.s	10	23	0.8	1.0	2.3
96 s	21	39	1.8	1.7	1.9
s.s	12	23	1.0	1.0	1.9
94 s	11	20	0.9	0.9	1.8
s.s	8	20	0.7	0.9	2.5

rates, determined with ^{210}Pb and clearly described and reported by Zuo *et al.* (1989; 1991) for these stations, we have indicated the 1890 horizon in the graphs of Figure 2 c and are thus able to demonstrate that the Pb and Zn increases started since that time.

The lowest concentrations of leachable Pb and Zn are found in the sandy sediment of station 94, close to the Spanish coast and beyond the influence of the Rhône sediment plume (Fig. 2 d). The Pb and the Zn profile show decreasing concentrations from the surface towards the depth interval of 1.5-2 cm and also for both metals there is a sub-surface maximum around 7 cm depth.

By comparison of profiles of all stations it becomes evident that the highest Pb and Zn contents are present in sediments closest to the Rhône outflow.

In contrast to the solid state profiles of Pb and Zn, those of Fe and Ca are generally constant with depth (Fig. 3). This uniformity implies that deposited sediments have not changed in basic composition in these cores. Concentrations of Fe and of Ca are location dependent with Fe having highest contents (up to 0.9 % leachable) near the Rhône mouth, while Ca shows the reversed trend with contents of 10 % near the Rhône mouth and up to 20-22 %, at the deepest station.

Examples of contrasting ^{210}Pb profiles (taken from Zuo *et al.*, 1991) at a station in the Rhône mouth and in the deeper part of the bay are given in Figure 4.

Table 2

Pb and Zn concentrations in different surface sediments of the world.

Concentrations du Pb et du Zn dans différents sédiments superficiels des océans mondiaux.

Pb $\mu\text{g}\cdot\text{g}^{-1}$	Zn $\mu\text{g}\cdot\text{g}^{-1}$	Area	Reference
20-30	50-70	Rhone, this study	This study
10-15	20-30	This study, water depth > 2 000 m	This study
246	285	Thermaikos Gulf Greece	Voutsinou and Satsmadjis (1983 b)
34	115	Thermaikos Gulf, water depth > 50 m	Voutsinou and Satsmadjis (1983 b)
11-20	50-80	Patraikos Gulf, Greece	Voutsinou and Satsmadjis (1983 a)
4-984	12-815	Raritan Bay USA	Greig and McGrath (1977)
6-50	5-270	Long Island Sound, USA	Greig <i>et al.</i> (1977)
5-20	9-26	Sicily	Castagna <i>et al.</i> (1987)
140	250	Narraganset Bay USA	Goldberg <i>et al.</i> (1977)
29	94	North Sea	Lichtfuss and Brümmer (1981)
10-40	125	California coast	Bruland <i>et al.</i> (1974)
36-84	121-395	Chesapeake Bay USA	Goldberg <i>et al.</i> (1978)
50	200	Baltic Sea	Müller <i>et al.</i> (1980)
8	-	Gulf of Thailand	Windom <i>et al.</i> (1984)

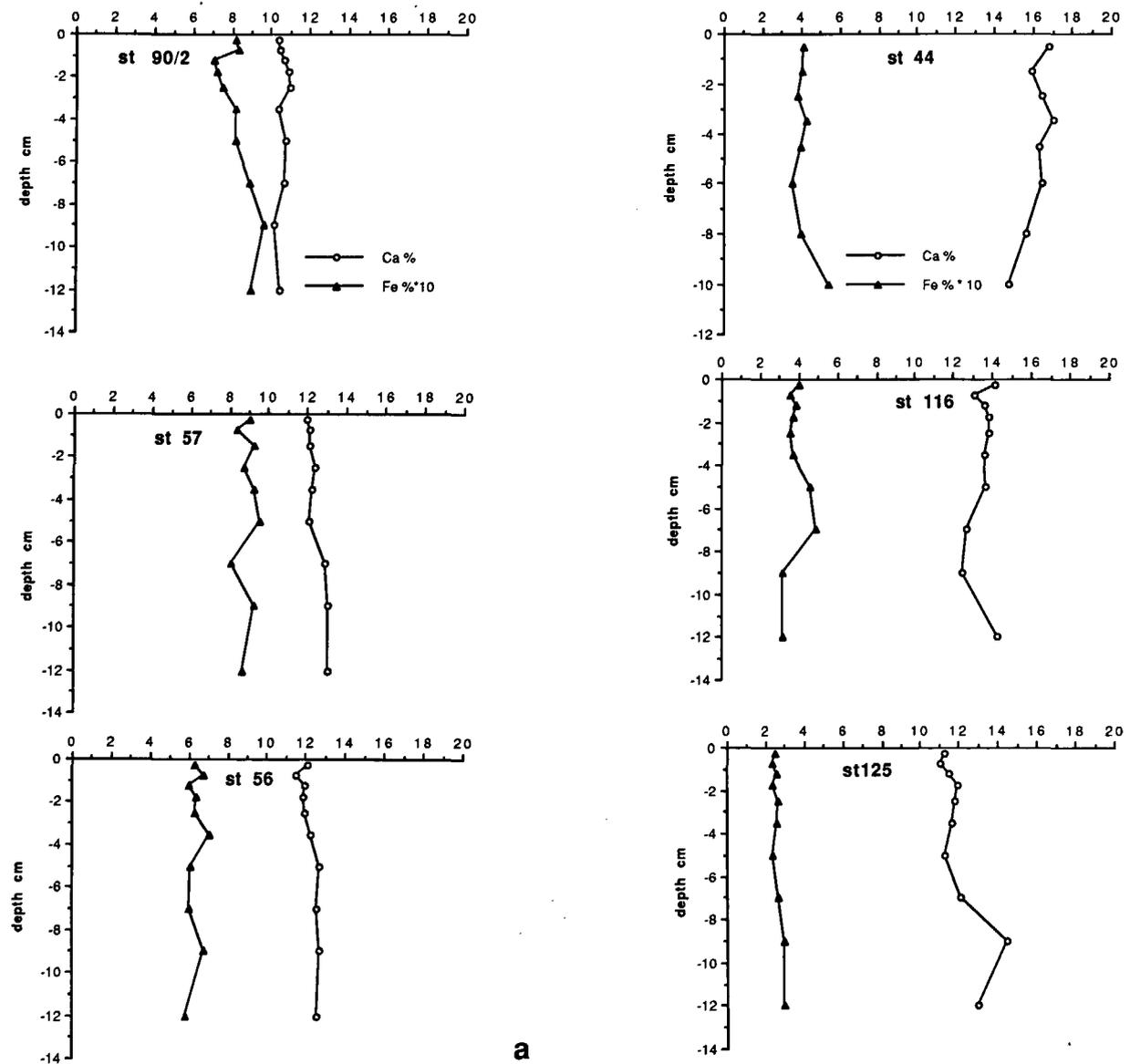


Figure 3 a, b, c, d
Depth profiles of Ca and Fe (%) in the same cores as in Figure 2 a, b, c, d.

Distribution verticale du Ca et du Fe (%) dans les mêmes prélèvements que ceux présentés dans les figures 2 a, b, c, d.

Porewater

Profiles of dissolved Zn and Pb are given in Figure 5 a, b and c. Stations are arranged in the same way as in Figure 2. The dissolved Zn profiles indicate a rather uniform distribution with depth at concentration levels of 500-1 000 nM. At some stations there are distinct maxima which coincide with maxima of dissolved Pb (stations 56, 57, 61 and 94). The profiles of dissolved Pb are rather "patchy", but consistent patterns among the profiles of dissolved Pb and those of dissolved Cd and dissolved Fe (data from Nolting, 1989) are present. This is illustrated in Figure 6 for station 56. These similarities suggest that the profiles of these metals are determined by common diagenetic processes. Both for dissolved Zn and for dissolved Pb pore-water concentrations are two orders of magnitude higher than in the overlying waters where concentrations of dissolved Pb

and dissolved Zn are < 600 pM and < 10 nM respectively (Copin-Montegut *et al.*, 1986; Laumond *et al.*, 1984; Elbaz-Poulichet *et al.*, 1989).

DISCUSSION

Leachable Pb and Zn

Before being able to interpret and to compare profiles of leachable Pb and Zn at individual stations, we should realize that the shape of these profiles is determined by the rate of sediment accumulation, the (biologically mediated) sediment mixing rate, and by the dilution of the anthropogenic Pb and Zn inputs by biogenous phases (in our case

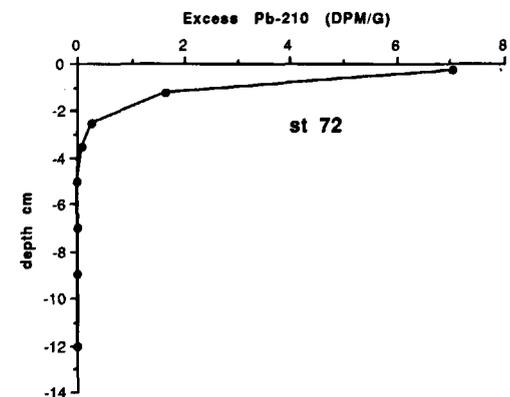
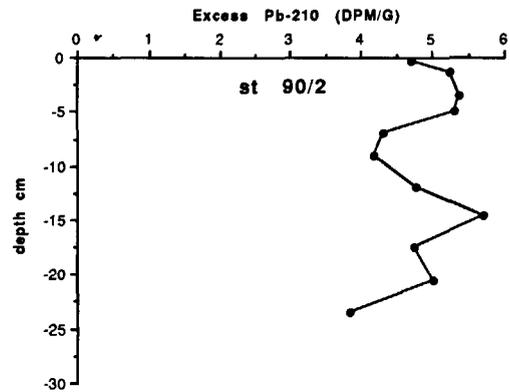
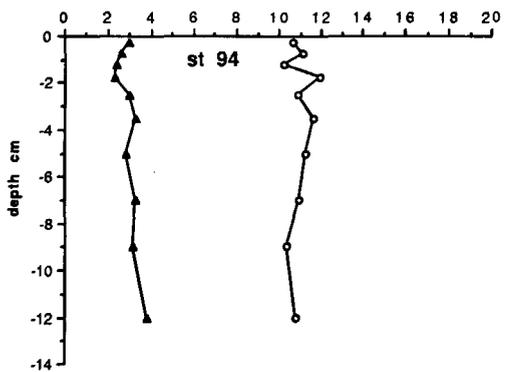
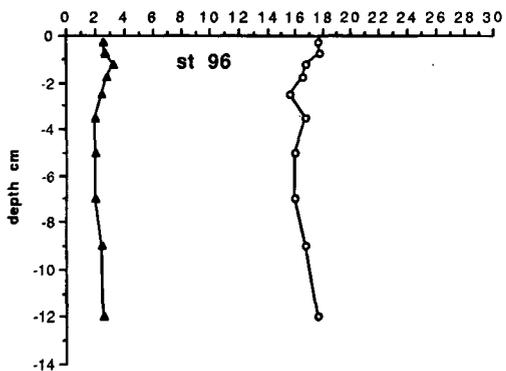
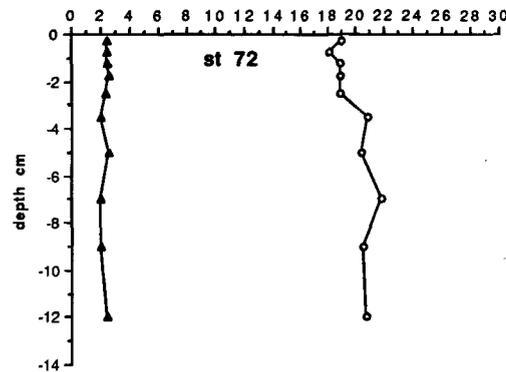
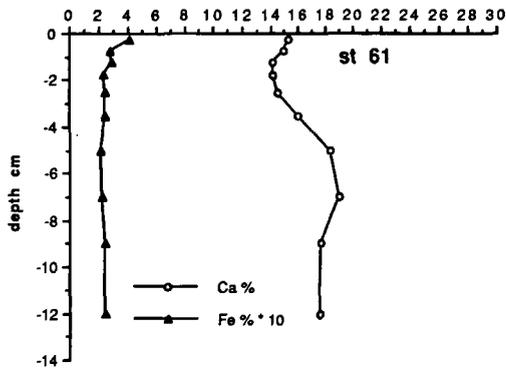


Figure 4

Profiles of excess ^{210}Pb at station 90/2 and 72 (data from Zuo *et al.*, 1991).

Excès de ^{210}Pb a stations 90/2 et 72 (résultats de Zuo *et al.*, 1991).

wing interpretation of the profiles: at the stations in the immediate vicinity of the Rhône outflow (Fig. 2 a), sediment accumulation rates are relatively high ($> 0.6 \text{ cm.yr}^{-1}$) and thus the profiles (up to a depth of 12 cm) represent a timespan of only 20 years. Potential decreases of these inputs for example due to the decreasing use of leaded automobile gasoline (Trefry *et al.*, 1985; Boyle *et al.*, 1986; Gobeil and Silverberg, 1989) will be masked by sediment mixing (mixed surface layers of 2-15 cm; see Fig. 2 a).

The stations which are summarized in Figure 2 b have in common that they are at intermediate waterdepths (70-750 m) and have sediment accumulation rates of $0.10\text{-}0.15 \text{ cm.yr}^{-1}$ (Zuo *et al.*, 1989; 1991). The base of the profiles (12 cm depth) thus originates from 80-120 years ago. From the base upwards the Pb and Zn signals are increasing until a sub-surface level at 3-5 cm depth, above which the concentrations vary little with depth. This behaviour is consistent with the depth of the mixed layer as derived from ^{210}Pb profiles at these locations (Zuo *et al.*, 1989; 1991).

Figure 2 c gives the profiles of leachable Pb and Zn of the deep stations ($> 2000 \text{ m}$ water depth). Given the sediment accumulation rates at the individual stations, we conclude that the 12 cm long cores represent periods of 300, 600 and 240 years at stations 61, 72 and 96 respectively. At all the

the increase of Ca-carbonate content in the sediment with water-depth).

Data on accumulation of recent sediments and on mixing rates became available, within the framework of the EROS-2000 project, from excess ^{210}Pb -profiles (Zuo *et al.*, 1989; 1991). Using these data we arrive at the follo-

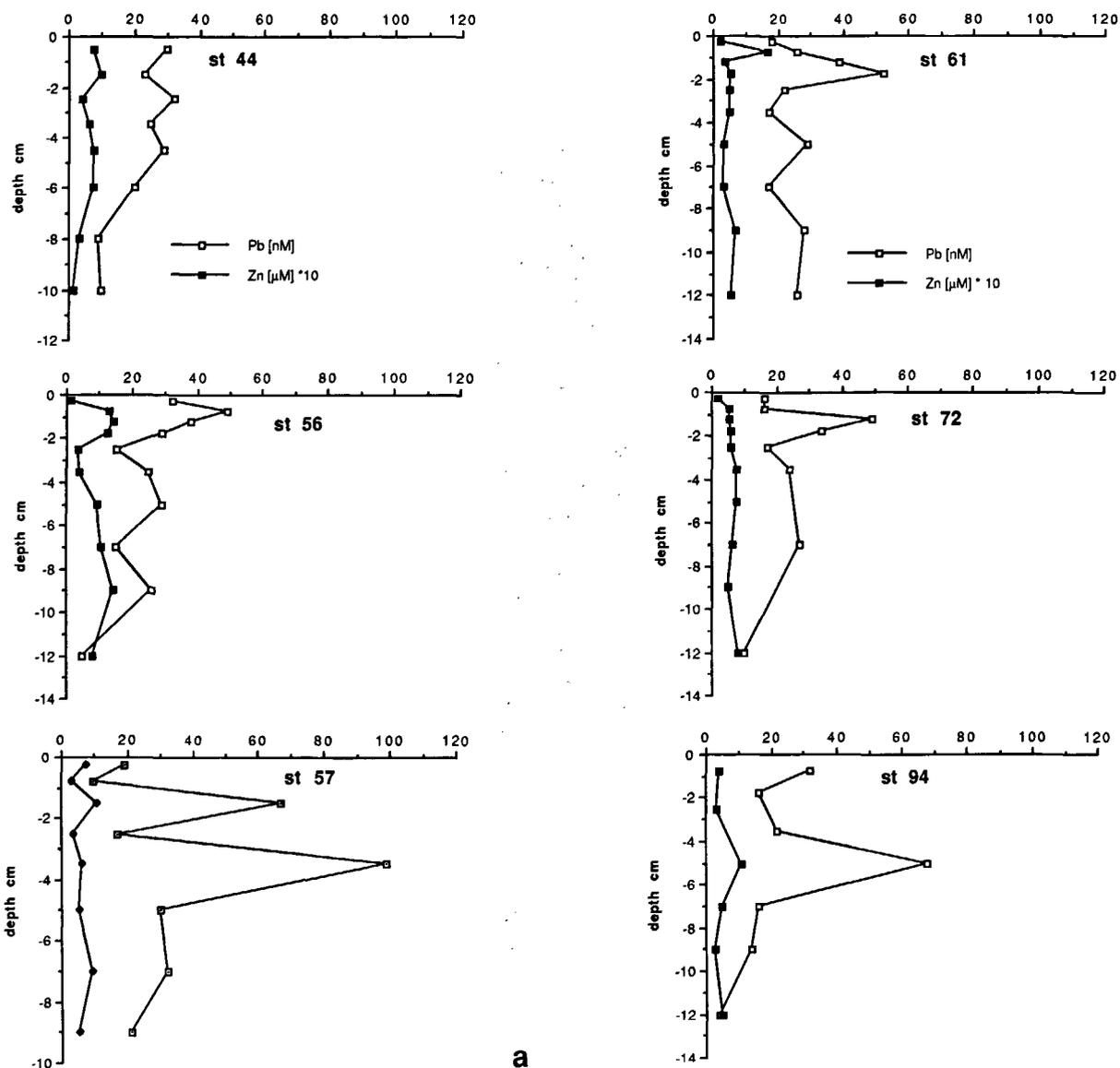


Figure 5 a, b, c

Depth profiles of Pb (nM) and Zn ($\mu\text{M} \cdot 10$) in the pore waters of the sediment cores collected at stations 44, 56, 57, 61, 72, 94, 116 and 125.

Distribution verticale du Pb (nM) et du Zn ($\mu\text{M} \cdot 10$) dans l'eau interstitielle des sédiments prélevés aux stations 44, 56, 57, 61, 72, 94, 116 et 125. \uparrow

stations the remarkable increases of Pb and Zn started about 100 years ago, in line with results from the Californian border basins (Bertine, 1980) and the Mississippi delta (Trefry *et al.*, 1985). The increases are manifest because sediment mixing at these stations is insignificant compared to mixing rates at the more shallow stations in the Gulf of Lions. The low values of leachable Pb and Zn at station 94 (Fig. 2 d) indicates that sedimentation at this location is not originating from the Rhône but that the sandy sediments originate predominantly from the Spanish coastline area.

Veron *et al.* (1987) calculated a background lead content of $\sim 15 \mu\text{g} \cdot \text{g}^{-1}$ in the silicate fraction and of $\sim 0.8 \mu\text{g} \cdot \text{g}^{-1}$ in the carbonate fraction in the subsurface samples of their North-East Atlantic cores. These calculated values are close to the reported world averaged values of $12 \mu\text{g} \cdot \text{g}^{-1}$

for the silicate (Taylor, 1964) and of $0.1\text{-}1 \mu\text{g} \cdot \text{g}^{-1}$ (Thompson, 1972) for the carbonate fraction respectively. Calculations with these last data, and the known carbonate content in the sub-surface samples from our deepest stations (61, 72 and 96) gives background levels of $6.5\text{-}7.3 \mu\text{g} \cdot \text{g}^{-1}$ Pb, close to the measured values of $5\text{-}7 \mu\text{g} \cdot \text{g}^{-1}$ (Fig. 2 c, d). Also at station 94 calculated background levels for Pb and the measured values agree.

To be able to compare the Pb and Zn content of all stations in the Gulf of Lions, we have to correct for the "dilution" caused by the increasing content of CaCO_3 in the sediment, when going from shallow to deeper stations. When the Pb and Zn content in the near-surface samples and in the deepest samples of all cores are expressed on a carbonate free basis (Tab. 1), it becomes possible to judge the distribution of anthropogenic Pb and Zn inputs. For the

deep stations (61, 72 and 96) and for the unaffected station 94 background Pb concentrations of 8-11 $\mu\text{g.g}^{-1}$ are calculated, similar to the world averaged content in silicates, and also similar to the background concentrations for Pb in the silicate fraction of North-East Atlantic sediments as given by Veron *et al.* (1987). For zinc the calculated background value is 20-23 $\mu\text{g.g}^{-1}$, similar to the values Rutgers van der Loeff and Waijers (1986) reported for North-East Atlantic sediments.

The data summarized in Table 1, indicate clearly that the highest anthropogenic Pb and Zn signals are found in

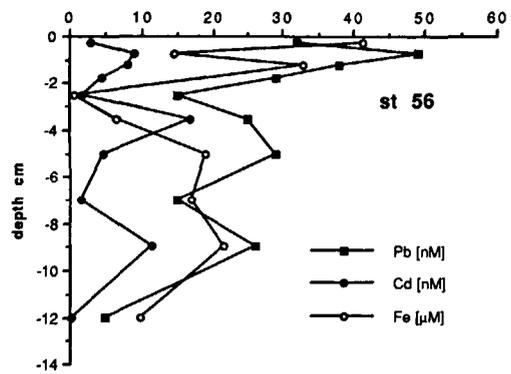
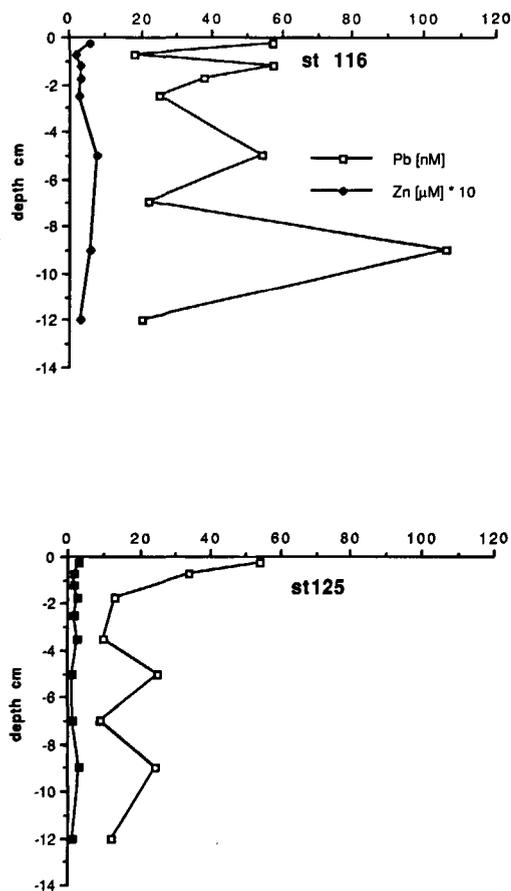


Figure 6

Depth profiles of Pb and Cd (nM) and Fe (μM) in the pore water of core 56, in the Rhône prodelta.

Distribution verticale du Pb, du Cd (nM) et du Fe (μM) dans l'eau interstitielle des sédiments du box-core 56 prélevé au niveau du prodelta du Rhône.

from various sources and tabulated by Chester, 1990). For both metals scavenging onto particles is an important transport route to the sediment. When we assume that the atmospheric inputs are homogeneously distributed to the surface waters of the Gulf of Lions, then the decreases in the surface sediment going from the Rhône outflow to the deep stations from 30 to 20 $\mu\text{g.g}^{-1}$ for Pb and from 115 to 40 $\mu\text{g.g}^{-1}$ for Zn (Tab. 1), suggest that the Zn content in the surface sediments of the shallower parts of the bay is relatively more influenced by riverine input, while the sediment Pb signal is more related to atmospheric inputs.

Our data do not permit a straightforward evaluation of the relative importance of riverine *versus* atmospheric deposition in the Gulf of Lions. Recently the importance of atmospheric deposition in our study area has been stressed (Chester *et al.*, 1989; Loye-Pilot *et al.*, 1989; Martin *et al.*, 1989), and given the relatively high enrichment factors of Pb and Zn in atmospheric deposits (Guerzoni *et al.*, 1989), atmospheric deposition could be an important source for Pb and Zn in the sediments.

sediments near the Rhône mouth at station 90-2 and station 57, where enrichments compared to background concentrations of > three times higher for Pb and > four times higher for Zn are found. Even at the deep stations far away from the Rhône outflow (61, 72 and 96) enrichment in surface sediments is 1.8-2.1 times for Pb and 1.5-2.0 times for Zn. Only at station 94 no anthropogenic Pb and Zn signals can be found, probably because fine-grained particles originating either from the Rhône and/or from atmospheric deposition do not settle here because of the current conditions.

The concentrations of both Pb and Zn in aerosols above the Mediterranean are on average about 26 ng.m^{-3} (Dulac *et al.*, 1987; Bergametti *et al.*, 1988; Guerzoni *et al.*, 1989). Upon arrival of aerosol particles in the surface water, partial dissolution of Pb and Zn will occur (data

From the sedimentation rates (cm.yr^{-1}) at stations 61, 72 and 96, assuming a dry sediment density of 2.5 g.cm^{-3} and a porosity of 0.8 in surface sediment, we can calculate the sediment accumulation rates ($\text{g.cm}^{-2}.\text{yr}^{-1}$). When we further assume a background value for Pb of 6 $\mu\text{g.g}^{-1}$ and using the surface sediment Pb data of Figure 2 c, we arrive at a "pollutant" Pb input to the sediment of $120 \pm 40 \text{ ng.cm}^{-2}.\text{yr}^{-1}$, which is similar to the data on pollutant atmospheric Pb input to the North Atlantic as summarized by Veron *et al.* (1987), based on data from Settle and Patterson, 1982; Jickells *et al.*, 1984; Buat-Menard and Chesselet, 1979; Chester *et al.*, 1983. This similarity suggests strongly that the increases of Pb in recent sediments in the offshore area of the Gulf of Lions can be, as in the North-East Atlantic, explained by atmospheric input alone. Calculations for Zn, indicate a pollutant atmospheric input to the surface sediments at the deep stations 61, 72 and 96 of $160 \pm 60 \text{ ng.cm}^{-2}.\text{yr}^{-1}$.

Pore water profiles and distribution coefficients (Kd)

The occurrence of dissolved Pb and Zn in the sediment pore waters at concentration levels of up to two orders of magnitude higher than the concentrations in the overlying bottom water, indicates that both Pb and Zn are mobilized in the sediment. The similarities of the profiles with those of dissolved Cd and dissolved Fe (Fig. 6) suggest that Pb and Zn are subjected to the same processes of early diagenesis as these just mentioned metals. This implies that they will be mobilized by oxidation of organic carbon compounds, as well as by dissolution of solid phase Fe- and Mn-oxide during sub-oxic diagenesis, with which they were associated. The correspondences between dissolved Pb profiles and those of dissolved Fe and dissolved Cd were reported before by Gobeil and Silverberg (1989) for sediments in the Laurentian Trough (Canada).

Although Pb and Zn are participating in diagenetic processes, the profiles of total Pb and -Zn are hardly affected by this behaviour. This is evident when the relative distribution of Pb and Zn over the dissolved and the solid phase is expressed as a Kd value. We calculate an average log Kd

for Pb and Zn, using data from all stations of 3.50 and 3.06 respectively (mean calculated Kd values for Pb and Zn were $3.50 \cdot 10^3$ and $1.14 \cdot 10^3$ respectively). The restricted mobility of Pb and of Zn thus warrants that the total Pb and Zn profiles can be interpreted in an historical context.

Comparison with other areas

As explained before, it is rather difficult to compare metal contents in sediments from different areas with each other, when not all information concerning sediment texture and composition is available. Keeping in mind this discrepancy, some results from other areas in the world are presented in Table 2. Compared to surface sediments in some other parts of the Mediterranean (Sicily, Greece), Pb and Zn concentrations in the Gulf of Lions are similar or lower. Comparison with environments outside the Mediterranean area also indicates that although lead and zinc concentrations in sediments of the Gulf of Lions have increased over the last century, this increase is not exceptionally high.

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