Fluxes and penetration rates of radionuclides and stable lead in sediments deposits from the Camargue (South France)

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Abstract . Since heavy metal deposition records are scarced in urbanized areas, we used saltmarsh and marine sediments as proxies to reconstruct heavy metal fluxes during the last century in the Camargue (South France). ^{210}Pb, ^{137}Cs and stable lead were analyzed in order to determine their inventories and to reconstruct temporal trends in concentrations and fluxes in two zones of the coastal environment. Two cores were collected in a saltmarsh environment and another one in the Gulf of Lions continental slope. Regarding the radionuclide profiles, one core from the saltmarsh appears to be influenced by Rhône flooding deposits. The other cores seem to reflect the atmospheric supply. Wether they were collected in different environment (saltmarsh and slope sediments), their pollutant lead inventories are in good agreement.
The ^{210}Pb excess inventories determinate in the same core are also very concomitant, and confirm the level of anthropogenic accumulation.

1. INTRODUCTION

There is a lack of records for heavy metal deposition and accumulation in urbanized coastal environments. While they can be quite precise, direct atmospheric inputs measurements are limited and do not reflect long term variations. Sediment record can be blurred by bioturbation or physical mixing. They also can include riverine input along with atmospheric deposition.

Here we propose to evaluate the validity of different proxies to match atmospheric deposition in coastal area located in Western Mediterranean. These proxies include salt marsh and continental margin sediments.

Our question are as followed :

• What is the inventory of heavy metal deposited in coastal Western Mediterranean ?
• How did this input vary with time ?
• How do compare input between different areas of the continental margin ?

2. SITE LOCALIZATION

Two cores were collected in Camargue area in 2000, close to the Rhône river : PAL-2 and, far from potential riverine flooding : CER-1 close to la *Tour du Valat*. A third core (HFF 6, 05°02'475 E, 42°47'001 N, 1240 m) was collected on the slope of the Gulf of Lions continental margin in the framework of the MTP-EUROMARGE program (fig. 1).

3. METHODS

This study was made in the framework of a CNRS-NSF program dedicated to the study of several heavy metal (Pb, Cu, Zn…) and radionuclide deposition in coastal area. However, we focus this paper on Pb. Pb is rapidly transported and scavenged away from its various industrial sources due to its strong affinity to submicron particles.

Furthermore, its stable isotopes (m = 204, 206, 207, 208) allow the discrimination of its different polluted source emissions vs. natural origin. The relative abundance of each stable isotope define the isotopic composition. It is unvariant from the mineral ore formation to its deposition. The sample isotopic composition is the result of a mixing between a pollutant/anthropic pole (^{206}Pb / ^{207}Pb = 1,16-1,17) and a natural pole (^{206}Pb / ^{207}Pb = 1,195-1,2 [1]).

Along with Pb, its radioactive analog [210]Pb (t = 22,3 y) is used to date Pb deposition and calculate fluxes to sediment. In order to evaluate the impact of bioturbation and physical mixing on deposition record, [137]Cs (t = 30 y) is analyzed along with [210]Pb. Both radionuclides have atmospheric origin.

The Pb concentration and isotopic composition are determined by Thermo Ionisation Mass Spectrometry (TIMS) at the CEREGE laboratory. The amount of pollutant Pb (*Pb xs*) is evaluated by substracting the detritic lead contribution (20±2 ppm in the Gulf of Lions sediments, [1] and [2]) to the total lead concentration measured. The radionuclide activities are measured by gamma spectrometry at Stony Brook (State University of New York). We use the CRS (Constant Rate of Supply) dating model [3] to date the deposition and calculatethe accumulation rates with ^{210}Pb excess. All the activity values expressed here were determined on dried material.

4. RESULTS

4. 1. Camargue sediment cores
4.1.1 CER-1 Core

Considering the [137]Cs(fig. 2), a mixed layer is evidenced in the 4 first cm (probably due to bioturbation or physical mixing). It is marked by a sub-surface maximum of 120 Bq.kg^{-1} while the surface activity is equal to 80 Bq.kg^{-1}. Under this mixed layer, the profile presents a regular decrease until cesium disappearance at10 cm.
The ^{210}Pb profile (fig. 2) shows the same trend as ^{137}Cs with a surficial mixed layer of 4 cm, followed by a regular decrease. The surface activity is equal to 150 Bq.kg^{-1}. [210]Pb is not in excess anymore at 10 cm deep.

The total lead concentration profile (fig. 2) displays an enrichment from the bottom to the top core with a sub-surface maximum of 75 ppm, at the base of the mixed layer. Bottom concentration (22 ppm) are close to natural values (20±2 ppm). The [206]Pb/[207]Pb ratio profile (fig. 2) shows a general trend from values close to natural ones (26 cm, [206]Pb/[207]Pb = 1.191) to less radiogenic isotopic compositions in the upper layers (1 cm, [206]Pb/[207]Pb = 1.179). The surficial 4 cm show a different evolution due to mixing clearly evidenced with the radionuclides profiles. We can expect this core CER-1 to be dominated by atmospherical supply (according with the radionuclides and lead behaviour). Even if it is affected by a surficial mixed layer.

Multiplicating the anthropogenic lead concentration (total lead concentration less detritical contribution) by the accumulation rates (obtained using ^{210}Pb excess), we are able to reconstruct the pollutant lead (Pb xs) fluxes during the last century (fig. 3). This graph evidences an increase of Pb flux from the beginning of the century to 1978 and a stabilization until now. This supply leads to a pollutant lead inventory equal to 350 µg.cm^{-2}.

4.1.2 PAL-2 Core

This ^{137}Cs profile is very disturbed (fig. 4). It shows increasing activity values from 6 to 14 cm (from 15 Bq.kg^{-1} to 98 Bq.kg^{-1}) followed by a clear mixed layer from 14 to 20 cm which presents the maximal values of the profile. The surface activity is equal to 30 Bq.kg^{-1}. The ^{137}Cs disappears at 35 cm deep.
The ^{210}Pb profile (fig. 4) presents the same trend with a 14-20 cm mixed layer showing maximal activity values around 50 Bq.kg^{-1}. The surface activity is equal to 37 Bq.kg^{-1}. The ^{210}Pb supported is probably reached at the bottom core since the activity at 35 cm value (20 Bq.kg^{-1}) is close to the ^{210}Pb supported value found in CER-1 (25 Bq.kg^{-1}).

We find the maximal total lead concentrations (fig. 4) in the lower part of the core (fig. 4). In sub-surface, we observe concentrations (16 and 18 ppm at 4 and 5 cm) lower than the detritical contribution (22 ppm in core CER-1). Globally, the concentrations decrease from the bottom to the top core and are low (maximum = 50 ppm).
The isotopic profile (fig. 4) is very disturbed with variations that do not show any clear trend. We note however that the [206]Pb/[207]Pb isotopic ratio values are less radiogenic than natural values ([206]Pb/[207]Pb = 1,195-1,2).

The core Pal-2 is likely affected by Rhône river flooding event as evidenced by the observed metal profile. Granulometry analysis will be done to confirm this flooding origin.
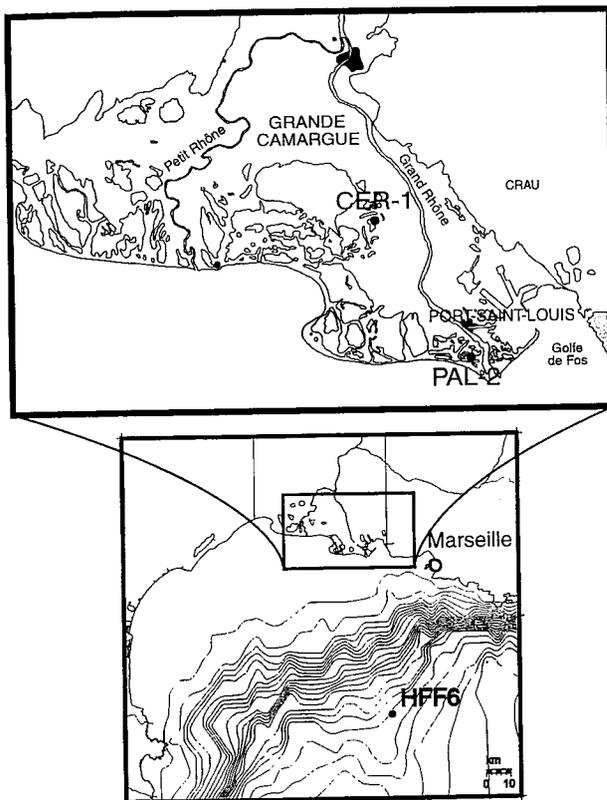

Figure 1 : collecting site map

4.2. Gulf of Lion sediments
4.2.1 HFF 6 Core

We observe low ^{137}Cs activity values (9.6 Bq.kg^{-1} is the surface activity value) (fig. 5). The ^{137}Cs is still present at 11 cm deep.

The ^{210}Pb profile presents a regular decay (fig. 5) with depth except a 3.5-5.5 cm mixed layer. The surface ^{210}Pb activity is equal to 420 Bq.kg^{-1} and the ^{210}Pb xs disappears at 8.5 cm (supported ^{210}Pb activity = 25 Bq.kg^{-1}). As the ^{137}Cs and the ^{210}Pb supported reach the same depth, it evidences the mobility of ^{137}Cs. The total lead concentration profile (fig. 5) shows an enrichment from the bottom to the top (from 23 ppm to 50 ppm). The maximum value is in sub-surface layer (54 ppm at 1.5 cm). At the bottom, the value (23 ppm) is close to the natural level. The ^{206}Pb/^{207}Pb ratios (fig. 5) evolute slightly from natural lead signatures (^{206}Pb/^{207}Pb = 1,196) at the bottom to more anthropogenic influenced signatures (^{206}Pb/^{207}Pb = 1,175) at the top of the core.

The reconstructed pollutant lead fluxes time evolution (fig. 6) shows two peaks in 1958 and 1971. From 1971 to 1999, they decrease. This anthropogenic Pb supply leads to a total anthropogenic Pb inventory equal to 376 µg.cm^{-2}.

5. DISCUSSION

The anthropogenic Pb inventories obtained in the cores CER-1 and HFF6 are in good agreement.

To compare our Pb deposition reconstruction with the direct measured atmospheric supply [4] in the area of La Tour du Valat, we calculate the anthropogenic Pb inventories corresponding to the last 10 year period. During this decade, the atmospheric supply is estimated at 3.5 $\mu g.cm^{-2}$ while we find inventories equal to 34.5 $\mu g.cm^{-2}$ in the Camargue core CER-1, and 44.5 $\mu g.cm^{-2}$ in the marine core HFF6. The core inventories are still in good agreement but they are higher than the atmospheric supply by a factor 10. To explain these higher inventory, a Rhône river supply could be invoke but, Pu isotopic composition determination analysis made on core CER-1 give atmosphere as material source. So, a local reconcentartion phenomenom appears to be the lonely responsible of higher Pb inventory in the Camargue area.

^{210}Pb xs inventories determined in each core are very similar (4065 $Bq.m^{-2}$ CER-1 ;4600 $Bq.m^{-2}$ HFF 6). They correspond to a ^{210}Pb flux respectively 126 ± 11 $Bq.m^{-2}.y^{-1}$ and 143 ± 18 $Bq.m^{-2}.y^{-1}$, which is higher than the atmospheric flux usually considered for this area
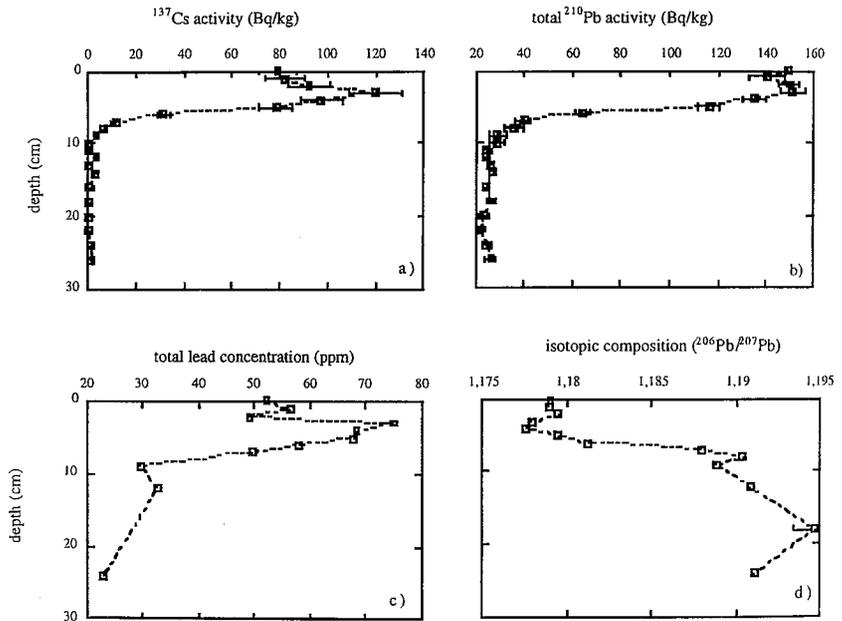

Figure 2: ^{137}Cs, total ^{210}Pb, total lead concentration, ^{206}Pb / ^{207}Pb isotopic ratio vs. depth in the CER-1 core

6. CONCLUSION

The use of radionuclides and anthropogenic tracers analysis allow a precise reconstruction of pollutant metal atmospheric deposition and of various input sources (flooding, atmosphere, riverine) in the coastal area of Camargue. This proceeding can be applied in other area to reconstruct the anthropogenic pollutant deposition.

7. REFERENCES

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[3] Appleby P. and Oldfield K., *Catena* **5** (1978) 1-5.
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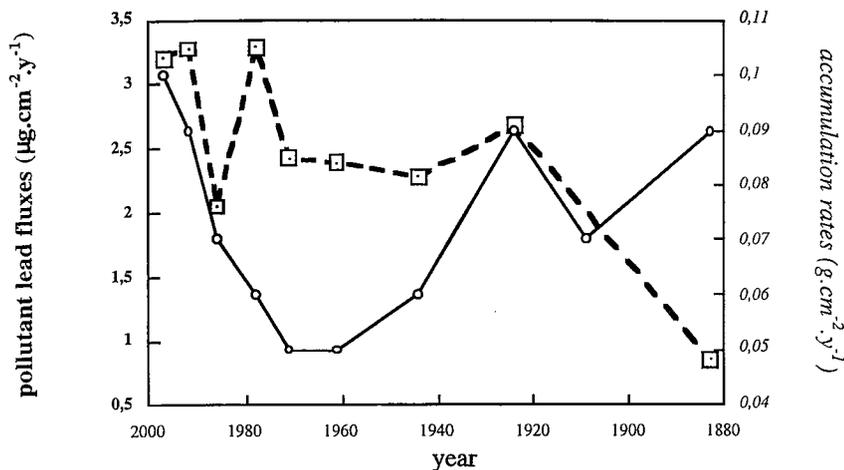[5]Radakovitch O., Cherry R. D., Heyraud M. and Heussner S., Oceanol. Acta, **21** (1998) 459-468.

Figure 3: Pollutant lead fluxes (μg.cm^{-2}.y^{-1}), **dotted line,** and accumulation rates (g.cm^{-2}.y^{-1}), filled line, during the last century from the CER-1 core
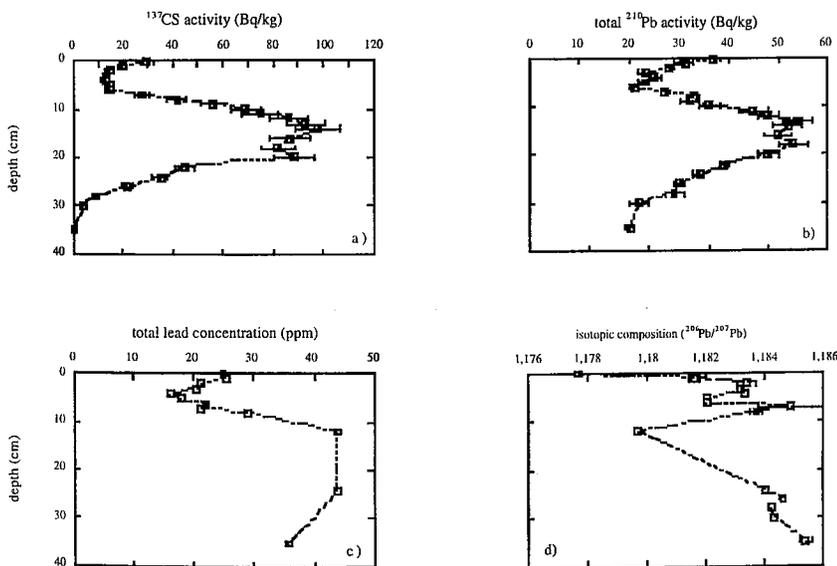

Figure 4: ^{137}Cs, total ^{210}Pb, total lead concentration, ^{206}Pb / ^{207}Pb isotopic ratio vs. depth in the PAL-2 core

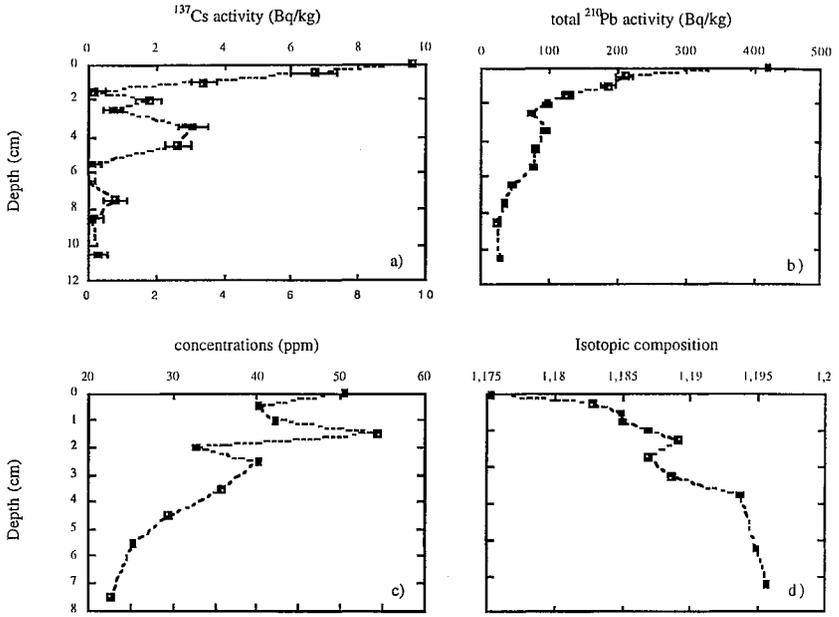**Figure 5:** [137]Cs, total ^{210}Pb, total lead concentration, [206]Pb / [207]Pb isotopic ratio vs. depth in the HFF 6 core
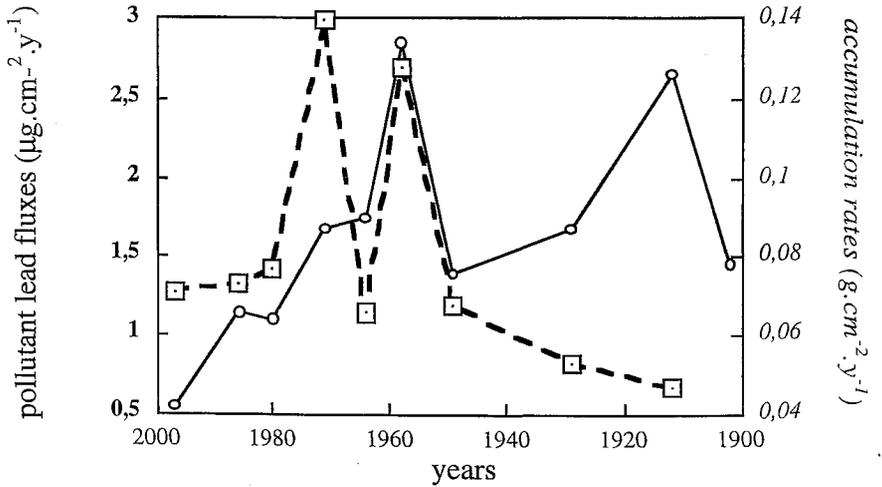
Figure 6: Pollutant lead fluxes (_g.cm [-2].y[-1]), **dotted line,** and accumulation rates (g.cm^{-2}.y[-1]), filled line, during the last century from the HFF6 core