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The role of large biogenic particles in the transport of atmospheric pollutant Pb down to North Atlantic sediments

Pb
Marine pollution
North Atlantic
Biogenic cycling

Pb
Pollution marine
Atlantique Nord
Cycle biogène

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ABSTRACT

Pb concentrations were measured on large particles (diameter >10 µm) at seven stations in North East Atlantic waters, and Pb isotopic composition was determined on one sediment core (Fluxatlante cruise, 1985). In intermediate and deep waters, Pb concentrations on large particles are about 0.5 ng l^{-1}, less than 1 % of total lead and show a close correlation with ^{210}Pb. This suggests that lead is primarily scavenged from the dissolved Pb pool in surface waters with little further scavenging in deep waters. Such an interpretation is supported by our observation of stable Pb isotopic ratios in surficial sediments which suggests that a rapid coupling exists between the atmospheric input of Pb to surface waters and its delivery to the water-sediment interface. Furthermore, the calculated large-particle lead flux leaving surface waters can account for our inventory of surficial sediments.

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RÉSUMÉ

Transport de Pb de pollution atmosphérique en Atlantique Nord. Rôle du transfert vertical par les particules biogènes.

Nous avons mesuré les concentrations de plomb sur les grandes particules (diamètre >10 µm) sur sept stations dans la colonne d'eau de l'Atlantique Nord-Est et les rapports isotopiques du plomb dans une carotte de sédiment. Dans les eaux intermédiaires et profondes, les concentrations en plomb des grandes particules sont environ de 0,5 ng l^{-1}, moins d'un pour cent du plomb total, et montrent une étroite corrélation avec le ^{210}Pb. Ces constatations nous font estimer que le plomb serait surtout adsorbé à partir du plomb dissous dans les eaux de surface, et que très peu d'adsorption interviendrait au cours de la chute de ces particules dans la colonne d'eau.

Nous observons en outre, la présence de plomb de pollution dans les sédiments de surface, ce qui implique un couplage rapide entre l'apport de plomb par l'atmosphère et l'arrivée de plomb au sédiment. Cela est probablement dû au rôle concentrateur des grandes particules d'origine biogénique suivi de leur transport à grande profondeur. Cette hypothèse est confirmée par l'analyse des rapports isotopiques du plomb dans le sédiment superficiel, qui sont proches de ceux du plomb de pollution dans l'atmosphère de cette région. De plus, le flux calculé de plomb quittant les eaux de surface avec les grandes particules peut rendre compte de l'inventaire du plomb de pollution sédimenté.

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INTRODUCTION

We and other colleagues have previously reported (Véron *et al.*, 1987; Hamelin *et al.*, 1990) the occurrence of recent pollutant lead in North Atlantic surficial sediments. Some 28-43 % of the inventory of anthropogenic Pb input delivered since the beginning of the industrial revolution was found in the sediment. However, the processes which control the coupling time between the atmospheric input and the arrival at the water-sediment interface have still to be investigated.

The concentration of Pb in surface seawater depends on the importance of the atmospheric input function, and of the Pb residence time in surface waters. Because Pb is incorporated in the biogeochemical cycle, it has a short residence time in surface waters and subsequently a variable proportion of this Pb will appear in the particulate phase. This should be a major transport process of Pb downwards to the sediment. How much of this Pb actually sediments with fecal material is still a matter of controversy. Such deposition is considered important by Jickells *et al.* (1984 a) who showed a good correlation between organic carbon and particulate Pb in Sargasso Sea sediment trap samples collected at a depth of 3 200 m. On the other hand, it was considered insignificant by Shen (1986).

Pollutant Pb is mainly emitted in the northern hemisphere. If one considers that in deep South Pacific waters, Pb concentrations are very close to a "natural background", then anthropogenic Pb is the largest part of total Pb in northern hemisphere marine waters, as shown by Schaule and Patterson (1981). In the North Atlantic, this anthropogenic Pb is seen in most of the water column. Its presence at great depths can be explained by vertical mixing, advective processes, or dissolution from large biogenic particles. The only detailed profiles that would have permitted determination of the precise contribution of each process in the North Atlantic (Boyle *et al.*, 1986; Shen and Boyle, 1987) were influenced by advective features, so that the modelization called for an adjustment of both the atmospheric Pb input and the horizontal advection at all depths. Although it is obvious from these studies that the shapes of the profiles may be primarily explained by vertical and advective mixing, we hypothesize that the loss of particulate Pb from large particles may also need to be invoked to explain the data adequately. These large, fast-settling particles come from the surface waters and their flux is known to decrease with depth (Suess, 1980). Since their settling velocity is high, of the order of 100 m d^{-1}, they could constitute a pool of pollutant Pb for the entire water column where most of them dissolve.

The importance of such a process was investigated during the Fluxatlante cruise (1985) using a large volume *in situ* filtration system (POP). Results are discussed in view of the sediment data.

METHODS

Large particles were collected from a large *in situ* pumping system (POP) wich made it possible to filter 150 to 1 000 l of seawater on precleaned Nuclepore membranes of 10 µm porosity and 142 mm in diameter.

Sample locations are shown in Figure 1. The filters were cut into four parts in the laboratory under ultra-clean conditions. We verified that for our analyses, sample inhomogeneity generated by this procedure was less than 20 %. Two quarters of each filter were pelletized for neutron activation measurements of Al, I, Mn and Ca. A third quarter was dissolved in suprapur HNO_3, HCl, and evaporated at 60°C. The residue was dissolved in 4 cc HNO_3 1% and analyzed for Pb by flameless atomic absorption (Véron, 1989). All these operations were carried out in teflon vials and performed under class-100 clean laminar flow benches. Total blank (1/2 filter plus reagents) was 12 ng and contributed to 8-15 % of the total particulate Pb. ^{210}Pb on large particle samples was analyzed according to Heyraud and Cherry (1979) by a standard technique involving acid digestion of samples and plating on silver discs prior to alpha-counting. Sediment samples were collected by using an interface corer system (CNRS, Bordeaux). The collection procedure and sediment description are reported in Véron *et al.* (1987) and Véron (1988).

Pb concentration and isotopic composition were determined by mass spectrometry on fine slices of sediment, using the chemical separation method of Manhès *et al.* (1978). Measurements were made in ultra-clean conditions. Chemical blanks were beyond the counting statistical error. Global error on Pb isotopic ratios is shown in the Table.

Table

Isotopic composition of sediment at station 7. Uncertainty in parentheses. Note that the first sample was measured on the three first millimetres of sediment. Recalculating ^{206}Pb/^{207}Pb for the first centimetre gives 1.192. Hamelin et al. *(1990) found 1.205 in a core of station 7 distant 1 metre from ours. The difference of 0.013 between the 2 sets of data is systematic. It induces a 2-year uncertainty on our estimate of the apparent age of this pollutant lead.*

Composition isotopique du sédiment à la station 7. L'incertitude est entre parenthèses. L'échantillon de surface représente une couche de 3 mm seulement. Le calcul du rapport ^{206}Pb/^{207}Pb pour le premier cm de sédiment donne un rapport ^{206}Pb/^{207}Pb de 1,192. Hamelin *et al.* (1990) ont mesuré un rapport de 1,205 dans une carotte de la station 7 distante d'un mètre de la nôtre. La différence de 0,013 entre les 2 sets est systématique. Elle induit une incertitude de 2 ans sur notre estimation de l'âge apparent de ce plomb de pollution.

Depth (cm)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{206}Pb/^{207}Pb
0 0.3	17.9128 (0.0121)	15.5925 (0.0160)	37.8375 (0.0491)	1.149
8 8.8	18.3775 (0.0115)	15.6340 (0.0144)	38.3386 (0.0482)	1.176
25 30	18.9673 (0.0134)	15.6368 (0.0155)	38.8102 (0.0485)	1.213

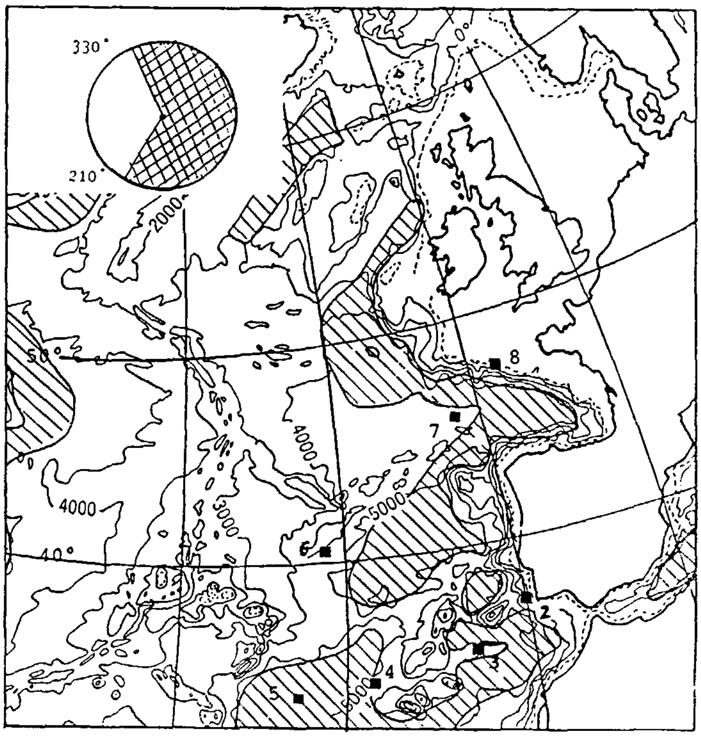

Figure 1

Map of large particle sampling stations during Fluxatlante cruise. Regions of significant turbidites are shown in hatched areas. After Davies and Laughton (1972). Insert: eastern and western wind sectors chosen for atmospheric Pb flux calculation.

Localisation des stations de prélèvement de grandes particules pendant la mission Fluxatlante, 1985. Les régions où les apports de turbidites sont importants sont marquées par les zones hachurées. D'après Davies et Laughton (1972). En haut à gauche, secteurs de vents d'est et d'ouest choisis pour les calculs de flux de plomb atmosphérique.

RESULTS

Large particles

Particles of large diameter collected during the Fluxatlante cruise were generally of biogenic origin. Most particles, examined by electron microscopy, were of the order of 100 µm, a very few being equal to or smaller than 20 µm. Most of this material was probably of fecal origin because of the nature of the contents : plankton, tests of organisms, silicate debris within large organic aggregates. It is known that these particles usually contain aluminosilicates (Dunbar and Berger, 1981; Deuser *et al.*, 1981; 1983; Scheidegger and Krissek, 1983; Krishnaswami *et al.*, 1985). Based on Al determination, we observed very large quantities of aluminosilicates, often more than 20% in weight per large aggregate. Pb data are presented in Figure 2.

The Pb concentrations measured on large particles represent less than 5 % of total Pb sampled with Go Flo bottles (dissolved + particulate, Lambert *et al.*, 1990). The highest concentrations are found in the first 50 metres of the water column (1.5 to 2.0 ng l^{-1}) and probably reflect the importance of Pb aeolian input and its incorporation in biogenic particulate matter. In the deeper water column, concentrations are significantly lower (0.2 to 0.6 ng l^{-1}). Data on ^{210}Pb activity measured on another portion of the same filters show that there is an excellent correlation between Pb and ^{210}Pb present in these large particles (Fig. 3). Such a correlation can be expected, because the settling velocity of these large particles is such that there is no radioactive decay of ^{210}Pb during transport. Similarly, there was a correlation between ^{210}Pb and Pb fluxes on Sargasso Sea sediment trap samples, when comparing data from Jickells *et al.* (1984 *a*) and Bacon *et al.* (1985).

Sediment

At Fluxatlante station 7 (water column depth : 3650 m) the sediment had a high carbonate content: 87 ± 6 %. The mean sedimentation accumulation rate measured by isotopic stratigraphy was low: 2.2 cm kyr^{-1} (Véron *et al.*, 1987) and the sediment was devoid of any advective input (this station was on a dome and away from the major turbidite influences, *see* Fig. 1). We therefore expected to see the major influence of pollutant Pb at the sediment surface. The first 3 mm exhibit 15 µg of Pb per g of dry sediment compared to a background in the first 10 cm of 2.8 ± 0.5 µg g^{-1} (Véron *et al.*, 1987). Isotopic Pb ratios at station Fluxatlante 7 are reported in the Table. We shall discuss $^{206/207}$Pb ratios in order to be consistent with the most frequent previous data sets. In the deepest sample (25 cm depth below the surface), these ratios fall in the range of natural sediments data. This is shown in Figure 4 by the good agreement

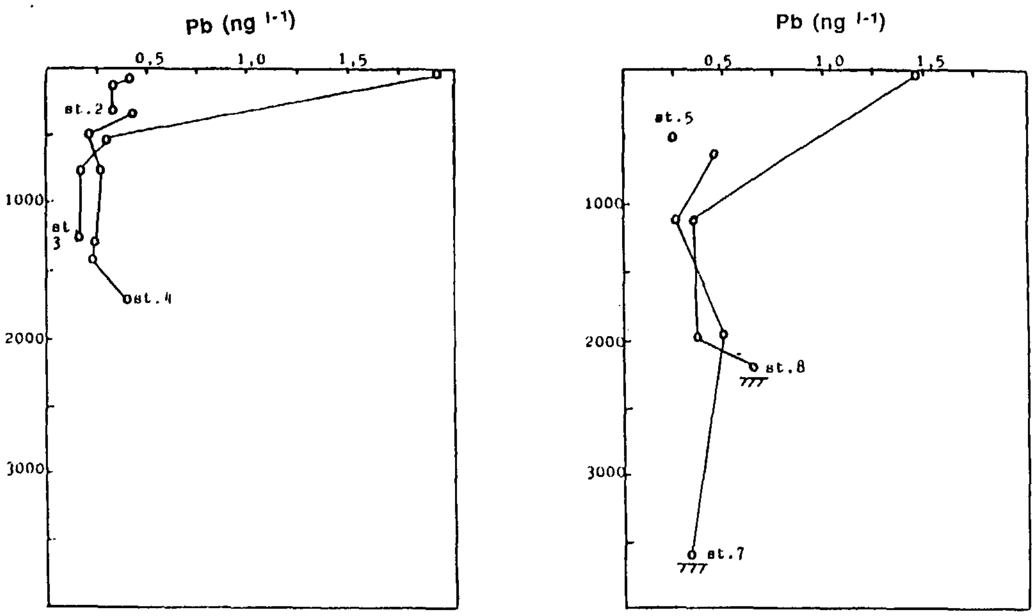

Figure 2

Pb concentrations (ng l^{-1}) on large particles collected at the various stations.
Concentrations en Pb (ng l^{-1}) des grandes particules collectées aux différentes stations

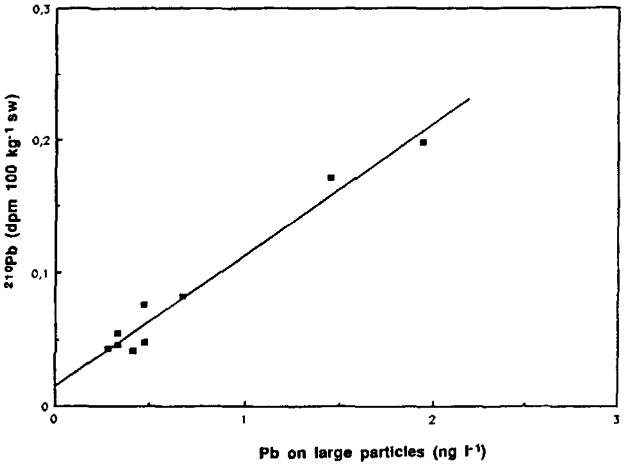

Figure 3

Pb (ng l^{-1}) and ^{210}Pb (dpm per 100 kg seawater) concentrations on large particles. Correlation = 0.015 + 0.099x (r=0.98)
Concentrations de Pb (ng l^{-1})et de ^{210}Pb (dpm par 100 kg d'eau de mer) dans les grandes particules. Correlation = 0.015 + 0.099x (r=0.98)

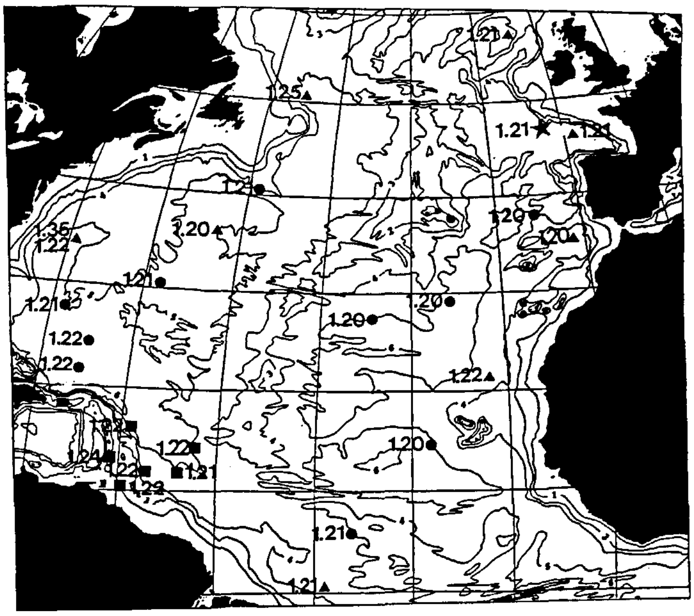

Figure 4

$^{206/207}Pb$ isotopic ratio in North Atlantic "pre-industrial" sediments
Rapports isotopiques $^{206/207}$Pb dans les sédiments Nord atlantiques de l'ère pré-industrielle :
● *Chow and Patterson, 1962;* ▲ *Chow* et al. *1980;* ■ *White* et al., *1985;* ∗ *This work*-Ce travail (station 7, 25-30 cm de profondeur)

between the $^{206/207}$Pb ratios in Atlantic preindustrial sediments from the literature (range 1.20-1.22) plotted along side our measurement . On the other hand, the surface and 8 cm depth samples in the core exhibit much lower radiogenic $^{206/207}$Pb ratios. Such a difference suggests the presence of some pollutant Pb with a composition different from the sedimentary background. The high ratio of the first mm appears to us as confirmation that pollutant Pb has reached the surface of the sediments.

If we consider that this Pb is in excess of the background level, we can calculate the Pb excess (Pb_{xs}) in this superficial zone:

$$(Pb_{xs}/3).M_H.(100 - W_s).1\ cm = Dxs$$

where D_{xs} is the lead in excess in the first cm of the sediment, M_H the density of wet sediment, W_s the porosity (in %). This yields 2.6 ± 0.3 μg of Pb_{xs} cm^{-2} in the first 3 mm of sediment. Then, the isotopic $^{206/207}$Pb ratio of the excess is (Shirahata *et al.*, 1980; Ng and Patterson, 1982):

$$^{206/207}Pb_{xs} = (^{206/207}Pb_T * Pb_T) - {}^{206/207}Pb_{BF}/Pb_{xs} = 1.135 \pm 0.001$$

Comparison of this isotopic ratio to the ratios of anthropogenic Pb in the atmosphere since 1900 (Fig. 5) suggests that it is similar to that of pollutant lead emitted in the European atmosphere after 1960.
The isotopic ratio found at 8 cm seems much too low to be explained by a pure diffusion process. We can only hypothesize that it was due to a burrow. Subsurface maxima due to macrofaunal distribution have also been reported by Hamelin *et al.* (1990).

DISCUSSION

Sediment

How do the results on surficial sediment station 7 compare with atmospheric isotopic ratios ? Pb isotopic ratios in the atmosphere have been used to characterize the different sources of lead and their strength (Chow and Johnstone, 1965; Chow e*t al.*, 1975; Elias and Patterson, 1980; Maring *et al.*, 1987; Hamelin *et al.*, 1989). The evaluation of isotopic ratios in the atmosphere between 1900 and 1960 was deduced from lacustrine data (Petit, 1974; Shirahata *et al.*, 1980).

Figure 5 shows that during this period, the $^{206/207}$Pb ratio of anthropogenic origin in the atmosphere was less radiogenic in Europe than in the United States. The temporal evolution of these ratios after 1960 is strongly influenced by the isotopic composition of lead ores used in gasoline (Chow and Earl, 1962; Chow *et al.*, 1975). Figure 5 also reflects that the use of radiogenic Missouri ores in US gasoline has increased the $^{206/207}$Pb ratio in the atmosphere of the United States, whereas the use of unradiogenic Australian ores in European gasoline has lowered $^{206/207}$Pb ratios in European air.
We have attempted to use the data in Figure 5 to calculate, as a gross approximation, the intensity of the western and eastern atmospheric pollutant Pb component in our surface sediment sample and its

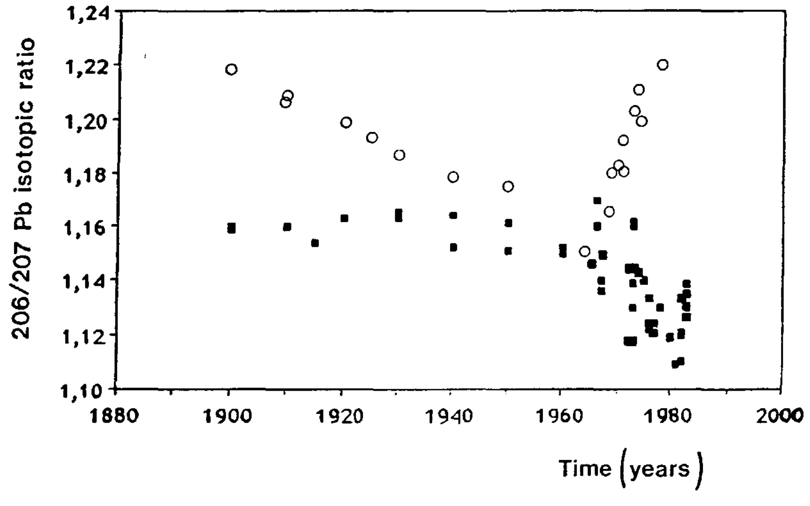

Figure 5

Change of $^{206/207}$Pb with time in north American (m) and European (n) atmosphere (from atmospheric and lacustrine data).
Évolution temporelle des rapports $^{206/207}$Pb dans l'atmosphère d'Amérique du Nord (m) et d'Europe (n). Données atmosphériques et lacustres.
Data from (Données extraites de) *Chow* et al., *1975*; *Shirahata* et al., *1980*; *Ng and Patterson, 1982; Elbaz-Poulichet* et al., *1984*; *Petit* et al., *1984; Flament, 1985; Petit (pers. comm.).*

apparent age. We have discarded any advective input from fluvial origin, since such inputs should be primarily scavenged at the margins by biological uptake, as suggested by the model of Bacon (1988).

The first information needed is how much Pb is deposited each year in surface waters at the site. Using the atmospheric data obtained during the same cruise (Véron, 1988), we have attempted to estimate the atmospheric input of lead to our site. This estimate is based on a limited number of aerosol samples, so that the following calculations are certainly fraught with large uncertainties. Nevertheless, it will be shown that they probably provide a correct estimate of the magnitude of total lead atmospheric deposition. Total deposition was probably primarily dominated by wet deposition processes. We have assumed a total deposition velocity (V) of 1.5 ± 0.5 $cm.s^{-1}$, based on Cambray *et al.* (1975) and Buat-Ménard (1986). We also assumed that the flux of atmospheric Pb over the North East Atlantic is equal to the sum of two fluxes, $F_1(C_1V)$ and $F_2(C_2V)$, F_1 from a western origin and F_2 from an eastern origin. F_3 is considered, as shown by Whelpdale *et al.* (1988), to have encountered an important number of rain events before reaching the eastern Atlantic. Because of this transport and deposition pattern, we could not use North East Atlantic deposition data since the western atmospheric Pb deposition at our site is likely to be lower than the flux observed in Sargasso Sea atmosphere during the same year (Jickells *et al.*, 1987). Four atmospheric samples taken during the Fluxatlante cruise in 1985 had wind trajectories indicating a western origin. The mean concentration was 1.7 ± 0.2 ng m^{-3}. To calculate F_2, we assumed that Pb concentrations C_2 in 1985 were comprised between 10 and 20 ng m^{-3} (15 ± 5 ng m^{-3}) based on two aerosol samples. As indicated by air mass trajectory analyses, these concentrations reflect fast transport of lead from Europe (in less than 2 days). The elevated Pb levels over Europe and this fast transport process probably explain the fact that C_2 is much greater than C_1. The calculated F_2 value is close to the wet deposition of Pb during that period which was determined from the analysis of 2 individual rain events.

The major constraint to calculate an integrated flux is then the frequency of the wind coming from the east and from the west. We defined a large eastern sector for station 7, so as to include influence from Spain and England (see insert Fig. 1). The data of the *Météorologie Nationale* in France between 1960 and 1980 show a wind frequency of that sector (fr_2) of 45 % of the time. Then, the deposition rate, D, of Pb and its isotopic ratio (RI) are respectively:

$D_{1985} = (C_1.V.fr_1) + (C_2.V.fr_2)$
with fr_1 = wind frequency from the western sector and $fr_1 + fr_2 = 1$

$RI_{1985} = \{(C_1.V.fr_1.R_1)+(C_2.V.fr_2.R_2)\}/\{(C_1.V_1.fr_1)+(C_2.V_2.fr_2)\}$

where R_1 is the isotopic ratio of aerosol lead from North America and R_2 from Europe in 1985, taken from Figure 5.

The atmospheric deposition estimated for our northeastern Atlantic site is then 370 ng cm^{-2} yr^{-1} with an isotopic ratio of 1.127. Thus, 85 % of the total Pb deposition flux would come from polluted eastern regions with an atmospheric transport time of less than 2 days and 15 % would come from the western sector with a transport time of 5 to 10 days over the ocean. There is obviously a large uncertainty on such a determination, but it is consistent with the inventory of Pb in surface waters at three Fluxatlante stations in 1985, considering a residence time of Pb of one year based on ^{210}Pb behaviour (Lambert *et al.*, 1990). Indeed, Pb inventory above the thermocline was 370 ng cm^{-2} at station 3; 370 ng cm^{-2} at station 4 and 420 ng cm^{-2} at station 5. This Pb atmospheric flux is about twice that of the western Atlantic in 1983 (Jickells *et al.*, 1984 *b*; 1987). This probably reflects the higher Pb pollution level over Europe (Lambert *et al.*, 1990) and its fast transport to the site.

For the years before 1985, we used the atmospheric deposition curve for pollutant Pb from Véron *et al.*, 1987. A step by step calculation from 1945 to 1985 allows us to calculate the atmospheric flux of Pb to the surface for each year, and to determine what fraction of this integrated flux our sedimented Pb represents.

There is a large error on each of these determinations, and it is therefore more interesting to test the sensitivity of each variable than to get an accurate "age" and proportion of eastern and western influences. We decided to use the following constraints:

- the $^{206/207}$Pb isotopic ratio obtained by this model for the pollution Pb accumulated between 1945 and 1985 must be equal to 1.135;
- the total integrated Pb deposited at the ocean surface must be less than 14 µg cm^{-2}, which is the maximum pollutant Pb input at the surface of this region since 1940 (Véron, 1988);
- The anthropogenic Pb in the first millimetres of sediment, defined as Pb$_{xs}$ (*see* above), must be equal to or greater than 2.6 µg cm^{-2}, which is the value we measured. There is indeed a possibility that some pollutant Pb is already mixed downwards in the sediment.

Taking all these constraints into account, our data are only compatible with Pb total deposition velocities in the atmosphere comprised between 1 and 1.75 cm s^{-1}. The frequencies of eastern winds at station 7 must be at least 45 %, but could be as high as 60 %. The atmospheric Pb concentrations under European influence (C$_2$) in 1985 are within the range we imposed: between 10 and 20 ng m^{-3}. Then, the "apparent age" of pollutant Pb at the surface of the sediment must be 8 to 12 years and the fraction of anthropogenic Pb transferred to the sediment must comprise between 40 and 70 % of the atmospheric input to surface waters. This estimate of the percentage of sedimented anthropogenic Pb is consistent with that of Jickells *et al.* (1987) in the Sargasso Sea.

This simple computation provides evidence of the internal coherence of the observed concentrations of Pb in surficial deep-sea sediments, the measured isotopic ratio, and the most likely hypotheses about the atmospheric flux. Therefore, it seems reasonable to think that there must be a rapid transfer process of Pb in the particulate form from surface waters to the sediment. This point is examined in the second part of the discussion.

Large particles

There seems to exist a common process for Pb and ^{210}Pb incorporation in large particles. Pb has been shown to be rapidly incorporated in biogenic particles by passive adsorption from the dissolved pool on the phytoplankton (Burnett and Patterson, 1980; Schaule and Patterson, 1981; Flegal and Patterson, 1983). This phytoplankton is then ingested by primary and secondary consumers, wich produce fecal aggregates that are the major component of particles of large

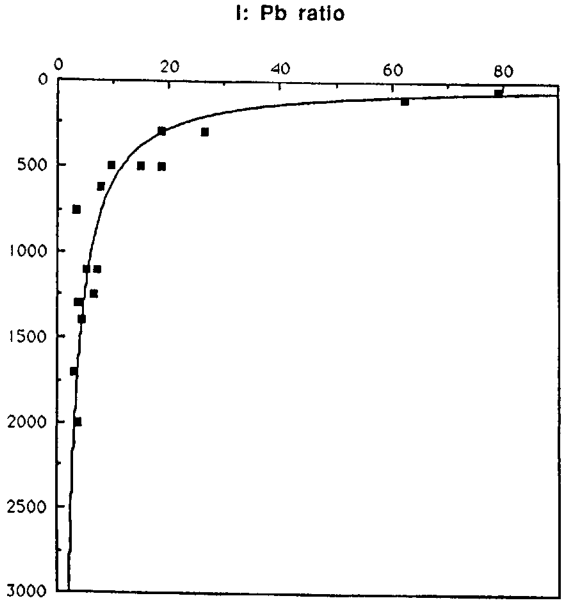

Figure 6

I: Pb ratios on all water column samples.
Rapports I/Pb sur tous les échantillons de la colonne d'eau.

diameter. The relative efficiency of these biological processes in concentrating Pb on large particles is evidenced by results of Pb concentrations in phytoplankton, zooplankton and their fresh fecal pellets, using clean sampling techniques. Zooplankton is reported to be 3-10 times less rich in Pb than phytoplankton: 2-7 ppm in zooplankton compared to about 20 ppm in average phytoplankton (Harstedt-Roméo, 1982; Roméo and Nicolas, 1986; Michaels and Flegal, 1990). This depletion is explained by the transfer of Pb to fecal material that is enriched by a factor of 20-200 relative to phytoplankton (Jickells *et al.*, 1984 *a*; Wallace *et al.*, 1977; Roméo and Nicolas, 1986).

It can then be hypothesized that the vertical flux of particulate Pb will be controlled by processes affecting fecal material (aggregation, disaggregation) as well as Pb exchange between dissolved and particulate phases. Processes specific to Pb can be evidenced by comparing the vertical variations of Pb and organic carbon particulate fluxes. In the absence of direct flux measurements using sediment traps, we have used an indirect approach as follows: a rough calculation of the particulate carbon flux at any depth can be made using the Suess (1980) equation :

$$C = PROD / \{0.0238\,z) + 0{,}212\} \qquad (1)$$

with PROD = productivity (g m^{-2} yr^{-1}); C = particulate organic carbon flux (g m^{-2} yr^{-1}); z = depth (m)

If we know the Pb: C relationship as a function of depth, we can estimate a particulate Pb flux.

Unfortunately, the nature of Nuclepore membranes prevents the measurement of POC on the filters. We therefore chose iodine (I) as a tracer of organic matter. We used a I: C molar ratio of 1 10^{-4} (Elderfield and Truesdale, 1980). Measurements were made on a portion of the same filters by neutron activation. Iodine : Pb ratios are displayed in Figure 6. Because of the scarcity of data, all samples have been pooled together. The I : Pb ratio does evolve in a non-linear way between surface waters and deep waters, because I decreases more rapidly than Pb.

The observed relationship is:

$$(I/Pb) = 4024 * (1/z)^{0.94} \quad (r = 0.95) \qquad (2)$$

Combining the two equations, the flux of Pb (F_{Pb}) is:

$$F_{Pb} = \{PROD_I / ((0.0238 * z) + 0{,}212)\} / \{4024 * (1/z)^{0.94}\} \qquad (3)$$

with $PROD_I$ = production of iodine in surface waters.

Considering a realistic average primary production rate for the open ocean of 200 g C m^{-2} yr^{-1} (Eppley and Peterson, 1979), yields a Pb flux from surface waters of 340 ng cm^{-2} yr^{-1}. This estimate is reasonable and close to our observations of total Pb in surface waters (Lambert *et al.*, 1990) and our estimate of atmospheric input. The flux of Pb at 4000 m is estimated by equation 3: 150 ng cm^{-2} yr^{-1} for 1985. Taking into account an atmospheric Pb flux for that region of 360 ng Pb cm^{-2} yr^{-1} (Véron, 1988) yields a Pb sedimentation representing 42% of the input. Within the uncertainties and limitations of our data set, this independent estimate is in good agreement with our sedimentary data.

These calculations indicate a recycling of Pb in the water column. Half of the flux from surface waters would be released in the dissolved and/or suspended particulate phases. According to Figure 6, this release occurs primarily below 750 m. This is coherent with Schaule and Patterson (1981) findings.

The residence time of Pb released in the water column can be assumed to be much longer than the apparent age of Pb in surficial sediments (10 years). Indeed, data on ^{210}Pb in the deep Atlantic suggest a residence time of about 50 years (Bacon, 1988). The apparent age of 10 years results essentially from the fast transport of Pb bound to fast sinking particles.

The evolution of I: Pb ratios in large particles with depth suggests a progressive concentration of Pb compared to biological components. The most likely explanation for this is biological re-packaging. This implies that at all depths, zooplankton consumes large particles and produces fecal pellets with less organic material, which is consumed, and more Pb, which is disposed of by zooplankton. This suggestion is in agreement with the fact that zooplankton is found at all depths in the North East Atlantic. An increasing volume of zooplankton has been found in deep waters in recent years, due to better sampling instrumentation (Angel, 1989). Therefore, a continuous re-packaging of fecal material with depth could be at work and explain that Pb and particulate organic matter do not decrease simultaneously. This process does not require advective inputs and can be interpreted in one-dimensional terms.

CONCLUSION

The vertical particulate flux of Pb scavenged in surface waters is not linearly related to that of organic matter. Indeed, previous work from sediment trap data and our data from large particle samples indicate that the abundance of these elements relative to that of labile organic components increases generally with depth. This pattern is apparently not primarily due to binding of trace metals with refractory components such as calcium carbonate and aluminosilicates. One possible explanation is biogenic repackaging of organic particulate matter at all depths. This transport induces a large and rapid Pb flux to the sediment. Pollutant Pb apparent age in the sediments is 8-12 years, reflecting the fact that 50 % of the present total inventory of Pb was emitted during the last 20 years (Véron, 1988). We suggest that the cycling of Pb in the ocean occurs on two time scales. There is a fast cycling in surface waters where Pb is scavenged and readily transported to the sediment, and a slow cycle where Pb transported by vertical mixing or released from large settling particles will be slowly delivered to the sediment. Our sedimentary data simply reflect the scale of the perturbation of Pb, which is much more pronounced in surface waters than in intermediate and deep waters. Such an apparent age is considerably shorter than the mean residence time of Pb in deep waters based on ^{210}Pb data.

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REFERENCES

Angel M.V. (1989) Vertical profiles of pelagic communities in the vicinity of the Azores front and their implications to deep-sea ecology. *Progr. Oceanogr.*, **22**, 1-46.

Bacon M.P. (1988) Tracers of chemical scavenging in the ocean: boundary effects and large-scale chemical fractionation, in: *Tracers in the ocean*, London, Royal Society, 147-160.

Bacon M.P., C. Huh, A.P. Fleer and W.G. Deuser (1985). Seasonality of the flux of natural radionuclides and plutonium in the deep Sargasso sea. *Deep-Sea Res.*, **32**, 273-286.

Boyle E.A., S.D. Chapnick, G.T. Shen and M.P. Bacon (1986) Temporal variability of lead in the Western North Atlantic Ocean. *J. geophys. Res.*, **91**, 8573-8593.

Buat-Ménard P. (1986). Air to sea transfer of anthropogenic trace metals, in: *The role of air-sea exchange in geochemical cycling*, NATO ASI Series, D. Reidel Oubl. Co., Doordrecht, 477-496.

Burnett M.W. and C.C. Paterson (1980). Perturbation of natural lead transport in nutrient calcium pathways of marine ecosystems by industrial lead. In: *Isotope Marine Chemistry*, E.D. Goldberg, Y.Horibe, K.Saruhashi and U. Rokakuho, editors, Tokyo,413-438.

Cambray R.S., D.F. Jefferies and G. Topping (1975). An estimate of the input of atmospheric trace elements into the North Sea and the Clyde sea. In: Report AERC-R7733, HMSO, United Kingdom Atomic Energy Authority, Harwell, London, 72-73.

Chow T.J. and C.C. Patterson (1962). The occurrence and significance of Pb isotopes in pelagic sediments. *Geochim. cosmochim. Acta*, **26**, 263-308.

Chow T.J. and M.S. Johnstone (1965) Lead isotopes in gasoline and aerosols of Los Angeles Basin, California. *Science*, **147**, 502.

Chow T.J., C.B. Snyder and J.L. Earl (1975). Isotope ratios of lead as pollutant source indicators. In: *Proceedings IAEASM 191/4, Vienna, Austria*, 95-105.

Chow T.J., J.L. Earl and C.B Snyder (1980). Lead isotopes in Atlantic DSDP sediment cores, in : Isotope Marine Chemistry, E.D. Goldberg, Y. Horibe, K.Saruhashi and U. Rokakuho, editors, Tokyo, 413-438.

Davies T.A. and A.S. Laughton (1972). Sedimentary processes in the North Atlantic, in: Sedimentary processes in the North Atlantic, *Initial Reports of the Deep-Sea Drilling Project, Washington, US Government Printing Office*, **12**, 905-934.

Deuser W.G., E.H. Ross and R.F. Anderson (1981). Seasonality in the supply of sediment to the deep Sargasso Sea and implications for the rapid transport of matter to the deep ocean. *Deep-Sea Res.*, **28**, 495-505.

Deuser W.G., P.G. Brewer, T.D. Jickells and R.F. Commeau (1983). Biological control of the removal of abiogenic particles from the surface ocean. *Science*, *219*, 388-391.

Dunbar R.B. and W.H. Berger (1981). Fecal pellet flux to modern bottom sediment of Santa Barbara Basin (California) based on sediment trapping, *Geol. Soc. Am. Bull., Part 1*, **92**, 212-218.

Elbaz-Poulichet F., P. Holliger, W.W. Huang and J.-M. Martin (1984) Lead cycling in estuaries, illustrated by the Gironde estuary, France. *Nature*, **308**, 409-414.

Elderfield H. and V.W. Truesdale (1980). On the biophilic nature of iodine in seawater. *Earth planet. Sci. Letts*, **50**, 105-114.

Elias R.W. and C.C. Patterson (1980). The toxicological implications of biogeochemical studies of atmospheric lead. In: *Polluted rain*, T.Y. Toribara, M.W. Miller and P.E. Morrow, editors, Plenum Press, N.Y., 391-400.

Eppley R.W. and B.J. Peterson (1979). Particulate organic matter flux and planktonic new production in the deep ocean. *Nature*, **282**, 677-680.

Flament P. (1985). Les métaux traces associés aux aérosols atmosphériques : apports au milieu marin du littoral Nord-Pas de Calais, *Thèse de Doctorat, Université des Sciences et Techniques de Lille*, 175 pp.

Flegal A.R. and C.C. Patterson (1983). Vertical concentration profiles of lead in the Central Pacific at 15°N and 20°S. *Earth planet. Sci. Letts*, **64**, 1983.

Hamelin B., F. Grousset, P.E. Biscaye, A. Zindler and J.-M. Prospero (1989). Lead isotopes in trade winds aerosols at Barbados: the influence of European emissions over the North Atlantic. *J. geophys. Res.*, **94**, C11, 16243-16250.

Hamelin B., F. Grousset and E.R. Sholkovitz (1990). Pb isotopes in surficial pelagic sediments from the North Atlantic. *Geochim. cosmochim. Acta*, **54**, 37-47.

Harstedt-Roméo M. (1982). Some aspects of the chemical composition of plankton from the North Western Mediterranean Sea. *Mar. Biol.*, **70**, 229-236.

Heyraud M. and R.D. Cherry (1979). Polonium-210 and lead-210 in marine food chains. *Mar. Biol.*, **52**,227-236.

Jickells T.D., T.M. Church and W.G. Deuser (1987). A comparison of atmospheric inputs and deep ocean particle fluxes for the Sargasso Sea. *Global biogeochem. cycles*, **1**, 117-130.

Jickells T.D., W.G. Deuser and A.H. Knap (1984 *a*). The sedimentation rates of trace elements in the Sargasso Sea measured by sediment trap. *Deep-Sea Res.*, **31**, 1169-1178.

Jickells T.D., A.H. Knap and T.M. Church (1984 *b*). Trace metals in Bermuda rainwater. *J. geophys. Res.*, **89**, 1423-1428.

Krishnaswami S., M. Baskarn, S.W. Fowler and M.Heyraud (1985). Comparative role of salps and other zooplankton in the cycling and transport of selected elements and natural radionuclides in Mediterranean waters. *Biogeochemistry*, **1**, 353-360.

Lambert C.E., E. Nicolas, A. Véron, P. Buat-Ménard, G. Klinkhammer, P. Le Corre and P. Morin (1990). Anthropogenic Pb cycle in North East Atlantic waters. *Oceanologica Acta*, this issue, 59-66.

Manhès G., J.-F. Minster and C.J. Allegre (1978). Comparative uranium-thorium-lead and rubidium-strontium study of the Saint-

Séverin amphoterie: consequences for early solar system chronology. *Earth planet. Sci. Letts*, **39**, 19-24.

Maring H., D.M. Settle, P. Buat -Ménard, F. Dulac and C.C. Patterson (1987). Stable lead isotope tracers of air mass trajectories in Mediterranean region. *Nature*, **330**, 154-156.

Michaels A.F. and Flegal A.R. (1990). Lead in marine planktonic organisms and pelagic foodwebs. *Limnol. Oceanogr.*, **35**, 287-295.

Ng A. and C.C. Patterson (1982). Changes of lead and barium with time in California off-shore basin sediments. *Geochim. cosmochim. Acta*, **46**, 2307-2321.

Petit D. (1974). ^{210}Pb et isotopes stables du plomb dans des sédiments lacustres. *Earth Sci. Letts*, **23**, 199-205.

Petit D. (1977). Étude sur la pollution de l'environnement par le plomb en Belgique. Les isotopes stables du plomb en tant qu'indicateurs de son origine, *Thèse de Doctorat ès Sciences, Université de Bruxelles.*

Petit D., J.-P. Menessier and L. Lamberts (1984). Stable lead isotopes in pond sediments as tracer of past and present atmospheric Pb pollution in Belgium. *Atm. Environ.*, **18**, 1189-1193.

Romeo M. and E. Nicolas (1986). Cadmium, copper, lead and zinc in three species of planktonic crustaceans from the east coast of Corsica. *Mar. Chem.*, **18**, 359-367.

Schaule B.K. and C.C. Patterson (1981). Lead concentrations in the North east Pacific: Evidence for global anthropogenic perturbations. *Earth planet. Sci. Letts*, **54**, 97-116.

Scheidegger K.F. and L.A. Krissek (1983). Zooplankton and nekton: natural barriers to the seaward transport of suspended terrigenous particles off Peru. In: *Coastal Upwelling: its sediment record. Part A: Responses of the sedimentary regime to present coastal upwelling*, E. Suess and J. Thiede, editors, Plenum Press, N.Y., 303-333.

Shen G.T. (1986). Lead and cadmium geochemistry of corals: reconstruction of historic perturbations in the upper ocean, *Ph.D. thesis, Woods Hole Oceanographic Institution and Massachusetts Institute of Technology.*

Shen G.T. and E.A. Boyle (1987). Lead in corals : reconstruction of historical industrial fluxes to the surface ocean. *Earth planet. Sci. Letts*, **82**, 289-304.

Shirahata H., R. W. Elias, C.C. Patterson and M. Koide (1980). Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. *Geochim. cosmochim. Acta*, **44**, 149-162.

Suess S. (1980) Particulate organic carbon flux in the oceans. Surface productivity and oxygen utilisation,. *Nature*, **288**, 260-263.

Véron A. (1988). Dynamique du transfert du plomb dans l'Océan Atlantique Nord-Est depuis l'atmosphère jusqu'au sédiment. *Thèse de Doctorat, Université Paris-Sud*, 248 pp.

Véron A., C.E. Lambert, A. Isley, P. Linet and F. Grousset (1987). Evidence of recent lead pollution in deep north-east Atlantic sediments. *Nature*, **326**, 278-281.

Wallace G.J. Jr., G.L. Hoffman and R.A. Duce (1977). The influence of organic matter and atmospheric deposition on the particulate trace metal concentration of North West Atlantic surface seawater. *Mar. Chem.*, **5**, 143-170.

Whelpdale D.M., A. Eliassen, J.N. Galloway, H. Dovland and J.M. Miller (1988).The transatlantic transport of sulfur. *Tellus*, **40B**, 1-15.

White W.M., B. Dupré and P. Vidal (1985). Isotope and trace element geochemistry of sediments from the Barbados Ridge - Demerara plain region, Atlantic ocean. *Geochim. cosmochim. Acta*, **49**, 1875-1886.