OCEANOLOGICA ACTA 1991 - VOL. 14 - N° 1

Anthropogenic lead cycle in the northeastern Atlantic

Total Pb
North Atlantic
Meddy
Pollution

Pb total
Atlantique Nord
Meddy
Pollution

Claude E. LAMBERT [a], **Emmanuel NICOLAS** [b], **Alain VÉRON** [a], **Patrick BUAT-MÉNARD** [a], **Gary KLINKHAMMER** [c], **Pierre LE CORRE** [d], **Pascal MORIN** [d]

[a] Centre des Faibles Radioactivités, CNRS-CEA, 91198 Gif-sur-Yvette Cedex, France.
[b] Université Pierre et Marie Curie (Paris VI), La Darse, 06230 Villefranche-sur-Mer, France.
[c] Massachussets Institute of Technology, Earth Sciences, Cambridge, Massachusetts, 02139, USA.
[d] Université de Bretagne Occidentale, Laboratoire de Chimie marine, avenue Victor Le Gorgeu, 29283 Brest Cedex, France.

Received 02/03/90, revised 10/07/90, 17/07/90

ABSTRACT

We have investigated total Pb distributions in the water column from various sites in the north-east Atlantic. Sea water samples were collected during the Fluxatlante cruise in 1985. Total Pb ranged from 35 to 45 ng.l^{-1} (170-220 pmol l^{-1}) in surface waters and decreased with depth in a manner consistent with previous findings. The high concentrations in surface waters probably reflect an important anthropogenic input of Pb from the atmosphere. Concentrations of total Pb are higher than in the western Atlantic. This difference seems to be closely related to the difference in atmospheric inputs of anthropogenic Pb. Three of the stations exhibit a specific Pb excess at the depth of the Mediterranean waters outflowing in the intermediate Atlantic waters; such an anomaly appears conservative over a distance of about 2 000 km. The east-west difference in concentrations is expected first to increase, because Pb in US-Canadian gasoline decreases faster than in European gasoline, and then to disappear when the new European anti-Pb regulations take full effect.

Oceanologica Acta, 1990. 14, 1, 59-66.

RÉSUMÉ

Cycle du plomb anthropogène dans l'Atlantique Nord-Est

Nous avons étudié les distributions de plomb total à différents sites de l'Atlantique Nord-Est en 1985. Le plomb total est de 35 à 45 ng l^{-1} (170 à 220 pmol l^{-1}) dans les eaux de surface et décroît avec la profondeur. Les concentrations élevées dans les eaux de surface reflètent probablement l'importance des apports en provenance de l'atmosphère. Trois stations montrent, dans les eaux intermédiaires, des concentrations de plomb en excès par rapport à celles des eaux atlantiques, et qui sont spécifiques de la présence d'eau méditerranéenne. Ce signal est conservatif sur plus de 2 000 km. Les concentrations en plomb de l'Atlantique Est sont plus élevées qu'à l'Ouest. Cette différence sera reliée à la différence de flux de plomb de pollution dans ces deux régions. Son évolution est liée à celle des émissions futures de Pb. Dans un premier temps, cette différence augmentera, car les émissions en provenance d'Amérique du Nord décroissent plus vite que les émissions européennes. La différence s'atténuera ensuite lors de la réduction de ces dernières.

Oceanologica Acta, 1990. 14, 1, 59-66.

CFR contribution n° 1121.

0399-1784/91/01 59 08/$ 2.80/© Gauthier-Villars

INTRODUCTION

It is now well established that Pb concentrations in sea water depend in great mesure on the intensity of the anthropogenic atmospheric input (Schaule and Patterson, 1981; Patterson and Settle, 1987; Jickells *et al.*, 1987).

At present, the atmospheric lead burden is entirely dominated by anthropogenic sources, primarily exhaust from gasoline, wich has increased dramatically in the past hundred years. Estimates of the global anthropogenic emission of atmospheric lead based on gasoline exhaust demonstrate that 50 % of the present inventory of this pollutant has been emitted during the last 20 years (Nriagu, 1979; Véron, 1988). The present lead cycle in the ocean is therefore not at steady state with respect to atmospheric inputs. ^{210}Pb-based calculations yield a Pb residence time of a few years in surface waters and at most a few centuries in deep waters (Bacon *et al.*, 1976; Nozaki *et al.*, 1976). Thus, Pacific surface and intermediate waters are less contaminated by Pb than Atlantic waters (Schaule and Patterson, 1981; Flegal and Patterson, 1983). Since the residence time of lead in the ocean is much shorter than the turnover time of deep waters, different vertical distributions of lead should be expected from one region to another, depending on the local atmospheric source strength and of the different physical and biogeochemical processes at work in surface waters.

At the present time, the North Atlantic Ocean is being subjected to two important Pb sources: atmospheric deposition from North America and from Europe. It has been shown by Boyle *et al.* (1986) that Pb concentrations in the surface waters of the Sargasso Sea have been decreasing recently, due to the decrease of Pb emission associated with North American gasoline exhausts. However, Pb emissions in Europe have not decreased to the same extent, during the present decade.

In this study, we present and discuss the distribution and concentrations of total Pb at seven sites occupied in 1985 in the northeastern Atlantic. We compare these data to those obtained by other workers in the northwestern Atlantic.

METHODS

Sea water samples were collected from the R/V *Le Suroît* during the Fluxatlante cruise in April-May 1985. Sampling stations are shown in Figure 1. Vertical profiles of Pb were obtained by analysis of unfiltered samples collected from specially treated 5 l Go-Flo sampling bottles. We used teflon spigots and air valves, viton o-rings.

Before the cruise, bottles were disassembled and soaked in HCl 1N for several days. Bottles were rinsed with distilled water. At sea, a "rinsing cast" was performed at 4 000 m for all bottles prior to use. Bottles were subsampled directly from a teflon tube in a clean laboratory aboard ship, acidified and measured immediately by Anodic Stripping Voltammetry (ASV).

A detailed description of the analytical method is presented by Laumond *et al.* (1984) and Nicolas (1985). Most of the total Pb should be in the dissolved form (Schaule and Patterson, 1981,1983). Calibration was done by standard additions. Precision was 5 %. Accuracy was verified by comparison with NASS-1 reference sea water (Berman *et al.*, 1983). We found 36 ± 1.4 ng l^{-1} for a certified value of 39 ± 6.

During the cruise, blanks were measured on sea water samples stripped of Pb by adsorption on Chelex. This blank sea water was measured the same manner as the samples; Pb blanks were typically smaller than the detection limit of 1 ng l^{-1}. Blanks were not subtracted from the measured concentrations. Surface water samples were taken with Go-Flo bottles which were rinsed each time by lowering the samplers down to 500 m and closing them during recovery.

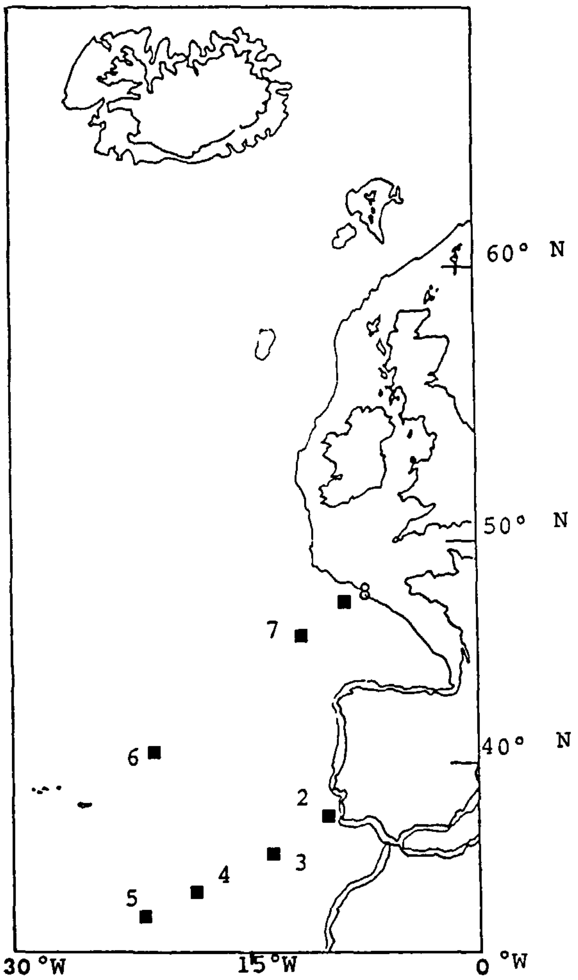


Figure 1

Map of Fluxatlante (2 to 8) sampling stations.
Carte des stations d'échantillonnage Fluxatlante.

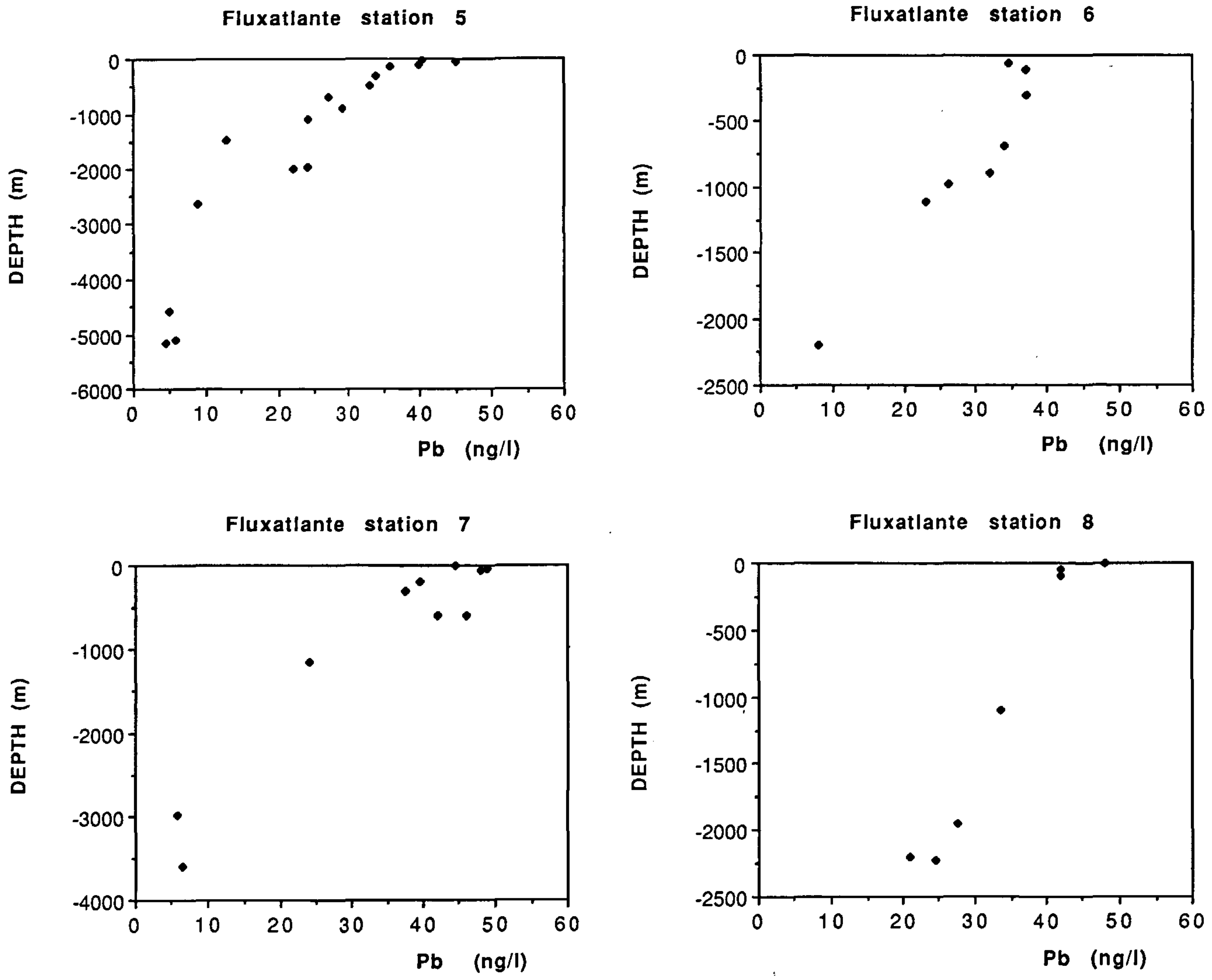
RESULTS

For all stations, surface Pb concentrations were found to be between 35 and 45 ng l^{-1} except st. 2 (60 ng l^{-1}). All profiles show a concentration decrease with depth to 4-6 ng l^{-1} (19-29 pmol l^{-1}) below 3 000 m. Concentrations below this depth are similar to those reported for the eastern Atlantic (Schaule and Patterson, 1983) and provide evidence of the lack of contamination of the methodology. The stations for this study can be organized into two broad classifications: those influenced by Mediterranean outflow and those lying outside Mediterranean influence.

From Brest to 33°N

The station closest to the coast (station 8, Fig. 2 *a*) exhibits relatively high Pb concentrations throughout the water column : 48 ng l^{-1} at the surface and 24 ng l^{-1} close to the bottom at 2 200 m. At station 7 (Fig. 2 *b*), which is further from the coast, the concentrations are highest at the surface and similar to surface concentration at station 8, but decrease steeply with depth. Pb levels at station 6 (Fig. 2 *c*) are similar to station 7, but are slightly lower in surface waters (35 ng l^{-1} compared to 45 ng l^{-1}) and decease sharply to 7 ng l^{-1} at 2 200 m. At the southern most station of this transect (station 5, Fig. 2 *d*) the level is systematically lower than at station 6, except for two points at 2 000 m. These two data points are supported by results from a second cast at the same station, using a different sampling bottle. An analysis of hydrographic data from this station suggests that the water mass at 2 000 m probably does not originate north of this site, where nutrient concentrations are lower. It is more likely that this water originated in the South Atlantic along the African coast (Fig. 3). We do not have sufficient information to explain the observed Pb increase at this depth.

The most important feature of the Pb profiles from this transect is the systematic decrease of Pb concentrations



Figures 2

Total Pb measured by ASV at each of the Fluxatlante stations. Pb concentration data are presented on the same scale.
Pb total mesuré par ASV à chaque station. Les concentrations sont à la même échelle pour chaque figure.

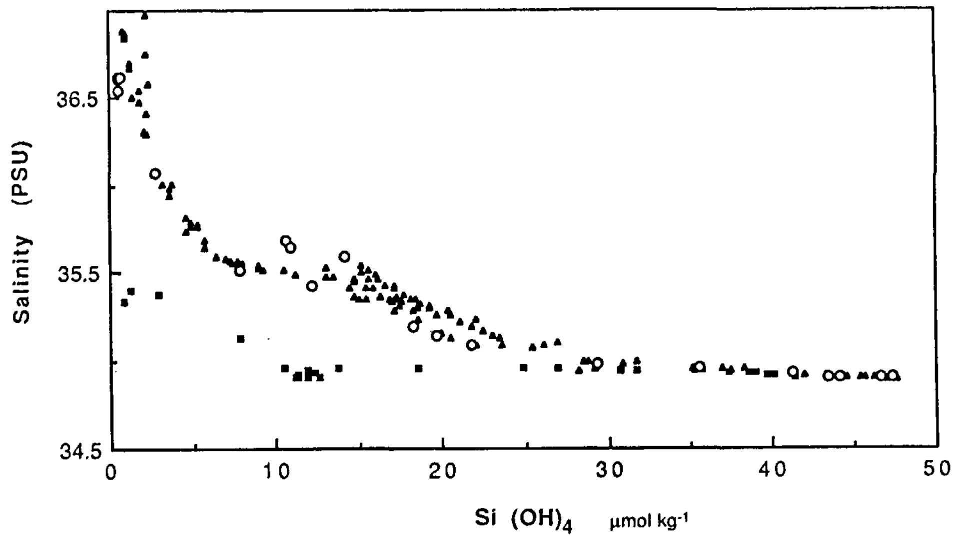


Figure 3

Salinity *versus* silicate are represented for: ■ TTO Atlantic north-east stations 119, 120; ▲ TTO Atlantic stations along the African Coast (71, 72, 76, 77, 78, 80, 81, 82); ○ Fluxatlante station 5 clearly belongs to this group.
■ Salinité et Si(OH)4 pour les stations TTO NE Atlantique 119,120 ; ▲ TTO le long de la côte africaine 71,72,76,77,78,80,81,82) ; ○ la station 5 Fluxatlante appartient clairement à ce groupe.

at all depths, proceeding from the shelf to the open ocean. To accentuate this point, the integrated Pb in the water column between the surface and 2 500 m is 7.9 µg cm^{-2} at station 8; 6.8 µg cm^{-2} at station 7; 5.6 µg cm^{-2} at station 6 and 5.2 µg cm^{-2} at station 5.

Stations influenced by the Mediterranean outflow

Like the station nearest to the French coast (station 8), closest to the Portuguese coast (station 2, Fig. 4 *a*) shows relatively high Pb concentrations throughout the water column and an integrated total Pb content of 7.5 µg cm^{-2}. Anomalously high concentrations of heavy metals along this coast and in the Bay of Cadiz have been observed by Van Geen *et al.* (1988). Station 2 has especially high concentrations of Pb in surface waters (60 ng l^{-1}). There is an obvious influence from the coast: Van Geen (pers. comm.) observed up to 94 ng l^{-1} Pb on the Spanish coast for surface waters of salinity S = 36.20.

Stations 3 and 4 exhibit the influence of Mediterranean outflow water (Fig. 4 *b* and *c*). At station 3, the Mediterranean outflow influence is apparent in high salinities and temperatures measured between 800 - 1 200 m (Fig. 5). These waters also exhibit lower nutrients than the interleaving Atlantic intermediate waters. Station 4 is further away from Gibraltar than station 3 but has higher Pb concentrations in the Mediterranean- influenced waters. This observation is consistent with the mid-depth salinity and temperature anomalies which are higher here (Fig. 6) than at station 3, revealing the presence of a lens of Mediterranean water; a Meddy with characteristics similar to those observed during the Transient Tracers in the Ocean (TTO) programme and by Armi *et al.* (1988).

This particular lens is made up of two different masses: the core at 800 -1 200 m and another highly saline but colder water mass above (300 - 800 m). A comparison of T, S and nutrient data from this study with TTO observations from the same area shows that the water at 300-800 m probably originates from the Gulf of Cadiz (Fig. 7), where it has been suggested that Meddies originate (Armi, 1988). Meddies with such double features seem to be common in the water column in this area (Armi and Zenk, 1984). Swallow (1969), first developed a hypothesis that they are created by Mediterranean waters which take different routes (canyons) when they leave Gibraltar.

Pb levels at stations 3 and 4 are lower in surface waters than at station 2 (45 ng l^{-1} compared to 60 ng l^{-1}), and decrease below the mixed layer and below the Mediterranean outflow (Fig. 4 *b* and *c*). At station 3, Pb concentrations within the Mediterranean outflow are 30 % greater than those predicted from the decreasing trend with depth (Fig. 4 *b*). These elevated Pb levels are correlated to the hydrographic structure of the Mediterranean outflow at this station (Fig. 5). At station 4, high Pb concentrations are associated with both parts of the lens, reaching 55 ng l^{-1} in the upper part (Fig. 4 *c*). By 1 700 m, Pb concentrations are similar to the concentrations at other stations. The presence of Mediterranean waters affects the total Pb inventory from surface to 2 500 m at both stations (5.8 µg.cm^{-2} at station 3 and 8.7 at station 4) compared to the other open ocean stations 5 and 6 (5.2 and 5.6 µg.cm^{-2}).

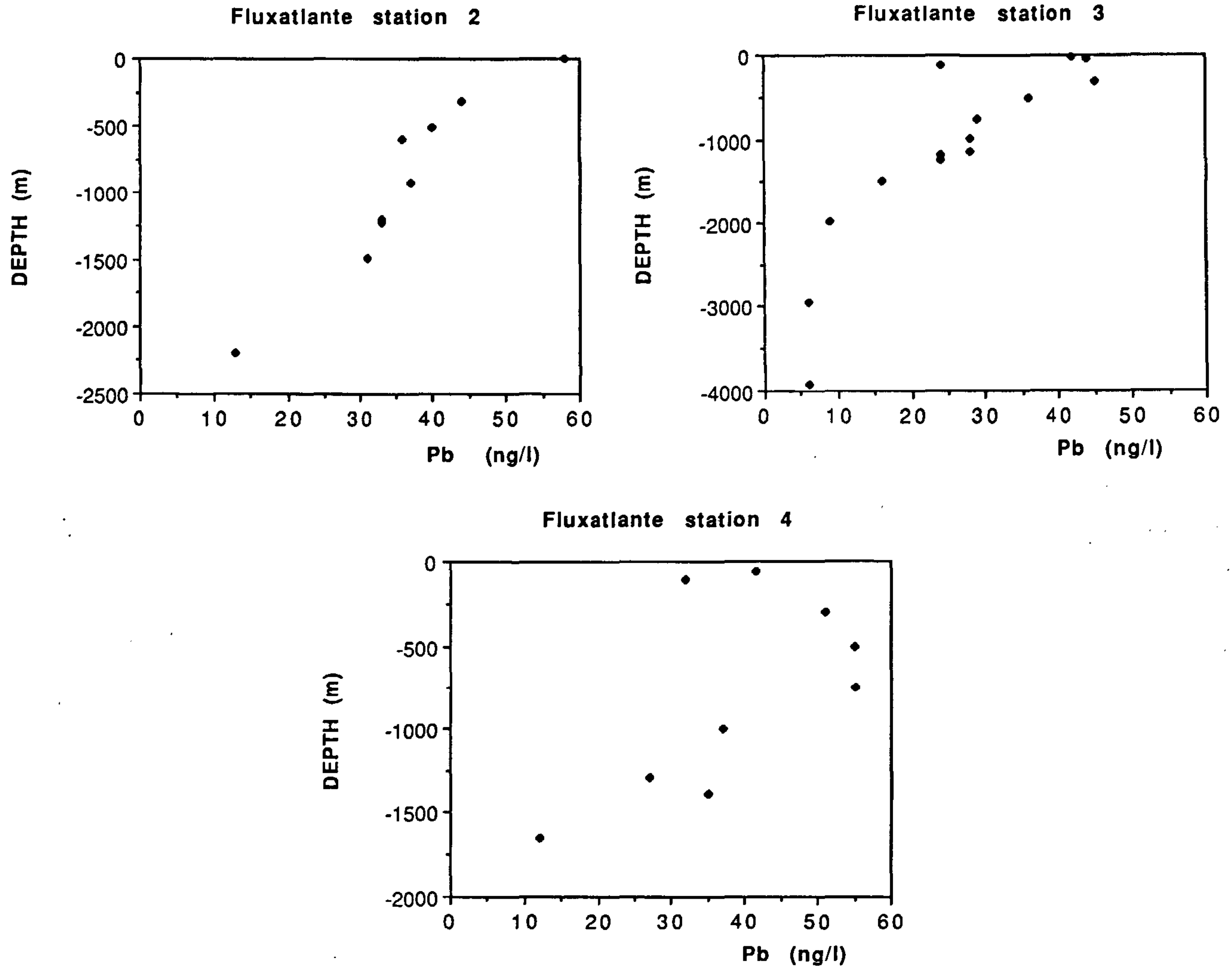


Figure 4

Total Pb measured by ASV at each of the Fluxatlante stations. Pb concentration data are presented on the same scale.
Pb total mesuré par ASV à chaque station. Les concentrations sont à la même échelle pour chaque figure.

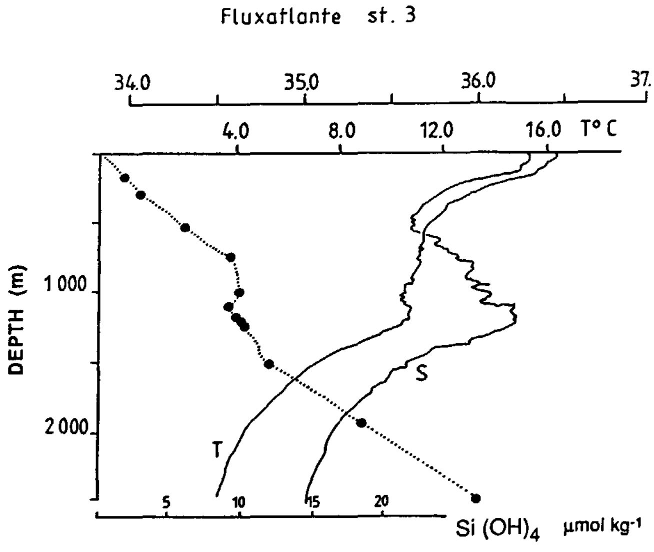


Figure 5

Temperature and salinity CTD profiles and $Si(OH)_4$ of Fluxatlante station 3 indicate the presence of Mediterranean waters.
Les profils de température, salinité et $Si(OH)_4$ à la station 3 Fluxatlante indiquent la présence des eaux Méditerrannéennes.

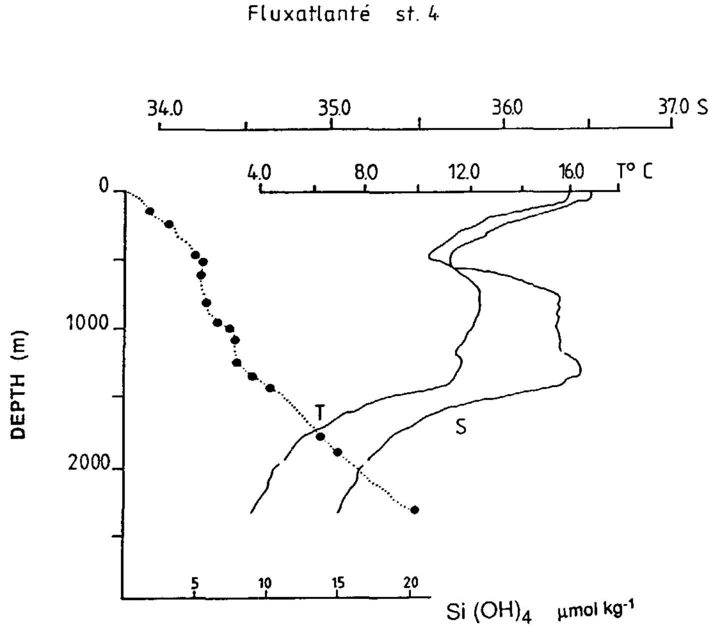


Figure 6

*Temperature and salinity CTD profiles and $Si(OH)_4$ of Fluxatlante station 4 indicate the presence of Mediterranean waters between 800 and 1 200 m. Above this, another part of this lens of water has characteristics similar to that of the Gulf of Cadiz (*see *Fig. 7).*
A la station 4, les profils de temparature, salinité et $Si(OH)_4$ indiquent la présence d'eaux méditerranéennes entre 800 et 1 200 m. Au-dessus de cette masse d'eau, une autre partie de la lentille a des caractéristiques proches de celles du Golfe de Cadix (fig. 7).

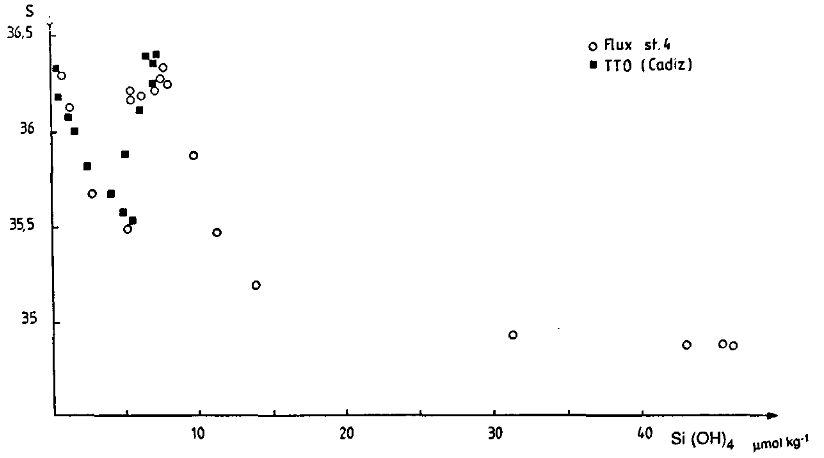


Figure 7

TTO $Si(OH)_4$: salinity relationship in the Gulf of Cadiz for a 800 m depth station, compared to Fluxatlante station 4 upper lens of water.
Relation $Si(OH)_4$: salinité pour une station dans le Golfe de Cadix à 800 m de profondeur comparée aux données de la station 4 Fluxatlante.

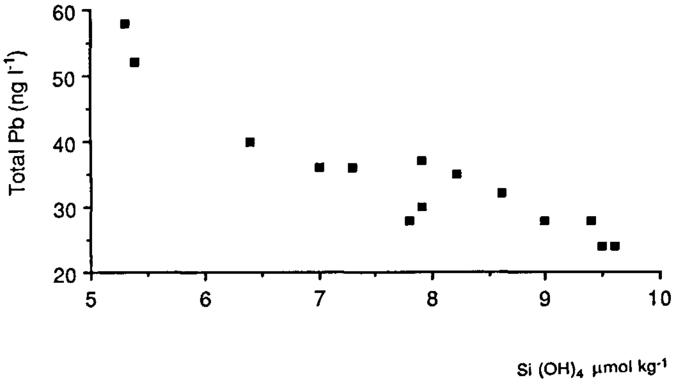


Figure 8

$Si(OH)_4$ and total Pb relationship in the Mediterranean outflow (maximum salinity waters).
Relation entre la salinité et $Si(OH)_4$ dans les eaux atlantiques méditerranéennes pour le maximum de salinité.

DISCUSSION

The overall distribution of Pb found at these sites is comparable to those observed at other locations, with a maximum in surface waters reflecting aeolian input and a progressive decrease of concentration with depth as a result of vertical mixing and scavenging of dissolved Pb by particles (Schaule and Patterson, 1981; Bruland, 1983). The advection of Mediterranean waters between 700 m and 1 500 m is responsible for anomalously high Pb concentrations at mid-depth on the order of 20-30 %. This observation is consistent with the fact that Mediterranean waters are very enriched in Pb (at Gibraltar Pb = 40 ng.l^{-1} for S = 36.5, Laumond *et al.*, 1984; Copin-Montégut *et al.*, 1986). Pb and silicate concentrations in Mediterranean outflow waters from stations 2 to 5 (500 to 1 200 m, high salinity) seem to be correlated (Fig. 8) suggesting that Pb in these waters behaves conservatively on the time scale of transport from Gibraltar. With an average horizontal velocity of 3 cm s^{-1}, transport over this distance would take about two years; apparently no more than a few percent of the total Pb inventory is scavenged from deep waters during this time.

We also observed a general decrease in surface Pb concentrations away from the shelf which is consistent with a westward decrease in Pb atmospheric input. This trend seems to support the observation that total atmospheric lead deposition is controlled by wet deposition (Buat-Ménard, 1986). In other words, the frequency of rains over the Atlantic is the major control on Pb deposition. Furthermore, this process is most influential nearest the coast where atmospheric Pb levels are the highest. This same effect has been demonstrated off the North American coast by Whelpdale *et al.* (1988) for SO_4. This process would result in a gradient in Pb surface water concentrations which would then be sustained by southwards surface water mass circulation along the transect.

Comparison with other data from the North Atlantic clearly shows that Pb concentrations are much higher in the northeastern Atlantic (in 1985) than in the northwestern Atlantic. Between 1979 and 1984, surface concentrations ranged between 20 - 31 ng.l^{-1} Pb at Bermuda (Schaule and Patterson, 1983; Boyle *et al.*, 1986), much lower than surface concentrations measured here in the eastern Atlantic (35- 45 ng.l^{-1}). This contrast can be enlighten by comparing surface concentrations in the same latitude range: 30°- 40°N. In 1980, surface waters in the western Atlantic (Boyle and Huested, 1983) exhibited low Pb concentrations ranging between 17 and 30 ng.l^{-1}. The Pb inventory of the western Atlantic measured in 1979 and 1984 (Boyle *et al.*, 1986) was 4 µg cm^{-2}, lower than values presented here. A comparison of mean Pb atmospheric fluxes calculated over the northwestern and northeastern Atlantic (Véron, 1988) is shown in the Table for the years 1980-1985. Surface inventories of Pb in the mixed layer (80 - 100 m depth) vary between regions (Tab.). Stations 3, 4, 5 are characterized by a well-mixed surface layer, whose thickness is 80 to 100 m. Pb inventories for these stations are shown in the same table. If we couple these inventories to an average atmospheric input over the northeast Atlantic of 360 ± 120 ng.cm^{-2}.yr^{-1} (Véron, 1988), a residence time of 1.1 ± 0.2 year is calculated for the surface mixed layer, in agreement with the general assessment of Pb residence time, as discussed by Boyle *et al.* (1986) for the Sargasso Sea and assessed for ^{210}Pb by Bacon *et al.* (1976) and Nozaki *et al.* (1976). These results are also consistent with the fact that the northwestern Atlantic fluxes are now much smaller than those of Eastern Atlantic reflecting the effect of national policies on the phasing out of lead in gasoline.

Table

Comparison of mean Pb atmospheric fluxes calculated over the northwestern and northeastern Atlantic (1980-1985).

Flux atmosphériques moyens comparés dans l'Atlantique du Nord-Ouest et du Nord-Est (1980-1985).

	Western Atlantic	Eastern Atlantic
Atmospheric input		
Pb ng.cm^{-2}.y^{-1}	160(1983)	360 ± 120 (1985)
ref	(1)	(2)
Surface water inventory		370 (station 3)
(mixed layer)	130(1980)	370 (station 4)
Pb ng.cm^{-2}	220(1980)	420 (station 5)
ref.	(3)	(this work)
Water column inventory		
Pb µg.cm^{-2}	4	5 - 7

(1) Jickells *et al.* (1984; 1987)
(2) Véron (1988)
(3) Boyle *et al.* (1986)

We believe that the contrast between Pb concentrations in the eastern and western North Atlantic reflects differences in atmospheric Pb inputs. The profiles in the eastern and western North Atlantic are consistent with the same residence time for Pb in surface waters. While the difference between eastern and western inputs has increased steadily since 1985, because the use of Pb in gasoline has decreased faster in the US than in Europe, this situation is expected to change soon with the application of new European regulations.

Acknowledgements

We acknowledge the help of the captain and crew of R/V *Le Suroît*. We are grateful to A. Van Geen, R. Sherrel and A. Isley for helpful discussions and comments and to C. Chaumery for his help during the cruise. This work was done with grants from the CNRS ATP "Chimie Marine" and PIROCEAN (now CNRS-INSU).

REFERENCES

Armi L., D. Hebert, N. Oakey, J. Price, P.L. Richardson, T. Rossby and B. Ruddik (1988). The history and decay of a Mediterranean salt lens. *Nature*, **333**, 649-651.

L. Armi and W. Zenk (1984). Large lenses of highly saline Mediterranean water. *J. phys. Oceanogr.*, **14**, 1560-1576.

Bacon M.P., D.W. Spencer and P.G. Brewer (1976). ^{210}Pb/^{226}Ra and 210Po/210Pb disequilibrium in seawater and suspended particulate matter. *Earth planet. Sci. Letts*, **32**, 277-296.

Berman S.S., R.E. Sturgeon, J.A.H. Desaulniers and A.P. Mykytink (1983). Preparation of seawater reference material for trace metals, NASS-1. *Mar. Pollut. Bull.*, **14**, 2, 69-73.

Boyle E.A. and S. Huested (1983). Aspects of the surface distributions of copper, nickel cadmium and lead in the North Atlantic and the North Pacific, in: *Trace Metals in seawater*, C.S. Wong, E.A. Boyle, K. Bruland, D. Burton and E.D. Goldberg, editors, NATO Series, Plenum Press, New York.

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 Publ. Co., Dordrecht, 477-496.

Copin-Montégut G., P. Courau and E. Nicolas (1986). Distribution and transfer of trace elements in the Western Mediterranean. *Mar. Chem.*, **18**, 189-195.

Flegal A.R. and Patterson C.C. (1983) Vertical concentration profiles of lead in the Central Pacific at 15°N and 20°S, *Earth planet. Sci. Letts*, **64**, 19-32.

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 Geochem. Cycles*, **2**, 117-130.

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

Laumond F., G. Copin-Montégut, P. Courau and E. Nicolas (1984). Cadmium copper and lead in the Western Mediterranean Sea, *Mar. Chem.*, **15**, 251-261.

Nicolas E. (1985). Application de la redissolution anodique impulsionnelle sur électrode tournante au dosage des ultra-traces Cd, Pb, Cu dans l'eau de mer, in: *Journées d'électrochimie, Florence, Université de Florence.*

Nozaki Y., J. Thomson and K.K. Turekian (1976). The distribution of ^{210}Pb and ^{210}Po in the surface waters of the Pacific Ocean. *Earth planet. Sci. Letts* **32**, 304-312.

Nriagu J. (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, *Nature*, **279**,409-411.

Patterson C.C. and D.M. Settle (1987). Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale. *Mar. Chem.*, **22**, 137-162.

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.

Schaule B.K. and C.C. Patterson (1983). Perturbations of the natural lead profile in the Sargasso sea by industrial lead, in: *Trace Metals in seawater*, C.S. Wong, E.A. Boyle, K. Bruland, D. Burton and E.D. Goldberg, editors, NATO Series, Plenum Press, New York.

Swallow J.C. (1969). A deep eddy off Cape St Vincent. *Deep-Sea Res., Suppl.*, **16**, 285-295.

TTO, Transient Tracers in the Ocean, North Atlantic study, Shipboard physical and chemical data report (1981) Scripps Institution of Oceanography (SIO), University of California, San Diego.

Van Geen A., P. Rosener and E. Boyle (1988). Entrainment of trace metal enriched Atlantic shelf water in the inflow to the Mediterranean Sea. *Nature*, **331**, 423-426.

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.*

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