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# Invasion of the abyssal North Atlantic by modern anthropogenic lead

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**Abstract.** While anthropogenic emissions have dramatically elevated lead concentrations in the North Atlantic troposphere and surface waters by orders of magnitude above natural levels [Murozumi et al., 1969; Schaule and Patterson, 1983; Boyle et al., 1986], it has been assumed that the relatively low lead levels in North Atlantic abyssal waters are not yet contaminated [Schaule and Patterson, 1981; Flegal and Patterson, 1983]. That misperception is redressed by the following stable lead isotopic composition data which reveal the advective transport of industrial lead into those deep basin waters through the formation of North Atlantic Deep Water (NADW). Additionally, spatial gradients in the isotopic signatures of anthropogenic lead within the North Atlantic abyss appear to serve as transient tracers of contaminant penetration rates.

Stable lead isotopic compositions, along with total lead concentrations, were analyzed in sea water samples collected during a suite of cruises in the far North Atlantic (IOC-II, 1993), western North Atlantic (OFP-BATS cruise, 1997), North African basins (MED-II, 1989 and EU-III, 1991), and equatorial North Atlantic (IOC-III, 1996). The samples were collected in modified Go-Flos$^{R}$; lead was concentrated by organic or resin extraction (chloroform/dithizone or Chelex-AG1X8 resin), using established trace metal clean techniques in HEPA filtered laboratories (blanks account for less than 3% of total lead analyzed for each sample). Stable lead isotopic ratios were measured by thermal ionization mass spectrometry (VG 5430), concurrently calibrated with NIST SRM 981. The lead concentrations of all the deep water samples, which ranged from 20 to 40 pM in the far North Atlantic and 30 to 60 pM in the deep North African basins, were oceanographically consistent with concentrations previously measured in deep waters near Bermuda [Schaule and Patterson, 1983] (25 to 45 pM) and Gibraltar [Lambert et al., 1991] (30 to 60 pM). All the isotopic compositions reported in Table 1 correspond to water samples from the NADW, as clearly identified by T/S diagrams [Worthington and Wright, 1970; Schmitz and McCartney, 1993].

While the $^{206}Pb/^{207}Pb$ ratios of those deep waters vary widely, from 1.154 to 1.187 (Fig. 1), all ratios are associated with various industrial lead emissions. Their anthropogenic origins are illustrated by the conformation of stable lead isotopic compositions ($^{206}Pb/^{207}Pb$: $^{208}Pb/^{206}Pb$) of abyssal ocean waters within the range of recent (< 15 years) industrial lead aerosols in the North Atlantic troposphere, which are markedly distinct from the isotopic compositions of preindustrial crustal lead in North Atlantic Holocene sediments (Fig. 2). Consequently, these data corroborate recent reports of the thermohaline ventilation of contaminant lead in the North Atlantic [Shen and Boyle, 1988; Véron et al., 1993], and they belie the earlier assumption that the aeolian fallout of industrial lead had not yet contaminated the deepest waters in the North Atlantic [Schaule and Patterson, 1983].

That assumption was, partially, based on the high partition coefficient (Kd ~ $10^5$) of lead in sea water [Kozelka et al., 1997], which accounts for the extensive scavenging of aeolian lead inputs in oceanic surface waters. The effective removal of industrial lead from the water column was further evidenced by the presence of particulate lead contamination in surficial abyssal sediments [Véron et al., 1987; Hamelin et al., 1990]. Therefore, initial observations of relatively conservative profiles of low lead concentrations in North Atlantic deep waters [Schaule and Patterson, 1983; Flegal and Patterson, 1983] were erroneously attributed to both the negligible remineralization of lead in deep oceanic waters and the inconsequential advection of lead along isopycnal horizons to those depths.

Although recent isotopic analyses in the North Atlantic attest to the negligible remineralization of lead in deep waters, they indicate the advection of lead along isopycnal horizons is much greater than originally assumed. The former is shown by the consistency of $^{206}Pb/^{207}Pb$ ratios of particulates collected in sediment traps at 1000 m (1.179 ± 0.003) and 2500m (1.181 ± 0.005) with those of overlaying surface waters (1.179 ± 0.003) in the equatorial North Atlantic (EU-III). The radiogenic signature found in these settling particles reflects the anthropogenic US emission since the late 1970's [Hamelin et al., 1997]. The deep advective transport is shown by the disparity between those particulates and the NADW (1.156 ± 0.012) at

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**Table 1.** Seawater sampling (Go-Flo bottles) and lead extraction (chloroform/dithizone or Chelex-AG1X8 resin) procedures were performed using established clean techniques [Schaule and Patterson, 1981; Flegal and Patterson, 1983] in HEPA filtered clean laboratories. Ratios of stable lead isotopes determined by thermal ionisation mass spectrometry (VG5430) were corrected using a SRM 981. Measured lead concentrations range from 20 to 40pM in the far North Atlantic and 30 to 60pM in the deep North African basins. They are similar to the only other deep samples reported in the North Atlantic near Bermuda [Schaule and Patterson, 1983] (25 to 45pM) and near Gibraltar [Lambert et al., 1991] (30 to 60pM). Here we only report lead isotope to demonstrate the penetration of pollutant lead into the North Atlantic Deep Waters (NADW) identified by T-S diagrams during the cruises [Worthington and Wright, 1970; Schmitz and McCartney, 1993]. ND and SD represent Non Determined ratios and the Standard Deviation of each ratio.

| Stations | Depth (m) | $^{206}Pb/^{204}Pb$ | SD | $^{206}Pb/^{207}Pb$ | SD | $^{208}Pb/^{206}Pb$ | SD |
|---|---|---|---|---|---|---|---|
| FAR NORTH ATLANTIC BASINS | | | | | | | |
| IOC II - 2 | 1410 | 18.75 | 0.06 | 1.197 | 0.007 | ND | |
| 54°30N; 48°30W | 2430 | 18.54 | 0.07 | 1.184 | 0.000 | ND | |
| | 3155 | 18.73 | 0.13 | 1.191 | 0.001 | 2.059 | 0.001 |
| IOC II - 11 | 782 | 18.66 | 0.33 | 1.181 | 0.001 | 2.072 | 0.003 |
| 65°16N; 30°24W | 1330 | ND | | 1.184 | 0.006 | 2.062 | 0.009 |
| | 1374 | ND | | 1.179 | 0.004 | 2.072 | 0.005 |
| IOC II - 13 | 2080 | 18.26 | 0.37 | 1.174 | 0.002 | ND | |
| 64°48N, 06°12E | 3065 | 18.35 | 0.10 | 1.177 | 0.001 | 2.075 | 0.001 |
| | 3732 | 18.48 | 0.38 | 1.174 | 0.002 | 2.080 | 0.004 |
| IOC II - 7 | 2563 | 18.50 | 0.34 | 1.184 | 0.002 | 2.068 | 0.003 |
| 63°42N; 33°00W | 2617 | 18.49 | 0.01 | 1.183 | 0.001 | ND | |
| | 2661 | 18.45 | 0.20 | 1.182 | 0.001 | 2.071 | 0.002 |
| IOC II - 12 | 298 | 18.29 | 0.47 | 1.178 | 0.002 | 2 075 | 0.004 |
| 68°12N; 22°42W | 992 | 18.37 | 0.41 | 1.178 | 0.003 | 2.072 | 0.004 |
| NORTH AMERICAN BASIN | | | | | | | |
| OFP - BATS | 2020 | 18.47 | 0.04 | 1.183 | 0.000 | 2.072 | 0.000 |
| 31°40N; 64°10W | 2400 | 18.47 | 0.19 | 1.189 | 0.001 | 2.063 | 0.002 |
| | 2950 | 18.64 | 0.17 | 1.189 | 0.001 | 2.059 | 0.002 |
| | 3300 | 18.47 | 0.13 | 1.186 | 0.001 | 2.065 | 0.001 |
| NORTH AFRICAN BASIN | | | | | | | |
| EU III | 2000 | 18.26 | 0.06 | 1.169 | 0.001 | 2.087 | 0.001 |
| 21°04N; 31°09W | 2500 | 17 95 | 0.07 | 1.152 | 0.000 | 2.104 | 0.001 |
| | 3000 | 17 83 | 0.04 | 1.146 | 0.000 | 2 112 | 0.001 |
| MED II | 2000 | 18.14 | 0.08 | 1.165 | 0.001 | 2.088 | 0.000 |
| 36°20N; 16°00W | 2500 | 18.09 | 0.02 | 1.160 | 0.000 | 2.098 | 0.000 |
| EQUATORIAL BASIN | | | | | | | |
| IOC III - 6 | 2900 | 18.12 | 0.10 | 1.164 | 0.000 | 2.087 | 0.001 |
| 8°00N; 45°00W | 3300 | 18 04 | 0.03 | 1.155 | 0.000 | 2.103 | 0.001 |
| | 4100 | 17.76 | 0.13 | 1.144 | 0.001 | 2 113 | 0.001 |

ND and SD represent Non Determined ratios and the Standard Deviation of each ratio.

that location (Fig. 1). Based on that isotopic disequilibrium, we do not expect a large impact of the short residence time particulate lead (months) by remineralization into the long residence time dissolved fraction (centuries). Then, the penetration of industrial lead into the North Atlantic abyss is primarily associated with the thermohaline circulation of NADW.

Moreover, the previously noted variations in stable lead isotopic compositions among NADW within the North Atlantic (Fig.1) indicate those ratios may be used as transient tracers of thermohaline circulation in deep ocean realms. For example, the isotopic signatures of lead in the deep waters of the North African ($1.146 < ^{206}Pb/^{207}Pb < 1.169$) and Equatorial ($1.144 < ^{206}Pb/^{207}Pb < 1.165$) basins are less radiogenic than those in the northwestern basin ($1.183 < ^{206}Pb/^{207}Pb < 1.189$), which corresponds with the isotopic signatures of more recent industrial lead emissions. The latter temporal variations are illustrated in Figure 3, which shows the relatively systematic evolution in predominant $^{206}Pb/^{207}Pb$ ratios of anthropogenic lead emissions to the North Atlantic troposphere over this century, derived from analyses of source loading [Wu and Boyle, 1997] and isotopic compositions of corals [Shen and Boyle, 1987], coastal marine sediments [Shirahata et al., 1980], ice cores [Rosman et al., 1993], and aerosols [Chow et al., 1975; Sturges and Barrie, 1987; Church et al., 1990; Véron et al., 1992]. The lead isotopic ratios have undergone a transient along with the time-variant legislation to delead gasoline in the USA (mid 70's) and more recently in western Europe (mid 80's). Prior to this phasing out, the isotopic signature of anthropogenic lead in the USA was altered by increasing use of lead ores from Missouri mines (US Bureau of Mines, 1962-1976) that are characterized by rather high $^{206}Pb/^{207}Pb$ ratios of 1.28-1.33. As a consequence, industrial $^{206}Pb/^{207}Pb$ ratios have evolved from 1.14-1.16 in the 60's to 1.22-1.24 in the 80's (Fig. 3). The isotopic evolution shown in Figure 3 can then be used as a time index for the recharge of the deep waters from the atmosphere.

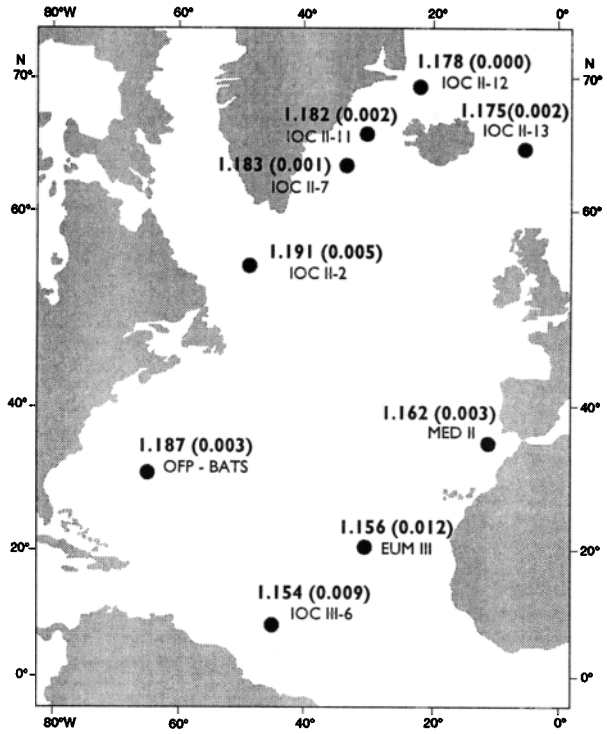


**FIG. 1.** Stations occupied as part of the IOC (International Oceanographic Commission, IOC II-1993 and III-1996), MEDATLANTE (MED II - 1989), EUMELI (EU III - 1991), OFP-BATS (1997) cruises. Average $^{206}Pb/^{207}Pb$ ratios measured in bulk seawater are reported that correspond to measurements in the far North Atlantic (source waters of the NADW) and in the NADW from the North American, North African and Equatorial basins. SD corresponds to the Standard Deviation of the mean $^{206}Pb/^{207}Pb$ ratios calculated at each deep station.

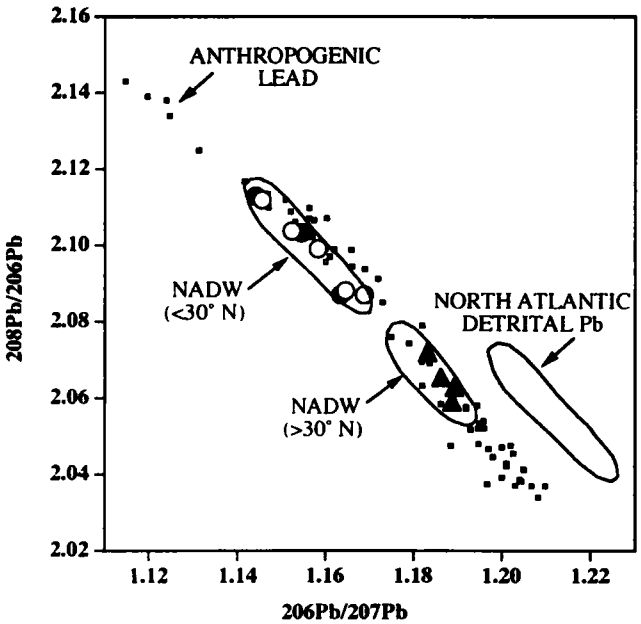


**FIG. 2.** Plot of $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ ratios of deep water samples collected during the North Atlantic cruises along with atmospheric anthropogenic lead (these aerosols sampled over the North Atlantic basin illustrate the range of recent pollutant lead isotopic signature) [Church et al., 1990; Véron et al., 1992; Hamelin et al., 1997; Véron and Church, 1997] (small open square), natural sedimentary from the North Atlantic (grey area) [Sun, 1980] and NADW (North American basin: closed triangle; North African basin: open circle; Equatorial basin: closed circle).

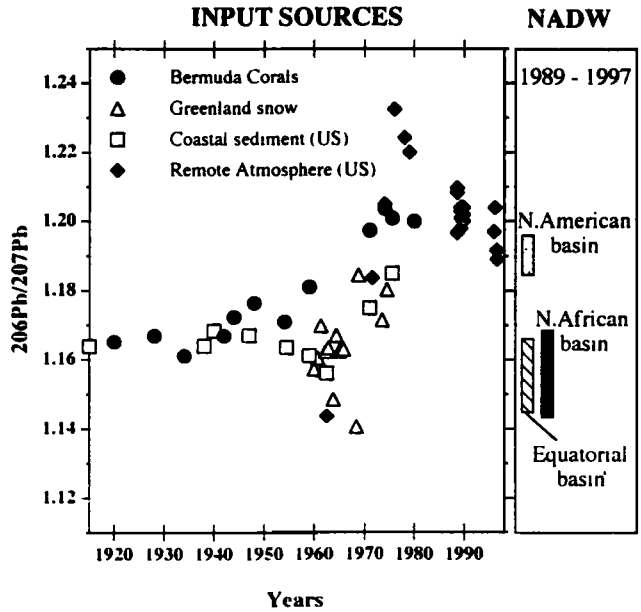


**FIG. 3.** Evolution of the industrial $^{206}Pb/^{207}Pb$ ratios in the USA troposphere for the past 70 years. Data are reported from coastal sediments (corrected for detrital contribution) [Shirahata et al., 1980], from aerosols collected in remote troposphere under the influence of USA temperate westerlies [Chow et al., 1975; Sturges and Barrie, 1987; Church et al., 1990; Véron et al., 1992] as well as for Greenland ice core [Rosman et al., 1993]. These results compare well to industrial $^{206}Pb/^{207}Pb$ ratios from Bermuda corals (as corrected for detrital contribution) [Shen and Boyle, 1987].

Assuming temporal variations in those isotopic signatures are characteristic of aeolian lead inputs to NADW source waters, penetration rates of NADW into North Atlantic basins may be determined by the isotopic composition of abyssal waters. Specifically, the NADW in the western North Atlantic basins (OFP-BATS and IOC-II) appears to have been formed approximately 20 years ago, since its $^{206}Pb/^{207}Pb$ ratios correspond with those of industrial lead emissions in the 1980s, and the NADW in the North African (MED-II, EU-III) and equatorial (IOC-III) basins appears to have been formed 30-50 years ago, since their $^{206}Pb/^{207}Pb$ ratios correspond with those of industrial lead emissions in the 1960's. Notably, both of those estimates are consistent with other, independent estimates of abyssal thermohaline ventilation rates based on $^{3}H$ (Western North Atlantic basins: 10-40 years) [Doney and Jenkins, 1994] and CFCs (UNADW in Equatorial region: 20-40 years) [Weiss et al., 1985; Smethie, 1993; Andrié et al., 1998].

Here, we demonstrate that lead encountered in the North Atlantic abyss originates from North American emissions of pollutant lead prior to the 70's. Further resolution of the penetration rates of this contaminant lead can be derived from subsequent isotopic analyses of NADW. This is evidenced by the relation between the pronounced temporal evolution of industrial lead imprint in the atmosphere and the spatial variations of NADW isotopic signatures in the northwestern and central basins of the North Atlantic.

The $^{206}Pb/^{207}Pb$ ratios of newly formed NADW in the far North Atlantic vary from 1.175±0.002 (ISOW) to 1.182±0.002 (DSOW) and 1.191±0.005 (LSW) (Fig. 1). These ratios are significantly different from recent USA signature ($1.195 < ^{206}Pb/^{207}Pb < 1.210$) [Chow et al., 1975; Sturges and Barrie, 1987] (Fig. 3) and like recent ice records [Rosman et al.,

1993], reflect mixing with less radiogenic western European emissions ($1.112 < {}^{206}Pb/{}^{207}Pb < 1.152$) [Chow et al., 1975; Sturges and Barrie, 1987; Véron and Church, 1997] owing to the phasing out of leaded gasoline in the US. Therefore, in the future, one can expect stable lead isotopes to continue both to uniquely fingerprint geographic sources of lead, and associated contaminants, and to trace transient fluxes of those contaminants into the abyssal North Atlantic over decadal scales.

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