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Isotopic evidence of contaminant lead in the South Atlantic troposphere and surface waters

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Abstract

The third Intergovernmental Oceanographic Commission (IOC) Baseline Contaminant cruise (May–June 1996) has established the first lead isotopic compositions in the surface water and the atmosphere of the Equatorial and South Atlantic Ocean. These ratios have evidenced both anthropogenic and natural origins of lead along the cruise transect (from 33°S to 10°N). The isotopic gradients tentatively have been, attributed to aeolian as well as surface-water advective inputs from a suite of rather local and remote sources to the Southern Hemisphere. Relatively low $^{206}Pb/^{207}Pb$ ratios (x ± sd) were encountered within the South Equatorial Current between 17°S and 5°S (1.156 ± 0.003). Those were bracketed by more radiogenic ratios at higher latitudes in the Southern Hemisphere (33°S to 23°S), within the Brazil Current and the Subtropical Gyre (1.163 ± 0.003), and in the Northern Hemisphere (0° to 10°N) (1.165 ± 0.005). The latter were comparable to ratios of surface water in the North Atlantic Equatorial Ocean (1.169 ± 0.006), under a combined contaminant influence of both North American westerlies (1.19–1.20) and European easterlies (1.155–1.165). That predominance of contaminant lead contrasts with the measurable presence of natural lead in surface waters of the Equatorial Ocean, which are attributed to aeolian inputs of Saharan dust. The ratios of lead in surface waters at higher latitudes in the South Atlantic are characteristic of anthropogenic lead aerosols also detected in Antarctic ice, and could substantiate as well the hypothesized aerosol recycling of lead by sea-spray emission in the far Southern Hemisphere. The atmospheric lead isotopic compositions ($^{206}Pb/^{207}Pb$) in bulk depositions (1.171 ± 0.006), precipitation (1.171 ± 0.006) and aerosols (1.168 ± 0.011) were, generally, more radiogenic than the surface waters (1.162 ± 0.005). Beside a poor representation of a short term atmospheric sampling, this difference could reflect a recent evolution in atmospheric lead emissions, which have not yet been reflected in oceanic surface waters. It may also be due, in part, to advective lead inputs from surface oceanic circulation of the South Equatorial Current. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Most heavy metal cycles in the ocean have been perturbed by atmospheric deposition from anthropogenic origins (Jickells et al., 1984; Maring et al., 1989; Duce et al., 1991). Studies of those contaminant metal sources, their transport dynamics, and their fates in the ocean in turn have, provided a better understanding of their impact on other global biogeochemical cycles (e.g., Morel et al., 1991). This is particularly true for lead, which, with its elevated concentrations and stable isotopes, has been used to deconvolute atmospheric metal sources (Schaule and Patterson, 1981; Church et al., 1990; Véron et al., 1992,1994,1998) and resolve exchange processes between dissolved and particulate fractions within the water column in the North Atlantic (e.g., Sherrell et al., 1992; Hamelin et al., 1997).

We recently have shown on a previous IOC cruise that lead can be used as a transient tracer of the invasion of the North Atlantic Deep Waters (NADW) by contaminant metals (Véron et al., 1999; Alleman et al., 1999). Presumably less anthropogenic lead should be found in the South Atlantic, because being surrounded by fewer industrialized countries and previously reported lead concentrations in its atmosphere (Maenhaut et al., 1979; Chester et al., 1983; Volkening et al., 1988; Volkening and Heumann, 1990; Radlein and Heumann, 1992), surface waters (Westerlund and Ohman, 1991; Helmers and Rutgers van der Loeff, 1993; Helmers and Schrems, 1995), and Antarctic ice (Dick and Peel, 1985; Boutron and Patterson, 1987; Suttie and Wolff, 1993; Wolff and Suttie, 1994) are relatively low. However, Nriagu et al. (1996) pointed out that in many developing countries from the Southern Hemisphere, the automobile tailpipe is still a major source of lead pollution, inducing high atmospheric lead concentrations in urban areas comparable to the levels in developed countries prior to the pollution control. Moreover, the sampling, extraction, and analytical techniques only recently have improved sufficiently to allow measurements of very low lead concentrations in relatively remote atmospheres and pristine sea waters. Those techniques have been incorporated only in a few measurements of lead isotopic compositions in surface waters of the South Atlantic Ocean (60° South) (Flegal et al., 1993) and snows in Antarctica (e.g., Rosman et al., 1994; Rosman et al., 1998).

Therefore, our objective in this study was to establish baseline signatures for lead isotopes in surface waters of the South Atlantic that could be used for future studies of contaminant lead invasion. Those signatures for both the atmosphere and the surface waters of the South Atlantic are presented in this initial report on samples collected during the third Intergovernmental Oceanographic Commission (IOC) Baseline Contaminant cruise (May–June, 1996), described by Cutter and Measures (1999).

2. Materials and methods

Surface sea-water sampling (Table 1) were performed during the third IOC cruise on the R/V Knorr from Uruguay to Barbados from May to June 1996 (Fig. 1). Surface-water samples were collected with a "fish sampler" laterally towed at the surface and connected to a peristaltic pump through an acid-clean Teflon-lined polyethylene tubing (Cutter and Measures, 1999). Subsurface samples were collected at five stations between 33°S and 10°N to characterize key water masses (Antarctic Bottom Water, North Atlantic Deep Water, Circum-Polar Deep Water, Antarctic

Table 1
Lead isotopic compositions (St. Dev: two standard deviations for a single measurement) of the surface sea water sampled with an underway towed "Fish" sampler during the IOC-III cruise (May–June 1996) from 33°S to 10°N

Samples (Location)	Date	Distance (Km)	$\frac{^{206}Pb}{^{204}Pb}$	St. Dev.	$\frac{^{208}Pb}{^{206}Pb}$	St. Dev.	$\frac{^{206}Pb}{^{207}Pb}$	St. Dev.
Fish 1 (33°49′S 46°17′W)	5/20/96	1000	18.38	0.71	2.090	0.006	1.165	0.003
Fish 4 Station 10 (33°04′S 40°27′W)	5/21/96	1520	18.21	0.12	2.086	0.001	1.165	0.001
Fish 6 (28°54′S 36°57′W)	5/24/96	1920	18.19	0.09	2.083	0.001	1.165	0.001
Fish 9 (25°23′S 33°20′W)	5/25/96	2700	18.17	0.05	2.087	0.001	1.164	0.000
Fish 10 (23°39′S 31°34′W)	5/26/96	2960	18.04	0.06	2.098	0.001	1.158	0.000
Fish 11 Station 8 (17°15′S 25°15′W)	5/28/96	3910	18.10	0.16	2.102	0.001	1.155	0.001
Fish 12 (14°07′S 24°06′W)	5/30/96	3980	18.05	0.05	2.103	0.001	1.156	0.000
Fish 14 (11°06′S 23°11′W)	5/31/96	4400	18.02	0.12	2.010	0.001	1.158	0.001
Fish 15 (10°24′S 23°01′W)	5/31/96	4680	18.02	0.07	2.103	0.001	1.156	0.000
Fish 18 (6°12′S 21°44′W)	6/1/96	5240	18.03	0.05	2.104	0.001	1.155	0.000
Fish 21 (2°23′S 20°33′W)	6/1/96	5700	18.16	0.18	2.098	0.001	1.161	0.001
Fish 22 Romanche (0°53′S 20°07′W)	6/2/96	5900	18.05	0.03	2.102	0.001	1.157	0.000
Fish 24 (2°42′N 21°36′W)	6/5/96	6420	18.19	0.30	2.105	0.003	1.158	0.002
Fish 26 (4°34′N 22°48′W)	6/6/96	7050	18.13	0.04	2.103	0.001	1.159	0.000
Fish 27 (5°09′N 26°50′W)	6/7/96	7150	18.16	0.03	2.101	0.001	1.161	0.000
Fish 29 (5°49′N 30°54′W)	6/8/96	7620	18.13	0.36	2.010	0.003	1.162	0.002
Fish 31 (6°28′N 35°06′W)	6/9/96	8100	18.15	0.13	2.096	0.001	1.163	0.001
Fish 34 (7°17′N 40°09′W)	6/10/96	8600	18.14	0.05	2.099	0.001	1.162	0.000
Fish 37 Station 6 (7°55′N 44°39′W)	6/11/96	9060	18.06	0.12	2.095	0.002	1.164	0.001
Fish 39 (6°07′N 46°21′W)	6/13/96	9350	18.11	0.04	2.103	0.001	1.159	0.000
Fish 40 Amazon 1 (5°28′N 48°01′W)	6/15/96	9560	18.53	0.21	2.084	0.002	1.177	0.001
RM Fish 1 (6°56′N 49°04′W)	6/17/96	9750	18.18	0.14	2.092	0.001	1.165	0.001
RM Fish 2 (7°44′N 50°10′W)	6/17/96	9900	18.12	0.04	2.096	0.000	1.163	0.000
RM Fish 3 (8°54′N 52°03′W)	6/18/96	10140	18.28	0.09	2.082	0.001	1.171	0.001

Intermediate Water, and South Atlantic Central Water) in the South Atlantic. A separate report on lead concentrations and isotopic compositions in those water profiles is presented elsewhere in this volume (Alleman et al., 2001).

Precipitation samples (LPT samples) (Table 2 (a and b)) were acquired using a 1-m diameter acid-clean (2 × -sub-boiling quartz distilled HNO$_3$) HDPE funnel cleaned between each sampling, which was exposed only during collections of rain events, and using ultra clean techniques (Patterson and Settle, 1976; Church et al., 1990). The total deposition samples (SPT samples) were collected with an acid-clean funnel (50-cm diameter) deployed atop a 10-m bow mast. These smaller funnels were open during a period of sampling time of 1–4 days, but only with the ship underway and headed into the wind. Aerosols were sampled by an inverted shield collecting system also located atop the 10-m mast, again sampling only with the ship to windward. Using a low-volume pump, Millipore cellulose acetate (type HA), acid-pre-cleaned filters (0.45 μm pore size; 47-mm diameter) were mounted with polycarbonate/Teflon Nucleopore holders (Maring et al., 1989). Each aerosol sampling covered a continuous period of 1–3 days at a pumping rate of $\sim 2\,\mathrm{m}^3\,\mathrm{h}^{-1}$, except during rain, shift of wind direction or wind speed below $0.5\,\mathrm{m\ s}^{-1}$. All the samples (atmospheric and sea water) were sub-sampled in 2-l low-density polyethylene (LDPE)

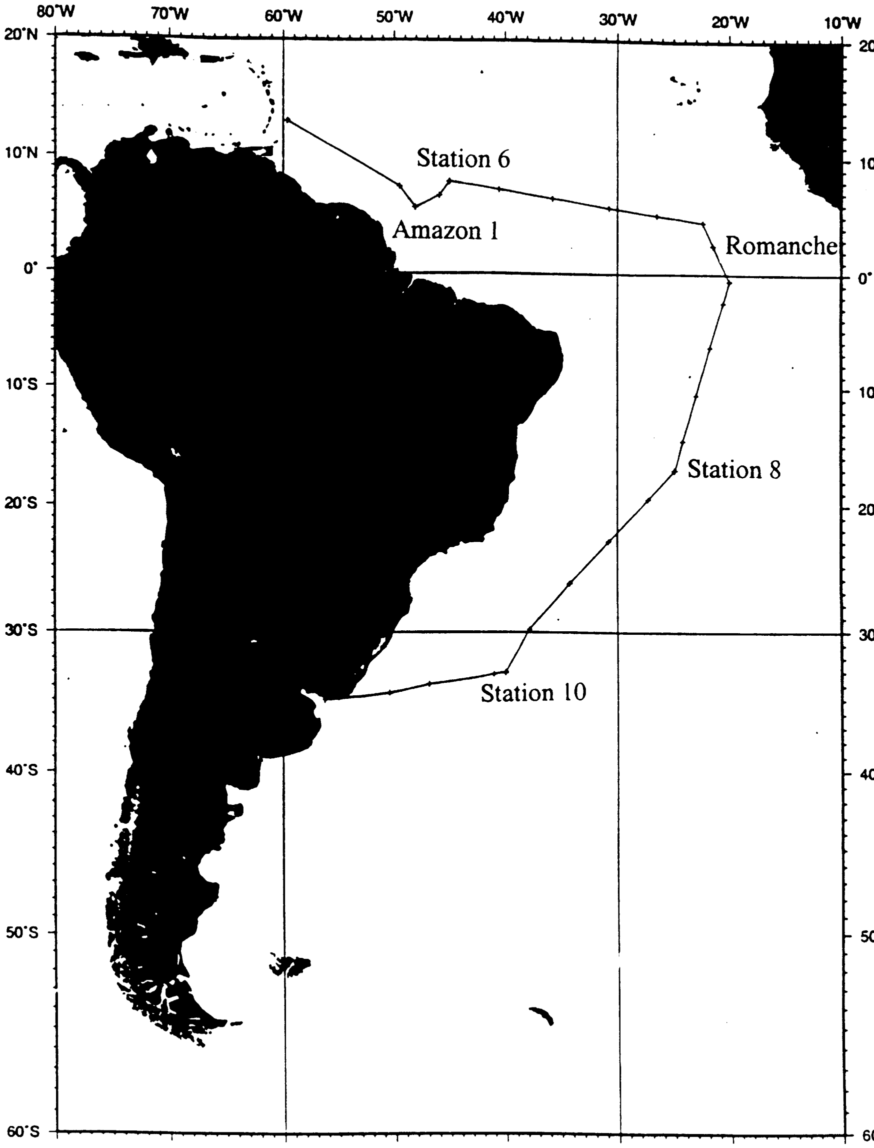

Fig. 1. The third IOC cruise track and the main sampling stations during May–June 1996.

acid-clean bottles under positive pressure of HEPA-filtered air inside a clean bench, triple bagged, and kept in the dark at 4°C until extraction (Patterson and Settles, 1976; Church et al., 1990).

Lead was extracted from unfiltered sea-water samples (about 900-ml pre-acidified to 0.1% with ultra-pure HNO_3) in a trace-metal-clean laboratory at the University of Delaware using a dithizone/chloroform extraction technique (Patterson and Settle, 1976). After evaporation, atmospheric samples were totally digested (HNO_3/HCl/HF) and double extracted by an anionic exchange resin technique (Manhés et al., 1978). Ratios of $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and

Table 2
(a) Lead isotopic compositions (St. Dev: two standard deviations for a single measurement) of the atmospheric samples (bulk deposition, precipitation and aerosols) collected during the IOC-III cruise. (b) Location, volume collected (ml and m^3) and lead concentrations for the bulk deposition, precipitation events and aerosols

Sample	Date	$^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$	St. Dev.	$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}$	St. Dev.	$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$	St. Dev.
Precipitation							
IOC LPT1	5/31/96	18.99	0.11	2.025	0.003	1.214[a]	0.003
IOC LPT2	6/5/96	18.37	0.03	2.092	0.000	1.174	0.000
IOC LPT3	6/6/96	18.27	0.01	2.095	0.000	1.170	0.000
IOC LPT4	6/7/96	18.16	0.07	2.102	0.001	1.163	0.000
IOC LPT5	6/10/96	18.27	0.11	2.099	0.001	1.164	0.001
IOC LPT7	6/13/96	18.51	0.00	2.078	0.000	1.183	0.000
IOC LPT8	6/14/96	18.54	0.32	2.082	0.001	1.173	0.002
IOC LPT10	6/14/96	18.33	0.18	2.095	0.002	1.167	0.001
Bulk deposition							
IOC SPT1	24-29/5/96	18.23	0.06	2.086	0.001	1.167	0.000
IOC SPT3	31/5-2/6/96	18.00	0.63	2.070	0.006	1.182	0.000
IOC SPT4	2-5/6/96	18.39	0.00	2.095	0.000	1.173	0.000
IOC SPT5	5-7/6/96	18.24	0.01	2.102	0.000	1.165	0.001
IOC SPT6	7-9/6/96	18.40	0.05	2.094	0.000	1.176	0.000
IOC SPT7	9-11/6/96	18.34	0.04	2.092	0.001	1.172	0.000
IOC SPT8	11-12/6/96	18.09	0.07	2.103	0.001	1.160	0.000
IOC SPT9	14-15/6/96	18.18	0.16	2.100	0.001	1.165	0.004
IOC SPT10	15-17/6/96	18.99	0.01	2.042	0.001	1.204[a]	0.000
IOC SPT11	17-18/6/96	18.44	0.03	2.087	0.000	1.179	0.000
IOC SPT12	18-19/6/96	18.37	0.04	2.088	0.001	1.175	0.000
Aerosols							
IOC A01 10B	22/5/96	18.48	0.39	2.072	0.003	1.179[a]	0.002
IOC A02 10B	22-23/5/96	18.00	0.16	2.107	0.001	1.154	0.001
IOC A04	27-29/5/96	18.43	0.21	2.089	0.002	1.177	0.001
IOC A08 PB	6-9/6/96	18.31	0.01	2.098	0.000	1.170	0.000
IOC A09 PB	9-11/6/96	18.32	0.01	2.107	0.000	1.165	0.000
IOC A10 PB	11-13/6/96	18.05	0.02	2.118	0.000	1.151	0.000
IOC A011 PB	14-16/6/96	18.47	0.09	2.088	0.001	1.180	0.001

Precipitation	Geographical location (from-to)	Rain volume (ml)	[Pb] (ppb)
IOC LPT1	11°S 23°W	2000	<0.05
IOC LPT2	3°07′N 21°47′W - 3°32′N 21°56′W	250	0.20
IOC LPT3	4°34′N 22°59′W	700	0.30
IOC LPT4	4°40′N 23°19′W	1800	0.20
IOC LPT5	7°11′N 39°34′W - 7°17′N 40°11′W	1300	<0.05
IOC LPT7	6°27′N 46°08′W	1700	0.30
IOC LPT8	4°40′N 47°20′W	1000	0.10
IOC LPT10	5°25′N 48°00′W	2000	0.10
Bulk deposition			
IOC SPT1	26°S 24°W – 17°S 25°W	50	0.40
IOC SPT3	9°56′S 22°52′W - 1°42′S 20°20′W	1900	<0.05
IOC SPT4	0°50′S 20°06′W - 4°17′N 22°22′W	700	0.30

Table 2 (*continued*)

Precipitation	Geographical location (from-to)	Rain volume (ml)	[Pb] (ppb)
IOC SPT5	4°17′N 22°22′W - 5°14′N 27°31′W	2000	0.20
IOC SPT6	5°14′N 27°31′W - 6°16′N 33°47′W	1300	0.10
IOC SPT7	6°31′N 35°31′W - 8°00′N 44°20′W	700	0.10
IOC SPT8	8°00′N 45°00′W	300	0.40
IOC SPT9	4°42′N 47°46′W - 6°15′N 48°26′W	2500	<0.05
IOC SPT10	5°48′N 47°57′W - 6°39′N 48°48′W	150	0.20
IOC SPT11	6°40′N 48°47′W - 9°35′N 53°18′W	2000	<0.05
IOC SPT12	9°35′N 53°18′W	100	0.10
Aerosols		Air volume (m^3)	
IOC A01 10B	33°49′S 40°27′W	6.8[b]	-
IOC A02 10B	33°00′S 40°01′W	73.7	-
IOC A04	18°12′S 26°09′W - 16°58′S 24°57′W	89.3	-
IOC A08 PB	4°28′N 22°55′W - 6°58′N 35°02′W	37.2	-
IOC A09 PB	6°31′N 35°30′W - 8°01′N 44°59′W	80.7	-
IOC A10 PB	7°59′N 44°59′W - 8°02′N 45°01′W	31.5	-
IOC A011 PB	5°49′N 47°58′W - 6°39′N 48°42′W	38.5	-

[a] Possible contamination during initial sampling containing high radiogenic US signature or due to low volume collected.

[b] Possible contamination from filter due to low volume pumped.

^{206}Pb/^{204}Pb (Tables 1 and 2a) were determined using a multi-collector Finnigan MAT 262 solid-source mass spectrometer located at the CEREGE (Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement, Aix en Provence, France). The mass spectrometer runs achieved usually a precision better than 0.1% for two standard deviations of the ^{206}Pb/^{207}Pb ratios. Calibration and mass fractionation corrections were determined by constant analyses of NIST (National Institute of Standards (NIST) and Technology, Gaitherburg, MD) SRM 981 (common lead standard reference material), inducing on average, a shift of 0.7% on the ^{206}Pb/^{207}Pb ratio. The ^{206}Pb/^{207}Pb ratios are used in the discussion because of a small fractionation factor, better detection limits, and for comparison with previous environmental studies. The average lead analytical blank for isotopic measurements (25 ± 12 pg; $n = 21$) in the sea-water samples, including the organic extraction and analytical processing, represented less than 3% of the lead analyzed in the sea water (surface sea-water lead concentrations in the South Atlantic range from 6.1 to 34.3 pM) (Ndung'u et al., 2001). Moreover, the isotopic homogeneity between successive samples (Fig. 2) suggests little contamination during the sampling, which otherwise would exhibit extremely variable isotopic signatures within the same water masses. The blanks for lead concentration measurements (236 ± 48 pg; $n = 16$) are reported and detailed in Ndung'u et al. (2001). The average lead analytical blanks ($n = 18$) for the precipitation and bulk samples (116 ± 54 pg) represented less than 10% of the total extracted lead from sub-samples (about 100 ml of precipitation with averaged lead concentrations of 0.17 ± 0.12 ppb Table 2b) obtained by Graphite Furnace Atomic Absorption Spectrometry (Perkin-Elmer 3300–Graphite Furnace HGA 600) (Church et al., 1990). The sampling blanks for the small and large funnels, estimated by pouring 1 l of acidified MilliQ water (0.1% HNO_3)

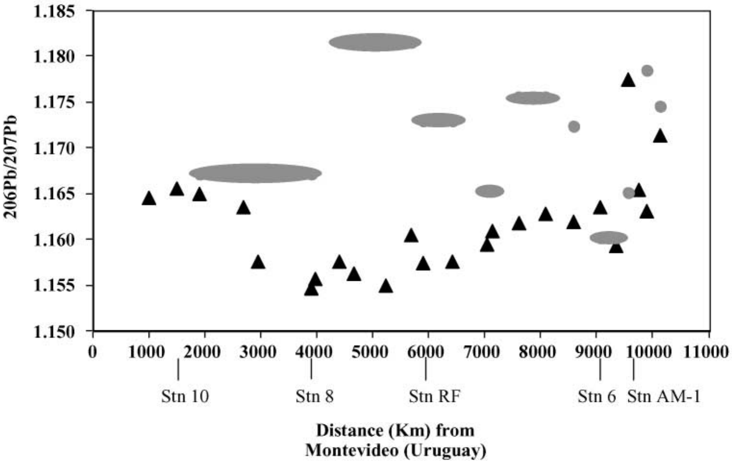

Fig. 2. Lead isotopic compositions in South Atlantic surface water (black triangles) compared to bulk deposition (gray areas). The data are plotted as a function of distance from departure (Montevideo, Uruguay) along the transect.

through the funnels, produce a blank under 5 pM. The average total blank for the entire aerosol filters (handling, acid digestion, extraction and analyses) was 450 ± 150 pg. The characteristic $^{206}Pb/^{207}Pb$ ratio of the blank filter was 1.181 ± 0.005. Finally, the overall homogeneity of the atmospheric lead signatures in the various type of samples suggests minor contamination during collection and analyses.

3. Results

3.1. Surface water signatures

The mean (x ± sd) stable lead isotopic compositions ($^{206}Pb/^{207}Pb$) in surface sea water for the entire south to north transect was 1.162 ± 0.005 (Table 1). This surprising homogeneity contrasted with the generally higher and much more variable range (1.164 to 1.195) in North Atlantic surface waters (e.g., Véron et al., 1994; Hamelin et al., 1997). As previously reported, that variation is caused by diverse aeolian inputs of relatively high and low radiogenic contaminant lead emissions from, respectively, North America and Western Europe for the past quarter century (e.g., Wu and Boyle, 1997; Alleman et al., 1999).

Although these first data in the South Atlantic indicate a much more narrow range (1.155–1.177) in surface waters, there still is a spatial gradient within those waters (Fig. 2). The lowest $^{206}Pb/^{207}Pb$ ratios (1.157 ± 0.002) were encountered between 17°S and the Equator, which is within the South Equatorial Current (Peterson and Stramma, 1991; Cutter and Measures, 1999). These are bracketed by more radiogenic lead in (a) more southerly surface waters (33° to 23°S) within the Brazil Current and the Subtropical Gyre (1.163 ± 0.003), and (b) more northerly surface waters, between the Equator and 10°N within the north Equatorial Atlantic (1.165 ± 0.005). There is a relatively substantial amount of US contaminant lead in the northernmost (8°54′N; 52°03′W) surface-water sample, showing a $^{206}Pb/^{207}Pb$ ratio of 1.1714. This is comparable to that (1.166–1.1713) measured in this region (7°–16°N; 36°–53°W) during the GCE/CASE/WATOX expedition in 1988 (Véron et al., 1994). In that study, Véron and colleagues suggested a small contribution of the lead content from the northward current into the equatorial waters. They attributed the relatively radiogenic lead to aeolian inputs from the North African trade easterlies mixed with North American air masses (Véron et al., 1994).

3.2. Atmospheric sample signatures

Characteristic lead isotopic compositions ($^{206}Pb/^{207}Pb$) of the atmospheric samples are illustrated in Fig. 2. It includes average ratios (x ± sd) of the aerosols (1.168 ± 0.011), bulk deposition (1.171 ± 0.006), and precipitation events (1.171 ± 0.006). Those data are tabulated in Table 2a. The lead concentrations for the precipitation and total deposition samples reported in Table 2b show an average of 0.17 ± 0.12 ppb (range from 0.05 to 0.4 ppb). This is lower than the lead concentrations found in total deposition at Bermuda (North Atlantic) in 1996–1998 (0.25 ± 0.22 ppb), and within the range of what has been measured in the Equatorial Ocean from 1985 to 1990 (0.091–1.03 ppb) (Helmers and Schrems, 1995). While these data present good correlation with other natural and anthropogenic elements (i.e. Cd, Cr, Zn, Fe, Al: G. Kim, personal com.), there is no significant relationship with the lead isotopes, probably due to the large variety of lead sources encountered during the cruise.

The larger isotopic variability of the various atmospheric samples, compared to their associated sea water samples, is attributed to (a) the presence of different transient sources of atmospheric lead during the sampling season, and (b) the short residence time of lead (<14 days) in the lower troposphere (Moore et al., 1973; Turekian et al., 1977; Talbot and Andren, 1983) relative to that of lead (1–2 years) in oceanic surface waters (Bacon et al., 1976; Nozaki et al., 1976; Flegal and Patterson, 1983; Lambert et al., 1991; Helmers and Schrems, 1995; Alleman, 1997). The atmospheric variability is also consistent with the proposal from Radlein and Heumann (1992) that atmospheric lead concentrations in the South Atlantic could vary as much as two orders of magnitude depending on meteorological conditions. This could include both changes in air mass sources that traversed more or less industrialized regions and in the extent of recycled sea spray that is assumed to represent a significant fraction of atmospheric lead in pristine areas (up to 20%) (Radlein and Heumann, 1992).

These results show that the $^{206}Pb/^{207}Pb$ ratios of all atmospheric samples (1.170 ± 0.008) are, on average (x ± sd) slightly more radiogenic than those of the surface sea water samples (1.162 ± 0.005) (Fig. 2). As previously noted, lead isotopic compositions in those surface waters tend to be relatively homogeneous due to both seasonally averaged advective transport and mixing processes within the water column. Therefore, the following discussion provides a preliminary proposal on factors governing lead isotopic compositions in the atmosphere and surface waters of the South Atlantic, based on our limited knowledge of tropospheric and oceanic circulation within that region.

There are other qualifications for interpreting the results. This includes concerns of extrapolating data from a relatively short sampling period for the atmospheric samples. In addition, the climatology of the South Atlantic includes a disproportionally large number of precipitation events within the Inter-tropical Convergence Zone (ITCZ) (Helmers and Schrems,

1995) that introduce biases compared to more southerly areas with less precipitation. Such a phenomenon was observed during the third IOC cruise with a significantly larger number of precipitation in the Equatorial Ocean (see Table 2b). It is also in agreement with a recent study on continental atmospheric lead isotopic compositions showing a significant gradient toward more radiogenic signatures in northern regions of Africa and South America (Bollhofer and Rosman, 2000).

4. Discussion

4.1. Isotopic characterization of lead in the South Atlantic

Although the presence of contaminant lead cannot be definitely established in oceanic waters by measurements of concentration alone, where physical and biogeochemical processes limit those concentrations, that contamination may be established by lead isotopic composition measurements (Véron et al., 1998; Alleman et al., 1999). Fig. 3 shows the unequivocal contrast between the low radiogenic anthropogenic lead isotopic compositions of the atmosphere and surface waters in the South Atlantic basin compared to the range of radiogenic natural lead signature represented by samples from pre-anthropogenic/Holocene sediments (Sun, 1980). Other potential natural sources in the Southern Hemisphere (Sandwich Island, Chilean volcanic rocks, regional sediment,

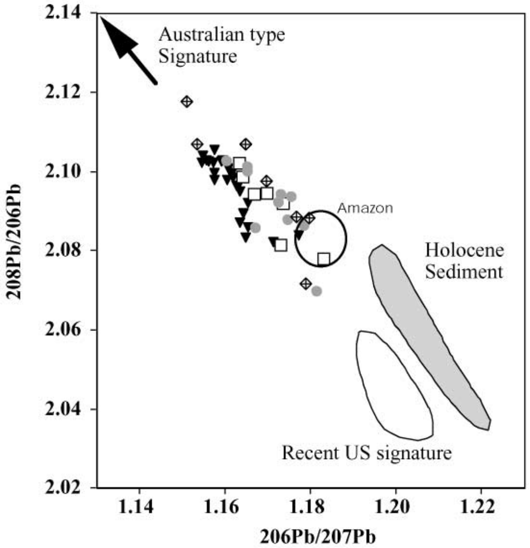

Fig. 3. Aerosols (diamonds), precipitation (squares), bulk deposition (gray circles), and surface sea water (black triangles) lead isotopic signatures in the South Atlantic Ocean on a ^{206}Pb/^{207}Pb versus ^{208}Pb/^{206}Pb diagram. Comparison with natural lead (Holocene sediment) (Sun, 1980) and recent US atmospheric lead signatures (Church et al., 1990; Véron et al., 1994; Véron and Church, 1997). The samples collected at the Amazon station are the closest to the natural end-member.

and Mount Erebus) also show distinct and more radiogenic isotopic compositions (1.185–1.275) (Barreiro, 1983; Boutron and Patterson, 1987) than the sea water anthropogenic fingerprint and are discussed in Alleman et al. (2001).

Unfortunately, the temporal and spatial origins of that anthropogenic lead cannot be quantified as it has in the North Atlantic, because there have been few direct measurements of contaminant leads within the Southern Hemisphere. Those few measurements include the following: Chow et al. (1975) measured the isotopic composition of leaded gasoline in two South American cities, where the $^{206}Pb/^{207}Pb$ ratio was 1.152 in Lima (Peru) in 1965 and 1.238 in Santiago (Chile) in 1969, with the latter believed to reflect a relatively large amount of North American (Missouri) lead used in Chilean gasoline. Doe (1970) reported a $^{206}Pb/^{207}Pb$ ratio of 1.187 for industrial lead in Brazil for 1978, which has been using unleaded gasoline since 1988. Some anthropogenic lead isotopic signatures ($^{206}Pb/^{207}Pb$) in South Africa were derived from blood samples (1.128 ± 0.013) in 1973 by Manton (1977). A more recent and comprehensive study on urban atmospheric particles presents a large range of isotopic signatures in South America (1.063–1.185) and Africa (1.066–1.153), attributed both to automobile exhausts (non-radiogenic Tetra-Ethyl lead mostly from Associated Octel) and radiogenic industrial emissions (Bollhofer and Rosman, 2000). The major Pb emitters of the Southern Hemisphere identified in this work are South Africa, Brazil, Argentina, Mexico and present a range of lead signatures between 1994 and 1999 of 1.067–1.085, 1.141–1.177, 1.147–1.153, 1.188–1.197, respectively. These measurements also evidenced an increase of $^{206}Pb/^{207}Pb$ ratios in a northerly direction of each continent. However, these data are still not sufficient to definitely identify the primary sources, much less temporal and spatial variations, of anthropogenic lead in the South Atlantic.

4.2. Lead enrichment factors in the South Atlantic

The anthropogenic origins of lead in the South Atlantic have previously been determined by calculations of its enrichment factor (EF), based on its crustal abundance relative to aluminum, $(Pb/Al)_{atm}$: $(Pb/Al)_{crust}$. Although aerosol lead concentrations (0.05 to $9.2\,ng\,m^{-3}$) in the South Atlantic troposphere in 1984–1985 (Volkening et al., 1988; Volkening and Heumann, 1990) were much lower than those ($0.1–800\,ng\,m^{-3}$) measured in the North Atlantic (Duce et al., 1975; Buat-Menard and Chesselet, 1979; Chester et al., 1983), the relatively high lead concentrations in coastal regions off urban areas located in western Africa (Dakar) and South America (Rio de Janeiro) were indicative of contaminant lead (Volkening et al., 1988; Radlein and Heumann, 1992). This was corroborated by EF calculations, based on an estimated natural background of atmospheric lead concentrations of $0.15\,ng\,m^{-3}$ (Lantzy and Mackenzie, 1979; Chester et al., 1983), that indicated essentially all (95%) of the lead in the South Atlantic equatorial atmosphere was anthropogenic. Our estimate of the lead enrichment factor, relative to iron (EF = 4–140), for the precipitation and total depositions collected during this cruise (G. Kim, personal com.) also suggest that more than 75% of the lead still originates from human activities. This is not surprising since many urban and industrial areas in the Southern Hemisphere present airborne lead levels matching or exceeding lead concentrations measured in the 1970s in northern industrial countries (Nriagu et al., 1996 and references therein).

4.3. Comparison with measurements of contaminant lead in the Antarctic

Even the most remote continent, Antarctica, has been shown to be under the manifest influence of contaminated atmospheric deposition (e.g., Boutron and Patterson, 1987). Thus, it is instructive to compare the signatures of the contaminant lead emissions found over the South Atlantic and the Antarctic region. Both the preceding isotopic compositions and EF calculations are consistent with recent measurements of lead contamination in adjacent surface waters of the polar South Atlantic or Southern Ocean. The latter was evidenced by the range in ^{206}Pb/^{207}Pb ratios (1.156 ± 0.025) and lead concentrations (9.8–103 pM kg^{-1}) in unfiltered surface sea water at ~60°S, which was attributed to mixtures of anthropogenic (low radiogenicity) and natural (high radiogenicity) aeolian lead inputs (Flegal et al., 1993). These concentrations match well the values from this cruise (6.1–34.3 pM kg^{-1}) (Ndung'u et al., 2001) as well as previous studies in the South Atlantic (5–118 pM kg^{-1}; Helmers and Rutgers van der Loeff, 1993) and the Weddell Sea (5–47 pM kg^{-1}; Westerlund and Ohman, 1991). Since the lead isotopic signatures of surface waters in the third IOC cruise transect from 33°S to 10°N are comparable, the entire South Atlantic appears to be contaminated with relatively non-radiogenic (low ^{206}Pb/^{207}Pb ratios), anthropogenic lead. Similarly, the tropospheric lead concentrations in Antarctica are relatively low, but still range over two orders of magnitude from 8 to 900 pg/m^3 (Maenhaut et al., 1979; Dick and Peel, 1985; Volkening et al., 1988; Volkening and Heumann, 1990; Radlein and Heumann, 1992). The variation is again attributed to varying inputs of anthropogenic lead sources and changing meteorological conditions over the area (Boutron and Patterson, 1987).

The contaminant origins of lead in the Antarctic troposphere are substantiated by measurements of both lead concentrations and isotopic compositions in recent Antarctic surface snow (Ng and Patterson, 1981; Boutron and Patterson, 1987; Rosman et al., 1993,1994; Suttie and Wolff, 1993; Wolff and Suttie, 1994). While clearly from anthropogenic sources, the significant variation of lead isotopic compositions (^{206}Pb/^{207}Pb) in Antarctic snow in 1983–84 (1.109–1.166) precludes obvious identification of specific contaminant lead sources (Rosman et al., 1994). These could include both (1) human activities on Antarctica and (2) anthropogenic lead emissions from Australia, South America, and Africa.

A second isotopic signature (e.g., ^{206}Pb/^{207}Pb ~ 1.163) is significantly different from the natural lead isotopic ratios (^{206}Pb/^{207}Pb ~ 1.252 in Antarctica) and has been characterized as a background source of contaminant lead in several Antarctic ice core samples (Rosman et al., 1994). Bollhofer and Rosman (2000) suggest that this signature reflects the anthropogenic lead emissions from the two main sources in South America, Brazil and Argentina, presenting similar range of atmospheric lead signatures (1.141–1.177). It matches our mean isotopic compositions of South Atlantic surface waters north of 33°S (^{206}Pb/^{207}Pb = 1.162 ± 0.005) and the Antarctic surface water at 60°S (Flegal et al., 1993). The similarity suggests that contamination extends throughout the entire South Atlantic but does not preclude a unique source, since a mixing of various lead sources in different proportions with variable signatures could lead fortuitously to the same final isotopic signal.

A conditional explanation for these resemblance in atmospheric and surface water samples has been proposed by Helmers and Schrems (1995). They suggested there is a relatively substantial sea water contribution of lead to the atmosphere (up to 20%) by recycled sea spray, especially in low atmospheric lead deposition regions (e.g., 30°S). Similarly, Radlein and Heumann (1992) assumed biogenic emissions from the Polar Antarctic Sea accounted for the high enrichment of lead, relative to iron (EF = 230–1800) in Antarctic (60°S to 77°S) aerosols in 1990. These scenarios have the ability to justify those similarities in such natural samples, which otherwise should present discrepancies due to various input sources and residence time.

4.4. Other potential lead origins: North–South interaction ?

The above discussion suggest there are multiple, relatively substantial, sources of lead in the South Atlantic. The isotopic composition of lead in South Atlantic surface water and atmospheric samples is more radiogenic (e.g., $^{206}Pb/^{207}Pb > 1.153$) than that of some of the known sources of anthropogenic lead emissions in the Southern Hemisphere (low radiogenic lead from Associated Octel). While this radiogenicity may be attributed to a mixture with natural lead sources that always show higher $^{206}Pb/^{207}Pb$ ratios (e.g., Holocene sediment: $^{206}Pb/^{207}Pb = 1.19$–1.21; Sun, 1980), the low concentrations of those natural inputs are usually overwhelmed by anthropogenic depositions even in remote oceanic surface waters, with the exception of Saharan dust storms (e.g., Church et al., 1990; Radlein and Heumann, 1992; Véron et al., 1993).

The latter is illustrated by the isotopic compositions of surface waters within the Amazon Plume in the North Equatorial Atlantic Ocean (Fig. 3). The lead isotopic composition in the plume is relatively radiogenic, with a $^{206}Pb/^{207}Pb$ ratio (1.177) fairly close to the natural signature (Fig. 3) and comparable to a previous determinations of Saharan $^{206}Pb/^{207}Pb$ ratios varying from 1.174 to 1.199 (Grousset et al., 1994; Alleman, 1997). This detrital isotopic signature of the surface waters is consistent with that of atmospheric samples collected concurrently (Table 2a). Their covariance indicates that lead in the Northwestern Equatorial Atlantic was primarily derived from Saharan dust, at least during the sampling period.

Alternatively, the relatively high radiogenicity of lead in South Atlantic surface waters may be due to inputs of contaminant lead from the Northern Hemisphere, where more than 85% of industrial lead emissions occur (Schaule and Patterson, 1981; Nriagu and Pacyna, 1988). The interhemispheric advection of industrial lead aerosols, however, is limited (1) by the formation of an air-mass barrier at the ITCZ (inter-tropical convergence zone) and (2) the short residence time (< 14 days) of lead aerosols in the troposphere (Turekian et al., 1977). Consequently, aeolian lead inputs from emissions in the northern hemisphere are not, generally, considered to be substantial in the southern hemisphere (Flegal and Patterson, 1983; Boutron and Patterson, 1987; Flegal et al., 1993). This is illustrated by previous reports of aerosol lead concentrations (e.g., Duce et al., 1975,1991; Helmers and Schrems, 1995), which show a two orders of magnitude decrease from the North Atlantic (0.1–800 $ng\,m^{-3}$) to the South Atlantic (0.05–9.2 ng/m^3). However, radiogenic lead sources (1.185–1.197) have been detected in Central America (Mexico) and the northern part of South America (Colombia) in 1997–1998 (Bollhofer and Rosman, 2000), which could increase the overall radiogenic character of the isotopic signature in the South Atlantic troposphere. Due to the annual shift of the Inter Tropical Convergence Zone to more northerly latitude during the northern summer, this industrial region is a potential source of radiogenic lead to the South Atlantic. Unfortunately, only two atmospheric samples (one aerosol and a bulk sample) were collected on the third IOC cruise with such a high radiogenic signature, making this conclusion tentative (Table 2a).

There is a similar, albeit smaller (4- 10-fold), gradient in lead concentrations in surface waters of the North and South Atlantic. This has been established in a previous transect across the equatorial waters of the eastern Atlantic (Helmers and Rutgers van der Loeff, 1993). That gradient also has been attributed to the limited interhemispheric transport of lead aerosols, as well as the convergence of the South Equatorial Current and the North Equatorial Counter Current between 0° and 10°N that limits advective mass transport of surface waters from the North to the South Atlantic (Peterson and Stramma, 1991). Based on a significant gradient of $^{206}Pb/^{207}Pb$ ratios in the equatorial waters (1.19–1.17 from 24 to 15°N), Véron et al. (1994) conclude that the ITCZ could inhibit effectively surface-water exchange between the North and the South.

The difference in magnitude between atmospheric and surface-water lead concentration gradients in the North and South Atlantic is related to differences in their residence times, which are based on ^{210}Pb normalization (Boyle et al., 1986; Véron et al., 1998). As shown above, aerosol-lead concentrations decrease approximately 100-fold from the North to the South Atlantic, while surface water lead concentrations decrease 4- to 10-fold. Declines in atmospheric lead concentrations in the North Atlantic have paralleled those of anthropogenic emissions of industrial lead aerosols in North America and Europe over the past two decades (i.e., the 5- to 8-fold reduction of aeolian lead deposition between 1979 and 1988-1991 corresponds with the reduction in leaded gasoline emissions during that period). On the other hand, decreases in surface-water lead concentrations in the North Atlantic have been much smaller (a factor 3 at best) (Church et al., 1984; Jickells et al., 1984; Wu and Boyle, 1997; Véron et al., 1998). This disparity is attributed to the biogeochemical cycling of lead in surface waters, along with physical water mass circulation processes. Therefore, this current transient evolution makes comparisons between atmospheric and surface water lead concentrations complex.

4.5. Anthropogenic versus natural lead sources in the South Atlantic

Plots of the isotopic compositions indicate that (1) lead in the troposphere is intermediate to that of predominant industrial and natural leads in the South Atlantic, and (2) there is relatively more detrital lead in the troposphere than in South Atlantic surface waters (Fig. 3). The gradients may be either a sampling artifact, due to the limited sampling period and the higher collection rate in the ITCZ (under the Saharan dust influence) or a reflection of the hemispheric reduction in emissions and/or isotopic signature of anthropogenic lead aerosols. The latter is consistent with large decadal (1979–1981 versus 1988–1989) decrease in atmospheric lead concentrations (Chester et al., 1983; Radlein and Heumann, 1992) as well as lead isotopes signature increase between 1994–95 and 1996–99 in the Southern Hemisphere (Bollhofer and Rosman, 2000).

The surface sea-water samples present similar radiogenic maxima in the southern (33–23°S), and the northern region (0–10°N), of the transect ($^{206}Pb/^{207}Pb = 1.163 \pm 0.003$ and $^{206}Pb/^{207}Pb = 1.165 \pm 0.005$, respectively) (Fig. 2). These maxima correlate exactly with the lead concentration maxima found by Helmers and Rutgers van der Loeff (1993) during a similar transect in 1990. One would expect a higher impact from anthropogenic lead emissions in the northern region of the transect due to the proximity of the largest industrial sources (US and Europe). Thus, one should have observed a mixed signature from US and Euro-African lead emissions in the North Atlantic samples and a clearer signal from natural lead sources in the South. Plotting the atmospheric and sea-water samples data on a $^{206}Pb/^{207}Pb$ versus

^{208}Pb/^{206}Pb graph (Fig. 3) indicates a three-component mixing scheme (high radiogenic lead of US origin, low radiogenic lead of Australian origin, and natural/detrital lead signal) for these values. Here, the South Atlantic clearly appears mostly disconnected from the natural/detrital signature (Holocene sediment; Sun, 1980). Interestingly, the samples closer to the natural signature are those collected in the North Equatorial Atlantic Ocean, not the more remote samples in the south. This result confirms the wide imprint over the Northern Hemisphere of a detrital dust fraction from the Sahara, typical for the late spring sampling, and recorded both in the atmospheric and surface water samples (Fig. 3). This detrital input was previously documented with Al and Pb concentration data during several transects across the Equator between 1985 and 1990 (Volkening and Heumann, 1990; Helmers and Rutgers van der Loeff, 1993; Helmers and Schrems, 1995).

On the contrary, the higher than average radiogenic signatures found in the southern part of the transect clearly display an anthropogenic signature slightly closer to the “US type” component (Fig. 3). These findings parallel former studies regarding the contamination of Antarctica surface waters (Flegal et al., 1993). The prevailing wind directions during the cruise were east/northeast, mostly under the influence of the remote South Atlantic marine troposphere except north of the Equator under the temperate easterlies and below 25°S, under the trade westerlies coming from the South American continent. The South American origin was confirmed by measurements of ^{222}Rn (half life: 3.8 days), a tracer of continental air origin, indicating a recent intrusion of continental air masses during the first week of the cruise (below 20°S) (G. Kim, personal com.). This sampling period corresponds to radiogenic surface sea water ($^{206}\mathrm{Pb}/^{207}\mathrm{Pb} = 1.163 \pm 0.003$) and total deposition signatures characteristic of the industrial lead sources from Brazil and Argentina (1.141–1.177; Bollhofer and Rosman, 2000).

The lowest ^{206}Pb/^{207}Pb ratios encountered between 17°S and 5°S (mean $^{206}\mathrm{Pb}/^{207}\mathrm{Pb} = 1.156 \pm 0.003$) could reflect the impact of the non-radiogenic South African anthropogenic lead emission advected through northward transport of surface sea water masses. The lead input from South Africa could be deposited directly into the Agulhas Current and the South Equatorial Current, reducing significantly the overall radiogenicity of the lead signature found in the South Atlantic surface sea water.

5. Conclusions

This study provides the first comprehensive data set on lead isotope determinations in the South Atlantic atmosphere and surface water. Contaminant lead is clearly evidenced in the atmosphere and surface water of the remote South Atlantic through the use of stable isotope signatures. In surface sea water, the mean ^{206}Pb/^{207}Pb ratio (1.162 ± 0.005) is substantially lower than in the North Atlantic. This low isotopic ratio probably originates from a mixing between emission of high and low radiogenic sources from the surrounding industrial countries (i.e. Brazil, Argentina and South Africa). The surface water isotopic signature is less radiogenic than the atmospheric, which contains also a larger imprint from at least one detrital source (Saharan dust). These dissimilarities could be related to (1) an advective transport of anthropogenic lead associated with the South Equatorial Current and/or (2) a recent decrease of contaminant lead input and/or the change of isotopic signatures from anthropogenic emissions. As expected, the Saharan dust imprint is most evidenced in the Equatorial Atlantic region. Overall, lead isotopic variations along the south-north transect do not reflect a direct influence of anthropogenic lead from the Northern Hemisphere into the South Atlantic Ocean, but more probably emissions from the main regional pollutant sources (Brazil, Argentina, South Africa, Mexico). Future stable lead isotope measurements should include atmospheric source determinations by coupling to other tracers and use of air mass trajectories.

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