

**Tracing the cycling of Pb and Cd from
natural and anthropogenic sources through
the troposphere and ocean**

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Declaration of originality

I declare that the content of this thesis is my own work unless otherwise stated, and that contributions to this thesis from others are fully acknowledged and referenced.

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Abstract

Anthropogenic emissions have been a major source of numerous trace elements to the environment during the past century, causing significant perturbations of their global biogeochemical cycles. This thesis focuses on the use of isotopic variations to study the cycling of Pb and Cd, derived from natural and anthropogenic sources, in the Tropical Atlantic Ocean.

To this end, a novel method to determine the Pb isotope composition and concentration of seawater is presented. This method is applied to (1) surface seawater and aerosol samples collected in the Tropical Atlantic, to reassess the relative importance of anthropogenic and natural Pb sources to the surface seawater of this region following the global phase out of leaded petrol, and (2) seawater depth profiles collected in the eastern Tropical Atlantic, to study the transient penetration of historic anthropogenic Pb emissions into the ocean interior.

The results reveal significant Pb contributions from mineral dust to surface seawaters of about 30 – 50 %. This is the first time a significant proportion of naturally derived Pb has been detected in Atlantic surface seawaters and can be viewed as the success of environmental policy. Furthermore, it is shown that the removal of atmospheric particles by dry deposition plays an important role in the observed mineral dust Pb contributions to surface seawater. The Pb isotope compositions and concentrations within the interior of the eastern Tropical Atlantic are consistent with values expected from the transport of transient anthropogenic Pb inputs by ocean circulation, thus enabling insights into ventilation timescales and pathways.

Finally, we present among the first data on the Cd isotope composition of atmospheric aerosols, which were collected in the eastern Tropical Atlantic. These results are used to assess the utility of isotope variations to trace the long-range atmospheric transport of anthropogenic and natural Cd sources to the ocean.

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Chapter 1

Introduction to the biogeochemical cycles of Pb and Cd

1.1 Anthropogenic perturbations of the biogeochemical cycles of Pb and Cd

Anthropogenic emissions from high temperature processes have significantly perturbed the global biogeochemical cycles of numerous trace elements (Nriagu & Pacyna, 1988). Of these, the most extensively documented and arguably the most extensively perturbed by anthropogenic activities is Pb (Reuer & Weiss, 2002, Boyle et al., 2014). The combustion of leaded petrol has been the dominant source of Pb to the environment in recent history, although emissions from non-ferrous metal smelting, coal combustion and waste incineration have also contributed as environmental Pb sources (Nriagu & Pacyna, 1988, Pacyna & Pacyna, 2001). The magnitude of anthropogenic Pb emissions to the environment has changed drastically during the past century, largely driven by the increased usage and subsequent phasing out of leaded petrol across the globe (Shotyk et al., 2005, Kelly et al., 2009, McConnell et al., 2014).

Similarly, emissions from high temperature industrial processes have perturbed the global biogeochemical cycle of Cd (Shen et al., 1987, Nriagu & Pacyna, 1988, Candelone et al., 1995, Eichler et al., 2014). The most important anthropogenic activity for the emission of Cd is considered to be non-ferrous metal smelting followed by coal combustion and municipal waste incineration (Nriagu & Pacyna, 1988, Pacyna & Paycna, 2001, Pacyna et al., 2009, Cheng et al., 2014). As with Pb, the magnitude of anthropogenic Cd emissions has changed during the past century, generally increasing to a peak in the 1960/70's before declining (Shen et al., 1987, Boutron et al., 1991, Candelone et al., 1995, Eichler et al., 2014). A pattern attributed to increasing industrialisation, followed by the implementation of stricter emission controls (Candelone et al., 1995, Eichler et al., 2014).

During these high temperature processes volatile trace elements such as Pb and Cd become vaporized and are emitted to the atmosphere where they rapidly condense onto fine particles ($<1\ \mu\text{m}$) (Galloway et al., 1982, Raes et al., 2000, Cloquet et al., 2006, Cziczo et al., 2009). Consequently, Pb and Cd are typically highly enriched over crustal concentrations in atmospheric aerosols (relative to a crustal reference element such as Al, Ti or Fe) (e.g. Chester et al., 1993a, Guieu et al., 1997). These fine particles are capable of undergoing long-range transport across the globe before removal to terrestrial and marine environments (Duce et al., 1991, Gelado-Caballero et al., 2012). The ocean therefore receives large quantities of these

anthropogenic derived elements, with atmospheric inputs of Pb and Cd estimated to dominate over riverine fluxes (Duce et al., 1991). Due to the short residence time of Pb in the ocean (1 – 2 years in ocean surface waters, increasing to decades/centuries in the ocean interior; Craig et al., 1973, Bacon et al., 1976) and the magnitude of historic anthropogenic emissions, Pb in the ocean is completely dominated by anthropogenic sources (Boyle et al., 2014). The Pb content of surface waters generally track temporal changes in atmospheric Pb emissions in the surrounding regions, whilst Pb contents within the ocean interior are generally controlled by the penetration of historic marine Pb inputs by ocean circulation (e.g. Shen & Boyle, 1988, Wu & Boyle et al., 1997a).

The marine biogeochemical cycle of Cd is heavily influenced by its role as a micronutrient, with dissolved Cd concentrations driven to low values in surface waters by biological uptake, then increasing with depth due to remineralisation of sinking organic material (Boyle et al., 1976, Bruland et al., 1978, Bruland, 1980). In contrast to Pb, the degree to which the marine Cd cycle has been perturbed by anthropogenic inputs is presently unclear, which comes despite the dominance of anthropogenic Cd emissions to the atmosphere. This is due to the much longer residence time of Cd in the ocean compare to Pb (estimated to be $\sim 10^4 - 10^5$ years, Simpson, 1981), with upwelling of Cd rich deep waters considered to be the dominant source of Cd to ocean surface waters rather than external inputs (Bruland, 1980). The relative importance of external inputs (predominantly anthropogenic) and upwelling deep water as a source of Cd to surface waters is likely to vary between regions. For example, reconstructions of historic surface water Cd concentrations over the past century using coral archives at Bermuda and the Galapagos Islands exhibit different trends (Shen et al., 1987). Temporal surface water Cd concentration variations at the Galapagos Islands were linked to changes in deep water upwelling strength, while temporal variations at Bermuda closely resembled the changes in the magnitude of North American industrial Cd emissions.

1.2 The use of isotopic variations to study the biogeochemical cycles of Pb and Cd

Variations in the isotopic composition of Pb and Cd can provide valuable insights to the sources and cycling of these elements in the atmosphere and the ocean. In particular Pb isotope composition variations have been extensively applied to trace

environmental Pb sources (e.g. Reuer & Weiss, 2002, Komárek et al., 2008, Boyle et al., 2014). Such studies exploit the fact that Pb has four stable isotopes; ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , of which only ^{204}Pb is non radiogenic. The isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are produced through the radioactive decay of ^{238}U , ^{235}U and ^{232}Th with half-lives of 4.47 Gyrs, 0.704 Gyrs and 14.01 Gyrs respectively (Dickin, 2005). Different geological reservoirs therefore develop distinct Pb isotope compositions depending on their parent/daughter ratios (i.e. U/Pb and Th/Pb), initial Pb isotope composition and age. This isotopic variability can be used to trace sources of Pb to the environment derived from different geological reservoirs.

Of particular importance are Pb ore deposits, which display significant Pb isotopic variability, since they are the geological source of Pb emissions from the combustion of leaded petrol and non-ferrous metal smelting (Sangster et al., 2000). For economic and political reasons, different countries have historically favored the use of Pb derived from particular ore deposits to supply their automotive and industrial needs (e.g. Hurst et al., 2002). This has resulted in regional differences in the isotope composition of anthropogenic Pb emissions that can often be distinguished from those of natural environmental Pb sources (e.g. Bollhofer & Rosman, 2001, Erel et al., 2006). Such regional isotopic variability can be used to determine the relative importance of different sources of Pb to ocean surface waters (Flegal et al., 1984, Flegal et al., 1993, Véron et al., 1993, Véron et al., 1994, Hamelin et al., 1997, Véron et al., 1998, Alleman et al. 2001a, Weiss et al., 2003, Noble et al., 2015).

Furthermore, there have been temporal changes in the isotope composition of Pb delivered to regions of the ocean in response to changes in anthropogenic activities and the Pb ores used to supply them (Kelly et al., 2009). These transient Pb isotope compositions have been transported into the interior predominantly by ocean circulation (Boyle, 1986, Shen & Boyle, 1988). Hence, mapping the distribution of Pb concentrations and isotope compositions in the ocean interior may enable insights into ventilation pathways and timescales similar to other anthropogenic transient tracers (e.g. CFC's, SF_6 , ^3H) (e.g. Doney et al., 1997, Fine, 2011).

Recently, Cd isotope variations have been employed to study its biogeochemical cycle. Unlike Pb, variations in the Cd isotope composition between materials arise through mass dependent fractionations during physiochemical processes (Rehkämper et al., 2012). Significant mass dependent Cd isotope fractionations have been shown to accompany the biological uptake of Cd in ocean

surface waters (e.g. Ripperger et al., 2007). The distribution of Cd isotope compositions in the ocean can therefore provide additional insights to its marine biogeochemical cycle over the distribution of Cd concentrations alone (e.g. Abouchami et al., 2011, Gault-Ringold et al., 2012, Conway & John, 2015a). One particular useful application of oceanic Cd isotope composition distributions may be identifying regions of the ocean where external inputs are an important source of Cd to ocean surface waters, i.e. regions of the ocean that are potentially perturbed by anthropogenic Cd inputs (Yang et al., 2012, Lambelet et al., 2013, Yang et al., 2014, Yang et al., 2015a).

In this regard, Cd isotope compositions have recently shown promise as a novel tracer to distinguish between anthropogenic and natural environmental Cd sources (Rehkämper et al., 2012, Gao et al., 2015). This is based on the finding that evaporation/condensation processes are capable of inducing significant Cd isotope fractionations, and have been shown to occur during the emission of Cd from Pb-Zn smelting operations (Wombacher et al., 2003, Wombacher et al., 2004, Cloquet et al., 2006, Shiel et al., 2010). Although studies have used such Cd isotope variability to trace Cd sources to sediments proximal to Pb-Zn smelters as well as to coastal waters (Cloquet et al., 2006, Gao et al., 2008, Shiel et al., 2012, Shiel et al., 2013, Gao et al., 2013, Chrastný et al., 2015, Wen et al., 2015), the application of Cd isotopes to trace the long-range atmospheric transport of anthropogenic and natural Cd sources has yet to be investigated.

1.3 Thesis outline

This thesis is a contribution to the international GEOTRACES program which aims to survey the distribution of key trace elements and their isotopes in the modern oceans in order to better understand their inputs, internal cycling and their application as proxies for past ocean changes (www.geotraces.org). In particular, this thesis focuses on the application of isotopic data to study the cycling of Pb and Cd from natural and anthropogenic sources in the Tropical Atlantic Ocean. To this end, a novel method to determine the Pb concentration and isotope composition of seawater is presented in Chapter 2. These analytical techniques are then applied to (1) surface seawater and aerosol samples collected in the Tropical Atlantic to document the changes in Pb sources to this region of the ocean following the global phase out of

leaded petrol (Chapter 3), and (2) seawater depth profile samples collected in the eastern Tropical Atlantic in order to trace the advection of historic Pb pollution into the ocean interior, gaining insights into ventilation timescales (Chapter 4). The first data on the Cd isotope composition of atmospheric aerosols, which were collected in the eastern Tropical Atlantic are presented in Chapter 5. These data are used to assess the utility of Cd isotopes to trace anthropogenic and natural external atmospheric inputs to surface waters of this region. Finally a summary of the findings and an outlook for future research is outlined in Chapter 6.

Chapter 2

**A novel method for the determination of Pb concentrations
and isotope compositions of seawater**

Abstract

A new method for the determination of seawater Pb isotope compositions and concentrations was developed, which combines and optimizes previously published protocols for the separation and isotopic analysis of this element. For isotopic analysis, the procedure involves initial separation of Pb from 1 to 2 L of seawater by co-precipitation with Mg hydroxide and further purification by a two stage anion exchange procedure. The Pb isotope measurements are subsequently carried out by thermal ionization mass spectrometry using a ^{207}Pb - ^{204}Pb double spike for correction of instrumental mass fractionation. These methods are associated with a total procedural Pb blank of 28 ± 21 pg (1sd) and typical Pb recoveries of 40 to 60 %. The Pb concentrations are determined by isotope dilution (ID) on 50 mL of seawater, using a simplified version of above methods.

Analyses of multiple aliquots of six seawater samples yield a reproducibility of about ± 1 to ± 10 % (1sd) for Pb concentrations of between 7 and 50 pmol/kg, where precision was primarily limited by the uncertainty of the blank correction (12 ± 4 pg; 1sd). For the Pb isotope analyses, typical reproducibilities (± 2 sd) of 150 to 1700 ppm and 1000 – 2000 ppm were achieved for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. These results are superior to literature data that were obtained using plasma source mass spectrometry and they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. Both Pb concentration and isotope data, furthermore, show good agreement with published results for two seawater intercomparison samples of the GEOTRACES program.

2.1. Introduction

Investigations that map the distribution of trace metals and their isotopes in seawater and which study their relationship to and potential impacts on global biogeochemical cycles in the oceans are an overarching goal of modern marine geochemistry and a key objective of the international GEOTRACES program. The global scale impact of human activities on natural Pb budgets was established more than 40 years ago by Chow and co-workers (Chow & Johnstone, 1965, Chow & Earl, 1970, Chow & Earl, 1972, Chow et al., 1973) and massive inputs of anthropogenic Pb into the oceans were soon thereafter identified by Patterson and co-workers based on the first accurate and precise Pb concentration measurements for seawater (Flegal & Patterson, 1983, Schaule & Patterson, 1981, Schaule & Patterson, 1983). Studies of the anthropogenic impact on marine Pb budgets were further advanced with the first successful Pb isotope analyses of seawater (Patterson et al., 1976, Flegal & Patterson, 1983, Flegal et al., 1984, Shen & Boyle, 1988, Flegal et al., 1989, Véron et al., 1994). Whilst these early measurements were all carried out by TIMS (thermal ionization mass spectrometry), the majority of seawater Pb analyses since the 1990's have been conducted using various types of ICP-MS instrumentation. At present, the most precise Pb isotope analyses of seawater apply either single collector high resolution or multiple collector ICP-MS (HR-ICP-MS and MC-ICP-MS, respectively), most commonly following low-blank pre-concentration of the element by co-precipitation with $\text{Mg}(\text{OH})_2$ (Weiss et al., 2000, Reuer et al., 2003).

These methodological advances are a consequence of the particular importance of seawater Pb isotope data to studies of environmental pollution and marine geochemistry. For example, analyses of corals yielded a seawater Pb isotope record for the North Atlantic over the last 220 yrs, which revealed significant isotopic variability through time, in accord with known changes in the extent and type of anthropogenic emissions (Kelly et al., 2009). Similarly, Pb isotope data for the modern ocean are used to infer the distribution of Pb from different anthropogenic and natural sources in surface seawater and to determine the lateral mixing and advection of subsurface water masses (see Boyle et al., 2014 for review).

Here, we present a new method for the accurate and precise determination of seawater Pb concentrations and isotope compositions. The methodology involves pre-concentration of Pb by $\text{Mg}(\text{OH})_2$ co-precipitation followed by ion exchange

chromatography (Strelow, 1978, Lugmair & Galer, 1992, Hirata, 1996), and subsequent isotopic analyses by TIMS using a ^{204}Pb - ^{207}Pb double spike to achieve precise control of instrumental mass fractionation (Hamelin et al., 1985, Galer, 1999). The technique is validated by analyses of both in-house and international seawater reference materials.

A number of previous investigations have shown that the application of Pb double or triple spikes enables Pb isotope measurements that are significantly more precise and accurate than conventional TIMS or MC-ICP-MS techniques and less susceptible to the analytical artifacts, which can be generated by instrumental mass bias effects (Gale, 1970, Woodhead, 1995, Woodhead, 1997, Galer, 1999, Thirlwall, 2000, Thirlwall, 2002, Baker et al., 2004). Our study is the first to apply the double spike methodology to seawater Pb isotope analyses. Using these techniques, we are not only able to analyze the commonly measured ratios $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ to high precision but $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ can also be determined to an uncertainty of better than about ± 3 ‰. Only very scarce seawater data are available for the latter ratios due to the analytical challenges but measurements of non-radiogenic ^{204}Pb are deemed to be important to fully exploit the potential of the Pb isotope system.

2.2. Experimental

2.2.1. Samples

A gravimetric solution of the well-characterized NIST standard reference material SRM 981 Pb was employed for calibration of the Pb double spike and to evaluate the precision of the mass spectrometric methods. Four filtered seawater samples that were available in large quantities were utilized as in house reference materials to further assess reproducibility. These encompass a surface water sample (Atlantic–S) and three subsurface water samples, Atlantic–D1, Atlantic–D2 (both from 2000 m depth), and Weddell (400 m depth). These samples were not specifically collected for Pb isotope analyses, and potential contamination during sampling and initial handling hence renders them unsuitable for evaluation of accuracy or an assessment of water mass properties.

To enable a comparison of our results with literature data for assessment of accuracy, we analyzed the international seawater reference samples GSI and GDI. These were collected at water depths of 7 m and 2000 m, respectively, at the Bermuda Atlantic Ocean Time Series station (BATS) during the 2008 GEOTRACES intercalibration cruise on the *R/V Knorr* (KN193-6). The collection and handling of these samples employed materials and procedures that were specifically designed for the intercalibration of contamination-prone trace metals and isotopes (Boyle et al., 2012).

2.2.3. Reagents

Water with a resistivity of $> 18.2 \text{ M}\Omega \text{ cm}$ from a Milli-Q water system was used throughout for reagent preparation and cleaning of labware. Purified concentrated HF ($\sim 28 \text{ M}$) and HBr ($\sim 8.5 \text{ M}$) were purchased from VWR as Optima (distilled) grade acids whilst concentrated (14.5 M) HNO_3 and 6 M HCl were prepared in-house by subboiling distillation of reagent grade acids in quartz stills. The Pb blanks of these acids were checked regularly and found to be consistently less than 2 pg/ml . The dilute mineral acids that were employed for the separation chemistry were freshly prepared for each batch of samples.

A purified aqueous solution of NH_3 was used to affect precipitation of $\text{Mg}(\text{OH})_2$ from seawater and prepared by cold vapor phase equilibration of reagent grade 28% (w/w) aqueous NH_3 with Milli-Q water in a Savillex Teflon elbow. Approximately 2 volumes of 28% aqueous NH_3 were employed for each volume of Milli-Q water, and these were equilibrated for about two weeks to obtain purified aqueous NH_3 (aq- NH_3) at a concentration of about 9 M . During this period, the Teflon elbow was stored double bagged in plastic, to limit contamination and loss of gaseous NH_3 . The aq- NH_3 was collected from the still just prior to use and each batch of three samples, plus a full procedural blank, was treated with the same solution. The Pb blank of the aqueous ammonia was stable at less than 0.3 pg/mL during the course of the study.

2.2.3. Preparation and calibration of ^{207}Pb - ^{204}Pb double spike

Highly enriched (>99 %) metallic ^{204}Pb and ^{207}Pb in wire form were purchased from Isoflex (USA). The wires were separately dissolved in 7.5 M HNO_3 and diluted with water to obtain solutions in 2 M HNO_3 . A dilute double spike solution was then prepared with a total Pb concentration of ~ 10 ng/ml and an optimal molar ratio of $^{207}\text{Pb}/^{204}\text{Pb} \approx 1$, based on the error propagation modeling of Galer (1999) and Rudge et al. (2009).

Spike calibration was performed using a gravimetric solution of NIST SRM 981 Pb. In a first step, the concentration of the double spike was determined by two reverse isotope dilution runs that were carried out with a Nu Plasma HR MC-ICP-MS, using external normalization to added Tl for mass bias control (Hirata, 1996, Rehkämper & Halliday, 1998, White et al., 2000). Initially, a preliminary concentration was obtained, based on an approximate spike isotope compositions, which was calculated from the mixing proportions of the ^{204}Pb and ^{207}Pb solutions, and the respective isotope compositions, as supplied by Isoflex.

The isotope composition of the double spike (Table 2.1) was then calibrated by analyses of different gravimetrically prepared double spike – NIST SRM 981 mixtures using TIMS (Dodson, 1963, Rudge et al., 2009). The instrumental mass fractionation correction (Hirata, 1996, Rehkämper & Halliday, 1998, White et al., 2000), the spike-standard mixing line, and the double spike composition were calculated by over-determining the system of equations (number of double spike – NIST SRM 981 mixtures > 2) and solving in the least-square sense, as described by Rudge et al. (2009). Finally, the calibrated double spike isotope composition was applied to the data from the initial reverse isotope dilution runs, to accurately define the double spike concentration.

Table 2.1. Lead isotope data of this study and reference values for NIST SRM 981 Pb. Also shown is the isotope composition of the Pb double spike used in this study.

Sample	Pb used (ng) ^a	n ^b	²⁰⁶ Pb/ ²⁰⁴ Pb ± 2sd ^c	²⁰⁷ Pb/ ²⁰⁴ Pb ± 2sd ^c	²⁰⁸ Pb/ ²⁰⁴ Pb ± 2sd ^c	²⁰⁶ Pb/ ²⁰⁷ Pb ± 2sd ^c	²⁰⁸ Pb/ ²⁰⁷ Pb ± 2sd ^c
<i>This study</i>							
SRM 981 Pb	2	59	16.9411 ± 16	15.4945 ± 15	36.7134 ± 39	1.09338 ± 21	2.36946 ± 32
± 2sd relative (ppm)			950	1006	1066	195	136
± 2se of typical (ppm) ^d			~400	~420	~440	~60	~50
SRM 981 Pb	10	9	16.9411 ± 19	15.4979 ± 21	36.7223 ± 66	1.09312 ± 06	2.36951 ± 14
± 2sd relative (ppm) ^e			109	140	180	56	51
± 2se of typical run			~70	~70	~80	~15	~15
<i>SRM 981 Reference values^e</i>							
Galer & Abouchami (1998) (TIMS)	~10		16.9405 ± 15	15.4963 ± 16	36.7219 ± 44	1.0932	2.3697
Thirlwall (2000)(TIMS)	~20		16.9409 ± 22	15.4956 ± 26	36.7228 ± 80	1.0933	2.3699
Todt et al. (1996) (TIMS)	80		16.9356 ± 23	15.4891 ± 30	36.7006 ± 113	1.0934	2.3694
Thirlwall (2002) (MC-ICP-MS)			16.9417 ± 29	15.4996 ± 31	36.724 ± 9	1.0930	2.3694
Baker et al. (2004) (MC-ICP-MS)	~50		16.9416 ± 13	15.5000 ± 13	36.7262 ± 31	1.0930	2.3694
²⁰⁷ Pb- ²⁰⁴ Pb double spike ^f			0.00240	1.03181	0.00820	0.002320	0.007950

^a Mass of Pb loaded on filament and/or used for a single analysis. ^b n = number of analyses. ^c 2sd = 2x standard deviation calculated from n separate runs; denotes long-term “external” reproducibility. ^d 2se = 2x standard error of the mean; denotes within-run (“internal”) precision of the data, based on individual results for measurement cycles. ^e All reference values were obtained using either double or triple spike techniques for correction of instrumental mass fractionation. ^f Isotope composition of the Pb double spike used in the current study.

2.2.4. Sample preparation for determination of Pb isotope compositions

2.2.4.1. Lead pre-concentration by co-precipitation with magnesium hydroxide

A number of previous studies have shown that co-precipitation of Pb with $\text{Mg}(\text{OH})_2$ is an effective, low-blank method for pre-concentration of Pb from seawater and this technique is retained in our procedure (Wu & Boyle, 1997b, Weiss et al., 2000). Initial tests showed that Pb is efficiently and reproducibly extracted from seawater at yields $\geq 80\%$ by precipitation with $\text{Mg}(\text{OH})_2$ at $\text{pH} \approx 10$. The yields were, furthermore, not correlated with the exact pH value that was adjusted or the amount of $\text{Mg}(\text{OH})_2$ precipitated. The $\text{Mg}(\text{OH})_2$ precipitate, however, was also found to scavenge a significant amount of sea salt, but the latter could be removed without noticeable reduction of the Pb yield by rinsing the precipitate with water.

In order to obtain sufficient Pb for precise analyses, even for Pb depleted seawater from the deep ocean, samples of up to about 2 L were processed. The seawater was transferred to 1 L pre-cleaned Teflon separating funnels, to aid the collection of the Mg hydroxide precipitate. Precipitation of $\text{Mg}(\text{OH})_2$ was affected by introduction of the purified aq- NH_3 until a final pH value of about 10 was obtained. As each seawater sample had been acidified to a slightly different extent, and because the precipitate forms only gradually, the applied volume of aq- NH_3 was optimized for each sample by slowly adding successive portions of the reagent to the separating funnel. This was achieved by an initial addition of 2 to 4 ml aq- NH_3 , whereupon the samples were stirred vigorously and then left to stand for least 3 hr to allow the $\text{Mg}(\text{OH})_2$ precipitate to form. If precipitation had not occurred after this time, an additional volume of 0.5 ml of aq- NH_3 was added every 2 to 3 hr until formation of precipitate was observed.

Once about 5 ml of $\text{Mg}(\text{OH})_2$ slurry had formed, the precipitate was drained through the bottom of the separating funnel, collected in a 15 ml Teflon centrifuge tube, centrifuged at 1700 rpm for about 10 min and the remaining solution poured off. This step was repeated several times until all precipitate was recovered from the funnel. The solids were then washed with 5 ml H_2O , centrifuged again and finally dissolved directly in the tubes by addition of 5 ml of a 2 M HBr – 0.01 M HF acid mixture. To aid dissolution, the centrifuge tubes were shaken whereupon the formation of many small bubbles within the solutions was observed for seawater

samples that had not been filtered following collection. Bubble formation is hence presumably related to the presence of residual organic compounds. It is important to remove the bubbles at this stage because they can otherwise lead to the formation of larger bubbles within the resin bed during the subsequent column chemistry, effectively blocking the flow. For removal of the bubbles, the centrifuge tubes were left to stand overnight, sealed and then gently heated on a hotplate for 10 min at 50° C. After cooling, bubbles should no longer be visible in the solutions, otherwise the heating was repeated.

2.2.4.2. Lead purification by anion exchange chromatography

The anion exchange purification procedure for Pb (Table 2.2) is based on previously published methods that apply strongly basic AG1X8 resin and dilute HBr – HNO₃ mixtures for elution, with modifications as detailed below.

Previous work has shown that silica is trapped by the Mg(OH)₂ precipitate, which is used for the separation of Pb from seawater (Wu & Boyle, 1997b, Weiss et al., 2000, Nicolaysen et al., 2003) . Relatively high Si concentrations of about 10 to 150 µmol/kg are, furthermore, found in seawater samples from depths >1000 m (de Souza et al., 2012). During method development we found that such concentrations suffice to form precipitates of silica on top of the resin column, when HF is not present in sample solutions. Hence, the 1st stage column chemistry of our final method (Table 2.2) applies a 2 M HBr - 0.01 M HF mixture for sample loading, whereby the small concentration of HF present enhances silica solubility to prevent precipitation of silicic acid. The same acid mixture is subsequently also used to completely flush silica from the resin, prior to elution of other matrix elements (Table 2.2). In 2 M HBr, Pb has a distribution coefficient K_D of about 200 towards the AG1X8 anion exchange resin that was used (Strelow et al., 1978, Manton, 1988, Guseva, 2007). Elution experiments confirmed that, whilst the Pb K_D value is reduced when HF is present, the use of trace HF in the elution scheme (Table 2.2) does not prevent retention of Pb on the resin bed during sample loading and matrix elution.

Following elution of Pb from the 1st stage columns, the samples were dried and further purified by a second column chemistry step, which is needed to eliminate remaining traces of Mg and improve the ionization of Pb during the TIMS analyses (Kamber & Gladu, 2009). To this end, the dried samples were redissolved in 0.2 M

HBr – 0.5 M HNO₃ and processed using established HBr – HNO₃ procedures on small 20 µL resin columns (Table 2.2), which help to minimize the procedural blank.

Table 2.2. Column chemistry procedure for the separation of Pb from seawater for isotope compositions (IC) and isotope dilution (ID) concentration measurements by TIMS

	Pb IC chemistry 1 st stage	Pb IC chemistry 2 nd stage	Pb ID chemistry
Resin ^a	100 µl AG1X8, 100-200 mesh	20 µl AG1X8, 100-200 mesh	20 µl AG1X8, 100-200 mesh
Clean resin	3 x 3 ml 0.1 M HNO ₃	3 x 1 ml 0.1 M HNO ₃	3 x 1 ml 0.1 M HNO ₃
Equilibrate resin	2 x 0.1 ml 2 M HBr – 0.01 M HF	2 x 0.1 ml 0.2 M HBr – 0.5 M HNO ₃	2 x 0.1 ml 0.5 M HBr – 0.2 M HNO ₃
Load sample	~5 ml in 2 M HBr – 0.01 M HF	~1 ml in 0.2 M HBr – 0.5 M HNO ₃	2 ml in 0.5 M HBr – 0.2 M HNO ₃
Elute matrix	2 x 0.1 ml 2 M HBr – 0.01 M HF	2 x 0.3 ml 0.2 M HBr – 0.5 M HNO ₃	2 x 0.3 ml 0.5 M HBr – 0.2 M HNO ₃
	2 x 0.5 ml 0.2 M HBr – 0.5 M HNO ₃		
	0.2 ml 0.03 M HBr – 0.5 M HNO ₃		
Elute Pb	3 ml 0.03 M HBr – 0.5 M HNO ₃	1 ml 0.03 M HBr – 0.5 M HNO ₃	1 ml 0.03 M HBr – 0.5 M HNO ₃

^a The resin is used in columns prepared from shrink-fit Teflon tubing. The columns have a reservoir volume of ~3 ml and a resin column with an internal Diameter of ~ 3 mm.

2.2.5. TIMS analyses of Pb isotope compositions

The accurate determination of Pb isotope compositions with precise correction of instrumental mass discrimination requires two separate mass spectrometric runs – one of the pure sample and a second analysis of a double spike – sample mixture. To this end, the purified Pb was divided into two aliquots and the double spike was admixed to one, prior to the TIMS measurements. The addition of the double spike after, rather than before, the chemical separation of Pb has a number of clear advantages. Conveniently, each sample needs to be processed through the (time-consuming) pre-concentration and purification steps only once, rather than twice. Furthermore, the impact of contamination from reagents and handling is minimized and uncertainties arising from different blanks impacting on the spiked and unspiked analyses are reduced (Hamelin et al., 1985).

In detail, our procedure involves splitting the Pb solutions from the 2nd stage column chemistry into a larger and a smaller aliquot. The larger aliquot comprising 2/3 of the sample remained unspiked, whilst Pb double spike was added to the remaining aliquot with 1/3 of the solution. The double spike addition was thereby carried out to obtain a molar ratio of natural (N) to spike-derived Pb (S) that approximates the optimum $S/N \approx 1.226$ (Rudge et al., 2009). This is equivalent to a molar proportion of spike, $S/(S+N)$, of 55.1%, corresponding to $^{206}\text{Pb}/^{204}\text{Pb} \approx 0.411$ (assuming a natural seawater $^{206}\text{Pb}/^{204}\text{Pb} = 18.4$). The amount of natural Pb present was thereby estimated from the Pb concentration measurements that were carried out first for all samples, and assuming a Pb recovery of 60% from the chemical separation (see below).

Following aliquoting and spiking, the Pb solutions were evaporated to dryness and redissolved in 1 μl 2 M HNO_3 . The samples were loaded on a single, previously outgassed zone refined Re filament (99.999%; H. Cross, USA), dried at 0.4 A, 0.5 μl of silica gel activator was then added and also dried at 0.4 A. The sample – activator mixture was finally heated at 2 A for ~ 1 s to evaporate phosphoric acid and fuse the silica gel.

Gerstenberger & Hasse (1997) prepared highly a highly successful activator for Pb isotope analyses by TIMS but this applies silica particles which are no longer commercially available. Hence, a new $\text{SiO}_2 - \text{H}_3\text{PO}_4$ activator mixture was made up for the current study. This mixture was prepared from SiO_2 nanoparticles (20-60 nm;

Io-Li-Tec Inc.) and Merck Ultrapur phosphoric acid, whereby a $\text{SiO}_2/\text{H}_3\text{PO}_4$ weight ratio of 0.43% was applied with respect to the addition of the silica to dilute 0.16 M H_3PO_4 . The amount of activator used for analysis was calibrated to optimize ionization yields, based on tests that were carried out with 2 ng NIST 981 Pb. These tests revealed that use of 0.5 μl activator solution was preferable to loading with 1 μl of activator – whilst the latter yielded more stable Pb ion beams the former produced ion beam intensities that were typically about 2 to 3 times higher.

The Pb isotope measurements were carried out on a TRITON TIMS instrument operating in static mode and using Faraday cups fitted with $10^{11} \Omega$ resistors. Prior to each measurement session, a gain calibration was carried out for all amplifiers. For analysis, the filaments were heated to a target temperature of about 1300°C within 30 min, and isotopic data were then collected in 15 blocks of 15 cycles with an integration time of 8.3 seconds. Half-mass baseline measurements (30 cycles x 1.05 s integrations following 5 s idle time) and an automatic peak centering routine (followed by 3 s idle time) were carried out prior to each block. Loads of 2 ng NIST 981 Pb provided stable and very reproducible ion beam intensities of 200 – 300 mV ^{208}Pb . For the seawater samples, the ion beam intensities were more variable and generally lower, whereby 2 ng Pb generally yielded ^{208}Pb ion beams of about 100 – 200 mV.

The measured isotopic data for the spiked and unspiked sample aliquots were processed using an iterative solver that employs published methods and which was implemented as a macro within a Microsoft Excel spreadsheet (Rudge et al., 2009). The method uses the exponential law to obtain mass bias corrected Pb isotope data and is employed on a cycle-by-cycle basis to provide an accurate assessment of the final propagated data uncertainties.

Following Doucelance & Manhès (2001), the TIMS source was baked for 3 hrs after the introduction of a new sample turret. This technique was observed to substantially reduce the formation of hydrocarbon species that can form interfering molecular ions during the Pb isotope runs (Thirlwall, 2000). The baking also significantly improved the vacuum within the ion source (to about 3.5 to 6×10^{-8} mbar, without use of a liquid N_2 cold trap) and enhanced Pb ion beam stability, thereby permitting analyses without interblock re-heating. The latter improvement is

presumably due to the efficient drying of the silica gel, which is achieved during heating in vacuum condition.

Barium-PO_x ions were mainly observed at temperatures, which are slightly higher compared to those employed for optimal Pb ionization (Thirlwall, 2000). The formation of such ions, and hence the presence of Ba in samples, is best avoided because they produce minor molecular interferences on ²⁰⁴Pb (from ¹³⁸Ba³¹P¹⁷O¹⁸O⁺, ¹³⁷Ba³¹P¹⁸O₂⁺) and, even more problematic, hinder the ionization of Pb whereby rapidly decaying Pb ion beams are observed. The presence of BaPO_x ions was routinely monitored during the analyses at mass 201, which corresponds primarily to ¹³⁸Ba³¹P¹⁶O₂⁺. The measured ion beam intensities at mass 201 were observed to rise during Pb sample runs but only to maximum values of 1 to 3 mV. At this level, the BaPO₂ interference contributes less than 15 ppm to the ²⁰⁴Pb ion beam, such that a correction was deemed unnecessary.

2.2.6. Determination of Pb concentrations

Lead concentrations were determined by isotope dilution (ID), and using a chemical separation method similar to that employed for the isotope ratio measurements but optimized for the processing of smaller seawater samples. In detail, 50 mL of seawater were weighed into clean polyethylene centrifuge tubes. Following addition of the Pb double spike, the mixtures were left to stand for at least 10 days to ensure full spike-sample equilibration. The amount of Pb spike added was based on an initial ‘guess’ of or any information available for the Pb concentration of the samples, to achieve an optimal S/N $\approx$ 2.61 (equivalent to ²⁰⁶Pb/²⁰⁴Pb $\approx$ 0.188) for minimal error propagation during ID data reduction.

Co-precipitation of Pb with Mg(OH)₂ was affected by adding 150 μ L of purified aq-NH₃. Following separation of the precipitate by centrifugation and dissolution in a dilute HNO₃ – HBr mixture, Pb was further purified using a single stage anion exchange chemistry. This employed small resin columns of only 20 μ L to minimize the procedural blank (Table 2.2). The anion exchange chemistry was slightly modified in comparison to the 2nd stage chemistry for Pb isotopes through use of a 0.5 M HBr – 0.2 M HNO₃ acid mixture for sample loading and matrix elution, because this was observed to facilitate the dissolution of the Mg(OH)₂ precipitate whilst ensuring quantitative retention of Pb on the small resin columns.

The ID TIMS analyses for Pb used the same techniques that were applied for the isotopic measurements but with shorter runs comprising 5 blocks of 15 cycles. During filament loading of some samples for the ID TIMS analyses, the presence of impurities, in the form of salts and possibly also organic compounds, was detected. When present, such impurities were associated with poor Pb ion beam intensities during the TIMS runs and in some extreme cases the analyses were even abandoned. Such contamination may also produce interfering molecular ions that could generate inaccurate ID results. Subsequent test showed that the impurities can be reduced to negligible levels, by allowing the resin bed to drain and dry completely (for about 10 min) after each step of the column chemistry procedure for Pb separation (Table 2.2) and, in particular, prior to the elution of Pb.

2.3. Results and discussion

2.3.1. Blanks

The total blank for the Pb isotope measurements was determined by carrying out the complete analytical procedure without an initial seawater sample being present. Over a 24-month period, the mean procedural blank was 28 ± 21 pg (1sd, $n = 25$; ignoring two abnormally high blanks of ~ 100 pg encountered during a single two-week period). The individual contributions to this total from (i) filament loading and (ii) reagents were also determined and found to be 1.9 ± 0.5 pg for the former, 5.0 ± 1.4 pg for the mineral acids used, and 2.5 ± 0.2 pg for the aq-NH₃ solutions. The contribution of the anion exchange resin and column chemistry (without reagents) to the total blank could hence be quantified as 17 ± 8 pg, by subtracting the reagent component from separately measured column chemistry blanks. The sum of the individual blank contributions is, therefore, 27 ± 10 pg, in accord with the full procedural blanks values determined during the study. Ignoring the individual contributions (and chemistry yields), a Pb blank of 10 to 50 pg contributes about 0.05 to 2.5% to the indigenous Pb budget of samples that were analyzed for isotopic compositions, assuming samples volumes and Pb concentrations of 1 to 2 L and 10 to 50 pmol/kg, respectively. The Pb isotope composition of the blank was also measured on several occasions with rather variable results, due to the low ion beam intensities and/or actual differences in blank compositions (e.g., $^{206}\text{Pb}/^{204}\text{Pb} = 18.34 \pm 0.62$,

$^{207}\text{Pb}/^{206}\text{Pb} = 1.196 \pm 0.028$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.422 \pm 0.021$; 2se, n = 10). Blank corrections were not applied to the isotopic data because such corrections did not improve the reproducibility of results from replicate sample analyses (see discussion below).

The total procedural blank for the Pb ID concentration measurements was determined using 100 μL seawater samples, as only negligible amounts of Pb (~ 0.2 to 1 pg) are present in such small volumes. These measurements revealed a relatively stable total Pb blank of 11.7 ± 4.3 pg (1sd, n = 36), which is equivalent to about 1 to 15% to the indigenous Pb in ID sample aliquots, assuming Pb abundances of 10 to 50 pmol/kg (for simplicity, this ignores variable chemistry yields and individual blank contributions). Blank corrections were applied to all measured Pb concentrations based on the mean blank value. The uncertainties of the Pb concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction.

2.3.2. Chemical separation of Pb

Stable isotope fractionation of Pb during anion exchange chromatography with HCl was recently documented and shown to vary systematically with Pb recovery (Baker et al., 2004, Blichert-Toft et al., 2010). Such fractionation can have a detrimental impact on the accuracy of subsequent Pb isotope measurements and may also occur during Pb purification with other anion exchange elution protocols. As part of this study it was therefore investigated whether incomplete recovery of Pb from the anion exchange chemistry applied here (Table 2.2) also has a systematic impact on the measured Pb isotope compositions. To this end, multiple 10 ng aliquots of NIST SRM 981 Pb were processed through the complete two stage column separation procedure and the purified Pb fractions were then analyzed using standard methods. The data (Fig. 2.1) illustrate that the column chemistry routinely affords Pb yields of about 50 to 70 %. Such recoveries are in accord with the total Pb yields of about 30 to 60 % that were determined for multiple analyses of five different seawater samples (Tables 2.3, 2.4). Assuming that the $\text{Mg}(\text{OH})_2$ co-precipitation achieves a recovery of ≥ 80 % for seawater Pb (see above), the Pb yield of the column chemistry is constrained to be about 40 to 75 %.

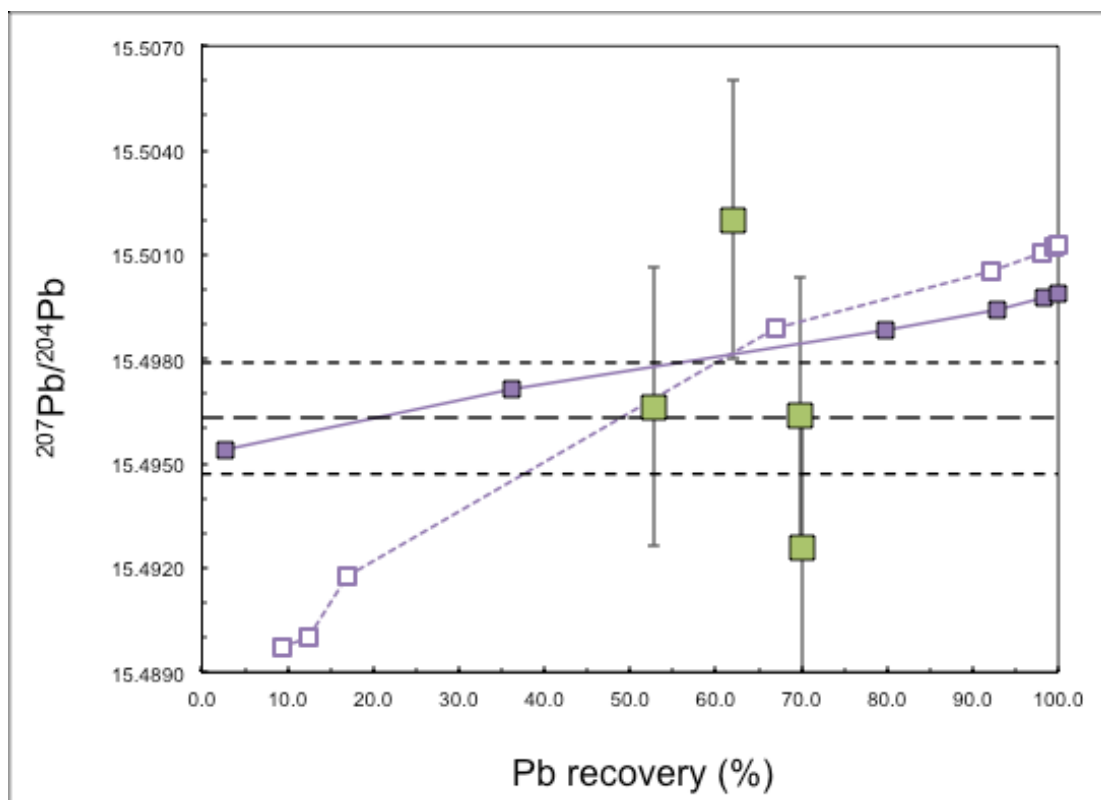


Figure 2.1. The recovery of Pb and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios obtained for 10 ng aliquots of NIST SRM 981 Pb that were processed through the 2-stage column chemistry (Table 2.2) are shown as full green squares with error bars that denote a $\pm 2\text{sd}$ uncertainty of about 240 ppm (Table 2.3). Shown for comparison are literature data for cumulative recovery and isotope composition of SRM 981 Pb that was collected in successive fractions from anion-exchange resin which was eluted with HCl: full purple squares and solid line – elution with 6 M HCl; open purple squares with hashed line – elution with 2 M and 8 M HCl (Baker et al. (2004)). The dashed black lines indicate the $^{207}\text{Pb}/^{204}\text{Pb}$ reference value determined for SRM 981 Pb (15.4963 ± 16 ; Table 2.1).

In a previous investigation, Reuer et al. (2003) reported essentially complete recovery of seawater Pb pre-concentrated by $\text{Mg}(\text{OH})_2$ co-precipitation, during purification on AG1X8 resin (as in this study) but using HBr and HCl for elution (Kamber & Gladu, 2009). Tests conducted during the course of the present study however showed that the method of Reuer et al. (2003) was associated with Pb recoveries similar to those reported here, when the procedure was modified to include additional use of HF to prevent precipitation of silicic acid during sample loading (Table 2.2). The use of dilute HF thus appears to be associated with either incomplete Pb retention on or elution from the anion exchange resin, regardless of the exact nature of the mineral acids, which are applied in the procedure. Ultimately, the current HBr- HNO_3 method (Table 2.2) was preferred to the elution method of Reuer et al. (2003), because the former applies only dilute mineral acids (which helps to

minimize the blank) and routinely produced cleaner Pb separates for subsequent isotopic analyses.

Importantly, the isotope data of Fig. 2.1 demonstrate that incomplete recovery of Pb from the column separation is not associated with significant shifts in isotopic composition. These results do not, however, rule out small, but barely resolvable, enrichments of heavier Pb isotopes following chemical purification. This follows from the observations of previous studies, which detected only minor Pb isotope fractionations, comparable to or smaller than the reproducibility of our results, as a result of incomplete elution of the element from anion exchange columns (Fig. 2.1).

2.3.3. Analyses of NIST SRM 981 Pb

Multiple measurements of 2 ng (n = 59) and 10 ng (n = 9) loads of NIST SRM 981 Pb were carried out for a basic validation for our double spike techniques of Pb isotope analysis. Notably, the mean isotopic data acquired for both the 2 ng and 10 ng runs are in excellent agreement with recent reference values that were acquired using various Pb double or triple spikes in conjunction with analyses by either TIMS or MC-ICP-MS (Table 2.1).

The 2sd between-run ('external') precision of the 10 ng data is ~50 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and ~250 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (where x = ^{206}Pb , ^{207}Pb , ^{208}Pb hereafter). This is similar to or only slightly worse than the reproducibility achieved by other workers with TIMS or MC-ICP-MS for comparable or somewhat larger Pb samples (10 to 80 ng; Table 2.1). Our data for the 2 ng loads, a sample size that is more relevant for seawater analyses (Table 2.3), is less precise than the 10 ng results, with a reproducibility ($\pm 2\text{sd}$ external) of ~150 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and ~1000 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 2.1). The significantly larger uncertainty of the $^{20x}\text{Pb}/^{204}\text{Pb}$ data presumably reflects that the 2 ng Pb analyses were hampered by the measurement of ^{204}Pb at low ion beam intensities (about 5 to 20 mV) using a Faraday cup and standard $10^{11} \Omega$ amplifiers. The within-run ('internal') precision (quantified by 2se; standard error of the mean) of both the 2 and 10 ng Pb measurements are about a factor of 2 to 3 better compared to the between-run uncertainties for all Pb isotope ratios (Table 2.1).

2.3.4. Analyses of in-house seawater reference samples

Multiple Pb concentration and isotope ratio analyses were carried out on four different in-house seawater reference samples (Table 2.3). These were available in sufficient quantity such that 5 to 7 repeat isotopic analyses could be carried out to rigorously investigate the reproducibility of the methods.

For the Pb contents, the precision (expressed as $\pm 1\text{sd}$, as is common for concentration data) varies between less than $\pm 1\%$ to about $\pm 12\%$ (Table 2.3). Notably, the reproducibility is worse for samples with low Pb contents. As similar samples sizes (of only $\sim 50\text{ ml}$) were employed for these measurements, the higher uncertainties for the Pb-depleted samples are most likely related to inaccuracies of the Pb blank correction, possibly due to spurious high blanks.

The isotopic results for the in-house seawater reference samples (Table 2.3) were acquired on individual aliquots of 1 to 2 L, from which about 2 to 10 ng of Pb were separated. The data display a $\pm 2\text{sd}$ reproducibility of ~ 150 to 1700 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and ~ 500 to 2000 ppm for $^{20\text{X}}\text{Pb}/^{204}\text{Pb}$ (Table 2.3). Clearly, this is inferior to the 2sd precision that was obtained for the comparable 2 ng and 10 ng loads of pure NIST SRM 981 Pb (Table 2.1). At the same time, the internal (within-run) $\pm 2\text{se}$ precision of the seawater measurements is similar to the NIST SRM 981 results, with uncertainties of ~ 30 to 100 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and ~ 300 to 700 ppm for $^{20\text{X}}\text{Pb}/^{204}\text{Pb}$ (Table 2.3). Given this discrepancy, it is most likely that the external 2sd reproducibility of the seawater Pb isotope data is limited by contamination of the samples by blanks of both variable magnitude and isotope composition. This interpretation is supported by two observations. First, the Weddell seawater, which has the lowest Pb concentration and thus the smallest Pb sample sizes, generally features the largest 2sd uncertainties (Table 2.3). Second, the application of a blank correction did not improve the 2sd reproducibilities for any of the samples, regardless of whether the corrections used mean blank values or only blank data that were linked to a specific batch of samples. In addition, it is also conceivable that the between-run 2sd uncertainties of the samples (Table 2.3) are, at least in part, limited by minor isotope fractionations that occur during the column chemistry (Fig. 2.1).

Table 2.3. Lead concentration and isotope composition data for the four in-house seawater reference materials and other key information relating to samples.

Sample	n-ID ^a	[Pb] ± 1sd pmol/kg ^b	± 1sd (%)	n-IC ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁶ Pb/ ²⁰⁷ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁷ Pb ± 2sd ^d	Sample size L ^e	Total Pb ng ^f	Meas. Pb (mean) ng ^g	Pb Yield (%) ^h
Atlantic – S ± 2sd relative (ppm) ^d ± 2se typical run (ppm) ⁱ	6	24.7 ± 1.0	4.0	5	18.429 ± 12 630	15.639 ± 9 560	38.307 ± 25 650	1.1784 ± 14 1157	2.4494 ± 04 174	~2	~11	3 – 6 (~4)	30 – 60
Atlantic – D1 ± 2sd relative (ppm) ^d ± 2se typical run (ppm) ⁱ	11	45.3 ± 0.5	1.1	7	18.499 ± 30 1610	15.625 ± 20 1280	38.287 ± 58 1520	1.1839 ± 07 586	2.4504 ± 06 251	1 – 2	10 – 20	3 – 10 (6)	30 – 50
Atlantic – D2 ± 2sd relative (ppm) ^d ± 2se typical run (ppm) ⁱ	2	47.4 ± 1.2	0.8	7	18.481 ± 30 1730	15.625 ± 22 1500	38.272 ± 59 1650	1.1828 ± 08 657	2.4494 ± 08 308	~2	~20	2 – 15 (7)	10 – 70
Weddell ± 2sd relative (ppm) ^d ± 2se typical run (ppm) ⁱ	8	7.6 ± 1.0	12.3	7	18.397 ± 48 2600	15.628 ± 20 1300	38.293 ± 70 1830	1.1772 ± 20 1727	2.4503 ± 20 822	~2	~3.8	~2.0	50 – 60

^a Number of individual sample aliquots analyzed for Pb concentrations. ^b Pb concentrations are corrected for a mean total blank of 11.7 ± 4.3 pg. The uncertainties of the concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction (see text). ^c Number of individual sample aliquots analyzed for Pb isotope compositions. ^d 2sd = 2x standard deviation calculated from results of n separate runs; denotes long-term “external” reproducibility. ^e Volume of individual aliquots used for Pb isotope analyses. ^f Original mass of Pb in sample aliquots used for Pb isotope analyses. ^g Mass of Pb in individual aliquots used for isotopic analyses, following chemical separation; a mean value is given in parentheses. ^h Pb recovery for the chemical separation process. ⁱ 2se = 2x standard error of the mean; denotes within-run (“internal”) precision of a run, based on individual results for measurement cycles.

2.3.5. GEOTRACES intercalibration samples GSI and GDI

Multiple Pb isotope and concentration measurements were also carried out for the two GEOTRACES intercomparison samples GSI and GDI (Table 2.4). For the Pb concentrations, GEOTRACES ‘consensus values’ were recently published, which are based on analyses of more than 10 independent laboratories (Group Consensus values, GEOTRACES, 2013). The mean Pb concentrations determined for the samples in this study from analyses of five or six separate aliquots have $\pm 1\text{sd}$ (external) reproducibilities that are similar to those obtained for the in-house seawater reference samples (Table 2.3), at about ± 4 to $\pm 6\%$ (Table 2.4). The results are, furthermore, identical to the reference values within the quoted uncertainties (Table 2.4).

The Pb isotope data for GSI and GDI were obtained on 2 to 3 sample aliquots of 2 L each, with originally about 10 to 15 ng Pb (Table 2.4). Following chemical separation, about 5 to 10 ng Pb were available for isotopic analysis. As for the seawater results of Table 3, the GSI and GDI measurements achieved (within-run) 2se reproducibilities that are similar to those obtained for similar loads of pure SRM 981 Pb, at ~ 30 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and 150 to 200 ppm for $^{20X}\text{Pb}/^{204}\text{Pb}$ (Table 2.4). In contrast, the external 2sd uncertainties, of ~ 350 to 1500 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and ~ 500 to 2200 ppm for $^{20X}\text{Pb}/^{204}\text{Pb}$, are typically significantly larger (Table 2.4). Again, this is most likely due to small Pb blank contributions of variable magnitude and isotope compositions and, potentially, minor isotope fractionation during Pb purification. Despite this, our results for the two samples compare favorably and are generally in agreement with the published reference results.

The reference Pb isotope data for the GEOTRACES samples were obtained at MIT (Massachusetts Institute of Technology) using MC-ICP-MS and at UCSC (University of California at Santa Cruz) by HR-ICP-MS (Boyle et al., 2012). These analyses did not apply a Pb double spike and were carried out using significantly smaller samples sizes (of about 0.25 to 0.5 L) compared to those utilized here.

For GSI, all Pb isotope ratios determined are identical to the MIT results within the 2sd uncertainties. There is also good agreement with the UCSC results for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ but the UCSC data are higher for $^{20X}\text{Pb}/^{204}\text{Pb}$ (Table 2.4). The uncertainties of the UCSC data are only poorly characterized, however, as they are based on only two analyses of a single seawater aliquot. Our new isotopic data for GDI are in excellent agreement with the MIT and USCS results for $^{206}\text{Pb}/^{207}\text{Pb}$,

$^{208}\text{Pb}/^{207}\text{Pb}$ and in reasonable agreement, just within uncertainty, with the UCSC $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Table 2.4). Hence, there are small but significant discrepancies for the remaining $^{20\text{X}}\text{Pb}/^{204}\text{Pb}$ data with the reference values, whereby our ratios are slightly lower. There is, however, also only marginal agreement between the MIT and UCSC results for these Pb isotope ratios, which are difficult to determine due to the low natural abundance of ^{204}Pb . This indicates that further analyses are needed to establish more reliable reference data for the $^{20\text{X}}\text{Pb}/^{204}\text{Pb}$ ratios of the GEOTRACES intercalibration samples.

The particular difficulty of ^{204}Pb measurements is also apparent in a comparison of the reproducibilities for the Pb isotope data obtained here and previously (Boyle et al., 2012). For the $^{20\text{X}}\text{Pb}/^{204}\text{Pb}$ ratios, the multiple MIT analyses reveal a $\pm 2\text{sd}$ uncertainty of ~ 5000 to $10,000$ ppm, whilst our data for GSI, GDI (Table 2.4) and the in-house test samples (Table 2.3) have uncertainties which are at least a factor of 5 better, at ~ 500 to 2000 ppm. For $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ the difference is less apparent, however as the reproducibility of the MIT results varies between 500 and 2500 ppm, whilst the data of this study (Tables 2.3, 2.4) typically have an uncertainty of about 500 to 1500 ppm.

Table 2.4. Lead concentration (ID) and isotope composition (IC) data for the GEOTRACES intercalibration samples GSI and GDI and reference values from the literature.

Sample	n-ID ^a	[Pb] ± 1sd pmol/kg ^b	n-IC ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁶ Pb/ ²⁰⁷ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁷ Pb ± 2sd ^d	Sample size L ^e	Total Pb ng ^f	Pb Yield (%) ^g
GSI											
This study	6	27.9 ± 1.2	3	18.359 ± 26	15.635 ± 7	38.246 ± 30	1.1741 ± 13	2.4463 ± 09	~2	~10	45 – 60
± 2sd relative (ppm) ^d				1430	480	790	1092	352			
± 2se typical run (ppm) ⁱ				~160	~170	~180	~30	~25			
Ref. – MIT			5	18.41 ± 11	15.67 ± 9	38.33 ± 23	1.1745 ± 06	2.4455 ± 28	0.25 – 0.5	1.5 – 3	
± 2sd relative (ppm) ^d				5870	5790	6020	511	1166			
Ref. – UCSC			2 ^h	18.46 ± 0	15.68 ± 1	38.36 ± 7	1.1775 ± 10	2.4468 ± 47	~0.5	~3	
Ref. – Consensus		29.5 ± 2.1									
GDI											
This study	5	45.7 ± 2.6	2	18.475 ± 41	15.624 ± 10	38.276 ± 60	1.1825 ± 19	2.4498 ± 22	~2	~17	50 – 55
± 2sd relative (ppm) ^d				2240	650	1570	1597	897			
± 2se typical run (ppm) ⁱ				~190	~200	~210	~30	~30			
Ref. – MIT			4	18.74 ± 17	15.83 ± 12	38.79 ± 31	1.1835 ± 35	2.4494 ± 18	0.25 – 0.5	2.5 – 5	
± 2sd relative (ppm) ^d				9320	7330	8000	2925	744			
Ref. – UCSC			4	18.54 ± 3	15.69 ± 2	38.43 ± 10	1.1815 ± 07	2.4491 ± 35	~0.5	2.5 – 5	
Ref. – Consensus		42.2 ± 1.3									

^a Number of individual sample aliquots analyzed for Pb concentrations. ^b Pb concentrations are corrected for a mean total blank of 11.7 ± 4.3 pg. The uncertainties of the concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction (see text). ^c Number of individual sample aliquots analyzed for Pb isotope compositions. ^d 2sd = 2x standard deviation calculated from results of n separate runs; denotes long-term “external” reproducibility. ^e Volume of individual aliquots used for Pb isotope analyses. ^f Original mass of Pb in sample aliquots used for Pb isotope analyses. ^g Pb recovery for the chemical separation process. ^h 2se = 2x standard error of the mean; denotes within-run (“internal”) precision of a run, based on individual results for measurement cycles. ⁱ Duplicate analyses of Pb separated from a single seawater sample. The Pb isotope reference data (Ref.) are from the labs of Ed Boyle at the Massachusetts Institute of Technology (MIT) and Russ Flegal at the University of California Santa Cruz (UCSC) (Boyle et al., 2012). Results in italics were calculated from data given in the literature. The ‘Consensus’ Pb concentrations are from (Group Consensus values, GEOTRACES, 2013).

2.4. Conclusions

A new analytical procedure has been developed for Pb isotope analysis of seawater and associated Pb concentration measurements by isotope dilution. This involves Mg hydroxide co-precipitation and anion exchange chromatography for Pb pre-concentration and isotopic analysis by TIMS in conjunction with a ^{207}Pb - ^{204}Pb double spike. Analyses of multiple aliquots of six seawater samples demonstrate typical reproducibilities ($\pm 2\text{sd}$) of about 150 to 1700 ppm and 1000 – 2000 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. With this precision, the new data are superior to literature results that were obtained by plasma source mass spectrometry. In particular, they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. Analyses of two GEOTRACES intercalibration samples from the Atlantic Ocean (GDI and GSI) display good agreement with recent results of two other laboratories.

2.5. Author contributions and acknowledgements

The work outlined in this Chapter has been previously published in *Analytica Chimica Acta* and was co-authored by Maxence Paul, Luke Bridgestock, Mark Rehkämper, Tina van de Flierdt and Dominik Weiss (Appendix 1). Specifically, M.P conducted the Pb double spike calibration and developed the chemical separation techniques in conjunction with M.R and T.vdF. The effects of isotopic fractionation accompanying incomplete yields were tested by M.P. The determination and monitoring of laboratory Pb blanks were conducted by M.P and L.B. The reproducibility of the measurements through measurements of NIST SRM and in house seawater standards was conducted by L.B (NIST, Atlantic S, Atlantic D1 and Weddell) and M.P (NIST and Atlantic D2). The assessment of accuracy of the method through measurement of GEOTRACES intercalibration samples was conducted by M.P and L.B (who contributed to Pb concentration determinations). The MAGIC research group, in particular Barry Coles and Katharina Kreissig are acknowledged for their support in keeping the laboratories functioning. Ed Boyle also provided useful tips during method development suggesting the use of HF during column chemistry. Financial support for this work was provided by NERC consortium grant

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Chapter 3

Tracing natural and anthropogenic Pb inputs to the tropical Atlantic using Pb isotopes

Abstract

It is well established that anthropogenic Pb emissions to the oceans completely overwhelmed natural Pb sources during the past century, predominantly due to leaded petrol usage. For example, Pb in Tropical Atlantic surface waters was completely dominated by anthropogenic sources in the 1980's and 1990's, despite receiving potentially large inputs of Pb from natural sources (North African mineral dust and the Amazon basin). Since then, leaded petrol has been phased out nearly everywhere. Here we present Pb concentration and isotope composition data for Tropical Atlantic surface waters collected during two GEOTRACES cruises (GA02, leg 2, 2010 and GA06, 2011) in order to reassess the relative importance of natural and anthropogenic Pb sources to this region.

Relative maxima (of about 30 to 50 %) in the contribution of mineral dust to Pb in ocean surface waters are observed to occur at different latitudes, of about 10 °N and 15 to 20 °N, between the two cruise transects. This observed latitudinal shift is consistent with changes in the position of the North African dust plume during its seasonal migration. This is the first time a significant proportion of Pb from natural sources has been detected in Atlantic surface waters, and can be viewed as the success of the global effort to reduce anthropogenic Pb emissions which started more than 40 years ago.

Furthermore, we present elemental concentration and Pb isotope composition data for aerosols collected in the eastern Tropical Atlantic (GEOTRACES, GA06 cruise). These data are used to assess the importance of differences in atmospheric concentration, deposition efficiency and solubility between Pb associated with mineral dust and anthropogenic sources, in producing the observed maxima in Pb contributions from natural sources (mineral dust) in ocean surface waters. In addition to elevated atmospheric mineral dust concentrations associated with the North African dust plume, the preferential removal of mineral dust relative to anthropogenic Pb from the atmosphere during dry deposition processes is found to be an important factor in setting the observed location and magnitude of the maximum contributions natural Pb sources to ocean surface waters.

Given that this region (1) exhibits the highest atmospheric mineral dust concentrations over the entire global ocean, and (2) is dominated by dry deposition, which preferentially removes mineral dust over anthropogenic Pb, it is reasonable to

assume that it receives the highest relative fluxes of mineral dust to anthropogenic Pb in the entire global ocean. Despite this, anthropogenic Pb sources still supply at least 50 % of the Pb to surface waters of this region. Hence, anthropogenic Pb emissions from other anthropogenic activities overall, remain the dominant source of Pb to the Atlantic ocean following the global phase out of leaded petrol.

3.1. Introduction

Anthropogenic emissions have completely overwhelmed natural environmental Pb sources during the last century, predominantly due to the use of leaded petrol (Pacyna & Pacyna et al., 2001, Reuer & Weiss, 2002, Shotyk et al., 2005, Boyle et al., 2014). The ocean has been heavily affected by this anthropogenic perturbation, with the North Atlantic historically receiving the highest anthropogenic Pb inputs due to its proximity to the industrialised regions of North America and Europe (Véron et al., 1993, Wu & Boyle, 1997, Kelly et al., 2009). Due to the short residence time of Pb in ocean surface waters (~ 2 years), their Pb contents closely track atmospheric inputs (Bacon et al., 1976, Schaule & Patterson, 1981, Véron et al., 1993, Wu & Boyle, 1997a). For example, Pb concentrations in North Atlantic surface waters rose to a peak of ~ 200 pmol/kg in the 1970's before sharply declining (by a factor of ~ 5) during the 1980's – 1990's, coinciding with the increased usage and subsequent phasing out of leaded petrol in the surrounding regions (Wu & Boyle, 1997a, Kelly et al., 2009).

The tropical Atlantic receives the largest inputs of mineral dust (i.e. from North Africa) out of any region in the global ocean (Goudie & Middleton, 2001). It also receives large riverine inputs from the Amazon basin. These are two potentially important natural Pb sources. However, Pb in surface waters of the tropical Atlantic was still completely dominated by anthropogenic sources in the 1980's – 1990's, despite dramatically decreasing anthropogenic inputs (Véron et al., 1994, Alleman et al., 2001a, Weiss et al., 2003). This likely reflected residual leaded petrol utilization in the surrounding regions. Complete leaded petrol cessation has since been achieved in the regions surrounding the tropical Atlantic, with all countries leaded petrol free except for Algeria as of 2010/2011 (United Nations Environment Program). Therefore natural Pb sources (North African mineral dust and Amazon River outflow) to the tropical North Atlantic are likely to have increased in importance.

The detection of Pb from natural sources in ocean surfaces waters would not only be a testament to the global effort to reduce anthropogenic Pb emissions, but would also provide a unique opportunity to study the factors governing marine Pb inputs from both anthropogenic and natural sources. In particular, the relative contribution of anthropogenic emissions and mineral dust to Pb in ocean surfaces waters will depend on (1) the relative concentration of these two sources of Pb in the

atmosphere, (2) the relative deposition efficiencies of Pb associated with these two sources to the ocean surface and (3) the relative solubility of Pb associated with these two sources in the ocean surface.

Anthropogenic Pb (Pb_{anth}) and Pb associated with mineral dust (Pb_{min}) behave differently with respect to their atmospheric emission, transport, subsequent removal and solubility in ocean surface waters. For example, the emission and transport of North African mineral dust over the Atlantic is highly sporadic, meaning atmospheric mineral dust concentrations over the Atlantic frequently vary by orders of magnitude over periods of several days (Prospero, 1996, Galado-Caballero et al., 2012, Prospero et al., 2014). In comparison, the atmospheric concentration of Pb_{anth} has been shown to be comparably constant over similar timescales, reflecting relatively constant rates of emission (Chester et al., 1981, Chester et al., 1993a, Chester et al., 1996, Guerzoni et al., 1999). The efficiency at which Pb_{anth} and Pb_{min} are removed from the atmosphere to the ocean surface furthermore depends on deposition mode (wet versus dry; Duce et al., 1991). While wet deposition is considered to be an efficient removal mechanism for both Pb_{min} and Pb_{anth} , dry deposition is thought to preferentially remove Pb_{min} over Pb_{anth} (Duce et al., 1991, Chester et al., 1999, Guerzoni et al., 1999, Baker et al., 2010, Baker et al., 2013). Furthermore, the solubility of Pb_{min} is known to be much lower than that of Pb_{anth} in ‘natural’ waters (seawater and precipitation) (Maring & Duce, 1990, Kersten et al., 1991, Chester et al., 1993b, Spokes et al., 1994, Guerzoni et al., 1999, Desboeufs et al., 2005, Hsu et al., 2005).

Difficulties in constraining each of these factors (atmospheric concentration, deposition efficiency and solubility) result in large uncertainties for estimates of atmospheric fluxes of trace elements to the ocean surface (e.g. Duce et al., 1991). Since ocean surface waters will integrate variable atmospheric Pb inputs over the residence time of Pb, the relative proportions of Pb_{anth} and Pb_{min} will provide a time averaged record of their relative fluxes. Hence, determining the relative proportions of Pb_{anth} and Pb_{min} in the ocean surface may enable unique insights into the factors influencing their atmospheric flux. This goal can be achieved with the aid of Pb isotope measurements, since Pb isotope composition variations can be used to assess the relative contributions of different Pb sources to atmospheric aerosols and ocean surface waters (e.g. Hamelin et al., 1997, Bollhofer & Rosman, 2001, Weiss et al., 2003, Witt et al., 2006, Noble et al., 2015).

In the current study we have obtained new elemental concentration and Pb isotope composition data for surface seawater and aerosol samples collected in the tropical Atlantic in 2010/2011. These results are evaluated with two main objectives. Firstly, we will reassess the relative proportion of Pb from natural and anthropogenic sources in surface waters of the tropical North Atlantic, following the global cessation of leaded petrol usage. Secondly, we will assess the relative importance of differences in atmospheric concentration, deposition efficiency and solubility between Pb_{anth} and Pb_{min} in setting their observed proportions in the ocean surface.

3.2. Samples

3.2.1 Seawater samples

Surface seawater from 2 – 3 m depth was collected using a towed ‘fish’ whilst underway on the RV Pelagia (GEOTRACES GA02 leg 2 cruise, 11th June – 8th July, 2010) and the RRS Discovery (GEOTRACES GA06 cruise, 7th February – 19th March, 2011) in the western and eastern tropical Atlantic respectively (Fig. 3.1, Table 3.1). In the western tropical Atlantic (WTA), 21 open ocean surface water samples were collected between 31.7 °N at the Bermuda Atlantic Time-series study site (BATS), and 0.7 °N. Water masses influenced by mixing with Amazon River water were encountered at 13 – 17 °N and 4 – 6 °N, identified by a decrease in salinity (Rijkenberg et al., 2014). In the eastern tropical Atlantic (ETA) four surface water samples were collected during a meridional transect between 3.3 °S and 17.4 °N, and one surface seawater sample was collected in East African coastal waters. None of the seawater samples were filtered so they feature both dissolved and particulate Pb. The latter typically contributes < 10 % of total Pb in open ocean seawater (Schaule & Patterson, 1981, Sherrell et al., 1992). Following collection, seawater samples were acidified to pH 2 by addition of ultra pure 6 M HCl.

The main focus of North African mineral dust transport across the tropical North Atlantic varies seasonally and is associated with the oscillation of the Inter Tropical Convergence Zone (ITCZ) (Swap et al., 1996, Moulin et al., 1997, Ben-Ami et al., 2012). During the first few months of the year the westward transport of North African mineral dust across the Atlantic is centered around 4 °N and gradually moves north until reaching a peak latitude of ~ 20 °N in the boreal summer (Ben-Ami et al.,

2012). Since the two cruises (GA02, leg 2 and GA06) were conducted at different times of the year, they transect the North African mineral dust plume at different stages of its seasonal migration (Fig. 3.1b,c).

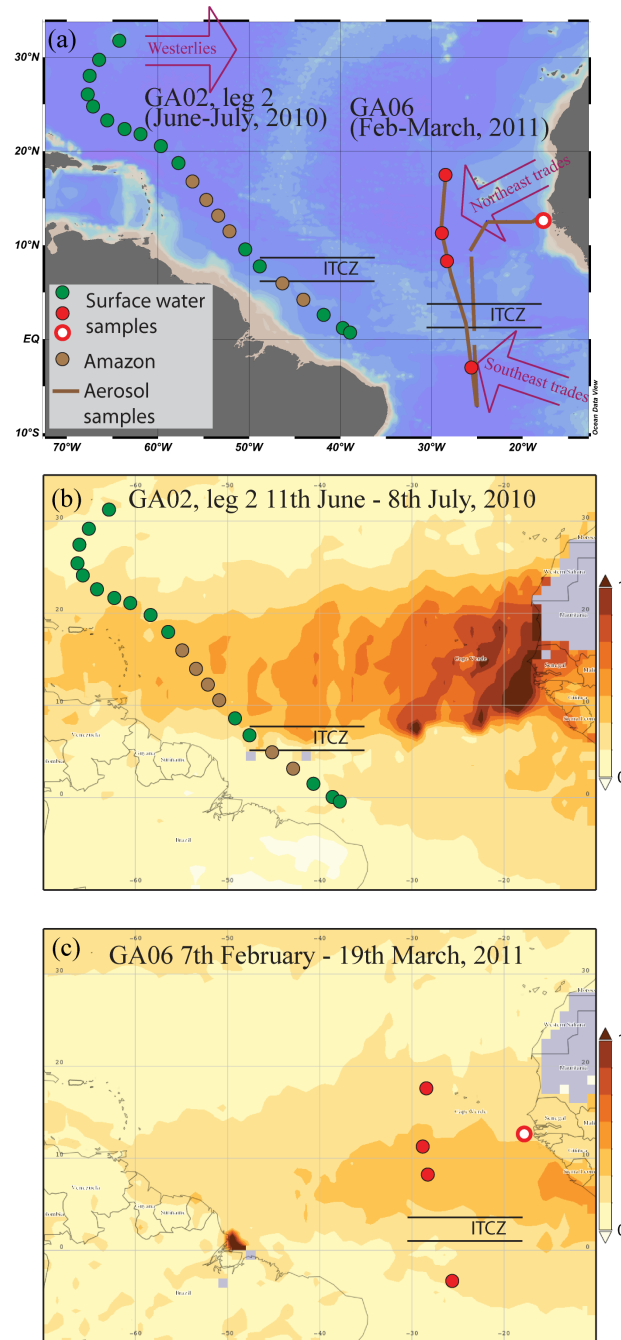


Figure 3.1; Panel (a), a map showing collection locations of surface seawater (circles) and aerosol samples (brown lines) during GEOTRACES GA02 and GA06 cruises. Brown circles indicate surface seawaters affected by mixing with Amazon outflow in the WTA. Arrows show the main meteorological regimes. Black lines show the position of the ITCZ (Inter Tropical Convergence Zone) during the time of each cruise. Produced using Ocean Data View (Schlitzer, 2002). Panels (b) and (c) are maps of aerosol optical depth (550 nm) averaged over the duration of the GA02, leg 2 and GA06 cruises respectively. The position of the North African mineral dust plume over the Atlantic can be clearly identified in each plot by higher values (darker colours). Visualisations were produced using the Giovanni online data system, NASA GES DISC (Acker & Leptoukh, 2007) and data from the MODIS instrument on board the Terra satellite.

3.2.2 Aerosol samples

Eleven aerosol samples were collected for elemental and Pb isotope analysis during the GA06 cruise in the ETA by high-volume sampling ($1 \text{ m}^3 \text{ min}^{-1}$) on to Whatman 41 cellulose fiber filters (203 mm x 241 mm) over $\sim 1 - 2$ days (Sarhou et al., 2003, Baker et al., 2006, Appendix 2). The filters were cleaned prior to aerosol collection at the University of East Anglia, in acid baths of 0.5 M HCl (1 hour) followed by 0.1 M HNO₃ (1 hour) with intermittent rinses with 18.2 M Ω cm water from a Millipore system. Three sampling blanks were collected during the cruise by placing clean filters into the sampling apparatus without turning on the pumping system. One clean, Whatman 41 filter was taken to assess the blank contribution from the filter material. Following sample collection, the filters were stored in zip-lock plastic bags and frozen.

Air mass back trajectories were calculated for the 5 days preceding the start of each aerosol collection period using the NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT, GDAS data set) (Draxler & Rolph, 2003) and are presented in Appendix 2. The aerosol samples are split into three groups based on their air mass back trajectories and collection location (Appendix 2, Table 3.2). The ITCZ separates the northeast trade winds and the southeast trade winds and was positioned at about 4 °N during the time of the GA06 cruise (Schlosser et al., 2014) (Fig. 3.1a). The samples collected north of the ITCZ feature air mass back trajectories typical of the northeast trade winds. They are split into two groups, whereby samples with air mass back trajectories indicating an Algerian origin were distinguished from the remainder (which had air mass back trajectories indicating North African origins). Such a distinction was made since leaded petrol was still available in Algeria at the time of sample collection (United Nations Environment Program). These groups have been termed ‘Algerian’ and ‘northeast trades’ respectively. Three of the samples were collected within/south of the ITCZ. They have air mass back trajectories indicating they did not encounter land in the 5 days preceding collection, and are termed ‘oceanic’.

3.3. Analytical techniques

All sample preparation was conducted in Class 10 laminar flow hoods within the Class 1000 clean rooms of the MAGIC laboratories at Imperial College London unless otherwise stated. Concentrated 15.6 M HNO₃ and 6 M HCl were purified by sub boiling distillation in either quartz or Savillex Teflon stills. Trace metal clean certified 8 M HBr, 28 M HF, 11.6 M HClO₄, 9.8 M H₂O₂ and 17.4 M acetic acid were purchased from commercial vendors. Reagent grade NH₃ was purified by cold vapor phase equilibration with 18.2 MΩ cm water for use in seawater co-precipitation (Chapter 2). Trace metal clean certified NH₃ was purchased from a commercial vendor for use in aerosol leaching (section 3.3.1.2). All acid dilutions were made using 18.2 MΩ cm water from a Millipore system.

The Pb concentrations and isotope compositions of the seawater samples were determined using analytical techniques described in Chapter 2. To distinguish measurements affected by spurious high blanks, Pb concentrations were measured in duplicate or triplicate for the majority of samples, and any anomalously high values were discarded.

3.3.1. Aerosol samples

A portion of each Whatman 41 filter (equivalent to about 25 to 50 % of the total exposed filter area) was subjected to a ‘total’ digestion procedure with the aim of liberating all available Pb and Al for analysis. In addition, a second portion of each Whatman 41 filter (equivalent to about 12 to 50 % of the total exposed filter area) was subjected to leaching, with the aim of liberating the Pb and Al that is readily soluble in ‘natural’ waters for analysis, following previously published methods (Sarhou et al., 2003, Baker et al., 2006, Baker et al., 2010, Baker et al., 2013). Details of these procedures are given in the following sections. The filter portions were taken by cutting the filters using ceramic scissors into pieces that were collected in 60 ml or 90 ml Teflon vials inside a laminar flow bench.

3.3.1.1 Total digestion procedure

In order to digest the Whatman 41 cellulose filter and organic material in the aerosol, the cut filter portions were sequentially digested on a hotplate in: (1) 10 – 20 ml 15.6 M HNO₃ at 90 – 120 °C, for ~ 12 – 15 hours, (2) 10 ml 15.6 M HNO₃ + 1ml 9.8 M H₂O₂ at 90 – 120 °C, for ~ 12 – 15 hours and (3) 4ml 15.6 M HNO₃ + 1ml 11.6 M HClO₄, starting at 120 °C increasing to 220 °C over ~ 12 – 15 hours. Residual HClO₄ was removed by repeated cycles of refluxing in 1 – 2 ml 15.6 M HNO₃ and evaporating to dryness at 140 – 220 °C.

During all of these steps, the lids were left off the Teflon vials to allow the gases produced to escape, resulting in progressive evaporation of the solutions. During step (3), 1 – 2 ml of 15.6 M HNO₃ was added periodically to dilute the HClO₄ and help control the rate of the reaction. Step 2 was omitted for filter portions representing less than 50 % of the total exposed area and step 3 was repeated if the digestion of organics was deemed incomplete. Following this, the aerosol samples were digested in 3ml 15.6M HNO₃ + 1ml 28M HF, at 120 – 140 °C for 4 days (with the lids of the Teflon vials closed), with regular treatments in an ultrasonic bath. Finally, the HNO₃ – HF solutions were evaporated to dryness and samples were re-dissolved in 4M HNO₃. The Pb blank of the total digestion procedure was 53 ± 48 pg (1sd, n = 7), which is < 0.05 % of the Pb processed in the samples and therefore deemed negligible.

3.3.1.2 Leaching procedure

For the leaching of filters, Whatman 41 filter portions were submersed in an ammonium-acetate solution (~ 0.5 M ammonia – 1 M acetic acid, pH 4.7) and shaken for 60 min at 200 rpm (25 ml of solution per 25 % of total exposed filter area). The solutions were then passed through 0.2 µm Whatman cellulose acetate filters within 60 to 75 min of the addition of the leaching solutions. The filtered solutions were evaporated to dryness and re-dissolved in 4M HNO₃. The Pb blank of the leaching procedure was 48 ± 27 pg (1sd, n = 6), which is < 0.05 % of the liberated Pb in the samples and is therefore deemed negligible.

3.3.2.3 Elemental concentrations of the aerosol samples

Elemental concentrations (Pb and Al) were determined on 10 % aliquots of the total digestion and leach solutions, which were evaporated to dryness and redissolved in suitable volumes of 1M HNO₃. Lead concentrations were determined by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) using an Agilent 7700x instrument in the ‘no gas’ mode of the collision-reaction cell, at the Natural History Museum, London. Aluminum concentrations were determined for the total digestion solutions by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo iCap 6500 Duo instrument at the Natural History Museum, London. Exceptions were samples ISO-5_{total} and ISO-11_{total}, where Al concentrations were determined by Q-ICP-MS. For the leach solutions, Al concentrations were determined using Q-ICP-MS.

The Pb blank content of the sampling procedure, as determined by analyses of ‘blank’ Whatman 41 filters were determined to be 25 ± 16 ng/filter (1sd, n = 4) for the total digestion procedure and 12 ± 7 ng/filter (1sd, n = 4) for the leaching procedure. Since these correspond to contributions of between 0.4 – 7.2 % to the Pb extracted by the total digestion and leach procedures, the Pb concentrations were corrected for this blank using the mean values. The uncertainty of the atmospheric Pb concentrations was calculated by propagating the 1sd of the mean blank values through the blank correction.

3.3.1.4 Lead isotope composition of the aerosol samples

Lead isotope compositions were determined on aliquots (0.6 – 53 %) of the total digestion and leach solutions, corresponding to 10 – 100 ng of Pb (typically 20 ng Pb). Lead was purified from the samples by processing them twice through an ion exchange chromatography procedure adapted from Chapter 2 (Appendix 3). The blank contribution of the ion exchange chromatography procedure was 14 ± 13 pg (2sd, n = 7), which is < 0.3 % of the Pb processed and is therefore deemed negligible. The isotope composition of the purified Pb was then analysed using the same measurement protocols as for the seawater samples (Chapter 2).

Loads of 10 ng and 20 ng SRM NIST 981 Pb were analysed at the start of every measurement session, with values in good agreement with literature results

(Appendix 3). Powder aliquots of the basaltic standard reference materials BCR-2 and BHVO-2, with about 20 ng of Pb, were also processed through the ion exchange procedure and analysed alongside the samples. Results given in Appendix 3 are in good agreement with published reference values (Woodhead & Hergt, 2000, Collerson et al., 2002, Baker et al., 2004, Weis et al., 2006). The reproducibility of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of BCR-2, of which 9 separate aliquots were analysed were taken to be representative for the samples (Appendix 3).

Since the blank from the Whatman 41 filters and sampling procedure contributes a significant portion of Pb to the total amount in the samples (0.4 – 7.2 %), a blank correction was implemented to the data using the mean Pb contents and isotope ratios of the blank filters. The isotope ratios determined for the blank filters subjected to the total digestion procedure were 18.3993 ± 0.6067 ($^{206}\text{Pb}/^{204}\text{Pb}$), 1.1745 ± 0.0368 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.4369 ± 0.0230 ($^{208}\text{Pb}/^{207}\text{Pb}$) (mean $\pm$ 2sd, n = 4). For the blank of the leach procedure the results were 18.3228 ± 0.2966 ($^{206}\text{Pb}/^{204}\text{Pb}$), 1.1724 ± 0.0220 ($^{206}\text{Pb}/^{207}\text{Pb}$) and 2.4371 ± 0.0120 ($^{208}\text{Pb}/^{207}\text{Pb}$) (mean $\pm$ 2sd, n = 4).

The uncertainty in the blank correction was calculated by separately propagating through the blank correction (1) the 1sd of the mean blank molar Pb content (since 2sd of the blank content yields unrealistic negative values) and (2) the 2sd of the blank isotope ratios. The total uncertainty for each sample was then calculated by standard addition of variances of (1) the propagated uncertainty in the blank contribution (1sd), (2) the propagated uncertainty of the blank isotope ratios (2sd) and (3) the 2sd of the replicate analyses of isotope ratios of 20 ng BCR-2 aliquots. The former two variances account for uncertainty generated by Pb blank encountered during sample collection, whilst the latter variance accounts for the uncertainty produced during chemical separation and mass spectrometric analysis.

3.4. Results

3.4.1 Seawater Pb concentrations and isotope compositions

Lead concentrations of the open ocean surface waters range between 15 – 24 pmol/kg, with the East African coastal surface water sample displaying a lower value (12 pmol/kg) (Fig. 3.2a, Table 3.1). In the WTA, Pb concentrations are lower in samples influenced by Amazon River water (15.0 – 18.1 pmol/kg) than the rest of the

data set (19.2 – 24.3 pmol/kg). Samples collected north of 20 °N in the WTA feature the highest Pb concentrations (21.5 – 24.2 pmol/kg). The spatial resolution of the open ocean surface water samples collected in the ETA is too low to confidently make inferences on Pb concentration patterns, however they show a similar range of values to those in the WTA (15.8 – 20.3 pmol/kg). The Pb concentrations in the WTA are generally in good agreement with those of filtered seawater samples (< 0.2 µm) (where available) collected during the GEOTRACES GA02 cruise (Fig. 3.2a) (R. Middag, K. Bruland & H. de Baar, personal communication). Exceptions are samples FISH 17 and FISH 20 (in the WTA), where lower Pb concentrations of filtered samples suggest a particulate Pb contribution of 15.5 and 8.3 % respectively to our unfiltered samples. Particulate Pb concentration data (> 0.2 µm) for samples collected during the meridional transect in the ETA at ~ 25 m depth range between 0.75 – 1.85 pmol/kg (A. Milne & M. Lohan, personal communication). Although not directly comparable to our ‘fish’ samples (due to difference in collection depth), they suggest a particulate Pb contribution of approximately 3.7 – 11.7 % to our unfiltered samples collected in the open ocean.

There is a strong correlation between $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ($r^2 = 0.99$) (Appendix 4). Although the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are also correlated ($r^2 = 0.71$), they do feature some independent variability outside of analytical uncertainty that can be used for source identification. Therefore, further discussion will focus on the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios. The Pb isotope compositions of the seawater samples range from 1.1651 to 1.1801 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.4429 to 2.4573 for $^{208}\text{Pb}/^{207}\text{Pb}$.

The Pb isotope ratios for the open ocean surface seawater samples vary with latitude in the WTA (Fig. 3.2b,c, Table 3.1). There is a general increase in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ from ~ 1.168 to ~ 1.177 and ~ 2.445 to ~ 2.457 respectively, between 0.7 and 13.1 °N. A relative maximum in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (1.1724 and 2.4513 respectively) occurs at 5.9 °N. A more pronounced relative maximum in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (1.1770–1.1788 and 2.4552 – 2.4570 respectively) is found between 13.1 and 20.6 °N. Between 20.6 and 31.7 °N, the two isotope ratios become decoupled with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios remaining relatively constant whilst $^{208}\text{Pb}/^{207}\text{Pb}$ ratios decrease to 2.4468. In the ETA, a similar trend in Pb isotope ratios of the open ocean surface waters with latitude is observed, with an increase in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ from 1.1651

and 2.4429 at 3.3 °S to a relative maximum of 1.1743 and 2.4508 at 11.9 °N. In contrast to the WTA, this is followed by a decrease in both ratios to 1.1691 and 2.4473 between 11.9 and 17.4 °N. It should be noted that this trend is poorly constrained due to the low spatial resolution of the sampling. The surface seawater sample collected in coastal waters in the ETA displays elevated $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of 1.1744 and 2.4567 respectively.

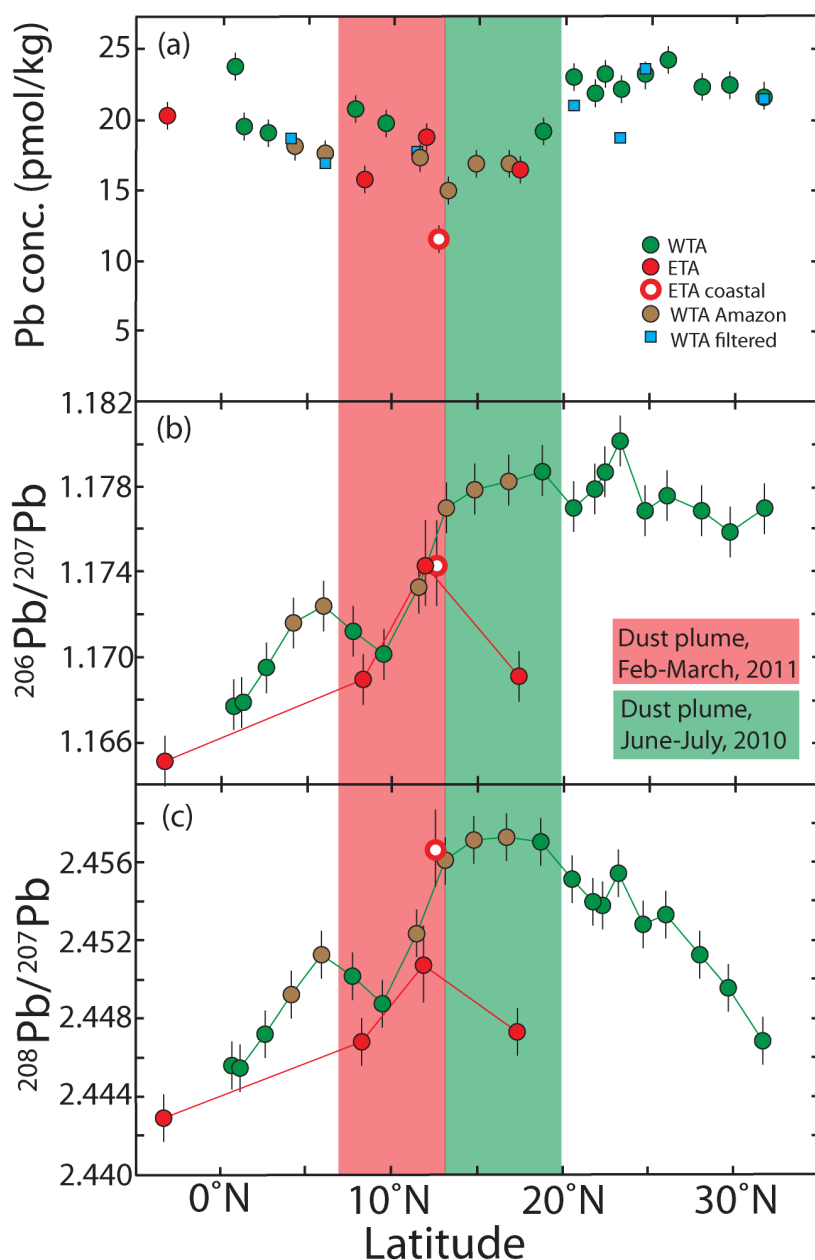


Figure 3.2; Plots of Pb concentrations (Panel a), $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (Panel b) and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (Panel c) for surface seawater samples against latitude. Symbols the same as Fig. 3.1. In addition, Pb concentrations of filtered samples collected during the GA02, leg 2 cruise are shown for comparison (blue squares), courtesy of R. Middig, H. de Baar and K. Bruland (pers. Communication). Red and green shaded fields denote the position of the North African dust plume during the GA06 and GA02, leg 2 cruise, in the ETA and WTA respectively.

Table 3.1, Lead concentration and isotope composition data for surface seawater samples collected during the 2nd leg of GEOTRACES GA02 cruise and the GEOTRACES GA06 cruise in the Tropical Atlantic.

Sample ID	Latitude (°N)	Longitude (°W)	Date	Pb concentration (pmol/kg)	n ^a	²⁰⁶ Pb/ ²⁰⁴ Pb	2se ^b (ppm)	²⁰⁶ Pb/ ²⁰⁷ Pb	2se ^b (ppm)	²⁰⁸ Pb/ ²⁰⁷ Pb	2se ^b (ppm)	Measured Pb quantity ^c (ng)
GA02, leg 2 (WTA) 11 th June – 8 th July, 2010												
Fish 13a	31.70	64.24	13/06	21.51	1	18.4093	150	1.1769	27	2.4468	21	6.0
Fish 13b	29.70	66.44	14/06	22.49	1	18.4034	368	1.1759	43	2.4496	35	3.4
Fish 14	28.04	67.51	16/06	22.28	1	18.4126	288	1.1768	30	2.4513	25	4.2
Fish 16a	26.06	67.72	16/06	24.24	2	18.4187	265	1.1776	32	2.4533	30	5.3
Fish 16b	24.75	67.10	17/06	23.32	1	18.4230	245	1.1769	32	2.4528	30	5.1
Fish 17	23.30	65.58	18/06	22.12	2	18.4650	205	1.1801	35	2.4555	32	4.6
Fish 18	22.38	63.67	19/06	23.20	1	18.4435	178	1.1787	23	2.4538	23	4.7
Fish 19	21.79	61.89	20/06	21.87	3	18.4345	267	1.1779	38	2.4540	35	2.3
Fish 20	20.56	59.72	21/06	23.03	1	18.4231	208	1.1770	30	2.4552	28	4.7
Fish 21	18.74	57.77	22/06	19.12	2	18.4555	241	1.1788	32	2.4570	25	4.8
Fish 22 ^{Amazon}	16.77	56.22	24/06	16.88	2	18.4383	541	1.1783	62	2.4573	50	1.6
Fish 23 ^{Amazon}	14.80	54.74	25/06	16.84	2	18.4529	267	1.1779	46	2.4572	37	4.0
Fish 24 ^{Amazon}	13.15	53.41	26/06	15.00	2	18.4112	459	1.1770	50	2.4561	49	3.3
Fish 25 ^{Amazon}	11.52	52.15	27/06	17.34	2	18.3623	181	1.1733	31	2.4524	24	4.3
Fish 26	9.50	50.43	28/06	19.78	2	18.3015	238	1.1701	31	2.4488	26	3.6
Fish 27	7.73	48.84	30/06	20.80	2	18.3240	271	1.1712	36	2.4502	29	4.7
Fish 28 ^{Amazon}	5.93	46.36	01/07	17.73	2	18.3450	206	1.1724	33	2.4513	26	4.6
Fish 29 ^{Amazon}	4.19	44.04	02/07	18.14	2	18.3336	314	1.1716	37	2.4493	29	3.5
Fish 30	2.62	41.81	03/07	19.19	2	18.2810	311	1.1695	40	2.4472	34	4.0
Fish 31	1.19	39.74	04/07	19.57	2	18.2710	253	1.1679	36	2.4455	27	5.1
Fish 32	0.70	38.97	05/07	23.88	2	18.2584	279	1.1677	34	2.4456	25	4.2
GA06 (ETA) 7 th February – 19 th March, 2011												
Fish 43* ^{Coastal}	12.59	17.65	22/02	11.52	1	18.3803	289	1.1744	37	2.4567	36	2.0
Fish 164	-3.31	25.49	05/03	20.31	1	18.2188	192	1.1651	29	2.4429	21	5.2
Fish 200	8.28	28.31	10/03	15.84	1	18.2834	198	1.1689	31	2.4468	25	4.4
Fish 211*	11.90	28.98	11/03	18.78	1	18.3767	274	1.1743	37	2.4508	26	3.2
Fish 277	17.37	28.39	14/03	16.46	1	18.2843	826	1.1691	102	2.4473	79	3.6

^{Amazon} Denotes samples affected by mixing with Amazon outflow water. ^{Coastal} Denotes sample collected off the coast of east Africa. ^a number of Pb concentration analyses conducted, quoted Pb concentrations are the mean of conducted analyses and have been corrected for an average blank of 11.7 ± 4.3 pg (1sd, n = 36) (Chapter 2). ^b relative within run precision (2se) of isotopic analysis. ^c Quantity of Pb utilized for the isotopic analysis. * Pb isotope ratios are assigned a higher level of uncertainty due to either the low quantity of Pb utilized in the analysis (< 3 ng) or poor within run precision. For these samples, isotope ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb are assigned relative uncertainties of 2.6, 1.7 and 0.8 ‰ respectively, for all other samples, these isotope ratios are assigned uncertainties of 1, 1 and 0.25 ‰ respectively based on replicate analyses (2sd) of in house seawater SRM's (Chapter 2). Likewise, the uncertainty of the Pb concentrations is taken as taken as ± 1 pmol/kg based on replicate analyses (1sd) of in house seawater SRM's (Chapter 2).

3.4.2. Aerosols; elemental concentrations, crustal enrichment factors, fractional solubilities and Pb isotope compositions

Crustal enrichment factors (EF_{crust}) were used to assess the relative amounts of Pb_{anth} and Pb_{min} in the aerosol samples (eqn. 3.1), where Pb/Al_{sample} represents the Pb/Al ratio of the aerosol sample and Pb/Al_{ucc} represents the Pb/Al ratio of the upper continental crust (2.09×10^{-4}), as given by Rudnick & Gao (2003).

$$EF_{\text{crust}} = (Pb/Al_{\text{sample}})/(Pb/Al_{\text{ucc}}) \quad (3.1)$$

The solubility of Pb in the leachates was calculated relative to the total digestions and expressed as a percentage (eqn. 3.2).

$$\text{Fractional solubility (\%)} = (\text{Concentration}_{\text{Leach}}/\text{Concentration}_{\text{Total}}) \times 100 \quad (3.2)$$

The uncertainty in the EF_{crust} values and fractional solubilities was calculated by propagating of the uncertainty (1sd) of the aerosol Pb concentrations.

The calculated atmospheric Pb concentrations based on aerosol measurements and filter exposure time (i.e. volume of air sampled; Appendix 2) range between $0.12 - 4.11 \text{ ngm}^{-3}$ for total Pb (total digestion procedure) and $0.10 - 1.94 \text{ ngm}^{-3}$ for soluble Pb (leachates), which correspond to a fractional solubility of 19 – 83 % (Table 3.2). The concentration of Al in the atmosphere is commonly used as a proxy for the concentration of mineral dust in the atmosphere (assuming mineral dust has an Al concentration of $\sim 8 \%$; e.g. Rahn, 1976, Chester et al., 1981, Chester et al., 1993a, Johansen et al., 2000). The total calculated atmospheric Al concentrations based on aerosol measurements and filter exposure time (i.e. volume of air sampled) range from $68 - 5808 \text{ ngm}^{-3}$, corresponding to atmospheric mineral dust concentrations of $0.85 - 72.6 \text{ } \mu\text{m}^{-3}$. Crustal enrichment factors range from 1.6 – 14.9 for the total digestion procedure and 44 – 411 for the leachates (Table 3.2). The aerosol samples collected within/south of the ITCZ, with ‘oceanic’ air mass back trajectories, feature total atmospheric Pb and Al concentrations at the lower end of the total range of the samples ($0.12 - 0.55 \text{ ngm}^{-3}$ Pb and $68 - 728 \text{ ngm}^{-3}$ Al). In contrast, the two samples featuring the highest total atmospheric Pb concentrations (4.11 & 2.94 ngm^{-3} Pb) are from the ‘Algerian’ group.

The Pb isotope compositions of the aerosol samples lie on a mixing line between North African mineral dust and anthropogenic emissions transported by the northeast trade winds in three isotope space ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$) (Fig. 3.3) (Chow & Patterson, 1962, Bollhofer & Rosman, 2001, Abouchami & Zabel, 2003, Witt et al., 2006, Abouchami et al., 2013a, Kumar et al., 2014). In detail, the Pb isotope composition of the total digestion samples trends towards the mineral dust endmember ($1.1520 - 1.1860$ $^{206}\text{Pb}/^{207}\text{Pb}$ and $2.4265 - 2.4710$ $^{208}\text{Pb}/^{207}\text{Pb}$), while the results for the leachate samples overlap the range of anthropogenic emissions within the northeast trade winds ($1.1338 - 1.1666$ $^{206}\text{Pb}/^{207}\text{Pb}$ and $2.4037 - 2.4466$ $^{208}\text{Pb}/^{207}\text{Pb}$).

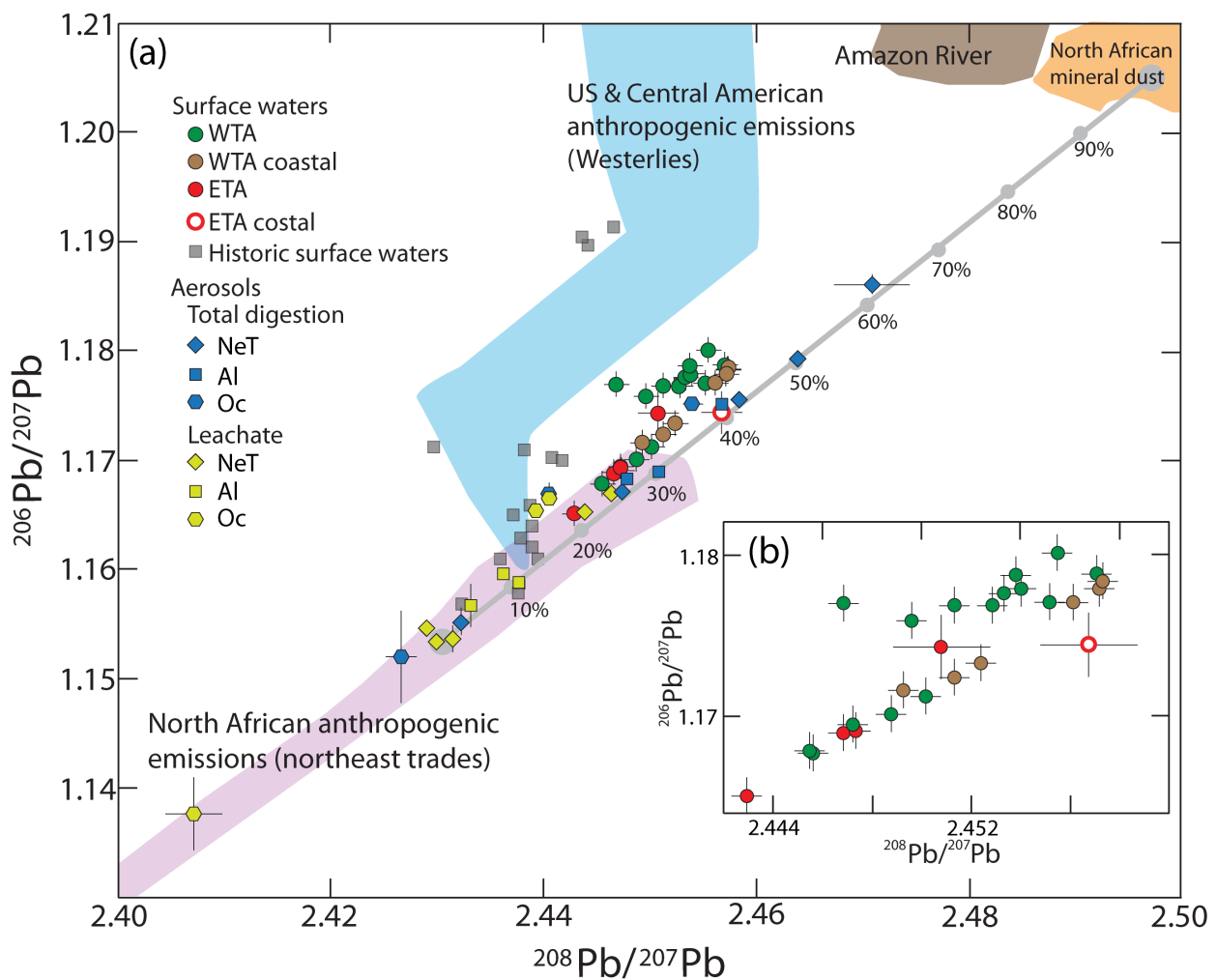


Figure 3.3; Panel (a), a plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ ratios for surface seawater and aerosol samples. Shown for comparison are the Pb isotope composition of (1) the major potential Pb sources to the Tropical Atlantic (coloured fields; see text for references), (2) surface seawaters collected in the region during the 1990's/80's (grey squares; Véron et al., 1994, Alleman et al., 2001a), as well as (3) a mixing line between Pb_{anth} transport by the northeast tradewinds and Pb_{min} (see Appendix 5 for details). Panel (b), displays a plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ ratios featuring the surface seawater samples only.

Table 3.2, Sampling information, elemental concentration and Pb isotope composition data for aerosols collected in the ETA during the GEOTRACES GA06 cruise

Sample ID	Latitude ^a (°N)	Longitude ^a (°W)	Collection date ^b	AMBT Group ^c	[Pb] (ngm ⁻³) ^d	Fractional solubility ^e (%)	[Al] (ngm ⁻³)	EF _{Crust} ^f	[Pb] _{aerth} (ngm ⁻³) ^g	²⁰⁶ Pb/ ²⁰⁴ Pb ^h	²⁰⁶ Pb/ ²⁰⁷ Pb ^h	²⁰⁸ Pb/ ²⁰⁷ Pb ^h
ISO-5 _{Total}	13.13	17.97	21/02	NeT	1.960 ± 0.008		5808*	1.62 ± 0.01	0.75	18.5819 ± 0.0176	1.1860 ± 0.0010	2.4710 ± 0.0036
ISO-5 _{Leach}	- 12.55	- 18.84	- 23/02		0.362 ± 0.008	18.5 ± 0.4	39	44.39 ± 0.98		18.2426 ± 0.0095	1.1668 ± 0.0003	2.4462 ± 0.0005
ISO-7 _{Total}	12.55	18.87	23/02	Al	4.113 ± 0.011		1935	10.19 ± 0.03	3.71	18.2792 ± 0.0087	1.1691 ± 0.0001	2.4508 ± 0.0004
ISO-7 _{Leach}	- 12.57	- 21.82	- 24/02		1.941 ± 0.011	47.2 ± 0.3	32	291.22 ± 1.63		18.1024 ± 0.0087	1.1587 ± 0.0002	2.4378 ± 0.0003
ISO-8 _{Total}	12.57	21.82	24/02	NeT	1.308 ± 0.009		3482	1.80 ± 0.01	0.58	18.4649 ± 0.0088	1.1792 ± 0.0002	2.4638 ± 0.0007
ISO-8 _{Leach}	- 12.57	- 23.76	- 25/02		0.225 ± 0.009	17.2 ± 0.7	15	70.68 ± 2.74		18.0165 ± 0.0214	1.1536 ± 0.0012	2.4314 ± 0.0004
ISO-11 _{Total}	12.54	23.92	25/02	Al	0.506 ± 0.016		1148	2.11 ± 0.07	0.27	18.3925 ± 0.0086	1.1750 ± 0.0001	2.4567 ± 0.0004
ISO-11 _{Leach}	- 9.46	- 25.66	- 27/02		0.214 ± 0.016	42.4 ± 3.4	9	108.50 ± 7.98		18.0679 ± 0.0341	1.1567 ± 0.0020	2.4331 ± 0.0005
ISO-12 _{Total}	8.67	25.62	27/02	Al	2.941 ± 0.012		3891	3.62 ± 0.01	2.13	18.2671 ± 0.0089	1.1682 ± 0.0002	2.4478 ± 0.0004
ISO-12 _{Leach}	- 1.02	- 25.33	- 01/03		1.220 ± 0.012	41.5 ± 0.4	30	193.28 ± 1.91		18.0990 ± 0.0093	1.1597 ± 0.0002	2.4360 ± 0.0003
ISO-14 _{Total}	-0.80	25.31	01/03	Oc	0.193 ± 0.005		137	6.74 ± 0.18	0.16	18.2323 ± 0.0235	1.1669 ± 0.0010	2.4405 ± 0.0007
ISO-14 _{Leach}	- -7.00	- 25.00	- 03/03		0.118 ± 0.005	61.3 ± 3.2	5	104.58 ± 4.67		18.2600 ± 0.0114	1.1666 ± 0.0006	2.4405 ± 0.0004
ISO-16 _{Total}	-7.15	24.99	03/03	Oc	0.117 ± 0.006		68	8.21 ± 0.41	0.10	18.0064 ± 0.0766	1.1520 ± 0.0043	2.4265 ± 0.0015
ISO-16 _{Leach}	- -3.15	- 25.54	- 05/03		0.097 ± 0.006	82.7 ± 6.4	2	308.35 ± 18.74		17.7103 ± 0.0589	1.1376 ± 0.0033	2.4070 ± 0.0027
ISO-19 _{Total}	-2.96	25.61	05/03	Oc	0.552 ± 0.007		728	3.63 ± 0.05	0.40	18.3829 ± 0.0101	1.1751 ± 0.0003	2.4540 ± 0.0008
ISO-19 _{Leach}	- 1.68	- 26.25	- 07/03		0.301 ± 0.007	54.5 ± 1.5	15	93.63 ± 2.22		18.2098 ± 0.0101	1.1654 ± 0.0004	2.4391 ± 0.0003
ISO-21 _{Total}	1.81	26.29	07/03	NeT	0.932 ± 0.006		1527	2.93 ± 0.02	0.61	18.4072 ± 0.0088	1.1756 ± 0.0002	2.4583 ± 0.0005
ISO-21 _{Leach}	- 6.74	- 27.80	- 09/03		0.383 ± 0.006	41.1 ± 0.6	28	64.93 ± 0.94		18.2042 ± 0.0092	1.1652 ± 0.0002	2.4438 ± 0.0004

Table 3.2 continued.

Sample ID	Latitude ^a (°N)	Longitude ^a (°W)	Collection date ^b	AMBT Group ^c	[Pb] (ngm ⁻³) ^d	Fractional solubility ^e (%)	[Al] (ngm ⁻³)	EF _{Crust} ^f	[Pb] _{anth} (ngm ⁻³) ^g	²⁰⁶ Pb/ ²⁰⁴ Pb ^h	²⁰⁶ Pb/ ²⁰⁷ Pb ^h	²⁰⁸ Pb/ ²⁰⁷ Pb ^h
ISO-23 _{Total}	6.84	27.84	09/03	NeT	0.500 ± 0.006		667	3.59 ± 0.04	0.36	18.2453 ± 0.0119	1.1669 ± 0.0004	2.4473 ± 0.0005
ISO-23 _{Leach}	11.31	28.86	11/03		0.314 ± 0.006	63.0 ± 1.3	13	112.59 ± 1.99		18.0142 ± 0.0122	1.1547 ± 0.0005	2.4292 ± 0.0004
ISO-25 _{Total}	11.45	28.89	11/03	NeT	0.230 ± 0.004		74	14.90 ± 0.27	0.21	18.0242 ± 0.0262	1.1552 ± 0.0013	2.4322 ± 0.0004
ISO-25 _{Leach}	17.42	28.38	14/03		0.170 ± 0.004	73.7 ± 2.2	2	411.00 ± 10.11		18.0048 ± 0.0153	1.1534 ± 0.0008	2.4298 ± 0.0004

^a Latitudes/longitudes between which samples were collected. ^b Dates (day/month) between which samples were collected. ^c AMBT = air mass back trajectory group, NeT = northeast trades, Al = Algerian, Oc = oceanic (Appendix 2). ^d Calculated atmospheric Pb concentration, uncertainty is estimated by propagation of the uncertainty in the sampling blank (1sd) (see text). ^e Solubility of Pb in leaching procedure express as a percentage of the Pb in the corresponding total aerosol digest, uncertainty is estimated by propagation of the uncertainty in leach and total aerosol digest atmospheric concentrations (1sd) (see text). ^f Crustal enrichment factors (defined in eqn. 3.1), uncertainty is estimated by propagation of the uncertainty of atmospheric concentrations (1sd) (see text). ^g Estimated atmospheric concentration of Pb from anthropogenic sources (see text). ^h Pb isotope ratios are corrected for the mean blank contribution and isotope composition of the sampling blank, with uncertainties (2sd) assessed as described in the text. * Al concentration above the calibrated range hence should be treated with caution.

3.5. Discussion

In the following, the surface seawater data are first discussed in context of the sources of Pb to the tropical Atlantic (section 3.5.1). The aerosol data are then applied to constrain the relative importance of atmospheric Pb concentrations, deposition efficiencies and solubilities in setting the observed relative contributions of Pb_{min} and Pb_{anth} to surface seawater (section 3.5.2).

3.5.1. Sources of Pb to Tropical Atlantic surface waters

The observed variability in surface water Pb isotope compositions can be explained by mixing between three endmembers; (1) a low $^{206}Pb/^{207}Pb$ - low $^{208}Pb/^{207}Pb$ endmember, (2) a high $^{206}Pb/^{207}Pb$ - low $^{208}Pb/^{207}Pb$ endmember and (3) a high $^{206}Pb/^{207}Pb$ - high $^{208}Pb/^{207}Pb$ endmember (Fig. 3.3). Endmember (1) is most likely anthropogenic Pb transported by the northeast trade winds that are characterised by low $^{206}Pb/^{207}Pb$ and low $^{208}Pb/^{207}Pb$ (1.1235 – 1.1698 and 2.4056 – 2.4540 respectively; Bollhofer & Rosman, 2001, Witt et al., 2006, Kumar et al., 2014, this study). Anthropogenic Pb emissions from central/southern Africa have been previously determined to feature similarly low Pb isotope ratios ($\sim 1.07 - 1.15$ $^{206}Pb/^{207}Pb$, 2.34 – 2.43 $^{208}Pb/^{207}Pb$) (Bollhofer & Rosman, 2000). Therefore, the presence of Pb in surface waters featuring low $^{206}Pb/^{207}Pb$ and low $^{208}Pb/^{207}Pb$ collected south of the ITCZ potentially reflects contributions of Pb transported by the southeast trade winds.

Anthropogenic Pb emissions transported by the Westerlies originating from the US and Central America feature high $^{206}Pb/^{207}Pb$ and relatively low $^{208}Pb/^{207}Pb$ and are most likely the sources of Pb for endmember (2) (Bollhofer & Rosman, 2001). While the synoptic meteorology is not optimal for the transport of South American Pb emissions over the tropical Atlantic, the range of Pb isotope compositions for anthropogenic emissions from this region suggest it could contribute to both endmembers (1) and (2) (Bollhofer & Rosman, 2000, Bollhofer & Rosman, 2001). The high $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{207}Pb$ ratios of endmember (3) are consistent with natural sources of Pb, namely North African mineral dust and riverine inputs from the Amazon basin (Chow & Patterson, 1962, Asmerom & Jacobsen, 1993, Allègre et al., 1996, Abouchami & Zabel, 2003, Abouchami et al., 2013a). A

compilation of the relevant literature data for assessing the Pb isotope compositions of these three endmembers is provided in Appendix 5.

In context of these endmembers, the surface waters close to the equator contain the largest contribution of low $^{206}\text{Pb}/^{207}\text{Pb}$ – low $^{208}\text{Pb}/^{207}\text{Pb}$ anthropogenic Pb transported by the north and/or southeast trade winds. The contribution of natural Pb sources increases with latitude in the WTA, with relative maxima at $\sim 5^\circ\text{N}$ and $\sim 15 - 20^\circ\text{N}$. Between $\sim 20^\circ\text{N} - 30^\circ\text{N}$ in the WTA there is an increase in the contribution of North/Central American anthropogenic Pb emissions transported by the Westerlies. The peak contribution of Pb from natural sources in the ETA occurs at $\sim 11^\circ\text{N}$, followed by an increased contribution of anthropogenic Pb transported by the northeast trade winds at 17°N . In the following section we discuss the importance of North African mineral dust and Amazon River inputs in forming the observed relative maxima in natural Pb contributions (i.e. high $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios).

3.5.1.1 Natural sources of Pb: the Amazon River and North African mineral dust

Since Pb inputs from the Amazon basin and North African mineral dust are both characterised by high $^{206}\text{Pb}/^{207}\text{Pb}$ and high $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, either source could potentially produce the concurrent isotopic maxima observed in the WTA (Fig. 3.2, Fig. 3.3). At $\sim 5^\circ\text{N}$ and between 13.2 and 16.8°N , decreases in salinity due to the mixing of seawater with Amazon River outflow coincide with increases in both $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (Fig. 3.4a). The Amazon may therefore be an important source of natural Pb at these locations. However, the Pb concentrations of these samples are positively correlated with salinity ($r^2 = 0.58$), indicating that the Amazon outflow endmember is characterised by a low Pb content ($\ll 10$ pmol/kg) (Fig. 3.4b). This is much lower than dissolved Pb concentrations in the Amazon River system ($\sim 300 - 800$ pmol/kg; Allègre et al., 1996), suggesting that Pb is efficiently removed by biogeochemical processes during mixing with seawater, consistent with previous findings in this region and for other river systems (Steding et al., 2000, Alleman et al., 2001a). The salinity of the samples affected by mixing with Amazon outflow water ($32.12 - 34.92$), furthermore indicate they are dominated by the ambient seawater with only small contributions from the Amazon outflow endmember. In addition, the samples collected north of 18°N in the WTA, feature

high $^{206}\text{Pb}/^{207}\text{Pb}$ and high $^{208}\text{Pb}/^{207}\text{Pb}$ ratios but are not associated with lower salinities (Fig. 3.2, Fig. 3.4a). Taken together, this suggests that North African mineral dust is likely to be the dominant source of Pb with high $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios in the WTA, with the Amazon exerting a minor additional influence on selected samples (Fig. 3.2, Fig. 3.4).

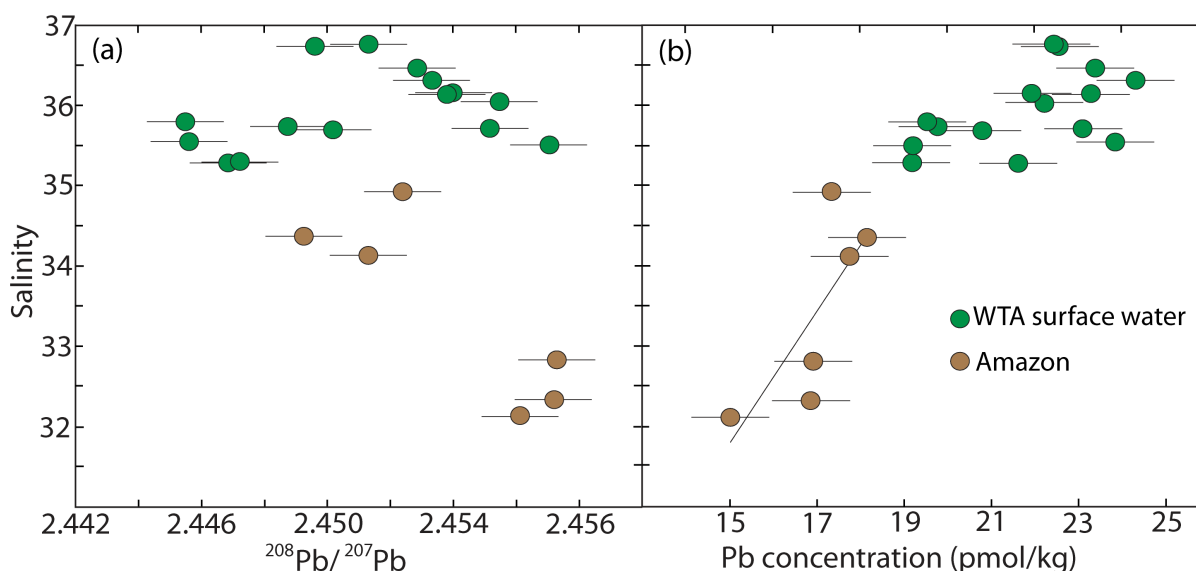


Figure 3.4; A plot of salinity versus $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (panel a), and Pb concentrations (panel b) for surface seawater samples collected in the WTA (GA02, leg 2). The samples influenced by mixing with Amazon River water, are denoted with brown circles, while other samples are denoted with green circles. Since the two potential anthropogenic Pb sources to the Tropical Atlantic feature lower $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than the two potential natural Pb sources (Fig. 3.3), increases in $^{208}\text{Pb}/^{207}\text{Pb}$ ratios can be as increases in the proportion of Pb from natural sources.

The position of the North African dust plume during the 2nd leg of the GA02 cruise in the WTA, coincides with the relative maxima in natural Pb contributions at 13.2 – 20.6 °N (Fig. 3.1b, Fig. 3.2). In the ETA, the relative maxima in natural Pb contributions occurs further to the south (11.9 °N), and is again consistent with the position of the North African mineral dust plume at the time of sample collection (Fig. 3.1c, Fig. 3.2). This supports the interpretation that North African mineral dust is the dominant natural source of Pb (Pb_{min}) to surface waters of the tropical Atlantic. Furthermore it indicates that peak contributions of Pb_{min} to ocean surface waters of this region follow the seasonal migration of the North African dust plume. This is reminiscent of the observed seasonal latitudinal shifts in Pb concentration maxima associated with the migration of the ITCZ (Pohl, et al., 1993, Helmers & Rutgers van der Loeff, 1993).

At the latitudes corresponding to the relative maxima in Pb_{min} contributions (taken as 18.7 °N in the WTA and 11.9 °N in the ETA), the relative proportion of Pb_{min} in surface waters are estimated using mass balance calculations to be between 30 and 50 % (Fig. 3.3). This calculation assumes a Pb_{min} endmember characterised by $^{206}Pb/^{207}Pb = 1.2051 \pm 0.0017$ (2se), $^{208}Pb/^{207}Pb = 2.4972 \pm 0.0029$ (2se), and a Pb_{anth} endmember characterised by $^{206}Pb/^{207}Pb = 1.1532 \pm 0.0057$ (2se), $^{208}Pb/^{207}Pb = 2.4304 \pm 0.0063$ (2se) (see Appendix 5 for details). The relative contribution of mineral dust (Pb_{min} endmember) in the WTA appears to be higher than that of the ETA transect, with a more pronounced maxima in both $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios (Fig. 3.2, Fig. 3.3). This is contrary to what might be expected based on the geographic relationship between the two cruise transects, as the cruise transect in the ETA is closer to the mineral dust source regions and hence should receive higher inputs of mineral dust (Prospero, 1996). This could be an artifact of the poor spatial resolution of sampling in the ETA, but it should be noted that it is also consistent with the observed interannual variability in the magnitude of mineral dust transport over the Atlantic at the time of the two cruises (Prospero et al., 2014) as highlighted in Figure 3.1. Hence the primary control on the relative contribution of Pb_{min} to surface waters seems to be the time dependent, latitudinal migration of the North African dust plume.

This ‘seasonality’ in the signal of atmospheric Pb inputs implies that the residence time of Pb in ocean surface waters in this region must be on the order of months to produce and preserve such spatially distinct isotopic fingerprints. In particular, the residence time must be long enough to allow highly variable atmospheric inputs to be averaged to produce the observed smooth/systematic spatial variability in isotope composition, but short enough to avoid a ‘memory’ of the dust plume’s previous position/redistribution of this input signal by ocean circulation (Fig. 3.2). Our results thus suggest a substantially shorter residence time than the 1 – 2 year value that is generally assumed to be the typical residence time of Pb in oligotrophic ocean surface waters (Bacon et al., 1976, Nozaki et al., 1976, Schaule & Patterson, 1981). Possibly, this discrepancy reflects enhanced scavenging rates due to the high biological productivity and large inputs of mineral dust in this region. Mineral dust is expected to be a sink in addition to a source of Pb through (1) re-adsorption of Pb onto the surfaces of mineral dust particles (Kersten et al., 1991, Chester et al., 1993b, Gueroni et al., 1999, Hsu et al., 2005, Mackey et al., 2015) and (2) by acting as

ballast, increasing the rate at which particulate organic material is removed from the ocean surface (Ternon et al., 2010).

An important question is whether the inferred Pb_{min} maxima represent Pb in the dissolved phase or suspended mineral dust particles in our unfiltered samples. Data from filtered and particulate samples indicates that the proportion of Pb in particulate form ($< 0.2 \mu m$) in our unfiltered samples is typically small ($< 5 \%$), but certain samples could contain up to $\sim 10 - 15 \%$ of particulate Pb (Fig. 3.2a). Therefore, although the majority of Pb in the ocean surface is likely to be in dissolved form, suspended mineral dust contributions could potentially contribute up to $20 - 50 \%$ of the estimated $30 - 50 \%$ Pb_{min} in the relative maxima. An argument against the importance of suspended mineral dust contributions to the inferred Pb_{min} maxima, is the smooth/systematic nature of these features, which suggests a residence time of total Pb on the order of months (see above). Since mineral dust inputs to the ocean surface are highly variable over periods of days (Ternon et al., 2010), and that the residence time of suspended mineral dust particles in the upper few meters of the ocean is likely to be similarly short (Croot et al., 2004), significant spatial variability in the Pb isotope composition of surface waters would be expected if this was controlled by changes in the amount of suspended mineral dust. For example, sample FISH 17 in the WTA, which features a 15.5% particulate contribution, also exhibits a deviation to higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios compared to adjacent samples (Table 3.1, Fig. 3.3). Such variability is likely the result of a sporadic input of mineral dust. We therefore infer that the consistency of the relative Pb_{min} maxima with the position of the North African dust plume indicates that Pb is predominantly in dissolved form. However, further studies that utilise filtered samples are needed to confirm this.

This is the first time a significant proportion (of about $30 - 50 \%$) of Pb from natural sources has been detected in Atlantic surface waters, and - with the exception of potential natural Pb contributions detected in surface waters of the remote Southern Ocean (Flegal et al., 1993) - the entire global ocean. This finding presumably reflects the now (almost) completed phase out of leaded petrol and is a testament to the success of the global effort to reduce anthropogenic Pb emissions which started over 40 years ago (Nriagu, 1990). However, the maximum contributions of Pb_{min} to ocean surface are still less than 50% and are restricted to relatively narrow latitudinal bands that correspond to the highest atmospheric mineral

dust concentrations over the entire global ocean (Fig. 3.2, Fig. 3.3) (Goudie & Middleton, 2001). Therefore, emissions from other anthropogenic activities, such as the combustion of unleaded petrol and coal as well as metal smelting, overall remain the dominant source of Pb to the Atlantic Ocean (Nriagu & Pacyna, 1988, Pacyna & Pacyna et al., 2001).

3.5.2 Constraining the factors governing the relative contribution of Pb_{min} and Pb_{anth} to ocean surface waters

The detection of Pb_{min} in the ocean surface enables the study of the factors that govern its atmospheric flux. The relative proportions of Pb_{min} and Pb_{anth} in the ocean surface (os) will depend on their relative atmospheric concentrations (at), deposition efficiencies (dp) and solubilities (sol) (eqn 3.3).

$$(Pb_{min}/Pb_{anth})_{os} = (Pb_{min}/Pb_{anth})_{at} \times (Pb_{min}/Pb_{anth})_{dp} \times (Pb_{min}/Pb_{anth})_{sol} \quad (3.3)$$

The coincidence of the relative Pb_{min} maxima in the ocean surface with the position of the North African dust plume suggests changes in atmospheric mineral dust concentrations (i.e. changes in $(Pb_{min}/Pb_{anth})_{at}$) are an important factor in driving changes in $(Pb_{min}/Pb_{anth})_{os}$. However, $(Pb_{min}/Pb_{anth})_{dp}$ and $(Pb_{min}/Pb_{anth})_{sol}$ are also likely to play an important role in setting the observed $(Pb_{min}/Pb_{anth})_{os}$. In order to investigate the relative influence of these factors on $(Pb_{min}/Pb_{anth})_{os}$ we discuss the aerosol data in the context of constraining $(Pb_{min}/Pb_{anth})_{at}$ (section 3.5.2.1) and $(Pb_{min}/Pb_{anth})_{sol}$ (section 3.5.2.2). Finally, within these constraints we investigate the importance of $(Pb_{min}/Pb_{anth})_{dp}$ in producing the observed maximum $(Pb_{min}/Pb_{anth})_{os}$ values (section 3.5.2.3).

3.5.2.1 Assessing the relative proportions of Pb_{min} and Pb_{anth} in the atmosphere

Lead EF_{crust} values (i.e. enrichment factors over the average Pb concentration in the upper continental crust) are commonly used to assess the proportion of Pb from anthropogenic relative to crustal sources (i.e. Pb_{min}) in the atmosphere. However it needs to be considered that such values are subject to certain limitations (Rahn, 1976). Firstly, other natural sources of Pb to the atmosphere, such as salt, biomass

burning and volcanic emissions can generate Pb enrichments that cannot be distinguished from Pb_{anth} . Due to the scale of the anthropogenic perturbation of Pb in the environment, which has been extensively documented (e.g. Reuer & Weiss, 2002, Boyle et al., 2014), it however seems reasonable to assume that any currently observed enrichments are dominated by Pb_{anth} . Secondly there is uncertainty in how well the chosen crustal Pb/Al reference ratio (Pb/Al_{ucc}) represents that of the mineral dust ($Pb/Al_{min\ dust}$). As a consequence, it has been convention to only consider EF_{crust} values over 5 or 10 as enriched relative to crustal sources (e.g. Völkening & Heumann et al., 1990, Chester et al., 1993a, Guerzoni et al., 1999, Erel et al., 2006, Galado-Caballero et al., 2012). Following this approach Pb_{min} would be considered to dominate the Pb budget in the majority of our total aerosol digests ($EF_{crust} = 1.6 - 14.9$; Table 3.2). However, if Pb/Al_{ucc} closely matches $Pb/Al_{min\ dust}$, then EF_{crust} values of 5 to 10 would indicate contributions from non-crustal sources of about 80 % to 90 %.

Lead isotopes are a complimentary tracer of atmospheric Pb sources that can help resolve this issue. When $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{207}Pb$ ratios determined for the aerosol total digests and leachates are plotted against EF_{crust} data they display negative correlations (Fig. 3.5a). Mixing lines between mineral dust with a $^{206}Pb/^{207}Pb$ ratio of 1.2051 (and $^{208}Pb/^{207}Pb = 2.4972$) and assuming $Pb/Al_{ucc} = Pb/Al_{min\ dust}$, fitted to the data suggest that the Pb isotope composition of the anthropogenic endmember is characterised by $^{206}Pb/^{207}Pb$ ratios between 1.135 – 1.165 (and $^{208}Pb/^{207}Pb = 2.405 - 2.445$). These values are within the range of the previously reported isotope compositions of anthropogenic Pb emission transported by the northeast trade winds (Bollhofer & Rosman, 2001, Witt et al., 2006, Kumar et al., 2014). This supports the assumption that the enriched Pb in the aerosol samples is dominated by Pb_{anth} . It also shows that isotope composition of Pb_{anth} transported by the trade winds displays considerable variability over timescales of several days.

The Pb isotope composition data can also help constrain $Pb/Al_{min\ dust}$ relative to Pb/Al_{ucc} . The isotopic compositions of the samples with the lowest EF_{crust} values (1.6 – 3.6) indicate a significant contribution from Pb_{anth} . The distribution of these data in Fig. 3.5a, furthermore implies that $Pb/Al_{min\ dust}$ is not significantly smaller Pb/Al_{ucc} , although it is possibly larger than Pb/Al_{ucc} . Guieu et al. (2002) estimated $Pb/Al_{min\ dust}$ to be $3.41 \times 10^{-4} \pm 1.16 \times 10^{-4}$ based on analyses of the fine ($< 20\ \mu m$) component of various North African soils. This result is similar but higher than

$\text{Pb}/\text{Al}_{\text{ucc}}$ (2.09×10^{-4} , Rudnick & Gao, 2003), and hence consistent with our independent estimate. Assuming $\text{Pb}/\text{Al}_{\text{min dust}} = \text{Pb}/\text{Al}_{\text{ucc}}$, the contribution of Pb from mineral dust in the total aerosol digests is estimated to be between 7 – 62 %. This corresponds to atmospheric Pb_{anth} concentrations of $0.10 - 3.71 \text{ ngm}^{-3}$ (assuming any Pb enrichment is dominated by Pb_{anth}) (Table 3.2). The proportion of Pb_{min} and Pb_{anth} in the atmosphere is therefore highly variable over short timescales (several days). In the following we show that this variability is largely driven by changes in the concentration of Pb_{min} in the atmosphere.

Previous studies found that EF_{crust} values are negatively correlated with atmospheric Al concentrations (in $\log_{10}$ space) in regions strongly affected by both anthropogenic and mineral dust emissions (i.e. the Mediterranean Sea and North West Atlantic Ocean; Chester et al., 1981, Chester et al., 1993a, Guerzoni et al., 1999). Such a relationship also exists for our data (Fig. 3.5b) and implies that, although the atmospheric concentration of Pb_{min} over the Atlantic is highly variable, the atmospheric concentration of Pb_{anth} remains relatively constant (Chester et al., 1996). Lines of constant atmospheric Pb_{anth} concentration are shown in Figure 3.5b (assuming $\text{Pb}/\text{Al}_{\text{min dust}} = \text{Pb}/\text{Al}_{\text{ucc}}$ and that any Pb enrichment is dominated by Pb_{anth}). It is reassuring to note that differences in the calculated atmospheric Pb_{anth} concentrations are broadly consistent with those expected based on the air mass back trajectory groupings. For example, samples of the ‘northeast trades’ group, feature intermediate Pb_{anth} concentrations of $0.21 - 0.75 \text{ ngm}^{-3}$. In contrast, two samples belonging to the ‘Algerian’ group have particularly high Pb_{anth} abundances of 2.13 and 3.71 ngm^{-3} , presumably reflecting the continued usage of leaded petrol in Algeria. Furthermore, the samples of the ‘oceanic’ group feature relatively low Pb_{anth} contents of $0.10 - 0.40 \text{ ngm}^{-3}$, presumably reflecting the lack of recent interaction with land and/or efficient removal of Pb_{anth} by wet deposition in the ITCZ (Table 3.2, Fig. 3.5b). In the following, we take the range of atmospheric Pb_{anth} concentrations for the ‘northeast trades’ group to be representative of those typically transported over the tropical North Atlantic.

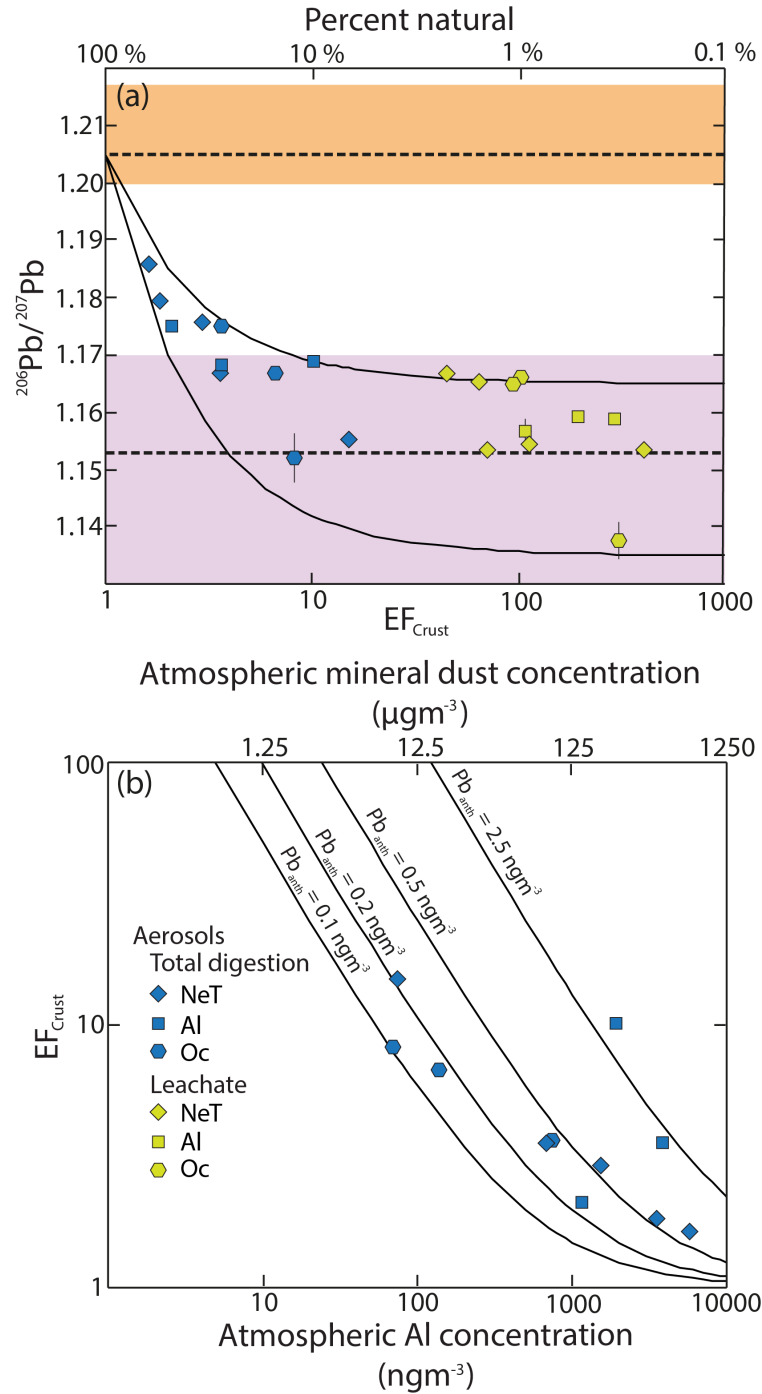


Figure 3.5; Panel (a) displays a plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios versus EF_{Crust} values (see eqn. 3.1) for the total aerosol digests (blue symbols) and leachates (yellow symbols). Shown for comparison, are the ranges of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for North African mineral dust (orange field) and anthropogenic Pb transported by the northeast trade winds (purple field) as well as the mean value of the compiled data sets (dashed lines) (see text for references and Appendix 5 for details). Solid black lines represent mixing lines between North African mineral dust, featuring a $^{206}\text{Pb}/^{207}\text{Pb} = 1.2051$ and $\text{Pb}/\text{Al} = \text{Pb}/\text{Al}_{\text{ucc}}$ (2.09×10^{-4} ; Rudnick & Gao, 2003), and anthropogenic Pb featuring $^{206}\text{Pb}/^{207}\text{Pb} = 1.135$ and $^{206}\text{Pb}/^{207}\text{Pb} = 1.165$. The convergence of data toward the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of North African mineral dust at $\text{EF}_{\text{Crust}} \approx 1$, indicates $\text{Pb}/\text{Al}_{\text{min}} \approx \text{Pb}/\text{Al}_{\text{ucc}}$. Panel (b) displays a plot of EF_{Crust} values versus atmospheric Al concentrations (and atmospheric mineral dust concentrations; see text) for the total aerosol digests. Black lines represent constant atmospheric Pb_{anth} concentrations mixing with mineral dust featuring a $\text{Pb}/\text{Al}_{\text{min}} \approx \text{Pb}/\text{Al}_{\text{ucc}}$. Different shaped symbols in the two panels denote air mass back trajectory groups (Appendix 2); Net = northeast trades (diamonds), Al = Algerian (squares) and Oc = Oceanic (hexagons).

As we previously concluded that the residence time of Pb in surface waters is on the order of several months in the study area (section 3.5.1.2), it is important to constrain the atmospheric Pb_{min} concentrations averaged over a comparable timescale, as this can be used to estimate the impact of the mineral dust flux on seawater Pb budgets. Continuous measurements of atmospheric mineral dust and PM_{10} concentrations at Barbados and Cayenne indicate mean monthly mineral dust concentrations of about $25 - 50 \mu g m^{-3}$ during peak seasonal North African mineral dust transport to those localities in 2010 and 2011 (Prospero et al., 2014). Assuming a mineral dust Al concentration of 8 % and $Pb/Al_{min\ dust} = 2.09 \times 10^{-4}$ (Rudnick & Gao, 2003), this corresponds to mean monthly atmospheric Pb_{min} concentrations of $0.4 - 0.8 ng m^{-3}$. When coupled with the typical Pb_{anth} concentration in the northeast trade winds ($0.21 - 0.75 ng m^{-3}$; Table 3.2, Fig. 3.5b) this results in $(Pb_{min}/Pb_{anth})_{at}$ ratios of $0.6 - 4.0$ (Table 3.3). This estimated range is subject to several sources of uncertainty, particularly (1) how well mineral dust concentrations averaged over monthly periods at coastal sites in the WTA reflect those over the entire tropical Atlantic, averaged over the residence time of Pb in the surface ocean and (2) how representative our estimated range of typical atmospheric Pb_{anth} concentrations is, given the relatively small sample set ($n = 5$) used for assessment. We nevertheless consider this range to be a reasonably conservative estimate.

3.5.2.2 Constraints on the relative solubility of Pb_{min} and Pb_{anth} in the ocean surface

Previous studies concluded that Pb_{anth} is more soluble than Pb_{min} in natural waters (precipitation and seawater) and attributed this to differences in solid state speciation (Maring & Duce, 1990, Kersten et al., 1991, Chester et al., 1993b, Spokes et al., 1994, Gueroni et al., 1999, Desboeufs et al., 2005, Hsu et al., 2005). This is supported by the anthropogenic Pb isotope compositions and high EF_{crust} values of our aerosol leachate samples, which demonstrated that they contain a much higher proportion of Pb_{anth} compared to the total aerosol digests. Furthermore, the estimated proportion of Pb_{min} in the total aerosol digests (section 3.5.2.1) is negatively correlated with fractional solubility with a gradient of -0.94 and an r^2 value of 0.73 (Fig. 3.6). This gradient suggests that $(Pb_{min}/Pb_{anth})_{sol}$ for our leaching procedure is ~ 0.01 (i.e. ~ 1 % decrease in fractional solubility per 1 % increase in the proportion of Pb_{min} in the aerosol). Uncertainty in this estimate arises not only from the scatter of

the results, but also in how well the conditions of the leaching procedure replicate relevant natural processes. A number of factors other than speciation are known to affect the dissolution of trace elements from aerosols in the natural environment, namely pH of the solvent (i.e. rainwater versus seawater), particle loading/size and aerosol history (i.e. chemical and physical processing in the atmosphere) (Lim et al., 1994, Gueroni et al., 1999, Chester et al., 2000, Desboeufs et al., 1999, Desboeufs et al., 2005, Baker & Croot, 2010). However, it is presently unclear how changes in these factors may influence $(Pb_{min}/Pb_{anth})_{sol}$. We therefore solely derived a conservative constraint on $(Pb_{min}/Pb_{anth})_{sol}$ of < 0.1 . Based on the observations of this and previous studies, it seems unlikely that relevant values of $(Pb_{min}/Pb_{anth})_{sol}$ significantly exceed this estimate but studies specifically investigating the effects of the aforementioned factors are warranted to obtain more robust constraints.

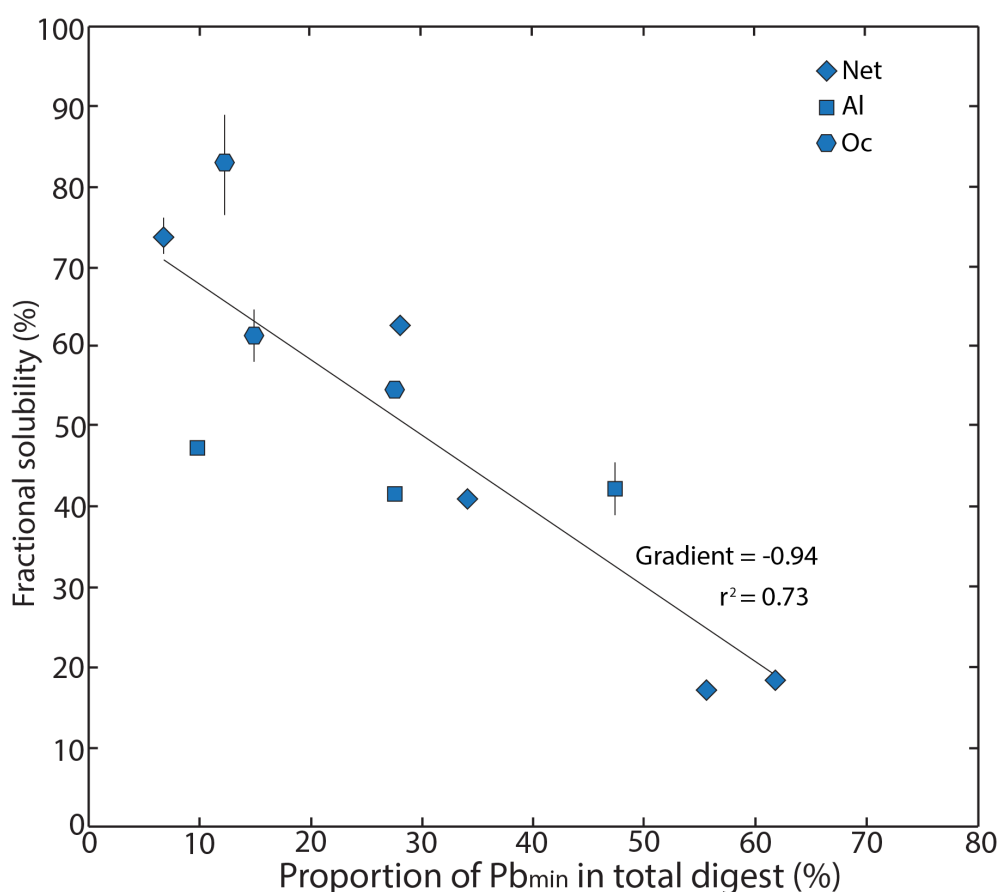


Figure 3.6; A plot of fractional solubility (eqn. 3.2) versus the estimated proportion (%) of Pb_{min} in the total aerosol digests (see section 3.5.2.1). The different symbols denote different air mass back trajectory groups (Appendix 2); Net = northeast trades (diamonds), Al = Algerian (squares) and Oc = Oceanic (hexagons).

3.5.2.3. *The importance of deposition mode*

Particles suspended in the atmosphere are removed to the ocean surface through either wet or dry deposition. The main removal mechanism in dry deposition is gravitational settling, which becomes less efficient with decreasing particle size (Raes et al., 2000). Anthropogenic enrichments of trace metals in aerosols are known to be concentrated in smaller particles ($\sim 0.1 - 1 \mu\text{m}$) than mineral dust ($\sim 2 \mu\text{m}$ following transport to the WTA) (Arimoto et al., 1997, Fomba et al., 2012). Models therefore predict mineral dust to be preferentially deposited over finer anthropogenic particles during dry deposition and this is supported by field observations (Duce et al., 1991, Chester et al., 1999, Guerzoni et al., 1999, Baker et al., 2010, Baker et al., 2013). In contrast, wet deposition is considered to efficiently remove both mineral dust and finer particles (Duce et al., 1991). Therefore, the relative deposition efficiency of Pb_{min} and Pb_{anth} depends on the relative importance of wet versus dry deposition, which in turn is determined by the amount of precipitation received by the region in question. In our study area, the ITCZ region receives intense precipitation (up to 10 mm/day, annual average) whilst the area immediately to the north has much lower precipitation rates (0 - 1 mm/day, annual average) (Kidd & Huffman, 2011). Consequently, wet deposition is thought to be the dominant deposition mode in the ITCZ (Helmerts & Schrems, 1995). Whereas further north, where the relative Pb_{min} maxima in seawater are situated, dry deposition is estimated to account of 95 % of the atmospheric dust flux (Gelado-Caballero et al., 2012).

Table 3.3. Results of sensitivity test on $(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{dp}}$ within the imposed constraints on $(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{at}}$ and $(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{sol}}$									
$(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{sol}}$	$(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{at}}$	1	1.5	2	2.5	3	3.5	4	
0.01	50.0–83.3	30.0–50.0	20.0–33.3	15.0–25.0	12.0–20.0	10.0–16.7	8.6–14.3	7.5–12.5	
0.02	25.0–41.7	15.0–25.0	10.0–16.7	7.5–12.5	6.0–10.0	5.0–8.3	4.3–7.1	3.8–6.3	
0.03	16.7–27.8	10.0–16.7	6.7–11.1	5.0–8.3	4.0–6.7	3.3–5.6	2.9–4.8	2.5–4.2	
0.04	12.5–20.8	7.5–12.5	5.0–8.3	3.8–6.3	3.0–5.0	2.5–4.2	2.1–3.6	1.9–3.1	
0.05	10.0–16.7	6.0–10.0	4.0–6.7	3.0–5.0	2.4–4.0	2.0–3.3	1.7–2.9	1.5–2.5	
0.06	8.3–13.9	5.0–8.3	3.3–5.6	2.5–4.2	2.0–3.3	1.7–2.8	1.4–2.4	1.3–2.1	
0.07	7.1–11.9	4.3–7.1	2.9–4.8	2.1–3.6	1.7–2.9	1.4–2.4	1.2–2.0	1.1–1.8	
0.08	6.3–10.4	3.8–6.3	2.5–4.2	1.9–3.1	1.5–2.5	1.3–2.1	1.1–1.8	0.9–1.6	
0.09	5.6–9.3	3.3–5.6	2.2–3.7	1.7–2.8	1.3–2.2	1.1–1.9	1.0–1.6	0.8–1.4	
0.10	5.0–8.3	3.0–5.0	2.0–3.3	1.5–2.5	1.2–2.0	1.0–1.7	0.9–1.4	0.8–1.3	

The values in each cell corresponds to the required $(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{dp}}$ values to produce a $(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{os}}$ of 0.3 and 0.5 respectively. The region of the domain where the preferential deposition of Pb_{min} over Pb_{anth} is not necessarily required ($(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{dp}} < 2$) is highlighted in dark grey. The region of the domain where the preferential deposition of Pb_{min} over Pb_{anth} agrees with the range used to model dry deposition ($(\text{Pb}_{\text{min}}/\text{Pb}_{\text{anth}})_{\text{dp}} = 10 - 20$) is highlighted in light grey

The largest atmospheric fluxes of Al (as a proxy for mineral dust) to the ocean surface in our study area occur in the ITCZ, associated with wet deposition (Helmers & Rutgers van der Loeff, 1993, Schlosser et al., 2014). Despite this, the surface seawater Pb_{min} maxima are found further to the north, which suggests that differences in deposition mode may significantly influence $(Pb_{min}/Pb_{anth})_{os}$. In particular, it indicates that the preferential removal of Pb_{min} relative to Pb_{anth} during dry deposition of mineral dust north of the ITCZ is important for producing the relative Pb_{min} maxima observed in the ocean surface. To test this hypothesis, Table 3 summarises the results of a sensitivity test, which investigates the $(Pb_{min}/Pb_{anth})_{dp}$ ratios needed to produce the observed $(Pb_{min}/Pb_{anth})_{os} = 0.3 - 0.5$ (section 3.5.2; eqn. 3.3), using the previously derived boundary conditions of $(Pb_{min}/Pb_{anth})_{at} = 0.6 - 4.0$ (section 3.5.2.1) and $(Pb_{min}/Pb_{anth})_{sol} < 0.1$ (section 3.5.2.2). The results of the test support the hypothesis, as they demonstrate that dry deposition, characterised by preferential removal of Pb_{min} over Pb_{anth} with $(Pb_{min}/Pb_{anth})_{dp} > 1$, is required within the majority of the constrained domain (Table 3.3). Only at the highest imposed limits of $(Pb_{min}/Pb_{anth})_{at}$ and $(Pb_{min}/Pb_{anth})_{sol}$ is preferential deposition of Pb_{min} over Pb_{anth} not required to produce the observed $(Pb_{min}/Pb_{anth})_{os}$.

Climatological models of aerosol deposition to the ocean surface have parameterized dry deposition velocities as $0.02 - 0.2 \text{ cms}^{-1}$ and $0.4 - 2 \text{ cms}^{-1}$ in the open ocean for fine (anthropogenic) and course mode particles (mineral dust) respectively, which correspond to $(Pb_{min}/Pb_{anth})_{dp}$ of about $10 - 20$ (Duce et al., 1991, Guerzoni et al., 1999, Baker et al., 2010, Baker et al., 2013). This is consistent with the predictions of the model across the range of constrained $(Pb_{min}/Pb_{anth})_{at}$, for lower $(Pb_{min}/Pb_{anth})_{sol}$ ratios of less than 0.05 (Table 3.3). Within this region of the domain, Pb_{min} would only contribute $2 - 5 \%$ of Pb in the ocean surface without the preferential deposition of Pb_{min} over Pb_{anth} . Taken together, the position of the relative Pb_{min} maxima in the ocean surface, and the model calculations suggest that deposition mode has a significant effect on the occurrence of detectable amounts of natural dust-derived Pb surface seawater.

3.6. Conclusions

A significant amount ($30 - 50 \%$) of Pb from natural sources (mineral dust) was detected in ocean surface waters of the tropical North Atlantic. This finding

presumably reflects the now (almost) complete global phase out of leaded petrol and can be viewed as a success of environmental policy. The relative Pb_{min} maxima in ocean surface waters occur in restricted latitudinal bands, the position of which are influenced by (1) the position of the North African dust plume, which features the highest atmospheric mineral dust concentrations, and hence the highest $(Pb_{min}/Pb_{anth})_{at}$, over any region of the global ocean and (2) the predominance of dry deposition which favors the preferential removal of Pb_{min} relative to Pb_{anth} . Given these factors, it can be expected that this region might receive the highest fluxes of Pb_{min} relative to Pb_{anth} for the entire global ocean following the global cessation of leaded petrol usage. Despite this Pb_{anth} still contributes up to 50 % of the Pb in these surface waters and this demonstrates that Pb emissions from other anthropogenic activities remain the dominant source of Pb to the ocean.

3.7. Author contributions and acknowledgements

For this chapter, I determined the Pb concentrations and isotope compositions of the seawater samples, digested/leached the aerosol samples and determined their Pb isotope compositions, in addition to leading the interpretation of the data set and presentation of the results. Further contributions were received from Tina van de Flierdt, Mark Rehkämper, Alex Baker, Rosie Chance, Stanislav Strekopytov, Emma Humphreys-Williams, Eric Achterberg, Micha Rijkenberg, Angela Milne, Maeve Lohan, Rob Middag, Roulin Khondoker, Hein de Baar and Ken Bruland. Specifically, T. van de Flierdt and M. Rehkämper are acknowledged for their support and guidance throughout this project. S. Strekopytov and E. Humphreys-Williams conducted the measurements of aerosol Pb and Al concentrations. R. Khondoker is thanked for advice on the total digestion and leaching procedures of the aerosols. For the samples collected during the GEOTRACES GA06 cruise credit goes to M. Lohan and E. Achterberg along with the other cruise participants and the captain and crew of the RRS Discovery. Whilst A. Baker and R. Chance are specifically credited with the collecting the aerosol samples during the GA06 cruise. For the samples collected during the GEOTRACES GA02 leg 2, cruise credit goes to M. Rijkenberg and H. de Baar along with the other cruise participants, and the captain and crew of the RV Pelagia. Finally, A. Milne and M. Lohan are thanked for sharing their particulate Pb concentration data (from the GA06 cruise), whilst R. Middag, H. de Baar and K.

Bruland are thanked for providing dissolved Pb concentration data (from the GA02 cruise).

Chapter 4

The utility of Pb isotopes as a transient tracer of ocean circulation in the eastern Tropical Atlantic

Abstract

The distributions of Pb concentrations and isotope compositions in the ocean interior have the potential to provide insights into ventilation timescales and pathways. However, the coverage of such data within the modern ocean is currently limited. Here we present Pb concentration and isotope composition data for three open ocean depth profiles collected in an approximately meridional transect in the eastern Tropical Atlantic (17 °N to 1 °S, between 25 and 28 °W), in addition to a depth profile collected on the continental shelf off the Senegalese coast (GEOTRACES section GA06).

In the open ocean, variations in Pb concentration and isotope composition are associated with hydrographic changes, with water masses ventilated in the southern hemisphere generally featuring lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than those ventilated in the northern hemisphere. These characteristics are consistent with differences in the isotope composition of historic anthropogenic Pb emissions within the two respective hemispheres. Furthermore, Pb concentration and isotope compositions in northern sourced waters are consistent with differences in their ventilation timescales. For example, a Pb concentration maximum at intermediate depth (600 – 900 m, 35 pmol/kg) in northern sourced waters from the Irminger/Labrador Seas, is associated with Pb isotope compositions indicative of northern hemispheric emissions during the 1950's and 1960's close to peak leaded petrol usage, and a transit time of ~ 50 – 60 years. In contrast, North Atlantic Deep Water (2000 to 4000 m water depth) features lower Pb concentrations and isotope compositions indicative of northern hemispheric emissions during the 1910's and 1930's and a transit time of ~ 80 – 100 years. This supports the notion that transient anthropogenic Pb inputs are predominantly transported into the ocean interior by ocean circulation.

However, the interpretation of Pb concentration and isotope composition distributions in terms of ventilation timescales and pathways, is complicated by (1) the chemical reactivity of Pb in the ocean and (2) mixing of waters ventilated at different times. The complex effects of water mass mixing on Pb isotope composition distributions is particularly apparent within the southern hemisphere water masses South Atlantic Central Water and Antarctic Intermediate Water, which are dominated by anthropogenic Pb emitted the last 50 – 100 years, despite being estimated to have

much older average ventilation ages in this region. As more data on the distribution of Pb concentrations and isotope compositions in the ocean interior become available, modeling efforts may help unravel the complex interplay between transient inputs, advection, mixing and chemical reactivity in producing the observed distribution of Pb in the ocean.

4.1. Introduction

Emissions from anthropogenic activities have dominated Pb inputs to the ocean during the past century (Schaule & Patterson, 1981, Kelly et al., 2009). Of particular importance was the use of leaded petrol along with high temperature industrial processes such as metal smelting, coal combustion and waste incineration (Nriagu & Pacyna, 1988, Pacyna & Pacyna, 2001). The isotope compositions of anthropogenic Pb emissions exhibit regional variations, which reflect the distinct Pb ores that were used in different economic regions to supply industrial and automotive activities (e.g. Bollhofer & Rosman, 2000, Bollhofer & Rosman, 2001). This has resulted in spatial variability in the Pb isotope composition of ocean surface waters which can be used to assess the relative contribution of anthropogenic Pb inputs from different regional sources (Flegal et al., 1984, Flegal et al., 1993, Véron et al., 1993, Véron et al., 1994, Hamelin et al., 1997, Véron et al., 1998, Alleman et al. 2001a, Weiss et al., 2003, Noble et al., 2015).

Furthermore, both the magnitude and isotope composition of anthropogenic Pb fluxes to the oceans have changed over time in response to known changes in anthropogenic activities (Boyle et al., 1986, Shen & Boyle, 1987, Véron et al., 1993, Wu & Boyle, 1997a, Desenfant et al., 2006, Kelly et al., 2009). For example, since the 1920's Pb concentrations in North Atlantic surface waters have closely tracked the utilisation of leaded petrol in the surrounding regions with a peak in the 1970's (Shen & Boyle, 1987, Desenfant et al., 2006, Kelly et al., 2009). Accompanying temporal changes in the Pb isotope composition of Atlantic surface waters have been attributed to changes in the relative magnitude of Pb emissions from different areas (i.e. the US and Europe) and changes in the market share of particular Pb ore deposits within regions (Wu & Boyle, 1997a, Véron et al., 1998, Hurst, 2002, Kelly et al., 2009). Due to the short residence time of Pb in the atmosphere (several days; Raes et al., 2000), and the heterogeneous distribution of emission sources, the history of anthropogenic marine Pb fluxes has been significantly different in the Northern and Southern hemispheres (Kelly et al., 2009, McConnell et al., 2014). Consequently, water masses formed in different hemispheres have been subject to different Pb input histories.

These transient Pb inputs were subsequently transported into the ocean interior predominantly by ocean circulation. This is highlighted by time series measurements of Pb concentrations and isotope compositions throughout the water column at the

Bermuda Time Series station between 1979 and 2011 (Schaule & Patterson, 1983, Boyle, 1986, Shen & Boyle, 1988, Sherrell et al., 1992, Véron et al., 1993, Véron et al., 1998, Lee et al., 2011, Boyle et al., 2012, Noble et al., 2015). The observed changes are broadly consistent with those expected from the transport of the known transient Pb inputs into the ocean interior by advection along neutral density surfaces (Boyle, 1986, Shen & Boyle, 1988). However, Pb is removed from the ocean by scavenging, which implies that Pb concentrations are not completely conservative tracers of advection and mixing (Bacon et al., 1976, Boyle, 1986, Shen & Boyle, 1988). Lead isotope compositions are thought to behave more conservatively, whereby differences in the Pb isotope composition of water masses in the Atlantic are interpreted to represent distinct formation locations and ventilation timescales (Alleman et al., 1999, Véron et al., 1999, Alleman et al., 2001b, Noble et al., 2015). Hence, mapping the distribution of Pb concentrations and isotope compositions within the ocean interior can provide insights into ventilation pathways and timescales, complementary to other transient tracers (i.e. CFC's, SF₆ and ³H) (e.g. Doney et al., 1997, Fine, 2011).

A particular advantage of anthropogenic Pb over other transient tracers is the earlier onset of Pb's anthropogenic perturbation, starting at around 1850 in the North Atlantic, compared to the more widely used CFC's and nuclear bomb test products (e.g. ³H), where the anthropogenic effects began in the 1930's to 1950's (Doney et al., 1992, Kelly et al., 2009, Fine, 2011). As a result, Pb allows the assessment of ventilation timescales within 'older' regions of the ocean. In addition, the regional variability of anthropogenic Pb inputs potentially enables insights into subtle differences in water mass formation regions. For example, slightly lower Pb isotope ratios (²⁰⁶Pb/²⁰⁷Pb) observed in Iceland Scotland Overflow Water relative to Denmark Strait Overflow Water have been attributed to the formation site of the former water mass being closer to Europe (Véron et al., 1999, Noble et al., 2015). However, the full potential of this tracer has yet to be realised largely due to limited coverage of the distribution of Pb concentrations and isotope compositions in the ocean interior and the limited understanding of the complex, regionally dependent boundary conditions. Moreover, improved knowledge of the chemical behavior of Pb in the ocean interior is required to confidently use this element as a tracer of ocean circulation, as the distribution of Pb concentrations and isotope compositions in some regions may be affected by particulate transport processes (Wu et al., 2010).

The Tropical Atlantic is a hydrographically complex region, where water masses subducted in the northern and southern hemispheres meet and a series of zonal currents are observed (Tsuchiya et al., 1992, Stramma & Schott, 1999, Schmid et al., 2003, Schott et al., 2003, Stramma et al., 2003, Stramma et al., 2005, Brandt et al., 2008). The eastern Tropical North Atlantic features variable oxygen concentrations with a distinct minimum around the Guinea dome ($\sim 10 - 25^{\circ}\text{N}$, $400 - 500\text{ m}$), resulting from poor ventilation (Karstensen et al., 2008). The deep waters ($> 1200\text{ m}$) of this region feature very low or even undetectable concentrations of commonly used transient tracers (CFC's, SF_6 , ^3H), reflecting transit times greater than ~ 60 years and weaker advection compared to the western Atlantic (Kuhlbrodt et al., 2007, Schneider et al., 2012, Jenkins et al., 2015a). Such decreased advection, as well as variable oxygen concentrations, may result in an increased importance of the vertical transport of Pb via sinking particles, similar to those observed for Nd in the region (Stichel et al., 2015).

A recent study, however showed Pb concentration and isotope composition distributions at about $\sim 17 - 25^{\circ}\text{N}$ in the eastern Atlantic which are broadly consistent with the transport of anthropogenic Pb inputs by ocean circulation (Noble et al., 2015). Here we present Pb concentration and isotope composition data of seawater profiles at three locations that describe a meridional transect in the eastern Tropical Atlantic from about 1°S to 17°N and between 25 and 28°W . In addition, results are presented for one location on the continental shelf off the Senegalese coast (12.4°N , 17.3°W) (Fig. 4.1). These data extend the coverage of the distribution of Pb concentrations and isotope compositions in the ocean interior across the North Atlantic oxygen minimum zone, transecting water masses formed in both the northern and southern hemispheres (Fig. 4.2).

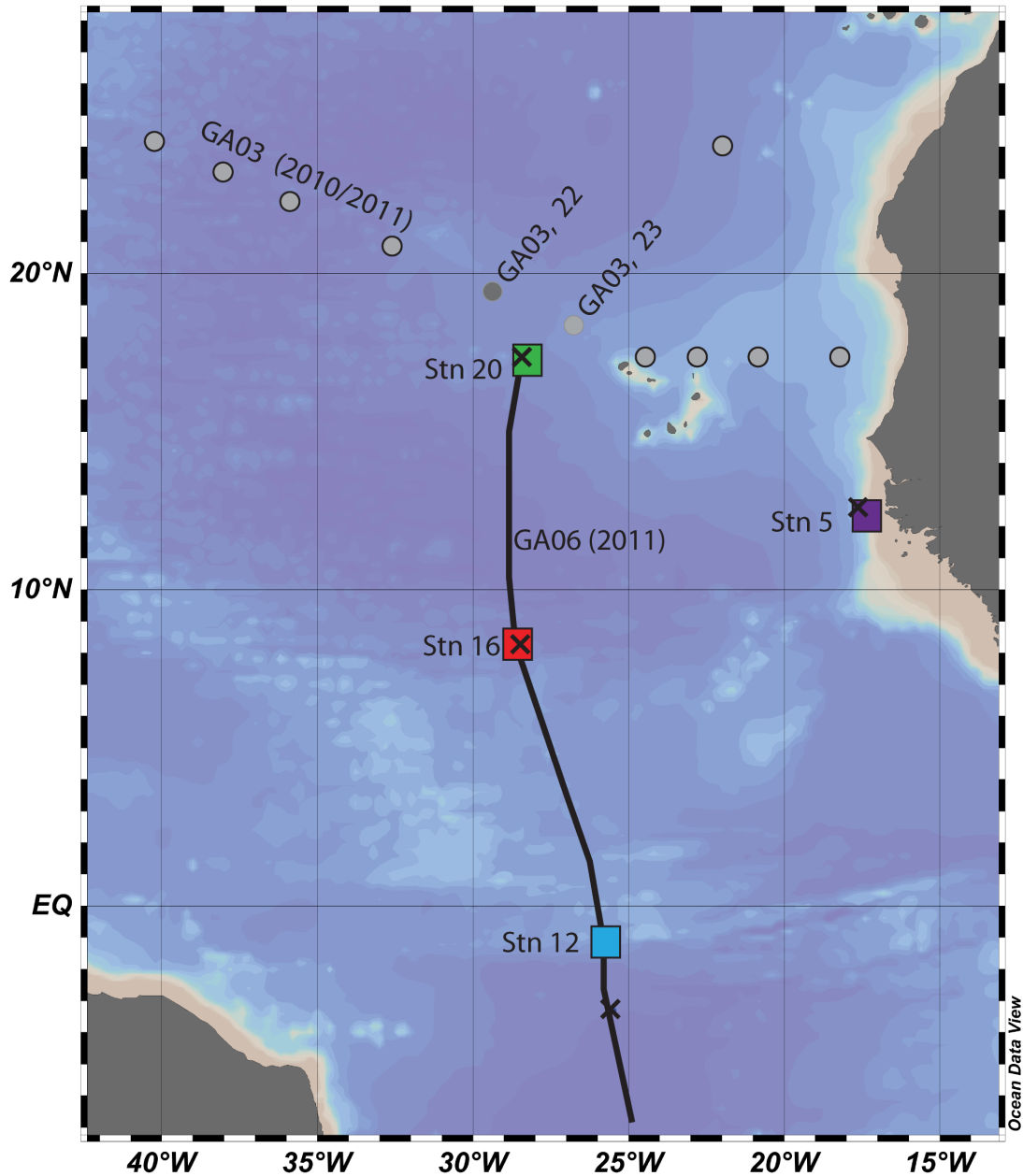


Figure 4.1; Locations of depth profiles collected for this study during the GEOTRACES GA06 cruise in 2011 (squares). Also shown are the locations of surface water samples collected close to each depth profile (previously presented in Chapter 3) (crosses), the line of the section presented in Fig 4.2 (black line) and the positions of depth profiles collected for Pb concentration and isotope composition analysis during the GEOTRACES GA03 cruise in 2010/2011 (grey circles) (Noble et al., 2015). This figure was produced using Ocean Data View (Schlitzer, 2002).

4.2. Samples, analytical techniques and hydrography

Seawater samples were collected during the GEOTRACES GA06 cruise on the RRS Discovery (7th February - 19th March 2011; D361) using a titanium rosette deployed from a non-conducting Kevlar cable and equipped with trace metal clean Niskin sample bottles (de Baar et al., 2008). In addition, data from (near) surface samples collected using a towed ‘fish’ sampler close to the locations of the depth profiles, are used to supplement this sample set (previously presented in Chapter 3) (Fig. 4.1). Following collection, each 2 L sample was transferred into pre-cleaned LPDE bottles inside a clean container and subsequently acidified to pH 2 using purified 6M HCl. No filtration was carried out.

The Pb concentrations and isotope compositions were determined at Imperial College London following analytical protocols outlined in Chapter 2. The Pb concentrations were measured in duplicate or triplicate for the majority of samples, in order to distinguish measurements affected by spurious high blanks, and any anomalous values were discarded. To assess the importance of dissolved and particulate Pb contributions to our unfiltered samples, particulate Pb concentration data are also presented. These data were provided by A. Milne and M. Lohan from the University of Plymouth (pers. communication).

The water masses encountered during the meridional open ocean transect originate from both the northern and southern hemisphere (Fig. 4.2). The upper 50 – 100 m ($\theta > 20\text{ }^{\circ}\text{C}$) of the water column is composed of Tropical Surface Water (TSW) (Stramma & Schott, 1999). Embedded within TSW is a thin, high salinity layer (36 to 37) known as Subtropical Underwater (STUW) (Stramma & Schott, 1999). This water mass is formed by subduction in the Northern and Southern Subtropical gyres and was sampled at 86 m at Station (Stn) 20 and 64 m at Stn 12 (O’Conner et al., 2005). Below TSW, the central waters ($\theta < 20\text{ }^{\circ}\text{C} > \sigma_{\theta} = 27.1$) are dominated by South Atlantic Central Water (SACW) and North Atlantic Central Water (NACW) which are separated by the Cape Verde Frontal Zone (CVFZ) at $\sim 15\text{ }^{\circ}\text{N}$ (Emery & Meincke, 1986, Zenk et al., 1991).

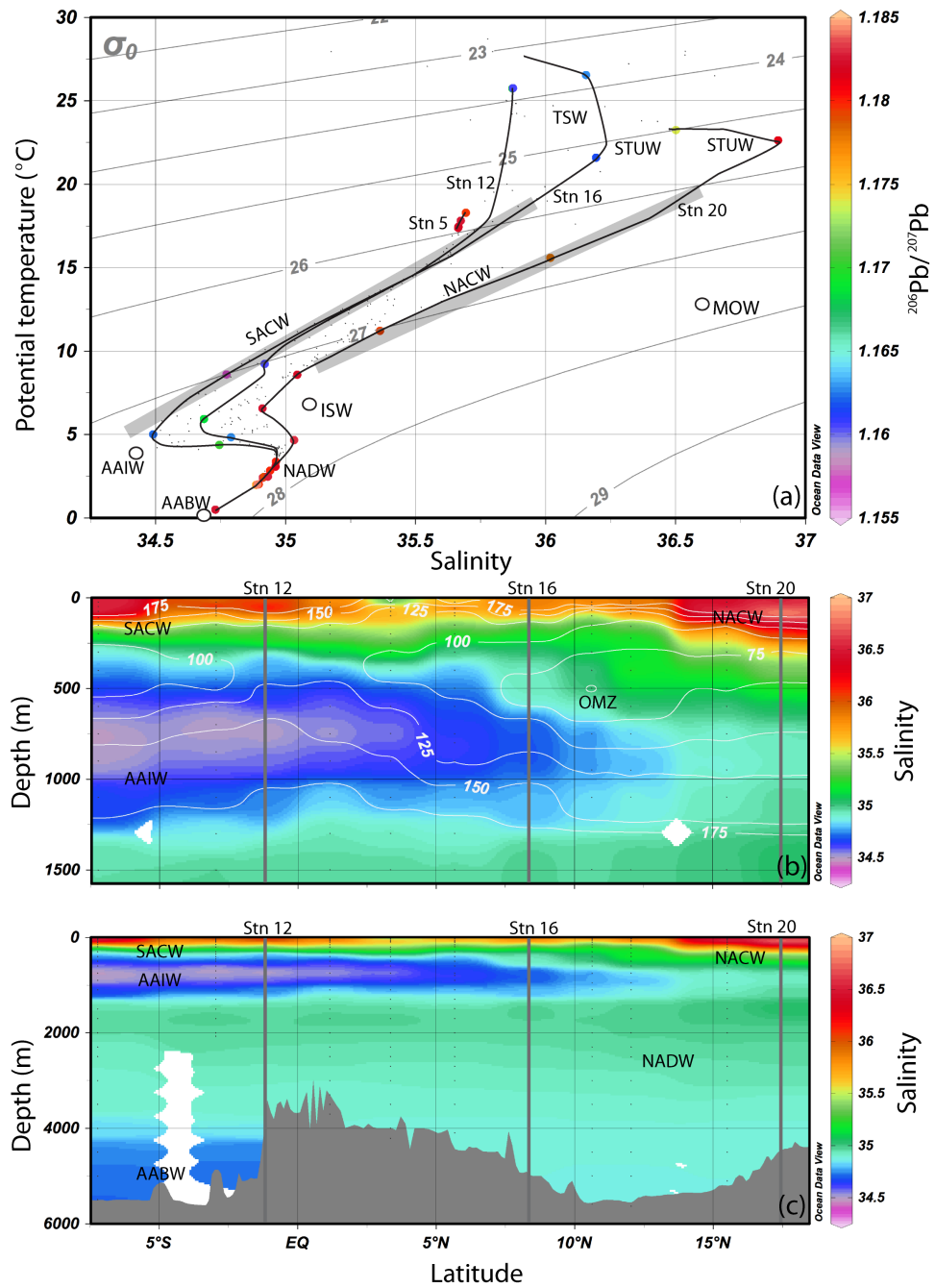


Figure 4.2; Panel (a), displays potential temperature versus salinity determined during the GEOTRACES GA06 cruise. Solid black lines denote the stations sampled for Pb concentration and isotope composition analysis. Open circles show compositions of water mass endmembers (see text for abbreviations), with grey shaded regions showing the compositions of SACW and NACW (after Emery & Meincke, 1986, Jenkins et al., 2015b). Light grey lines denote neutral density horizons (σ_0). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for the analysed samples are shown by the coloured points. Panel (b), Section of salinity (colours) for intermediate depth waters (< 1500 m), with positions of stations 20, 16 and 12 show by the grey lines. Contours of oxygen concentrations (in $\mu\text{mol/kg}$) are denoted by the white lines, and show the position of the oxygen minimum zone (OMZ). Panel (c), section of salinity (colours) for the entire water column. This figure was made using Ocean Data View (Schlitzer, 2002).

Intermediate depth waters (~500 – 1200 m, $\sigma_0 = 27.1 - 27.6$) are composed of Antarctic Intermediate Water (AAIW) in the southern end of the transect (Stn 12) and

northern sourced waters from the Labrador Sea (LSW), Irminger Sea (ISW) and/or Mediterranean outflow (MOW) at the most northerly station (Stn 20) (Emery & Meincke, 1986, Jenkins et al., 2015b). Samples collected along the $\sigma_\theta = 27.3 - 27.4$ neutral density horizons, represent the core of AAIW in various stages of mixing with more saline northern sourced waters (Fig. 4.2).

Below about 1200 m ($\sigma_\theta = 27.6$) North Atlantic Deep Water (NADW) dominates the water column (Tsuchiya et al., 1992). The Mid Atlantic Ridge separates the bottom waters (below ~ 3500 m) in the western and eastern basins (Schlitzer, 1987). At 1 °S, the section crosses the Mid Atlantic Ridge into the western basin (Fig. 4.2), where a decrease in salinity and θ below about 4000 m indicates the presence of dilute Antarctic Bottom Water (AABW), which was sampled at Stn 12 (4500 m).

4.3. Results

4.3.1. Lead concentrations

Lead concentrations for the three open ocean depth profiles range from 7.5 to 43.2 pmol/kg (Fig. 4.3a, Table 4.1). Particulate Pb concentrations ($> 0.2 \mu\text{m}$) range from 0.72 – 2.90 pmol/kg in the open ocean depth profiles, such that particulate Pb contributes approximately 5 – 10 % to the total Pb content of our unfiltered samples. The exception is the single sample collected within AABW (Stn 12, 4500 m), which features a particulate Pb contribution of 24 %. Samples collected within TSW ($> 50 - 100$ m, $\theta > 20$ °C), display relatively uniform Pb concentrations of 17.1 – 18.6 pmol/kg for all open ocean stations except at Stn 16, which features a near surface maximum (24.9 pmol/kg, depth 26 m). This is higher than the sample in the mixed layer directly below (18.6 pmol/kg, depth 56 m) as well as a sample collected at ~ 5 m water depth using a towed “fish” sampler close to the position of this station (15.8 pmol/kg) (Chapter 3). The anomalously high Pb concentration of this sample is also associated with a pronounced positive excursion in $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (see section 4.4.2). Such a high degree of variability in the mixed layer could potentially reflect contamination during sample collection and the results obtained for this sample should hence be treated with caution. However, this region does feature a complex, alternating zonal current system that could result in significant hydrographic changes over small length scales (tens of meters) in this depth range (e.g. Brandt et

al., 2008). At Stn 20, the occurrence of STUW is accompanied by an increase in Pb concentration to 21.5 pmol/kg, whilst at Stn 12 the Pb concentration of this water mass is indistinguishable to that of the overlying TSW.

Lead concentrations increase to a relative maximum in central and intermediate water masses at all three open ocean stations (Fig. 4.3a). This maximum is most pronounced at the most northerly station (Stn 20), reaching ~ 35 pmol/kg between 600 – 900 m, and extends down to at least 1500 m. The Pb distribution is in general agreement with data reported by Noble et al. (2015) for the same depth range from stations that were occupied slightly further north in 2011 (Fig. 4.1, Fig. 4.3a). These depths correspond to northern sourced intermediate waters from the Labrador Sea, Irminger Sea and/or Mediterranean outflow. The Pb concentration maximum in the southern most station (Stn 12, 23.7 pmol/kg) occurs at 395 m, corresponding to SACW. Below this, Pb concentrations drop to a minimum of 11.8 pmol/kg at 750 m within the core of AAIW. At Stn 16, the Pb concentration maximum (25.7 pmol/kg) is situated at 750 m and is intermediate to Pb concentrations at comparable depths (and neutral density horizons) at the adjacent stations (Stn 20, 35 pmol/kg & Stn 12, 11.8 pmol/kg). Based on salinity, this sample represents a mixture of AAIW sampled at Stn 12 (750 m) and the northern sourced intermediate waters (Labrador Sea, Irminger Sea and/or Mediterranean outflow) sampled at Stn 20 (600 – 900 m) (Fig. 4.2).

Between about 2000 and 4000 m, the depth level corresponding to NADW, Pb concentrations at Stns 16 and 20 show a steady decrease with depth from 17 pmol/kg to 11 pmol/kg. These Pb concentrations are in excellent agreement with those determined by Noble et al. (2015) for the same depth range at stations occupied slightly further north in 2011 (Fig. 4.1, Fig. 4.3a). In contrast, the sample at 3000 m at Stn 12 has an anomalously high Pb concentration of 43.2 pmol/kg. The adjacent samples at 2500 m and 3700 m (Stn 12) also show slightly elevated Pb contents (18.4 pmol/kg and 21.4 pmol/kg) relative to those of comparable depths at Stns 16 and 20. The deepest sample at this Stn (12), taken within AABW, features the lowest Pb concentration of the data set (7.5 pmol/kg).

Table 4.1; Results of Pb concentrations and isotope composition analyses for seawater samples from four depth profiles collected in the eastern Tropical Atlantic during the GEOTRACES GA06 cruise

Station	Depth (m)	Total Pb concentration (pmol/kg)	n ^a	Particulate Pb concentration ^b (pmol/kg)	Particulate Pb contribution (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	2se ^c (ppm)	²⁰⁶ Pb/ ²⁰⁷ Pb	2se ^c (ppm)	²⁰⁸ Pb/ ²⁰⁷ Pb	2se ^c (ppm)	Measured Pb ^c (ng)
5	24	17.5	1	12.6 (26 m)	73	18.4753	319	1.1794	36	2.4660	28	3.5
	34	17.4	1	20.9 (36 m)	120	18.5320	257	1.1824	30	2.4737	26	4.4
	49	20.2	1	20.1 (51 m)	99	18.5236	202	1.1818	27	2.4730	21	5.1
	64	20.0	2	16.4 (66 m)	82	18.5143	222	1.1815	29	2.4724	24	4.1
	78*	10.0	2	16.7 (80 m)	166	18.5034	1281	1.1785	172	2.4676	159	1.1
	93	23.1	2	23.8 (107 m)	103	18.5220	224	1.1818	37	2.4709	28	4.3
12	45	16.3	1	0.9 (45 m)	5	18.1826	290	1.1626	49	2.4388	46	3.9
	64	16.8	1	0.6 (60 m)	4	18.1592	277	1.1615	34	2.4368	27	2.7
	395	23.7	1	1.9 (400 m)	8	18.0622	286	1.1566	41	2.4313	36	4.0
	750*	11.8	2	0.7 (750 m)	6	18.1592	449	1.1621	55	2.4360	54	2.0
	1100*	12.1	1	0.9 (1100 m)	8	18.3123	528	1.1702	60	2.4436	61	2.0
	2500	18.4	2	1.2 (2500 m)	6	18.4343	322	1.1797	39	2.4500	30	4.6
	2999	43.2	2	1.6 (2999 m)	4	18.5382	420	1.1829	52	2.4571	46	3.2
	3699*	21.4	2	1.3 (3699 m)	6	18.4419	2634	1.1798	161	2.4519	130	3.4
	4498*	7.5	1	1.8 (4498 m)	24	18.4909	956	1.1823	139	2.4550	131	1.5

Stn 5 was occupied on the 22nd February, 2011 at 12.36 °N, 17.34 °W. Stn 12 was occupied on the 6th March, 2011 at 1.1 °S, 25.36 °W. Stn 16 was occupied on the 10th March, 2011 at 8.20 °N, 28.20 °W. Stn 20 was occupied on the 14th March, 2011 at 17.23 °N, 28.23 °W. ^a Number of Pb concentration analyses conducted. Quoted Pb concentrations are the mean of conducted analyses and were all corrected for a Pb blank of 11.7 ± 4.3 pg (1sd, n = 36) (Chapter 2). ^b Concentration of particulate Pb at the same depth or a depth close to the sample collected for total Pb concentration and isotope composition analysis (data courtesy of Angela Milne and Maeve Lohan), depth of the sample in brackets. ^c The reproducibility of the individual isotopic analysis in ppm (2se). ^d The quantity of Pb available for isotopic analysis (ng).

Table 4.1 continued.

Station	Depth (m)	Total Pb concentration (pmol/kg)	n ^a	Particulate Pb concentration ^b (pmol/kg)	Particulate Pb contribution (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	2se ^c (ppm)	²⁰⁶ Pb/ ²⁰⁷ Pb	2se ^c (ppm)	²⁰⁸ Pb/ ²⁰⁷ Pb	2se ^c (ppm)	Measured Pb ^d (ng)
16	26	24.9	2	1.8 (25 m)	7	18.1251	124	1.1604	27	2.4359	24	7.0
	56	18.6	2	2.0 (54 m)	11	18.2667	169	1.1695	24	2.4456	24	4.4
	404	19.0	2	1.4 (400 m)	7	18.1266	193	1.1603	32	2.4349	23	4.4
	750	25.7	1	1.9 (750 m)	7	18.2683	336	1.1683	41	2.4415	34	4.1
	1099	19.5	1	1.9 (1099 m)	10	18.1540	200	1.1626	29	2.4366	26	3.7
	1999	17.2	1	2.3 (1999 m)	13	18.4451	304	1.1799	38	2.4508	31	4.4
	2999*	13.6	1	1.5 (2999 m)	11	18.4434	537	1.1789	62	2.4520	54	2.3
	3999*	12.6	2	0.7 (3999 m)	5	18.3874	1216	1.1762	114	2.4482	102	2.7
20	26	17.1	1	1.3 (24 m)	8	18.3636	240	1.1737	28	2.4481	26	3.7
	86	21.2	1	1.4 (83 m)	7	18.4815	175	1.1811	37	2.4503	31	5.7
	200	21.7	1	2.1 (200 m)	10	18.4172	243	1.1778	64	2.4468	61	5.0
	405	26.9	1	2.9 (400 m)	11	18.4371	186	1.1792	31	2.4469	29	6.4
	600	33.2	2	1.6 (600 m)	5	18.4868	138	1.1818	25	2.4472	21	7.5
	899	35.7	2	2.5 (899 m)	7	18.4987	28	1.1824	30	2.4483	27	6.4
	1499	29.0	2	2.3 (1499 m)	8	18.5040	304	1.1829	35	2.4523	29	5.1
	2300*	15.0	2	0.9 (2300 m)	6	18.5024	1915	1.1813	182	2.4519	141	3.4
	3000	13.0	2	1.0 (3000 m)	8	18.4948	627	1.1826	83	2.4548	74	3.0
	3999*	11.3	2	1.3 (3999 m)	12	18.5105	708	1.1841	96	2.4545	90	2.9

The relative uncertainty of the isotope ratios is taken as 1, 1 and 0.25 ‰ for the ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios respectively, based on replicate analyses of in-house seawater standards (Chapter 2). * Denotes samples assigned higher relative uncertainties of 2.6, 1.7 and 0.8 ‰ for the ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios respectively based on replicate analyses of in-house seawater standards (Chapter 2), due to high within run uncertainties of low quantities of Pb available for analysis (< 3 ng).

The Pb concentrations of the depth profile collected on the continental shelf off the coast of Senegal (Stn 5) show a general increase with depth from 17.5 pmol/kg to 23.1 pmol/kg (Fig 4.3e). The sample at 78 m features an anomalously low Pb content of 10.0 pmol/kg. Particulate Pb concentrations indicate that the vast majority of Pb (up to 100%) in these samples is in particulate form (Table 4.1, Fig 4.3e).

4.3.2. Lead isotope compositions

The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios display a strong correlation ($r^2 = 0.98$), similar to that exhibited by surface waters and aerosol samples presented in Chapter 3. In contrast, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios feature some independent variability that exceeds analytical uncertainty and which can hence be used for source assessment (Appendix 4). We therefore limit our discussion to the latter two ratios, and only present $^{206}\text{Pb}/^{204}\text{Pb}$ ratio data for completeness (Table 4.1). The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios range between 1.1566 and 1.1841, and 2.4313 and 2.4571 respectively for the open ocean depth profiles (Fig. 4.3bcd, Table 4.1).

The distribution of Pb isotope compositions in the TSW layer generally agrees with data for samples collected in the upper few meters using the “fish” sampler, which are attributed to the variations in atmospheric Pb inputs (see Chapter 3). There are, however a few of exceptions. Firstly, the composition of the anomalous sample from Stn 16 at 26 m depth (see section 4.4.1), may reflect contamination during sampling or small-scale hydrographic variations linked to the complex zonal current system in this region. Secondly, the subsurface sample from within TSW, collected at Stn 20, 26 m, has slightly higher $^{206}\text{Pb}/^{207}\text{Pb}$ and lower $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than the nearby “fish” sample. This deviation trends towards the isotope composition of the underlying STUW, which features a higher Pb concentration (21.5 pmol/kg) and may reflect mixing with Pb transported within this layer. This is supported by a continuous increase in salinity from the surface to the salinity maximum within STUW at this station. Subtropical Underwater at this location features a distinct Pb isotope composition relative to the underlying NACW and overlying TSW (Fig. 4.3bcd). Noble et al. (2015) recently mapped the distribution of Pb isotope compositions in STUW along a quasi-zonal transect across the North Atlantic at ~20 to 40 °N. They found that this layer featured low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the western basin, characteristic

of European Pb emissions, and higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the eastern basin consistent with our finding.

Below the TSW and STUW layers, variations in Pb isotope compositions are associated with hydrographic changes, with water masses formed in the southern hemisphere generally featuring lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than those formed in the northern hemisphere. The lowest $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (1.1566 – 1.1603 and 2.4313 – 2.4349 respectively) are found in SACW (~ 400 m depth, Stns 12 & 16). At Stn 12 at 750 m, AAIW sampled at its most concentrated form also features low Pb isotope ratios, with $^{206}\text{Pb}/^{207}\text{Pb} = 1.1621$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4360$. These isotope compositions are consistent with data previously determined for these water masses in the South and Tropical Atlantic for samples collected in 1996 (Alleman et al., 2001b). In contrast, NACW sampled at Stn 20 at 200 – 405 m depth, features higher $^{206}\text{Pb}/^{207}\text{Pb}$ (1.1778 – 1.1792) and $^{208}\text{Pb}/^{207}\text{Pb}$ (2.4468 – 2.4469) ratios. This isotope signature can be distinguished from the underlying intermediate water (600 m – 900 m,) which has slightly higher $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (2.4472 – 2.4483) in addition to a Pb concentration maximum of ~35 pmol/kg.

At Stn 16, the sample collected at 750 m ($\sigma_\theta = 27.3$) shows isotope ratios that are approximately intermediate ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1683$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4415$) to those determined at Stns 12 and 20 for the same density horizon ($\sigma_\theta = 27.3 - 27.4$). Below this depth and near the boundary between AAIW and NADW (1099 m, $\sigma_\theta = 27.5$) there is an observed decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ (to 1.1626) and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (to 2.4366).

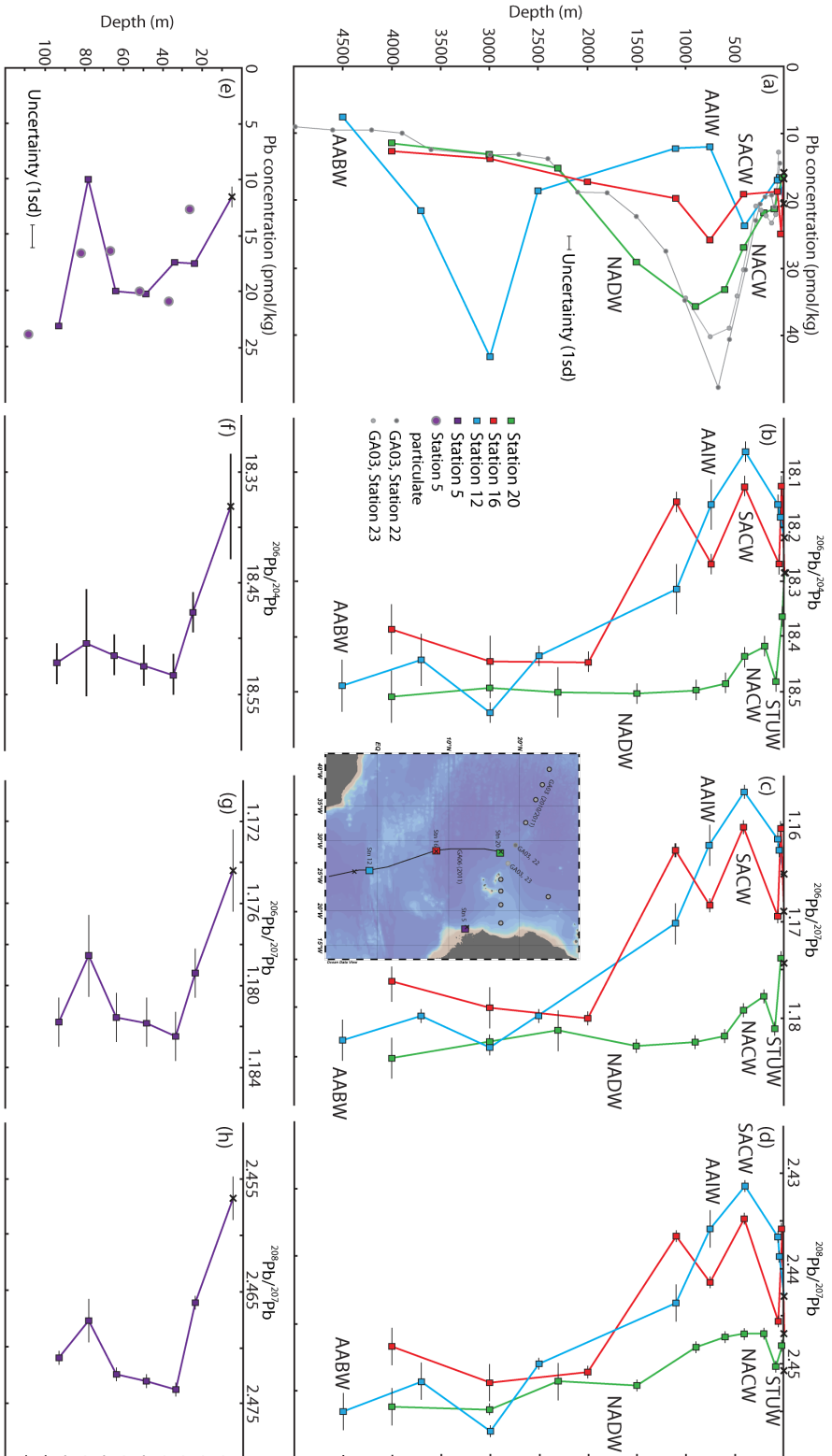


Figure 4.3: Depth profiles of Pb concentration and Pb isotope ratios at Stn 12, 16 and 20 (panels (a) to (d)) and Stn 5 (panels (e) to (h)). Lead concentration depth profiles collected during the GEOTRACES GA03 cruise (Stn 22 and 23) (panel (a)) and particulate Pb concentration data for Stn 5 (panel (e)) are shown for comparison.

North Atlantic Deep Water features a relatively uniform Pb isotope composition ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1762 - 1.1841$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4482 - 2.4500$), which is in good agreement with the NADW composition determined for samples from the eastern Atlantic collected during the GEOTRACES GA03 cruise (Noble et al., 2015). Samples featuring elevated Pb concentrations near the Mid Atlantic Ridge (Stn 12, depth 2500 – 3700 m), show identical Pb isotope compositions to samples from comparable depths at Stns 16 and 20. The single sample collected within AABW features the lowest Pb concentration of 7.5 pmol/kg and has relatively high $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios (of 1.1823 and 2.4550 respectively) that resemble NADW. These values are consistent with previously reported results for dilute AABW in the region by Alleman et al., (2001b). Samples from the depth profile collected off the Senegalese coast feature relatively uniform and high $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, of 1.1785 – 1.1824 and 2.4660 – 2.4737 respectively.

4.4. Discussion

The Pb isotope compositions of the open ocean depth profiles are consistent with anthropogenic emissions during the past century and this highlights the pervasive nature of anthropogenic perturbation of Pb in the environment (Fig. 4.4). Samples from the depth profile collected off the Senegalese coast (Stn 5) lie closest to the composition of pre-anthropogenic (naturally sourced) Pb in three isotope space, with Pb being in predominately particulate form (Fig. 4.3e, Fig. 4.4). This likely reflects the importance of re-suspended shelf sediments, which feature a mixture of Pb derived from anthropogenic sources and North African mineral dust.

The distinct Pb isotope compositions and concentrations of the different water masses suggest that ocean circulation is the dominant transport mechanism for anthropogenic Pb into the interior of the Atlantic. This is in agreement with previous interpretations (Véron et al., 1999, Alleman et al., 1999, Alleman et al., 2001b, Noble et al., 2015). However, vertical transport of Pb via sinking particles through aggregation/disaggregation and chemical equilibrium processes may also play a minor role and cannot be completely ruled out (Sherrell et. al., 1992, Wu et al., 2010). In the following, the data are discussed in the context of penetration of historic anthropogenic Pb emissions into the ocean interior by ocean circulation, and compared to existing constraints on ventilation pathways/timescales.

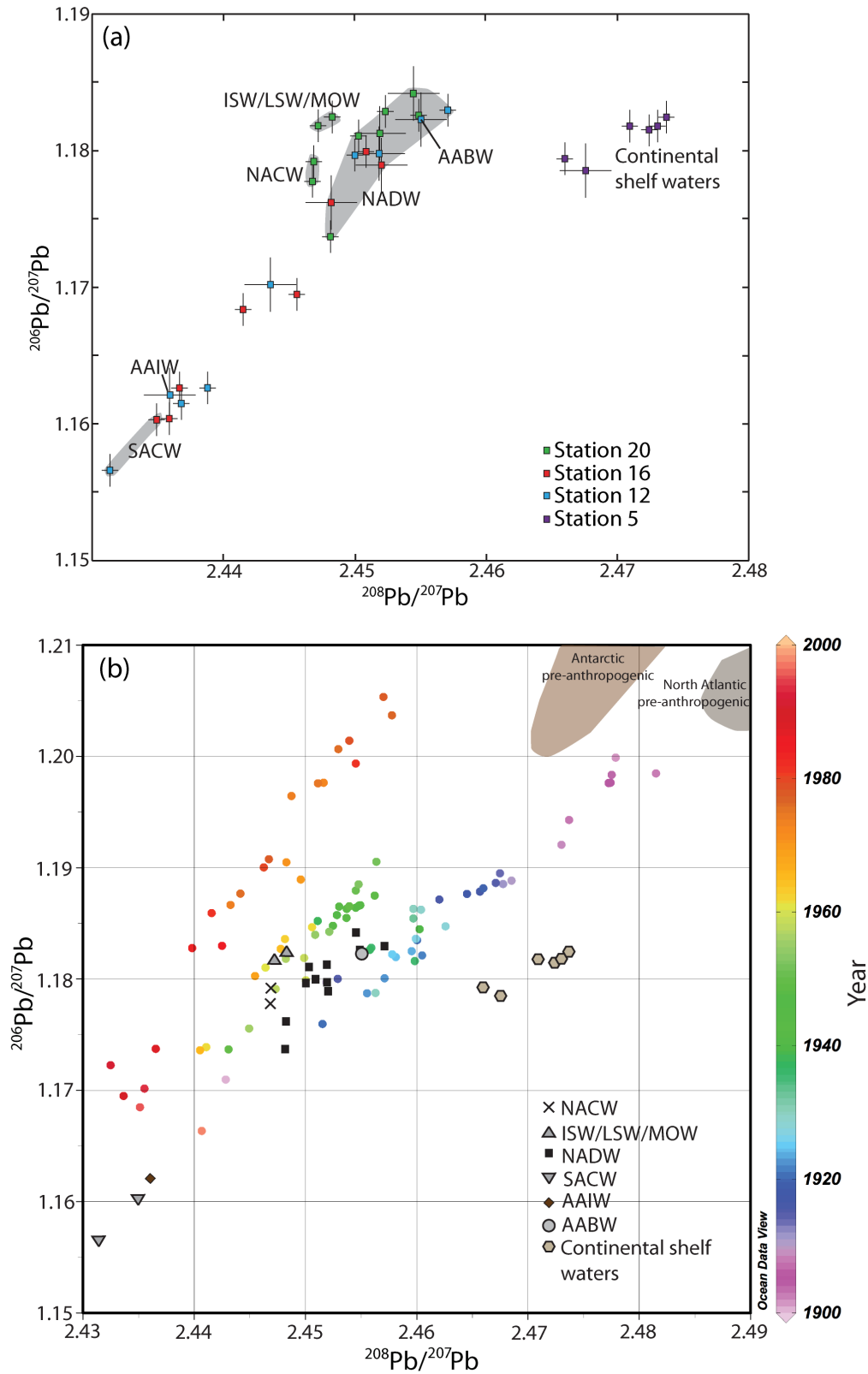


Figure 4.4; Panel (a) three isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$) for seawater samples from the four depth profiles in the eastern tropical Atlantic. Compositions of the main water masses are highlighted (grey fields). Colours denote the different stations Panel (b) three isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$) showing the composition of the major water masses relative (1) to pre-anthropogenic Pb from Antarctic ice cores (Vallelonga et al., 2002, Van de Velde et al., 2005) and North Atlantic Holocene sediments (Chow & Patterson, 1962, Abouchami & Zabel, 2003) and (2) the coral reconstruction of seawater Pb isotope compositions in the western North Atlantic during the last century (Sargasso Sea, Kelly et al., 2009) (coloured dots, with the colours corresponding to the age) . This figure was made using Ocean Data View (Schlitzer, 2002).

4.4.1. Southern hemispheric water masses

South Atlantic Central Water and AAIW are formed by subduction of surface waters within the Antarctic Circumpolar Current (ACC), north of the Polar Front, with the more northerly, less dense variety contributing to SACW (Tomczak & Godfrey, 1994, Stramma & England 1999). Although no direct historic records of Pb inputs to surface waters exist for this region (i.e. reconstructions from coral achieves and/or time series measurements of surface waters; e.g. Kelly et al., 2009)), ice cores and firn provide records of the historic delivery of anthropogenic Pb to Antarctica (Rosman et al., 1994, Barbante et al., 1997, Planchon et al., 2003, Vallelonga et al., 2002, Van de Velde et al., 2005, McConnell et al., 2014). Such records, are generally consistent across the continent suggesting they are representative of the Antarctic region (and potentially the southern hemisphere) as a whole and not subject to significant local bias (McConnell et al., 2014).

Two major periods of southern hemispheric anthropogenic Pb emissions are identified in the Antarctic ice core/firn records. Between about 1890 and 1910, enrichments of anthropogenic Pb are attributed to metal smelting in Australia (Vallelonga et al., 2002, Van de Velde et al., 2005, McConnell et al., 2014). Following a period of reduced anthropogenic Pb fluxes (~ 1930 to 1950), a subsequent rise and fall of anthropogenic Pb enrichments peaking in the 1970's is attributed to the increased use and subsequent phasing out of leaded petrol in southern hemisphere countries (Planchon et al., 2003, Vallelonga et al., 2002, Van de Velde et al., 2005, McConnell et al., 2014). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios associated with the anthropogenic enrichments are much lower (at ~ 1.10 – 1.20) compare to the pre-anthropogenic background (at ~ 1.20 – 1.25) (Planchon et al., 2002, Vallelonga et al., 2002, Van de Velde et al., 2005, McConnell et al., 2014). The low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of SACW and AAIW at Stn 12 (1.1566 – 1.1621) are therefore consistent with anthropogenic southern hemisphere Pb emissions during the past century.

Alleman et al. (2001b) determined similar Pb isotope compositions for these two water masses to our values that were relatively constant across a large area in the South and Tropical Atlantic in 1996 ($^{206}\text{Pb}/^{207}\text{Pb}$ = 1.150 – 1.165, between ~ 10 °N and 35 °S). This suggests a lack of temporal and spatial variability for the isotope composition of anthropogenic Pb transported by these water masses, despite considerable temporal variability in the isotope composition of historic southern hemispheric anthropogenic Pb inputs ($^{206}\text{Pb}/^{207}\text{Pb}$ ≈ 1.10 – 1.20) (McConnell et al., 2014). This observation may be partly explained differences in how the ice core/firn

records integrate variable atmospheric inputs relative to surface waters, whereby ice/firn layers often represent distinct seasons whilst Pb has a typical residence time of 1 – 2 in ocean surface waters (Bacon et al., 1976, Nozaki et al., 1976, Schaule & Patterson, 1981, McConnell et al., 2014). However, another factor could be effective homogenisation of variable anthropogenic Pb inputs during recirculation within in the South Atlantic Subtropical Gyre (Stramma & England 1999). Mixing of water parcels exposed to the atmosphere at different times will produce an average Pb isotope composition which will be biased towards the composition of the water that was ventilated during the period with the highest Pb fluxes, similar to the non-linear mixing effects imposed on other transient tracers (e.g. Doney et al., 1997). The highest Pb fluxes to surface waters of the ACC were likely produced during peak leaded petrol usage in the 1970's, and this was generally associated with low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of about 1.15 – 1.16 (Barbante et al., 1997, McConnell et al., 2014). Hence, the Pb isotope composition of waters in the ocean interior will not necessarily represent the average ventilation age for a mixture of waters ventilated at different times.

The effect of 'non-linear mixing' of water parcels with different ventilation ages on the Pb isotope composition of these waters becomes apparent in a comparison with the ventilation constraints provided by other transient tracers. A transit time distribution model of CFC and SF₆ data yields mean ventilation ages of ~ 150 years and ~ 300 years at neutral density horizons corresponding to SACW ($\sigma_\theta = 27.1$) and AAIW ($\sigma_\theta = 27.3$) respectively, for water along the equator the the eastern Tropical Atlantic, close to the position of Stn.12 (Schneider et al., 2012). These mean ventilation ages pre-date the onset of the anthropogenic Pb perturbation in the southern hemisphere and seem in contrast with the observation of anthropogenic Pb emitted in the past ~ 50 – 100 years at similar neutral density horizons ($\sigma_\theta = 27.0$ & 27.2). This apparent discrepancy results from the mixing of waters that were ventilated during the past century (with high concentrations of anthropogenic Pb) with older waters that feature much low contents of pre anthropogenic Pb. The effect of this large difference in the Pb concentration between waters with difference 'ages' will be to dilute the Pb content of the recently ventilated waters without significantly altering its isotope composition. Antarctic ice and firn records indicate that anthropogenic Pb was enriched by a factor of about 70 over the pre-anthropogenic background during the past century (McConnell et al., 2014). Hence, pre-anthropogenic ocean surface water likely featured much lower Pb concentrations than those affected by anthropogenic Pb inputs. In this context, the lower Pb concentration

of AAIW relative to SACW (by a factor of about 2) is consistent with its older mean ventilation age, which reflects greater dilution of recently ventilated water with older, pre-anthropogenic water.

Antarctic bottom water is formed by the subduction of surface waters close to the Antarctic margin (notably in the Weddell and Ross Seas) with entrainment of Circumpolar Deep Water (Mantyla & Reid, 1983, Orsi et al., 1999, Orsi et al., 2002). The Pb isotope composition of this water mass lies towards to the pre-anthropogenic background in three isotope space, featuring much higher $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than SACW and AAIW (Fig. 4.4). This likely reflects that a smaller proportion of this water mass was ventilated during the past century (characterized by the anthropogenic Pb perturbation of the southern hemispheric) in comparison to SACW and AAIW. The low Pb concentration of AABW (7.5 pmol/kg) is consistent with this interpretation. A larger proportion of pre-anthropogenic Pb is expected for this water mass because significant quantities of poorly ventilated Lower Circumpolar Deep Water, including a component of NADW, are involved in its formation (Orsi et al., 2002). It should, however, be noted that the Pb isotope composition of AABW at Stn 12 is likely to be significantly influenced by the particulate phases, which contribute 24 % to the Pb content of the analysed sample.

4.4.2. Northern hemispheric water masses

Emissions from North America and Europe have dominated the input of Pb into the North Atlantic during the past century (Wu & Boyle, 1997a, Kelly et al., 2009). Reconstructions of Pb concentrations and isotope compositions of surface waters during the last few centuries in the Sargasso Sea are available for comparison to our seawater data (Shen & Boyle, 1987, Desenfant et al., 2006, Kelly et al., 2009). These records are located far from the deep water formation sites in the northern North Atlantic and are likely biased towards North American inputs, relative to the deep water formation sites. However, since US Pb emissions completely dominated over those from Europe between the 1940's and the 1980's, these records are likely a good approximation for the waters that were subducted in the North Atlantic during this period (Wu & Boyle, 1997a, Weiss et al., 2003).

The highest Pb inputs to the North Atlantic were in the 1970's during peak use of leaded petrol in the surrounding regions, similar to the southern hemispheric records (Shen & Boyle, 1987, Desenfant et al., 2006, Kelly et al., 2009). Hence, the Pb isotope composition of mixtures of water parcels ventilated at different times, will

be biased towards the composition of the water parcels that were ventilated closest to the 1970's. A comparison of our Pb isotope data with those from the coral-based reconstruction of Kelly et al. (2009), show that the signature of our NADW samples best matches the Pb emissions during the 1910's to 1930's (Fig. 4.4b). A similar signature was detected by Noble et al. (2015) in NADW collected in the eastern Atlantic in 2011, and suggests a transit time of approximately 80 – 100 years for at least the most recently ventilated components of this water mass. Schlitzer et al. (1985) used the radioactive nuclides ^{14}C and ^{39}Ar to estimate a transit time of $\sim 100 - 200$ years for northern hemispheric derived waters of waters below 3000 m in the eastern Atlantic, which agrees well with our interpretation.

Previous studies furthermore suggested difference in Pb isotope composition between upper and lower NADW in the Tropical and South Atlantic in the 1990's, whereby lower NADW was characterized by lower Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.14 - 1.16$) than upper NADW ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.17 - 1.18$) (Alleman et al., 1999, Alleman et al., 2001b). This is in contrast to our findings and those of Noble et al. (2015), which imply a relatively constant Pb isotope composition throughout the various NADW layers. Notably, the values previously determined for lower NADW by Alleman et al. (1999, 2001b) are lower than any $^{206}\text{Pb}/^{207}\text{Pb}$ ratios found in the available western North Atlantic coral records (Kelly et al., 2009). We speculate that the discrepancy between our data versus the results reported by Alleman et al. (1999, 2001b) may reflect the transient evolution of the composition of NADW in the region between the 1990's and 2011. While the discrepancy between the Sargasso Sea coral record versus the results reported by Alleman et al. (1999, 2001b) may reflect regional differences in the historic Pb emissions to the Nordic Seas relative to the Sargasso Sea. For example, emissions from Europe featuring low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ($\sim 1.14 - 1.15$) have been shown to influence Pb in lake sediments from southwest Greenland (Bindler et al., 2001). Reconstructions of Pb concentrations and isotope compositions for surface waters closer to northern hemispheric deep water formation sites are thus needed, for improved interpretation of these data sets.

The Pb concentration maximum at Stn 20 at 600 – 900 m ($\sigma_\theta = 27.2 - 27.4$) has a Pb isotope composition that matches Sargasso Sea Pb inputs during the 1950's to 1960's, and is similar to the isotope composition of the peak Pb inputs from the 1970's (Fig 4.4b). This Pb signature may therefore originate from waters subducted in the Labrador and/or Irminger Seas with a transit time of about 50 – 60 years. Noble et al. (2015) found Pb concentration maxima at intermediate water depths in the centre of the subtropical gyre that were associated with similar Pb isotope compositions and

SF₆ ventilation ages of ~ 40 years, consistent with our interpretation. They also found a Pb concentration maximum along the east of the basin (18 – 23 °W) that was associated with MOW and featured a similar isotope composition (Noble et al., 2015). Based on the location of Stn 20 (28 °W), the Pb concentration maximum is most likely related to that observed by Noble et al. (2015) in the centre of the subtropical gyre. However, MOW may also contribute some Pb to this signature, highlighting the complexity of advective Pb sources to this region at intermediate depths.

4.4.3. *Mixing of historic northern and southern hemispheric Pb emissions*

The sample collected within AAIW at Stn 16 (750 m) has a Pb concentration and isotope composition that is intermediate to those at comparable depths (and neutral density horizons, $\sigma_\theta = 27.3 - 27.4$) at Stn 20 and Stn 12 (Fig. 4.3). These three samples span a salinity gradient along this neutral density horizon, with northward increasing salinity as AAIW mixes with saltier, northern hemispheric waters (either MOW or LSW/ISW Sea water; Fig. 4.2). The Pb concentration and isotope composition of the Stn 16 sample at 750 m, may therefore be explained by mixing between water with lower concentrations of historic southern hemispheric Pb emissions (featuring low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, i.e. Stn 12) and water with higher concentrations of historic northern hemispheric Pb emissions (featuring high $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, i.e. Stn 20). Based on salinity, the sample from Stn 16, 750 m is a 6+4 mixture of waters at Stn 12 and Stn 20 (along the $\sigma_\theta = 27.3 - 27.4$ neutral density horizons). Taking the samples at Stn 12, 750 m and Stn 20, 899 m as endmembers (Table 4.1) a mass balance calculation predicts that the water mixture at Stn 16, 750 m should be characterised by $[\text{Pb}] = 20.9 \text{ pmol/kg}$ of Pb, $^{206}\text{Pb}/^{207}\text{Pb} = 1.1753$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4437$. Compared to the actual observation, with $[\text{Pb}] = 25.69 \text{ pmol/kg}$, $^{206}\text{Pb}/^{207}\text{Pb} = 1.1683$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4415$, the calculated Pb concentration is too low and the predicted $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios are too high (Fig. 4.5).

Our simplistic mixing model assumes purely isopycnal mixing of water in one dimension (approximately north-south), conservative behavior of Pb in the water column and that the two endmembers are in steady state with respect to Pb in this region. Obviously, these assumptions are likely invalid, so it is not surprising that the observed data do not conform to this model. However, comparing the data point at Stn 16 (750 m) with the model prediction may prove useful for deciphering the complex mixing behavior of this region. The distribution of Pb concentrations and isotope

compositions in the over- and underlying waters make diapycnal mixing an unlikely candidate for reconciling the discrepancy. Furthermore, the removal of Pb by scavenging should offset the observed value to lower Pb concentrations relative to the mixing line, whilst the measurements reveal a higher Pb content (Fig. 4.5). The data point at Stn 16 (750 m) has an estimated particulate Pb contribution of 7 %, which on its own is insufficient to explain the observed excess Pb of about 20 %. However, it is possible that Pb released into solution via sinking particles could play a role in generating the discrepancy, although without additional constraints this hypothesis is difficult to test.

Although the net transport of AAIW is northward, its detailed circulation pattern in this region is complex, involving a series of zonal, alternating currents (Stramma & Schott, 1999, Stramma et al., 2005). Antarctic Intermediate Water enters the Tropical Atlantic via the Intermediate Western Boundary Current off the northeast coast of Brazil (Stramma & Schott, 1999). Likewise, northern sourced water masses enter the region via the Deep Western Boundary Current (Stramma & Schott, 1999). The western Tropical Atlantic is therefore an important region for the mixing of northern and southern sourced water masses (Stramma & Schott, 1999). These waters are then transported into the eastern basin via a series of zonal currents. In particular, a northern branch of the eastward flowing North Equatorial Countercurrent that extends down into AAIW, has been identified at 8 – 10 °N coinciding with the position of Stn 16 (Stramma et al., 2005). Hence, the majority of mixing between historic northern and southern hemispheric Pb emissions likely occurs in the western Tropical Atlantic. This invalidates the assumption of one-dimensional (north – south) isopycnal mixing and hence our choice of endmembers. For the observed Pb concentration at Stn 16, 750 m to lie on a mixing line between northern and southern hemispheric emissions, one or both of the endmembers needs to feature a higher Pb concentration and/or lower Pb isotope ratios than those determined for Stn 12 and 20.

The complexity of hydrological variations and associated distribution of Pb concentrations and isotope compositions at intermediate depth in this region were recently highlighted by Noble et al. (2015). Two depth profiles collected just 16 hours apart at the same location (17.4 °N, 24.5 °W), revealed rapid temporal variability of Pb concentration and isotope composition variability that were tentatively attributed to hydrographic changes linked to variability in the zonal current system (Noble et al., 2015). Given the differences in Pb isotope composition between Atlantic water masses derived from the northern and southern hemisphere, Pb isotopes may prove a useful tracer of water mass mixing in this hydrographically complex region.

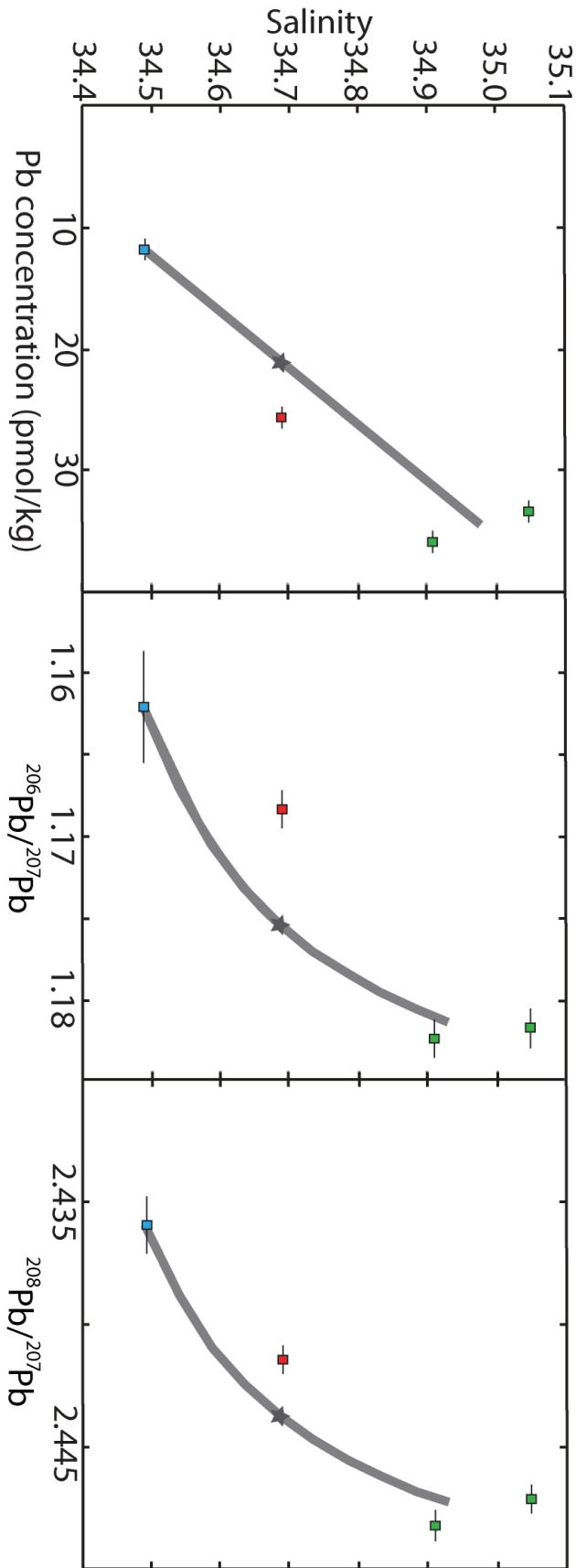


Figure 4.5, Plots of salinity versus Pb concentration, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios for samples collected along the $\sigma_0 = 27.3 - 27.4$ neutral density horizon. Grey lines show idealized mixing lines between endmember compositions determined at Stn 12 (blue symbol) and 20 (green symbol) at the same neutral density horizons. Grey star denotes the compositions predicted to occur at Stn 16 in the case of simple two component mixes (see main text), while the red square indicates the measured composition

4.4.4. *The effects of hydrothermal activity on Pb in the deep ocean?*

The elevated Pb concentrations of samples from between 2500 and 3699 m at Stn 12 relative to those from comparable depths at Stn 16 and 20 may be due to contamination during sampling. However, their location above the Mid Atlantic Ridge and the systematic distribution suggest they may be a real feature associated with hydrothermal venting. As the Pb concentrations at 3000 m for Stn 16 and 20 is 13 pmol/kg, the elevated concentration of 43 pmol/kg for Stn 13 at 3000 m potentially signifies a 70 % contribution of hydrothermal inputs. Such hydrothermally derived Pb is expected to have a Pb isotope composition similar to that of the mid ocean ridge basalt (MORB) (LeHuray et al., 1988, Godfrey et al., 1994). Close to the location of Stn 12, MORB features a significantly different Pb isotope composition ($^{206}\text{Pb}/^{207}\text{Pb} = 1.121 - 1.125$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.461 - 2.456$) to the ambient seawater ($^{206}\text{Pb}/^{207}\text{Pb} = 1.17 - 1.18$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.45$) (Ito et al., 1987). A large contribution of hydrothermally derived Pb should therefore be detectable by a significant shift in the seawater Pb isotope composition. This stands in contrast to the similarity of the Pb isotope composition for samples from Stn 12 at 2500 – 3699 m to those from comparable depths at Stn 16 and Stn 20 (Fig 4.3). An alternative source of this excess Pb could be the leaching of historic anthropogenic Pb from the sediments by hydrothermal fluids, that are known to feature a range of Pb isotope compositions that encompass the values determined for the seawater at this location (Hamelin et al., 1990).

The particulate Pb concentration at this station and depth indicate only a 4 % particulate Pb contribution, hence the vast majority of the excess Pb must be in dissolved form. In any case, the occurrence of a Pb concentration maximum from hydrothermal inputs stands in contrast to previous studies, which found that Pb is rapidly removed from vent fluids upon mixing with seawater, by co-precipitation with and scavenging by sulphides (LeHuray et al., 1988, Godfrey et al., 1994, Noble et al., 2015). Furthermore, the lower dissolved Pb concentrations and concurrent higher particulate Pb concentrations in the vicinity of the TAG hydrothermal vent field suggest that Pb is scavenged from the ambient seawater by hydrothermal particles (Noble et al., 2015).

4.5. Conclusions

The distributions of Pb concentrations and isotope compositions in the interior of the eastern Tropical Atlantic are related to hydrographic variations, and are generally consistent with those expected for the penetration of transient anthropogenic Pb inputs via ocean circulation. In particular, the southern hemisphere derived water masses SACW and AAIW feature low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios whilst northern hemispheric water masses have higher $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios. This is consistent with the differences in the isotope compositions of historic anthropogenic emissions from the southern and northern hemisphere. Furthermore, variations in Pb concentration and isotope composition within northern-sourced water masses are consistent with those expected due to differences in ventilation timescales. In particular, a Pb concentration maximum of about 35 pmol/kg in northern sourced intermediate waters features a Pb isotope composition indicative of northern hemispheric Pb emissions in the 1950 to 1960's, close to the peak use of leaded petrol. In contrast, NADW features lower Pb concentrations and an isotope composition indicative of northern hemispheric Pb emissions during the 1910's to 1930's. These findings are consistent with other ventilation timescale estimates for this region based on other transient tracers. However, the interpretation of Pb concentration and isotope composition distributions in terms of ventilation timescales and pathways can be complicated by water mass mixing, in a similar fashion to non-linear the mixing effects imposed on other transient tracers. Furthermore, vertical transport of Pb via sinking particles cannot be completely ruled out. With increasing data coverage of seawater Pb concentrations and isotope composition, modeling studies will provide an invaluable tool to decipher the various controls and unlock the potential of Pb as a ventilation tracer.

4.6. Author contributions and acknowledgements

For this chapter, I determined the Pb concentration and isotope composition of the samples and lead the interpretation/presentation of the results. Additional contributions to the work were received from Maxence Paul, Mark Rehkämper, Tina van de Flierdt, Angela Milne, Maeve Lohan and Eric Achterberg. Thanks go to M. Paul for providing advice and guidance on the analytical techniques as well as M.

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Chapter 5

The Cd isotope composition of atmospheric aerosols

Abstract

Isotope composition variations in have recently shown promise for tracing anthropogenic Cd emissions to environment. Furthermore, Cd isotope variations may also prove to be a useful tracer of external atmospheric inputs to the ocean. Despite these potentially important applications, the Cd isotope composition of atmospheric aerosols has yet to be investigated. Here we present Cd isotope composition data for atmospheric aerosol samples collected in the eastern Tropical Atlantic, during the GEOTRACES GA06 cruise (2011).

The Cd isotope compositions of the aerosols samples are indistinguishable from the estimated composition of the upper continental crust ($\epsilon^{114/110}\text{Cd} \approx 0$), with the exception of a single sample that yielded a $\epsilon^{114/110}\text{Cd}$ value of -5.4 ± 1.3 . This comes despite the aerosol samples exhibiting a wide range of Cd contributions from North African mineral dust and anthropogenic sources. Due to the remote collection locations, the anthropogenic Cd content of our samples likely represents a mixture of numerous emission sources, which feature an average $\epsilon^{114/110}\text{Cd}$ value identical to North African mineral dust. This observation negates the use of Cd isotope variations to distinguish between anthropogenic and natural Cd sources transported by the northeast trade winds over the Tropical Atlantic.

However, our data do not rule out potential regional variations in the isotope composition of anthropogenic Cd in the atmosphere. In particular, the sample that yielded a distinct a $\epsilon^{114/110}\text{Cd}$ value of -5.4 ± 1.3 was the only sample analysed that was collected south of the Inter Tropical Convergence zone, and may hence reflect regional differences between the isotope composition of anthropogenic Cd transported by the northeast and southeast trade winds. Further investigations into the Cd isotope composition of atmospheric aerosols are clearly needed, and will advance our understanding of anthropogenic impacts on the global biogeochemical cycling of this element.

5.1. Introduction

The global biogeochemical cycle of Cd has been significantly perturbed by anthropogenic activities during the past century (Shen et al., 1987, Nriagu & Pacyna, 1988, Candelone et al., 1995, Eichler et al., 2014). Atmospheric emissions from high temperature processes represent an important transport pathway for anthropogenic Cd to the environment (e.g. Shao et al., 2013). Non-ferrous metal smelting (e.g. Pb-Zn smelting) is thought to be the most important activity for the emission of anthropogenic Cd, followed by combustion of fossil fuels (primarily coal) and municipal waste incineration (Nriagu & Pacyna, 1988, Pacyna & Paycna, 2001, Pacyna et al., 2009, Cheng et al., 2014). During these high temperature processes Cd becomes vaporised (due to its low boiling point) and is emitted to the atmosphere where it rapidly condenses onto fine ($<1\ \mu\text{m}$) particles (Galloway et al., 1982, Raes et al., 2000, Cloquet et al., 2006). Such particles are capable of under going long-range transport across the globe before removal to terrestrial and marine environments (Duce et al., 1991, Gelado-Caballero et al., 2012).

Recently, Cd isotope variations have shown promise as a new geochemical tool to distinguish between natural and anthropogenic sources of Cd to the environment (Rehkämper et al., 2012, Gao et al., 2015). This is based on the finding that evaporation/condensation processes are capable of inducing significant mass dependent Cd isotope fractionations (Wombacher et al., 2003, Wombacher et al., 2004). Hence, atmospheric emissions of Cd by high temperature industrial processes are expected to be associated with isotope fractionation, providing that evaporation of Cd is incomplete or that vaporised Cd is continually removed from the solid residue (Wombacher et al., 2004, Cloquet et al., 2006). Although a recent study found no significant difference between the Cd isotope compositions of fume-derived dust and ore materials of a Pb-Zn smelting operation in Poland (Chrastný et al., 2015), support comes from the observation that fume-derived dusts of Pb-Zn smelting operations feature ‘light’ Cd isotope compositions whilst the residual slag and metal products have ‘heavy’ Cd isotope signatures relative to the precursor ores (Cloquet et al., 2005, Cloquet et al., 2006, Shiel et al., 2010).

Such Cd isotope variability has been exploited to trace anthropogenic (fume-derived dust and slag) and natural sources of Cd to sediments proximal to Pb-Zn mining and smelting operations (Cloquet et al., 2006, Gao et al., 2008, Gao et al.,

2013, Chrastný et al., 2015, Wen et al., 2015). Furthermore, Shiel et al. (2012, 2013) interpreted Cd isotope variability of marine bivalves in context of anthropogenic and natural Cd sources to coastal waters. However, the application of Cd isotopes to trace the long-range atmospheric transport of anthropogenic emissions has yet to be investigated.

In addition, the use of Cd isotope variations to study the internal cycling of this element in the ocean where Cd is an important micronutrient has recently gained a lot of attention (Lacan et al., 2006, Ripperger & Rehkämper, 2007, Ripperger et al., 2007, Schmitt et al., 2009, Abouchami et al., 2011, Gault-Ringold et al., 2012, Yang et al., 2012, Lambelet et al., 2013, Xue et al., 2013, Abouchami et al., 2014, Yang et al., 2014, Conway & John, 2015a, Conway & John, 2015b, Yang et al., 2015a). These studies have found that dissolved Cd is fractionated to 'heavier' isotope compositions in the upper 1 km of the ocean, relative to the comparatively uniform composition of the deep ocean. In many instances, the extent this fractionation is also related to decreases in dissolved Cd concentrations and this covariance was broadly explained by biological uptake of Cd associated with isotope fractionation following closed-system Rayleigh fractionation models (e.g. Ripperger et al., 2007, Abouchami et al., 2011, Abouchami et al., 2014).

However, the currently available global data set of seawater Cd isotope compositions and concentrations features significant deviations from a single closed-system Rayleigh fractionation model, potentially reflecting differences in vital effects between phytoplankton communities (e.g., Abouchami et al., 2011), water mass mixing (e.g., Conway & John, 2015a), deviations from close-system behavior through external inputs (e.g. Ripperger et al., 2007, Yang et al., 2012, Yang et al., 2014, Yang et al., 2015a) or other processes (e.g. Gault-Ringold et al., 2012). Constraining the Cd isotope composition of external inputs to the ocean is therefore essential to advance our understanding of the marine biogeochemical cycle of this element. In particular it may prove to be a useful tracer of regions of the ocean where external inputs dominate the supply of Cd to ocean surface waters over the upwelling of deep waters (e.g., Shen et al., 1987). At present only limited Cd isotope data for riverine inputs have been published (Lambelet et al., 2013), while only preliminary results from a single conference abstract, are currently available for the Cd isotope composition of atmospheric aerosols (Yang et al., 2015b). This comes even though the global

atmospheric flux of Cd to the ocean has been estimated to be larger than riverine inputs (Duce et al., 1991).

Here we present Cd isotope composition data for atmospheric aerosols, on samples that were collected in the eastern Tropical Atlantic (Fig. 5.1). Whilst this region is subject to the transport of large quantities of mineral dust emitted from North Africa (Prospero et al., 2014), aerosols in this region are commonly also highly enriched in anthropogenic Cd (Gelado-Caballero et al., 2012). The aerosol samples feature variable proportions of Cd from natural (mineral dust) and anthropogenic emissions, allowing assessment of the isotope composition of these two important environmental Cd sources. These data enable the investigation of the utility of Cd isotopes to trace the sources of Cd to the atmosphere and provide important constraints for studies concerning the marine biogeochemical cycling of this element.

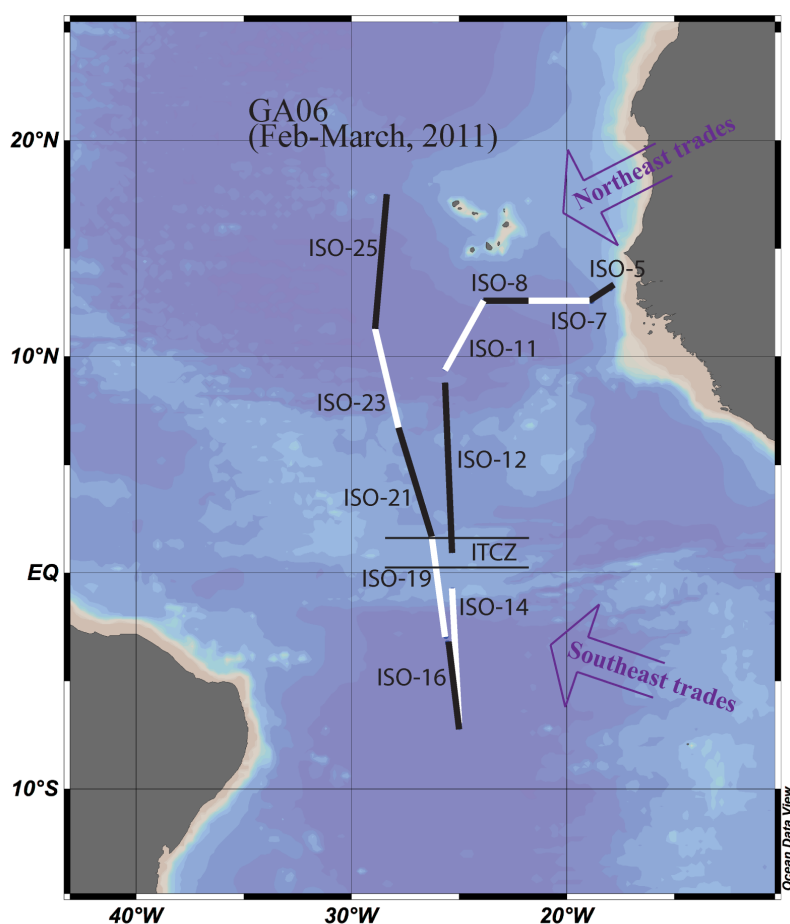


Figure 5.1. Locations of transects over which aerosol samples were collected (alternating black and white lines) during the GEOTRACES GA06 cruise. Also shown is the position of the ITCZ at the time of the cruise as well as the major meteorological regimes (purple arrows). Produced using Ocean Data View (Schlitzer, 2002)

5.2. Samples and analytical techniques

Aerosol samples were collected onto Whatman 41 filters in the eastern Tropical Atlantic during the GEOTRACES GA06 cruise (2011), for which Pb isotope compositions were previously presented (Chapter 3). Details of their collection and digestion/leaching are given in Chapter 3, with only a brief description provided below. The majority of aerosol samples were collected north of the Inter Tropical Convergence Zone (ITCZ), with air mass back trajectories indicating a North African origin (groups ‘Northeast trades’ and ‘Algerian’). Three of the aerosol samples are from within/south of the ITCZ, with air mass back trajectories indicating no interaction with land in the 5 days preceding collection (group ‘oceanic’) (Chapter 3, Appendix 2). Sample preparation was conducted within the clean rooms of the MAGIC laboratories, using trace metal clean reagents as described in Chapter 3. In addition, heptane was pre-cleaned through liquid-liquid extraction with distilled 6M HCl.

Each aerosol sample was split into two portions, with 25 – 50 % and 12 – 50 % of the total exposed filter area subjected to a total digestion procedure (featuring concentrated HF, HClO₄ and HNO₃) and a leaching procedure (dilute ammonium acetate solution, pH 4.7) respectively (Chapter 3, Appendix 2). Aliquots of these subsamples (10 %) were taken for determination of elemental concentrations (Chapter 3), with the Cd contents determined by quadrupole inductively coupled plasma mass spectrometry using an Agilent 7700x with 5ml/min He in the collision reaction cell, at the Natural History Museum, London. The Cd blank encountered during aerosol collection and digestion/leaching was assessed to be 0.9 ± 0.5 ng (1sd, n = 4) per filter (through the use of filter blanks, Chapter 3), which corresponds to 1.4 – 12.6 % of the aerosol sample Cd contents. Atmospheric Cd concentrations were calculated based on the Cd content determinations and filter exposure time (i.e. volume of air sampled; Appendix 2) and were blank corrected using the mean value. Uncertainties were calculated by propagation of blank variability (1sd).

5.2.1 Cadmium isotope measurements

Precise determination of Cd isotope compositions of atmospheric aerosols is challenging due to the low concentration of Cd in the atmosphere ($\sim 1 - 100$ pgm⁻³,

Guerzoni et al., 1999, Gelado-Caballero et al., 2012). Hence, only total digestion and leachate subsamples corresponding to 50 % of the total exposed filter area were analysed for Cd isotope composition, as other subsamples contained insufficient quantities of Cd to yield precise measurements. For these selected samples, the blank encountered during sample collection and digestion/leaching amounted to 1.4 – 4.3 % of the total Cd content. Aliquots (66 – 85 %) of the total digestion and leachate solutions were taken for Cd isotope analysis, which contained approximately 5 – 25 ng of Cd. The Cd aliquot of subsample ISO-21_{Total}, featuring 25 ng of Cd, was further split into two separate aliquots (ISO-21a_{Total} and ISO-21b_{Total}, featuring approximately 15 and 10 ng of Cd respectively) in order to assess the external reproducibility of the analytical procedure (chemical separation and mass spectrometric analysis).

Cadmium isotope compositions were determined using multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), in conjunction with a Cd double spike (DS), prepared from enriched ¹¹¹Cd and ¹¹³Cd for correction of instrumental mass bias (Xue et al., 2012). To this end, appropriate quantities of Cd DS were equilibrated with the sample aliquots prior to chemical separation of Cd from the sample matrix (see below). Cadmium was purified from the sample aliquots by processing through a three stage ion exchange chromatography procedure, which utilized Biorad AG 1X8 and Eichrom TRU-spec ion exchange resins (Table 5.1) (adapted from Xue et al., 2012). Previous studies have found that the presence of organics leached from Eichrom TRU-spec resin during ion exchange chromatography can cause anomalous results during the mass spectrometric measurement of Cd isotope ratios if the final elutes are not sufficiently diluted prior to analysis (Gault-Ringold & Stirling, 2012, Murphy et al., 2015). Since our samples featured low Cd contents, dilution was not a viable option. Therefore, a heptane liquid-liquid extraction technique was employed following the final ion exchange chromatography stage in order to remove organic compounds from the eluted Cd (Murphy et al., 2015). Whereby, 1.2 ml of heptane was added to the Cd elutes (in 1.8 ml of 6 – 8M HCl, Table 1), twice shaken for 30 seconds and left to stand for 3 minutes, before removal of the heptane (which forms an immiscible layer on top of the HCl). This entire process was then repeated. Finally, purified Cd solutions were evaporated to dryness and re-dissolved in 1 ml of 0.1 M HNO₃ ready for isotopic analysis. The Cd blank for the chemical separation procedure (ion exchange chromatography and heptane extraction) was consistently determined to be < 10 pg which was considered

to be negligible relative to quantity of natural Cd processed in the samples (5 – 20 ng).

Table 5.1, Details of the three stage ion exchange chromatography procedure used to purify Cd prior to mass spectrometric analysis

	1 st Stage ^a	2 nd Stage ^b	3 rd Stage ^b
Resin	2 ml AG1 X8 100-200 mesh	100 µl AG1 X8 200-400 mesh	100 µl Eichrom TRU-Spec
Clean resin	15 ml 2 M HNO ₃	0.75 ml 2 M HNO ₃	10 ml 6 M HCl
	2 ml H ₂ O	0.1 ml H ₂ O	
	26 ml 6 M HCl	1.3 ml 6 M HCl	
	12 ml 0.5 M HCl	0.6 ml 0.5 M HCl	
Equilibrate resin	6 ml 3 M HCl	0.3 ml 3 M HCl	
Load sample	in 10 ml 3M HCl	in 0.5 ml 3M HCl	in 0.2 ml 8 M HCl ^c
Elute matrix	2 ml 3M HCl	0.1 ml 3M HCl	
	30 ml 0.5 M HCl	1.5 ml 0.5 M HCl	
	10 ml 1 M HCl	0.5 ml 1 M HCl	
	10 ml 2 M HCl	0.5 ml 2 M HCl	
	12 ml 6 M HCl	0.6 ml 6 M HCl	
	16 ml 0.1 M HBr	0.6 ml 0.1 M HBr	
	– 0.5 M HNO ₃	– 0.5 M HNO ₃	
	2 ml 2 M HNO ₃	0.1 ml 2 M HNO ₃	
Elute Cd	8 ml 2 M HNO ₃	0.75 ml 2 M HNO ₃	0.2 ml 8 M HCl
			1.4 ml 6 M HCl

^a The resin is used in quartz columns with a 3 ml resin bed, 50 ml reservoir, and quartz fiber frits.

^b The resin is used in columns prepared from shrink-fit Teflon tubing. The columns have a reservoir volume of ~3 ml and a resin column with an internal diameter of ~ 3 mm.

^c Cadmium is eluted in sample loading solution.

Cadmium isotope measurements were conducted using a Nu Plasma MC-ICP-MS instrument (Nu instruments) at Imperial College London. Sample solutions were introduced using an Aridus II desolvation unit (CETAC Technologies) equipped with a Micromist glass nebulizer operated at flow rates of 0.110 to 0.115 µl/min. The sensitivity obtained for Cd was between 200 and 300 V/ppm. Depending on the quantity of Cd available in each sample aliquot, Cd DS was added with the aim of achieving a molar spike/sample (S/N) ratio for Cd of either approximately 2 (if > 10 ng Cd in sample) or 3 (if < 10 ng Cd in sample), resulting in total Cd solution concentrations of 15 – 45 ng/ml (featuring between 5 – 20 ng of natural Cd). The S/N ratio for optimal error propagation is considered to be 1 (Xue et al., 2012). Higher S/N ratios were chosen, however, as previous empirical tests have found that the accuracy and precision of Cd standard solution measurements are consistent within the S/N

ratio range of 0.6 – 6, relative to those of S/N = 1 (Xue et al., 2012). Furthermore, our samples featured low Cd contents, so the addition of higher quantities of Cd DS increased the ion beam intensities of spiked isotopes (^{113}Cd and ^{111}Cd) without requiring further dilution of the natural Cd. Initial tests showed that this resulted in a slight improvement of the internal reproducibility of the analyses relative to solutions featuring a comparable concentration of ‘natural’ Cd and S/N = 1.

Analyses of sample solutions were bracketed by measurements of mixed solutions of the standard reference material (SRM) NIST 3108 Cd with the Cd DS at comparable S/N ratios and dilutions. Measurement protocols followed those previously described (Xue et al., 2012, Murphy et al., 2015). In brief, the ion beam intensities at mass numbers 111 (Cd), 112 (Cd + Sn), 113 (Cd + In), 114 (Cd + Sn), 115 (In) and (Sn) were simultaneously measured with Faraday cups equipped with $10^{11} \Omega$ resistors. The data acquisition sequence comprised of 3 blocks of 20 integrations lasting 5 seconds each, with a 15 second measurement of the electronic baseline prior to each block whilst the ion beams were deflected by the electrostatic analyser. Between analyses, the sample introduction system and instrument were rinsed for approximately 4 minutes with 0.1 M HNO_3 .

Data are presented as $\epsilon^{114/110}\text{Cd}$ values relative to NIST 3108 Cd (eqn. 5.1) (Abouchami et al., 2013b).

$$\epsilon^{114/110}\text{Cd} = [({}^{114}\text{Cd}/{}^{110}\text{Cd}_{\text{Sample}}/{}^{114}\text{Cd}/{}^{110}\text{Cd}_{\text{NIST 3108}}) - 1] \times 10^4 \quad (5.1)$$

The raw isotopic ratios were processed offline to calculate the $\epsilon^{114/110}\text{Cd}$ values corrected for instrumental mass bias and isobaric interferences following iterative techniques developed by Siebert et al. (2001) using an Excel spreadsheet based approach (Ripperger & Rehkämper et al., 2007, Xue et al., 2012, Murphy et al., 2015).

5.2.2 Assessment of data quality

The uncertainty of the Cd isotope data was taken as the reproducibility of the bracketing analyses of matching SRM NIST 3108 Cd – Cd DS mixtures, and this was ± 1 to $2 \epsilon^{114/110}\text{Cd}$ (2sd, n = 6 – 25). Additional SRMs were analysed to validate the accuracy and precision of the isotopic measurements (Table 5.2). Analyses of the Cd

SRM BAM-I012 were conducted every measurement session and yielded results in good agreement with literature consensus values (Abouchami et al., 2013b), thereby demonstrating the accuracy of the mass spectrometric measurements and instrumental mass bias correction.

Table 5.2, Results for SRM's Cd isotope analyses

SRM	$\epsilon^{114/110}\text{Cd}_{\text{NIST 3108}}$	n ^e	Blank % ^f
BAM-I012	-12.91 ± 0.65	13	
Abouchami et al, 2013b ^a	-13.32 ± 0.43		
BIR-1	0.71 ± 0.70	4	
Wombacher et al., 2003 ^b	1.51 ± 4.90	5	
AGV-2	1.13 ± 1.25	3	
AGV-2 FT1 ^c	1.22 ± 1.04		1.9 %
AGV-2 FT2 ^c	0.55 ± 1.04		2.6 %
AGV-2 (All) ^d	1.03 ± 1.04	5	

All SRM analyses were run at concentrations of 15 ng/ml of natural Cd. BAM-I012 analyses were conducted at S/N ratios of either 1, 2 or 3, whilst all other SRM analyses were conducted at S/N of 2. The typical external reproducibility of bracketing analyses of NIST 3108 Cd (at comparable concentrations and S/N ratios) was ± 1 epsilon (2sd). Quoted uncertainties are 2sd of replicate analyses of the SRM's, unless otherwise stated. ^a Consensus value from measurements conducted by six separate laboratories. ^b Data converted to $\epsilon^{114/110}\text{Cd}_{\text{NIST 3108}}$ values from $\epsilon\text{Cd}/\text{amu}$ relative to SRM Munster JMC, using consensus values given by Abouchami et al., 2013b. ^c AGV-2 aliquots doped with digested filter material, uncertainty given as reproducibility (2sd) of bracketing NIST 3108 analyses. ^d Mean and 2sd of all AGV-2 analyses. ^e Number of analyses conducted. ^f Percentage blank contribution from digested filter material added to AGV-2 FT samples,

In addition, Cd isotope analyses were conducted for the geological SRMs BIR-1 (basalt) and AGV-2 (andesite) from US Geological Survey. To this end, powdered aliquots of these SRM's were digested in 28 M HF + 15 M HNO₃ (3 + 1) on a hotplate at 140 °C for several days with regular treatments in an ultrasonic bath. Sub-aliquots of these digested solutions were taken (corresponding to about 15 ng of Cd), equilibrated with Cd DS (to achieve a S/N ratio of about 2) and processed through the chemical separation procedure before mass spectrometric analysis. The results obtained for BIR-1 are in good agreement with those previously published, although display a much better reproducibility (Wombacher et al., 2003). Whilst no published Cd isotope data is currently available for AGV-2, results are in good agreement with the estimated composition of the upper continental crust (Schmitt et al., 2009, Rehkämper et al., 2012). Furthermore, the reproducibility's of multiple determinations of these SRM's were comparable to the reproducibility of the

bracketing standard analyses (NIST 3108 Cd). This validates the assessment of data uncertainty through replicate analyses of SRM NIST 3108 Cd.

However, the Cd isotope measurements of the aerosol samples are subject to additional factors that can affect their accuracy and precision, relative to those of pure Cd (NIST 3108 Cd, BAM-I012) and geological SRMs (BIR-1 and AGV-2). Namely, (1) the blank encountered during aerosol collection and digestion/leaching procedures and (2) potential effects of residual matrix associated with the digestion of large quantities of the cellulose filter material (for the total digestion samples only). To test the effect of these factors, two portions of blank Whatman 41 filters (corresponding to the equivalent size of 50 % of the total exposed area) were subjected to the total digestion procedure (described in Chapter 3). Aliquots of these filter solutions (85 %, comparable to those taken for the samples) were doped with quantities of AGV-2 and Cd DS (corresponding to 15 ng of natural Cd, $S/N \approx 2$), processed through the chemical separation procedure and analysed. The blank contribution from the digestion of the filter material was 1.6 – 2.6 % of the natural Cd content, which is comparable those estimated for the samples (1.4 – 4.3 %). The $\epsilon^{114/110}\text{Cd}$ values determined for these two test samples (AGV-2 FT1 and AGV-2 FT2) agree within uncertainty with those determined for the other AGV-2 aliquots. Furthermore, the reproducibility of AGV-2 data set is comparable to that of the bracketing analysis of NIST 3108 Cd. This suggests that the sample analyses do not suffer from increases in uncertainty (relative to analyses of the pure Cd SRM's) or inaccuracy due to blank contributions and potential matrix effects.

5.3. Results

Atmospheric Cd concentrations range between 3.8 – 40.3 pgm^{-3} for the total digests and 3.8 – 28.0 pgm^{-3} for the leachates, whilst atmospheric Al concentrations, a commonly used proxy for mineral dust, vary from 68 – 5808 ngm^{-3} for the total digests (Chapter 3, Table 5.3). The proportion of Cd derived from mineral dust and from anthropogenic sources in the aerosols was assessed using crustal enrichment factors (EF_{crust} ; eqn. 5.2). If $\text{Cd}/\text{Al}_{\text{sample}}$ represents the Cd/Al ratio of the aerosol sample and $\text{Cd}/\text{Al}_{\text{ucc}}$ represents the Cd/Al ratio of the upper continental crust (1×10^{-6}), as given by Rudnick & Gao, (2003), then;

$$EF_{\text{crust}} = (Cd/Al_{\text{sample}})/(Cd/Al_{\text{ucc}}) \quad (5.2)$$

The solubility of Cd in the leachates were calculated relative to the total digestions and expressed as a percentage (eqn. 5.3).

$$\text{Fractional solubility (\%)} = (\text{Concentration}_{\text{Leach}}/\text{Concentration}_{\text{Total}}) \times 100 \quad (5.3)$$

The uncertainty in the EF_{crust} values and fractional solubilities were calculated by propagation of the uncertainty (1sd) of the aerosol Cd concentrations. The EF_{crust} values range between 3.8 and 107 for the total digests, whilst the fractional solubilities vary between 50 and 85 %, with the exception of sample ISO-16 that yielded a fractional solubility of 279 ± 13 % (Table 5.3). Such an unrealistic value could represent heterogeneous distribution of Cd on the filter or may have resulted from contamination during the leaching or chemical separation procedure. The latter seems unlikely as the blank of the leaching and chemical separation procedures were consistently assessed to be < 1 ng and < 10 pg respectively, which are much lower than the blank required to produce the anomalous fractional solubility (i.e. > 100 %) of at least 16 ng of Cd. Interpretation regarding this sample should hence be treated with caution.

The aerosol total digests and leachates analysed for Cd isotope compositions all yielded $\epsilon^{114/110}\text{Cd}$ values within uncertainty of ± 0 , except for ISO-16_{Leach} that was characterised by $\epsilon^{114/110}\text{Cd} = -5.4 \pm 1.3$ (Table 5.3, Fig. 5.2). Replicate analyses of ISO-21_{Total} (ISO-21a_{Total} and ISO-21b_{Total}) yield results identical within analytical uncertainty (Table 5.3). Where total digests and leachates from the same aerosol sample were analysed (ISO-21, ISO-12 & ISO-23), results were identical within uncertainty (Fig. 5.2). This is not surprising given the high fractional solubilities of the leachates and the findings of previous studies that abiotic processes (other than evaporation and condensation) are generally not associated with significant Cd isotope fractionation (Rehkämper et al., 2012). The Cd isotope composition of leachates for which no data are available for the corresponding total digest, are therefore interpreted to represent that of the bulk aerosol.

Table 5.3. Aerosol sample details, elemental and Cd isotopic data											
Sample ID	Latitude (°N)	Longitude (°W)	Collection date	AMBT Group	[Cd] (pgm ⁻³)	Fractional solubility (%)	[Al] (ngm ⁻³)	EF _{Crust}	ε ^{114/110} Cd ^a	n ^b	Blank % ^c
ISO-5 _{Total}	13.13	17.97	21/02	NeT	24.2 ± 0.2	58 ± 1	5808*	3.8 ± 0.04	0.15 ± 1.46	8	1.8
	-	-	-		14.1 ± 0.2		39				3.1
ISO-5 _{Leach}	12.55	18.84	23/02								
ISO-7 _{Total}	12.55	18.87	23/02	Al	26.1 ± 0.3	70 ± 2	1935	12.2 ± 0.2	1.47 ± 1.30	25	2.3
	-	-	-		18.2 ± 0.3		32				3.3
ISO-7 _{Leach}	12.57	21.82	24/02								
ISO-8 _{Total}	12.57	21.82	24/02	NeT	20.1 ± 0.3	55 ± 1	3482	5.2 ± 0.1	1.91 ± 2.05	6	2.4
	-	-	-		11.0 ± 0.3		15				4.3
ISO-8 _{Leach}	12.57	23.76	25/02								
ISO-11 _{Total}	12.54	23.92	25/02	Al	8.1 ± 0.5	77 ± 7	1148	6.4 ± 0.4			10.0
	-	-	-		6.2 ± 0.5		9				12.6
ISO-11 _{Leach}	9.46	25.66	27/02								
ISO-12 _{Total}	8.67	25.62	27/02	Al	40.3 ± 0.3	69 ± 1	3891	9.4 ± 0.1	1.37 ± 1.30	25	1.7
	-	-	-		28.0 ± 0.4		30		1.23 ± 1.06	23	2.4
ISO-12 _{Leach}	1.02	25.33	01/03								
ISO-14 _{Total}	-0.80	25.31	01/03	Oc	7.6 ± 0.2	50 ± 2	137	50.2 ± 1			3.8
	-	-	-		3.8 ± 0.2		5				7.3
ISO-14 _{Leach}	-7.00	25.00	03/03								
ISO-16 _{Total}	-7.15	24.99	03/03	Oc	3.8 ± 0.2	279 ± 13	68	50.1 ± 2.3	-5.40 ± 1.30	25	8.1
	-	-	-		10.6 ± 0.2		2				3.1
ISO-16 _{Leach}	-3.15	25.54	05/03								

Table 5.3 continued.

Sample ID	Latitude (°N)	Longitude (°W)	Collection date	AMBT Group	[Cd] (pgm ⁻³)	Fractional solubility (%)	[Al] (ngm ⁻³)	EF _{Crust}	$\epsilon^{114/110}\text{Cd}^a$	n ^b	Blank % ^c
ISO-19 _{Total}	-2.96	25.61	05/03	Oc	13.5 ± 0.2	63 ± 2	728	16.7 ± 0.3			2.9
ISO-19 _{Leach}	-	-	-		8.5 ± 0.2		15				4.6
	1.68	26.25	07/03								
ISO-21a _{Total}	1.81	26.29	07/03	NeT	22.9 ± 0.2	53 ± 1	1527	13.6 ± 0.1	0.88 ± 1.06	23	1.4
ISO-21b _{Total}	-	-	-						-0.33 ± 1.30	25	
ISO-21 _{Leach}	6.74	27.80	09/03		12.1 ± 0.2		28		0.51 ± 1.06	23	2.6
ISO-23 _{Total}	6.84	27.84	09/03	NeT	10.8 ± 0.2	85 ± 2	667	14.6 ± 0.2	-1.88 ± 1.47	10	2.9
ISO-23 _{Leach}	-	-	-		9.1 ± 0.2		13		0.41 ± 1.30	25	3.4
	11.31	28.86	11/03				74				
ISO-25 _{Total}	11.45	28.89	11/03	NeT	8.7 ± 0.1	81 ± 2	2	107 ± 1.5	1.11 ± 1.06	23	2.6
	-	-	-								
ISO-25 _{Leach}	17.42	28.38	14/03		7.0 ± 0.1						3.3

AMBT = air mass back trajectory group, NeT = northeast trades, Al = Algerian, Oc = oceanic. * Al concentration above the calibrated range, hence should be treated with caution. ^a Uncertainty quoted as 2sd of the bracketing analyses of NIST 3108 Cd analysed at comparable 'natural' Cd concentrations and S/N ratios as the samples. ^b Number of bracketing analyses of NIST 3108. ^c Percentage blank contribution from the collection and digestion/leaching procedures. See Appendix 2 for additional aerosol metadata and air mass back trajectory analyses.

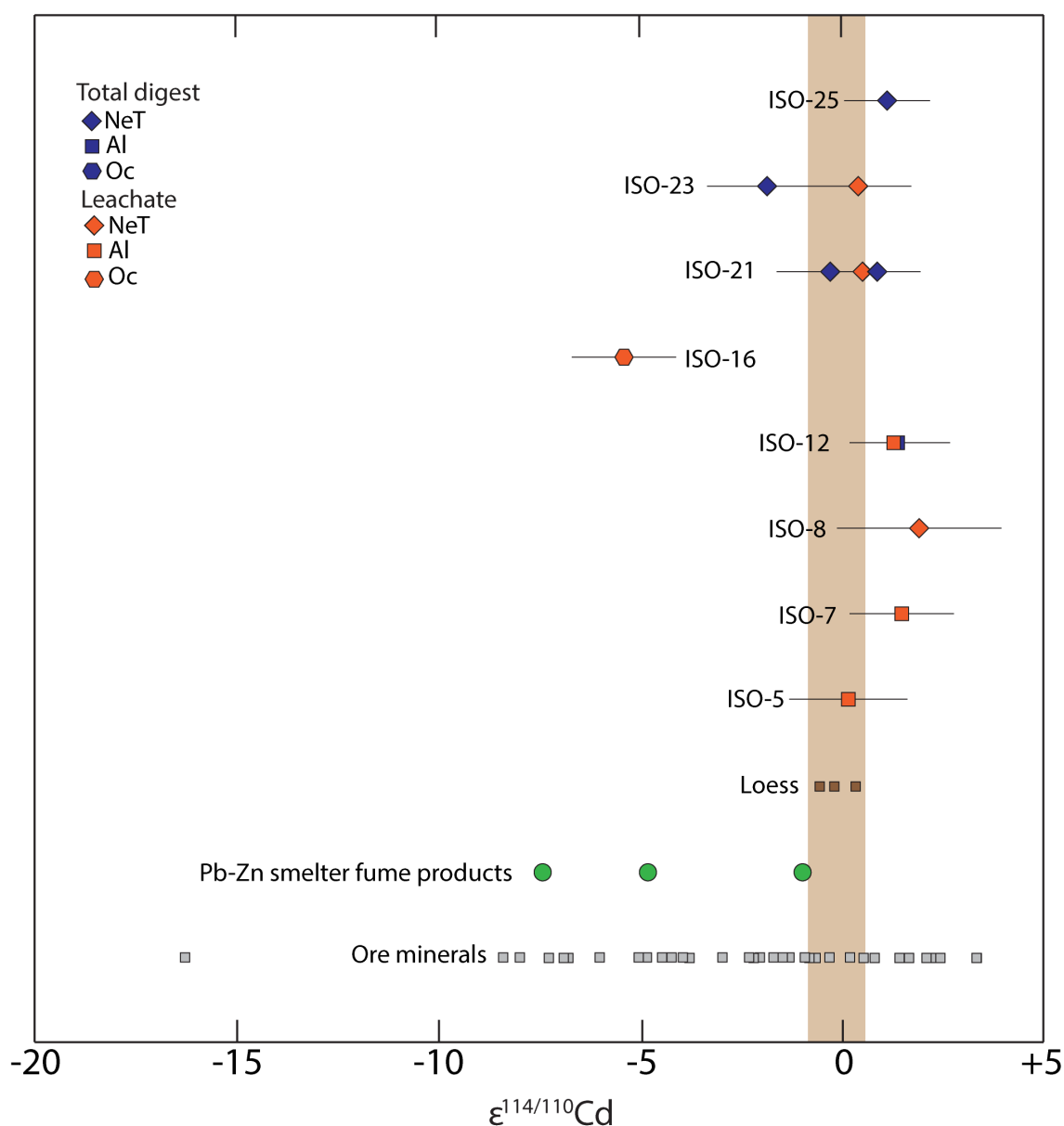


Figure 5.2. $\epsilon^{114/110}\text{Cd}$ values for aerosol total digests and leachates, compared to fume derived Pb-Zn smelter dust (green circles; Cloquet et al., 2006, Shiel et al., 2010, Chrastný et al., 2015), ore materials used to supply smelting operations (grey squares; Wombacher et al., 2003, Shiel et al., 2010, Zhu et al., 2013, Chrastný et al., 2015, Wen et al., 2015) and the estimated composition of the upper continental crust (brown shaded box) based on results for three loess samples (brown squares; Schmitt et al., 2009). The shapes of the aerosol samples symbols correspond to their air mass back trajectory groups, with NeT = northeast trades (diamonds), Al = Algerian (squares) and Oc = oceanic (hexagons).

5.4. Discussion

The range of EF_{crust} values displayed by the samples indicate variable Cd contributions from mineral dust and anthropogenic sources. There is a negative

correlation between EF_{crust} values and Al atmospheric concentrations (in $\log_{10}$ space; Fig. 5.3a), which is characteristic of a relatively constant ‘background’ concentration of anthropogenic Cd, which becomes periodically diluted by sporadic emissions of mineral dust (Chester et al., 1993a, Chester et al., 1996, Guerzoni et al., 1999). Although it is uncertain how closely the chosen Cd/Al_{ucc} reference ratio approximates that of North African mineral dust, the extension of this trend down to the lowest EF_{crust} values (3.8 – 5.2) suggests that at the very least, values of > 5 represent increases in anthropogenic Cd contributions. Without additional constraints it is unclear, however, how important anthropogenic Cd contributions are for the samples featuring the lowest EF_{crust} values (ISO-5, ISO, 11 and ISO-8). Two samples from the ‘oceanic’ group (ISO-14 and ISO-16) collected south/within the ITCZ along with ISO-25 of the ‘Northeast trades’ group feature the lowest atmospheric Al concentrations and the highest EF_{crust} values (50 – 107). These samples are likely completely dominated by anthropogenic Cd. The remaining aerosols (ISO-7, ISO-12, ISO-19, ISO-21 and ISO-23) with EF_{crust} values of 9.4 – 16.7 are likely to contain anthropogenic Cd contributions of at least 50 – 60 %, assuming an EF_{crust} value of ~ 5 represents that of North African mineral dust.

The currently available Cd isotope data for terrestrial rocks indicates limited isotopic variability (Wombacher et al., 2003, Schmitt et al., 2009). Based on results for three loess samples, the Cd isotope composition of the upper continental crust is assumed to be $\epsilon^{114/110}\text{Cd} = -0.1 \pm 0.7$ (mean $\pm$ 2sd; Fig. 5.2), which is identical to the estimated composition of the bulk silicate earth with $\epsilon^{114/110}\text{Cd} = -0.3 \pm 1.0$ (mean $\pm$ 2sd; data from Schmitt et al., 2009, converted to $\epsilon^{114/110}\text{Cd}$ notation by Rehkämper et al., 2012). North African mineral dust is therefore also likely to be characterised by $\epsilon^{114/110}\text{Cd} \approx 0$. In contrast, atmospheric emissions of Cd from high temperature anthropogenic processes are expected to have lower $\epsilon^{114/110}\text{Cd}$ values due to isotope fractionation of the vapor phase to ‘lighter’ isotope compositions, with fume-derived dusts from Pb-Zn smelting operations featuring $\epsilon^{114/110}\text{Cd}$ values as low as -7 (Fig. 5.2; Cloquet et al., 2006, Shiel et al., 2010).

The observation that the aerosol samples with the lowest EF_{crust} values (> 5) are characterized by $\epsilon^{114/110}\text{Cd} \approx 0$ is consistent with the interpretation that their Cd inventory is dominated by mineral dust (Fig. 5.3b). With the exception of ISO-16 the

remaining samples, which likely contain significant quantities of anthropogenic Cd, however also display Cd isotope compositions indistinguishable from the upper continental crust (Fig. 5.3b). Of particular significance is sample ISO-25 that features the highest EF_{crust} value of 107 ± 1.5 , and an $\epsilon^{114/110}\text{Cd}$ value of 1.11 ± 1.06 (Fig. 5.3b). Sample ISO-16, which features an EF_{crust} value of 50 and is hence likely dominated by anthropogenic Cd, yielded an $\epsilon^{114/110}\text{Cd}$ value of -5.4 ± 1.3 . This result is consistent with that expected for the long-range transport of isotopically light Cd emitted by high temperature anthropogenic processes.

Although two studies of Pb-Zn smelting operations in France and Canada have shown that fume-derived Cd is fractionated to lower $\epsilon^{114/110}\text{Cd}$ values (-5 to -7; Cloquet et al., 2006, Shiel et al., 2010, Fig. 5.2), a recent study of emissions from a Pb-Zn smelting operation in Poland found no significant Cd isotope fractionation of fume derived dusts relative to the precursor ore materials (Chrastný et al., 2015). Furthermore, preliminary data from a study of Cd isotope fractionation during coal combustion suggest that the Cd isotope composition of the fly ash is strongly fractionated, with $\epsilon^{114/110}\text{Cd}$ values of +10 to +50 relative to the combusted coal, which featured $\epsilon^{114/110}\text{Cd}$ values of +0.4 to +10 (Fouskas et al., 2014). This result is not in line with the expected fractionation of the fume products to lower $\epsilon^{114/110}\text{Cd}$ values. Hence, the isotope fractionation of Cd during atmospheric emission by high temperature processes is not necessarily consistent and likely depends on the specific conditions during processes at individual emission sources.

In addition to the direction and magnitude of isotope fractionation during emission, the isotope composition anthropogenic Cd in the atmospheric will also be influenced by the composition of the starting materials. Although initial studies found that commonly used ore minerals displayed a relatively limited range of $\epsilon^{114/110}\text{Cd}$ values, that were generally similar to the continental crust at $\epsilon^{114/110}\text{Cd} \approx -2$ to +3 (Wombacher et al., 2003, Schmitt et al., 2009, Shiel et al., 2010), a more recent study found much larger Cd isotope variability for ore minerals from different Chinese Pb-Zn deposits with $\epsilon^{114/110}\text{Cd}$ of between -16 and +2 (Fig. 5.2, Zhu et al., 2013). Taken together, this suggests that it may be difficult to predict the isotope composition of Cd emitted from a particular source, which will dependent on the nature of the

combustion processes and any emission control steps (e.g. electrostatic filters) as well as the compositions of the source materials.

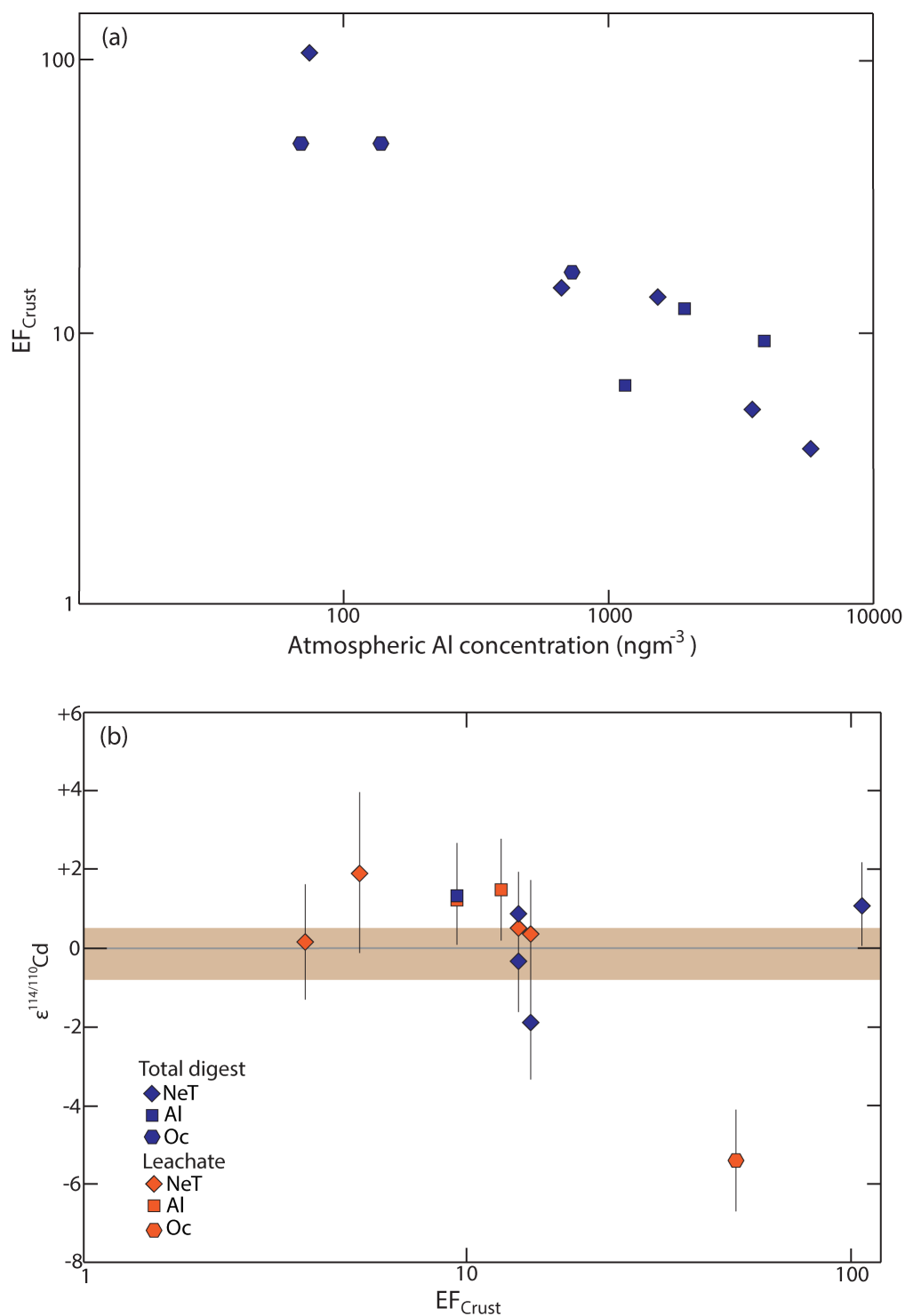


Figure 5.3. Panel (a), EF_{Crust} values versus atmospheric Al concentrations for the total digests (EF_{Crust} value uncertainties (1sd) are smaller than symbols). Panel (b), of $\epsilon^{114/110}Cd$ values versus EF_{Crust} values. For the leachate samples, EF_{Crust} values are taken from the corresponding total digest. The estimated Cd isotope composition of the upper continental crust is marked by the brown rectangle (Schmitt et al., 2009).

Since our aerosols were collected over the open ocean, in remote locations, their Cd content likely reflects a mixture of numerous emission sources. The observation that anthropogenic Cd transported by the northeast trade winds exhibits a seemingly identical isotope composition to the upper continental crust (and North African mineral dust) therefore likely reflects the average $\epsilon^{114/110}\text{Cd}$ of anthropogenic emission sources in a wide area of North Africa. It is nevertheless conceivable that, different regions featuring different collections of emission sources could feature isotopic variability for anthropogenic Cd. For example, ISO-16, the only sample collected south of the ITCZ that was analysed for Cd isotope composition, is characterised by a distinct $\epsilon^{114/110}\text{Cd}$ value of -5.4 ± 1.3 . This may therefore signify a difference in the isotope composition of anthropogenic Cd transported by the northeast trade winds ($\epsilon^{114/110}\text{Cd} \approx 0$; e.g., ISO-25) and the southeast trade winds ($\epsilon^{114/110}\text{Cd} \approx -5$; e.g., ISO-16). However this interpretation should be treated with caution due to the limited size of our data set, and the possibly suspect nature of sample ISO-16_{leach} (see section 5.3). Support for potential regional variations in the isotope composition of anthropogenic Cd in the atmosphere, come from preliminary results obtained in the South China Sea, with aerosols dominated by anthropogenic Cd exhibiting a distinctly difference range of $\epsilon^{114/110}\text{Cd}$ values, +1 to +18, to those determined in our study (Yang et al., 2015b).

5.5. Conclusions

With a single exception, all of the aerosols samples collected in the Tropical Atlantic Ocean yielded Cd isotope compositions indistinguishable from the upper continental crust at $\epsilon^{114/110}\text{Cd} \approx 0$, despite displaying a wide range of relative Cd contributions from mineral dust and anthropogenic sources. This composition is consistent with that expected for North African mineral dust, a finding which may provide useful constraints for marine mass balance estimates of Cd. The seemingly identical isotope composition of anthropogenic and natural Cd transport by the northeast trade winds over the Tropical Atlantic negates the use of Cd isotopes to distinguish between these two sources of Cd in this particular region. Due to the

remote location of these aerosols, they likely reflect homogenised mixtures of anthropogenic Cd from numerous emission sources, which feature an average $\epsilon^{114/110}\text{Cd}$ of about 0.

However, it is conceivable that anthropogenic emissions originating from different regions, which feature different emission sources, may display distinct Cd isotope signatures. Support for this idea comes from the distinct Cd isotope composition of ISO-16, of $\epsilon^{114/110}\text{Cd} = -5.4 \pm 1.3$, the only sample collected south of the ITCZ. Further studies into (1) Cd isotope fractionation during high temperature anthropogenic sources (i.e. non-ferrous metal smelting facilities, coal fired power stations and municipal waste combustion), (2) the Cd isotope composition of source materials (i.e ore minerals, coal and municipal waste) and (3) Cd isotope composition of atmospheric aerosols in different regions are therefore warranted to develop the use of Cd isotopes to trace environmental Cd sources.

5.6. Author contributions and acknowledgements

For this chapter I determined the Cd isotope composition of the aerosol samples and lead the interpretation and presentation of the results. Additional contributions were received from Katy Murphy, Mark Rehkämper, Tina van de Flierdt, Stanislav Strekopytov, Emma Humphreys-Williams, Alex Baker, Rosie Chance, Eric Achterberg and Maeve Lohan. Specifically K. Murphy is thanked for her expert guidance on the Cd isotope composition measurements. T. van de Flierdt and M. Rehkämper are acknowledged for their support and guidance throughout this project. The determination of the Cd and Al contents of the aerosol samples, were conducted by S. Strekopytov and E. Humphreys-Williams. A. Baker and R. Chance collected the aerosol samples during the GEOTRACES GA06 cruise, which was organised by E. Achterberg and M. Lohan. Additional thanks go to the other participants of the GA06 cruise, along with the captain and crew of the RRS Discovery. Finally Carl Palk is thanked for useful advice on ion exchange chromatography procedures.

Chapter 6

Summary and future work

It is well established that emissions from anthropogenic processes have been an important environmental source of numerous trace elements, including Pb and Cd, during the past century (Nriagu & Pacyna, 1988). Isotopic variations provide a useful tool to distinguish between different environmental sources of these elements, and to study their biogeochemical cycling (Komárek et al., 2008, Rehkämper et al., 2012, Boyle et al., 2014). The focus of this thesis is to apply isotopic measurements of Pb and Cd in seawater and atmospheric aerosol samples collected in the Tropical Atlantic Ocean, in order to assess the sources and cycling of these elements within this region of the troposphere and the ocean. Here we summarise the key findings of this thesis and highlight areas that should be the subject of future investigations.

A novel method to measure the Pb concentration and isotope composition of seawater samples is presented in Chapter 2. The method involves purification of Pb from the sample matrix by $\text{Mg}(\text{OH})_2$ co-precipitation and a two stage ion exchange chromatography procedure. Subsequently, isotopic analyses are conducted by thermal ionisation mass spectrometry in conjunction with a ^{207}Pb - ^{204}Pb double spike. The precision of this method was assessed through replicate analyses of six seawater samples, with typical reproducibilities ($\pm 2\text{sd}$) of about 150 to 1700 ppm and 1000 – 2000 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. Notably, the precision of these data is superior to those found in the literature. In particular they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. The accuracy of this method was assessed through analyses of two GEOTRACES intercalibration samples from the Atlantic Ocean and display good agreement with results from two other laboratories.

In Chapter 3, this method is applied to determine the Pb concentration and isotope compositions of surface seawater samples collected during two GEOTRACES cruise transects in the western and eastern Tropical Atlantic, in addition to the Pb isotope compositions of aerosol samples collected in the eastern Tropical Atlantic. These data are employed to (1) reassess the relative importance of natural and anthropogenic sources of Pb to surface waters of this region following the global phase out of leaded petrol, and (2) to study the factors governing the relative atmospheric flux of Pb associated with mineral dust and anthropogenic sources (i.e. relative atmospheric concentrations, deposition efficiencies and solubilities).

Relative maxima in the contribution of Pb from North African mineral dust to ocean surface waters, of about 30 to 50 % were detected at different latitudes (of 10 °N and 15 to 20 °N) for the two cruise transects. These observed changes in latitude are consistent with changes in the position of the North African dust plume during its seasonal migration. Using constraints provided by the aerosol data, we are able to show that the preferential removal of mineral dust over finer particles, on which anthropogenic Pb is known to be concentrated, during dry deposition is an important factor in governing the observed position and magnitude of the relative maxima in mineral dust Pb contributions to surface seawaters.

This is the first time a significant quantity of Pb from natural sources has been detected in Atlantic surface waters, and this can be viewed as the success of environmental policy. However, given that this region (1) features the highest atmospheric mineral dust concentrations over the global ocean (Goudie & Middleton et al., 2001) and (2) is dominated by dry deposition (Gelado-Caballero et al., 2012), it is reasonable to assume that it receives the highest relative fluxes of mineral dust compared to anthropogenic Pb of the entire global ocean. In this light, the observation that anthropogenic Pb still accounts for at least 50 % of the Pb in surface waters of this region suggests that other anthropogenic activities (i.e. unleaded petrol and coal combustion, as well as non-ferrous metal smelting; Pacyna & Pacyna et al., 2001) remain the dominant source of Pb to the ocean following the phasing out of leaded petrol.

In fact, due to differences in solubility, atmospheric concentrations of anthropogenic Pb need to be reduced to a much lower level compared to mineral dust, in order for the latter to become an important marine Pb source overall. At present, it is difficult to confidently constrain relative solubility of these two sources of Pb in the environment. Further investigations into the relative solubility Pb from mineral dust and anthropogenic sources and the environmental factors which exert a potentially control on their relative solubility (i.e. pH, chemical and physical processing in the atmosphere etc), are therefore required to further our understanding to the relative flux of these two Pb sources to the ocean.

In Chapter 4, Pb concentration and isotope composition data for depth profiles collected in the eastern Tropical Atlantic are presented. The distributions of these

chemical properties in the interior of this region of the ocean were found to be generally consistent with those expected from the transport of historic anthropogenic emissions by ocean circulation. Hence, these data enable insights into ventilation timescales and pathways in a similar fashion to other more commonly exploited transient tracers (e.g. CFC's, SF₆ and ³H; e.g. Fine et al., 2011). However, interpretation of the observed distribution of anthropogenic Pb in the ocean is complicated by mixing of waters ventilated at different times and locations, similar to the 'non-linear' mixing effects imposed on other transient tracers (e.g. Doney et al., 1997).

Further complications arise from the chemical reactivity of Pb in the ocean, in addition to the complex, regionally dependent boundary conditions of marine Pb inputs. The latter potentially enables insights into subtle differences in water mass formation sites (e.g. Véron et al., 1999, Noble et al., 2015). However, improved knowledge on regional Pb input histories is required to adequately constrain the role of transient inputs on the distribution of Pb in the ocean interior. This can be achieved through the acquisition of Pb concentration and isotope composition data from suitable environmental archives, such as corals, ice/firm cores, lake sediments etc. (e.g. Kelly et al., 2009, McConnell et al., 2014). Through efforts related to the international GEOTRACES program (www.geotraces.org), data on the distribution of Pb concentrations and isotope compositions in the ocean interior is set to increase in the near future. Modeling efforts, constrained by this expanding global data set may help unravel the complex interplay between transient inputs, advection, mixing and chemical reactivity in producing the observed distribution of Pb in the ocean.

In Chapter 5, we present some of the first data on the Cd isotope composition of atmospheric aerosols, which were collected in the eastern Tropical Atlantic. These data are used to assess the utility of Cd isotopic variations to distinguish between anthropogenic and natural sources of Cd in the atmosphere. Despite, containing a wide range of Cd contributions from mineral dust and anthropogenic sources, the Cd isotope composition of the majority of the aerosol samples were identical within analytical uncertainty, displaying the same composition as the upper continental crust (Schmitt et al., 2009). We speculate that this reflects the homogenisation of anthropogenic Cd emitted from numerous sources, by mixing during atmospheric

transport, resulting in an average isotope composition of anthropogenic Cd that is indistinguishable from that of North African mineral dust. Hence isotopic variations may not be useful in differentiating anthropogenic and natural atmospheric Cd sources in this region.

However, this does not rule out the possibility of regional variations in the isotope composition of anthropogenic Cd in the atmosphere, an idea support by the unique Cd isotope composition of a single aerosol sample collected south of the Inter Tropical Convergence Zone. Further support comes from preliminary results from aerosols collected in the South China Sea, which display a much larger range in Cd isotope compositions than our aerosol samples (Yang et al., 2015b). Hence, additional investigations in the Cd isotope composition of atmospheric aerosols are needed, and will advance our understanding on the anthropogenic perturbation to the global biogeochemical cycling of this element.

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Appendices

**Appendix 1: Paper arising from the work described in Chapter 2:
“High-precision measurements of seawater Pb isotope compositions
by double spike thermal ionization mass spectrometry”**



High-precision measurements of seawater Pb isotope compositions by double spike thermal ionization mass spectrometry



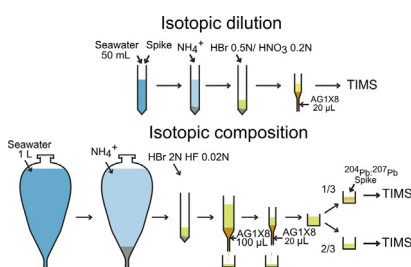
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HIGHLIGHTS

- Precise and accurate determination of seawater Pb isotope compositions.
- Uncertainties (2sd) for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ are better than $\pm 3\%$.
- Analysis of a GEOTRACES depth profile from the South Atlantic Ocean.
- Pb isotopic compositions reflect the different water masses that were sampled.
- The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios display a correlation.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method for the determination of seawater Pb isotope compositions and concentrations was developed, which combines and optimizes previously published protocols for the separation and isotopic analysis of this element. For isotopic analysis, the procedure involves initial separation of Pb from 1 to 2 L of seawater by co-precipitation with Mg hydroxide and further purification by a two stage anion exchange procedure. The Pb isotope measurements are subsequently carried out by thermal ionization mass spectrometry using a ^{207}Pb – ^{204}Pb double spike for correction of instrumental mass fractionation. These methods are associated with a total procedural Pb blank of 28 ± 21 pg (1sd) and typical Pb recoveries of 40–60%. The Pb concentrations are determined by isotope dilution (ID) on 50 mL of seawater, using a simplified version of above methods. Analyses of multiple aliquots of six seawater samples yield a reproducibility of about ± 1 to $\pm 10\%$ (1sd) for Pb concentrations of between 7 and 50 pmol/kg, where precision was primarily limited by the uncertainty of the blank correction (12 ± 4 pg; 1sd). For the Pb isotope analyses, typical reproducibilities (± 2 sd) of 700–1500 ppm and 1000–2000 ppm were achieved for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. These results are superior to literature data that were obtained using plasma source mass spectrometry and they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. Both Pb concentration and isotope data, furthermore, show good agreement with published results for two seawater intercomparison samples of the GEOTRACES program. Finally, the new methods were applied to a seawater depth profile from the eastern South Atlantic. Both Pb contents and isotope compositions display a smooth evolution with depth, and no obvious outliers. Compared to previous Pb isotope data for seawater, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are well correlated with $^{207}\text{Pb}/^{206}\text{Pb}$, underlining the significant improvement achieved in the measurement of the minor ^{204}Pb isotope.

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1. Introduction

Investigations that map the distribution of trace metals and their isotopes in seawater and which study their relationship to and potential impacts on global biogeochemical cycles in the oceans are an overarching goal of modern marine geochemistry and a key objective of the international GEOTRACES program [1]. The global scale impact of human activities on natural Pb budgets was established more than 40 years ago by Chow and co-workers [2–5] and massive inputs of anthropogenic Pb into the oceans were soon thereafter identified by Patterson and co-workers [6–8], based on the first accurate and precise Pb concentration measurements for seawater. Studies of the anthropogenic impact on marine Pb budgets were further advanced with the first successful Pb isotope analyses of seawater [6,9–13]. Whilst these early measurements were all carried out by TIMS (thermal ionization mass spectrometry), the majority of seawater Pb analyses since the 1990s have been conducted using various types of ICP-MS instrumentation. At present, the most precise Pb isotope analyses of seawater apply either single collector high resolution or multiple collector ICP-MS (HR-ICP-MS and MC-ICP-MS, respectively), most commonly following low-blank pre-concentration of the element by co-precipitation with $\text{Mg}(\text{OH})_2$ [14,15].

These methodological advances are a consequence of the particular importance of seawater Pb isotope data to studies of environmental pollution and marine geochemistry. For example, analyses of corals yielded a seawater Pb isotope record for the North Atlantic over the last 220 years [12,15,16], which revealed significant isotopic variability through time, in accord with known changes in the extent and type of anthropogenic emissions. Similarly, Pb isotope data for the modern ocean are used to infer the distribution of Pb from different anthropogenic and natural sources in surface seawater [9,13,17,18] and to determine the lateral mixing and advection of subsurface water masses [19–23]. Shen and Boyle [12], furthermore, highlighted that temporal changes in the Pb content and isotope composition of different water masses can be applied to trace ventilation times.

In this paper, we present a new method for the accurate and precise determination of seawater Pb concentrations and isotope compositions. The methodology involves pre-concentration of Pb by $\text{Mg}(\text{OH})_2$ co-precipitation [24] followed by ion exchange chromatography [25,26], and subsequent isotopic analyses by TIMS using a ^{204}Pb – ^{207}Pb double spike to achieve precise control of instrumental mass fractionation [27,28]. The technique is validated by analyses of both in-house and international seawater reference materials and its utility demonstrated by data obtained for a GEOTRACES seawater depth profile from the South Atlantic Ocean.

A number of previous investigations [28–34] have shown that the application of Pb double or triple spikes enables Pb isotope measurements that are significantly more precise and accurate than conventional TIMS or MC-ICP-MS techniques and less susceptible to the analytical artifacts, which can be generated by instrumental mass bias effects. Our study is the first to apply the double spike methodology to seawater Pb isotope analyses. Using these techniques, we are not only able to analyze the commonly measured ratios $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ to high precision but $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ can also be determined to an uncertainty of better than about $\pm 3\%$. Only very scarce seawater data are available for the latter ratios due to the analytical challenges but measurements of non-radiogenic ^{204}Pb are deemed to be important to fully exploit the potential of the Pb isotope system.

2. Experimental

2.1. Samples

A gravimetric solution of the well-characterized NIST standard reference material SRM 981 Pb was employed for calibration of the Pb double spike and to evaluate the precision of the mass spectrometric methods. Four filtered seawater samples that were available in large quantities were utilized as in house reference materials to further assess reproducibility. These encompass a surface water sample (Atlantic – S) and three subsurface water samples, Atlantic – D1, Atlantic – D2 (both from 2000 m depth), and Weddell (400 m depth). These samples were not specifically collected for Pb isotope analyses, and potential contamination during sampling and initial handling hence renders them unsuitable for evaluation of accuracy or an assessment of water mass properties.

To enable a comparison of our results with literature data for assessment of accuracy, we analyzed the international seawater reference samples GSI and GDI. These were collected at water depths of 7 m and 2000 m, respectively, at the Bermuda Atlantic Ocean Time Series station (BATS) during the 2008 GEOTRACES intercalibration cruise on the R/V Knorr (KN193-6). The collection and handling of these samples employed materials and procedures that were specifically designed for the intercalibration of contamination-prone trace metals and isotopes [35].

The seawater for a Pb isotope and concentration depth profile was collected in the South Atlantic Ocean off the African coast at 36.46°S, 13.39°E in October 2010 during the eastern part of the GEOTRACES GA10 transect along 40°S on the R.R.S. Discovery (D357; 18 October–22 November 2010) [1]. This depth profile from station 3 encompasses 12 samples that cover the entire 4500 m of the water column at the sampling location. Station 3 serves as a 'cross over station', which means that it was sampled by three separate GEOTRACES cruises (UK GEOTRACES cruise D357 – this study; UK GEOTRACES cruise JC068 in 2011/2012; MD166 BONUS – GoodHope Cruise in 2008, Boye et al. [36]), thereby enabling a comparison of results for samples from a single location but that were collected at different times and analyzed using different methodologies. The samples from cruise D357 analyzed here were obtained with a titanium rosette deployed from plasma rope and equipped with trace metal clean sample bottles and supplemented by underway surface water sampling (2–3 m depth) using a towed 'fish' (Wyatt et al. [37]). All bottle handling was conducted in a clean container and each sample was transferred into two pre-cleaned 1 L LPDE bottles without filtration or acidification. About one year after collection and two weeks prior to analysis, the samples were acidified to pH 2 with 6 M HCl.

2.2. Reagents

Water with a resistivity of $>18.2 \text{ M}\Omega \text{ cm}$ from a Milli-Q water system was used throughout for reagent preparation and cleaning of labware. Purified concentrated HF ($\sim 28 \text{ M}$) and HBr ($\sim 8.5 \text{ M}$) were purchased from VWR as Optima (distilled) grade acids whilst concentrated (14.5 M) HNO_3 and 6 M HCl were prepared in-house by subboiling distillation of reagent grade acids in quartz stills. The Pb blanks of these acids were checked regularly and found to be consistently less than 2 pg/mL. The dilute mineral acids that were employed for the separation chemistry were freshly prepared for each batch of samples.

A purified aqueous solution of NH_3 was used to affect precipitation of $\text{Mg}(\text{OH})_2$ from seawater and prepared by cold vapor phase equilibration of reagent grade 28% (w/w) aqueous NH_3 with Milli-Q water in a Savillex Teflon elbow. Approximately 2 volumes of 28% aqueous NH_3 were employed for each

volume of Milli-Q water, and these were equilibrated for about two weeks to obtain purified aqueous NH_3 (aq- NH_3) at a concentration of about 9 M. During this period, the Teflon elbow was stored double bagged in plastic, to limit contamination and loss of gaseous NH_3 . The aq- NH_3 was collected from the still just prior to use and each batch of three samples, plus a full procedural blank, was treated with the same solution. The Pb blank of the aqueous ammonia was stable at less than 0.3 pg/mL during the course of the study.

2.3. Preparation and calibration of ^{207}Pb – ^{204}Pb double spike

Highly enriched (>99%) metallic ^{204}Pb and ^{207}Pb in wire form were purchased from Isoflex (USA). The wires were separately dissolved in 7.5 M HNO_3 and diluted with water to obtain solutions in 2 M HNO_3 . A dilute double spike solution was then prepared with a total Pb concentration of ~ 10 ng/mL and an optimal molar ratio of $^{207}\text{Pb}/^{204}\text{Pb} \approx 1$, based on the error propagation modeling of Galer [28] and Rudge [38].

Spike calibration was performed using a gravimetric solution of NIST SRM 981 Pb. In a first step, the concentration of the double spike was determined by two reverse isotope dilution runs that were carried out with a Nu Plasma HR MC-ICP-MS, using external normalization to added Tl for mass bias control [24,39,40]. Initially, a preliminary concentration was obtained, based on an approximate spike isotope compositions, which was calculated from the mixing proportions of the ^{204}Pb and ^{207}Pb solutions, and the respective isotope compositions, as supplied by Isoflex.

The isotope composition of the double spike (Table 1) was then calibrated by analyses of different gravimetrically prepared double spike – NIST SRM 981 mixtures using TIMS [38,41]. The instrumental mass fractionation correction [24,39,40], the spike-standard mixing line, and the double spike composition were calculated by over-determining the system of equations (number of double spike – NIST SRM 981 mixtures >2) and solving in the least-square sense, as described by Rudge et al. [38]. Finally, the calibrated double spike isotope composition was applied to the data from the initial reverse isotope dilution runs, to accurately define the double spike concentration.

2.4. Sample preparation for determination of Pb isotope compositions

2.4.1. Lead pre-concentration by co-precipitation with magnesium hydroxide

A number of previous studies have shown that co-precipitation of Pb with $\text{Mg}(\text{OH})_2$ is an effective, low-blank method for pre-concentration of Pb from seawater [14,42] and this technique is retained in our procedure. Initial tests showed that Pb is efficiently and reproducibly extracted from seawater at yields $\geq 80\%$ by precipitation with $\text{Mg}(\text{OH})_2$ at $\text{pH} \approx 10$. The yields were, furthermore, not correlated with the exact pH value that was adjusted or the amount of $\text{Mg}(\text{OH})_2$ precipitated. The $\text{Mg}(\text{OH})_2$ precipitate, however, was also found to scavenge a significant amount of sea salt, but the latter could be removed without noticeable reduction of the Pb yield by rinsing the precipitate with water.

In order to obtain sufficient Pb for precise analyses, even for Pb depleted seawater from the deep ocean, samples of up to about 2 L were processed. The seawater was transferred to 1 L pre-cleaned Teflon separating funnels, to aid the collection of the Mg hydroxide precipitate. Precipitation of $\text{Mg}(\text{OH})_2$ was affected by introduction of the purified aq- NH_3 until a final pH value of about 10 was obtained. As each seawater sample had been acidified to a slightly different extent, and because the precipitate forms only gradually, the applied volume of aq- NH_3 was optimized for each sample by slowly adding successive portions of the reagent to the separating funnel. This was achieved by an initial addition of 2–4 mL aq- NH_3 , whereupon the samples were stirred vigorously and then left to stand for least 3 h to allow the $\text{Mg}(\text{OH})_2$ precipitate to form. If precipitation had not occurred after this time, an additional volume of 0.5 mL of aq- NH_3 was added every 2–3 h until formation of precipitate was observed.

Once about 5 mL of $\text{Mg}(\text{OH})_2$ slurry had formed, the precipitate was drained through the bottom of the separating funnel, collected in a 15 mL Teflon centrifuge tube, centrifuged at 1700 rpm for about 10 min and the remaining solution poured off. This step was repeated several times until all precipitate was recovered from the funnel. The solids were then washed with 5 mL H_2O , centrifuged again and finally dissolved directly in the tubes by addition of 5 mL of a 2 M HBr –0.01 M HF acid mixture. To aid dissolution, the centrifuge tubes were shaken whereupon the formation of many small bubbles within the solutions was observed for seawater

Table 1

Lead isotope data of this study and reference values for NIST SRM 981 Pb. Also shown is the isotope composition of the Pb double spike used in this study.

Sample	Pb used (ng) ^a	<i>n</i> ^b	$^{206}\text{Pb}/^{204}\text{Pb} \pm 2\text{sd}^c$	$^{207}\text{Pb}/^{204}\text{Pb} \pm 2\text{sd}^c$	$^{208}\text{Pb}/^{204}\text{Pb} \pm 2\text{sd}^c$	$^{207}\text{Pb}/^{206}\text{Pb} \pm 2\text{sd}^c$	$^{208}\text{Pb}/^{206}\text{Pb} \pm 2\text{sd}^c$
This study							
SRM 981 Pb	2	42	16.943 ± 16	15.496 ± 15	36.716 ± 38	0.91460 ± 18	2.16710 ± 61
$\pm 2\text{sd}$ relative (ppm)			920	970	1050	200	280
$\pm 2\text{se}$ of typical (ppm) ^d			~ 500	~ 500	~ 550	~ 60	~ 80
SRM 981 Pb	10	25	16.9419 ± 31	15.4968 ± 38	36.7224 ± 91	0.91470 ± 11	2.16755 ± 20
$\pm 2\text{sd}$ relative (ppm) ^e			180	240	250	120	90
$\pm 2\text{se}$ of typical run			~ 90	~ 100	~ 100	~ 40	~ 60
SRM 981 Reference values ^e							
Galer and Abouchami (TIMS) [57]	~ 10		16.9405 ± 15	15.4963 ± 16	36.7219 ± 44	0.91475 ± 4	2.16771 ± 10
Thirlwall (TIMS) [31]	~ 20		16.9409 ± 22	15.4956 ± 26	36.7228 ± 80	0.91469 ± 7	2.16770 ± 21
Todt et al. (TIMS) [58]	80		16.9356 ± 23	15.4891 ± 30	36.7006 ± 113	0.91459 ± 13	2.16701 ± 43
Thirlwall (MC-ICP-MS) [32]			16.9417 ± 29	15.4996 ± 31	36.724 ± 9	0.91488 ± 8	2.16770 ± 24
Baker et al. (MC-ICP-MS) [29]	~ 50		16.9416 ± 13	15.5000 ± 13	36.7262 ± 31	0.91491 ± 4	2.16781 ± 12
^{207}Pb – ^{204}Pb double spike ^f			0.00240	1.03181	0.00820	431.03	3.4267

^a Mass of Pb loaded on filament and/or used for a single analysis.

^b *n* = number of analyses.

^c $2\text{sd} = 2 \times$ standard deviation calculated from *n* separate runs; denotes long-term “external” reproducibility.

^d $2\text{se} = 2 \times$ standard error of the mean; denotes within-run (“internal”) precision of the data, based on individual results for measurement cycles.

^e All reference values were obtained using either double or triple spike techniques for correction of instrumental mass fractionation.

^f Isotope composition of the Pb double spike used in the current study.

samples that had not been filtered following collection. Bubble formation is hence presumably related to the presence of residual organic compounds. It is important to remove the bubbles at this stage because they can otherwise lead to the formation of larger bubbles within the resin bed during the subsequent column chemistry, effectively blocking the flow. For removal of the bubbles, the centrifuge tubes were left to stand overnight, sealed and then gently heated on a hotplate for 10 min at 50 °C. After cooling, bubbles should no longer be visible in the solutions, otherwise the heating was repeated.

2.4.2. Lead purification by anion exchange chromatography

The anion exchange purification procedure for Pb (Table 2) is based on previously published methods that apply strongly basic AG1X8 resin and dilute HBr–HNO₃ mixtures for elution, with modifications as detailed below.

Previous work [14,43,44] has shown that silica is trapped by the Mg(OH)₂ precipitate, which is used for the separation of Pb from seawater. Relatively high Si concentrations of about 10–150 µmol/kg are, furthermore, found in seawater samples from depths >1000 m [45,46]. During method development we found that such concentrations suffice to form precipitates of silica on top of the resin column, when HF is not present in sample solutions. Hence, the 1st stage column chemistry of our final method (Table 2) applies a 2 M HBr–0.01 M HF mixture for sample loading, whereby the small concentration of HF present enhances silica solubility to prevent precipitation of silicic acid. The same acid mixture is subsequently also used to completely flush silica from the resin, prior to elution of other matrix elements (Table 2). In 2 M HBr, Pb has a distribution coefficient K_D of about 200 toward the AG1X8 anion exchange resin that was used [25,47,48]. Elution experiments confirmed that, whilst the Pb K_D value is reduced when HF is present, the use of trace HF in the elution scheme (Table 2) does not prevent retention of Pb on the resin bed during sample loading and matrix elution.

Following elution of Pb from the 1st stage columns, the samples were dried and further purified by a second column chemistry step, which is needed to eliminate remaining traces of Mg [49] and improve the ionization of Pb during the TIMS analyses. To this end, the dried samples were redissolved in 0.2 M HBr–0.5 M HNO₃ and processed using established HBr–HNO₃ procedures on small 20 µL resin columns (Table 2), which help to minimize the procedural blank.

2.5. TIMS analyses of Pb isotope compositions

The accurate determination of Pb isotope compositions with precise correction of instrumental mass discrimination requires

two separate mass spectrometric runs – one of the pure sample and a second analysis of a double spike – sample mixture. To this end, the purified Pb was divided into two aliquots and the double spike was admixed to one, prior to the TIMS measurements. The addition of the double spike after, rather than before, the chemical separation of Pb has a number of advantages. Conveniently, each sample needs to be processed through the (time-consuming) pre-concentration and purification steps only once, rather than twice. Furthermore, the impact of contamination from reagents and handling is minimized and uncertainties arising from different blanks impacting on the spiked and unspiked analyses are reduced.

In detail, our procedure involves splitting the Pb solutions from the 2nd stage column chemistry into a larger and a smaller aliquot. The larger aliquot comprising 2/3 of the sample remained unspiked, whilst Pb double spike was added to the remaining aliquot with 1/3 of the solution. The double spike addition was thereby carried out to obtain a molar ratio of natural (N) to spike-derived Pb (S) that approximates the optimum S/N ≈ 1.226 [38]. This is equivalent to a molar proportion of spike, S/(S + N), of 55.1%, corresponding to ²⁰⁶Pb/²⁰⁴Pb ≈ 0.411 (assuming a natural seawater ²⁰⁶Pb/²⁰⁴Pb = 18.4). The amount of natural Pb present was thereby estimated from the Pb concentration measurements that were carried out first for all samples, and assuming a Pb recovery of 60% from the chemical separation (see below).

Following aliquoting and spiking, the Pb solutions were evaporated to dryness and redissolved in 1 µL 2 M HNO₃. The samples were loaded on a single, previously outgassed zone refined Re filament (99.999%; H. Cross, USA), dried at 0.4 A, 0.5 µL of silica–gel activator was then added and also dried at 0.4 A. The sample–activator mixture was finally heated at 2 A for ~1 s to evaporate phosphoric acid and fuse the silica gel.

Gerstenberger and Hasse [50] prepared a highly successful activator for Pb isotope analyses by TIMS but this applies silica particles which are no longer commercially available. Hence, a new SiO₂–H₃PO₄ activator mixture was made up for the current study. This mixture was prepared from SiO₂ nanoparticles (20–60 nm; Iolitec Inc.) and Merck Ultrapur phosphoric acid, whereby a SiO₂/H₃PO₄ weight ratio of 0.43% was applied with respect to the addition of the silica to dilute 0.16 M H₃PO₄. The amount of activator used for analysis was calibrated to optimize ionization yields, based on tests that were carried out with 2 ng NIST 981 Pb. These test revealed that use of 0.5 µL activator solution was preferable to loading with 1 µL of activator – whilst the latter yielded more stable Pb ion beams the former produced ion beam intensities that were typically about 2–3 times higher.

The Pb isotope measurements were carried out on a TRITON TIMS instrument operating in static mode and using Faraday cups

Table 2

Column chemistry procedure for the separation of Pb from seawater for isotope compositions (IC) and isotope dilution (ID) concentration measurements by TIMS

	Pb IC chemistry 1st stage	Pb IC chemistry 2nd stage	Pb ID chemistry
Resin ^a	100 µL AG1X8, 100–200 mesh	20 µL AG1X8, 100–200 mesh	20 µL AG1X8, 100–200 mesh
Clean resin	3 × 3 mL 0.1 M HNO ₃	3 × 1 mL 0.1 M HNO ₃	3 × 1 mL 0.1 M HNO ₃
Equilibrate resin	2 × 0.1 mL 2 M HBr–0.01 M HF	2 × 0.1 mL 0.2 M HBr–0.5 M HNO ₃	2 × 0.1 mL 0.5 M HBr–0.2 M HNO ₃
Load sample	~5 mL in 2 M HBr–0.01 M HF	~1 mL in 0.2 M HBr–0.5 M HNO ₃	2 mL 0.5 M HBr–0.2 M HNO ₃
Elute matrix	2 × 0.1 mL 2 M HBr–0.01 M HF	2 × 0.3 mL 0.2 M HBr–0.5 M HNO ₃	2 × 0.3 mL 0.5 M HBr–0.2 M HNO ₃
Elute Pb	2 × 0.5 mL 0.2 M HBr–0.01 M HNO ₃ 0.2 mL 0.03 M HBr–0.5 M HNO ₃ 3 mL 0.03 M HBr–0.5 M HNO ₃	1 mL 0.03 M HBr–0.5 M HNO ₃	1 mL 0.03 M HBr–0.5 M HNO ₃

^a The resin is used in columns prepared from shrink-fit Teflon tubing. The columns have a reservoir volume of ~3 mL and a resin column with an internal diameter of ~3 mm.

fitted with $10^{11} \Omega$ resistors. Prior to each measurement session, a gain calibration was carried out for all amplifiers. For analysis, the filaments were heated to a target temperature of about 1300°C within 30 min, and isotopic data were then collected in 15 blocks of 15 cycles with an integration time of 8.3 s. Half-mass baseline measurements (30 cycles $\times$ 1.05 s integrations following 5 s idle time) and an automatic peak centering routine (followed by 3 s idle time) were carried out prior to each block. Loads of 2 ng NIST 981 Pb provided stable and very reproducible ion beam intensities of 200–300 mV ^{208}Pb . For the seawater samples, the ion beam intensities were more variable and generally lower, whereby 2 ng Pb generally yielded ^{208}Pb ion beams of about 100–200 mV.

The measured isotopic data for the spiked and unspiked sample aliquots were processed using an iterative solver that employs published methods [38] and which was implemented as a macro within a Microsoft Excel spreadsheet. The method uses the exponential law to obtain mass bias corrected Pb isotope data and is employed on a cycle-by-cycle basis to provide an accurate assessment of the final propagated data uncertainties.

Following Doucelance and Manhès [51], the TIMS source was baked for 3 h after the introduction of a new sample turret. This technique was observed to substantially reduce the formation of hydrocarbon species that can form interfering molecular ions during the Pb isotope runs [31]. The baking also significantly improved the vacuum within the ion source (to about 3.5 to 6×10^{-8} mbar, without use of a liquid N_2 cold trap) and enhanced Pb ion beam stability, thereby permitting analyses without interblock reheating. The latter improvement is presumably due to the efficient drying of the silica gel, which is achieved during heating in vacuum condition.

Barium- PO_x ions were mainly observed at temperatures, which are slightly higher compared to those employed for optimal Pb ionization [31]. The formation of such ions, and hence the presence of Ba in samples, is best avoided because they produce minor molecular interferences on ^{204}Pb (from $^{138}\text{Ba}^{31}\text{P}^{17}\text{O}^{18}\text{O}^+$, $^{137}\text{Ba}^{31}\text{P}^{18}\text{O}_2^+$) and, even more problematic, hinder the ionization of Pb whereby rapidly decaying Pb ion beams are observed. The presence of BaPO_x ions was routinely monitored during the analyses at mass 201, which corresponds primarily to $^{138}\text{Ba}^{31}\text{P}^{16}\text{O}_2^+$. The measured ion beam intensities at mass 201 were observed to rise during Pb sample runs but only to maximum values of 1–3 mV. At this level, the BaPO_2 interference contributes less than 15 ppm to the ^{204}Pb ion beam, such that a correction was deemed unnecessary.

2.6. Determination of Pb concentrations

Lead concentrations were determined by isotope dilution (ID), and using a chemical separation method similar to that employed for the isotope ratio measurements but optimized for the processing of smaller seawater samples. In detail, 50 mL of seawater were weighed into clean polyethylene centrifuge tubes. Following addition of the Pb double spike, the mixtures were left to stand for at least 10 days to ensure full spike–sample equilibration. The amount of Pb spike added was based on an initial ‘guess’ of or any information available for the Pb concentration of the samples, to achieve an optimal $\text{S/N} \approx 2.61$ (equivalent to $^{206}\text{Pb}/^{204}\text{Pb} \approx 0.188$) for minimal error propagation during ID data reduction.

Co-precipitation of Pb with $\text{Mg}(\text{OH})_2$ was affected by adding 150 μL of purified aq- NH_3 . Following separation of the precipitate by centrifugation and dissolution in a dilute HNO_3 – HBr mixture, Pb was further purified using a single stage anion exchange chemistry. This employed small resin columns of only 20 μL to minimize the procedural blank (Table 2). The anion exchange chemistry was slightly modified in comparison to the 2nd stage

chemistry for Pb isotopes through use of a 0.5 M HBr –0.2 M HNO_3 acid mixture for sample loading and matrix elution, because this was observed to facilitate the dissolution of the $\text{Mg}(\text{OH})_2$ precipitate whilst ensuring quantitative retention of Pb on the small resin columns.

The ID TIMS analyses for Pb used the same techniques that were applied for the isotopic measurements but with shorter runs comprising 5 blocks of 15 cycles. During filament loading of some samples for the ID TIMS analyses, the presence of impurities, in the form of salts and possibly also organic compounds, was detected. When present, such impurities were associated with poor Pb ion beam intensities during the TIMS runs and in some extreme cases the analyses were even abandoned. Such contamination may also produce interfering molecular ions that could generate inaccurate ID results. Subsequent test showed that the impurities can be reduced to negligible levels, by allowing the resin bed to drain and dry completely (for about 10 min) after each step of the column chemistry procedure for Pb separation (Table 2) and, in particular, prior to the elution of Pb.

3. Results and discussion

3.1. Blanks

The total blank for the Pb isotope measurements was determined by carrying out the complete analytical procedure without an initial seawater sample being present. Over a 24-month period, the mean procedural blank was 28 ± 21 pg (1sd, $n=25$; ignoring two abnormally high blanks of ~ 100 pg encountered during a single two-week period). The individual contributions to this total from (i) filament loading and (ii) reagents were also determined and found to be 1.9 ± 0.5 pg for the former, 5.0 ± 1.4 pg for the mineral acids used, and 2.5 ± 0.2 pg for the aq- NH_3 solutions. The contribution of the anion exchange resin and column chemistry (without reagents) to the total blank could hence be quantified as 17 ± 8 pg, by subtracting the reagent component from separately measured column chemistry blanks. The sum of the individual blank contributions is, therefore, 27 ± 10 pg, in accord with the full procedural blanks values determined during the study. Ignoring the individual contributions (and chemistry yields), a Pb blank of 10–50 pg contributes about 0.05–2.5% to the indigenous Pb budget of samples that were analyzed for isotopic compositions, assuming samples volumes and Pb concentrations of 1–2 L and 10–50 pmol/kg, respectively. The Pb isotope composition of the blank was also measured on several occasions with rather variable results, due to the low ion beam intensities and/or actual differences in blank compositions (e.g., $^{206}\text{Pb}/^{204}\text{Pb} = 18.34 \pm 0.62$, $^{207}\text{Pb}/^{206}\text{Pb} = 1.196 \pm 0.028$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.422 \pm 0.021$; 2se, $n=10$). Blank corrections were not applied to the isotopic data because such corrections did not improve the reproducibility of results from replicate sample analyses (see discussion below).

The total procedural blank for the Pb ID concentration measurements was determined using 100 μL seawater samples, as only negligible amounts of Pb (~ 0.2 to 1 pg) are present in such small volumes. These measurements revealed a relatively stable total Pb blank of 11.7 ± 4.3 pg (1sd, $n=36$), which is equivalent to about 1–15% to the indigenous Pb in ID sample aliquots, assuming Pb abundances of 10–50 pmol/kg (for simplicity, this ignores variable chemistry yields and individual blank contributions). Blank corrections were applied to all measured Pb concentrations based on the mean blank value. The uncertainties of the Pb concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction.

3.2. Chemical separation of Pb

Stable isotope fractionation of Pb during anion exchange chromatography with HCl was recently documented and shown to vary systematically with Pb recovery [29,52]. Such fractionation can have a detrimental impact on the accuracy of subsequent Pb isotope measurements and may also occur during Pb purification with other anion exchange elution protocols. As part of this study, it was, therefore, investigated whether incomplete recovery of Pb from the anion exchange chemistry applied here (Table 2) also has a systematic impact on the measured Pb isotope compositions. To this end, multiple 10 ng aliquots of NIST SRM 981 Pb were processed through the complete 2-stage column separation procedure and the purified Pb fractions were then analyzed using standard methods. The data (Fig. 1) illustrate that the column chemistry routinely affords Pb yields of about 50–70%. Such recoveries are in accord with the total Pb yields of about 30–60% that were determined for multiple analyses of five different seawater samples (Tables 3 and 4). Assuming that the Mg(OH)₂ co-precipitation achieves a recovery of ≥80% for seawater Pb (see above), the Pb yield of the column chemistry is constrained to be about 40–75%.

In a previous investigation, Reuer et al. [15] reported essentially complete recovery of seawater Pb pre-concentrated by Mg(OH)₂ co-precipitation, during purification on AG1X8 resin (as in this study) but using HBr and HCl for elution [49]. Test conducted during the course of the present study showed, however, that the method of Reuer et al. [15] was associated with Pb recoveries similar to those reported here, when the procedure was modified to include additional use of HF to prevent precipitation of silicic acid during sample loading (Table 2). The use of dilute HF thus appears to be associated with either incomplete Pb retention on or elution from the anion exchange resin, regardless of the exact nature of the mineral acids, which are applied in the procedure. Ultimately, the current HBr-HNO₃ method (Table 2) was preferred to the elution method of Reuer et al. [15], because the former applies only dilute mineral acids (which helps to minimize the blank) and routinely produced cleaner Pb separates for subsequent isotopic analyses.

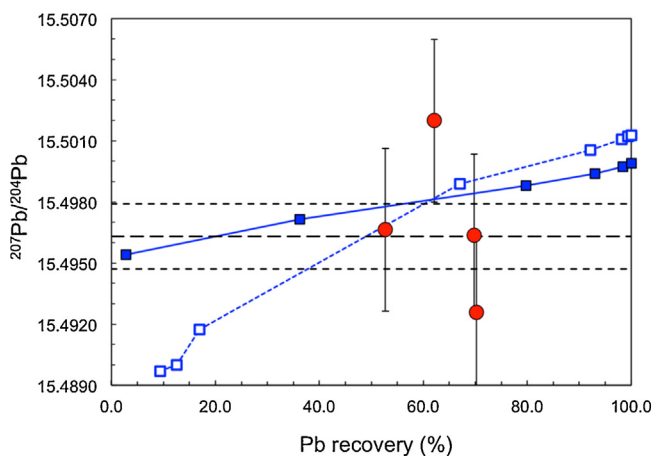


Fig. 1. The recovery of Pb and ²⁰⁷Pb/²⁰⁴Pb ratios obtained for 10 ng aliquots of NIST SRM 981 Pb that were processed through the 2-stage column chemistry (Table 2) are shown as full red circles with error bars that denote a ±2sd uncertainty of about 240 ppm (Table 3). Shown for comparison are literature data for cumulative recovery and isotope composition of SRM 981 Pb that was collected in successive fractions from anion-exchange resin which was eluted with HCl: full blue squares and solid line—elution with 6M HCl; open blue squares with dashed line—elution with 2 M and 8 M HCl (Baker [29]). The dashed black lines indicate the ²⁰⁷Pb/²⁰⁴Pb reference value determined for SRM 981 Pb (15.4963 ± 16; Table 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Lead concentration and isotope composition data for the four in-house seawater reference materials and other key information relating to samples.

Sample	n-ID ^a	[Pb] ± 1sd ^b pmol/kg ^b	±1sd (%)	n-IC ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ±2sd ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ±2sd ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ±2sd ^d	²⁰⁶ Pb/ ²⁰⁶ Pb ±2sd ^d	²⁰⁷ Pb/ ²⁰⁶ Pb ±2sd ^d	²⁰⁸ Pb/ ²⁰⁶ Pb ±2sd ^d	Sample size L ^e	Total Pb ng ^f	Meas. Pb (mean) ng ^g	Pb yield (%) ^h
Atlantic – S ±2sd relative (ppm) ^d ±2se typical run (ppm) ⁱ	6	24.7 ± 1.0	4.0	5	18.429 ± 12 630 ~300	15.639 ± 9 560 ~300	38.307 ± 25 650 ~300	0.84862 ± 98 1150 ~40	2.0787 ± 25 1220 ~50	2.0697 ± 12 580 ~50	~2	~11	3–6 (~4)	30–60
Atlantic – D1 ±2sd relative (ppm) ^d ±2se typical run (ppm) ⁱ	11	45.3 ± 0.5	1.1	7	18.499 ± 30 1610 ~350	15.625 ± 20 1280 ~350	38.287 ± 58 1520 ~350	0.84464 ± 50 590 ~100	2.0697 ± 10 550 ~90	2.0697 ± 10 550 ~90	1–2	10–20	3–10 (6)	30–50
Atlantic – D2 ±2sd relative (ppm) ^d ±2se typical run (ppm) ⁱ	2	47.4 ± 1.2	0.8	7	18.481 ± 30 1730 ~650	15.625 ± 22 1500 ~650	38.272 ± 59 1650 ~700	0.84540 ± 59 760 ~80	2.0707 ± 10 550 ~90	2.0707 ± 10 550 ~90	~2	~20	2–15 (7)	10–70
Weddell ±2sd relative (ppm) ^d ±2se typical run (ppm) ⁱ	8	7.6 ± 1.0	12.3	7	18.397 ± 48 2600 ~600	15.628 ± 20 1300 ~600	38.293 ± 70 1830 ~600	0.84945 ± 147 1730 ~60	2.0814 ± 20 980 ~90	2.0814 ± 20 980 ~90	~2	~3.8	~2.0	50–60

^a Number of individual sample aliquots analyzed for Pb concentrations.

^b Pb concentrations are corrected for a mean total blank of 11.7 ± 4.3 pg. The uncertainties of the concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction (see text).

^c Number of individual sample aliquots analyzed for Pb isotope compositions.

^d 2sd = 2 × standard deviation calculated from results of n separate runs; denotes long-term “external” reproducibility.

^e Volume of individual aliquots used for Pb isotope analyses.

^f Original mass of Pb in sample aliquots used for Pb isotope analyses.

^g Mass of Pb in individual aliquots used for isotopic analyses, following chemical separation; a mean value is given in parentheses.

^h Pb recovery for the chemical separation process.

ⁱ 2se = 2 × standard error of the mean; denotes within-run (“internal”) precision of a run, based on individual results for measurement cycles.

Table 4
Lead concentration (ID) and isotope composition (IC) data for the GEOTRACES intercalibration samples GSI and GDI and reference values from the literature.

Sample	<i>n</i> -ID ^a	[Pb] ± 1sd pmol/kg ^b	<i>n</i> -IC ^c	²⁰⁶ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁷ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁴ Pb ± 2sd ^d	²⁰⁷ Pb/ ²⁰⁶ Pb ± 2sd ^d	²⁰⁸ Pb/ ²⁰⁶ Pb ± 2sd ^d	Sample size I ^e	Total Pb ng ^f	Pb yield (%) ^g
GSI											
This study	6	27.9 ± 1.2	3	18.359 ± 26	15.635 ± 7	38.246 ± 30	0.85162 ± 93	2.0833 ± 16	~2	~10	45–60
±2sd relative (ppm) ^d				1430	480	790	1100	750			
±2se typical run (ppm) ⁱ				~160	~170	~180	~30	~40			
Ref. – MIT			5	18.41 ± 11	15.67 ± 9	38.33 ± 23	0.85143 ± 39	2.0821 ± 15	0.25 to –0.5	1.5–3	
±2sd relative (ppm) ^d				5870	5790	6020	460	700			
Ref. – UCSC			2 ^h	18.46 ± 0	15.68 ± 1	38.36 ± 7	0.84929 ± 50	2.0780 ± 40	~0.5	~3	
Ref. – Consensus		29.5 ± 2.1									
GDI											
This study	5	45.7 ± 2.6	2	18.475 ± 41	15.624 ± 10	38.276 ± 60	0.84568 ± 134	2.0718 ± 14	~2	~17	50–55
±2sd relative (ppm) ^d				2240	650	1570	1590	670			
±2se typical run (ppm) ⁱ				~190	~200	~210	~30	~60			
Ref. – MIT			4	18.74 ± 17	15.83 ± 12	38.79 ± 31	0.84493 ± 214	2.0696 ± 50	0.25 to –0.5	2.5–5	
±2sd relative (ppm) ^d				9320	7330	8000	2530	2410			
Ref. – UCSC			4	18.54 ± 3	15.69 ± 2	38.43 ± 10	0.84640 ± 42	2.0729 ± 27	~0.5	2.5–5	
Ref. – Consensus		42.2 ± 1.3									

The Pb isotope reference data (Ref.) are from the labs of Ed Boyle at the Massachusetts Institute of Technology (MIT) and Russ Flegel at the University of California Santa Cruz (UCSC) [35]. Results in italics were calculated from data given in the literature. The 'Consensus' Pb concentrations are from [53].

^a Number of individual sample aliquots analyzed for Pb concentrations.

^b Pb concentrations are corrected for a mean total blank of 11.7 ± 4.3 pg. The uncertainties of the concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction (see text).

^c Number of individual sample aliquots analyzed for Pb isotope compositions.

^d 2sd = 2 × standard deviation calculated from results of *n* separate runs; denotes long-term "external" reproducibility.

^e Volume of individual aliquots used for Pb isotope analyses.

^f Original mass of Pb in sample aliquots used for Pb isotope analyses.

^g Pb recovery for the chemical separation process.

ⁱ 2se = 2 × standard error of the mean; denotes within-run ("internal") precision of a run, based on individual results for measurement cycles.

^h Duplicate analyses of Pb separated from a single seawater sample.

Importantly, the isotope data of Fig. 1 demonstrate that incomplete recovery of Pb from the column separation is not associated with significant shifts in isotopic composition. These results do not, however, rule out small, but barely resolvable, enrichments of heavier Pb isotopes following chemical purification. This follows from the observations of previous studies, which detected only minor Pb isotope fractionations, comparable to or smaller than the reproducibility of our results, as a result of incomplete elution of the element from anion exchange columns (Fig. 1).

3.3. Analyses of NIST SRM 981 Pb

Multiple measurements of 2 ng ($n = 42$) and 10 ng ($n = 25$) loads of NIST SRM 981 Pb were carried out for a basic validation for our double spike techniques of Pb isotope analysis. Notably, the mean isotopic data acquired for both the 2 ng and 10 ng runs are in excellent agreement with recent reference values that were acquired using various Pb double or triple spikes in conjunction with analyses by either TIMS or MC-ICP-MS (Table 1).

The 2sd between-run ('external') precision of the 10 ng data is ~ 100 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and ~ 250 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (where $x = ^{206}\text{Pb}$, ^{207}Pb , ^{208}Pb hereafter). This is similar to or only slightly worse than the reproducibility achieved by other workers with TIMS or MC-ICP-MS for comparable or somewhat larger Pb samples (10–80 ng; Table 1). Our data for the 2 ng loads, a sample size that is more relevant for seawater analyses (Table 3), is less precise than the 10 ng results, with a reproducibility (± 2 sd external) of ~ 250 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and ~ 1000 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 3). The significantly larger uncertainty of the $^{20x}\text{Pb}/^{204}\text{Pb}$ data presumably reflects that the 2 ng Pb analyses were hampered by the measurement of ^{204}Pb at low ion beam intensities (about 5–20 mV) using a Faraday cup and standard $10^{11} \Omega$ amplifiers. The within-run ('internal') precision (quantified by 2se; standard error of the mean) of both the 2 and 10 ng Pb measurements are about a factor of 2–3 better compared to the between-run uncertainties for all Pb isotope ratios (Table 1).

3.4. Analyses of in-house seawater reference samples

Multiple Pb concentration and isotope ratio analyses were carried out on four different in-house seawater reference samples (Table 3). These were available in sufficient quantity such that 5–7 repeat isotopic analyses could be carried out to rigorously investigate the reproducibility of the methods.

For the Pb contents, the precision (expressed as ± 1 sd, as is common for concentration data) varies between less than $\pm 1\%$ to about $\pm 12\%$ (Table 3). Notably, the reproducibility is worse for samples with low Pb contents. As similar samples sizes (of only ~ 50 mL) were employed for these measurements, the higher uncertainties for the Pb-depleted samples are most likely related to inaccuracies of the Pb blank correction, possibly due to spurious high blanks.

The isotopic results for the in-house seawater reference samples (Table 3) were acquired on individual aliquots of 1–2 L, from which about 2–10 ng of Pb were separated. The data display a ± 2 sd reproducibility of ~ 500 – 1500 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and ~ 500 – 2000 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 3). Clearly, this is inferior to the 2sd precision that was obtained for the comparable 2 ng and 10 ng loads of pure NIST SRM 981 Pb (Table 1). At the same time, the internal (within-run) ± 2 se precision of the seawater measurements is similar to the NIST SRM 981 results, with uncertainties of ~ 40 – 100 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and ~ 300 – 700 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 3). Given this discrepancy, it is most likely that the external 2sd reproducibility of the seawater Pb isotope data is limited by contamination of the

samples by blanks of both variable magnitude and isotope composition. This interpretation is supported by two observations. First, the Weddell seawater, which has the lowest Pb concentration and thus the smallest Pb sample sizes, generally features the largest 2sd uncertainties (Table 3). Second, the application of a blank correction did not improve the 2sd reproducibilities for any of the samples, regardless of whether the corrections used mean blank values or only blank data that were linked to a specific batch of samples. In addition, it is also conceivable that the between-run 2sd uncertainties of the samples (Table 3) are, at least in part, limited by minor isotope fractionations that occur during the column chemistry (Fig. 1).

3.5. GEOTRACES intercalibration samples GSI and GDI

Multiple Pb isotope and concentration measurements were also carried out for the two GEOTRACES intercomparison samples GSI and GDI (Table 4). For the Pb concentrations, GEOTRACES 'consensus values' were recently published, which are based on analyses of more than 10 independent laboratories [53]. The mean Pb concentrations determined for the samples in this study from analyses of five or six separate aliquots have ± 1 sd (external) reproducibilities that are similar to those obtained for the in-house seawater reference samples (Table 3), at about ± 4 to $\pm 6\%$ (Table 4). The results are, furthermore, identical to the reference values within the quoted uncertainties (Table 4).

The Pb isotope data for GSI and GDI were obtained on 2–3 sample aliquots of 2 L each, with originally about 10–15 ng Pb (Table 4). Following chemical separation, about 5–10 ng Pb were available for isotopic analysis. As for the seawater results of Table 3, the GSI and GDI measurements achieved (within-run) 2se repeatabilities that are similar to those obtained for similar loads of pure SRM 981 Pb, at 30–60 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and 150–200 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 4). In contrast, the external 2sd uncertainties, of ~ 650 – 1500 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and ~ 500 – 2200 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$, are typically significantly larger (Table 4). Again, this is most likely due to small Pb blank contributions of variable magnitude and isotope compositions and, potentially, minor isotope fractionation during Pb purification. Despite of this, our results for the two samples compare favorably and are generally in agreement with the published reference results.

The reference Pb isotope data for the GEOTRACES samples were obtained at MIT (Massachusetts Institute of Technology) using MC-ICP-MS and at UCSC (University of California at Santa Cruz) by HR-ICP-MS [35]. These analyses did not apply a Pb double spike and were carried out using significantly smaller samples sizes (of about 0.25–0.5 L) compared to those utilized here.

For GSI, all Pb isotope ratios determined are identical to the MIT results within the 2sd uncertainties. There is also good agreement with the UCSC results for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ but the UCSC data are higher for $^{20x}\text{Pb}/^{204}\text{Pb}$ (Table 4). The uncertainties of the UCSC data are only poorly characterized, however, as they are based on only two analyses of a single seawater aliquot. Our new isotopic data for GDI are in excellent agreement with the MIT and UCSC results for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and in reasonable agreement, just within uncertainty, with the UCSC $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Table 4). Hence, there are small but significant discrepancies for the remaining $^{20x}\text{Pb}/^{204}\text{Pb}$ data with the reference values, whereby our ratios are slightly lower. There is, however, also only marginal agreement between the MIT and UCSC results for these Pb isotope ratios, which are difficult to determine due to the low natural abundance of ^{204}Pb . This indicates that further analyses are needed to establish more reliable reference data for the $^{20x}\text{Pb}/^{204}\text{Pb}$ ratios of the GEOTRACES intercalibration samples.

The particular difficulty of ^{204}Pb measurements is also apparent in a comparison of the reproducibilities for the Pb isotope data obtained here and previously [35]. For the $^{20x}\text{Pb}/^{204}\text{Pb}$ ratios, the multiple MIT analyses reveal a $\pm 2\text{sd}$ uncertainty of ~ 5000 – $10,000$ ppm, whilst our data for GSI, GDI (Table 4) and the in-house test samples (Table 3) have uncertainties which are at least a factor of 5 better, at ~ 500 – 2000 ppm. For $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ the difference is less apparent, however, as the reproducibility of the MIT results varies between 500 and 2500 ppm, whilst the data of this study (Tables 3 and 4) typically have an uncertainty of about 500–1500 ppm.

3.6. Depth profile for Pb isotopes and concentrations in the eastern South Atlantic Ocean

Twelve seawater samples from a depth profile in the eastern part of the GEOTRACES GA10 section in the South Atlantic Ocean were analyzed (Fig. 2a and Table 5), to (i) demonstrate that our new methodology is suitable for routine acquisition of high precision seawater Pb isotope data and (ii) highlight the important insights, which can be gained from such results.

Lead concentrations are highest in the uppermost part of the water column with a surface (~ 3 m water depth) concentration of 17.7 pmol/kg, increasing to a relative maximum of 25.2 pmol/kg at 49 m and decreasing again to 22.4 pmol/kg at 397 m depth. From 400 m downwards, the Pb concentrations decrease, until they reach relatively constant and low values of 5 – 10 pmol/kg below 2000 m (Fig. 2a). A comparison with the dissolved Pb concentrations for a depth profile collected at the exact same location during the second expedition along the South Atlantic GA10 transect (cruise JC068; same station; Schlosser et al., pers. comm.) demonstrates excellent agreement for the entire water column. In contrast, data reported from IPY cruise MD166 (Boye et al. [36]) for the same location show significant deviations from our results, as the dissolved Pb concentrations are elevated by up to a factor of 2 and they define a pattern which is less smooth with depth.

Overall, our Pb concentrations for seawater from the southeast Atlantic Ocean, sampled in 2010, are significantly lower than the values of 29.5 pmol/kg and 42.2 pmol/kg that were reported for 2008 samples from the surface and 2000 m depth at the BATS station in the northwest Atlantic Ocean (Table 4). Lead concentrations in seawater have been strongly affected by anthropogenic Pb emissions over the past century. Such emissions were generally higher in the northern Hemisphere compared to southern regions but peaked in the 1970s. Since then, they have decreased by almost

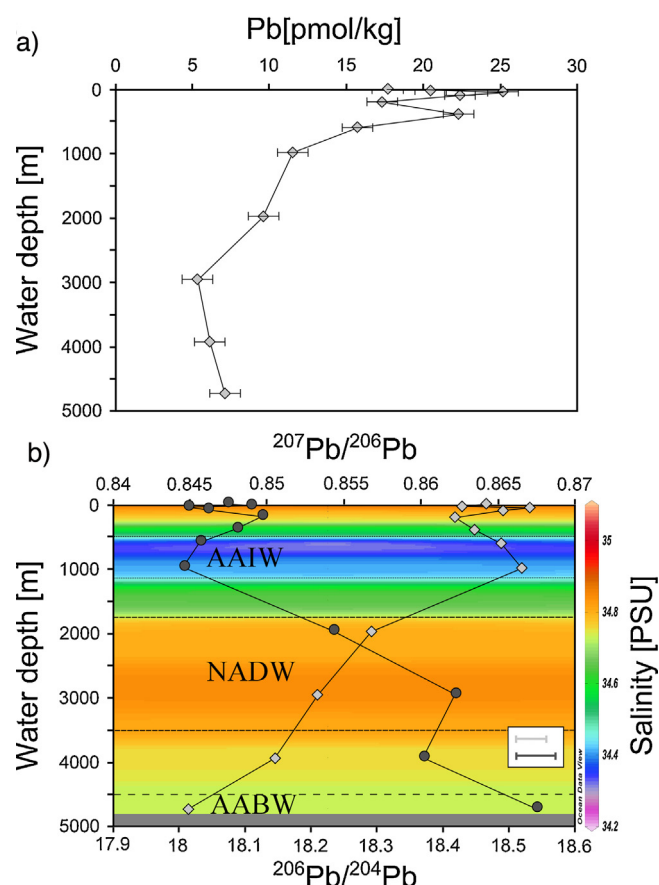


Fig. 2. Lead data for the seawater depth profile collected at station 3 (36.46°S , 13.39°E) of the GEOTRACES GA10 cruise. (A) Vertical distribution of Pb concentrations, with uncertainties as reported in Table 4 and (B) vertical distribution of $^{207}\text{Pb}/^{206}\text{Pb}$ (grey diamonds) and $^{206}\text{Pb}/^{204}\text{Pb}$ (dark grey dots) ratios, with uncertainties as reported in Table 4. The background colors from Ocean Data View [59] display the salinity of the water column during the time of sample collection [37].

a factor of 10 due to the phasing out of leaded gasoline, first in the US and then in Europe (e.g., Kelly et al. [16]). Consequently, northwest Atlantic surface waters now contain less anthropogenic Pb (and exhibit a different isotopic composition) than deeper North Atlantic waters, which were contaminated in the past [13,19]. A

Table 5

Lead isotope and concentration data for a seawater profile from the southeastern Atlantic Ocean (D357 station 3, GEOTRACES transect GA10; latitude: 36.46°S , longitude: 13.39°E ; sampled in October 2010).

Sample	Depth (m)	[Pb] pmol/kg ^a	$\pm 1\text{sd}^b$	$^{206}\text{Pb}/^{204}\text{Pb}^c$	$^{207}\text{Pb}/^{204}\text{Pb}^c$	$^{208}\text{Pb}/^{204}\text{Pb}^c$	$^{207}\text{Pb}/^{206}\text{Pb}^c$	$^{208}\text{Pb}/^{206}\text{Pb}^c$
Fish 113	2–3	17.7	0.9	18.073	15.620	38.030	0.86428	2.1040
183	25	20.5	0.4	18.111	15.624	38.017	0.86266	2.0991
180	49	25.2	0.5	18.013	15.618	37.922	0.86707	2.1053
177	99	22.4	0.8	18.044	15.614	37.941	0.86533	2.1027
174	198	17.3	0.6	18.125	15.627	38.015	0.86221	2.0975
171	397	22.3	0.6	18.087	15.618	37.970	0.86350	2.0993
170	594	15.7	0.5	18.031	15.600	37.885	0.86518	2.1011
169	989	11.5	0.5	18.007	15.604	37.911	0.86655	2.1052
167	1975	9.6	0.4	18.234	15.623	38.159	0.85677	2.0927
166	2955	5.3	0.4	18.418	15.717	38.452	0.85331	2.0879
164	3931	6.1	0.4	18.370	15.625	38.266	0.85050	2.0830
163	4724	7.1	0.4	18.540	15.664	38.537	0.84492	2.0785

^a Pb concentrations are corrected for a mean total blank of 11.7 ± 4.3 pg.

^b The uncertainties of the concentration data propagate both the (within-run) precision of the isotopic analyses and the uncertainty of the blank correction (see text).

^c For the Pb isotopes, assumed external 2sd reproducibilities of ± 1250 ppm for $^{20x}\text{Pb}/^{204}\text{Pb}$ and of ± 800 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ are larger than the $\pm 2\text{se}$ internal uncertainties in all cases. Based on this, appropriate 2sd uncertainties are ± 0.023 for $^{206}\text{Pb}/^{204}\text{Pb}$, ± 0.020 for $^{207}\text{Pb}/^{204}\text{Pb}$, ± 0.047 to 0.048 for $^{208}\text{Pb}/^{204}\text{Pb}$, ± 0.00068 to 0.00069 for $^{207}\text{Pb}/^{206}\text{Pb}$ and ± 0.0017 for $^{208}\text{Pb}/^{206}\text{Pb}$.

comparison of our (sub-) surface Pb concentrations (18–25 pmol/L) with data for eastern South Atlantic surface waters sampled in 1990 (with [Pb] = 11–29 pmol/kg at 21–32°S and 7–13°E; [47]) reveals similar results. This implies that there was no major change in the Pb supply to the southeast Atlantic Ocean between 1990 and 2010.

The $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios for our seawater profile from the South Atlantic exhibit the highest values in the subsurface and at mid depth (0.867 at 49 m and 989 m water depth) and slightly lower values at the surface and at 198 m ($^{207}\text{Pb}/^{206}\text{Pb} \approx 0.862$ –0.863; Fig. 2b). Below ~1000 m water depth, $^{207}\text{Pb}/^{206}\text{Pb}$ decreases all the way to the bottom of the profile ($^{207}\text{Pb}/^{206}\text{Pb} = 0.845$ at 4723 m water depth). These trends in $^{207}\text{Pb}/^{206}\text{Pb}$ are mirrored by the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, which are lowest at the subsurface ($^{206}\text{Pb}/^{204}\text{Pb} = 18.01$; 49 m) and at intermediate depth ($^{206}\text{Pb}/^{204}\text{Pb} = 18.01$; 989 m), and increase to $^{206}\text{Pb}/^{204}\text{Pb} = 18.54$ at the bottom of the profile (Fig. 2b). The correlation between the seawater $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios ($r^2 = 0.97$) observed here is significantly improved compared to the results of previous studies [13,19,20,23,54]. We assign this improvement to the accurate and precise determination of the minor isotope ^{204}Pb (and hence $^{208}\text{Pb}/^{204}\text{Pb}$ ratios) with our new methodology, and surmise that previous claims of poor correlations may be due to analytical artifacts and should hence be assessed with care.

The major deep and intermediate water masses encountered at station 3 in the eastern South Atlantic are indicated by the salinity contouring in Fig. 2b. In brief, most of the water column is dominated by water masses sourced from high southern latitudes – cold and dense Antarctic bottom water (AABW) at >4500 m depth, and fresh Antarctic intermediate water (AAIW) at ~500–1100 m – whilst saline, nutrient-poor North Atlantic Deep Water (NADW) is present at ~1700–3500 m depth (see Wyatt et al. [37] for further details on the transect hydrography). Since we are presenting the first Pb isotope depth profile for the eastern South Atlantic, there are no data available for direct comparison. However, our results confirm previously suggested differences [23] in the Pb isotope fingerprints of two main Southern Ocean water masses, AAIW ($^{207}\text{Pb}/^{206}\text{Pb} = 0.865$ –0.867, $^{206}\text{Pb}/^{204}\text{Pb} = 18.01$ –18.03; $n = 2$) and AABW ($^{207}\text{Pb}/^{206}\text{Pb} = 0.845$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.54$; $n = 1$). These isotopic differences are a consequence of different water mass formation mechanisms and regions (e.g., Orsi et al. [55]), and hence different proportions of anthropogenic versus natural Pb. prior to ventilation into the deeper ocean. The Pb isotopic composition of NADW in the southeast Atlantic Ocean ($^{207}\text{Pb}/^{206}\text{Pb} = 0.853$ –0.857, $^{206}\text{Pb}/^{204}\text{Pb} = 18.42$ –18.23 at ~2000–3000 m water depth; $n = 2$) appears distinct from NADW in the northwestern North Atlantic (BATS Station at 2000 m; Table 4), and values previously reported for the equatorial western Atlantic Ocean [23]. This points to older ventilation ages in the eastern basins of the Atlantic Ocean compared to the western basins (e.g., England [56]). Further interpretation of the results will, however, have to await the acquisition of Pb isotope and concentration data for additional profiles from the GEOTRACES GA10 transect.

4. Conclusions

A new analytical procedure has been developed for Pb isotope analysis of seawater and associated Pb concentration measurements by isotope dilution. This involves Mg hydroxide co-precipitation and anion exchange chromatography for Pb pre-concentration and isotopic analysis by TIMS in conjunction with a ^{207}Pb – ^{204}Pb double spike. Analyses of multiple aliquots of six seawater samples demonstrate typical reproducibilities ($\pm 2\text{sd}$) of about 700–1500 ppm and 1000–2000 ppm for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. With this

precision, the new data are superior to literature results that were obtained by plasma source mass spectrometry. In particular, they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. Analyses of two GEOTRACES intercalibration samples from the Atlantic Ocean (GDI and GSI) display good agreement with recent results of two other laboratories.

Our methods were applied to samples from a seawater depth profile from the eastern South Atlantic Ocean at ~40°S. For these samples, both Pb concentrations and isotope compositions show a smooth pattern with depth and no obvious outliers. Furthermore, $^{206}\text{Pb}/^{204}\text{Pb}$ shows a clear correlation with $^{207}\text{Pb}/^{206}\text{Pb}$, underlining the improvement that was achieved for the challenging Pb isotope analyses, particularly of $^{206}\text{Pb}/^{204}\text{Pb}$. The depth profile results permit the identification and characterization of several key water masses, including AAIW, AABW and NADW. Considering that our profile is not located far from the formation regions of AAIW and AABW, the data provide the most precise Pb isotope characterization of these water masses published to date, but substantiation of the results by analyses of additional seawater samples from this region is needed.

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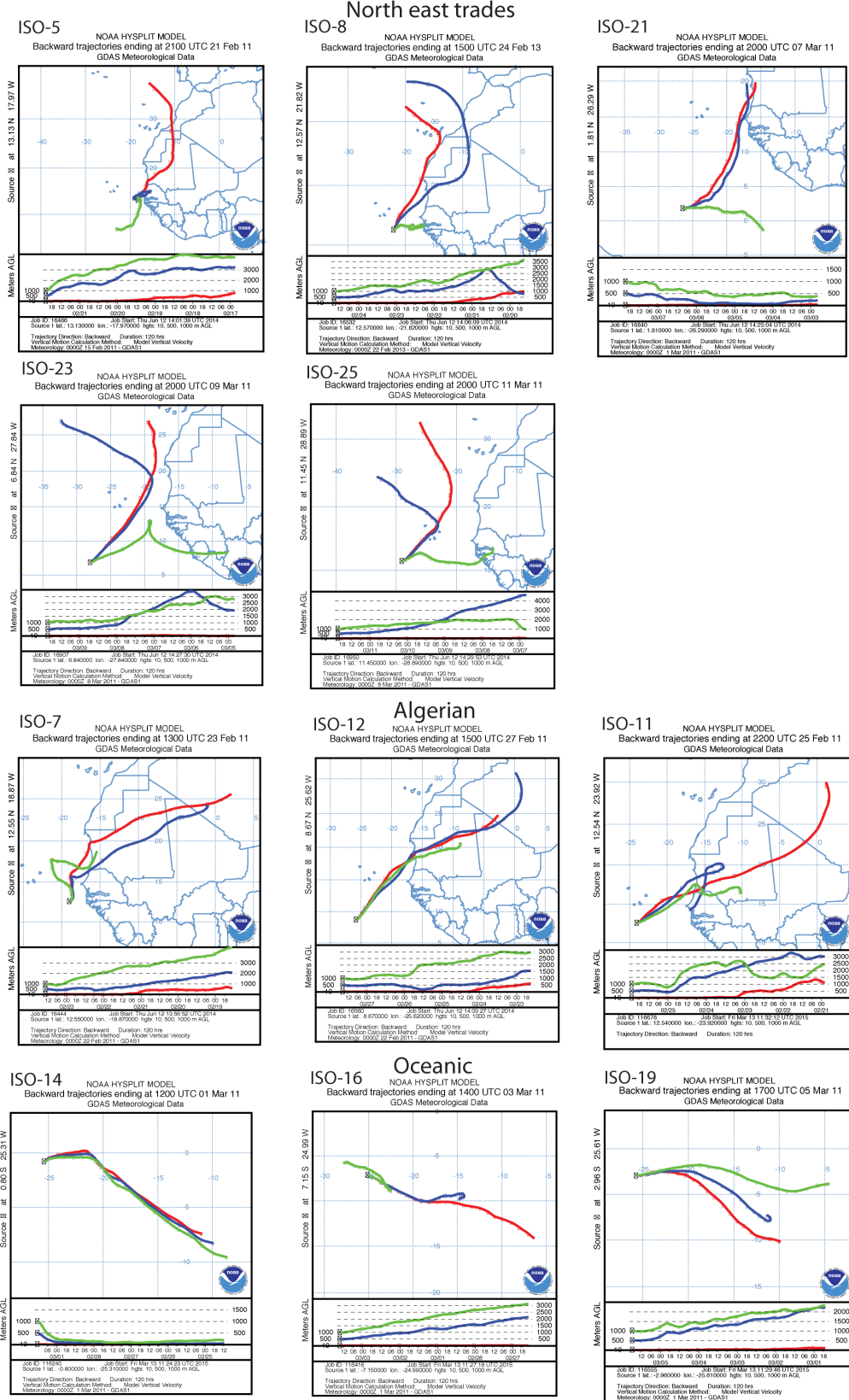
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Appendix 2: Aerosol sample metadata and air mass back trajectories

Sample ^a	Starting Latitude (°N) ^b	Ending Latitude (°N) ^b	Starting Longitude (°W) ^b	Ending Longitude (°W) ^b	Start date/time ^c	End date/time ^c	Volume of air sampled (m ³) ^d	Proportion of exposed filter area (%) ^e
ISO-5 _{Total}	13.13	12.55	17.97	18.84	21/02/2011	23/02/2011	1981.9	12.5
ISO-5 _{Leach}					21:24	11:38		37.5
ISO-7 _{Total}	12.55	12.57	18.87	21.82	23/02/2011	24/02/2011	1462.2	50
ISO-7 _{Leach}					13:10	13:29		50
ISO-8 _{Total}	12.57	12.57	21.82	23.76	24/02/2011	25/02/2011	1813.8	50
ISO-8 _{Leach}					14:49	20:57		50
ISO-11 _{Total}	12.54	9.46	23.92	25.66	25/02/2011	27/02/2011	1006.2	50
ISO-11 _{Leach}					22:00	10:28		50
ISO-12 _{Total}	8.67	1.02	25.62	25.33	27/02/2011	01/03/2011	1315.2	37.5
ISO-12 _{Leach}					14:59	10:17		50
ISO-14 _{Total}	-0.80	-7.00	25.31	25.00	01/03/2011	03/03/2011	3000.6	50
ISO-14 _{Leach}					11:41	13:15		50
ISO-16 _{Total}	-7.15	-3.25	24.99	25.54	03/03/2011	05/03/2011	2698.2	25
ISO-16 _{Leach}					14:17	11:10		25
ISO-19 _{Total}	-2.96	1.68	25.61	26.25	05/03/2011	07/03/2011	2219.4	25
ISO-19 _{Leach}					17:16	19:15		50
ISO-21 _{Total}	1.81	6.74	26.29	27.80	07/03/2011	09/03/2011	2855.4	50
ISO-21 _{Leach}					20:05	19:24		50
ISO-23 _{Total}	6.84	11.31	27.84	28.86	09/03/2011	11/03/2011	2845.8	50
ISO-23 _{Leach}					20:05	19:18		50
ISO-25 _{Total}	11.45	17.42	28.98	28.38	11/03/2011	14/03/2011	3798.6	50
ISO-25 _{Leach}					20:07	11:05		50

^a Name of sample, subscripts “Total” and “Leach” denote subsamples subjected the total digestion and leaching procedures respectively (Chapter 3). ^b Latitude and longitude of start and end of each aerosol sample collection. ^c Date (day/month/year) and time (hour:minute) of the start and end of each aerosol collection. ^d Volume of air sampled during each aerosol collection period. ^e The proportion of the total exposed filter area taken for the total digestion and leachate subsamples.

Figure A2.1: Air mass back trajectories were calculated for the 5 days preceding the start of each aerosol collection using the NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory Model, (HYSPLIT, GDAS data set) (Draxler & Rolph, 2003). Arrival heights of 10, 500 and 1000 m were used along with model vertical velocity for calculation of vertical motion.



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Appendix 3: Aerosol ion exchange chromatography procedure and SRM results

Aliquots from the aerosol total digestion and leachate solutions were processed twice through an ion exchange chromatography procedure, adapted from Chapter 2, in order to purify Pb prior to isotopic analysis (Table A3.1). The adaptations, involved (1) the absence of HF (0.01 M) from the loading solution and (2) a second iteration of the procedure (which utilizes 100 μ l of anion exchange resin (AG1 X8 100 – 200 mesh) as opposed to a second stage which utilizes 20 μ l of anion exchange resin. The former was implemented as low concentrations of HF, which were necessary to prevent precipitation of silica from seawater during the procedure (Chapter 2), were not required for the aerosol samples. The latter, as the use of 20 μ l of anion exchange resin was found to reduce the yield from 90 – 100 %, to 50 – 60 %, when compared to use of 100 μ l of anion exchange resin. The increase in reagent volumes as a result of this adaptation was not associated with a significant rise in the Pb blank of the procedure (14 ± 13 pg, mean $\pm$ 2SD, $n = 7$), which was considered negligible relative to the quantity of Pb processed in the samples (3 – 100 ng).

The accuracy and precision of the ion exchange chromatography procedure and the mass spectrometric analyses were assessed by replicate analyses of the SRM's BCR-2 and BHVO-2. Powdered aliquots of 0.04 – 0.2 g of these SRM's were digested in 3:1 solutions of 28 M HF and 15.6 M HNO₃ (total volume of 6 – 8 ml), at 140 °C for 4 days with regular treatments in an ultrasonic bath. The digested solutions were then evaporated to dryness, re-dissolved in 2 M HNO₃, prior to being separated into aliquots corresponding to $\sim$ 20 ng of Pb. These aliquots were then evaporated to dryness, re-dissolved in 3 ml 2 M HBr and processed through the ion exchange chromatography procedure prior to Pb isotope analysis (Chapter 2). The results are in good agreement with values from the literature and demonstrate reproducibilities comparable to equivalent loads on SRM NIST 981 (Table A3.2). We take the reproducibility of the Pb isotope ratios from replicate analyses of the BCR-2 aliquots, featuring the larger data set ($n = 9$), to be representative of the uncertainty generated during chemical separation and mass spectrometric analysis of the samples.

Table A3.1. Details of ion exchange chromatography procedure for the separation of Pb from the aerosol total digests and leachates

Resin	100 µl AG1 X8 100 – 200 mesh
Clean resin	3 x 3 ml 0.1 M HNO ₃
Equilibrate resin	2 x 0.1 ml 2 M HBr
Load sample	in 3 ml 2 M HBr
Elute matrix	2 x 0.1 ml 2 M HBr
	2 x 0.5 ml 0.5 M HNO ₃ – 0.2 M HBr
	0.2 ml 0.5 M HNO ₃ – 0.03 M HBr
Elute Pb	3 ml 0.5 M HNO ₃ – 0.03 M HBr

Table A3.2. Results of analyses of SRM's

Sample ID	n ^a	²⁰⁶ Pb/ ²⁰⁴ Pb ^b	²⁰⁶ Pb/ ²⁰⁷ Pb ^b	²⁰⁶ Pb/ ²⁰⁸ Pb ^b
10 ng NIST 981	9	16.9411 ± 19	1.0931 ± 01	2.3695 ± 01
relative 2sd (ppm) ^c		109	56	51
typical within run 2se (ppm) ^d		70	15	15
20 ng NIST 981	6	16.9418 ± 23	1.0931 ± 01	2.3695 ± 02
relative 2sd (ppm) ^c		133	49	82
typical within run 2se (ppm) ^d		40	15	15
Literature				
Galer & Abouchami, 1998 (TIMS)		16.9405	1.0932	2.3697
Thirlwall, 2000 (TIMS)		16.9409	1.0933	2.3699
Todt et al., 1996 (TIMS)		16.9356	1.0934	2.3694
Thirlwall, 2002 (MC-ICP-MS)		16.9417	1.0930	2.3694
Baker et al., 2004 (MC-ICP-MS)		16.9416	1.0930	2.3694
20 ng BCR-2	9	18.7603 ± 85	1.2006 ± 01	2.4692 ± 03
relative 2sd (ppm) ^c		453	105	131
typical within run 2se (ppm)		90	20	16
Literature				
Baker et al., 2004 (MC-ICP-MS)		18.7650	1.2011	2.4804
Woodhead & Hergt, 2000 (TIMS)		18.7500	1.2008	2.4786
Collerson et al 2002 (MC-ICP-MS)		18.7570	1.2005	2.4784
Weis et al., 2006 (TIMS & MC-ICP-MS)		18.7529	1.2002	2.4783
20 ng BHVO-2	4	18.6398 ± 63	1.1998 ± 02	2.4612 ± 03
relative 2sd (ppm) ^c		336	127	121
typical within run 2se (ppm) ^d		100	25	25
Literature				
Baker et al., 2004 (MC-ICP-MS)		18.6490	1.1997	2.4605
Woodhead & Hergt, 2000 (TIMS)		18.6410	1.1997	2.4603
Collerson et al 2002 (MC-ICP-MS)		18.6790	1.2003	2.4602
Weis et al., 2006 (TIMS & MC-ICP-MS)		18.6474	1.2005	2.4616

^aNumber of replicate analyses conducted. ^bMean and absolute uncertainty (2sd) of the replicate analyses. ^cRelative uncertainty (2sd) of the replicate analyses. ^dTypical relative internal precision (2se) of a single analysis.

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Appendix 4: The Pb isotope systematics of seawater and aerosol data presented in Chapters 3 and 4

Studies tracing the environmental sources of Pb have typically focused on the relative abundances of ^{206}Pb , ^{207}Pb and ^{208}Pb , whilst neglecting the use of ^{204}Pb (e.g. Weiss et al., 2003). This is largely due to analytical difficulties in the precise determination of Pb isotope ratios featuring ^{204}Pb , which has a low relative abundance of about 1 % (Komárek et al., 2008). Hence, source appointment is typically conducted using only two of three potential independently varying isotope ratios. Our new method allows the determination of Pb isotope ratios featuring ^{204}Pb in seawater at an unprecedented level of precision (Chapter 2). Here we assess the utility of different Pb isotope ratios for source appointment by comparing the variance observed for various Pb isotope ratios for the seawater and aerosol data sets presented in Chapters 3 and 4, relative to analytical uncertainty. This assessment is used to choose which Pb isotope ratios are best presented for optimal source appointment in the thesis.

Included in this assessment are the Pb isotope ratios; $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. The typical reproducibilities ($\pm 2\text{sd}$) of replicate analyses six seawater samples of about 150 – 1700 ppm for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ and 1000 – 2000 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, are taken as analytical uncertainty for the seawater samples (Chapter 2), whilst details of the assessment of the analytical uncertainty of the aerosol samples are given in Chapter 3. The data for seawater and aerosol samples presented in Chapters 3 and 4 show strong correlations in plots of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, with no deviations from these correlations exceeding analytical uncertainty (Fig. A4.1, Fig. A4.3). In contrast, although still correlated, these data display independent variability, exceeding analytical uncertainty in plots of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ (Fig. A4.2, Fig. A4.4), thus providing the greatest information on source apportionment. Furthermore, the variance in the data sets is best resolved outside of analytical uncertainty by the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios, hence these ratios are chosen for presentation in the thesis.

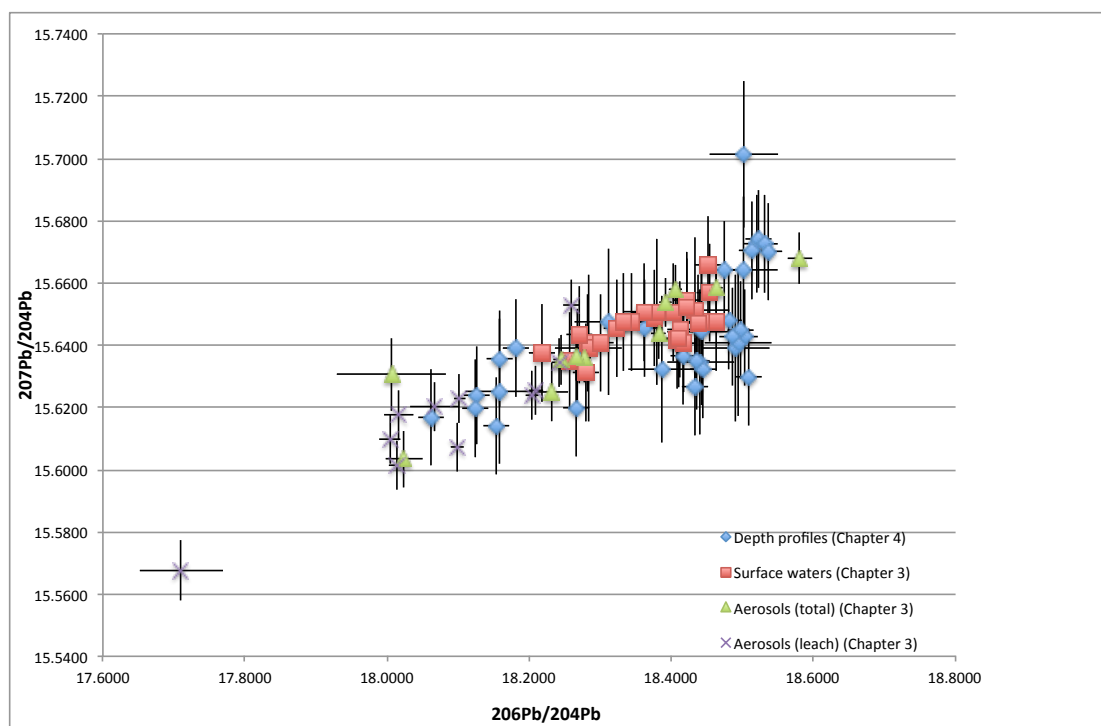


Figure A4.1. $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the depth profile seawater samples presented in Chapter 4, as well as the surface seawater samples, aerosol total digests and aerosol leachate samples presented in Chapter 3.

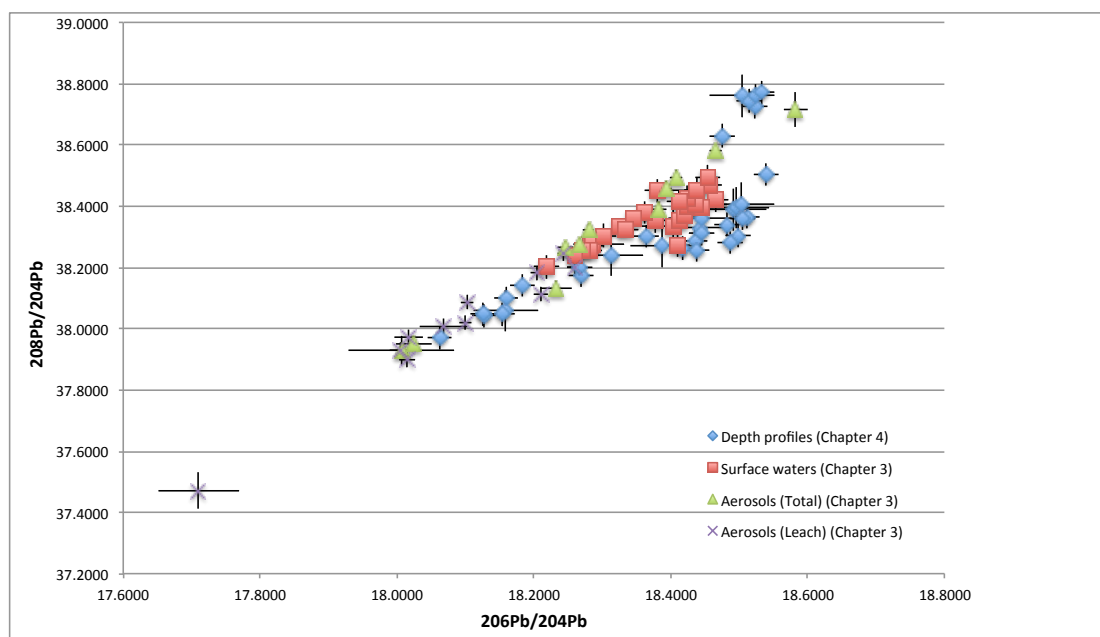


Figure A4.2. $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the depth profile seawater samples presented in Chapter 4, as well as the surface seawater samples, aerosol total digests and aerosol leachate samples presented in Chapter 3.

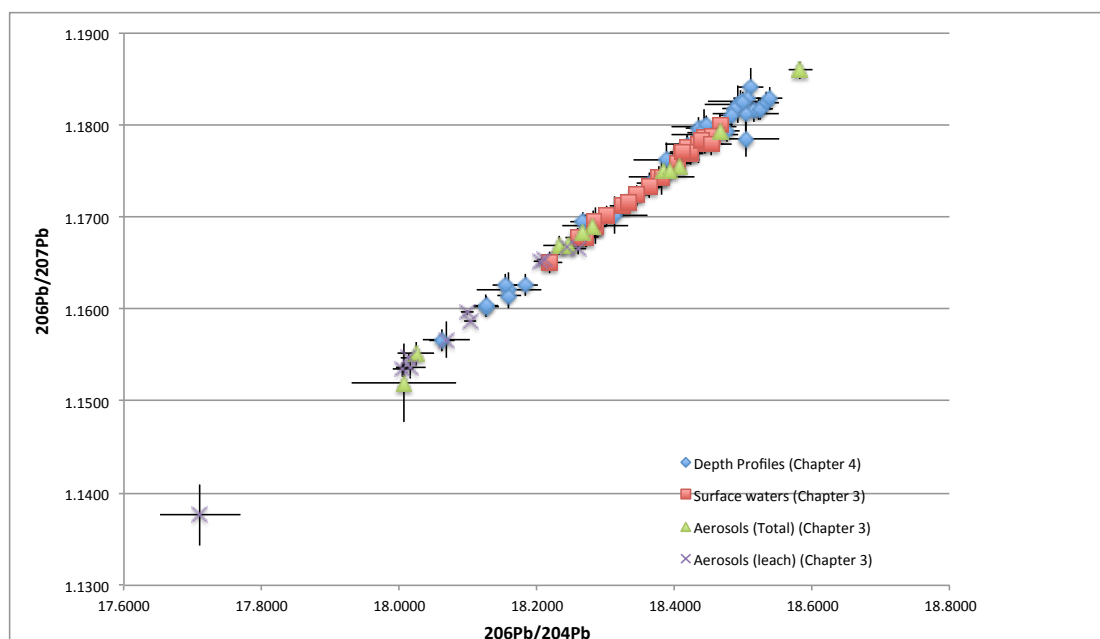


Figure A4.3. $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the depth profile seawater samples presented in Chapter 4, as well as the surface seawater samples, aerosol total digests and aerosol leachate samples presented in Chapter 3.

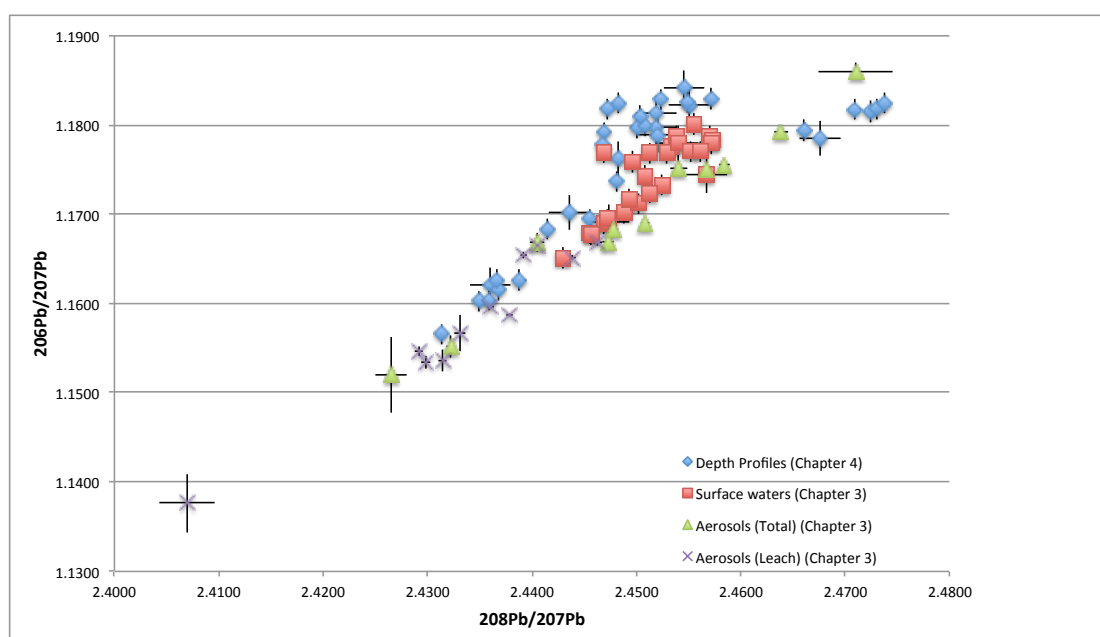


Figure A4.4. $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ for the depth profile seawater samples presented in Chapter 4, as well as the surface seawater samples, aerosol total digests and aerosol leachate samples presented in Chapter 3.

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Appendix 5: Assessment of the isotope compositions of potential Pb sources to the Tropical Atlantic

Here we provide (1) details of the literature data selected to assess the Pb isotope compositions of the 3 endmembers used to interpret the sources of Pb to ocean surface waters (Chapter 3, section 3.5.1.1) and (2) details of the mass balance estimates of the maximum relative proportions of Pb_{min} in ocean surface waters (Chapter 3, section 3.5.1.2).

A5.1 Literature compilation of the isotope composition of potential Pb sources to the tropical Atlantic

The selection criteria for literature data used to assess the isotope composition of anthropogenic Pb transported by the northeast trade winds (endmember (1)) were (1) aerosols collected either within the northeast trade winds (as assessed by air mass back trajectories) in the tropical North Atlantic (Witt et al., 2006) or collected within North Africa (Bollhofer & Rosman, 2001, Kumar et al., 2014), (2) that feature information on at least the isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb , and (3) that were produced from dilute acid leaching procedures (typically dilute HBr), rather than from total digestions (featuring concentrated HF) (Table A5.1). The latter was to ensure that the Pb isotope compositions reflected those of anthropogenic emissions, unaffected by mineral dust contributions. The selected data were from aerosols collected during the mid 1900's and 2000's. Recent data is preferable as the isotope composition of anthropogenic Pb emissions from particular regions can change over decadal time scales, due to changes in the market share of Pb ores use to supply anthropogenic activities and/or changes in anthropogenic activities (e.g. Hurst et al., 2002). It is reassuring to note that the compiled data span a similar range to our leachate samples, indicating lack of temporal variability between the collection of the different sample sets.

For the assessment of the isotope composition of anthropogenic Pb transported by the Westerlies (endmember (2)), we use the comprehensive the data set of Bollhofer & Rosman (2001) for aerosols collected in the eastern US and Central America in the 1990's. In accord with the previously stated selection criteria, these data were produced from dilute HBr leachates (Table A5.2).

For endmember (3) the Pb isotope composition of the Amazon outflow has been assessed through Pb isotope composition data for suspended particles collected within the Amazon River system, in lieu the availability of data for dissolved Pb

(Asmerom & Jacobsen, 1993, Allègre et al., 1996) (Table A5.3). The Pb isotope composition of North African mineral dust has been assessed through (1) data for pre-anthropogenic (Pleistocene) marine sediments in the eastern tropical North Atlantic (Chow & Patterson, 1962, Abouchami & Zabel, 2003) and (2) data for dust collected within the Bodélé depression (located in Chad) (Abouchami et al 2013) (Table A5.4). The former are interpreted to represent accumulations of North African mineral dust on the ocean floor whilst the latter represent dust samples from the most important mineral dust source area in North Africa (and the world) (Goudie & Middleton, 2001). It is reassuring to note the isotopic similarity of the two data sets. A single outlier from the data set of Abouchami & Zabel (2003) was omitted from the compilation.

Table A5.1; Compiled literature data used to assess the isotope composition of anthropogenic Pb transported by the northeast trade winds

Location	Year	Leaching protocols	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	Reference
Tunisia	1995	0.4 HBr (1 hr)	1.1430	2.4200	Bollhofer & Rosman, 2001
Morocco	1997	0.4 HBr (1 hr)	1.1410	2.4180	Bollhofer & Rosman, 2001
Egypt	1995	0.4 HBr (1 hr)	1.1530	2.4310	Bollhofer & Rosman, 2001
Senegal	1995	0.4 HBr (1 hr)	1.1010	2.3750	Bollhofer & Rosman, 2001
Mali	2008	0.5 HBr (15 mins)	1.1536*	2.4349*	Kumar et al., 2014
Mali	2008	0.5 HBr (15 mins)	1.1698*	2.4530*	Kumar et al., 2014
Mali	2008	0.5 HBr (15 mins)	1.1590*	2.4418*	Kumar et al., 2014
Mali	2008	0.5 HBr (15 mins)	1.1596*	2.4408*	Kumar et al., 2014
Cape Verde	2008	0.5 HBr (15 mins)	1.1235*	2.4056*	Kumar et al., 2014
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1450	2.4180	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1600	2.4350	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1650	2.4240	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1560	2.4300	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1540	2.4300	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1660	2.4540	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1630	2.4380	Witt et al., 2006
Tropical Atlantic	2001	0.1 M HNO ₃ (24 hr)	1.1490	2.4230	Witt et al., 2006
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1668	2.4462	This study (ISO-5 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1587	2.4378	This study (ISO-7 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1536	2.4314	This study (ISO-8 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1567	2.4331	This study (ISO-11 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1597	2.4360	This study (ISO-12 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1652	2.4438	This study (ISO-21 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1547	2.4292	This study (ISO-23 _{leach})
Tropical Atlantic	2011	AA (pH 4.7) (1 hr)	1.1534	2.4298	This study (ISO-25 _{leach})

AA - ammonium acetate. * Pb isotope ratios quoted in the table ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) were calculated from $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios quoted in the publication.

Table A5.2; Compiled literature data used to assess the isotope composition of anthropogenic Pb transported by the Westerlies

Location	Year	Leaching protocols	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	Reference
Argonne (US)	1995	0.4 M HBr (1 hr)	1.2110	2.4570	Bollhofer & Rosman, 2001
Wilmington (US)	1995	0.4 M HBr (1 hr)	1.2330	2.4610	Bollhofer & Rosman, 2001
South Holland (US)	1995	0.4 M HBr (1 hr)	1.2200	2.4590	Bollhofer & Rosman, 2001
Sioux (US)	1996	0.4 M HBr (1 hr)	1.1950	2.4500	Bollhofer & Rosman, 2001
Dallas (US)	1997	0.4 M HBr (1 hr)	1.2020	2.4450	Bollhofer & Rosman, 2001
New York (US)	1998	0.4 M HBr (1 hr)	1.1970	2.4590	Bollhofer & Rosman, 2001
Tampa (US)	1994	0.4 M HBr (1 hr)	1.2140	2.4520	Bollhofer & Rosman, 2001
Tampa (US)	1998	0.4 M HBr (1 hr)	1.2080	2.4590	Bollhofer & Rosman, 2001
Woods Hole (US)	1998	0.4 M HBr (1 hr)	1.1730	2.4380	Bollhofer & Rosman, 2001
Havanna	1997	0.4 M HBr (1 hr)	1.1610	2.4380	Bollhofer & Rosman, 2001
Mexico City	1998	0.4 M HBr (1 hr)	1.1900	2.4600	Bollhofer & Rosman, 2001
Mexico City	1998	0.4 M HBr (1 hr)	1.1880	2.4520	Bollhofer & Rosman, 2001
Santa Ana	1994	0.4 M HBr (1 hr)	1.2150	2.4600	Bollhofer & Rosman, 2001
Puerto Rico	1994	0.4 M HBr (1 hr)	1.1760	2.4290	Bollhofer & Rosman, 2001
Cuba-Habana	1995	0.4 M HBr (1 hr)	1.1610	2.4380	Bollhofer & Rosman, 2001

Table A5.3; Compiled literature data of the Pb isotope composition of suspended riverine particles in the Amazon basin

River	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	Reference
Negro	1.2071	2.4715	Allègre et al., 1996
Solimoes	1.2077	2.4785	Allègre et al., 1996
Amazon	1.2062	2.4788	Allègre et al., 1996
Madeira	1.1923	2.4804	Allègre et al., 1996
Amazon	1.2089	2.4829	Allègre et al., 1996
Urucara	1.2131	2.4780	Allègre et al., 1996
Trombetas	1.2528	2.5075	Allègre et al., 1996
Tapajos	1.2093	2.4825	Allègre et al., 1996
Amazon	1.2058	2.4849	Allègre et al., 1996
Amazon	1.2024	2.4957	Asmerom & Jacobsen, 1993

All Pb isotope ratios quoted in the table ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) were calculated from $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios quoted in the publications.

Table A5.4; Compilation of literature data used to assess the Pb isotope composition of North African mineral dust.

Type	Location	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	Reference
PMS	Sierra Leone Rise	1.2051	2.4918	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2048	2.4916	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2039	2.4930	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2035	2.4905	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2025	2.4905	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2029	2.4906	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2029	2.4931	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2027	2.4919	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2028	2.4923	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2021	2.4918	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2022	2.4918	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2028	2.4918	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2055	2.4924	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2027	2.4883	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2019	2.4915	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2026	2.4924	Abouchami & Zabel, 2003
PMS	Sierra Leone Rise	1.2024	2.4914	Abouchami & Zabel, 2003
PMS	ETA	1.2000	2.5000	Chow & Patterson, 1962
PMS	ETA	1.2010	2.5021	Chow & Patterson, 1962
PMS	ETA	1.2030	2.5010	Chow & Patterson, 1962
PMS	ETA	1.2030	2.4959	Chow & Patterson, 1962
PMS	ETA	1.2020	2.4990	Chow & Patterson, 1962
N.A dust	Bodélé depression	1.2112	2.5076	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2046	2.4966	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2037	2.4977	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2115	2.5134	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2167	2.5117	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2153	2.5105	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2100	2.5138	Abouchami et al., 2013
N.A dust	Bodélé depression	1.2161	2.5105	Abouchami et al., 2013

PMS = Pleistocene marine sediment, N.A dust = North African dust collected in source region (Bodélé depression, Chad), ETA = eastern Tropical Atlantic. The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios quoted in the table were calculated from $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios quoted in Abouchami & Zabel, 2003 and Abouchami et al., 2013, and from $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ quoted in Chow & Patterson, 1962.

A5.2. Mass balance estimates of the relative proportions of Pb_{min} and Pb_{anth} in ocean surface waters

The proportion of Pb_{min} relative to Pb_{anth} in ocean surface waters corresponding to the relative Pb_{min} maxima have been estimated using mass balance. The estimates assume (1) that Pb in these surface waters consists of a binary mixture of Pb_{min} and Pb_{anth} transported by the northeast trade winds, and (2) that the Pb isotope composition of these two endmembers is represented by the mean of the relevant compiled data sets. For the isotope composition of Pb_{anth} (transported by the northeast trade winds), the compiled literature data are combined with the leachate data for aerosols collected north of the ITCZ (groups ‘northeast trades’ and ‘Algerian’) from this study. The Pb isotope compositions of Pb_{anth} transported by the northeast trade winds span a relatively large range (Fig. 3.5), with this variability occurring over periods of several days (section 3.5.2.1). This likely reflects the relatively short residence time of atmospheric aerosols (~ several days) (Raes et al., 2000). Due to the longer residence time of Pb in ocean surface waters (likely ~ months, section 3.5.1.2), it can be expected that inputs of Pb_{anth} featuring variable isotope compositions will be integrated towards an average. This is supported by the smooth/systematic spatial distribution of Pb isotope compositions in the ocean surface (Fig. 3.2) and forms the premise for assumption (2).

Based on the compiled data, Pb_{anth} (transported by the northeast trade winds) is characterized by an isotope composition of 1.1532 ± 0.0057 ($^{206}Pb/^{207}Pb$) and 2.4304 ± 0.0063 ($^{208}Pb/^{207}Pb$) (mean $\pm$ 2se, n = 25), whilst Pb_{min} is characterized by an isotope composition of 1.2051 ± 0.0017 ($^{206}Pb/^{207}Pb$) and 2.4972 ± 0.0029 ($^{208}Pb/^{207}Pb$) (mean $\pm$ 2se, n = 30). Using these endmembers we have constructed a mixing line in three isotope space ($^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$) which is displayed in Fig. 3.3 (Chapter 3). Comparison of the Pb isotope compositions of the surface seawater samples to this mixing line indicates a maximum Pb_{min} contribution of 30 – 50 % (Fig. 3.3, Chapter 3).

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