UNIVERSITY OF CALIFORNIA
SANTA CRUZ

ASIAN ANTHROPOGENIC LEAD CONTAMINATION IN THE NORTH PACIFIC OCEAN AS EVIDENCED BY STABLE LEAD ISOTOPIC COMPOSITIONS

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by

Cheryl M. Zurbrick

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This dissertation of Cheryl M. Zurbrick is approved:

Professor A. Russell Flegal, Chair

Professor Donald R. Smith

Professor Kenneth W. Bruland

Professor Doris B. Ash

Tyrus Miller
Vice Provost and Dean of Graduate Studies

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Abstract

Cheryl M. Zurbrick

Asian anthropogenic lead contamination in the North Pacific Ocean as evidenced by stable lead isotopic compositions

This dissertation work determined the changing scope of lead (Pb) contamination in the North Pacific Ocean since the phase-out of leaded gasoline in most of the world. Chapters 1 and 2 consisted of validating our method for determining Pb concentrations and isotopic compositions in seawater. Chapter 3 established a baseline of Pb isotopic compositions (PbICs) in the western and central North Pacific in 2002. This was an ideal time to establish such a baseline because China had recently (mid-2000) ceased their use of leaded gasoline and simultaneously began consuming increasingly large amounts of coal, known to have relatively high Pb concentrations. We found subsurface waters were contaminated with Asian industrial Pb, predominantly Chinese coal emissions. In contrast, the abyssal waters were a mix of Asian industrial Pb and background (i.e., natural) Pb.

Chapter 4 revisited the western and central North Pacific in 2009 – 2011 to determine what, if any, changes had occurred in this short time period. We found that Pb in subsurface and abyssal waters of the western North Pacific were similar to Chinese aerosols. Such a large change in the PbICs of abyssal water in 9 years was unanticipated and attributed to the relatively large flux of particle-bound Pb from the euphotic zone to the deep ocean, which was in isotopic equilibrium with the reservoir of dissolved Pb. In contrast, the central North Pacific abyssal water PbICs were similar to values previously reported because of the relatively lower particulate

export. Based on comparisons to baseline PbIC data, we determined that abyssal waters in the western and central North Pacific would be isotopically indistinguishable from surface waters in the next three decades.

Sources of Pb to coastal California waters were reevaluated in Chapter 5. Prior studies had found that surface waters of the California Current System (CCS) were isotopically consistent with both Asian industrial Pb and US leaded gasoline, still in use at that point in time. In 2010 and 2011, we found that surface and subsurface waters of the CCS were isotopically similar to Asian industrial emissions. However, remobilized US gasoline Pb from sediments in the San Francisco Bay, California, were accumulating in the “mud belt” on the continental shelf and changing the isotopic composition of overlying waters. During periods of intense upwelling, this historic Pb was brought to the surface of the water. However, the much larger quantity of Pb from Asian industrial emissions made the isotopic composition of Pb from historic US gasoline unidentifiable in off-shore waters.

A secondary research focus of this dissertation was to improve my own teaching abilities. Chapter 6 explored the intersection of system thinking and aquatic toxicology in undergraduate education. Among a wealth of information, I found that group concept mapping was no more useful to student learning than the same activity done individually. This was due to poor implementation of team learning strategies by me and inadequate time for students to adjust to non-traditional instruction methodologies.

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The chapters of this dissertation include reprints of the following published manuscripts, and three prepared manuscripts:

Chapter 1: Zurbrick, C.M., P.L. Morton, C. Gallon, A.M. Shiller, W.M. Landing and A.R. Flegal. (2012) Intercalibration of Cd and Pb concentration measurements in the Northwest Pacific Ocean. *Limnology and Oceanography: Methods*. 10: 270 - 277

My contributions to this chapter were to organize the three participating groups, analyze the subsamples for UCSC, and write the manuscript. P.L. Morton analyzed the samples for FSU and C. Gallon helped analyze the samples for UCSC. A.M. Shiller, W.M. Landing, and A.R. Flegal oversaw the analyses at their respective institutions and provided help in writing the manuscript.

Chapter 2: Zurbrick, C.M., C. Gallon and A.R. Flegal. A new method for stable lead isotope extraction from seawater. (2013) *Analytica Chimica Acta*. 800: 29 – 35.

I contributed to this chapter by generating the data, developing the instrument portion of the method, and writing the manuscript. C. Gallon developed the chemistry portion of the method. A.R. Flegal oversaw the method development and contributed to the writing of the manuscript.

Chapter 3: Zurbrick, C.M., C. Gallon and A.R. Flegal. Submitted. Asian industrial lead within the Northwest Pacific Ocean evidenced by lead isotopes in seawater. *Environmental Science and Technology*.

My contributions to this chapter were analyzing half of the samples, interpreting the data and writing the manuscript. C. Gallon analyzed the other half of the samples. A.R. Flegal oversaw the work for this chapter, assisted with data interpretation, and helped in the writing of this manuscript.

Chapter 4: Zurbrick, C.M., K. Horikawa, J. Zhang and A.R. Flegal. In prep. Recent increases of anthropogenic lead in North Pacific Ocean abyssal waters. *Geochimica et Cosmochimica Acta.*

I contributed to this chapter by analyzing the seawater for Pb concentrations and isotopic compositions, doing the data analysis, and writing the manuscript. K. Horikawa participated in the sampling and J. Zhang was the chief scientist of the research expedition. Both K. Horikawa and J. Zhang assisted in the writing of the manuscript. A. R. Flegal oversaw the laboratory work for this chapter and assisted in writing the manuscript.

Chapter 5: Zurbrick, C.M., D.V. Biller, R.C. Till, K.W. Bruland and A.R. Flegal. In prep. Lead in coastal California impacted by current and past sources of contamination. *Proceedings of the National Academy of Sciences.*

My contributions to this chapter were to analyze the off-shore profiles for Pb concentrations and selected samples for Pb isotope compositions, interpreting the data and writing the manuscript. D.V. Biller assisted in the collection of samples and analyzed surface waters and benthic stations for Pb concentrations. R.C. Till collected and analyzed particulate leachable Pb concentrations. K.W. Bruland was chief scientist on the two research cruises and assisted in the data interpretation. A.R. Flegal oversaw the Pb isotope analyses and contributed to the writing of the manuscript.

Introduction

Humans have perturbed the elemental cycle of lead (Pb) in the environment for many centuries (Martinez-Cortiza et al., 2002; Flegal et al., 2010). In the past century this pollution increased markedly through the worldwide use of leaded gasoline. These Pb emissions were subsequently deposited in remote parts of the globe (Flegal et al., 1993a; Rosman et al., 2000). In addition, the human body burden of Pb increased dramatically (Patterson, 1965) which generated much attention because it is a potent neurotoxin (ATSDR, 2007; Bellinger, 2007), associated with behavioral problems (Cervantes et al., 2005; Wright et al., 2008) and developmental delays in children (Chia et al., 2004). A global effort to ban the use of leaded gasoline began in the 1970s and that phase-out was nearly completed by the early 2000s. A concomitant decrease in the Pb content of aerosols (Flegal et al., 1996), seawater (Wu and Boyle, 1997), and humans (Muntner et al., 2005) was documented during that phase-out. However, environmental Pb contamination and human exposure persists today through industrial emissions (Chen et al., 2005; Ren et al., 2006; Duzgoren-Aydin, 2007; Gallon et al., 2011) and contaminated foods (Zhang et al., 1996; Moreda-Piñeiro et al., 2003; Bao et al., 2009; Chen et al., 2009; Shi et al., 2010).

The approximate source(s) of Pb can be established through the stable Pb isotopic compositions (PbICs) of a sample. This is possible because of the natural variations in the abundances of the four stable isotopes of Pb (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) which are not altered by biological, chemical, geological processes. This variation is due to the natural abundance of primordial Pb (^{204}Pb) and the abundance of radiogenic ^{238}U, ^{235}U and ^{232}Th which decay slowly (~ > 1 billion years) to ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively. The provenance of Pb in the ocean is established by comparing the PbICs of modern Pb-containing materials (e.g., coal, loess) to the PbICs found in the ocean.

The burning of coal, which has a high Pb content (~35 ppm, Díaz-Somoano et al., 2009), releases large quantities of Pb to the atmosphere. Over Asia, prevailing Westerlies winds blow aerosols over the North Pacific Ocean and beyond, where dust is deposited (Jaffe et al., 1999; Buck et al., 2006; Gallon et al., 2011). Because of the rapid increase in coal consumption in China since 2000 (BP, 2012), the changing quantity and composition of Pb in the North Pacific was investigated in this dissertation.

In Chapter 1, the method for analyzing Pb concentrations in seawater (Zurbrick et al., 2012) was validated by comparing measurements with two other groups and analyzing reference seawater samples provided by the GEOTRACES and SAFe intercalibration programs. In Chapter 2, the method for PbICs (Zurbrick et al., 2013) was developed and similarly validated. The relatively low concentration of Pb in open ocean seawater (< 10 ~ 100 pmol kg^{-1}, Lee et al., 2011; Biller and Bruland, 2012) requires ultraclean sample handling, reagents, and apparatuses in order to prevent contamination of these samples. By using a chelating resin as opposed to organic solvents or co-precipitation, the reagent blank was kept relatively low and the method was both inexpensive and environmentally friendly with this method.

In Chapter 3, baseline concentrations and isotopic compositions of subsurface Northwest Pacific seawater from 2002 were determined. This was an ideal time for such a baseline because China had recently ceased their use of leaded gasoline (mid-2000, Li et al., 2012), and their large consumption of coal had just begun (BP, 2012).

By 2011, Chinese coal consumption had increased 155%, and constituted 49% of the coal consumed globally. Lead concentrations and PbICs in seawater samples collected in the central (2009) and western North Pacific (2011) were determined in Chapter 4. Similarities and differences in the PbICs for the two regions were documented, and a simple model of changing PbICs in the deep ocean was constructed using the previous 2002 samples from Chapter 3 as a baseline.

In Chapter 5, Pb contamination was documented off the coast of northern California in the Northeast Pacific Ocean. This location was chosen because prior studies of Pb in these neritic waters during the 1980s found a mix of contamination from the ongoing use of leaded gasoline in the U.S. and Asian industrial emissions (Flegal et al., 1989; Flegal et al., 1993b). Coastal samples were collected in 2010 and 2011 and compared with recent reports of Asian Pb aerosols impacting the West Coast of North America (Bollhöfer and Rosman, 2001).

Finally, in Chapter 6 I explored the intersection of system thinking and aquatic toxicology in undergraduate education in an effort to improve my own teaching abilities. Among the wealth of quantitative and qualitative data generated, four forms of assessment (multiple choice, short answer, individual concept mapping, and group concept mapping) were analyzed for their utility to students and the instructor. In addition, social factors which influence the success of active learning in undergraduate classes were evaluated.

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Zurbrick C. M., Morton P. L., Gallon C., Shiller A. M., Landing W. M. and Flegal A. R. (2012) Intercalibration of Cd and Pb concentration measurements in the northwest Pacific Ocean. Limnol. Oceanogr. Methods **10**, 270–277.

CHAPTER 1. INTERCALIBRATION OF Cd AND Pb CONCENTRATION MEASUREMENTS IN THE NORTHWEST PACIFIC OCEAN

Cheryl M. Zurbrick, Peter L Morton, Céline Gallon, Alan M.
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Intercalibration of Cd and Pb concentration measurements in the northwest Pacific Ocean

C. M. Zurbrick[1], P. L. Morton[2], C. Gallon[3], A. M. Shiller[4], W.M. Landing[2], and A.R. Flegal[1,3]*
[1]Department of Microbiology and Environmental Toxicology, University of California, Santa Cruz, CA 95064
[2]Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, FL 32306
[3]Institute of Marine Sciences, University of California, Santa Cruz, CA 95064
[4]Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529

Abstract

Dissolved and total Cd and Pb concentration measurements in seawater were intercalibrated using 33 samples collected on the fourth cruise of the Intergovernmental Oceanographic Commission's (IOC-4) Global Investigation of Pollution in the Marine Environment (GIPME) in the northwest Pacific Ocean, as well as in three seawater reference materials (SAFe S1, SAFe D2, and NASS-5). Laboratories from Florida State University (FSU), University of California at Santa Cruz (UCSC), and University of Southern Mississippi (USM) participated in the Pb intercalibration, and two of them (FSU and UCSC) participated in the Cd intercalibration. While each of the laboratories employed different extraction techniques before analysis by inductively coupled plasma–mass spectrometry (ICP-MS), the measurements of Cd and Pb concentrations for the IOC-4 samples agreed to within 4% and 15%, respectively, and those of the reference materials agreed to within 13% and 8%, respectively. This successful intercalibration demonstrates that there now are multiple techniques available for accurately measuring Cd and Pb concentrations in seawater.

The study of trace metals in the oceans is important because many are essential trace elements (e.g., Co, Fe, Mn, Zn), others (e.g., Ag, Hg, Pb) evidence the global magnitude of anthropogenic contamination of the oceans, and some (e.g., Cd, Cu) fall into both categories (Bruland and Lohan 2004). Because concentrations of those metals and their species in the oceans are truly trace (e.g., parts-per-billion and parts-per-trillion), extremely sensitive, accurate, and precise measurements are needed to determine their role as limiting nutrients and/or as tracers of industrial contamination. These determinations often involve the synthesis of data generated by several research groups, which necessitates ongoing intercalibrations among those laboratories to ensure the data are comparable. Consequently, one of the principal objectives of the Intergovernmental Oceanographic Commission's (IOC) Global Investigation of Pollution in the Marine Environment (GIPME) has been to encourage intercalibrations among different laboratories measuring trace element concentrations in seawater (Landing et al. 1995). These intercalibrations serve as a crucial means to both ensure accurate measurements and validate different laboratory procedures and instrumental analytical methods.

Here we report the results of our intercalibration of filtered (0.2–0.4 µm) and total (unfiltered) Cd and Pb concentrations of seawater samples collected on the fourth IOC baseline contaminant survey in the northwest Pacific Ocean (IOC-4). These comparisons are noteworthy because there has never been a published intercalibration of dissolved or total Pb concentration measurements in the northwest Pacific Ocean; and the last published intercalibration of Cd measurements for the entire North Pacific was with samples collected in 1979 (Bruland et al. 1985). However, Bruland has recently initiated an

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*Corresponding author: E-mail: czurbric@ucsc.edu

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intercalibration of trace element concentrations in two homogenous water samples (SAFe S1 and SAFe D2) collected in the northeast Pacific in 2004 (Johnson et al. 2007), which provide informal consensus values (unpublished) for both Cd and Pb in those waters (Bruland 2011).

These new intercalibrations are especially important because of (1) advances in analytical methodologies, (2) pronounced changes in anthropogenic inputs of metals to the North Pacific, and (3) accelerating impacts of climate change over the past three decades, which may be altering the biogeochemical cycling of metals in those waters. For example, emissions from the combustion of leaded gasoline—which dominated atmospheric Pb fluxes to the North Pacific in the preceding century (Flegal and Patterson 1983; Flegal et al. 1986)—have become inconsequential with the virtual elimination of leaded gasoline in North America and most of Asia. Conversely, aeolian fluxes of Pb and other anthropogenic elements (e.g., Ag, Se) to the North Pacific now appear to be increasing with the rapid industrial development of Asia and the burning of coal for electricity generation (Ranville and Flegal 2005; Ranville et al. 2010; Wu et al. 2010; Gallon et al. 2011). Therefore, extremely sensitive, accurate, and precise measurements are needed to resolve temporal and spatial variations of trace elements in the North Pacific, as well as in other oceanic waters.

Materials and procedures

Before the cruise, sample bottles were cleaned at each university with different methods, all of which were determined to be sufficient. Florida State University (FSU) washed 500 mL bottles with acetone, rinsed with deionized (DI) water (10 MΩ cm), washed with 5% (v/v) Micro detergent, rinsed with DI water, immersed in 3 M HCl (trace metal grade) for 5 d at room temperature, rinsed with DI water, immersed in ultra-high purity (UHP) 0.5 M HCl for 5 d, rinsed five times with UHP water (18 MΩ cm), filled with UHP water and acidified to 0.024 M HCl (UHP), and stored full until use. University of California at Santa Cruz (UCSC) soaked 2 L bottles in 5% (v/v) Citranox (Alconox) for ≥ 1 week, rinsed with DI water, filled with 6.0 M HCl (reagent grade) for 4 weeks, rinsed with UHP water, filled with 0.15 M HNO_3 (trace metal grade) and stored (≥ 3 weeks). University of Southern Mississippi (USM) washed 500 mL bottles overnight at 60°C in 1.2 M HCl (reagent grade), cooled upside-down in a trace metal clean fume hood, rinsed with UHP water, and then stored empty before use.

Samples for the intercalibration were collected on the R/V *Melville* during the IOC-4 cruise in the North Pacific from 1 May–5 June 2002, as previously detailed by Measures et al. (2006). Briefly, trace metal clean techniques were used to collect surface seawater samples with a FISH and subsurface seawater samples with modified (trace metal clean) GO-FLO bottles on a Kevlar line. Filtered (0.2 µm) surface waters collected for FSU and USM were passed through Pall Gelman Acropak 500 (polyethersulfone) capsule filters, while filtered (0.4 µm) subsurface waters were pressure-filtered through 142 mm Nuclepore polycarbonate membrane filters; all samples were stored in acid-cleaned HDPE bottles (500 mL). Unfiltered waters collected for UCSC were stored in acid-cleaned LDPE bottles (2 L). All samples were subsequently acidified (pH 1.8) with 6.0 M HCl (UHP) to 0.024 M HCl and handled with trace metal clean techniques in HEPA filtered air (Class 100) laminar flow hoods.

At FSU, Cd and Pb were concentrated and extracted from the seawater matrix using an off-line chelating resin extraction method and then analyzed with a quadrupole ICP-MS (HP Agilent 7500), using established techniques (Milne et al. 2010). In brief, 12 mL aliquots of acidified seawater were spiked with a multi-element–enriched isotope standard that included ^{111}Cd and ^{207}Pb and then UV-oxidized for 1.5 h. [Although UV oxidation may not be necessary for Cd and Pb analyses, it is necessary when using this method to release other trace metals (e.g., Co and Cu) bound to organic ligands, which are analyzed simultaneously with Cd and Pb (Bruland 2011).] Before extraction, the samples were pH-adjusted and buffered to pH 5.9 ± 0.1 using 2 M ammonium acetate ($CH_3CO_2NH_4$) solution (pH 9.0) before passing over a 200 µL column of Toyopearl AF-Chelate 650 M resin (Tosohaas). Samples were eluted with 1 mL of 1.0 M HNO_3 (UHP), collected into trace metal clean 4 mL polypropylene vials, and capped until analysis. On average, the complete cycle of loading and eluting a sample took 7.5 min. The samples were analyzed using an isotope dilution method on a quadrupole ICP-MS (HP Agilent 7500c) with an octopole reaction–collision cell (ORC), operated in reaction mode. The ORC effectively eliminates the potential polyatomic isobaric interference on ^{111}Cd from ^{95}Mo^{16}O by both energy discrimination and charge transfer mechanisms. The ORC is an off-axis chamber, 2 mL in volume, with a positive potential difference along the ion flow path. It is flooded with low molecular weight gases (He for collision mode or H_2 for reaction mode) to increase the probability of the passing ions colliding with the gases. The polyatomic interference MoO$^+$ has a larger diameter (effective nuclear volume) than monoatomic Cd$^+$, and therefore has a higher collision frequency than the analyte, resulting in both energy discrimination (MoO$^+$ cannot traverse the chamber) and charge transfer (MoO$^+$ absorbs an electron from H_2, rendering it mute to the detector).

At UCSC, Cd and Pb concentrations were analyzed with an on-line chelating resin extraction, using the methodology developed by Ndung'u et al. (2003). This involved micro-columns filled with Toyopearl AF-Chelate 650 M resin (Tosohaas) connected directly to a magnetic sector ICP-MS (Thermo ELEMENT XR) operated in low resolution mode with acid-cleaned Watson-Marlow manifold pump tubing and Teflon tubing. Four milliliters of acidified seawater was buffered to a pH of 8.5 with 0.8 M $CH_3CO_2NH_4$ buffer (pH 9.0) and loaded onto the column. The column was washed with 4 mL of 0.1 M $CH_3CO_2NH_4$ buffer (pH 9.0), then the analytes were eluted

Table 1. Blanks and detection limits for Cd and Pb associated with each laboratory's method. USM's method of using small sample volumes did not achieve Cd at an accurate enough level due to MoO interferences.

	Cd (pmol/kg)		Pb (pmol/kg)	
Laboratory	**Blank**	**Detection Limit**	**Blank**	**Detection Limit**
FSU	3.12 ± 0.97 *n* = 6	2.9	1.98 ± 0.94 *n* = 6	2.9
UCSC	3.8 ± 1.7 *n* = 33	5.2	5.0 ± 1.3 *n* = 33	3.8
USM	—	—	1.3 ± 0.6 *n* = 17	1.9

directly into the ICP-MS with 2 mL of 1.5 M HNO_3 (UHP) doped with In and Bi as internal standards. The system was flushed with 1.5 M HNO_3 (UHP) before the next sample loading. The complete cycle took an average of 6 min. The Cd and Pb analyses were calibrated using a set of standards prepared with high-purity single element solutions added to seawater that was previously stripped of its metal content using Toyopearl AF-Chelate 650 M resin. MoO interferences on Cd were monitored by spiking Cd-free seawater with varying concentrations of Mo. Counts on masses 110 and 111 were related to Mo concentrations and the false Cd to Mo ratio was used to calculate and subtract the MoO interference from each sample; in most samples this difference was < 0.5%.

Unlike FSU and UCSC, USM did not use chelating resins to separate trace metals from the seawater matrix. Instead, 5 mL acidified seawater samples were spiked with isotopically-enriched ^{207}Pb, allowed to equilibrate for 30 s, and then dissolved Pb was extracted using a magnesium hydroxide [$Mg(OH)_2$] coprecipitation method (Wu and Boyle 1997; Shiller and Bairamadgi 2006). Measurements of Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) were made with the extracts using a magnetic sector field ICP-MS (Thermo ELEMENT 2) operated in low resolution. Because of the small sample volumes used with this method for Pb concentrations, MoO interferences precluded concurrent measurements of Cd that were sufficiently accurate and precise for this intercalibration.

Assessment

Blanks and detection limits

The three laboratories determined their analytical blanks differently. At FSU, the blanks were derived from a series of analyses that quantified the contributions from (1) the $CH_3CO_2NH_4$ buffer solution and (2) the extraction and analysis procedure, which were then extrapolated to the volume (12 mL) of the samples (Milne et al. 2010). At UCSC, the blanks were derived from analyses of UHP water acidified to pH 1.8 with 0.024 M HCl (UHP) and then processed in the same manner as samples. While this blank includes both that of the UHP water and the procedural blank, subsequent work has shown that the majority of the blank was from the reagents. UCSC has, consequently, addressed the issue by cleaning the buffer with an on-line column packed with Toyopearl AF-Chelate 650 M resin (Tosohaas) just prior to buffering samples on-line, which has dramatically reduced the total blank (1.8 pmol/kg Cd, 3.3 pmol/kg Pb) for future work. At USM, the blanks were derived from analyses of a small quantity of seawater after it had been stripped of its metal content by $Mg(OH)_2$ co-precipitation, as described previously (Shiller and Bairamadgi 2006).

The methods used by FSU and UCSC had comparable analytical blanks for Cd (Table 1). FSU's off-line resin extraction had blanks of 3.12 ± 0.97 pmol/kg ($n = 6$), while UCSC's on-line resin extraction had blanks of 3.7 ± 1.7 pmol/kg ($n = 33$). The formal detection limit for each method (calculated as three times the standard deviation of the blank) was 2.9 pmol/kg for FSU and 5.2 pmol/kg for UCSC. These formal detection limits exceeded the lowest levels of Cd found in surface seawater (~1 pmol/kg), but were generally much lower than Cd concentrations found throughout the rest of the water column (20-1000 pmol/kg).

Similarly, the methods used by all 3 groups had comparable analytical blanks for Pb (Table 1). These were 1.98 ± 0.94 pmol/kg ($n = 6$) for FSU, 5.0 ± 1.3 pmol/kg ($n = 33$) for UCSC, and 1.3 ± 0.6 pmol/kg ($n = 17$) for USM. The formal Pb detection limits were 2.9, 3.8, and 1.9 pmol/kg for FSU, UCSC, and USM, respectively. All detection limits were relatively low compared to seawater concentrations of Pb (typically ≥ 20 pmol/kg).

Whereas the differences in detection limits and blanks are laboratory dependent, some general conclusions can be drawn from contrasts in analytical protocols at FSU and UCSC. This was partially due to differences in the analytical set-up. While the ICP-MS at FSU is part of a shared-use facility, the Landing group uses method-specific sets of ICP-MS cones (platinum) and sample introduction systems for different applications. These components are regularly cleaned and/or polished between uses, ensuring that blanks are minimized. The ICP-MS at UCSC is also part of a shared-use facility, and the cones and nebulizer employed for this intercalibration were shared with a wide group of other instrument users. As a consequence, it is clear that Pb contamination from those cones and nebulizer was more problematic at UCSC, despite several

Table 2. Results from the analysis of standard reference materials SAFe S1 and D2 and certified reference material NASS-5 with their accepted concentration values for Cd and Pb.

Reference material	Laboratory	Cd (pmol/kg)	Pb (pmol/kg)
SAFe S1	Consensus value	1.0 ± 0.2	47.6 ± 2.4
	FSU	0.8 ± 0.7 ($n = 5$)	44.3 ± 1.5 ($n = 5$)
	UCSC	1.1 ± 0.2 ($n = 6$)	49.9 ± 0.9 ($n = 6$)
	USM	—	49 ± 1 ($n = 6$)
SAFe D2	Consensus value	986 ± 27	27.7 ± 1.8
	FSU	1008 ± 32 ($n = 5$)	26.2 ± 0.4 ($n = 5$)
	UCSC	991 ± 39 ($n = 9$)	29.0 ± 1.3 ($n = 9$)
	USM	—	27.7 ± 0.6 ($n = 6$)
NASS-5	Certified value	205 ± 27	38 ± 24
	FSU	195 ± 7 ($n = 3$)	29.2 ± 2.0 ($n = 3$)
	UCSC	225 ± 10 ($n = 3$)	28 ± 2 ($n = 3$)
	USM	—	34 ± 1 ($n = 6$)

hours of running acid through the instrument before each analysis for this intercalibration. Another reason for differences in the blanks was the larger volume of buffer used by the UCSC method, which elevated the blank. Regardless, both the FSU and UCSC methods were near the limit of detection to accurately measure the lowest seawater Cd concentrations, as evidenced by the high variability in the analysis of the low SAFe S1 concentration of 1 pmol/kg (see below). Both the FSU and UCSC resin extraction methods allow for an increase in the signal-to-blank ratio by increasing the volume of sample loaded onto the column. Increasing the volume of sample to be extracted requires the use of either more buffer solution or a higher pH buffer, while striving to minimize any increase in the Cd and Pb blanks contributed by the buffer.

Standard reference materials

To validate the accuracy of the three methods, each laboratory analyzed three different reference seawater materials: SAFe S1 and SAFe D2, which were distributed by Bruland (2011), and a National Research Council Canada certified reference material (NASS-5) (Table 2). The agreement among the three laboratories on the reference material concentrations demonstrated that each method is capable of accurately measuring the levels of Cd and Pb found in open ocean samples, with FSU and UCSC reporting Cd concentrations that agree within 30 pmol/kg (≤13%), and all three laboratories reporting Pb concentrations that agreed within 5 pmol/kg (≤8%). These differences are consistent with the differences (one standard deviation) of the methods for SAFe S1 and SAFe D2 (Bruland 2011)—i.e., the three laboratories' values were not statistically different from the consensus SAFe values (t-test, $P = 0.05$).

IOC-4 seawater samples

Eleven IOC-4 seawater samples collected for each laboratory were analyzed (Table 3). Each group (FSU, UCSC, and USM) had sent precleaned subsample bottles on the IOC-4 research cruise. The bottles were filled using trace-metal clean protocols, then returned to each group for acidification and storage. We selected five surface water samples collected underway with the FISH sampling system and six subsurface water samples from Station 8 with the GO-FLO system. Each group took two 30 mL subsamples from their original sample bottles and sent them to the other laboratories for analysis. The depth profile from Station 8 (Figure 1A-C) shows that the 3 groups had similar results for each depth, and better agreement at lower concentrations of both Cd and Pb. One UCSC sample (Station 8, 300 m), which was leaking and clearly contaminated when it arrived at USM, was excluded from this intercalibration.

While samples provided by each laboratory for the intercalibration should have similar concentrations because they were aliquots taken from the same GO-FLO bottles, the FSU and USM samples were filtered and the UCSC samples were not filtered. In general, the difference between dissolved and unfiltered concentrations of Cd is ~5% in oceanic regions with moderate productivity (Bruland et al. 1979). The greatest difference between dissolved and unfiltered samples in our study was in FISH sample 20, where unfiltered concentrations of Cd exceeded filtered samples by 200 pmol/kg (Table 3). This sample was collected off the coast of the Kuril-Kamchatka margin, where seasonal productivity can result in enhanced biological uptake of Cd and higher particulate (and unfiltered seawater) Cd concentrations.

There was good agreement among the laboratories in their measurements of a wide range of Cd and Pb concentrations in surface water samples (Figure 2A-C). The Cd concentrations agreed within 20 pmol/kg (≤4%), and the Pb concentrations agreed within 8 pmol/kg (≤15%).

The intercalibration data were also comparable to previous measurements of Cd and Pb in the North Pacific. For example, Cd concentrations in the vertical profile at Station 8 were similar to those reported for the central North Pacific Ocean by Bruland et al. (1994). Lead concentrations in that vertical profile are higher than those reported by Boyle et al. (2005) in a

Table 3. Summary of seawater sample concentration measurements for Cd and Pb made on IOC-4 subsamples provided by FSU, UCSC, and USM. FSU and UCSC reported both Cd and Pb, whereas USM reported Pb only. ND = not detected, BDL = below detection limit. Reported concentrations from different labs on individual subsamples are in agreement.

		Cd (pmol/kg) Subsample source			Pb (pmol/kg) Subsample source		
Sample ID	**Lab**	**FSU**	**UCSC**	**USM**	**FSU**	**UCSC**	**USM**
IOC-4 Station 8,	FSU	1.7	2.8	BDL	57.8	67.3	55.6
26.0°N, 175.0°W	UCSC	0.4	2.2	1.2	63.8	74.8	69.4
80 m	USM	ND	ND	ND	66.0	80.2	64.8
IOC-4 Station 8,	FSU	51.9	52.9	51.1	77.6	76.4	114.6
26.0°N, 175.0°W	UCSC	50.2	53.8	54.2	87.5	85.3	128.4
170 m	USM	ND	ND	ND	89.6	88.6	130.6
IOC-4 Station 8,	FSU	145.2	159.4	150.2	65.8	71.6	70.3
26.0°N, 175.0°W	UCSC	164.3	159.8	159.1	77.0	77.8	76.5
300 m	USM	ND	ND	ND	78.7	118.9	78.3
IOC-4 Station 8,	FSU	790.6	819.2	851.7	47.1	49.3	48.4
26.0°N, 175.0°W	UCSC	878.8	824.5	898.4	53.3	57.0	54.2
700 m	USM	ND	ND	ND	56.9	58.2	53.6
IOC-4 Station 8,	FSU	972.8	935.2	952.2	55.8	48.5	63.0
26.0°N, 175.0°W	UCSC	1008.1	967.4	1019.9	60.2	52.4	69.8
900 m	USM	ND	ND	ND	65.1	60.3	75.0
IOC-4 Station 8,	FSU	978.7	1016.7	922.0	25.8	22.2	22.0
26.0°N, 175.0°W	UCSC	984.8	951.6	964.3	27.8	19.4	22.3
1500 m	USM	ND	ND	ND	29.9	24.6	25.8
IOC-4 FISH 20	FSU	541.4	778.4	576.4	59.2	63.7	60.1
45.9°N, 158.6°E	UCSC	565.6	748.7	565.2	66.9	72.8	63.3
	USM	ND	ND	ND	72.6	75.6	67.6
IOC-4 FISH 24	FSU	655.2	653.8	616.1	45.3	48.1	44.0
49.8°N, 166.6°E	UCSC	647.4	672.1	632.0	49.8	53.1	48.4
	USM	ND	ND	ND	52.0	60.2	50.6
IOC-4 FISH 31	FSU	109.1	174.8	122.9	65.9	72.1	68.8
39.6°N, 170.6°E	UCSC	109.1	170.3	124.7	74.9	83.7	61.9
	USM	ND	ND	ND	77.0	88.2	79.5
IOC-4 FISH 48	FSU	2.5	4.4	2.0	45.6	41.9	42.2
26.0°N, 175.0°W	UCSC	3.4	1.1	1.4	56.9	40.2	46.8
	USM	ND	ND	ND	53.6	52.2	50.4
IOC-4 FISH 62	FSU	2.5	2.9	2.0	29.1	37.1	27.6
24.9°N, 153.6°W	UCSC	1.4	1.8	1.2	31.5	39.1	31.0
	USM	ND	ND	ND	34.9	42.4	33.4

vertical profile ~1700 km to the east of Station 8. As previously documented, this trend is consistent with the expectation that Pb concentrations are higher in the surface and intermediate waters as one moves westward, toward aeolian emission sources of anthropogenic Pb from Asia (Wu et al. 2010; Gallon et al. 2011).

Discussion

Methods used by FSU and UCSC for Cd had blanks and detection limits lower than several previously reported analytical procedures. This includes analyses with graphite furnace absorption atomic spectrometry (GFAAS), which had blanks of 78 pmol/kg and detection limits of 41 pmol/kg (Colbert et al. 1998), and analyses with an aluminum hydroxide coprecipitation method and flameless atomic absorption spectrometry (FAAS), which had a detection limit > 10 nmol/kg (Doner and Ege 2005). In contrast, Lee et al. (2011) recently described a method similar to the chelating resin extractions reported here, that had comparable blanks of 0 ± 2 pmol/kg and a slightly higher detection limit (6 pmol/kg).

For Pb concentration analyses, the overall figures of merit for the laboratories were comparable to some of those previously reported. For example, in a previous IOC intercalibration, Ndung'u et al. (2001) reported Pb measurements per-

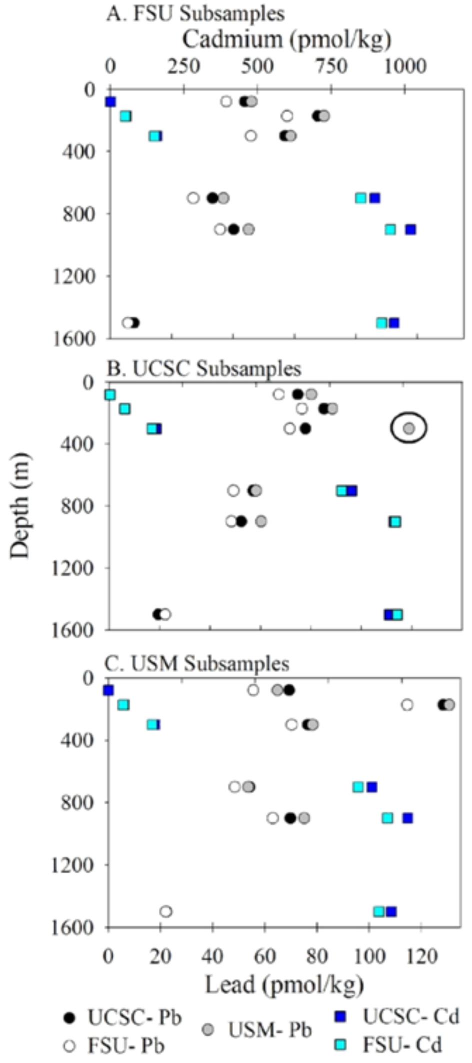

Figure 1. Cadmium and Pb concentrations in IOC-4 Station 8 subsamples from A) FSU, B) UCSC and C) USM. Analyses conducted by FSU, UCSC and USM were in agreement. The data point circled in black (IB) was a sample that leaked during shipping and became contaminated for Pb. Note that the symbol sizes are larger than the analytical error of the measurements.

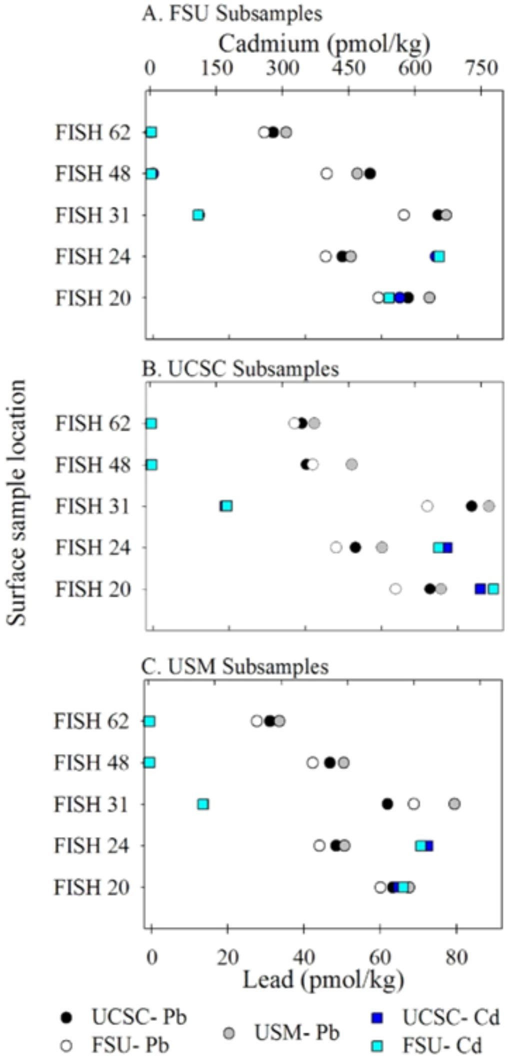

Figure 2. Cadmium and Pb concentrations at five locations in IOC-4 towed-FISH surface water subsamples from A) FSU B) UCSC and C) USM. Analyses conducted by FSU, UCSC and USM were in agreement. For locations see Table 3. Note that the symbol sizes are larger than the analytical error of the measurements.

formed at UCSC and Old Dominion University (ODU) with organic solvent extraction followed by ICP-MS or GFAAS analysis; those had blanks of 1.2 ± 0.2 and 3.2 ± 1.1 pmol/kg, respectively, and detection limits of 0.7 and 3.3 pmol/kg, respectively. The Pb blanks for USM (1.3 ± 0.1 pmol/kg) and FSU (1.95 ± 0.93 pmol/kg) were also are similar to that (1.3 pmol/kg) reported by Lee et al. (2011).

Comments and recommendations

Methods employed in this intercalibration were determined to be suitable for measuring concentrations of Cd and Pb in seawater, while each of those methods has its relative strengths and weaknesses. The off-line resin extraction isotope dilution technique used by FSU provides extremely low blanks, good precision, and uses lower buffer and elution acid volumes compared with the methods at UCSC and USM. The FSU method also allows for simultaneous extraction and analysis of six other metals (Mn, Fe, Co, Ni, Cu, and Zn) (Milne et al. 2010). The on-line resin extraction method used by UCSC requires virtually no sample preparation time in the laboratory, and sample volumes may be as little as 5 mL per analysis. The downside of this convenience is that more ICP-MS instrument time is required. The $Mg(OH)_2$ co-precipitation method used by USM yields better blanks and detection limits than the procedures employed at FSU and UCSC for Pb analyses and simultaneously generates data for six other metals (Ga, Fe, Cr, Cu, Ni, and Zn). However, the 5 mL of sample required by the $Mg(OH)_2$ co-precipitation method was insufficient for concurrent Cd concentration measurements.

Overall, these three methods demonstrate several improvements over many of the techniques previously employed. They require smaller sample volumes, involve less toxic chemicals (such as the carcinogen chloroform used in solvent extraction), and provide faster sample throughput than most previously reported methods; they also allow for simultaneous multi-element analyses from a single aliquot. While the blanks and detection limits vary slightly among methods, each is sufficient for providing reproducible data (≤4% and ≤15% for Cd and Pb, respectively) over a wide range of open-ocean seawater concentrations.

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<u>CHAPTER 2.</u> A NEW METHOD FOR STABLE LEAD ISOTOPE EXTRACTION FROM SEAWATER

Cheryl M. Zurbrick, Céline Gallon and A. Russell Flegal

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A new method for stable lead isotope extraction from seawater

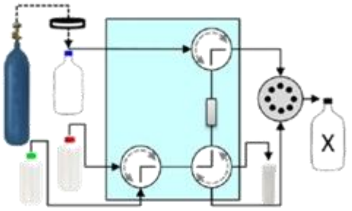
Cheryl M. Zurbrick[a,*], Céline Gallon[b,1], A. Russell Flegal[a,b]

[a] WIGS, Department of Microbiology and Environmental Toxicology, University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, United States
[b] Institute of Marine Sciences, University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064, United States

HIGHLIGHTS

- We present a relatively fast (2.5–6.5 h), semi-automated system to extract Pb from seawater.
- Extraction requires few chemicals and has a relatively low blank (0.7 pmol kg^{-1}).
- We compare analyses of Pb isotopes by HR ICP-MS with those by MC-ICP-MS.

GRAPHICAL ABSTRACT



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ABSTRACT

A new technique for stable lead (Pb) isotope extraction from seawater is established using Toyopearl AF-Chelate 650 M® resin (Tosoh Bioscience LLC). This new method is advantageous because it is semi-automated and relatively fast; in addition it introduces a relatively low blank by minimizing the volume of chemicals used in the extraction. Subsequent analyses by HR ICP-MS have a good relative external precision (2σ) of 3.5‰ for ^{206}Pb/^{207}Pb, while analyses by MC-ICP-MS have a better relative external precision of 0.6‰. However, Pb sample concentrations limit MC-ICP-MS analyses to ^{206}Pb, ^{207}Pb, and ^{208}Pb. The method was validated by processing the common Pb isotope reference material NIST SRM-981 and several GEOTRACES intercalibration samples, followed by analyses by HR ICP-MS, all of which showed good agreement with previously reported values.

1. Introduction

Much of the lead (Pb) in the oceans is derived from the atmospheric deposition of industrial Pb emissions [1]. Stable Pb isotope analyses are an important tool in tracing the sources of those lead inputs. The GEOTRACES program, whose aim is to better understand the processes controlling trace metal distributions in the oceans, has designated Pb as a "metal of interest" [2]. As a result, the ability of many research groups to make highly accurate measurements of Pb isotopes is needed, as highlighted by recent intercalibration efforts (e.g., [3]). Unfortunately, measurements of Pb isotopes in seawater are confounded by the difficulty of extracting adequate quantities of the metal from a highly saline matrix, when sample volumes are often limited by sampling logistics.

Lead concentrations in seawater typically range from <10 pmol kg^{-1} to a few hundred pmol kg^{-1} [4,5]. Prior to instrumental analysis, Pb must therefore be extracted from the seawater matrix and concentrated to levels suitable for analysis, reaching a few nmol kg^{-1}. The original isotope extraction methods for Pb in seawater involved organic solvent extraction using either chloroform and dithizone in two-steps [6] or ammonium pyrrolidine dithiocarbamate (APDC) [7]. Both of these methods proved successful (e.g., [8–10]), but had relatively high blanks (~30 pmol kg^{-1}) [6,11] when compared with newer methods. One of the more recent avenues explored is the use of chelating resins, which provides a faster extraction. McLaren et al. [12] developed

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[*] Corresponding author. Tel.: +1 831 459 5336; fax: +1 831 459 3524.
E-mail address: CZurbric@ucsc.edu (C.M. Zurbrick).

[1] Present address: California Regional Water Quality Control Board, 320 W. 4th Street #200, Los Angeles, CA, United States.

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a Pb isotope extraction chemistry utilizing silica-immobilized 8-hydroxyquinoline (I-8-HOQ) resin which was improved by Halicz et al. [13] but still had a relatively high blank (~30 pmol kg^{-1}) compared to the current organic solvent extraction methods. However, Miyazaki and Reimer [14,15] developed a similar resin extraction method using Chelex-100® resin (Bio-Rad) that had a relatively lower blank (~15 pmol kg^{-1}), likely due to the inherently cleaner reagents than the organic solvents used previously. Finally, Reuer et al. [16] developed Pb isotope extraction by $Mg(OH)_2$ co-precipitation which was subsequently streamlined as detailed in Boyle et al. [3]. This low blank method (0.01–1 pmol kg^{-1}) [3,16–18] was advantageous for seawater samples with extremely low Pb concentrations (<10 pmol kg^{-1}). While not time-consuming for the analyst, this method does require an overnight precipitate settling step which lengthens the extraction procedure.

With GEOTRACES sampling efforts underway in all major ocean basins, improved analytical efficiency is more imperative than ever before. This need has already prompted the development of several new and promising methods. Notably, Sohrin et al. [19] and Biller and Bruland [5] recently developed methods for a simultaneous resin extraction of multiple trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) using Chelate-PA1® resin (Nobias, Hitachi-Hitec). These techniques proved efficient to extract Pb with low blanks (~1 pmol kg^{-1}), but the relatively low amount of seawater extracted (40–120 mL) would be insufficient for most Pb isotope measurements.

Here, we present a method with relatively low blanks and high processing efficiency to extract Pb from seawater, along with subsequent analyses by high resolution inductively coupled plasma mass spectrometry (HR ICP-MS, magnetic sector) and multi-collector ICP-MS (MC-ICP-MS).

2. Experimental

2.1. Reagents

All reagents used were the purest available. Ultra high purity (UHP) water (Millipore Milli-Q Academic with Ultrapure Ionex Cartridge; 18 MΩ cm) was used exclusively for all dilutions and cleaning steps. Quartz (Q) grade HCl and HNO_3 were prepared in-house from trace metal grade (TMG) HCl and HNO_3 by sub-boiling distillation in a quartz still. Likewise, TMG 99.5% acetic acid (CH_3COOH, 17.4 M) was purified by quartz distillation; Optima™ grade 21% ammonium hydroxide (NH_4OH, 11 M) was purchased (Fisher Scientific). All plastic (LDPE, PTFE) materials (bottles, tubing, fittings, etc.) were acid cleaned prior to use.

Toyopearl AF-Chelate 650 M® resin (65 μm; Tosoh Bioscience LLC, #14475) was used for Pb extraction. This iminodiacetate-based cation exchange resin has been utilized successfully to extract both metals and rare earth elements from seawater for concentration analysis using micro columns in automated systems [20,21]. Prior to use, the resin was cleaned by mixing ~5 mL of stock slurry with 25 mL of 0.8 M TMG HNO_3 in an LDPE bottle, shaking the mixture for 1 h, letting the particles settle by gravitation, and decanting the acid. The resin solution was rinsed with UHP water until the pH was raised to 5. The clean resin was then stored in a refrigerator to inhibit bacterial growth.

Sample pH was adjusted with a 10 M ammonium acetate solution. This solution was prepared with 485 mL of NH_4OH and 238 mL of CH_3COOH in a total volume of 1 L, adjusted to a final pH of 9.50 ± 0.05. Prior to use, the solution was passed twice through a "clean up" column filled with Toyopearl AF-Chelate 650 M® resin, providing a significant reduction in the blank. Column wash was prepared as a 1:10 dilution of this cleaned solution in UHP water.

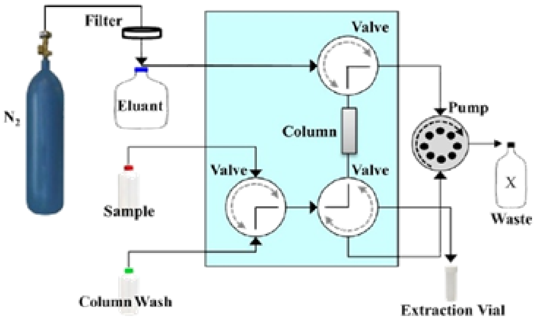

Fig. 1. A schematic representing one of the four offline Pb extraction setups, as described in Section 2.2. The sample Pb is loaded on a column, the column is flushed with column wash to minimize salts, and the Pb is eluted to a vial for analysis.

2.2. Online setup

The semi-automated system was operated in a HEPA filtered air (Class 100) laminar flow hood in a trace metal clean laboratory. The set-up was built with four parallel lines to process four separate extractions at a time. It consisted of four parallel columns, sample bottles (500 mL) and extract bottles (7 mL), linked to a common column wash (500 mL) and an eluant bottle (2 L). It was controlled by four-port switching valves (Upchurch Scientific, #V-101 L), connected with Teflon tubing (1.59 mm I.D.) and flangeless Teflon ferrules with nuts (Western Analytical #P245x, #P200Nx). Fig. 1 shows a simplified representation of the system with 1 line.

Cleaned resin was used to fill columns made in-house. These columns were made from 4 mm internal diameter (I.D.) Teflon tubing that was cut to 2 cm lengths, fitted with 3.2 mm thick frits (pore size <50 μm) on both ends. This gave an effective volume of 0.05 cm^2 for each column, which was packed with 60 ± 5 mg of Toyopearl resin. These columns were connected to Teflon tubing (1.59 mm I.D.) using Teflon compression reducing unions (Cole Parmer, #EW-06391-75), and connected to the online system.

The flow of solutions through the extraction system was driven by two different mechanisms. Sample and column wash were drawn through the system using a peristaltic pump (Masterflex Console drive model 7521-50, Cole Parmer) programmed to run using a timed digital controller (Fisher Scientific, #06-662-24). Both solutions could flow across the column and then pass through the manifold pump tubing (1.14 mm; Fisher Scientific #14190507) to waste, avoiding the addition of contamination from the pump tubing. The eluant acid (1.5 M Q HNO_3 + 15 nmol kg^{-1} Tl) was set up to be pushed through the column by N_2 gas at 5 psi. The gas first passed through a 0.2 μm PTFE vent filter (Pall Corporation #4401) to prevent particulate contamination of the acid.

After assembly the entire setup was thoroughly cleaned. First, the system was slowly flushed with 6 M TMG HNO_3 for 1 h (flow rate 0.83 mL min^{-1}). The lines and column were then filled with 1.5 M Q HNO_3 and left to soak for 1 week. Finally the system was flushed with additional 1.5 M Q HNO_3 for 30 min (flow rate 0.83 mL min^{-1}).

2.3. Extraction procedure

An appropriate volume of seawater to yield 1 ng of Pb (50–500 mL) was calculated based on a previous analysis of Pb concentration [20]. Seawater samples, previously acidified to 24 mM HCl and stored, were brought to pH ≈ 5 by adding 10 M ammonium acetate solution at a ratio of 100 mL sample:1 mL solution just prior (<1 h) to extraction.

Before each extraction, the system was cleaned and conditioned. Each column was washed with 7.5 mL of 1.5 M Q HNO_3 which flowed through the sample line, across the column, and to the waste. The columns were then conditioned with 8 mL of UHP water followed by 4 mL of column wash, each, which flowed through the wash line, over the column, and to the waste. The sample lines located before the columns were then flushed with 1.3 mL of sample which flowed through the sample line and directly to waste.

At that time, the samples were pumped across the column and to waste at a rate of 2 mL min^{-1}, allowing Pb to bind to the resin while matrix salts were flushed through. When the samples had loaded, 8 mL of column wash flowed across each column to waste. Lastly, the eluant was pushed across the columns into the extraction vials at ~1 mL min^{-1}, moving the Pb off the resin and into the extract. Roughly 1 mL of eluant was collected resulting in a ~5 nmol kg^{-1} extract.

After each extraction, the system was cleaned. First, 45 mL of 6 M TMG HNO_3 was flushed through each sample line, across the column, and to the waste. Then, the eluant line was re-opened so that 3 mL of 1.5 M Q HNO_3 flowed across the columns to waste extraction vials. Additional extractions were then performed, or if the system remained unused for greater than 1 week the sample-column-waste lines were filled with 0.2 M Q HNO_3 to prevent bacterial growth on the resin.

The total time required for an extraction depended on the volume of sample processed. Including the cleaning stage between extractions, this time ranged from 2.5 h for 50 mL of seawater to 6.5 h for 500 mL.

2.4. HR ICP-MS

Analyses were made on a Thermo Element XR HR ICP-MS (magnetic sector) located in the Marine Analytical Laboratory at UC Santa Cruz. The instrument was equipped with an "H" skimmer cone and a standard interface pump (30 $m^3 h^{-1}$). The samples were nebulized in an ESI-PC^3 Peltier cooling spray chamber at 4 °C at 120 μL min^{-1}. The HR ICP-MS was tuned prior to each instrument session by adjusting the torch position, the sample gas (Ar) flow rate (~0.75 L min^{-1}), and additional Ar gas (~0.19 L min^{-1}). The signal of the ^{208}Pb for a 5 nmol kg^{-1} solution was typically $2.0 \pm 0.3 \times 10^6$ counts per second, an efficiency of 0.06%.

All four stable lead isotopes were analyzed (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb), while ^{200}Hg and ^{202}Hg were monitored for isobaric interference correction of the 204 counts, and ^{203}Tl and ^{205}Tl were monitored for mass bias corrections. Samples were analyzed in low resolution mode and consisted of the integration of 10 runs comprised of 20 scans with the detector held in counting mode. Each scan was 0.40 s, and total sample processing time including uptake, analysis, and flushing out the sample line was approximately 3 min, consuming $\leq$0.35 mL of sample.

Detector dead time was characterized during each measurement session. NIST SRM-981 common lead isotopic standard (wire dissolved in Q HNO_3) was analyzed at varying concentrations and a dead time that minimized the slopes of the $^{208}Pb/^{206}Pb$, $^{208}Pb/^{207}Pb$ and $^{208}Pb/^{204}Pb$ isotope ratios versus concentration was chosen (as in Nelms' Method 2 [22]). This was usually 1–9 ns.

2.5. MC-ICP-MS

In order to explore analytical improvement with a multi-collector instrument, several replicate analyses of the HR ICP-MS measurements were made on a ThermoFinnigan Neptune MC-ICP-MS located in the W.M. Keck Isotope Laboratory at UC Santa Cruz. Similar to the single collector, this instrument was equipped with a standard interface pump (30 $m^3 h^{-1}$); enhanced sensitivity was achieved using the "X" skimmer cone. The samples were drawn through a Cetac MCN 6000 micro concentric nebulizer (spray chamber 85 °C, desolvator 160 °C) at 100 μL min^{-1} by Ar sample gas (1 L min^{-1}) and an additional Ar sweep gas (4 L min^{-1}).

Table 1
MC-ICP-MS cup configuration (measured displacements, in mm, of the Faraday cups on each side of the center "C" cup) for Pb isotope analyses.

	L3	L2	L1	C	H1	H2	H3
Isotope	^{202}Hg	^{203}Tl	^{204}Pb	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb
Position	28.400	17.720	7.000	–	7.460	17.755	28.206

Prior to each instrument session, gain and baseline calibrations were performed. Additionally, the instrument was tuned each day by optimizing gas flow rates as well as the source lenses, peak shape, and the inlet system settings. The typical beam on ^{208}Pb for a 5 nmol kg^{-1} solution was 370 mV, an efficiency of 0.9%.

The cup configuration, or measured displacements of the Faraday cups, was set with seven isotopes in one line (Table 1; ^{200}Hg was not monitored). Sample measurements, made in low resolution mode, were 1 block of 50 cycles, with each cycle consisting of 1 integration lasting 4.194 s. Electronic baselines (30 cycles of 1.05 s each) and peak centering were performed prior to the analysis of each sample. The typical take-up, analysis, washout sequence time was 7 min, consuming <0.6 mL of sample. Output data were corrected online for the amplifier gains and baseline.

2.6. Corrections

Data from both instruments were corrected offline for ^{204}Hg isobaric interference on ^{204}Pb, instrument blank, and mass bias. First, the HR ICP-MS ^{200}Hg and ^{202}Hg counts were checked for agreement, assuming natural abundances of 23.096% and 29.863%, respectively. ^{204}Hg was calculated from ^{202}Hg assuming a natural abundance of 6.865%, and this signal was subtracted from the total $^{204}(Hg + Pb)$ counts to yield counts of ^{204}Pb. Next, the blank – the average of all 1.5 M Q HNO_3 analyzed throughout the analyses on a given day – was subtracted from the samples. Last, the data were corrected for mass bias.

Mass bias corrections for the HR ICP-MS were investigated using the exponential law and normalization to Tl. However, the non-log-linear relationship between $^{203}Tl/^{205}Tl$ to any Pb ratio (Fig. 2a) demonstrated that this correction scheme did little to improve the accuracy of the Pb isotope ratios and made the internal precision worse. As a result, mass bias was corrected by normalization to the accepted NIST SRM-981 values (Table 4 [23]). Because the mass bias of the HR ICP-MS did not drift in a linear fashion over the course of an analysis (Figs. 2 and 3), samples were not corrected by bracketing to NIST SRM-981 values, but rather by normalization on a per ratio basis to the average percent difference between all measured NIST SRM-981 values throughout a run and the accepted value. NIST SRM-981 was analyzed 5–10 times per hour (between every 1 to 3 samples).

Conversely, mass bias on the MC-ICP-MS was well characterized by Tl (Fig. 2b). Corrections for the MC-ICP-MS were done using the exponential law and $^{203}Tl/^{205}Tl = 2.3888$. In addition, samples were corrected using the average percent difference between accepted and analyzed Pb isotope ratios of NIST SRM-981 (Fig. 3).

3. Results and discussion

Unless otherwise noted, all statistics reported here are within the 95.4% confidence interval (2σ), and $x \pm y$ represents the average plus or minus 2 standard deviations.

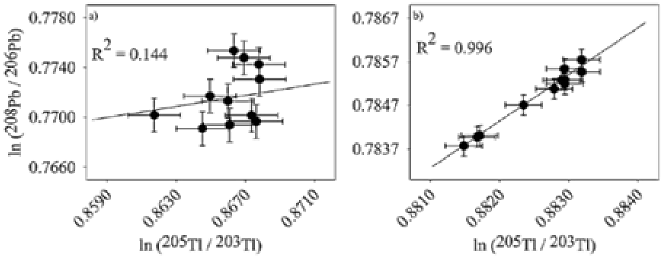

Fig. 2. The log-linear relationship between $^{205}Tl/^{203}Tl$ and $^{208}Pb/^{206}Pb$ for analyses on the (a) HR ICP-MS shows that Tl does not characterize mass bias in an accurate way, whereas (b) analyses on the MC-ICP-MS show that Tl and Pb have a clear relationship and mass bias can be accurately described.

Table 2
Blanks and recoveries associated with various methods for extracting stable Pb isotopes from seawater.

Method	Pb blank (pmol kg^{-1})	Pb blank (pg)	% yield	Source
Dithizone organic solvent	28	620	–	Patterson and Settle [6]
APDC organic solvent	28	6000	93%	Munksgaard et al. [10]
Chelex-100 resin	14–48	10–30	96%	Reimer and Miyazaki [14] and Miyazaki and Reimer [15]
I-8-HOQ resin	27	27	95%	Halicz et al. [13]
$MgOH_2$ co-precipitation	1	6	90%	Weiss et al. [17] and Wu and Boyle [25]
$MgOH_2$ + AG1 X8	0.01–0.12	1–20	100%	Boyle et al. [3], Reuer et al. [16], Wu et al. [18]
Toyopearl resin	0.1 ± 1.3	1–30	92 ± 13%	This method

– denotes unknown value.

Table 3
Precision (2σ) and accuracy of analyses of NIST SRM-981 spiked into 300 mL and 400 mL Pb-free seawater, respectively (extracts = 5 nmol kg^{-1}).

	HR ICP-MS				MC-ICP-MS			
	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	*n*	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	*n*
Internal precision	3.5‰	2.2‰	9.3‰	25	0.6‰	0.2‰	0.7‰	4
External precision	4.8‰	6.0‰	6.3‰	94, 6 days	2.5‰	3.1‰	2.8‰	19, 3 days
Accuracy[a]	99.6%	99.8%	99.7%	3	99.9%	99.8%	89.6%	3

[a] For accuracy tests, the same extracts were measured on both instruments to ensure no changes in chemistry or blank occurred and that differences were in the accuracy of instrumental measurements.

3.1. Blanks

The combined system and reagent blank was evaluated by treating UHP water as a sample. The extracted blanks were doped with a well characterized ^{208}Pb spike and analyzed, giving an accurate value for the 1–30 pg Pb blanks. When normalized for the volume of UHP water concentrated (100–250 mL), the blanks were 0.1–1.3 pmol kg^{-1} ($n = 61$), corresponding to 0.02–2% of a 5 nmol kg^{-1} sample extract. This blank is relatively low compared with other methods (Table 2).

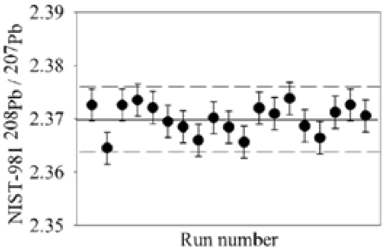

Fig. 3. Repeat measurements of NIST SRM-981 over the course of a day on the HR ICP-MS shows no clear pattern in drift. The solid line represents the average of the data while the dashed lines represent 2σ.

3.2. Pb elution

Lead elution and recovery were checked to ensure the column functioned properly. First, Pb-free seawater was produced by adjusting the pH of 1 L of open ocean water to pH ~ 5 with the 10 M ammonium acetate solution, 400 mg of Toyopearl resin was added and the bottle was shaken for 24 h. After settling, the Pb-free seawater was decanted and spiked with NIST SRM-981 which was loaded onto the column and eluted in small (~0.1 mL) increments. These fractions showed that >99% of the Pb recovered was eluted from the column in the first 1 mL (Fig. 4), confirming that this was a sufficient volume of eluant for collecting the sample extracts. Typical

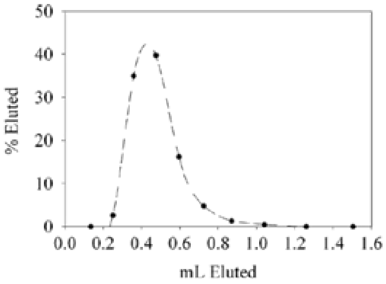

Fig. 4. Elution curve of NIST SRM-981 spiked into Pb-free seawater.

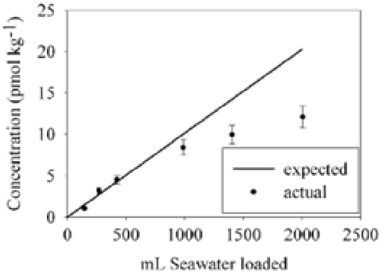

Fig. 5. Recovery of NIST SRM-981 in various volumes of seawater, showing 65 mg of Toyopearl resin in the columns has a saturation capacity of just less than 1000 mL of seawater. Therefore, seawater concentrations as low as ~1 pmol kg^{-1} Pb can be extracted with these columns.

recoveries were 92% ± 13% ($n = 6$). This is comparable to other methods which had 92 ± 10% [24], 96% [14], 95 ± 3% [13], and 90 ± 0.05% [25] recoveries (Table 2). For the precision achieved in this work, any fractionation due to <100% recovery is minimal as evidenced by spiking NIST SRM-981 into Pb-free seawater and processing it as a sample (Section 3.4).

3.3. Resin saturation

Resin saturation with salts and other metals would result in ≪100% yield. To test the capacity of the resin, 100–2000 mL aliquots of NIST SRM-981 were spiked into Pb-free seawater and extracted (Fig. 5). From this, it appears that 65 mg of Toyopearl resin reaches saturation after ~1000 mL of seawater is loaded. These columns are capable of extracting a sufficient amount of Pb for isotope analysis in seawater samples with ≥1 pmol kg^{-1} Pb. For applications requiring greater than 1000 mL to be concentrated, samples should be divided in two or more extractions. However, most samples require <500 mL of seawater to provide 1 ng of Pb, so very few samples would need to be split. Alternatively, columns with a greater resin capacity could be built, and the volumes of solutions used for the extraction adjusted to the new quantity of resin.

3.4. Precision and accuracy

Replicate analyses of NIST SRM-981 extracted from 300 mL of Pb-free seawater were used to establish the precision of the measurements. On the HR ICP-MS, typical internal precision for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, ^{206}Pb/^{204}Pb was 3.5‰, 2.2‰, and 9.3‰, respectively ($n = 25$; Table 3). External precision (over 6 days) of NIST SRM-981 measurements for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, ^{206}Pb/^{204}Pb was 4.8‰, 6.0‰, and 6.3‰, respectively ($n = 94$; Table 3). These figures compare well with other measurements; the average external precision for ^{206}Pb/^{207}Pb of other ICP-MS (quadrupole and magnetic sector) instruments is ~5.0‰ [13,15,17,26,27]. For multi-collector instruments external precision for ^{206}Pb/^{207}Pb is typically much better, on average 0.2‰ for both TIMS [28–32] and MC-ICP-MS [16,23,33–36].

Accuracy was determined by comparing the difference between the accepted value of NIST SRM-981 and measurements of NIST SRM-981 spiked into 400 mL of Pb-free seawater and processed through the extraction procedure like a sample. The accuracy of ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, ^{206}Pb/^{204}Pb was 99.6%, 99.8%, and 99.7%, respectively ($n = 3$; Table 3). These differences from the accepted values were statistically insignificant ($p < 0.025$, t-test) given the precision limits of the instrument.

3.5. HR ICP-MS versus MC-ICP-MS

MC-ICP-MS is advantageous, in part, because of its enhanced precision for all isotope ratios. The viability of analyzing 5 nmol kg^{-1} extracts was investigated by spiking NIST SRM-981 into Pb-free seawater and extracting it as a sample. These extracts were all found to have much greater precision than 5 nmol kg^{-1} solutions on the HR ICP-MS (Table 3). Internal precision for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb was 0.6‰, 0.2‰, and 0.7‰, respectively ($n = 4$). External precision (over 3 days) for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb was 2.5‰, 3.1‰, and 2.8‰, respectively ($n = 19$). These values were 2–20 times better than the precision measurements on the HR ICP-MS. The accuracy of the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios (99.9% and 99.8% respectively) on the MC-ICP-MS was statistically the same ($p < 0.025$, t-test) as the accepted value for NIST SRM-981. However, the accuracy of the ^{206}Pb/^{204}Pb ratio (89.6%) was statistically different ($p < 0.025$, t-test) than the accepted value.

In a 5 nmol kg^{-1} solution, the 204 beam is ~6 mV. While the measurements are very reproducible as evidenced by the high precision, the low intensity signal, potentially variable blank and subsequent ^{204}Hg correction results in inaccurate results. A difference as small as 0.1 mV in the mass 204 measurement produces a change of 4% in the final, corrected ^{206}Pb/^{204}Pb ratio. This problem could be resolved by analyzing a greater concentration sample, or analyzing mass 204 with an ion counter. Higher concentrations (25 nmol kg^{-1}) of Pb in the extract were analyzed and did have improved accuracy, but the volume of seawater required to provide that much analyte is often unavailable in oceanographic research. We also tried shifting the cup configuration so that mass 204 was in the center cup (the only cup equipped with an ion counter on our ThermoFinnigan Neptune), but due to cup motor limits we were unable to simultaneously analyze mass 208. Analyzing all 7 isotopes in "dynamic mode" requires more than twice as much analyte per analysis, which requires twice as much seawater sample. Newer MC-ICP-MS models are often equipped with multiple ion counters, and thus able to circumvent this problem.

Analysts are then left to decide what is more valuable for their purposes: high precision ^{206}Pb, ^{207}Pb, ^{208}Pb values or compromising precision for the ^{204}Pb value. In a survey of 151 Pb deposits, Sangster et al. [37] found that a majority of the discriminating power in source determination (86%) comes from the ^{206}Pb, ^{207}Pb, and ^{208}Pb values; only a small proportion of environmental samples require ^{204}Pb to identify sources. For the purposes of exploring the merits of this new extraction technique, all further analyses were carried out using the HR ICP-MS.

3.6. GEOTRACES intercalibration seawater

The data generated by this method was evaluated by processing several GEOTRACES intercalibration samples. These include surface ("GSI", 7 m) and deep ("GDI", 2000 m) water as well as a full depth profile ("GPrI"). Replicate extractions and analyses ($n = 2$–5) of all 10 samples were done. To date, Pb isotopes in the GEOTRACES intercalibration samples have been reported by one other group at MIT [3]. Although our results have relatively larger errors associated with them than the MIT group, this disparity is almost certainly because our analyses were made on an HR ICP-MS while MIT used an MC-ICP-MS in conjunction with a Daly-style ion counting unit. Within error, most of our samples agree with the previously published data (Table 4, Fig. 6). Moreover, a consensus value will remain uncertain until further analyses are performed by more groups.

Table 4
Analyses of GEOTRACES intercalibration samples surface water (GSI), deep water (GDI), and the IC1 (GPrI) profile at BATS (31.67°N, 64.17°W) sampled in 2008. Note the precision values are standard error (2σ) for n analyses. Comparison data are available in Boyle et al. [3].

Sample	Depth (m)	Pb (pmol kg^{-1})[a]	^{206}Pb/^{207}Pb		^{208}Pb/^{207}Pb		^{206}Pb/^{204}Pb		n[b]
			avg	2 s.e.	avg	2 s.e.	avg	2 s.e.	
GSI	7	22.7 ± 5.7	1.1742	0.0013	2.4466	0.0024	18.31	0.05	4
GDI	2000	41.5 ± 7.5	1.1831	0.0007	2.4517	0.0064	18.46	0.04	5
GPrI	75	22.4	1.1757	0.0013	2.4497	0.0021	18.38	0.12	3
GPrI	125	20.5	1.1766	0.0007	2.4495	0.0018	18.41	0.01	3
GPrI	250	23.2	1.1780	0.0015	2.4498	0.0010	18.44	0.04	3
GPrI	500	29.6	1.1799	0.0010	2.4467	0.0037	18.45	0.03	3
GPrI	1000	35.3	1.1854	0.0005	2.4542	0.0021	18.55	0.08	3
GPrI	1500	36.3	1.1848	0.0005	2.4549	0.0008	18.50	0.02	3
GPrI	2500	23.2	1.1822	0.0009	2.4497	0.0045	18.42	0.05	2
GPrI	3500	16.1	1.1816	0.0031	2.4555	0.0031	18.44	0.05	3
NIST SRM-981 accepted value [23]			1.0931		2.3696		16.94		

[a] Measured as in Ndung'u et al. [20].
[b] Number of analyses.

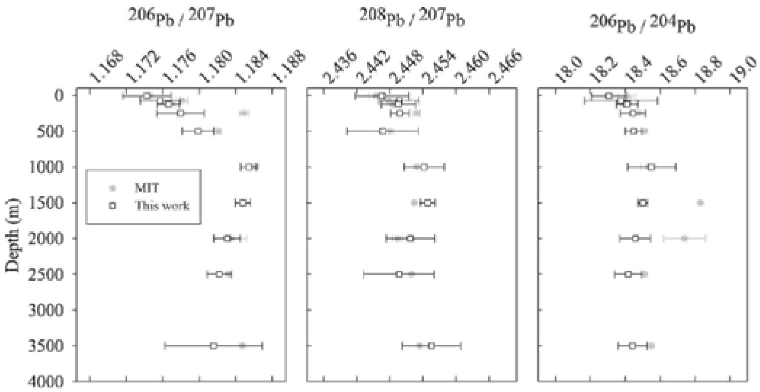

Fig. 6. The GEOTRACES Intercalibration 1 station (BATS, Atlantic Ocean) data for the method presented here (white squares) and values previously reported by MIT researchers (gray circles) [3]. Error bars represent 2σ on analyses of replicate extractions.

4. Conclusion

The extraction technique described here has a low blank comparable to the $MgOH_2$ co-precipitation method [16,17,38] and is also highly efficient, like other resin-based extraction techniques [12–15]. Additionally, the method is capable of extracting Pb from a large (1000 mL) volume of seawater. While better precision is achieved using an MC-ICP-MS, isotope analyses on the available MC-ICP-MS at UC Santa Cruz are limited to ^{206}Pb, ^{207}Pb, and ^{208}Pb in extracts <25 nmol kg^{-1}. This challenge could be overcome by utilizing a MC-ICP-MS with ion counter(s) in conjunction with Faraday cups, which would allow for highly precise and accurate analyses of all four stable Pb isotopes. This said, the precision and accuracy of analyses by HR ICP-MS on 5 nmol kg^{-1} extracts is scientifically useful and sufficient for differentiating Pb origins in the North Pacific Ocean [39] using all four stable isotopes of Pb.

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CHAPTER 3. ASIAN INDUSTRIAL LEAD WITHIN THE NORTHWEST PACIFIC OCEAN EVIDENCED BY LEAD ISOTOPES IN SEAWATER

Cheryl M. Zurbrick, Céline Gallon and A. Russell Flegal

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Abstract

We found continued lead (Pb) contamination of the Northwest Pacific Ocean in 2002 which was attributed to Chinese industrial emissions. Elevated Pb concentrations (64 – 113 pmol kg^{-1}) in the Kuroshio Current and subsurface North Pacific Subtropical Gyre (NPSG) corresponded to ^{206}Pb/^{207}Pb ratios (1.160 – 1.170) which were similar to industrial Pb aerosols over China. Those aerosols were previously attributed to the large quantity of Pb contained in coal consumed by China (30% of global total in 2000 – 2002). In water depths greater than 1,000 m the Pb concentrations (6 – 37 pmol kg^{-1}) were lower. The ^{206}Pb/^{207}Pb isotope ratios of this deep water were relatively lower (1.170 – 1.185) in the Western Subarctic Gyre (WSAG) than in the NPSG (1.176 – 1.194). Previously reported data regarding aerosol Pb inputs to surface waters and particle fluxes were used to calculate a ~ 200-fold relative difference in the flux of Pb to WSAG deep water versus NPSG deep water. This larger flux to the WSAG supports our observations of deep water in the WSAG reflecting modern Asian Pb inputs and Pb isotope ratios which change on the timescale of several years to a decade, while the NPSG changes on the timescale of a century.

1. Introduction

Despite the essentially global phase-out of leaded gasoline over the past four decades, there has not been a dramatic decrease in lead (Pb) concentrations in North Pacific surface waters similar to that observed in the North Atlantic Ocean. [1–3] That disparity may be due, in part, to the lower surface water Pb levels in the North Pacific (~ 60 pmol kg^{-1}) prior to the phase-out of leaded gasoline in North America and Europe [4] compared with surface water in the North Atlantic Ocean (~160 pmol kg^{-1}) at that time. [5] However, it was commonly assumed that there would still have been a large decrease in Pb concentrations following the elimination of leaded gasoline in both North America in the 1990s and Asia in the proceeding decade.

Subsequent measurements of Pb in the central North Pacific Ocean documented a surprisingly limited and relatively constant range of surface water concentrations from 30 – 50 pmol kg^{-1}. [1, 2, 6–8] The minimal decrease observed has been attributed to the phase-out of leaded gasoline in Japan by the 1990s and in smaller part North American countries. [2, 9] This persistence can somewhat be attributed to the fact that many Asian countries (e.g., China) did not phase out their use of leaded-gasoline until mid-2000. [10] An alternative hypothesis is that other sources are emitting increasing amounts of Pb to the North Pacific Ocean.

The phase-out of leaded gasoline eliminated contributions from China's single largest atmospheric Pb source at that point in time. [10] However, the rapid industrialization of many Asian countries that began in 2000 and continues today has increased the Pb aerosol emissions from industrial processes and coal combustion. Countries such as India, Indonesia, the Philippines, and South Korea have all more than doubled the amount of coal consumed between 1990 and 2011. [11] China's increase in both coal production and consumption more than tripled during this same time period, and in 2011 was responsible for 49% of the coal consumed globally – highlighting the major changes happening in that region of the world (Figure 1). As a result, the aerosol Pb emissions from power generation and industrial activities in China are nearing their pre-2000 levels, [10, 12] in spite of the limited emissions controls instituted in China in 2005. [12] Due to the high density of metal smelters and coal consumption in the eastern provinces of China, [10, 12] prevailing winds blow Pb into the Northwest Pacific Ocean or further. [1, 13, 14]

Studies conducted prior to the rapid acceleration in Asian industrialization documented Pb aerosol concentrations of 0.03 – 0.32 ng m^{-3} at Enewetak Atoll (11.34˚N, 162.34˚E) in the western North Pacific Ocean. [6, 15] Experiments on the solubility of aerosol Pb found that 60 % – 90 % of it was readily soluble. [16] Maring and Duce also found that Pb from Asian emissions was more soluble in seawater than aerosol Pb from North and Central American sources, possibly due to differential transformation of Pb speciation during atmospheric transport. [16] Based on these observations, Duce [17] estimated the flux of aerosol Pb near the Asian continent (100 µg m^{-2} yr^{-1}) to be 10 times higher than the flux of aerosol Pb to the central North Pacific Ocean (100 µg m^{-2} yr^{-1}).

In 2002, Gallon et al. [1] found total aerosol Pb concentrations ranging from 0.02 – 5.5 ng m^{-3} between the Asian mainland and central North Pacific Ocean. These highly variable concentrations were, in part, attributed to the limited sampling period, episodic nature of seasonal dust storms, and varying distances from Asia. [13] Regardless, the highest Pb concentrations were attributed to industrial Pb emissions from Asia, [1] indicating that current oceanic inputs from Asian industrial Pb emissions are similar in magnitude to what they were when leaded gasoline was still being used in Asian countries.

Recent seawater data collected for this region in 2002 – 2005 support the proposal that on-going industrial Pb emissions from Asia are now comparable to previous emissions of leaded gasoline. Wu et al. [8] determined that there were similar Pb concentrations (25 – 50 pmol kg^{-1}) in North Pacific Subtropical Gyre (NPSG) surface waters in 2004 – 2005 as previous cruises in 2002 (30 – 50 pmol kg^{-1}) [1] and in 1979 (30 – 60 pmol kg^{-1}). [7] Dissolved Pb in oceanic surface waters has an estimated ~ 2 year residence time. [18] Therefore, the sustained elevation of Pb concentrations in the NPSG must be from Pb inputs to surface waters since the phase-out of leaded gasoline. Further to the west, the Pb concentrations of surface waters in the Kuroshio Current were found to be much higher (> 100 pmol kg^{-1}) than the NPSG. [1] This spatial difference in Pb concentrations was attributed to the proximity of the Kuroshio Current to the Asian continent, [1] which has higher dust inputs and therefore higher Pb inputs. [17]

Stable Pb isotope data further validated Gallon et al.'s attribution of Pb to Asian sources. Gallon et al. [1] reported $^{206}Pb/^{207}Pb$ isotope ratios (1.157 – 1.161) in the surface waters of the Kuroshio Current, which closely matched that of aerosols measured over mainland Asia ($^{206}Pb/^{207}Pb \approx 1.16$), predominantly China. [19, 20] In addition, they found Asian Pb isotope signatures in surface waters of the Western Subarctic Gyre (WSAG; ^{206}Pb/^{207}Pb = 1.157 – 1.162) and the NPSG (^{206}Pb/^{207}Pb = 1.163 – 1.169) in 2002. The more recent ^{206}Pb/^{207}Pb isotope ratios are in contrast to the surface water ^{206}Pb/^{207}Pb isotope ratios of the NPSG measured in 1979 (1.184-1.196). [6, 7] At that time, Flegal et al. [7] attributed the major sources of Pb to the NPSG to emissions of leaded gasoline in North America and Asia.

While there have been very few measurements of Pb concentrations in North Pacific surface waters, there have been even fewer measurements of those concentrations in subsurface waters in the North Pacific Ocean. The lone stable Pb isotope profile in the NPSG, collected in 2004, was used in conjunction with concentration profiles in a mixing model as evidence that anthropogenic Pb emissions from Asia have begun to impact abyssal waters. [8] They found ^{206}Pb/^{207}Pb ratios (1.18) in deep waters were lower than the background ^{206}Pb/^{207}Pb ratios (1.20 – 1.21) of sediments in the same region.

With the rapid industrialization of Asia as evidenced by China’s coal consumption, there is concern over the continued Pb input to the ocean. In this work, we analyzed the Pb concentrations and isotope ratios at 9 vertical profiles. These measurements were then compared with the known isotope signatures of potential Pb sources in order to examine the influence of Chinese Pb to the subsurface waters of the North Pacific.

2. Experimental Section

Seawater samples were collected from 1 May to 3 June, 2002, aboard the R/V Melville during the Intergovernmental Oceanographic Commission's 4th Global Investigation of Pollution in the Marine Environment expedition (Figure 2). This cruise began offshore of Japan and had stations in both the Western Subarctic Gyre (WSAG) and the North Pacific Subtropical Gyre (NPSG). During this transect, waters were also sampled in the Kuroshio Current, Oyashio Current and Kuroshio Extension.[21]

Subsurface waters were collected at 9 vertical profile stations using 30 L GOFLO ™ bottles, which were modified for trace metal clean sampling, hung on a Kevlar ® line. [22] Unfiltered subsamples were taken in an onboard trace metal clean laboratory under HEPA filtered air (Class 100) and collected in acid-cleaned 2 L low-density polyethylene bottles. Samples were acidified to pH ≈ 2 using ultrapure (sub-boiling quartz distilled) HCl.

Lead concentrations in seawater were measured at the UC Santa Cruz Marine Analytical Lab using an on-line chelating resin extraction [23] connected to a Thermo ELEMENT XR™ magnetic sector high resolution inductively coupled plasma mass spectrometer (HR ICP-MS) as detailed in Zurbrick et al. [24] The Pb procedural blanks, which were analyzed concurrently, were < 6 pmol kg^{-1}, the precision was ≤ 5 %, and the detection limit was ≤ 5 pmol kg^{-1}. The inter-laboratory reproducibility (analytical and across subsamples) of these Pb concentration measurements was ≤ 15%, based on intercalibration with Bill Landing's laboratory at Florida State University and Alan Shiller's laboratory at the University of Southern Mississippi. [24]

Lead isotopes in these samples were processed and subsequently analyzed at the UC Santa Cruz Marine Analytical Lab using the method of Zurbrick et al. [25] Briefly, Pb was extracted from seawater (50 – 800 mL) using Toyopearl AF-Chelate 650 M ™ ion-exchange resin and eluted in a 1 mL extract of ultrapure 1.5 N HNO_3; the Pb concentration in these extracts was ~ 5 nmol kg^{-1}. Extraction blanks comprised of ultra high purity (18 MΩ cm) water (Millipore Milli-Q ® Academic with Ultrapure Ionex Cartridge) acidified to pH ≈ 2 were $\leq$ 30 pg (0.1 – 1.3 pmol kg^{-1}). The extracts were analyzed by the HR ICP-MS in counting mode. Measurements of ^{204}Pb were corrected for isobaric interferences from ^{204}Hg by monitoring ^{202}Hg and assuming natural abundances of mercury isotopes ($^{204}Hg/^{202}Hg = 0.22988$). Isotope ratios were calibrated with concurrent measurements of National Institute of Standards and Technology (NIST) standard reference material 981 (common lead). [25] Replicate extractions and analyses of samples (n = 2 – 9) produced data with average standard errors (2 σ) of 2‰, 4‰, and 74‰ for $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$ respectively. This precision agreed well with our previously reported reproducibility for GEOTRACES intercalibration seawater. [25]

3. Results and Discussion

The Pb concentrations and isotope ratios showed similar trends across the entire cruise track (Figures 3, 4). Waters with elevated Pb concentrations (64 – 113 pmol kg^{-1}) had low $^{206}Pb/^{207}Pb$ ratios (1.157 – 1.167), whereas waters with relatively lower Pb concentrations (6 – 37 pmol kg^{-1}) had higher $^{206}Pb/^{207}Pb$ ratios (1.170 –

1.194). In addition, the Pb concentrations and ^{206}Pb/^{207}Pb ratios were both correlated with depth (r = -0.73 and r = 0.71, respectively, Pearson's correlation).

3.1 Subsurface Waters

The most striking feature of the Pb distribution was the subsurface Pb maxima that persisted throughout the Kuroshio Current, its Extension and the NPSG. In the Kuroshio Current near the coast of Japan, elevated Pb concentrations (78 – 113 pmol kg^{-1}) extended to a depth of 500 m (station 1; Table 1). The corresponding ^{206}Pb/^{207}Pb isotope ratios in the Kuroshio Current were low (1.160 – 1.167), and ^{208}Pb/^{206}Pb ratios were high (2.104 – 2.112). Similar concentrations and isotope ratios were observed in the surface and subsurface waters offshore, where the Kuroshio and Oyashio Currents mixed (station 4) and in the Kuroshio Extension (stations 5, 6). The Pb concentrations decreased as the water mass diffused to the east (station 7, 8, 9), but the ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios maintained values similar to the Kuroshio Current (1.160 – 1.170; 2.099 – 2.111). This subsurface Pb maxima was also observed by Wu et al. [8] At a nearby station (30˚N, 140˚W) in October 2004 they found a low ^{206}Pb/^{207}Pb isotope ratio (1.159) that corresponded with a subsurface dissolved Pb maxima (73 pmol kg^{-1}) between 200 – 400 m depth.

Of note, the 20 m sample at station 5 had the highest Pb concentration of the entire dataset, and anomalous ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios. The authors found the isotope ratios were not an analytical artifact through replicate measurements, and decided the distinct values were a result of bottle or sampling contamination. As such, this data point was not included in the interpretation of these data.

The subsurface Pb maxima contrasted with the surface waters (upper 100 m) of the NPSG which had lower Pb concentrations (35 – 75 pmol kg^{-1}). In addition, the NPSG surface waters had ^{206}Pb/^{207}Pb isotope ratios (1.161 – 1.800) which were slightly elevated and ^{208}Pb/^{206}Pb isotope ratios (2.080 – 2.110) which were slightly lower than the subsurface Pb feature. In the depths below the subsurface maxima (> 500 m), the concentrations of Pb decreased to less than 60 pmol kg^{-1} and there was a corresponding change in ^{206}Pb/^{207}Pb ratios to greater than 1.172 and ^{208}Pb/^{206}Pb ratios to less than 2.090.

The WSAG was the only region of the Northwest Pacific Ocean where the subsurface Pb concentration maxima was not observed, with Pb concentrations of 54 – 83 pmol kg^{-1}. While this water mass is very different from the Kuroshio Current because it is dominated by upwelling conditions throughout the year, [26, 27] its isotope ratios (^{206}Pb/^{207}Pb = 1.158 – 1.170, ^{208}Pb/^{206}Pb = 2.095 – 2.117) were similar to those of the other subsurface waters collected on the cruise. The similarity in Pb isotope ratios suggested that the dominant source of Pb in WSAG surface waters was the same source as the rest of the subsurface waters in the Northwest Pacific Ocean.

Previous work has shown that atmospheric deposition is the major contributor of Pb to North Pacific waters. [28, 29] Because of the relatively short residence time of dissolved Pb in oceanic surface waters (< 2 years) [18] and particles in the euphotic zone (~ 1 week) [30, 31] we focused on the most recent aerosol data available, generally 1998 or later. From a comparison of the Pb isotope ratios in seawater versus possible Pb sources, it was determined that the Pb in the upper 500 m probably came from multiple sources (Figure 5). The seawater samples had isotopic signatures similar to aerosols from Russia (1998 – 1999) [32], Mongolia (1994 – 1995) [33], Japan (1998 – 1999) [32] and China (1999 – 2003). [19, 20] These aerosols are the integrated signatures of several sources of Pb, including coal combustion, industrial processing of Pb ore and naturally occurring Pb such as in Asian loess. [34–36]

Russian and Mongolian aerosols have similar Pb isotope signatures, which are enriched in ^{208}Pb relative to the seawater samples. A mixing line of Russian leaded gasoline (phased out in 2002) with Russian coal could produce the ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios observed in the seawater, but the relatively small consumption of coal (Figure 1, 4% world total in 2000 – 2002) [11] was not enough to produce the observed isotope ratios in the water. Mongolia, similarly to Russia, does not produce nearly enough coal combustion emissions to be a dominant influence on these seawater samples. [1]

Japanese aerosols, which have been relatively constant in composition since the 1980s [33] closely reflect fly ash from municipal solid waste (MSW) incineration in Japan. [33, 37, 38] The isotope ratios of the MSW fly ash are very similar to Pb in aerosols transported from the Asian continent, [39] confounding which is the dominant source of Pb in Japanese aerosols. However, the MSW emissions are an unlikely source of the observed seawater isotope ratios due to the relatively small amount of Pb that comes from this source. [28]

Since the phase-out of leaded gasoline in China in the mid-1990s, the atmospheric Pb isotope ratios have shifted in much of the country, from ^{206}Pb/^{207}Pb

~1.150 to 1.160 and ^{208}Pb/^{206}Pb ~2.123 to 2.115. [19, 20] The change in isotope ratios is a reflection of the lesser contribution of vehicle emissions to atmospheric Pb pollution since that phase-out, and the greater contribution from industrial activities. [19] The present-day aerosol Pb isotope signatures (^{206}Pb/^{207}Pb = 1.157 – 1.170; ^{208}Pb/^{206}Pb = 2.072 – 2.120) [19, 20] are within the large range of measured values for Chinese coals (^{206}Pb/^{207}Pb =1.075 – 1.220; ^{208}Pb/^{206}Pb = 2.020 – 2.220). [38, 40]

Moreover, Mukai et al. [40] found that coal combustion was not the only important source of atmospheric Pb over China, and that industrial processing of Chinese ore was also an important factor. Chinese ore has a wide range of Pb isotope signatures depending on whether it is from the northern (^{206}Pb/^{207}Pb = 1.08 – 1.14; ^{208}Pb/^{206}Pb = 2.14 – 2.22) or southern (^{206}Pb/^{207}Pb =1.18, ^{208}Pb/^{206}Pb = 2.10) regions of China. [40] The isotopic compositions of seawater samples most closely resembled those of ore from southern China, which is less enriched in ^{208}Pb and ^{207}Pb than in ores from northern China. The aerosol Pb signatures for China, combined with the wide range of values for Asian loess, are indistinguishable from the isotopic ratios of Pb in the upper 500 m of seawater samples. Therefore, it appears that atmospheric emissions from coal combustion in China, which accounted for 30% of the global consumption in 2000 – 2002, [11] are now the dominant source of aerosol Pb deposition to the North Pacific Ocean.

Our findings support previous work conducted by Gallon et al. [1] on surface water samples from this same cruise. They substantiated the transport of anthropogenic Pb to surface waters using enrichment factors of Pb in aerosols. Those surface waters had similar Pb isotope ratios (^{206}Pb/^{207}Pb =1.157 – 1.169; ^{208}Pb/^{206}Pb = 2.095 – 2.118) as the upper 500 m samples analyzed in this work. Gallon et al. [1] attributed the dominant source of Pb in the surface waters to Chinese industrial emissions from coal burning and ore smelting, and considered the contribution of Asian loess to be minimal. In this work, we determined that some subsurface seawater samples (20 – 500 m) had Pb isotopic compositions comparable to those of Asian loess which we tentatively attributed to the differing residence times for Pb in surface and subsurface waters. Surface waters reflect their most recent Pb inputs due to the short residence time of aerosol Pb, [7] but subsurface waters integrate Pb signatures over 2 or more years. [18, 41]

3.2 Deep Water

Below 1000 m, Pb concentrations decreased and Pb isotopic ratios varied with depth. At depths > 1000 m, the concentrations of Pb decreased from 40 pmol kg^{-1} to as low as 5.9 pmol kg^{-1} (Table 1). The ^{206}Pb/^{207}Pb ratios increased with depth from 1.172 to ratios greater than 1.185 at the three deepest stations (Figure 6); similarly, ^{208}Pb/^{206}Pb ratios decreased to less than 2.087. The three deepest profiles (stations 2, 7 and 9) exhibited a spatial trend in increasing ^{206}Pb/^{207}Pb ratios (1.172 – 1.193) and decreasing ^{208}Pb/^{206}Pb (2.086 – 2.064) ratios from west to east. The ratios in the deepest depths (^{206}Pb/^{207}Pb = 1.185 – 1.193; ^{208}Pb/^{206}Pb = 2.086 – 2.064) were similar to those of FeMn nodules (^{206}Pb/^{207}Pb = 1.184 – 1.195; ^{208}Pb/^{206}Pb = 2.062 – 2.102) [42] and pelagic sediments (^{206}Pb/^{207}Pb = 1.191 – 1.196; ^{208}Pb/^{206}Pb = 2.052 – 2.071) [43–45] in the Northwest Pacific Ocean.

Pb isotopic ratios in the deepest sample (5,400 m) at station 7 deviated from this trend ($^{206}Pb/^{207}Pb$ =1.173; $^{208}Pb/^{206}Pb$ = 2.101), and were most similar to those in the upper ocean ($^{206}Pb/^{207}Pb$ =1.171; $^{208}Pb/^{206}Pb$ = 2.095). Repeated extractions and analyses of separate aliquots of that sample confirmed these anomalous isotope ratios. Moreover, this anomaly could not be attributed to inputs of Pb from the benthic nepheloid layer, because the sample was collected 400 m above the bottom of the ocean. Work by Nagaoka et al. [28] has shown that particles in deeper depths can have statistically different isotope ratios than particles higher in the water column, but the differences they documented (7‰) were much smaller than those observed at station 7 (20‰). In addition, the Pb concentration was elevated relative to the sample collected above it. Therefore, the authors concluded that the sample was contaminated and data for it were excluded in the following discussion.

We had hypothesized that the deep water profiles would be in good agreement, as they were composed of the same water masses. Despite the close agreement in Pb concentrations of stations 7 and 9 (Table 1), their isotope ratios were not identical. This discrepancy could be due to the proximity of station 9 to the volcanically active Hawai'ian Island chain, and/or due to differential Pb inputs from aerosols. Station 2 was highly dissimilar from stations 7 and 9, with Pb concentrations 2 – 6 times higher and Pb isotope ratios, particularly at 2,500 m, relatively lower in ^{206}Pb (Figure 6).

3.3 Implications

Aerosol dust and Pb inputs to the North Pacific have been both modeled [17, 46, 47] and measured. [1, 6, 15] As expected, they have shown that aerosol Pb inputs are up to ten times higher near the Asian mainland than they are in the central North Pacific Ocean. Surface waters are a reflection of the isotopic composition of their Pb inputs, [1] which are dominated by aerosol deposition in the North Pacific Ocean. [28, 29] We believe that the isotopic compositions of Pb in North Pacific deep water are also a reflection of these aerosol inputs now.

Wu et al. [8] created a model to show how Pb inputs to the deep ocean have doubled the concentration of Pb in the deep waters of the NPSG in the past 100 years. In addition, this model shows a large change in $^{206}Pb/^{207}Pb$ isotope ratios (1.203 to 1.189) over the same time period. These changes were mainly attributed to vertical Pb inputs by particulate Pb, because particles have a short residence time (< 3 months) in oceanic waters [30, 31] relative to that of dissolved Pb in deep seawater (≥ 150 years). [41] Despite the short residence time of particles, Sherrell et al. [48] documented that particle-bound Pb isotopes were in equilibrium with dissolved Pb on a time scale more rapid than the rate at which the particles sank.

The Pb isotopic ratios of our deep NPSG seawater samples are similar to those of Wu et al. [8] collected 2.5 years after ours (Figure 6). This similarity in isotope ratios suggests several possibilities. The most obvious explanation is that the Pb inputs to the ocean in the NPSG were isotopically consistent over that time period. Another reason could be that although Pb aerosol isotope ratios changed with time, the concentration flux of this aerosol Pb input was very low. The small magnitude of Pb inputs relative to the existing quantity of Pb in the deep water would have negligible effects on the isotope ratios of the deep water. Lastly, the observed similarity in isotope ratios of deep water could be a combination of similar aerosol Pb isotope ratios with time and minimal concentration fluxes of Pb to the deep ocean.

In contrast, the Pb isotope ratios of deep waters in the WSAG (station 2) had much different Pb isotope ratios than those in the NPSG. We assume the isotope ratios of aerosol Pb inputs were the same in both the WSAG and NPSG because of the similarity of the isotopic ratios in the surface waters of the WSAG (^{206}Pb/^{207}Pb = 1.157 – 1.162; ^{208}Pb/^{206}Pb =2.099 – 2.118) and the NPSG (^{206}Pb/^{207}Pb =1.163 – 1.169; ^{208}Pb/^{206}Pb = 2.093 – 2.104). [1] Therefore, we attribute the isotopic difference in the deep waters of the WSAG and NPSG to a larger flux of Pb from surface waters to abyssal waters in the WSAG than the NPSG.

During the VERTIGO program, Lamborg et al. [49] documented a greater particulate flux in the WSAG as compared with the central NPSG (22.75°N, 158°W). They found the particulate total mass flux in the WSAG (200 – 1000 mg m^{-2} d^{-1}) to be much larger than in the NPSG (50 – 80 mg m^{-2} d^{-1}). Furthermore, the flux attenuation in the upper 500 m of the WSAG (20 – 45%) was much lower than in the NPSG (60 – 80%). [49, 50] Together, the flux and attenuation measurements indicate two to three times as many particles sink below 500 m in the WSAG versus the NPSG. At increasing depths (> 500 m) the attenuation markedly decreased to ~10% in both the WSAG [28] and NPSG. [50]

Using particle flux as a proxy for Pb inputs to the deep ocean, we estimate the differential particulate Pb fluxes to the deep water as:

$\Delta F = \Delta_{atmos} \bullet \Delta_p \bullet \Delta_{sink}$

where ΔF is the difference in Pb flux to waters below 500 m between the WSAG and NPSG, Δ_{atmos} is the ratio of aerosol Pb inputs to the surface waters of the WSAG versus the NPSG (10), [1, 17] Δ_p is the ratio of particle flux in the lower euphotic zone of the WSAG versus the NPSG (9 ± 6), [49] and Δ_{sink} is the ratio of particles that sink below 500 m without remineralizing in the WSAG versus the NPSG (2.7 ± 1.3). [49, 50]

The calculated difference in particulate Pb flux to deep waters (ΔF) is ~ 200 times greater in the WSAG than the NPSG. However, the relatively greater flux does not equate with a 200 fold increase in the concentration of Pb in those waters, as a majority of that Pb flux remains in the particulate phase [41] and the particles settle rapidly (70 – 330 m d^{-1}). [30, 31] Rather, this elevated Pb flux in the WSAG means there is a larger pool of exchangeable particulate Pb in the deep waters of the WSAG versus the NPSG. Based on this larger pool of exchangeable Pb in the WSAG relative to the NPSG, we hypothesize there will be accelerated changes in Pb concentrations and isotopic compositions in WSAG deep water compared to those in NPSG deep water.

Finally, we use the differing Pb flux to deep water in conjunction with Wu et al.'s model for the NPSG [8] to estimate the rate of change in WSAG deep water. In that model, the NPSG changes on the timescale of ~ a century. We estimate that the WSAG can change on the timescale of several years to a decade because of the ~

200-fold difference in Pb flux to this basin. Previous studies have documented the relatively rapid (4 years) change in Pb isotope signatures (1.21 to 1.19) of surface water [51] during the phase-out of US leaded gasoline in the Atlantic Ocean. In addition, Alleman et al. [52] found that the isotopic composition of abyssal waters was rapidly changed by the formation of North Atlantic Deep Water which had entrained Pb from surface waters. Although the mechanism for change of deep water Pb isotope ratios is different in the North Pacific Ocean, the first deep Pb isotopic profile of the WSAG shows that the vertical transport of Pb sorbed onto particulates can produce large isotopic changes quickly relative to that of the NPSG.

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Table 1. Lead concentrations, isotopic ratios, and water density at the nine depth profiles.

Depth (m)	Sigma-theta	Pb (pmol kg^{-1})	^{206}Pb/^{207}Pb	2 s.e.	^{208}Pb/^{206}Pb	2 s.e.	^{206}Pb/^{204}Pb	2 s.e.	number of analyses
Station 1 (34.47 °N, 146.99 °E)									
*0 **		*103.5*	*1.165*	*0.001*	*2.107*	*0.001*	*18.16*	*0.04*	*3*
40	24.49	105.0	1.167	0.002	2.104	0.003	18.27	0.07	2
200	25.18	113.1	1.164	0.001	2.111	0.005	18.18	0.04	8
455	26.43	77.6	1.160	0.002	2.112	0.007	18.07	0.08	4
527	26.69	66.9	1.174	0.001	2.089	0.004	18.29	0.20	4
1342	27.50	54.5	1.167	0.001	2.099	0.007	18.30	0.06	2
Station 2 (44 °N, 155 °E)									
*0 **		*72.4*	*1.157*	*0.002*	*2.114*	*0.006*	*17.97*	*0.18*	*3*
20	26.33	71.7	1.159	< 0.001	2.113	0.005	18.06	0.03	2
60	26.43	82.8	1.164	0.002	2.108	0.007	18.19	0.02	4
100	26.47	62.5	1.158	< 0.001	2.117	0.003	18.07	0.09	2
300	27.05	54.4	1.168	0.002	2.098	0.004	18.20	0.04	2
1200	27.54	30.8	1.172	0.001	2.093	0.005	18.25	0.08	6
2525	27.73	25.2	1.172	< 0.001	2.086	0.005	18.21	0.08	2
5000	27.79	30.1	1.185	0.002	2.073	0.001	18.49	0.08	2
Station 3 (50 °N, 167 °E)									
*0 **		*55.8*	*1.162*	*0.002*	*2.099*	*0.003*	*18.02*	*0.04*	*5*
24	26.38	68.6	1.170	0.003	2.095	0.008	18.20	0.06	4
103	26.48	63.7	1.166	0.003	2.097	0.005	18.07	0.01	2

300	27.08	54.7	1.170	0.003	2.098	0.005	18.27	0.11	2
1500	27.61	34.2	1.173	0.004	2.098	0.010	18.29	0.10	4

Station 4 (39.36 °N, 170.58 °E)

0 *		*87.2*	*1.160*	*0.002*	*2.109*	*0.001*	*18.02*	*< 0.01*	*2*
20	25.91	88.7	1.164	0.001	2.105	0.003	18.19	0.04	7
80	26.32	92.1	1.164	0.002	2.106	0.004	18.16	0.06	7
175	26.41	78.5	1.157	0.002	2.113	0.005	18.07	0.05	5
250	26.58	79.4	1.163	< 0.001	2.107	0.003	18.22	0.02	2
300	26.67	69.9	1.162	< 0.001	2.109	0.003	18.13	< 0.01	2
900	27.33	47.5	1.173	0.003	2.095	0.009	18.34	0.05	4
1500	27.55	57.5	1.169	0.002	2.097	0.003	18.30	0.08	6

Station 5 (33.77 °N, 170.58 °E)

0 *		*103.5*	*1.163*	*0.002*	*2.105*	*0.005*	*18.20*	*< 0.01*	*2*
20**	*24.82*	*127.6*	*1.176*	*0.001*	*2.087*	*0.003*	*18.39*	*0.05*	*9*
175	25.33	101.1	1.160	0.002	2.113	0.005	18.12	0.08	7
300	25.74	84.5	1.164	0.001	2.106	0.004	18.18	0.07	7
500	26.32	77.7	1.162	< 0.001	2.108	0.003	18.15	0.06	3
1500	27.50	48.6	1.172	0.002	2.094	0.002	18.21	0.08	2

Station 6 (30.50 °N, 170.58 °E)

0 *		*84.1*	*1.162*	*0.001*	*2.106*	*0.003*	*18.17*	*0.03*	*5*
20	24.47	92.1	1.167	0.001	2.100	0.004	18.20	0.06	2
150	25.44	105.4	1.164	0.002	2.109	0.004	18.23	0.02	3
300	25.88	83.5	1.164	0.001	2.108	0.002	18.16	0.06	3
1500	27.55	36.9	1.170	0.003	2.099	0.006	18.31	0.03	2

Station 7 (24.25 °N, 170.33 °E)

*0 **		*45.0*	*1.163*	*0.001*	*2.104*	*0.004*	*18.16*	*0.19*	*4*
20	23.90	51.3	1.171	0.002	2.095	0.003	18.31	0.04	6
60	24.11	54.8	1.169	0.001	2.099	0.002	18.26	0.03	2
100	24.36	59.6	1.163	0.002	2.106	0.003	18.15	0.03	6
299	25.66	83.4	1.167	0.001	2.101	0.006	18.21	0.07	4
648	26.75	55.6	1.167	0.001	2.100	0.002	18.19	0.06	6
997	27.30	41.1	1.169	0.002	2.097	0.003	18.24	0.07	4
1196	27.45	27.7	1.174	0.001	2.089	0.005	18.32	0.06	4
1196	27.45	27.8	1.173	0.001	2.093	0.002	18.29	0.06	6
2998	27.75	8.9	1.185	0.002	2.087	0.005	18.51	0.07	5
4496	27.79	10.1	1.191	0.001	2.065	< 0.001	18.56	0.03	2
5396	27.81	11.9	1.173	0.002	2.100	0.007	18.32	0.11	4

Station 8 (26.00 °N, 175.00 °W)

*0 **		*47.4*	*1.164*	*0.003*	*2.103*	*0.013*	*18.21*	*0.25*	*3*
43	24.49	66.8	1.171	0.002	2.088	0.005	18.29	0.05	4
80	24.78	75.3	1.167	0.002	2.099	0.004	18.25	0.03	4
173	25.45	86.0	1.162	0.002	2.111	0.003	18.15	0.06	4
300	25.95	78.7	1.163	0.001	2.108	0.004	18.13	0.09	4
700	26.93	58.7	1.164	0.003	2.106	0.006	18.22	0.06	4
900	27.24	54.3	1.176	0.003	2.086	0.008	18.42	0.17	2
1500	27.58	21.8	1.176	0.001	2.093	0.005	18.37	0.09	2

Station 9 (22.75 °N, 158.00 °W)

*0 **		*32.8*	*1.166*	*< 0.001*	*2.093*	*< 0.001*	*18.19*	*0.26*	*2*
20	23.80	44.2	1.180	< 0.001	2.080	0.003	18.47	0.08	4

60	24.48	54.3	1.177	0.001	2.086	0.002	18.40	0.01	2
100	24.78	52.4	1.169	0.001	2.099	0.002	18.25	0.01	2
200	25.51	54.3	1.160	0.003	2.110	0.007	18.12	0.07	5
300	26.09	74.3	1.162	0.003	2.105	0.004	18.24	0.23	4
500	26.74	67.4	1.171	0.005	2.086	0.018	18.44	0.13	3
950	27.37	32.9	1.177	0.001	2.090	0.003	18.40	< 0.01	2
1750	27.63	12.4	1.179	0.001	2.086	< 0.001	18.41	0.05	2
2508	27.72	15.1	1.194	0.004	2.064	0.010	18.51	0.16	3
4508	27.79	5.9	1.193	0.002	2.064	0.003	18.63	0.14	2

** Values from Gallon et al. (2011), listed here for reference purposes.*

** Suspected of contamination; values excluded in discussion of results.

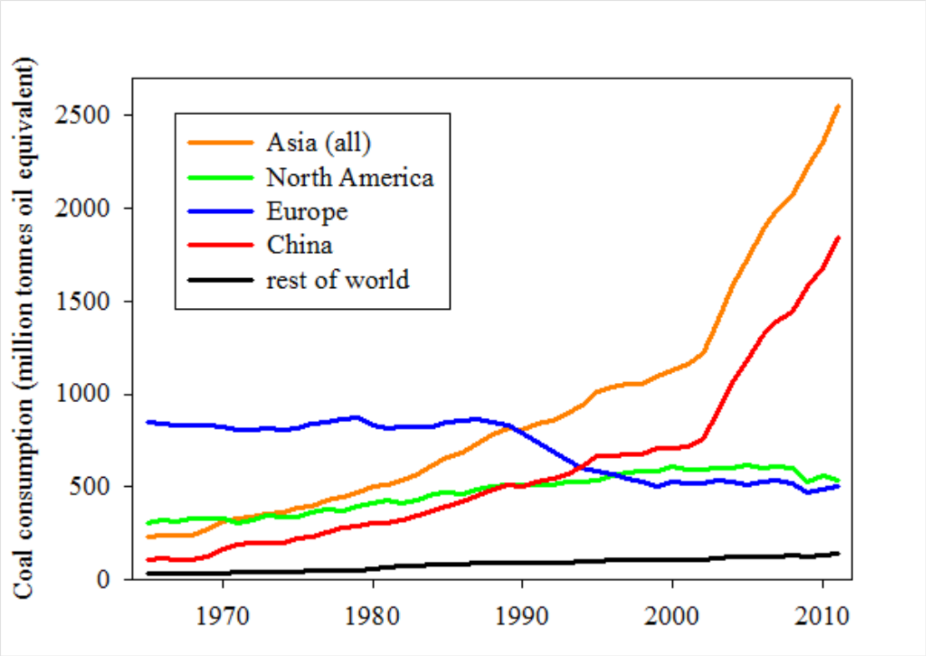

Figure 1. The global coal consumption from 1965 – 2011 shows that China dramatically increased their usage in the early 2000’s. [11]

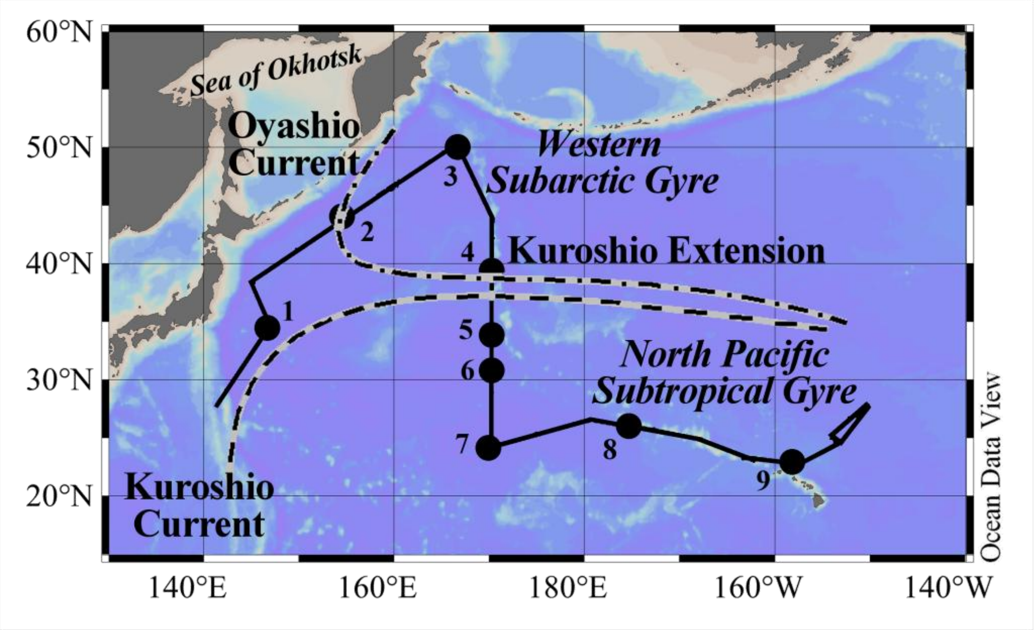

Figure 2. Map of IOC-4 cruise path with station numbers, prominent currents and hydrographic regions.

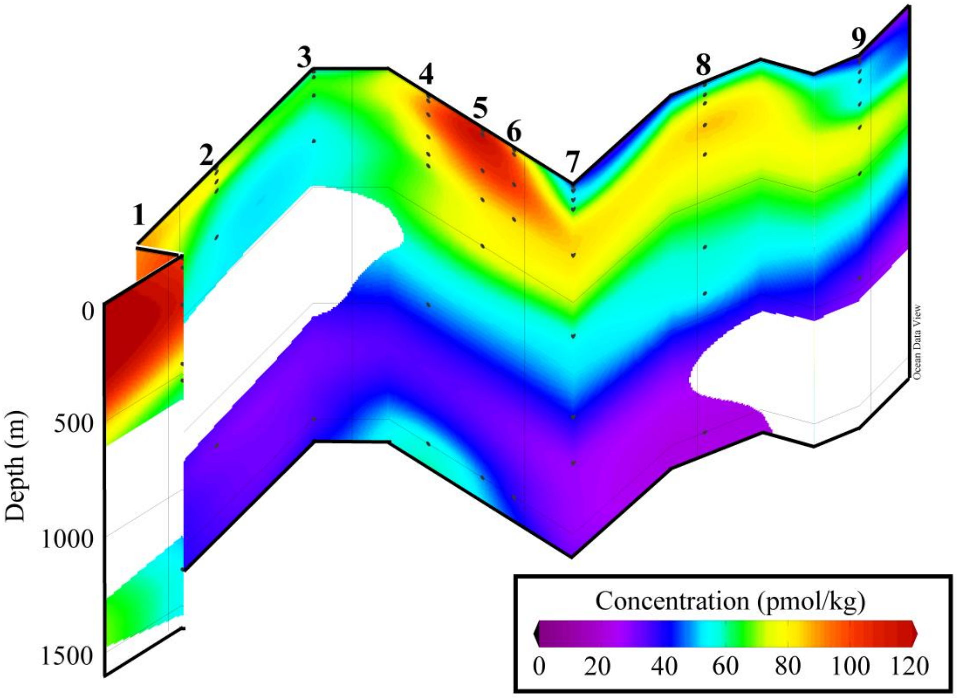

Figure 3. Lead concentrations in the upper 1,500 m of the cruise, contoured to the approximate cruise track. The Pb concentrations are highest in the surface waters of the Kuroshio Current (station 1), the mixed water region (station 4), and in the Kuroshio Extension (stations 5, 6). There is a subsurface Pb concentration maxima in the NPSG (stations 7, 8, 9).

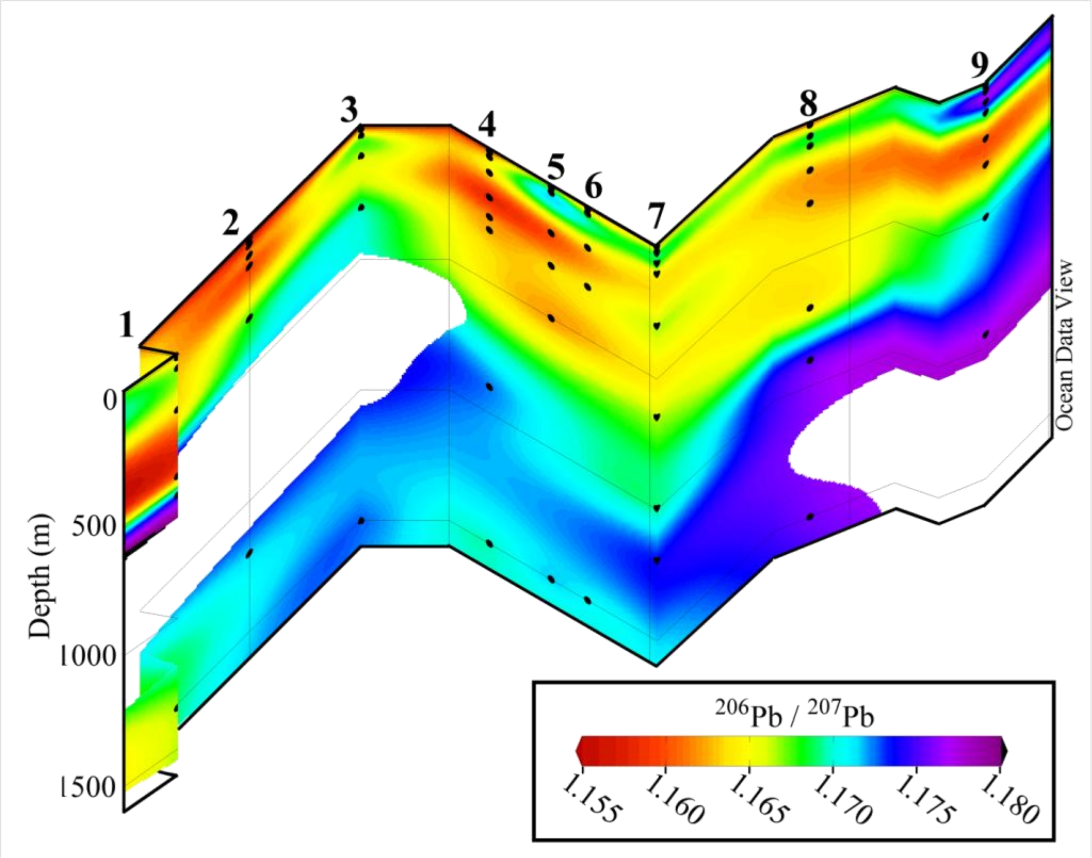

Figure 4. The plot of ^{206}Pb/^{207}Pb isotopes reveals a similar trend as the Pb concentrations plot. The surface waters (stations 1, 2, 3, 4) and subsurface Pb concentration maxima (stations 5, 6, 7, 8, 9) have similar isotopic compositions to those of Chinese coal.

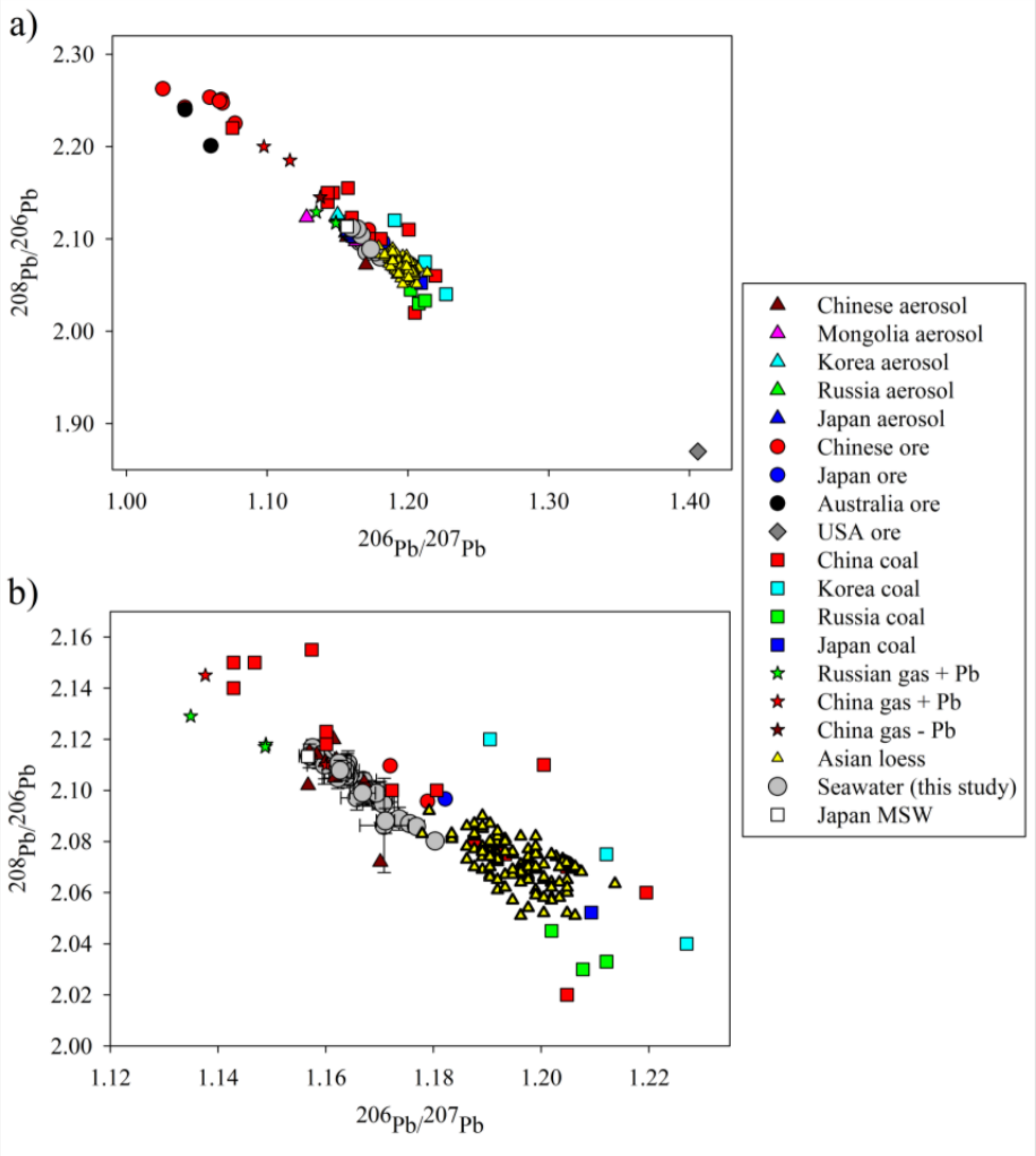

Figure 5. Triple isotope plots of stations 1 – 9 in the upper 500 m of the water column along with a) global sources and b) possible sources which contributed to the Pb in these seawater samples. Global sources: Chinese aerosols, [19, 20] Mongolian and Korean aerosols, [33] Russian and Japanese aerosols, [32] Chinese, Japanese, and USA ores, [53] Australian Ore, [33, 38] Chinese coal, [38, 40] Korean coal, [38] Russian coal, [54] Japanese coal and Municipal Solid Waste (MSW) aerosols, [39] Russian gasoline, [55] Chinese gasoline, [20] and Asian loess. [34–36]

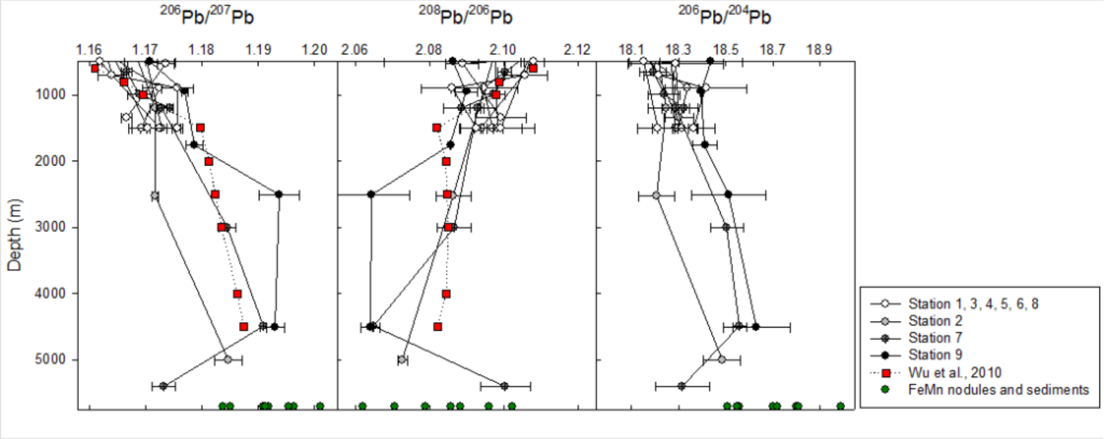

Figure 6. The Pb isotopic profiles > 500 m for this cruise as well as Wu et al. (2010) at 30˚N, 140˚W (red squares) and FeMn nodules [42] and sediments [43–45] collected around the North Pacific Ocean (green circles).

CHAPTER 4. RECENT INCREASES IN ANTHROPOGENIC LEAD IN NORTH PACIFIC OCEAN ABYSSAL WATERS

Cheryl M. Zurbrick, Keiji Horikawa, Jing Zhang and A. Russell Flegal

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Abstract

In this study, we further document lead (Pb) pollution to the North Pacific Ocean. Near-surface water Pb isotope compositions (PbICs) homogenously reflect Chinese industrial emissions. Deep water Pb isotope ratios are compared with other recent Pb data (2002 – 2004) and show that PbICs in the western edge of the basin are changing at twice the rate of the central North Pacific. That rate difference highlights the extensive Pb emissions currently entering this ocean.

In the western North Pacific near-surface and abyssal waters have similar PbICs (^{206}Pb/^{207}Pb = 1.160 – 1.170, ^{208}Pb/^{206}Pb = 2.100 – 2.111). These seawater PbICs reflect current Chinese atmospheric industrial Pb emissions (^{206}Pb/^{207}Pb = 1.161, ^{208}Pb/^{206}Pb = 2.110), which indicate anthropogenic contamination has spread throughout the entire water column. In contrast, PbICs in near-surface and abyssal waters in the central North Pacific (^{206}Pb/^{207}Pb = 1.160 to 1.182, ^{208}Pb/^{206}Pb = 2.112 to 2.090) are dissimilar, with the surface waters reflecting current aeolian Pb inputs and the deep waters exhibiting a mixture of industrial and preindustrial Pb inputs. However, our estimates for the rate of isotopic change in all North Pacific deep waters indicate that their PbICs will be indistinguishable from those of Asian industrial Pb inputs within the next few decades.

1. Introduction

Humans have perturbed the environment to the point that we have dramatically altered the cycles of as many as 62 elements (Sen and Peucker-Ehrenbrink, 2012), and scientists have deemed our current epoch the “anthropocene” (Steffen et al., 2011; Zalasiewicz et al., 2011). The cycling of lead (Pb), one of the most contaminated elements, has received much attention in the last 50 years because it is a potent neurotoxin (ATSDR, 2007; Bellinger, 2007). Consequently, concerns with human exposure to Pb have prompted studies of its sources, transport and fate as well as global efforts to reduce exposure.

Prior to the phase-out of leaded gasoline in the 1970s, humans contributed an estimated 92% of the total Pb emitted to the environment annually – more than 10 times what was emitted by natural sources (Nriagu and Pacyna, 1988; Nriagu, 1989). Since the elimination of leaded gasoline by most nations, the estimated human contribution of total Pb emissions has dropped to 65% (Sen and Peucker-Ehrenbrink, 2012). However, emissions from rapidly developing nations are again increasing the amount of anthropogenically-mobilized Pb to the environment. In China, the phase-out of leaded gasoline in 2000 temporarily halted that nation’s skyrocketing Pb emissions (Li et al., 2012). However, coal has a relatively high concentration of Pb (35 ppm, Díaz-Somoano et al., 2009), and its increased consumption along with other industrial activities in China are leading atmospheric Pb emissions (9,500 – 12,000 t yr^{-1} in 2009) to approach pre-2000 levels (~ 13,000 t yr^{-1}, Tian et al., 2012; Li et al., 2012).

Models and measurements of atmospheric aerosol transport show a large amount of Asian dust is dumped into the North Pacific Ocean (Duce et al., 1991; Ginoux et al., 2001; Zender et al., 2003; Uno et al., 2009). Moreover, measurements of aerosol Pb have documented Asian inputs in the North Pacific (Settle and Patterson, 1982; Duce et al., 1983) and West Coast of the United States (Bollhöfer and Rosman, 2001). Previous work has shown that the Pb in aerosols over the North Pacific Ocean is highly soluble in seawater (Maring and Duce, 1990). Conversely, nutrients also associated with that dust stimulate plankton growth (Yuan and Zhang, 2006) which can scavenge Pb and export it to the deep ocean as shown for Al (Bruland et al., 2012; Yuan and Zhang, 2006). Recent measurements of Pb in North Pacific aerosols had typical enrichment factors of 1 – 17, and as high as 131 (Gallon et al., 2011). Seawater collected concurrently with those aerosols had Pb isotope compositions (PbICs; $^{206}Pb/^{207}Pb = 1.157 – 1.169$, Gallon et al., 2011) consistent with Chinese industrial emissions ($^{206}Pb/^{207}Pb = 1.157 – 1.170$, Zheng et al., 2004; Chen et al., 2005; Toshiaki et al., 2012).

We have previously documented the relatively faster change in PbICs of deep water in the western North Pacific as compared with the central North Pacific due to their spatial gradient in vertical inputs (i.e., particulate-Pb) from overlaying waters (Zurbrick et al., 2014). We attributed that spatial difference to a combination of the greater flux of atmospheric Pb and relatively larger flux of particles to deep water at the western edge of the ocean basin. In this study, we investigated the ongoing impact of industrial Pb emissions by revisiting the North Pacific and documenting changes in near-surface and deep waters after a 5 – 9 year time period.

2. Experimental Section

Seawater samples were collected during two cruises in the North Pacific Ocean. The GEOTRACES Intercalibration 2 (IC2) cruise was in May 2009 aboard the R/V Knorr, which collected water at 30˚N, 140˚W (station SAFe) in the central North Pacific Subtropical Gyre (NPSG) (Figure 1). Samples were collected using trace metal clean techniques as described by Cutter et al. (Cutter et al., 2010) and detailed by Fitzsimmons and Boyle (Fitzsimmons and Boyle, 2012). These samples were filtered using 0.2 µm Osmonics capsule filters and collected in acid cleaned 2 L low-density polyethylene (LDPE) bottles.

The second set of samples was collected on the GEOTRACES Western North Pacific Ocean baseline cruise (KH11-07) aboard the R/V Hakuho-Maru which sailed from 16 July – 4 August, 2011. This cruise sampled waters in the Western Subarctic Gyre (WSAG) (stations K1, K2, N2) and the western edge of the NPSG (stations N3, N4). Seawater samples were collected in acid-cleaned Teflon® coated 12-L Niskin-X™ bottles (General Oceanics), filtered using 0.2 µm AcroPak™ filters (Pall Corp.) and subsampled into acid-cleaned 2 L LDPE bottles using trace metal clean techniques in a HEPA-filtered room (Nishioka et al., 2013).

Upon returning to the WIGS lab, samples from both expeditions were immediately acidified to pH ≈ 2 using ultrapure (sub-boiling quartz-distilled) HCl. The samples were vigorously shaken and left to de-sorb any scavenged Pb from the walls of the bottles for > 2 months prior to analyses. Lead concentrations in seawater were measured at the UC Santa Cruz Marine Analytical Lab using an on-line chelating resin extraction (Ndung'u et al., 2003) connected to a Thermo ELEMENT XR™ magnetic sector high resolution inductively coupled plasma mass spectrometer (HR ICP-MS) as detailed in Zurbrick et al. (2012). The procedural Pb blanks were < 2 pmol kg^{-1} (n = 18) and the detection limit was $\leq$ 4 pmol kg^{-1}. Concurrent analyses of GEOTRACES intercalibration samples were similar to the range of concentrations reported by others (Table 1).

Lead isotopes were extracted and subsequently analyzed at the UC Santa Cruz Marine Analytical Lab using the method of Zurbrick et al. (2013). Briefly, Pb from seawater (65 – 100 mL) was pre-concentrated using Toyopearl AF-Chelate 650 M ™ ion-exchange resin and eluted in 1 mL of ultrapure 1.5 N HNO_3. The Pb concentration in the extracts was ~ 5 nmol kg^{-1}. The analysis and correction procedures were the same as detailed in Zurbrick et al. (2013). Extraction blanks (ultra high purity water; 18 MΩ cm) acidified to pH ≈ 2 were $\leq$ 40 pg (0.2 – 2 pmol kg^{-1}). Replicate extractions and analyses of samples (n = 2 – 6) produced data with average standard errors (2 σ) of 3‰, 5‰, and 73‰ for ^{206}Pb/^{207}Pb, ^{208}Pb/^{206}Pb, ^{206}Pb/^{204}Pb respectively. This precision agreed well with our previously reported reproducibility for GEOTRACES intercalibration seawater (Zurbrick et al., 2013; Boyle et al., 2012).

3. Results

Near-surface waters of the WSAG (stations K1, K2, N2) were distinctly lower in Pb concentrations (25 – 45 pmol kg^{-1}) than the western NPSG (stations N3, N4; 60 – 66 pmol kg^{-1}) or central NPSG (station SAFe; 67 pmol kg^{-1}; Table 2). The elevated concentrations in the NPSG extended to a depth of ~ 500 m (Figure 2), consistent with the depth of the permanent thermocline (Figure 3). Below 1,500 m, all five stations had identical temperatures and salinities, indicating they were of the same water mass. Despite their common water mass, the Pb concentrations at the five stations were not identical. The western NPSG waters at 1500 m and 2000 m were higher in concentration (20 – 30 pmol kg^{-1}) than the WSAG waters (15 – 20 pmol kg^{-1}) and the central NPSG (9 – 13 pmol kg^{-1}) at corresponding water densities. Those spatial differences in Pb concentrations diminished with depth, and they were quite similar (5 ± 2 pmol kg^{-1}) below 4000 m at all five stations.

Lead concentrations showed a ~10 fold difference between near-surface and deep waters, but the PbICs in the WSAG and western NPSG varied less. Water at stations closest to the Asian continent (K1, K2), had PbICs (^{206}Pb/^{207}Pb = 1.161 – 1.172, ^{208}Pb/^{206}Pb = 2.098 – 2.111) that were relatively invariant with depth (Figure 4a). Similarly, stations in the western NPSG (N3, N4) had PbICs (^{206}Pb/^{207}Pb = 1.160 – 1.173, ^{208}Pb/^{206}Pb = 2.096 – 2.116) that were similar in the near-surface and deep water (Figure 4b). The subtle changes in isotope ratios with depth at these four stations contrasted with the large variation in PbICs in the central NPSG (SAFe). At that station, the PbICs of near-surface waters (^{206}Pb/^{207}Pb ≈ 1.160, ^{208}Pb/^{206}Pb ≈

2.112) were isotopically distinct from those of the deep waters (^{206}Pb/^{207}Pb ≈ 1.182, ^{208}Pb/^{206}Pb ≈ 2.090; Figure 4c).

4. Discussion

4.1 Sources of Pb

The seawater PbICs fit the isotopic signature for current Chinese aerosols (Zheng et al., 2004; Chen et al., 2005; Toshiaki et al., 2012). Those aerosols are a mix of industrial emissions, such those from as coal and smelting (Mukai et al., 1993; Sangster et al., 2000; Mukai et al., 2001), and natural Asian loess (Figure 5). The majority of the seawater samples' PbICs matched anthropogenic sources of Pb, which suggests pervasive Pb contamination of the entire water column. In contrast, the PbICs of station SAFe deep water were closer to the range for PbICs of Asian loess (Jones et al., 2000; Sun and Zhu, 2010; Wu et al., 2011), North Pacific FeMn crusts (Ling et al., 1997), and North Pacific benthic sediments (Chow and Patterson, 1962; Chow and Tatsumoto, 1964; Kersting, 1995). Together, these geologic materials represent background PbICs to the North Pacific, prior to industrial Pb inputs. Consequently, Pb in station SAFe deep water currently appears to be a mix of contemporary industrial and preindustrial Pb inputs to the North Pacific.

These PbICs are consistent with previous reports that Pb in North Pacific abyssal water is predominantly transported into the deep ocean by vertical inputs, rather than by lateral advection (Wu et al., 2010; Zurbrick et al., 2014), and are consistent with the observation of rapid Al and Cs injection into deep waters (Yuan and Zhang, 2006; Honda et al., 2013). The PbICs of deep water, which are similar to modern (past ~3 decades) Chinese aerosols, must have been derived from surface inputs and subsequent vertical export because those abyssal waters are ~ 1,000 years old (Matsumoto, 2007). In surface waters, Pb scavenges onto particles (Bruland et al., 2012) which sink through the water column rapidly (1 – 2 months, Honjo and Manganini, 1993; Berelson, 2002; Yuan and Zhang, 2006; Honda et al., 2013). During that transport, the net change in dissolved Pb concentration remains low, but the rapid exchange of Pb between particle surfaces and dissolved Pb results in isotopic equilibrium between the two Pb phases, as reported by Sherrell et al. (1992). That apparent isotopic equilibrium is supported by the similarity in PbICs of our seawater and those of particles collected at 770 m and 5100 m in the WSAG between 2005 and 2007 (Nagaoka et al., 2010) (Figure 4a).

4.2 Lead concentrations, 2002 - 2011

We find close agreement in the NPSG between station SAFe and a previous occupation at this location in 2004 (Figure 2, Wu et al., 2010). Below 200 m, the two Pb concentration profiles are in close agreement (± 4 pmol kg^{-1}) with each other. In the near-surface water, Pb concentrations are more variable (± 13 pmol kg^{-1}). We attribute the concentration differences in the mixed layer (0 – 150 m) (Tupas et al., 1997 – 2000) to seasonal and annual variations in atmospheric inputs and scavenging onto sinking particles, as proposed by Boyle and colleagues (2005). In their study, they found relatively large Pb concentration fluctuations (± 20 pmol kg^{-1}) in the mixed layer during a 3 year time series.

Agreement in Pb concentrations was worse between the WSAG and western NPSG and an Intergovernmental Oceanographic Commission (IOC) cruise in 2002. In the WSAG (stations K1, K2), Pb concentration differences of 5 – 20 pmol kg^{-1} persisted throughout the entire water column as compared with IOC station 2 (Figure 2, Zurbrick et al., 2014). In addition, near-surface waters in both the WSAG and western NPSG (stations N3, N4) were 20 – 50 pmol kg^{-1} lower in concentration in 2011 than in 2002 (IOC 2 – 6). The variation in Pb concentrations between 2011 and 2002 was relatively large, but we do not believe it was due to a decrease in Pb concentration with time for two reasons.

First, a direct comparison of Pb concentrations between the two cruises is hindered because the 2002 samples were not filtered, whereas the 2011 samples were filtered. It is plausible that seasonal particle fluxes resulted in a large portion of the total Pb in the particulate phase (> 0.2 μm) during the 2011 sampling. Particle export in the WSAG is high relative to the NPSG (Lamborg et al., 2008) and can vary seasonally by a factor of 10 (Nagaoka et al., 2010). In addition, low particle attenuation in the WSAG results in high export throughout the water column (Lamborg et al., 2008). Therefore we suspect a large portion of the total Pb was in the particulate phase, because of the high scavenging rate of Pb onto particles (Nozaki et al., 1976; Nozaki et al., 1980; Benoit et al., 2010).

Second, the main source of the Pb to the surface waters did not change between 2002 and 2011, as evidenced by the similarity of their PbICs in mixed layer waters (Figure 4, Gallon et al., 2011). The predominant source of Pb in both studies was determined to be atmospheric deposition of Chinese industrial Pb emissions, notably those from coal combustion. China's coal consumption in the decade leading up to the 2011 GEOTRACES cruise increased 155% (BP, 2012). Since it is very unlikely that the aeolian Pb flux to North Pacific surface waters decreased between the 2002 IOC and 2011 GEOTRACES cruises, we assume the higher Pb concentrations in 2002 relative to 2011 are an artifact of the latter samples' filtration.

4.3 Changing abyssal waters

Over the past nine years, the PbICs of deep water (2500 – 5000 m) have changed substantially in the WSAG and western NPSG (Figure 4a, b). As previously noted, the deep water ^{206}Pb/^{207}Pb (1.165 – 1.173) was isotopically lighter in 2011 than it was in 2002 (1.172 – 1.185, IOC 2), while the ^{208}Pb/^{206}Pb (2.096 – 2.116) was isotopically heavier than in 2002 (2.073 – 2.087, Zurbrick et al., 2014). The PbICs of WSAG deep water in 2002 were similar to those of North Pacific FeMn crusts (^{206}Pb/^{207}Pb = 1.19, ^{208}Pb/^{206}Pb = 2.07) (Ling et al., 1997) and North Pacific benthic sediments (^{206}Pb/^{207}Pb = 1.18 – 1.20, ^{208}Pb/^{206}Pb = 2.06 – 2.10) (Chow and Patterson, 1962; Chow and Tatsumoto, 1964; Kersting, 1995). In contrast, the 2011 WSAG and western NPSG deep water PbICs (^{206}Pb/^{207}Pb = 1.165 – 1.173, ^{208}Pb/^{206}Pb = 2.096 – 2.116) were similar to those of Chinese aerosols (^{206}Pb/^{207}Pb = 1.161, ^{208}Pb/^{206}Pb = 2.110) (Zheng et al., 2004; Chen et al., 2005). Consequently, we interpret those relatively homogeneous PbICs to mean anthropogenic Pb has now contaminated both near-surface and deep waters in the western edge of the North Pacific Ocean basin.

Although less pronounced, PbICs were different at station SAFe in NPSG deep water between 2004 and 2009 (Figure 4c). Wu et al. (2010) reported deep water PbICs (^{206}Pb/^{207}Pb = 1.182 – 1.188, ^{208}Pb/^{206}Pb = 2.082 – 2.085) that were a mix of anthropogenic and background (i.e., geologic) Pb. We measured similar PbICs at corresponding depths (^{206}Pb/^{207}Pb = 1.182 – 1.183, ^{208}Pb/^{206}Pb = 2.084 – 2.090). Within analytical error (2 σ), many of the Pb isotope ratios between 2004 and 2009 were indistinguishable. However, the overall isotopic trend in deep water was similar to the WSAG and western NPSG in that the more recent seawater PbICs looked less like background Pb and more like modern aerosol inputs.

The larger change in PbICs in the WSAG and western NPSG as compared with that in the central NPSG is attributed to the relatively greater Pb flux to the former's deep waters (Lamborg et al., 2008; Honda et al., 2013). In our previous work, we estimated the Pb flux in the WSAG was ~ 200 times higher than the central NPSG (Zurbrick et al., 2014). Using the differences in the PbICs of the deepest samples ($\geq$ 4000 m) in 2011 and 2009 versus 2004 (Wu et al., 2010) and 2002 (Zurbrick et al., 2014), the change per mil per year was calculated. In the WSAG and western NPSG the rate of change (^{206}Pb/^{207}Pb ≈ 2‰ yr^{-1}; ^{208}Pb/^{206}Pb ≈ 4‰ yr^{-1}) was twice that of the central NPSG (^{206}Pb/^{207}Pb ≈ 1‰ yr^{-1}; ^{208}Pb/^{206}Pb ≈ 2‰ yr^{-1}). Assuming atmospheric sources of Pb do not change in the coming years, we propose that PbICs of deep water in the WSAG and western NPSG will become indistinguishable from those of aerosols by ~ 2020. Similarly, we estimate changes in

PbICs in the central NPSG will continue to shift until ~2040, at which point the deep water will also match those of aeolian inputs to North Pacific surface waters.

4.4 Summary

Previously, we hypothesized that the change in deep water PbICs would occur faster in the WSAG than the NPSG (Zurbrick et al., 2014). We based our hypothesis on the greater atmospheric Pb inputs to WSAG surface waters (due to their relative proximity to Asia), and the greater particulate flux in the WSAG compared to the central North Pacific (Zurbrick et al., 2014). These new measurements of seawater, collected in 2011 confirm that deep water PbICs are changing more rapidly in the WSAG and western NPSG than in the central NPSG. Finally, if anthropogenic emissions continue at present day levels, we predict the PbICs of essentially all deep waters in the western and central North Pacific will be characterized by industrial Pb inputs within a few decades.

5. Acknowledgements

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Table 1. Analytical blanks, detection limit, and values for measured concensus samples.

Concentrations				
	average	2 x standard deviation	n	
Blank	1.9		18	
detection limit	3.4			*consensus***
GEOTRACES Surface*	23.3	3.0	4	*28.6 (± 1.0)*
GEOTRACES Deep*	40.4	9.3	4	*42.7 (± 1.5)*
SAFe Surface*	43.4	1.4	3	*48.0 (± 2.2)*
SAFe Deep2*	27.3	3.6	3	*27.7 (± 1.5)*
Isotopes				
Blank	< 40 pg (0.2 - 2 pmol kg^{-1})			
average standard error	3‰	^{206}Pb/^{207}Pb	2 - 6	
(2 σ)	5‰	^{208}Pb/^{206}Pb	2 - 6	
	73‰	^{206}Pb/^{204}Pb	2 - 6	

* Intercalibration samples obtained from Geoffrey Smith, www.GEOTRACES.org

** Consensus values as reported May 2013

Table 2. Lead concentrations, isotopic compositions, and hydrographic parameters at each station.

Depth	Concentration (pmol kg^{-1})	^{206}Pb/^{207}Pb	2 s.e.	^{208}Pb/^{206}Pb	2 s.e.	^{206}Pb/^{204}Pb	2 s.e.	n	Temperature (°C)	Salinity (PSU)
Station SAFe IC2 (30.00 °N, 140.00 °W)										
25	67.0	1.160	0.001	2.112	0.002	18.18	0.05	4	19.0	34.8
100	68.4	1.161	0.001	2.111	0.002	18.19	0.04	5	18.2	34.9
200	62.1	1.161	0.002	2.113	0.003	18.21	0.07	4	12.8	34.1
350	68.8	1.159	0.002	2.112	0.003	18.13	0.05	4	8.9	34.0
500	62.2	1.160	0.001	2.110	0.001	18.14	0.04	4	6.4	34.0
750	43.1	1.166	0.002	2.101	0.004	18.37	0.04	6	4.4	34.2
1000	26.4	1.172	0.001	2.095	0.001	18.51	0.10	6	3.7	34.4
1500	13.1	1.177	0.001	2.091	0.002	18.46	0.03	6	2.6	34.6
2000	9.3	1.180	0.001	2.092	0.003	18.57	0.07	4	1.9	34.6
3000	6.9	1.183	0.002	2.084	0.007	18.63	0.04	3	1.3	34.7
4000	8.0	1.182		2.095		18.90		1	1.2	34.7
4500	6.2	1.183	< 0.001	2.090	0.008	18.77	0.23	2	1.1	34.7
Station K2 (47.00 °N, 160.05 °E)										
20	34.9	1.163	< 0.001	2.105	0.002	18.07	0.04	3	5.1	32.9
*100**	*55.4*	*1.243*	*0.001*	*1.993*	*0.002*	*19.52*	*0.07*	*4*	*0.8*	*33.2*
200	41.1	1.163		2.106		18.15		1	3.6	33.9
300	40.9	1.166		2.101		18.16		1	3.7	34.0
600	33.9	1.166	0.002	2.103	0.007	18.15	0.13	4	3.2	34.3
1001	27.3	1.167		2.102		18.18		1	2.5	34.4
1500	19.6	1.165	0.006	2.097	0.007	18.10	0.23	3	1.9	34.6

2000	17.2	1.169	0.003	2.100	0.004	18.15	0.06	4	1.6	34.6
3000	14.7	1.169	0.001	2.102	0.002	18.23	0.05	6	1.3	34.7
4000	9.4	1.169	0.004	2.104	0.012	18.14	0.06	4	1.1	34.7
5000	5.3	1.169	0.002	2.111	0.004	18.26	0.06	4	1.1	34.7

Station K1 (51.00 °N, 165.00 °E)

20	24.7	1.162	0.001	2.107	0.008	18.17	0.02	2	9.0	32.8
99	40.6	1.161	0.003	2.111	0.006	18.09	0.06	4	3.0	33.1
200	36.7	1.163	0.002	2.108	0.003	18.11	0.05	3	4.1	33.8
300	44.3	1.164	0.001	2.105	0.001	18.10	0.11	2	3.9	34.0
600	34.2	1.164	0.001	2.105	0.006	18.19	0.10	3	3.3	34.2
1000	24.4	1.164	0.003	2.106	0.006	18.25	0.14	3	2.7	34.4
1500	16.9	1.168	0.002	2.100	0.008	18.20	0.10	2	2.1	34.5
2000	15.1	1.172	< 0.001	2.098	0.004	18.27	0.09	2	1.7	34.6
3000	10.3	1.171	0.001	2.100	0.004	18.27	0.05	2	1.3	34.7
4000	9.3	1.167	0.003	2.106	0.002	18.08	< 0.01	2	1.2	34.7
4878	3.7	1.172	0.001	2.102	0.005	18.33	0.05	2	1.1	34.7

Station N2 (44.99 °N, 165.02 °W)

19	46.2	1.153	0.007	2.119	0.003	18.08	0.17	3	8.6	32.9

Station N3 (40.00 °N, 165.00 °W)

19	66.0	1.167	< 0.001	2.109	0.015	18.23	0.02	2	18.2	34.5
100	64.7	1.165	0.002	2.104	0.002	18.18	0.09	2	12.9	34.3
200	62.8	1.166	0.002	2.112	0.004	18.17	0.09	2	11.0	34.2
300	54.7	1.163	0.006	2.106	0.006	18.16	0.02	2	9.3	34.1
601	35.2	1.164	0.005	2.115	0.009	18.29	0.09	2	4.2	34.0

1002	33.6	1.165	0.003	2.111	0.006	18.15	0.10	3	3.3	34.3
1506	25.1	1.158	0.007	2.113	0.005	18.06	0.28	3	2.4	34.5
2000	23.6	1.165	0.001	2.105	0.002	18.30	0.09	3	1.9	34.6
2999	13.2	1.168	0.007	2.108	0.009	18.39	0.15	2	1.4	34.7
3499	11.8	1.168	0.001	2.116	0.008	18.20	0.03	2	1.2	34.7
5000	5.2	1.165		2.108		18.17		1	1.1	34.7

Station N4 (30.00 °N, 165.01 °W)

20	60.0	1.165	0.002	2.102	0.001	18.18	0.04	2	23.7	34.9
101	71.8	1.164	0.006	2.107	0.012	18.12	0.05	2	17.8	34.7
201	74.8	1.160	0.002	2.108	0.005	18.26	0.02	2	16.9	34.7
300	66.4	1.164	0.002	2.107	0.003	18.20	0.01	2	16.2	34.6
601	46.9	1.159	0.002	2.114	0.004	18.11	0.04	4	7.9	34.1
1003	38.0	1.161	0.001	2.109	0.003	18.15	0.05	3	3.8	34.3
1502	29.6	1.164	0.003	2.107	0.008	18.31	0.02	3	2.4	34.5
2001	19.3	1.167	0.002	2.108	0.004	18.24	0.06	3	1.8	34.6
2999	15.3	1.173	0.002	2.102	0.002	18.32	0.06	2	1.3	34.7
4001	8.4	1.169	0.008	2.096	0.012	18.28	< 0.01	2	1.2	34.7
5000	5.5	1.168	0.001	2.110	0.003	18.31	0.05	2	1.0	34.7

* The authors presumed this sample was contaminated because of its elevated Pb concentration and outlier isotopic composition. It was not included in the analyses and discussion od this dataset.

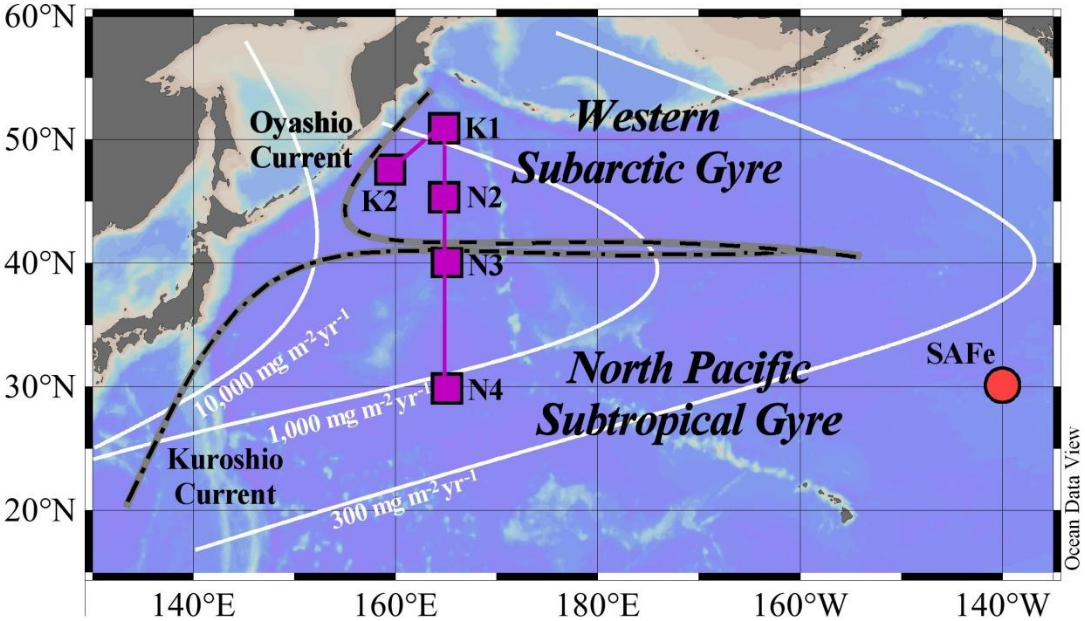

Figure 1. The two cruises sampled waters in the North Pacific Ocean. The GEOTRACES Intercalibration 2 (IC2) cruise sampled the central NPSG in May, 2009 (red circle), and the GEOTRACES KH11-07 cruise sampled the WSAG and western NPSG in July – August 2011 (purple squares).

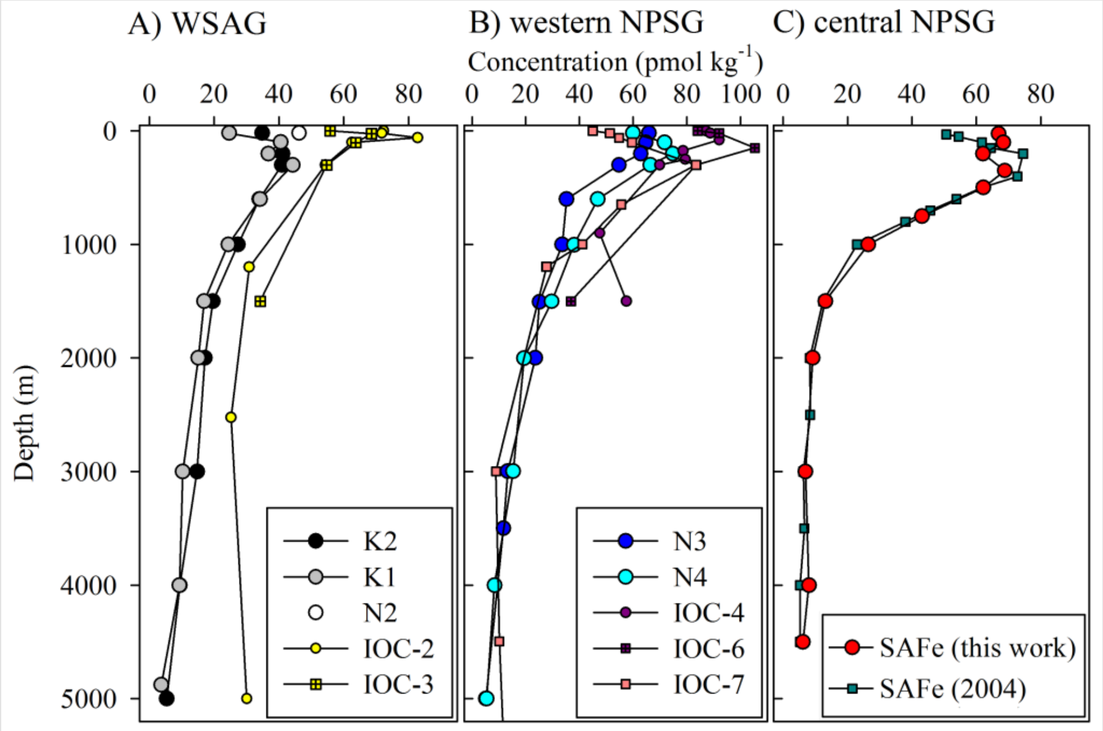

Figure 2. Dissolved (0.2 µm) Pb concentrations had a subsurface maximum and diminished in concentration with depth. A) In the WSAG the 2011 data (grey, black and white circles) were lower in concentration than data previously reported for total dissolvable Pb (yellow circles and squares, Zurbrick et al., 2014) throughout the entire water column. B) In the western NPSG, 2011 subsurface waters (blue circles) were similar to data previously reported for total dissolvable Pb (purple circles and squares, Zurbrick et al., 2014). C) In the central NPSG, 2011 near-surface waters (red circles) were elevated relative to dissolved Pb (blue squares) data previously reported (Wu et al., 2010) but were similar in concentration below the mixed layer depth.

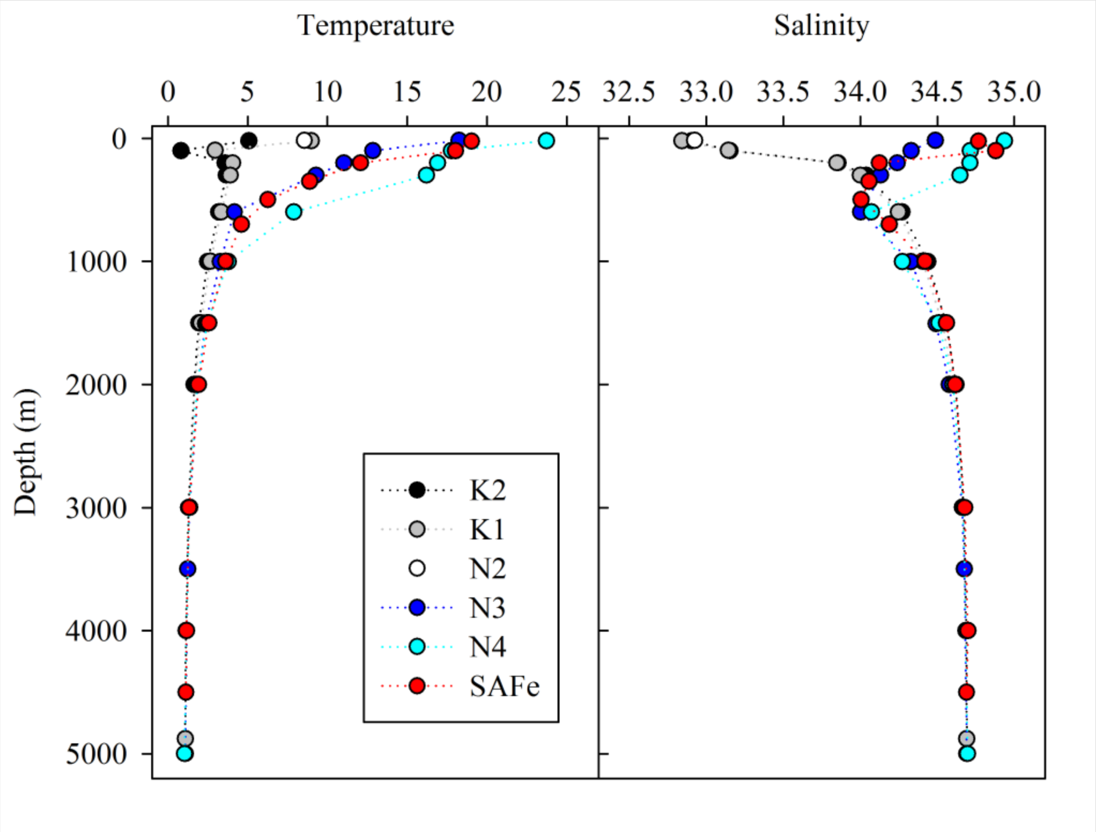

Figure 3. Temperature and salinity plots of the 5 depth profiles showed that the waters below 1,500 m were similar in both parameters, implying they were the same water mass.

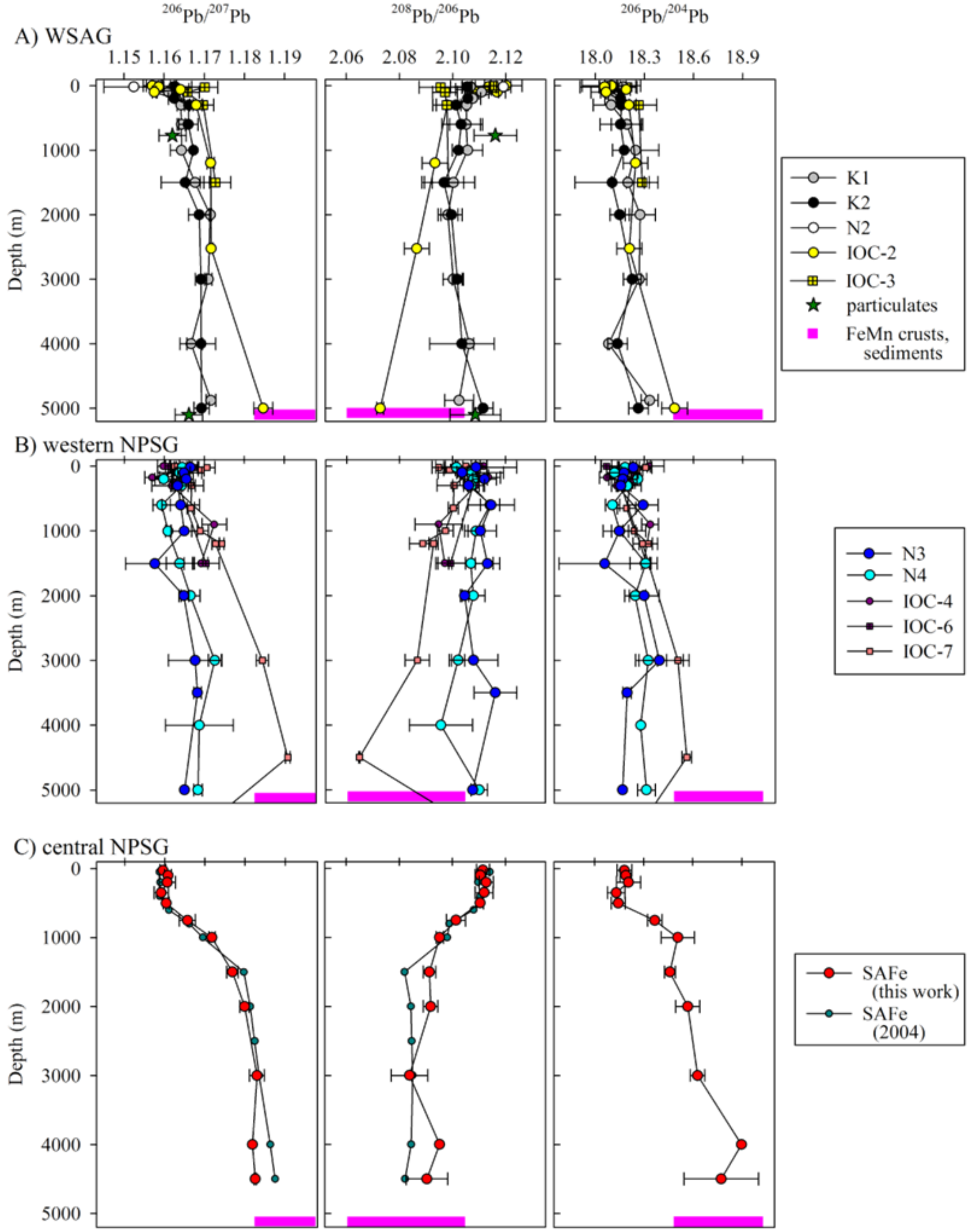

Figure 4. Lead isotope compositions versus depth in the a) WSAG, b) western NPSG and c) central NPSG. The data are compared with previously published data: IOC 2002 (Zurbrick et al., 2014), particles (Nagaoka et al., 2010), SAFe 2004 (Wu et al., 2010), FeMn crusts (Ling et al., 1997) and sediments (Chow and Patterson, 1962; Chow and Tatsumoto, 1964; Kersting, 1995).

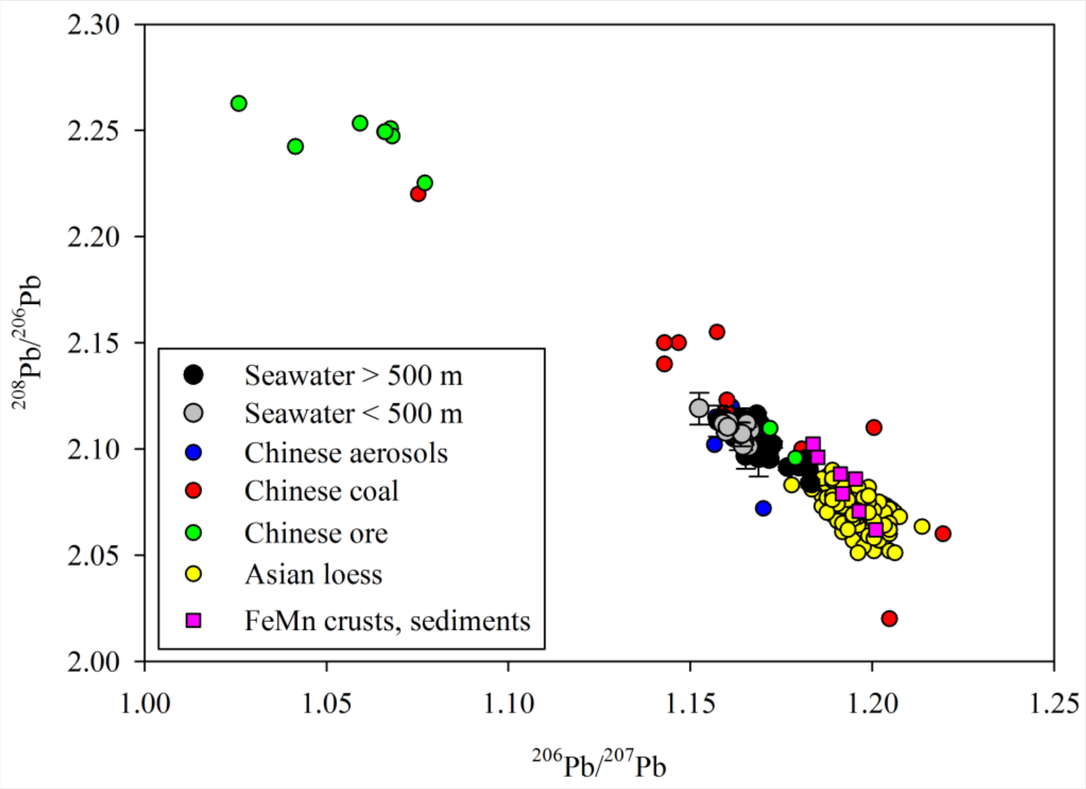

Figure 5. The triple isotope plot of $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ showed this seawater data (> 500 m or < 500 m depth) compared with PbICs of possible sources reported by others. Several of the deep water samples (black circles) were more similar to FeMn crusts and sediments (magenta squares; references same as Figure 4). Most deep water and near-surface water samples (grey circles) were very similar to Chinese aerosols (blue circles, Zheng et al., 2004; Chen et al., 2005). These aerosols are composites of Chinese ores (green circles, Sangster et al., 2000 and references therein), Chinese coal (red circles, Mukai et al., 1993; Mukai et al., 2001) and Asian loess (yellow circles, Jones et al., 2000; Sun and Zhu, 2010; Wu et al., 2011).

CHAPTER 5. LEAD IN COASTAL CALIFORNIA IMPACTED BY CURRENT AND PAST SOURCES OF CONTAMINATION

Cheryl M. Zurbrick, Dondra V. Biller, Ralph C. Till, Kenneth W. Bruland and A. Russell Flegal

Prepared for *Proceedings of the National Academy of Sciences*

Abstract

In this study, we found lead (Pb) in coastal surface waters was a mix of remobilized US leaded gasoline from 20 + years ago which flushes out of San Francisco Bay (SFB) and Asian industrial Pb aerosols deposited in the North Pacific. Lead concentrations of off-shore surface (11 – 31 pmol kg^{-1}) and subsurface (18 – 67 pmol kg^{-1}) waters were isotopically indistinguishable ($^{206}Pb/^{207}Pb = 1.158 – 1.174$; $^{208}Pb/^{206}Pb = 2.092 – 2.113$) from those Pb isotopic compositions (PbICs) of Chinese aerosols ($^{206}Pb/^{207}Pb = 1.157 – 1.170$; $^{208}Pb/^{206}Pb = 2.072 – 2.115$) (Zheng 2004, Chen 2005). Near-shore seawater had a wide range in Pb concentrations (16 – 78 pmol kg^{-1}) above the continental shelf, where surface water PbICs ($^{206}Pb/^{207}Pb = 1.167 – 1.179$; $^{208}Pb/^{206}Pb = 2.089 – 2.102$) were similar to those Chinese aerosols but benthic water PbICs ($^{206}Pb/^{207}Pb = 1.182 – 1.187$; $^{208}Pb/^{206}Pb = 2.075 – 2.081$) were more radiogenic. These benthic waters were isotopically alike with benthic particles ($^{206}Pb/^{207}Pb = 1.189 – 1.196$; $^{208}Pb/^{206}Pb = 2.061 – 2.069$) which was attributed to rapid isotopic equilibrium. Benthic particle Pb concentrations were negatively correlated (r = -0.63, Pearson correlation coefficient) with distance from the mouth of San Francisco Bay (SFB). In addition, these particles were isotopically consistent

with Pb from SFB ($^{206}Pb/^{207}Pb = 1.181 – 1.187$; $^{208}Pb/^{206}Pb = 2.065 – 2.080$) which were previously attributed to persistent contamination from historic US gasoline Pb deposits in its drainage basin.

Although coastal surface water Pb concentrations were higher than those off-shore, the correlation (r = 0.75, Pearson correlation coefficient) between Pb concentrations and salinity indicated that this spatial elevation was a result of upwelled subsurface waters and not a large diffusive flux of Pb out of benthic sediments along the continental shelf. That attribution was substantiated by our calculation that directly above the continental shelf 31% of Pb came from remobilized historic US leaded gasoline and 69% was from contemporary Asian industrial Pb. The contribution from US gasoline Pb was diminished by the relatively greater amounts of Asian industrial Pb in offshore CCS waters. Therefore, we determined that the predominant source of Pb was from the deposition of Asian industrial aerosols.

1. Introduction

Previous studies have documented lead (Pb) contamination in the immediate coastal region of California. In one case, this contamination was due to a point source contaminant located in Monterey Bay (Flegal et al., 1987). Using mussels as biomonitors of contamination, Flegal and colleagues documented exceptionally high Pb concentrations (3 – 1826 $\mu g\ g^{-1}$) in the mussels in Monterey Bay compared with typical concentrations found along the coast (0.5 $\mu g\ g^{-1}$). Stable Pb isotope compositions (PbICs) were used to identify the source of Pb contamination as a Pb slag deposit beside the Bay, and determined very little of the Pb in the mussels was from seawater or industrial aerosols. In another case, Pb contamination from non-point sources was documented in otters around Monterey Bay (Smith et al., 1992). In that study, Pb concentrations in the teeth of modern (1980s) otters were twice as high as the Pb concentrations in pre-industrial (pre-1800) otters. Lead isotopic compositions were used to identify the source of Pb in pre-industrial otters as natural and continental derived Pb, while the modern otters had Pb contributions from the point source slag and contemporary US industrial aerosols. Those industrial aerosols were attributed to the ongoing use of leaded gasoline in the United States at that point in time and to a much lesser degree Asian industrial Pb.

Neritic waters off of California were also found to be contaminated by Pb of both local and remote origins. Using PbICs, Flegal and colleagues (1989) documented that PbICs (^{206}Pb/^{207}Pb = 1.181 – 1.204; ^{208}Pb/^{206}Pb = 2.029 - 2.063) in surface waters of the California Current System (CCS) were similar to those of US industrial Pb (^{206}Pb/^{207}Pb ≈ 1.22, ^{208}Pb/^{206}Pb ≈ 2.02), while upwelled water PbICs (^{206}Pb/^{207}Pb = 1.174 – 1.175; ^{208}Pb/^{206}Pb = 2.069 – 2.079) were more like those of Asian industrial Pb (^{206}Pb/^{207}Pb ≈ 1.16, ^{208}Pb/^{206}Pb ≈ 2.09).

The upwelling of Asian Pb in California’s coastal waters occurs because Pb deposited to Northwest Pacific surface waters subducts with surrounding water to the subsurface in the North Pacific, and is then advected to the California coast through its eastward, shoaling flow (You et al., 2000). Dissolved Pb in subsurface waters has a longer residence time (≥ 150 years; Nozaki et al., 1980) relative to the movement of this water mass across the Pacific Ocean (10 – 30 years; Fine et al., 2001). As a result, Asian industrial Pb emissions, which deposit in the Northwest Pacific Ocean (Gallon et al., 2011) are upwelled in the Northeast Pacific (Flegal et al., 1989; Flegal et al., 1993).

Furthermore, Pb contamination from non-point sources has been documented along the entire West Coast of North America and in the central North Pacific Ocean in the 1980s. Stukas and Wong (1981) and Flegal et al. (1986) documented the PbICs (^{206}Pb/^{207}Pb = 1.191 – 1.253; ^{208}Pb/^{206}Pb = 1.975 - 2.048) of waters off British Columbia (5 – 750 km) as being contaminated by modern US industrial Pb from aerosol deposition. Farther from shore (~1200 km), surface water PbICs (^{206}Pb/^{207}Pb = 1.164; ^{208}Pb/^{206}Pb = 2.124) were less radiogenic (Flegal et al., 1986). Flegal et al. attributed that Pb to Asian (Japanese) industrial Pb aerosols (^{206}Pb/^{207}Pb ≈ 1.16; ^{208}Pb/^{206}Pb ≈ 2.09), derived from atmospheric deposition. However, these values differed from central Pacific surface water PbICs (^{206}Pb/^{207}Pb = 1.184 – 1.196; ^{208}Pb/^{206}Pb = 2.044 – 2.057) also collected in 1980 (Flegal et al., 1984), which were primarily attributed to atmospheric deposition of North American industrial Pb.

In contrast to those previous measurements, today the central North Pacific surface water no longer has measurable signatures of US industrial Pb. In 2002, the Northwest and central Pacific surface water PbICs (^{206}Pb/^{207}Pb = 1.153 – 1.169; ^{208}Pb/^{206}Pb = 2.093 - 2.119) were relatively homogenous. Those PbICs were attributed to deposition of Chinese industrial Pb emissions (Wu et al., 2010; Gallon et al., 2011; Zurbrick and Flegal, 2014) because of their similarity to aerosol PbICs in

China (^{206}Pb/^{207}Pb = 1.157 – 1.170; ^{208}Pb/^{206}Pb = 2.072 – 2.115, Zheng et al., 2004; Chen et al., 2005). In addition, Gallon et al. (2011) found relatively high enrichment factors (up to 131) for Pb in aerosol samples across the western and central North Pacific Ocean which indicated that aerosol Pb was predominantly anthropogenic. The temporal change in PbICs of North Pacific surface water was attributed to the completed phase-out of leaded gasoline in most of the world since the initial studies (Nriagu, 1990) and the increase in coal consumption by China (Tian et al., 2012; Li et al., 2012), which has relatively high (~ 35 ppm) Pb concentrations (Díaz-Somoano et al., 2009). These growing atmospheric Pb emissions are subject to long-distance transport and subsequent deposition in remote waters.

There are several possible sources of Pb in coastal waters off California. Water that flushes San Francisco Bay (SFB) could contribute relatively large concentrations of Pb to coastal waters. The Bay has a history of contamination, particularly for high seasonal sediment loadings (McKee et al., 2002) and trace metals (Flegal et al., 1991; van Geen and Luoma, 1999; Steding et al., 2000; Hurst and Bruland, 2008). Lead measured in sediment cores was three times higher in the 1990s and isotopically distinct (^{206}Pb/^{207}Pb = 1.181 – 1.189; ^{208}Pb/^{206}Pb = 2.066 – 2.074) compared with pre-industrial times (^{206}Pb/^{207}Pb = 1.221 – 1.222; ^{208}Pb/^{206}Pb = 2.034 – 2.036, Ritson et al., 1999). Ritson et al. (1999) attributed more than 50% of the Pb in the post-industrial sediments to US industrial Pb sources (i.e., leaded gasoline, mining, smelting), which persisted in the Bay because of the strong affinity of Pb for sediments (Dunlap et al., 2000; Steding et al., 2000).

Furthermore, modern SFB surface water PbICs (^{206}Pb/^{207}Pb = 1.175 – 1.185; ^{208}Pb/^{206}Pb = 2.072 – 2.076) and sediments (^{206}Pb/^{207}Pb = 1.175 – 1.190; ^{208}Pb/^{206}Pb = 2.063 – 2.068) were isotopically alike (Dunlap et al., 2000). This agreement was attributed to the rapid exchange of particulate and dissolved Pb which establishes isotope equilibrium in 1 – 9 days (Gee, 2003), consistent with observations in the Atlantic Ocean (Sherrell et al., 1992) and studies of particulate and dissolved ^{210}Pb in river water (Benoit and Hemond, 1991).

Although ~ 90% of Pb in SFB is in the particulate phase (Gee, 2003), it is relevant to the coastal waters because relatively large amounts of suspended sediments are flushed out of the Bay with the ebb tide (Hurst and Bruland, 2008). The high concentration of leachable particulate Pb was previously found to be a good tracer of the Bay's plume as it flowed into coastal waters (Hurst and Bruland, 2008). Despite the recent decrease in Pb contamination to SFB, the persistence of historic Pb in the sediments was projected to be a continued source of Pb for many decades (Dunlap et al., 2000; Steding et al., 2000).

Although dissolved Pb in the plume dilutes as it mixes with CCS waters, many of the particulates that flush out of SFB and coastal rivers settle and accumulate in the "mud belt" on the continental shelf, operationally defined as the region between the 50 – 90 m isobaths (Wheatcroft et al., 1997; Xu et al., 2002). Prior work by Biller et al. (2013) investigated benthic iron (Fe) concentrations derived from riverine sediments. They found a correlation between dissolved and particulate leachable Fe concentrations and the continental shelf mud belt width. Due to the behavior of both

Fe and Pb scavenging onto particles (Bruland et al., 2012), it was anticipated that Pb concentrations would also be correlated with mud belt width. Furthermore, the physical process of upwelling over the mud belt was documented to pick up Fe from the continental shelf and bring it to coastal surface waters (Biller et al., 2013). Eddies can then carry coastal waters off-shore, mixing them with CCS surface water (Strub et al., 1991). Through this process, subsurface Pb from off-shore can become coastal surface water, and possibly entrain Pb from the benthic layer on the continental shelf.

Several known changes in Pb inputs to the California coast have occurred in the last two decades. The point source (Pb slag deposit) in Monterey Bay has been removed, leaded gasoline has been phased-out for most vehicles since the early 1990s (aviation gasoline is still leaded), and aerosol Pb concentrations have decreased (Flegal et al., 1996). Corresponding changes in PbICs from 1990 (^{206}Pb/^{207}Pb = 1.200 – 1.216; ^{208}Pb/^{206}Pb = 2.022 – 2.044; Sanudo-Wilhelmy and Flegal, 1994) to 1998 (^{206}Pb/^{207}Pb = 1.159 – 1.186; ^{208}Pb/^{206}Pb = 2.058 – 2.099; Bollhöfer and Rosman, 2001) also documented a change in the dominant source of Pb to California, with the more recent aerosols being attributed to long-range transport of Asian industrial Pb emissions (Bollhöfer and Rosman, 2001).

Because CCS surface waters reflect aerosol inputs as documented by (Flegal et al., 1989), we anticipated that the off-shore surface waters would have PbICs more similar to those of Asian industrial Pb than those of US industrial Pb. However, we expected the PbICs of the SFB and portion of the mud belt near upwelling to continue reflecting their historic contamination of US industrial Pb inputs. Therefore, this study’s objective was to re-evaluate the current sources of Pb in the California coast through measurements of Pb concentrations and PbICs in seawater and marine particulates in the California Current upwelling zone.

2. Methods

2.1 Cruise overview

Seawater and particulate samples were collected aboard the R/V Point Sur on two expeditions in May 2010 and August 2011, as detailed in Biller and Bruland (2013) and Biller et al. (2013). During these voyages samples were collected from upwelling and downwelling cores, eddies moving off-shore, and the SFB and its plume during an ebb tide (Figure 1). These hydrographic features were located using temperature and salinity via the shipboard underway data acquisition system and daily satellite imagery of sea surface temperature from the NOAA POES AVHRR satellite (coastwatch.pfeg.noaa.gov).

2.2 Sampling methods

2.2.1 Seawater

Surface waters were collected by a towed trace metal clean GeoFISH (Bruland et al., 2005), and subsurface seawater was collected for trace metals in 8 L Teflon™ coated GO-FLO™ bottles (General Oceanics) deployed on a Kevlar® hydroline (Bruland et al., 1979). Vertical hydrographic data were collected using the R/V Pt. Sur's rosette system with a conductivity, temperature, depth (CTD) sensor (Seabird). All trace metal samples from the surface and subsurface waters were filtered using 0.2 µm pore size Acropak™ 200 capsule filters and subsampled using trace metal clean techniques (Bruland et al., 1979). Subsamples were collected and stored in trace metal clean 1 – 2 L low density polyethylene (LDPE) bottles for off-shore profiles, or 100 mL LDPE bottles for surface and near-shore profiles. While at sea, samples were acidified to pH ≈ 2 with 4 mL of ~ 6 M ultrapure (sub-boiling quartz-distilled, “Q”) HCl per liter of seawater.

2.2.2 Particulates

Particulate samples were collected by filtering 200 – 2000 mL of seawater through acid-cleaned 47 mm diameter 0.4 μm Nuclepore™ polycarbonate track-etched membrane filters (Whatman®). Filters were mounted on a polypropylene filter sandwich, and the filtration apparatus was pressurized with filtered nitrogen gas. After filtration, the filters were folded and stored frozen in acid-cleaned high-density polyethylene vials.

2.3 Analyses

2.3.1 Concentrations in seawater

The off-shore profiles were analyzed for dissolved Pb using an on-line preconcentration step in the Marine Analytical Lab (MAL) at UC Santa Cruz (UCSC) as detailed by Ndung’u et al. (2003). Briefly, Pb was concentrated on microcolumns filled with Toyopearl AF-Chelate 650 M ™ ion-exchange resin and controlled by a Finnigan μ-sampler flow injection manifold. Samples were eluted directly into the Thermo ELEMENT XR™ magnetic sector high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) and analyzed in low resolution mode. Procedural extraction blanks in acidified (24 mM Q HCl) ultrapure (18 MΩ cm) water (Millipore Milli-Q ® Academic with Ultrapure Ionex Cartridge) were 3.5 ± 1.2 (1 s.d.) pmol kg^{-1} (n = 43, Table 1). The detection limit (3X s.d. of the blank) was 3.7 pmol kg^{-1}. Seawater reference materials from the SAFe and GEOTRACES programs which were extracted and analyzed concurrently were in agreement with consensus values (Table 2).

Surface seawater samples from transects and shallow profiles over the continental shelf were analyzed using the multi-element method of Biller and Bruland (2012). In brief, Pb was quantitatively extracted and analyzed along with seven other trace metals (values reported in Biller and Bruland, 2013). This method involved off-line preconcentration of the trace metals on columns filled with Nobias-chelate PA1® resin, eluted with 1 M Q HNO_3 and analyzed by HR-ICP-MS in the MAL at UCSC. Extraction blanks of column-cleaned seawater (as detailed in Biller and Bruland, 2012) were 0.6 ± 0.3 pmol kg^{-1} (n = 32); the detection limit was 0.7 pmol kg^{-1} (Table 1). Lead concentrations of SAFe seawater reference samples extracted concurrently were in excellent agreement with consensus values (Table 2).

2.3.2 Concentrations in particulates

Particulate samples were leached using the method of Berger et al. (2008). This method used a weak acetic acid leach (25%, pH = 2) with a mild reducing agent (0.02 M hydroxylamine hydrochloride) and heat (10 min, 90 – 95 ˚C). Leachates were analyzed for Pb concentrations using the HR-ICP-MS. The filter blanks were 0.5 ± 0.1 pmol (n = 4), while process blanks (50 – 150 mL of 0.2 µm filtered seawater) were 6.3 ± 2.1 pmol kg^{-1} (n = 7) and the detection limit (3X s.d. of the instrument blank) was 0.1 pmol kg^{-1} (Table 1).

2.3.3 PbICs

Select samples were analyzed for PbICs. Seawater samples (100 – 350 mL) were preconcentrated off-line on Toyopearl AF-Chelate 650 M ™ ion-exchange resin and eluted in 1.5 M Q HNO_3 following the method of Zurbrick et al. (2013). Extraction blanks in acidified (24 mM Q HCl) ultrapure water were 18 ± 12 pg of Pb (0.6 pmol kg^{-1}, n = 26, Table 1). Isotope abundances were determined on the HR-ICP-MS in the MAL at UCSC in counting mode and corrected for ^{204}Hg isobaric interference. Mass bias was corrected by bracketing with National Institute of Standards and Technology standard reference material 981 (common lead) as detailed in Zurbrick et al. (2013). The analytical reproducibility of 981 (2 s.d.) was ^{206}Pb/^{207}Pb = 7‰, ^{208}Pb/^{206}Pb = 2‰ and ^{206}Pb/^{204}Pb = 92‰ (n = 64), which was in good agreement with our previously reported reproducibility for GEOTRACES IC1 (Zurbrick et al., 2013; Boyle et al., 2012).

When enough Pb was present, PbICs were determined for particulate samples. Leachates were either diluted with 1.5 M Q HNO_3 or dried in trace metal clean Teflon™ vials on a hotplate and reconstituted in 1.5 M Q HNO_3 to a concentration of 5 pmol kg^{-1} for analysis. Samples were then analyzed in the same manner as described for seawater extracts.

3. Results

3.1 Off-shore Pb profiles

There was a subsurface Pb concentration maximum in the off-shore profiles (Figure 2a, Table 3). Dissolved Pb concentrations (20 – 40 pmol kg^{-1}) were lower in surface and deep waters than in the subsurface (100 – 500 m) waters (50 – 65 pmol kg^{-1}). This subsurface maxima corresponded to water densities of σ_Θ = 25.6 – 26.9 (Figure 2a, b), and varied between 100 – 200 m depending on whether the station was located in upwelling favorable or downwelling favorable conditions.

Lead isotopic compositions (^{206}Pb/^{207}Pb = 1.158 – 1.174; ^{208}Pb/^{206}Pb = 2.092 – 2.113) of the 2011 off-shore stations (13, 14, 18, 26, 30) were relatively homogenous (Figure 2c, d). At four of these stations (14, 18, 26, 30) the subsurface Pb maxima had the least radiogenic PbICs (^{206}Pb/^{207}Pb = 1.158 – 1.165; ^{208}Pb/^{206}Pb = 2.105 – 2.112). Of note, the 40 m sample at Station 30 had anomalous isotopic ratios (^{206}Pb/^{207}Pb = 1.156; ^{208}Pb/^{206}Pb = 3.972). Repeated extractions (3) of this sample ruled out the possibility of the anomalous isotopes being an analytical artifact. Because the abundance of ^{208}Pb was quite high, we assumed the sample was contaminated and this data point was not included in the discussion of this dataset.

3.2 Surface Pb

Dissolved Pb concentrations in surface waters varied with their distance to the coast (Table 4, Figure 3a). In surface waters along the coast (< 50 km off-shore) Pb concentrations (30 – 50 pmol kg^{-1}) were relatively high with the exception of one transect just south of the mouth to SFB (17 – 36 pmol kg^{-1}). In the waters further off-shore (> 50 km), surface concentrations (11 – 30 pmol kg^{-1}) were lower than near-shore.

Some of the highest dissolved and particulate Pb concentrations were measured on the transect out of SFB. Dissolved Pb concentrations within the Bay (42 – 47 pmol kg^{-1}) and ebb plume waters (37 – 46 pmol kg^{-1}) were relatively high (Figure 4a) while those of coastal waters outside the plume were lower (32 pmol kg^{-1}). Particulate Pb concentrations within the SFB (6 – 11 nmol kg^{-1} of water) and plume (2.4 – 7 nmol kg^{-1} of water) were the highest of all samples collected, while particles outside the plume had a much lower concentration (0.2 nmol kg^{-1} of seawater). The lower particulate Pb concentration outside the Bay was typical of coastal waters which had very low concentrations (< 0.2 nmol kg^{-1} of seawater, Table 5), and the high particulate Pb concentrations in the plume were consistent with the previous report of Hurst and Bruland (2008).

Lead isotopic compositions of SFB surface waters were isotopically distinct from those of off-shore waters. In the Bay and its plume the PbICs (^{206}Pb/^{207}Pb = 1.181 – 1.187; ^{208}Pb/^{206}Pb = 2.071 – 2.080) were more radiogenic than coastal water PbICs (^{206}Pb/^{207}Pb = 1.171 – 1.176; ^{208}Pb/^{206}Pb = 2.071 – 2.080, Table 6, Figure 4b and c). Similarly, particulate PbICs (^{206}Pb/^{207}Pb = 1.183 – 1.187; ^{208}Pb/^{206}Pb = 2.067 – 2.080) were isotopically indistinguishable from the dissolved PbICs within SFB and its plume. Just outside the plume, particulate PbICs (^{206}Pb/^{207}Pb = 1.178; ^{208}Pb/^{206}Pb = 2.080) and dissolved PbICs (^{206}Pb/^{207}Pb = 1.176; ^{208}Pb/^{206}Pb = 2.088) were similar to one another but isotopically different than SFB and its plume.

3.3 Benthic shelf

Along the coast, benthic waters (39 – 340 m) were elevated in Pb concentration (46.1 ± 11.0 pmol kg^{-1}) relative to overlying surface waters (35.0 ± 10.3 pmol kg^{-1}, Table 5). We attributed this difference in concentrations over a relatively shallow distance to the variable upwelling intensity along the coast during our sampling period. Elevated chlorophyll *a* concentrations (6 ± 6 µg kg^{-1}) in these surface waters also suggested Pb could have scavenged onto particles (i.e., plankton).

Leachable Pb concentrations in particles over the continental shelf varied with depth (Table 5). In the benthic layer, particle Pb concentrations (111 ± 139 pmol kg^{-1} of seawater) were higher than in overlying surface waters (32 ± 33 pmol kg^{-1} of seawater, Table 5). Benthic particles had PbICs (^{206}Pb/^{207}Pb = 1.189 – 1.196; ^{208}Pb/^{206}Pb = 2.061 – 2.069) comparable to both benthic waters (^{206}Pb/^{207}Pb = 1.182 – 1.187; ^{208}Pb/^{206}Pb = 2.075 – 2.081) and SFB particles (Table 6). The similarity in PbICs between benthic particles and water supports previous studies of isotopic equilibrium between these two pools of Pb in oceanic waters (Sherrell et al., 1992; Gee, 2003). In contrast, the overlying surface waters had less radiogenic PbICs (^{206}Pb/^{207}Pb = 1.167 – 1.179; ^{208}Pb/^{206}Pb = 2.089 – 2.102), more similar with those of Asian industrial Pb emissions.

4. Discussion

4.1 Off-shore Pb: coming from Asia

Dissolved Pb in surface waters had PbICs (^{206}Pb/^{207}Pb = 1.160 – 1.166; ^{208}Pb/^{206}Pb = 2.101 – 2.113) which were isotopically consistent with those of Chinese aerosols (^{206}Pb/^{207}Pb = 1.162 ± 0.004, ^{208}Pb/^{206}Pb = 2.107 ± 0.013; Zheng et al., 2004;

Chen et al., 2005, Figure 5). The Pb in those aerosols has been traced to Asian industrial Pb emissions, primarily from fossil fuel burning (i.e., coal combustion) (Zheng et al., 2004; Chen et al., 2005). Those Asian industrial aerosols are transported long distances by the Westerlies winds and have been documented to deposit in the North Pacific Ocean and along the West Coast of North America (Gallon et al., 2011; Jaffe et al., 1999; McKendry et al., 2008; Uno et al., 2009). Recent models have projected that ~ 0.3 g m^{-2} yr^{-1} of dust derived from Asia, or 10 – 20% of the dust from Asia (over Japan), is deposited in the Northeast Pacific coastal region annually (Takemura et al., 2002; Uno et al., 2009). These models have been corroborated by measurements of aerosols PbICs (^{206}Pb/^{207}Pb = 1.172 ± 0.008; ^{208}Pb/^{206}Pb = 2.080 ± 0.011) in California in 1998 (Bollhöfer and Rosman, 2001), which were consistent with declining US industrial Pb emissions and increasing Chinese industrial Pb emissions.

These analyses show that the primary source of Pb to off-shore surface water in the CCS has changed since the 1980s. Previous studies demonstrated that Pb was predominantly derived from US industrial and leaded gasoline emissions (Flegal et al., 1984, 1989). In 2010 and 2011, the CCS surface waters reflected inputs of Asian industrial Pb emissions, akin to the changes in PbICs of surface water in the central North Pacific (Wu et al., 2010; Gallon et al., 2011; Zurbrick and Flegal, 2014). The change in both the central and eastern North Pacific PbICs was attributed to the phase-out of leaded gasoline usage since the initial studies of Flegal and colleagues (C.E.C., 1990; Nriagu, 1990). Lead isotopic compositions of surface waters reflected the changes in atmospheric Pb on this timescale because of the short (6 – 10 day) residence time of Pb in atmospheric dust (Settle and Patterson, 1991; Jaffe et al., 1999) and in surface waters (< 2 years; Nozaki et al., 1976).

Like off-shore surface waters, sub-surface waters (15 – 500 m) reflected Asian industrial Pb signatures (Figure 5). The CCS subsurface Pb concentration maxima (50 – 65 pmol kg^{-1}) had a similar density (σ_Θ = 25.6 – 26.9) to the subsurface Pb concentration maxima (70 – 86 pmol kg^{-1}) in the Northwest Pacific Ocean (σ_Θ = 25.5 – 27, Zurbrick et al., 2014). In addition, PbICs (^{206}Pb/^{207}Pb = 1.158 – 1.165; ^{208}Pb/^{206}Pb = 2.105 – 2.112) of the subsurface Pb feature in the CCS matched the PbICs (^{206}Pb/^{207}Pb = 1.157 – 1.167; ^{208}Pb/^{206}Pb = 2.100 – 2.113) of the subsurface Northwest Pacific water at similar densities (Zurbrick and Flegal, 2014; Zurbrick et al., 2014). Previous work by Fine et al. (2001) used chloroflulorocarbon (CFC) data to approximate the age of waters at this density between 10 and 30 years, meaning the off-shore subsurface waters reflected Asian industrial Pb inputs from 1980 – 2000. In addition, the agreement between subsurface CCS water and the upwelled water analyzed by Flegal et al. (1989) demonstrates that Asian industrial Pb inputs to the Northwest Pacific Ocean have not changed appreciably in the past 30 years.

4.2 Upwelled waters supply Pb to surface waters

Surface water concentrations of Pb (30 – 50 pmol kg^{-1}) near the coast (< 50 km off-shore) were higher than those of waters off-shore (> 50 km, 11 – 30 pmol kg^{-1}, Figure 3a). These surface water concentrations were positively correlated (r = 0.75, Pearson correlation coefficient) with salinity, with lower salinity waters (≈ 32) having lower Pb concentrations (11 – 20 pmol kg^{-1}) and higher salinity waters (≈ 34) having higher Pb concentrations (40 – 50 pmol kg^{-1}, Figure 6). High salinity surface water near the coast originated from the off-shore subsurface Pb concentration maxima (45 – 67 pmol kg^{-1}) which was corroborated by their similar water densities (σ_{Θ} = 25.5 – 26 and 25.6 – 26.9, respectively). In contrast, the less saline waters off-shore in the CCS were stratified from the subsurface Pb maxima, keeping the Pb concentrations lower. In addition, they were relatively older waters compared with the freshly upwelled coastal waters, and could have lost Pb to scavenging and vertical export.

The exception to the relationship between salinity and Pb concentrations was in the SFB plume where there were high Pb concentrations (37 – 47 pmol kg^{-1}) and low salinities (≈ 32). However, this anomaly was not seen far beyond the mouth of the Bay. Satellite imagery of sea surface temperature (Figure 1) confirmed that warm SFB waters mixed with coastal waters near the mouth of the Bay on short timescales (at most days), which diluted the high Pb concentrations and simultaneously elevated the salinity.

4.3 Remobilization: SFB and the mud belt

Similar to upwelled waters, Pb in the SFB had not changed in recent history. Dissolved and particulate Pb concentrations (37 – 47 pmol kg^{-1} and 2 – 11 nmol kg^{-1} of water, respectively) within the SFB and plume were some of the highest measured in surface waters during the cruises (Figure 4a). In addition, the PbICs ($^{206}Pb/^{207}Pb$ = 1.181 – 1.187; $^{208}Pb/^{206}Pb$ = 2.067 – 2.080) of SFB water and particulates from this transect were isotopically indistinguishable from sediment PbICs ($^{206}Pb/^{207}Pb$ = 1.175

– 1.190; ^{208}Pb/^{206}Pb = 2.063 – 2.076) previously reported in the SFB (Ritson et al., 1999; Dunlap et al., 2000; Steding et al., 2000, Figure 5). Those earlier works attributed the Pb in SFB to persistent inputs of US gasoline Pb which accumulated in the sediments. The isotopic similarity of the water and particles supported the rapid (days) isotopic equilibration of dissolved and particulate Pb documented previously (Benoit and Hemond, 1991; Gee, 2003) and observed above the mud belt in this work. As a result of this isotopic equilibrium, the ebb tide carried old US gasoline Pb out to the coast with SFB water and particles.

We expected particulate Pb concentrations to correlate with mud belt width as was previously documented for Fe (Biller et al., 2013). However, the correlation ($r = 0.52$, Pearson correlation coefficient) between mud belt width and particulate Pb was relatively weak (t-test, $p < 0.05$). In addition, dissolved manganese concentrations (Biller and Bruland, 2013) were not correlated ($r = -0.34$, Pearson correlation coefficient) with dissolved Pb concentrations in the benthic layer, suggesting manganese oxides had a limited role in influencing Pb concentrations. However, there was a negative correlation ($r = -0.63$, Pearson correlation coefficient) between benthic particulate Pb concentrations and distance from the SFB between 37º – 38º N, indicating particulate Pb concentrations decreased with increasing distance from the mouth of SFB (Figure 7). Furthermore, the benthic particulate PbICs (^{206}Pb/^{207}Pb = 1.189 – 1.196; ^{208}Pb/^{206}Pb = 2.061 – 2.069) were isotopically indistinguishable from SFB particulate PbICs (^{206}Pb/^{207}Pb = 1.188 – 1.193; ^{208}Pb/^{206}Pb = 2.061 – 2.066).

Therefore, we concluded that the Pb in the mud belt was from the SFB, and the Bay was releasing Pb derived from US gasoline from the 1980s or earlier.

In addition to the Pb within SFB, particle Pb in the mud belt continued to remobilize in benthic waters. Benthic layer particulates and dissolved Pb concentrations were positively correlation (r = 0.70, Pearson correlation coefficient, Table 5). Benthic particle PbICs (^{206}Pb/^{207}Pb = 1.189 – 1.196; ^{208}Pb/^{206}Pb = 2.061 – 2.069) and benthic seawater PbICs (^{206}Pb/^{207}Pb = 1.182 – 1.187; ^{208}Pb/^{206}Pb = 2.075 – 2.081) were more similar to each other than those of CCS surface water (^{206}Pb/^{207}Pb = 1.167 – 1.183; ^{208}Pb/^{206}Pb = 2.074 – 2.102, Table 6). This isotopic difference was surprising because the benthic seawater (σ_Θ = 26.5 ± 0.3, 46.1 ± 11.0 pmol kg^{-1}) originated from upwelled CCS subsurface water (σ_Θ = 26.5 ± 0.5; 43.7 ± 12.9 pmol kg^{-1}). The PbICs of the benthic water suggest that a rapid isotopic exchange occurs between the Pb in the mud belt and the upwelling benthic waters, with no measurable concentration change. As a result, old US gasoline Pb which flushed out to the California shelf on particles was remobilized into coastal waters as dissolved Pb. Periodic, variably intense upwelling (Biller et al., 2013), brought the remobilized Pb to the ocean surface.

Lead isotopic compositions in overlying waters evidenced the mixing of remobilized US gasoline Pb deposits in the benthic layer with surface CCS water. Benthic water PbICs (^{206}Pb/^{207}Pb = 1.182 – 1.187; ^{208}Pb/^{206}Pb = 2.075 - 2.081) were isotopically distinguishable from coastal surface water PbICs (^{206}Pb/^{207}Pb = 1.167 – 1.179; ^{208}Pb/^{206}Pb = 2.089 – 2.102). The average isotopic difference between the benthic and respective overlying waters for these stations was 12 ± 4‰ (^{206}Pb/^{207}Pb) and 17 ± 7 ‰ (^{208}Pb/^{206}Pb) (Table 6).

The difference in PbICs between benthic and overlying waters was used to estimate the quantities of remobilized US gasoline Pb and Asian industrial Pb in surface waters directly over the mud belt. We constructed a simple linear mixing model:

$$(B * {}^{R}Pb_{benthic}) + (S * {}^{R}Pb_{off\text{-}shore}) = {}^{R}Pb_{overlying}$$

where $^{R}Pb_{benthic}$ are the PbICs of benthic particles just above the mud belt (^{206}Pb/^{207}Pb = 1.189 – 1.196; ^{208}Pb/^{206}Pb = 2.061 – 2.069), $^{R}Pb_{off\text{-}shore}$ are the PbICs of surface waters in the CCS (^{206}Pb/^{207}Pb = 1.160 – 1.166; ^{208}Pb/^{206}Pb = 2.101 – 2.113), and $^{R}Pb_{overlying}$ are the PbICs of the overlying waters (^{206}Pb/^{207}Pb = 1.167 – 1.179; ^{208}Pb/^{206}Pb = 2.089 – 2.102). S is the percentage of Pb contributed by CCS off-shore waters and B is the percentage of Pb contributed by the benthic layer. This simple model assumed that CCS surface water and benthic water were the only two sources of Pb, thus the sum of S and B was 100%. Lead concentrations were substituted for PbICs to validate this assumption, and the calculated concentrations were consistent with the observed values in overlying surface waters.

We calculated coastal surface waters directly over the shelf were 31 ± 9 % remobilized historic US gasoline Pb (benthic water) and 69 ± 9 % contemporary Asian industrial aerosol Pb (CCS surface water). The isotopic signature of historic US gasoline Pb was diminished by the relatively greater amount of Pb from the deposition of Asian industrial Pb as eddies carried these coastal waters off-shore.

Overall, the contribution of remobilized, old US gasoline Pb in coastal waters was minimal compared with the much greater amount of newer Pb from Asian industrial emissions in the CCS surface and subsurface waters.

5. Conclusions

Previous studies of Pb in the coastal waters of California revealed the predominant source of Pb to surface waters was from US industrial emissions, primarily those of leaded gasoline (Flegal et al., 1989). In contrast, this study determined that CCS surface waters are now dominated by contemporary Asian industrial Pb inputs (mainly Chinese coal combustion). Upwelled waters over the mud belt on the continental shelf remobilized US industrial Pb from SFB to the surface waters. However, the old US industrial Pb was unidentifiable in off-shore waters due to the relatively greater contribution of Asian industrial Pb from the CCS and upwelled waters.

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Table 1. Blanks and detection limits for the dissolved Pb extractions and particulate Pb leaches.

Blank (pmol kg^{-1})	n	detection limit (pmol kg^{-1})	corresponding analyses
3.5 ± 1.2	43	3.7	dissolved Pb in offshore profiles
0.6 ± 0.3	32	0.7	dissolved Pb in shelf stations and surface transects
6.3 ± 2.1*	7	0.1**	particulate Pb leaches
0.6 (18 pg)	26		PbIC extraction (seawater)

* process blanks of 50 - 150 mL 0.2 μm filtered seawater

** based on instrument blank

Table 2. Values for measured reference materials SAFe Surface and Deep, GEOTRACES (GTC) Surface and Deep. The ± values correspond to 1 standard deviation. Reference materials obtained from Geoffrey Smith, www.GEOTRACES.org.

	SAFe Deep 2	SAFe Surface 1	GTC Deep	GTC Surface	corresponding analyses
Pb (pmol kg^{-1})	28.0 ± 4.4	43.9 ± 3.9	38.5 ± 2.4	25.5 ± 4.0	dissolved Pb in offshore profiles
n	8	5	5	5	

Pb (pmol kg^{-1})	26.3 ± 0.9	47.6 ± 0.9	-	-	dissolved Pb in shelf stations and surface transects
n	16	16	-	-	

Table 3. Lead concentrations and isotopic compositions in the off-shore profiles. n refers to the number of analyses for PbICs.

Depth (m)	Sigma-theta	Salinity	Dissolved Pb (pmol kg^{-1})	^{206}Pb/^{207}Pb	S.E. (2 σ)	^{208}Pb/^{206}Pb	S.E. (2 σ)	^{206}Pb/^{204}Pb	S.E. (2 σ)	n
Station 14, May 2010 (40.50˚N, 125.76˚W)										
0	24.68	32.5	24.8							
20	24.68	32.5	29.3							
95	25.41	33.1	39.8							
175	26.31	33.9	55.4							
240	26.54	34.0	55.2							
490	26.90	34.1	56.0							
740	27.17	34.3	40.2							
Station 15, May 2010 (39.50˚N, 125.21˚W)										
0	24.55	32.4	26.1							
20	24.56	32.4	19.5							
80	24.98	32.7	23.0							
145	26.04	33.6	31.9							
240	26.50	34.0	49.2							
490	26.88	34.1	43.5							
740	27.16	34.3	40.4							
Station 16, May 2010 (38.74˚N, 124.50˚W)										
0	25.34	33.1	21.8							
15	25.36	33.2	18.4							
70	26.23	33.8	50.9							

140	26.50	34.0	61.0							
240	26.69	34.1	61.3							
490	27.01	34.2	47.6							
740	27.23	34.3	36.5							
Station 31, May 2010 (36.50˚N, 122.50˚W)										
0	25.36	33.4	31.3							
45	25.87	33.6	43.1							
180	26.49	34.1	47.6							
460	26.93	34.2	46.4							
700	27.17	34.3	41.3							
920	27.33	34.4	22.0							
Station 40, May 2010 (34.80˚N, 122.00˚W)										
25	24.88	33.2	27.8							
100	25.62	33.3	53.5							
150	26.14	33.8	57.1							
230	26.48	34.0	67.3							
480	26.92	34.2	65.0							
720	27.18	34.3	33.5							
Station 13, August 2011 (41.01˚N, 125.02˚W)										
0	25.04	33.0	26.7	1.163	0.003	2.104	0.009	18.14	0.01	2
15	25.09	33.0	24.1	1.165	< 0.001	2.103	0.009	18.23	0.06	2
50	25.97	33.6	38.7	1.168	0.001	2.102	0.002	18.30	0.02	3
100	26.29	33.9	43.2	1.168	< 0.001	2.103	0.002	18.21	0.03	3
150	26.50	34.0	45.4	1.174	0.001	2.092	0.006	18.34	0.01	2

300	26.73	34.1	51.7	1.167	0.001	2.104	0.001	18.26	0.04	3
500	26.93	34.2	36.5	1.166	0.001	2.105	0.005	18.37	0.19	2

Station 14, August 2011 (39.00˚N, 126.34˚W)

0	23.68	32.6	21.0	1.160	0.002	2.113	0.005	18.19	0.01	3
20	23.69	32.6	29.5	1.172	0.001	2.092	0.002	18.36	0.05	3
60	24.70	32.7	25.7	1.164	0.001	2.105	0.002	18.20	0.02	2
100	25.29	33.0	36.9	1.162	0.001	2.105	0.006	18.18	0.01	2
200	26.29	33.8	42.9	1.165	0.001	2.107	0.003	18.23	0.01	3
300	26.61	34.0	55.9	1.164	0.001	2.108	0.003	18.16	0.04	3
500	26.92	34.2	40.2	1.166	< 0.001	2.104	0.002	18.25	0.03	3

Station 18, August 2011 (38.01˚N, 126.37˚W)

0	23.96	32.9	23.9	1.162	0.002	2.109	< 0.001	18.19	0.07	3
20	24.09	32.9	26.6	1.160	0.002	2.103	0.003	18.15	0.05	2
38	25.39	33.3	30.7	1.164	0.007	2.103	0.009	18.22	0.17	2
75	25.92	33.4	37.3	1.162	0.003	2.104	0.001	18.15	0.01	2
150	26.41	33.9	58.0	1.165	0.002	2.106	0.003	18.25	0.08	3
300	26.75	34.1	52.6	1.165	0.002	2.106	0.001	18.23	0.04	3
500	27.02	34.3	34.5	1.167	0.003	2.102	0.004	18.26	0.05	3

Station 26, August 2011 (36.66˚N, 125.01˚W)

0	23.61	32.7	24.6	1.162	0.002	2.105	0.005	18.13	0.07	2
20	23.62	32.7	21.9	1.163	0.002	2.104	0.002	18.13	0.07	2
60	24.30	32.8	27.0	1.161	< 0.001	2.111	< 0.001	18.18	0.03	3
100	25.13	33.0	38.1	1.158	0.002	2.112	< 0.001	18.13	0.11	3
150	25.83	33.4	52.2	1.161	< 0.001	2.106	0.002	18.15	0.03	2

300	26.59	34.0	61.3	1.165	0.002	2.105	0.002	18.23	0.05	5
500	26.92	34.1	41.3	1.163	0.001	2.105	0.002	18.24	0.08	2

Station 30, August 2011 (35.34˚N, 124.67˚W)

0	24.12	33.3	25.2	1.166	0.001	2.101	0.004	18.26	0.05	2
15	24.20	33.3	20.6	1.167	0.001	2.101	0.001	18.29	0.05	3
*40**	*25.58*	*33.6*	*33.9*	*1.156*	*0.003*	*3.972*	*0.005*	*18.27*	*0.08*	*3*
60	25.94	33.4	45.3	1.162	0.003	2.111	0.004	18.17	0.04	3
75	26.11	33.6	48.0	1.162	0.001	2.108	0.004	18.16	0.05	2
100	26.28	33.8	55.4	1.163	0.002	2.109	0.004	18.26	0.11	2
150	26.45	34.0	54.6	1.163	0.001	2.107	0.004	18.19	< 0.01	2
200	26.59	34.1	54.4	1.164	0.002	2.105	0.005	18.18	0.12	2
300	26.74	34.1	49.4	1.166	0.003	2.104	0.005	18.26	0.03	2
500	27.02	34.2	31.7	1.166	0.002	2.103	0.006	18.36	0.07	2

* Repeated extractions and analyses of this sample consistently yielded anomlous isotopic ratios relative to the other samples. Although unable to definitively identify a source, this sample was deemed contaminated and not discussed in this data set.

Table 4. Dissolved and particulate Pb concentrations in surface waters.

Latitude (˚N)	Longitude (˚W)	Date	Salinity	dissolved Pb (pmol kg^{-1})	particulate Pb (pmol kg^{-1} of seawater)
38.95	123.78	5/8/2010	33.49	41.9	
39.10	123.78	5/8/2010	33.38	40.8	
39.23	123.85	5/8/2010	33.61	46.3	
39.36	123.90	5/8/2010	33.43	42.1	
39.56	123.84	5/8/2010	33.87	37.6	
39.68	123.87	5/8/2010	33.47	38.1	
39.74	123.91	5/8/2010	34.05	45.5	
39.87	124.00	5/8/2010	33.67	44.9	
39.98	124.12	5/9/2010	34.02	49.4	
40.11	124.26	5/9/2010	33.82	33.6	
39.87	124.90	5/9/2010	32.11	15.1	
39.72	124.77	5/9/2010	32.26	11.5	
39.64	124.71	5/9/2010	32.28	11.7	
39.45	124.55	5/9/2010	32.33	17.3	
39.39	124.50	5/9/2010	32.42	20.6	
39.27	124.48	5/9/2010	32.43	17.3	
39.14	124.45	5/9/2010	32.49	15.5	
39.00	124.42	5/10/2010	32.72	40.8	
38.91	124.40	5/10/2010	32.57	27.3	
38.76	124.37	5/10/2010	32.52	15.2	
38.60	124.34	5/10/2010	32.72	16.9	
38.42	124.30	5/10/2010	32.74	18.8	
38.70	124.26	5/14/2010	32.95	18.7	
38.79	124.31	5/14/2010	32.97	21.4	
38.86	124.35	5/14/2010	32.71	21.2	
38.95	124.40	5/14/2010	32.97	19.5	
39.07	124.47	5/14/2010	32.84	24.6	
39.11	124.49	5/14/2010	32.93	20.2	
39.33	124.62	5/14/2010	32.83	15.1	
39.50	124.72	5/15/2010	32.98	17.2	
39.54	124.75	5/15/2010	32.76	22.1	
39.62	124.79	5/15/2010	32.70	18.2	
39.75	124.86	5/15/2010	32.45	17.1	
39.85	124.92	5/15/2010	32.28	17.7	
38.93	123.99	5/16/2010	32.27	16.9	
38.95	123.94	5/16/2010	32.44	18.5	

38.98	123.85	5/16/2010	32.47	35.7	
36.54	122.52	5/20/2010	33.19	32.9	
36.59	122.52	5/20/2010	33.14	31.2	
36.70	122.44	5/20/2010	33.67	32.3	
36.76	122.39	5/20/2010	33.71	34.6	
36.84	122.31	5/20/2010	33.71	32.9	
36.82	122.19	5/20/2010	33.76	27.6	
36.83	121.99	5/20/2010	33.74	33.6	
36.92	121.94	5/20/2010	33.80	26.8	
36.49	121.97	5/21/2010	33.66	43.7	
36.39	121.96	5/21/2010	33.75	47.3	
36.28	121.91	5/21/2010	33.83	45.5	
36.18	121.74	5/21/2010	33.87	48.5	
36.06	121.65	5/21/2010	33.82	47.9	
35.96	121.56	5/21/2010	33.77	47.2	
35.88	121.49	5/21/2010	33.75	46.0	
35.77	121.41	5/22/2010	33.87	49.8	
35.67	121.32	5/22/2010	33.85	43.7	
35.52	121.17	5/22/2010	33.86	47.6	
35.56	121.21	5/22/2010	33.86	46.8	
35.45	121.17	5/22/2010	33.81	45.5	
35.36	121.13	5/22/2010	33.76	42.0	
35.29	121.11	5/22/2010	33.61	41.3	
35.08	121.01	5/22/2010	33.64	39.8	
35.00	120.98	5/22/2010	33.55	36.4	
34.90	120.92	5/23/2010	33.50	40.3	
34.77	120.85	5/23/2010	33.65	42.6	
34.63	120.77	5/23/2010	33.74	35.8	
34.54	120.67	5/23/2010	33.87	37.5	
38.02	123.09	8/17/2011	33.65	36.5	
38.06	123.08	8/17/2011	33.55	34.2	
38.20	123.11	8/17/2011	33.61	38.1	
38.34	123.17	8/17/2011	33.64	34.5	2.9
38.45	123.27	8/17/2011	33.75	40.2	1.6
38.56	123.41	8/17/2011	33.78	39.5	1.4
38.68	123.54	8/17/2011	33.86	38.1	10
38.77	123.64	8/17/2011	33.55	41.3	2.2
38.87	123.75	8/17/2011	33.44	39.7	1.7
38.99	123.83	8/17/2011	33.46	37.9	2.8
39.12	123.80	8/18/2011	33.79	41.7	30

39.25	123.87	8/18/2011	33.81	43.4	19
39.39	123.90	8/18/2011	33.53	37.9	3.0
39.54	123.85	8/18/2011	33.48	33.8	1.7
39.66	123.88	8/18/2011	33.50	34.5	60
39.74	124.68	8/18/2011	32.65	25.4	
39.59	124.59	8/18/2011	32.68	26.7	
39.47	124.50	8/18/2011	32.73	25.9	
39.35	124.40	8/18/2011	32.81	25.7	
39.23	124.30	8/18/2011	32.97	35.6	
39.10	124.20	8/18/2011	32.89	33.4	
38.98	124.10	8/18/2011	33.13	32.9	
38.87	124.01	8/18/2011	33.30	33.6	
38.77	123.90	8/18/2011	33.08	35.3	
38.67	123.78	8/18/2011	33.06	37.1	
38.57	123.66	8/19/2011	33.56	43.5	
38.47	123.54	8/19/2011	33.82	39.4	
38.37	123.42	8/19/2011	33.77	41.4	
40.84	124.52	8/20/2011	33.41	32.4	
40.89	124.68	8/20/2011	33.58	30.2	41
40.95	124.84	8/20/2011	33.22	30.3	3.0
38.94	126.34	8/21/2011	32.60	23.8	1.2
38.81	126.34	8/21/2011	32.50	25.2	
38.69	126.35	8/21/2011	32.58	25.0	
38.57	126.34	8/21/2011	32.68	27.7	
38.43	126.37	8/22/2011	32.71	29.7	0.2
38.25	126.34	8/22/2011	33.07	26.3	
38.00	126.33	8/22/2011	32.87	29.4	
37.92	126.36	8/22/2011	32.84	27.0	
37.78	126.26	8/22/2011	33.15	26.4	
37.85	126.10	8/22/2011	32.97	27.7	
37.91	125.94	8/22/2011	32.93	27.8	1.7
37.98	125.78	8/22/2011	32.99	28.9	
38.01	125.70	8/22/2011	33.14	28.7	
38.04	125.61	8/22/2011	33.31	32.6	1.3
38.11	125.47	8/23/2011	32.76	27.6	0.9
38.18	125.35	8/23/2011	32.72	27.7	0.7
38.19	125.20	8/23/2011	32.71	28.0	
38.12	125.06	8/23/2011	32.76	27.8	14
37.91	124.98	8/23/2011	33.22	30.7	
37.78	124.98	8/23/2011	33.00	28.8	

37.65	124.98	8/23/2011	32.94	27.9	
37.72	124.88	8/23/2011	32.95	29.1	
37.81	124.77	8/23/2011	33.15	29.0	
37.89	124.66	8/23/2011	33.14	29.1	
37.98	124.55	8/23/2011	33.20	32.1	
38.07	124.44	8/23/2011	33.18	31.9	
38.16	124.32	8/24/2011	33.23	31.2	
38.26	124.19	8/24/2011	33.31	33.2	
38.35	124.07	8/24/2011	32.89	36.3	
38.44	123.95	8/24/2011	33.32	32.3	
38.45	123.94	8/24/2011	33.38	32.1	
38.53	123.83	8/24/2011	33.06	33.3	
38.61	123.72	8/24/2011	32.86	36.6	
36.79	121.96	8/25/2011	33.71	32.5	
36.78	122.32	8/25/2011	33.63	31.8	7.8
36.77	122.58	8/25/2011	33.57	29.9	16
36.76	122.94	8/25/2011	33.30	30.3	11
36.75	123.37	8/26/2011	33.38	30.4	15
36.74	123.64	8/26/2011	33.37	31.0	6.8
36.50	124.98	8/26/2011	32.66	27.4	
36.39	124.95	8/26/2011	32.69	27.0	
36.13	124.90	8/26/2011	32.80	28.7	
35.97	124.86	8/27/2011	32.71	27.6	
35.80	124.86	8/27/2011	33.19	28.7	
35.69	124.81	8/27/2011	33.25	25.9	
35.42	124.57	8/27/2011	33.21	27.8	
35.49	124.44	8/27/2011	33.16	27.7	
35.54	124.32	8/27/2011	33.08	29.0	
35.62	124.21	8/27/2011	33.22	29.8	
35.69	124.10	8/27/2011	33.18	28.0	
35.78	123.98	8/27/2011	33.19	27.7	
35.93	123.70	8/28/2011	33.27	25.6	
35.91	123.52	8/28/2011	33.17	27.7	
35.89	123.34	8/28/2011	33.31	25.0	
35.87	123.16	8/28/2011	33.33	26.3	
35.69	121.65	8/28/2011	33.48	34.2	
35.68	121.57	8/28/2011	33.56	32.4	
35.66	121.49	8/28/2011	33.49	36.1	
35.64	121.40	8/28/2011	33.38	27.5	
36.13	122.00	8/29/2011		33.0	

36.02	121.87	8/29/2011	33.51	28.2	7.7
35.89	121.74	8/29/2011	33.47	34.5	19
35.76	121.63	8/29/2011	33.45	34.1	15
35.72	121.54	8/29/2011	33.52	31.2	
35.69	121.45	8/29/2011	33.47	33.8	15
35.66	121.37	8/29/2011	33.51	34.8	
35.66	121.34	8/29/2011	33.42	36.2	
35.74	121.40	8/29/2011	33.55	38.4	23
35.80	121.45	8/29/2011	33.41	38.2	26
35.85	121.50	8/29/2011	33.47	40.4	22
35.91	121.54	8/30/2011	33.54	41.7	30
35.97	121.57	8/30/2011	33.58	41.0	22
36.00	121.64	8/30/2011	33.45	40.3	38
36.06	121.69	8/30/2011	33.68	44.0	
36.09	121.77	8/30/2011	33.67	44.0	
36.14	121.83	8/30/2011	33.68	45.6	40
36.90	122.16	8/30/2011	33.65	36.6	
36.97	122.24	8/30/2011	33.77	32.4	
37.04	122.33	8/30/2011	33.71	30.0	147
37.11	122.42	8/30/2011	33.68	18.6	21
37.20	122.48	8/30/2011	33.61	24.4	9.0
37.30	122.53	8/30/2011	33.45	20.6	40
37.40	122.59	8/30/2011	33.38	17.1	0.7
37.50	122.70	8/30/2011	33.20	23.7	9.4
38.02	123.36	8/31/2011	33.52	43.0	
38.07	123.42	8/31/2011	33.39	46.5	
38.11	123.46	8/31/2011	33.35	46.5	17
38.16	123.52	8/31/2011	33.44	42.6	14
38.21	123.57	8/31/2011	33.64	39.2	11
38.24	123.62	8/31/2011	33.54	44.2	12
38.27	123.65	8/31/2011	33.35	38.4	21
38.28	123.66	8/31/2011	33.32	38.5	21
38.25	123.58	8/31/2011	33.72	37.8	
38.21	123.51	8/31/2011	33.63	42.1	14
38.17	123.43	8/31/2011	33.41	46.5	
38.13	123.34	8/31/2011	33.65	39.7	
38.09	123.25	9/1/2011	33.67	34.5	
38.04	123.17	9/1/2011	33.66	39.0	17
38.01	123.10	9/1/2011	33.65	41.2	
37.98	123.01	9/1/2011	33.56	27.5	21

37.99	122.96	9/1/2011	33.10	26.2	33
37.93	122.95	9/2/2011	33.40	22.6	
37.89	122.87	9/2/2011	33.26	26.4	
37.84	122.79	9/2/2011	33.23	28.6	
37.66	122.58	9/2/2011	33.37	31.8	217
37.69	122.58	9/2/2011	33.17	36.9	
37.72	122.58	9/2/2011	32.45	39.8	2406
37.74	122.58	9/2/2011	32.40	42.0	
37.76	122.58	9/2/2011	32.14	44.8	5529
37.77	122.58	9/2/2011	31.92	44.4	
37.79	122.55	9/2/2011	31.62	43.8	7433
37.81	122.50	9/2/2011	31.32	45.9	
37.82	122.48	9/2/2011	30.97	42.1	6018
37.83	122.46	9/2/2011	30.60	45.4	
37.84	122.44	9/2/2011	29.55	47.3	10998

Table 5. Dissolved and particulate Pb concentrations over the continental shelf.

Station	Depth (m)	Sigma-theta	Salinity	Latitude (˚N)	Longitude (˚W)	dissolved Pb (pmol kg^{-1})	particulate Pb (pmol kg^{-1} water)
				May 2010			
5	0	26.08	34.0	37.78	122.95	36.7	
5	60	26.63	34.0	37.78	122.95	42.6	
6	0	25.90	33.7	37.87	123.09	44.3	
6	85	26.62	33.9	37.87	123.09	51.3	
7	0	26.00	33.8	38.11	123.12	44.2	
7	70	26.72	34.0	38.11	123.12	38.4	
8	0	26.09	33.9	38.11	123.03	37.2	
8	56	26.62	34.0	38.11	123.03	48.7	
9	0	26.22	34.0	38.26	123.08	28.6	
9	64	26.70	34.0	38.26	123.08	43.9	
10	0	26.30	34.0	38.46	123.25	47.0	
10	62	26.71	34.0	38.46	123.25	35.2	
11	0	26.39	34.0	38.64	123.43	42.4	
11	68	26.79	34.1	38.64	123.43	41.8	
12	0	26.29	34.0	38.78	123.62	45.7	
12	65	26.77	34.0	38.78	123.62	47.3	
17	0	26.18	33.9	39.03	123.77	43.1	
17	69	26.80	34.1	39.03	123.77	54.3	
18	0	26.13	33.9	39.17	123.79	37.7	
18	69	26.79	34.1	39.17	123.79	54.5	
19	0	26.12	33.9	39.33	123.84	35.9	
19	83	26.84	34.0	39.33	123.84	57.1	
20	0	26.12	33.9	39.54	123.83	28.1	
20	69	26.79	34.0	39.54	123.83	52.9	
23	0	26.34	33.9	38.64	123.44	37.5	
23	69	26.52	34.0	38.64	123.44	40.8	
26	0	25.69	33.7	37.42	122.62	42.4	
26	63	26.58	34.0	37.42	122.62	39.9	
27	0	25.26	33.4	37.30	122.52	27.2	
27	63	26.54	34.0	37.30	122.52	50.2	
28	0	25.32	33.5	37.16	122.45	23.7	
28	52	26.35	33.9	37.16	122.45	51.5	
28	66	26.54	34.0	37.16	122.45	49.6	

29	0	25.59	33.8	37.04	122.33	25.8	
29	67	26.54	34.0	37.04	122.33	66.2	
30	0	25.64	33.8	36.93	122.15	33.1	
30	65	26.50	34.0	36.93	122.15	57.0	
33	0	25.93	33.8	36.43	121.95	48.8	
33	88	26.78	34.0	36.43	121.95	54.7	
34	0	25.94	33.8	36.32	121.90	50.4	
34	73	26.62	34.0	36.32	121.90	54.2	
36	0	25.81	33.8	35.20	120.89	51.4	
36	67	26.65	34.1	35.20	120.89	56.3	
37	0	26.06	33.9	35.46	121.05	46.4	
37	64	26.64	34.1	35.46	121.05	57.2	
38	0	26.05	33.9	35.60	121.22	46.5	
38	57	26.53	34.0	35.60	121.22	52.0	

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2	0	25.77	33.7	38.78	123.62	39.3	5.5
2	64	26.46	33.9	38.78	123.62	25.7	31
3	0	25.87	33.8	38.82	123.65	37.6	18
3	48	26.39	33.9	38.82	123.65	34.8	2.2
4	0	25.86	33.8	38.82	123.66	40.5	8.9
4	61	26.47	34.0	38.82	123.66	27.9	25
5	0	25.52	33.5	38.80	123.69	38.5	24
5	90	26.62	34.0	38.80	123.69	37.0	25
6	0	25.72	33.7	39.17	123.79	39.0	2.2
6	70	26.45	33.9	39.17	123.79	28.4	140
7	0	25.89	33.9	39.33	123.84	36.2	5.5
7	81	26.54	33.9	39.33	123.84	34.0	23
8	0	25.52	33.6	39.54	123.83	24.2	116
8	68	26.49	33.9	39.54	123.83	33.2	18
9	0	25.48	33.6	40.74	124.33	27.0	5.9
9	40	26.39	33.9	40.74	124.33	26.1	43
10	0	25.59	33.6	40.77	124.39	32.6	4.5
10	64	26.55	33.9	40.77	124.39	34.5	44
11	0	25.22	33.4	40.79	124.42	32.6	3.5
11	100	26.81	34.0	40.79	124.42	45.7	48
12	0	25.03	33.4	40.82	124.47	29.0	1.5
12	340	28.17	34.1	40.82	124.47	45.9	9.5
21	0	24.90	33.5	37.19	122.74	25.7	2.6

21	185	27.05	34.0	37.19	122.74	45.6	4.5
22	0	24.93	33.7	37.25	122.61	21.0	2.3
22	90	26.48	33.9	37.25	122.61	46.6	27
23	0	25.04	33.5	37.28	122.53	23.0	42
23	75	26.31	33.9	37.28	122.53	43.5	198
24	0	24.95	33.6	37.30	122.48	20.2	75
24	44	25.99	33.8	37.30	122.48	36.0	166
25	0	25.21	33.6	37.18	122.48	29.3	69
25	70	26.24	33.8	37.18	122.48	41.5	330
31	0	25.34	33.6	35.65	121.30	35.0	19
31	58	26.08	33.7	35.65	121.30	43.3	22
33	0	25.27	33.5	36.06	121.61	36.1	54
33	49	25.97	33.7	36.06	121.61	39.3	63
34	0	25.40	33.6	36.17	121.70	34.8	55
34	52	25.98	33.7	36.17	121.70	44.3	50
35	0	25.49	33.7	36.22	121.81	35.6	52
35	79			36.22	121.81	46.7	58
36	0	25.36	33.6	36.32	121.96	34.8	12
36	74	26.30	33.8	36.32	121.96	52.2	28
37	0	24.70	33.4	37.42	122.61	16.1	
37	64	26.27	33.9	37.42	122.61	38.8	
38	0	24.95	33.3	37.60	122.83	20.4	87
38	67	26.30	33.9	37.60	122.83	38.7	154
39	0	24.92	33.3	37.76	123.00	24.1	15
39	62	26.24	33.8	37.76	123.00	48.9	103
41	0	25.18	33.4	37.93	122.95	22.6	
41	54	26.22	33.8	37.93	122.95	78.4	516
42	0	25.02	33.3	37.89	122.87	26.4	59
42	50	26.17	33.8	37.89	122.87	75.0	392
43	0	24.96	33.2	37.84	122.79	28.6	68
43	39	26.08	33.8	37.84	122.79	58.8	369

Table 6. Lead isotopic compositions of dissolved and particulate Pb in select waters from August 2011 over the continental shelf. (Particulate data in bold italics.)

Stn	Depth (m)	Salinity	Latitude (˚N)	Longitude (˚W)	dis. Pb (pmol kg^{-1})	part. Pb (pmol kg^{-1})	^{206}Pb/^{207}Pb	S.E. (2 σ)	^{208}Pb/^{206}Pb	S.E. (2 σ)	^{206}Pb/^{204}Pb	S.E. (2 σ)	n
2	64	33.9	38.78	123.62	25.7		1.185	0.001	2.075	0.006	18.53	0.03	4
4	61	34.0	38.82	123.66	27.9		1.185	0.001	2.075	0.004	18.55	0.04	4
6	70	33.9	39.17	123.79	28.4		1.182	0.001	2.080	0.003	18.51	0.03	4
6	***70***	***33.9***	***39.17***	***123.79***		***140***	***1.189***	***0.001***	***2.069***	***0.001***	***18.93***	***0.08***	***2***
7	0	33.9	39.33	123.84	36.2		1.174	0.001	2.090	0.004	18.39	0.06	4
7	81	33.9	39.33	123.84	34.0		1.182	0.001	2.081	0.005	18.47	0.04	4
8	0	33.6	39.54	123.83	24.2		1.167	0.002	2.101	0.005	18.19	0.02	4
8	68	33.9	39.54	123.83	33.2		1.182	0.001	2.078	0.005	18.52	0.05	4
10	0	33.6	40.77	124.39	32.6		1.167	0.001	2.102	0.004	18.24	0.02	4
10	64	33.9	40.77	124.39	34.5		1.185	0.001	2.075	0.004	18.55	0.03	4
22	0	33.7	37.25	122.61	21.0		1.174	0.001	2.091	0.004	18.37	0.02	4
22	90	33.9	37.25	122.61	46.6		1.184	0.001	2.079	0.003	18.52	0.03	4
24	0	33.6	37.30	122.48	20.2		1.179	0.001	2.089	0.006	18.46	0.07	4
24	44	33.8	37.30	122.48	36.0		1.187	0.001	2.075	0.002	18.62	0.05	4
24	***44***	***33.8***	***37.30***	***122.48***		***166***	***1.196***	***0.003***	***2.065***	***0.003***	***19.01***	***0.02***	***2***
41	0	33.4	37.93	122.95	22.6		1.171	0.001	2.095	0.003	18.33	0.04	3
41	***54***	***33.8***	***37.93***	***122.95***		***516***	***1.193***	***< 0.001***	***2.064***	***0.002***	***18.57***	***0.23***	***2***
42	0	33.3	37.89	122.87	26.4		1.172	0.001	2.093	0.005	18.27	0.09	2
42	***50***	***33.8***	***37.89***	***122.87***		***392***	***1.194***	***0.001***	***2.063***	***< 0.001***	***18.27***	***0.25***	***2***
43	0	33.2	37.84	122.79	28.6		1.173	0.001	2.094	0.003	18.40	0.04	2
43	39	33.8	37.84	122.79	58.8		1.187	0.001	2.076	0.004	18.63	0.04	2
43	***39***	***33.8***	***37.84***	***122.79***		***369***	***1.193***	***0.001***	***2.061***	***0.002***	***18.50***	***0.15***	***2***

t16	0	33.4	37.66	122.58	31.8		1.176	< 0.001	2.088	0.002	18.49	0.12	2
t16	***0***	***33.4***	***37.66***	***122.58***		***217***	***1.178***	***0.002***	***2.080***	***< 0.001***	***18.58***	***0.03***	***2***
t16	0	33.2	37.69	122.58	36.9		1.187	0.001	2.071	0.002	18.60	0.04	3
t16	0	32.5	37.72	122.58	39.8		1.182	< 0.001	2.076	0.003	18.48	0.01	2
t16	***0***	***32.5***	***37.72***	***122.58***		***2406***	***1.184***	***< 0.001***	***2.070***	***0.001***	***18.39***	***0.15***	***2***
t16	0	32.4	37.74	122.58	42.0		1.183	< 0.001	2.080	0.005	18.55	0.16	2
t16	0	32.1	37.76	122.58	44.8		1.184	0.001	2.072	0.003	18.54	0.02	2
t16	***0***	***32.1***	***37.76***	***122.58***		***5529***	***1.186***	***0.003***	***2.065***	***0.001***	***18.42***	***0.21***	***2***
t16	0	31.9	37.77	122.58	44.4		1.181	0.002	2.080	0.003	18.48	0.06	3
t16	0	31.6	37.79	122.55	43.8		1.185	0.001	2.073	0.001	18.55	0.06	3
t16	***0***	***31.6***	***37.79***	***122.55***		***7433***	***1.184***	***0.003***	***2.072***	***0.002***	***18.42***	***0.19***	***2***
t16	0	31.3	37.81	122.50	45.9		1.183	0.003	2.076	0.002	18.51	0.06	3
t16	0	31.0	37.82	122.48	42.1		1.183	0.001	2.072	0.002	18.51	0.04	4
t16	***0***	***31.0***	***37.82***	***122.48***		***6018***	***1.183***	***0.001***	***2.070***	***0.002***	***18.39***	***0.09***	***2***
t16	0	30.6	37.83	122.46	45.4		1.183	0.001	2.071	0.005	18.51	0.09	2
t16	0	29.6	37.84	122.44	47.3		1.183	0.001	2.074	0.004	18.53	0.05	3
t16	***0***	***29.6***	***37.84***	***122.44***		***10998***	***1.184***	***0.001***	***2.068***	***0.003***	***18.41***	***0.16***	***2***

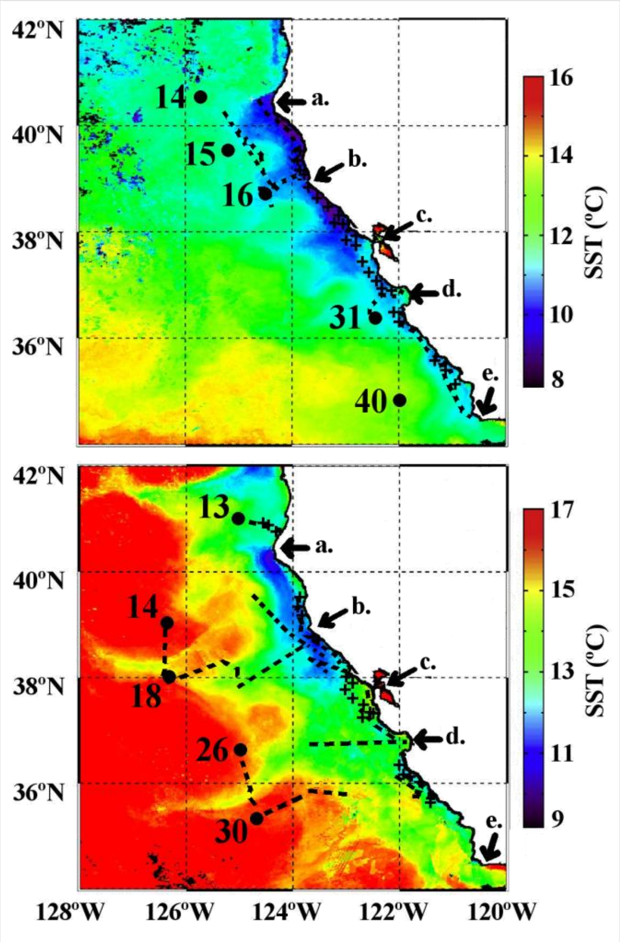

Figure 1. Samples collected on the May 2010 expedition (upper panel) and August 2011 expedition (lower panel) overlaid on satellite-derived sea surface temperature (note the different temperature scales for the two plots). Samples were collected from off-shore profile stations (•), benthic stations over the continental shelf (+), and surface water transects (---). Major landmarks are: a.) Cape Mendocino, b.) Point Arena, c.) San Francisco Bay, d.) Monterrey Bay, and e.) Point Conception. Figure adapted from Biller and Bruland, 2013.

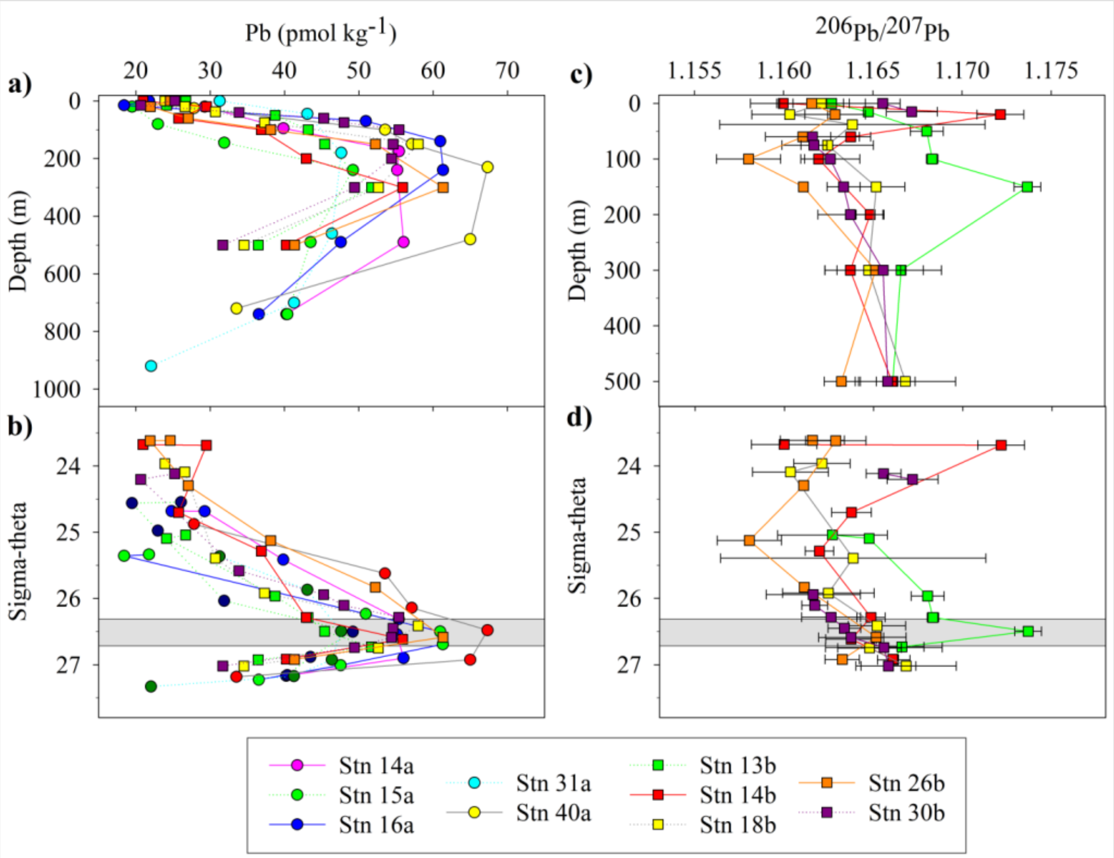

Figure 2. Off-shore profiles of dissolved Pb concentration (pmol kg^{-1}) versus a) depth and b) sigma-theta (σ_Θ) showed that the subsurface maxima changed depth depending on upwelling or downwelling favorable conditions, but that this feature occurred at the same density ($\sigma_\Theta \approx 26.5 \pm 0.2$) in all of the stations. The ^{206}Pb/^{207}Pb isotopic composition versus c) depth and d) sigma-theta were relatively homogenous throughout the water column. Error bars correspond to standard error (2 σ). In the legend, "a" refers to samples collected in May 2010 and "b" refers to samples collected in August 2011.

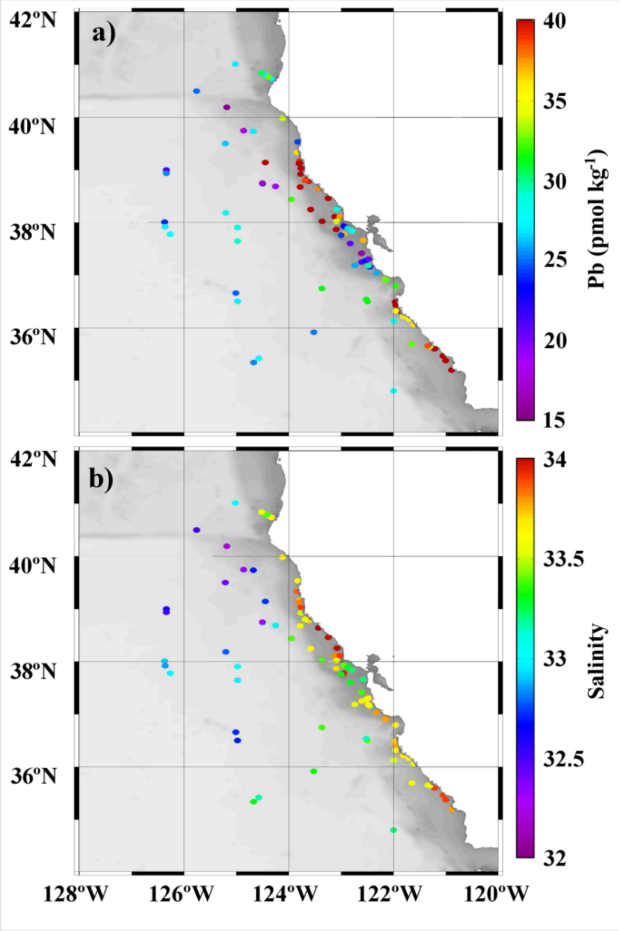

Figure 3. Surface water plots of a) dissolve Pb concentrations (pmol kg^{-1}) and b) salinities. These two parameters were positively correlated (r = 0.75, Pearson correlation coefficient) with high values near the coast due to upwelling and lower values off-shore.

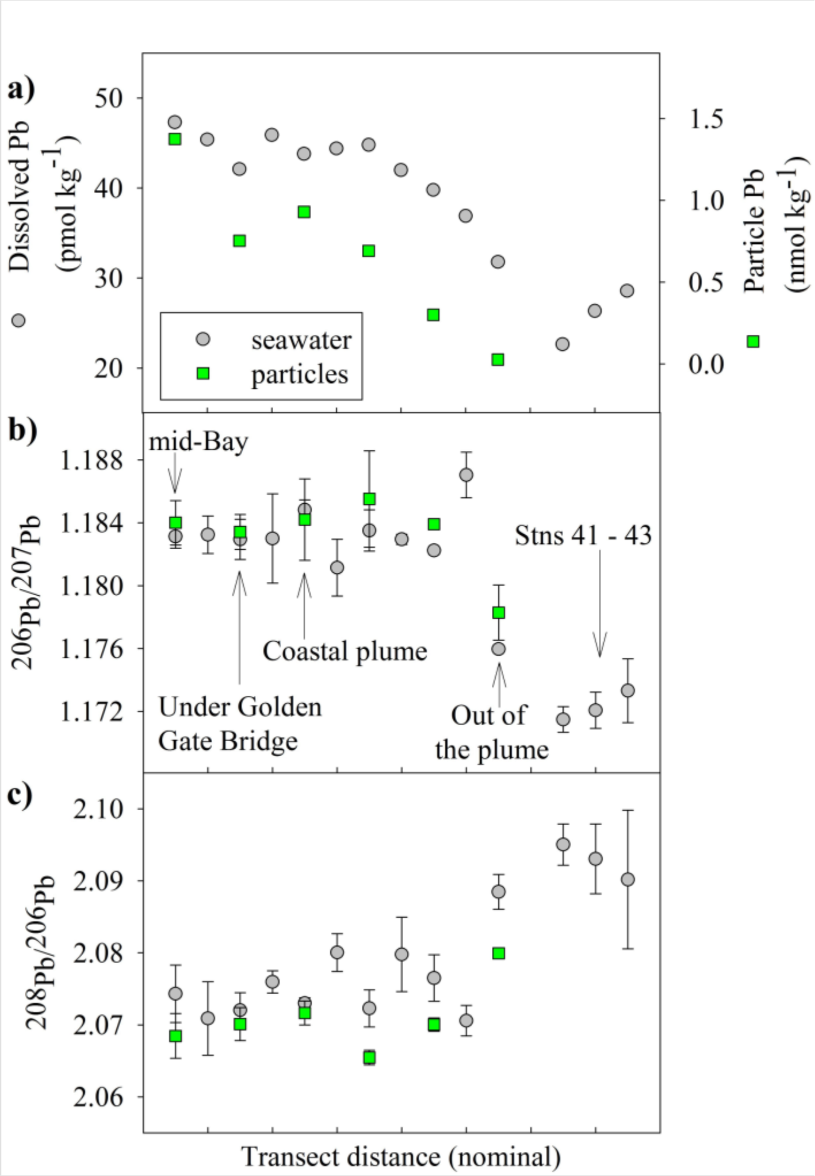

Figure 4. Dissolved and particulate Pb a) concentrations, b) $^{206}Pb/^{207}Pb$ isotope ratios and c) $^{208}Pb/^{206}Pb$ isotope ratios on the transect out of San Francisco Bay into coastal waters. Concentrations were higher in the Bay and its plume than in coastal waters. Similarly, PbICs within SFB and the plume were distinguishable from coastal surface water and particles. In general, there was good agreement between the PbICs of dissolved and particle Pb.

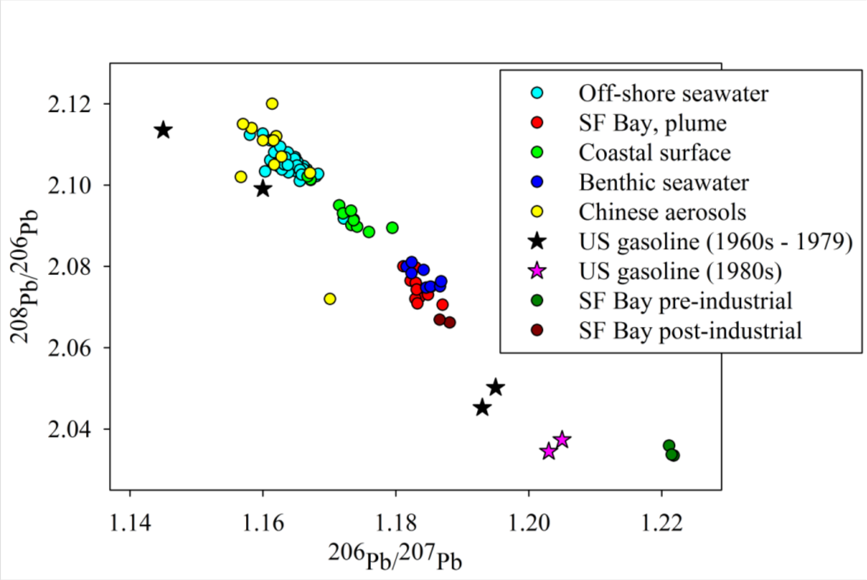

Figure 5. The triple isotope plot of ^{206}Pb/^{207}Pb versus ^{208}Pb/^{206}Pb was used to identify the sources of Pb to these waters. Off-shore seawater was isotopically consistent with Chinese aerosols (Zheng et al., 2004; Chen et al., 2005). In contrast, the benthic water over the mud belt was more like water from SFB. Both of these were similar to previous measurements of Pb in sediments of the Bay (Ritson et al., 1999). The coastal surface water PbICs were intermediate to the off-shore and benthic PbICs.

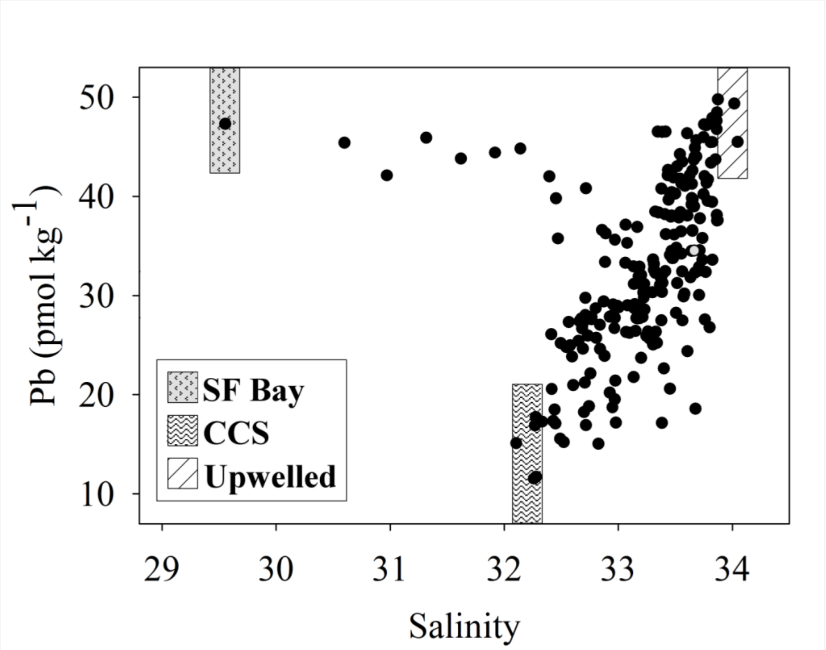

Figure 6. Dissolved Pb concentrations plotted against salinities. In seawater, concentrations and salinities were positively correlated (0.75, Pearson correlation coefficient, SFB samples excluded). Lower salinities (≈ 32) corresponding to the CCS surface waters had relatively less Pb than the more saline (≈ 34) upwelled waters along the coast. The San Francisco Bay samples had much less saline (≈ 29.5) waters due to fresh-water inputs from the San Joaquin and Sacramento Rivers, but were elevated in Pb concentration.

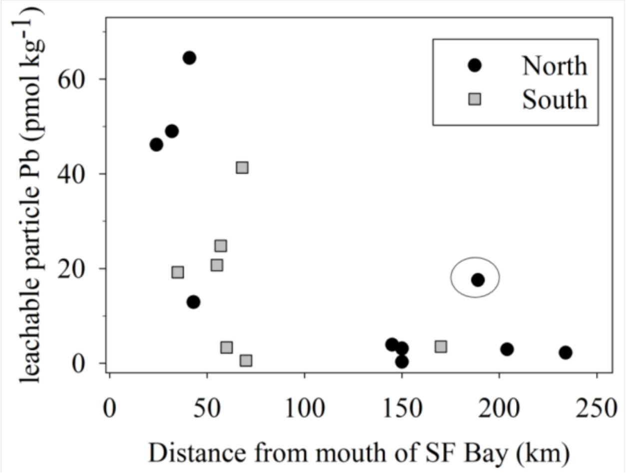

Figure 7. Lead concentrations of leachable particle Pb along coastal California decreased with increasing distance both to the north (●) and the south (■) of SFB. The circled point 190 km from the Bay was located 3.5 km directly off-shore of the Navarro River. This river has been previously documented to have high sediment loadings (C.A.R.W.Q.C.B., 2000), which could have elevated the Pb concentrations at this location.

CHAPTER 6. EXPLORING THE USE OF SYSTEM THINKING, CONCEPT MAPPING AND GROUP LEARNING IN UNDERGRADUATE TOXICOLOGY EDUCATION

Cheryl M. Zurbrick

"Research has taught us a great deal about effective teaching and learning in recent years, and scientists should be no more willing to fly blind in their teaching than they are in scientific research."

- Bruce Alberts, Biochemist and former President, National Academy of Sciences

"There is a crucial difference between simply putting students into groups to learn and in structuring cooperative interdependence among students."

- Teed et al. 2012

Abstract

In this research project, using social constructivist learning theory, I explored the intersection of system thinking and environmental toxicology using case studies, active learning techniques, such as think-pair-share, in-class debate, and group work, as well as a variety of assessments, such as multiple choice, constructed response (short answer), and concept mapping. Results regarding system thinking indicated that most students were capable of reading and interpreting concept maps, but a third of the students struggled with predicting temporal trends in the system. Analysis of

assessments indicated that multiple choice questions were best suited for checking whether or not learners held common, scientifically correct or incorrect prior conceptions. Constructed response questions were best at exploring the reasoning behind students' conceptions. Individual concept mapping revealed 11 kinds of prior conceptions, while group concept mapping revealed 5 kinds of prior conceptions; group discussions of the co-constructed concept maps revealed 12 kinds of prior conceptions. Concept mapping was important because it revealed a variety of conceptions broadly related to the given prompt, which then informed the instructor about specific topics to discuss in class. These topics might have otherwise have gone unaddressed. Group concept mapping, in this particular case, did not reveal detailed differences between individual concept maps and collaborative group created maps. This latter phenomenon likely occurred because students lacked practice in fundamental collaborative learning techniques. The socially mediated activities would have been more productive had the students been given more instructional scaffolds and time to develop their roles as active learners.

1. Introduction

I am interested in students' understanding of toxins as part of a large, global ecological system, as well as students' abilities to predict change in these systems. I used multiple assessment methods to consider how students' scientifically incorrect prior ideas could be best elicited for subsequent collaborative transformation. Additionally, I compared how information elicited in groups differed from information elicited from individuals. In this study, I explored two questions:

1. How are students' prior conceptions differentially revealed by multiple choice questions, constructed response questions, and talk during the construction of concept maps?
2. How are prior conceptions on concept maps different in individual or group situations, and how might group learning be improved?

I start by briefly reviewing selected theories of learning over the last half century, including constructivism, social constructivism and conceptual change theory (Figure 1). In the broad spectrum, these theories of learning are relatively new and focus on learning as a conceptual process as opposed to the acquisition of skills (Greeno et al., 1996). In addition, these learning theories emphasize the importance of the individual learners' role in the knowledge-construction process.

1.1 Constructivism

The constructivist framework, heavily influenced by Swiss psychologist Jean Piaget, stipulates that students are not passive recipients of knowledge, but must be actively engaged in developing their ideas (Piaget, 1970; Hammond et al., 2001). Learning is defined as both building new knowledge and reorganizing existing concepts (Piaget, 1964; Greeno et al., 1996). In addition, students do not come to class with an empty head or open mind (Greeno et al., 1996). Rather, they already have formed conceptions, which are initial ideas that humans develop to explain the physical phenomena in their everyday experiences (Vosniadou, 2012); by the time students arrive in school they have firmly held beliefs. These views are often not in agreement with scientific views, and sometimes are completely contradictory to scientific beliefs (Duit and Treagust, 2003). Conceptions can be corrected through education, but are sometimes compounded by rushed or partial lessons. For example, conceptions can be reinforced when new information is added to existing, incompatible prior knowledge instead of transforming it to be aligned with scientific beliefs (Vosniadou et al., 2008).

Experts refer to initial conceptions in a variety of ways (preconceptions, alternative conceptions, misconceptions), but here I use the term *prior conceptions* to refer to the scientifically incorrect ideas that learners have, and the term *conceptions* to more generally refer to learners' scientifically correct and incorrect ideas. I chose this term because it gives value to students' ideas (Abimbola, 1988) which are, after all, erroneous extensions of otherwise productive knowledge rooted in their experiences (Smith et al., 1994). Prior conceptions stem from a variety of sources, including observations, self-constructed explanations, can be taught-and-learned, are due to vernacular language use, or can be religious or myth-based (Alters and Nelson, 2002; Moore et al., 1997).

1.2 Social constructivism

Russian psychologist Lev Vygotsky is credited as the father of social constructivism, an elaboration of constructivist learning theory (Sjøberg, 2007). This learning theory studies how people socially co-construct knowledge, thus it focuses on the social aspects influencing individual participants (Vygotsky, 1978; Lave, 1991). Social interactions necessarily impact the process of knowledge construction (Vygotsky, 1978; Atwater, 1996). Vygotsky introduced the concept of the "zone of proximal development" as the difference between what a learner can do independently versus what they could do with assistance from a "more knowledgeable other" (Vygtostky, 1978). Therefore, differences in knowledge between group participants inevitably allow for one or more members to act as a "more knowledgeable other" to the group (Gould-Kreutzer, 1993).

Although their interpretations of learning theories differ considerably, both Piaget and Vygotsky would agree that cooperative learning among peers could lead to healthy disagreements which help promotes learning (Johnson et al., 1998; Greeno et al., 1996). Although a potentially powerful learning tool, social constructivism has not played a major role in many college classrooms.

In an effort to change this, Johnson and colleagues (1998) discussed the return of group learning to undergraduate education. They detailed five "keys elements" to fostering productive disagreement in the classroom: positive interdependence, individual accountability, promotive interaction, social skills and group processing. Positive interdependence means that students need to rely on one another for success, while individual accountability is ensuring that each student is evaluated for their performance. Promotive interaction means that students need to help support each other through encouragement and assistance in a face to face manner. Working together in person is important because nonverbal communication skills (i.e., facial expressions) can provide critical feedback to teammates. Social skills are a critical component of teamwork, and are needed for success in the workforce. Students need to have the opportunity to see these skills modeled by their classmates and practice using them in appropriate ways. Lastly, group processing is a chance for teammates to give each other feedback on what was helpful and what could be improved for the future. Put into practice, these keys help promote successful social constructivism through teamwork.

1.3 Conceptual change theory

Since the 1980s, conceptual change theory has explored the role of how initial conceptions, or ideas formed prior to formal education, influence how people learn (Posner, 1982). Conceptual change theory was founded with four tenets: in order to change what a person believes, they must be dissatisfied with their existing idea(s); the new idea must be intelligible to the learner; the new idea appears plausible and coherent with other existing knowledge held by the learner; and the new idea holds promise for being a productive way to move forward (Posner, 1982). Continued development of this theory has found that students' prior conceptions include productive ideas that can become the basis for achieving a more sophisticated scientific understanding (Smith et al., 1994); novice learners, unlike expert learners, have not yet developed the realization that their knowledge is a hypothesis until tested and justified (diSessa 1988, 1993, 2008; Vosniadou, 2003); while conceptual change can be fast, it is often a slow and gradual shift (Vosniadou, 2012); and social processes such as comfort participating in class can significantly influence conceptual change (Hatano and Inagaki, 2003). Understanding students' existing prior conceptions is essential to promoting learning in this learning theory.

Some researchers have found that learners' prior conceptions are not easy to change through teaching. This difficulty arises either due to a lack of motivation by students to engage in learning activities or because of the human tendency to favor one's own knowledge over new knowledge (Vosniadou, 2003; Hatano and Inagaki, 2003). One result of college-level conceptual change research in the classroom suggested that students can memorize facts and do well on a test without truly learning the new information. For example, even after college chemistry courses, some learners maintain their prior conception that atoms are something *in* matter as opposed to being the basic constituents of matter (Andersson, 1990; Pozo and Gomez-Grespo, 2005). Many other examples demonstrate instances where learners revert to their prior conceptions either on finals exams, or shortly thereafter (Jaakkola et al., 2011; Driver et al., 1994; Prince et al., 2012; Alters and Nelson, 2002).

In part, reverting to prior conceptions can be attributed to the human tendency of favoring one's own ideas and explanations over new and sometimes less intuitive information, as mentioned previously (Vosniadou, 2003; Hatano and Inagaki, 2003). However, it can also be attributed to poor teaching methods such as traditional instruction (i.e., didactic lecture) which fail to make learners interrogate their prior conceptions (Alters and Nelson, 2002; Vosniadou, 2012). Other experts attribute the reverting to the inadequacies of conceptual change theory (D. Ash, 2008; Smith et al., 1994). They argue that, instead of viewing students as wrong or having a deficit, students need an environment that adequately fosters development of their prior conceptions to factually correct STEM knowledge. Vosniadou (2012) suggests that the risk of not fully engaging prior conceptions is that new, factually correct information is merely overlaid on deeply held prior conceptions, the two of which are often in disagreement. The result is new and correction information which is easy to discard. Resolving these prior conceptions requires student-centered teaching and learning instead of traditional, teacher-centered instruction.

1.4 Student-centered teaching and learning

Teacher-centered instruction focuses on teachers disseminating knowledge typically through lectures and provides instructors with very little feedback on student understanding outside of exams. The traditional college lecture is not designed around the principles of learning produced by research in psychology, education, and other fields (e.g., NRC, 2000), but stems from the historical period in time when books were scarce and lecturing was the most effective means to disseminate information broadly (Boyer Commission Report, 2003). This method of teaching has persisted “largely because it was familiar, easy and required no imagination” (Boyer Commission Report, 2003). In addition, learning theories rooted in “stamping out” students’ factually incorrect prior conceptions such as early versions of conceptual change theory support teacher-centered teaching.

In contrast, student-centered teaching and learning, which is supported by a variety of socially-supported learning theories, emphasizes what learners know and makes the instructor a facilitator of learning. Instead of overriding students’ knowledge, the student-centered approach to conceptual change is concerned with transforming and building on students’ prior conceptions. Active learning is one such approach, and involves students “doing things and thinking about what they are doing” (Bonwell and Eison, 1991). Constructivists and social constructivists believe that active learning benefits students because they are able to explore new information, discuss why it does or does not fit with their prior conceptions, and ultimately construct new ideas for themselves. Internal and verbalized dialogue is a key component to helping students interrogate their ideas, which makes group learning particularly fruitful.

1.5 Active learning

In addition to the pedagogical evidence which supports why active learning works, there is strong empirical evidence on the effectiveness of this approach. Recent investigations into team learning (Michaelsen and Sweet, 2011), collaborative learning and testing (Leight et al., 2012), and collaborative writing (Sawey and Sawey, 2013) all provide evidence of students co-creating knowledge. In addition to promoting individual students’ greater knowledge when learned in groups (e.g., Johnson et al., 1998; Duffrin, 2003), there are several other benefits to active learning. These include: better science literacy, promotion of diversity, and an improved ability to teach. Through active learning approaches, students have more opportunities to learn about and practice science through use of critical thinking and problem-solving skills (Handelsman et al., 2004; Allen et al., 2011; Hmelo-Silver, 2004). In addition, using problem based learning or case studies to teach content has helped students see that science is not a series of disjointed facts but are cohesive concepts and relevant to their lives (Pelaez, 2002; Wood, 2009; Momsen et al., 2010).

Overall, active learning has numerous benefits. Hake (1998) conducted an extensive survey of physics students nationwide and found learning gains were nearly twice as high in active learning courses than in traditional courses; Knight and Wood (2005) found similar results in their upper-division biology students. Attendance was improved in classes that employed active learning and group work, likely because of the added social pressure to not disappoint classmates (Herreid, 1998). Work by Watkins and Mazur (2013) further showed that active learning promotes the retention of STEM majors at the undergraduate level. Haak et al. (2011) found that active learning was able to disproportionately benefit students of disadvantaged backgrounds (educationally and socioeconomically) which led to reduced achievement gaps between advantaged and disadvantaged college learners.

Besides student benefits, instructors are better able to do their job. By using active learning, teachers have more feedback on student understanding every class period, not just after an exam (Silverthorn, 2006). With a better sense of what students do and do not understand, teachers can focus their teaching efforts on the most appropriate topics.

1.6 Concept mapping

One active learning approach that is particularly useful in allowing students to see how they think about a problem is concept mapping, pioneered by Joseph Novak (Novak et al., 1983). Concept maps are pictorial and/or word diagrams that students create to organize their thinking about the relationships and processes between discrete components of a system (BSCS 2002). These maps are physical representations of students’ mental models, or how they understand information (BSCS 2002; Brandt et al., 2001). As such, concept maps are a useful way for teachers to see what prior conceptions students may hold about a particular topic. For example, the connections between photosynthesis and cellular respiration in plant biology can be lost on students; concept mapping allows teachers to evaluate whether or not students see these two processes as related (Brown, 2003).

In addition, concept maps can act as a framework for complex topics. By creating a map, students build a cohesive “bigger picture” of integrated topics within a system instead of learning fragmented knowledge (Kinchin et al., 2000). As an example, a concept map used as an ocean system can help students relate Saharan dust storms with high fisheries catches off of Brazil.

Concept maps are also useful tools in team learning (Roth and Roychoudhury, 1993; Brown, 2003). While benefits to individual students can vary, working as a group on concept mapping requires students to articulate their thoughts and explain ideas with evidence and reasoning, which are key practices in STEM fields (Vanides et al., 2005; NGSS 2013). The act of working as a team on a concept map trains students to act like scientists. In addition, co-constructed concept maps are fodder for productive disagreement among students who have different ways of understanding and explaining concepts. In this way, concept maps promote metacognition (how you know what you know) by encouraging students to explain their ideas to others (Brown, 2003).

Finally, concept maps can be a powerful tool for teachers. They can be administered as pre-test assessments of what knowledge and prior conceptions students bring with them to the classroom. Concept maps can also be used as post-test assessments, allowing teachers to evaluate students' conceptual changes (Markham et al., 1994; Brandstädter et al., 2012; Vanides et al., 2005).

1.7 System thinking

The structural thought organization used in concept mapping readily lends itself to use in "system thinking" (e.g., Assaraf and Orion, 2005). System thinking is a dynamic way of thinking fostered through a holistic approach to learning about a subject from many sides, as opposed to isolated components of that system. This way of thinking means students know both details about small, crucial components as well as the bigger picture. One of the benefits of system thinking is learning to recognize patterns across multiple systems, as this helps learners apply existing knowledge to new subjects and develop critical thinking skills (Lyneis, 1995).

Assaraf and Orion (2005) distill the critical elements of system thinking to 7 components. First is the ability to identify system components and system processes. In environmental toxicology this would include the toxin, its sources and its various forms, and processes such as evaporation, diffusion, decay, biomagnification, etc. The second step is identifying relationships among components. In our example this could be wind *moves* the toxin from land to the ocean or cadmium in the ocean *is consumed by* plankton *which is biomagnified in* fish. The third step is being able to organize the system’s components and processes in a framework of relationships, often in the form of a concept map.

Once a framework is built, students must be able to make generalizations about a system (step 4). For example, the dilution of a toxin typically reduces its effects, or that changing wind patterns will result in different parts of the environment being contaminated. The fifth step is identifying the dynamic relationships within the system, such human-derived sources of industrial pollution influencing acid rain, or how climate change can alter wind and weather patterns which will impact the transport of toxins.

The sixth and seventh steps involve more critical thinking skills: understanding “hidden dimensions” and the cyclic nature of the system, respectively. Hidden dimensions refer to patterns that are not readily visible such as why plastic pollution can kill populations of frogs. This step includes understanding how changing a component can influence the system’s emergent properties. Finally, students must understand that the system is a cycle. Changes on the part of one component can feed back into many components, and these changes can often be predicted.

By using concept maps in representing system thinking, students’ conceptions regarding what components are involved in the system and what processes are important in influencing changes in the system are made apparent. This makes concept maps as pre-tests and post-tests useful for gauging both student’s system thinking capabilities (Assaraf and Orion, 2005) as well as investigating what prior conceptions students hold.

1.8 Prior conceptions

In this study, I focus on prior conceptions because this is where the chief power of concept maps lie. Constructivist and conceptual change theories both emphasize the importance of eliciting students' prior conceptions. By making prior conceptions visible, the instructor has a better sense of what information to address in class to help students re-appropriate their prior conceptions in fruitful ways. Concept maps are a tool in drawing out these scientifically incorrect conceptions in a student-centered way that promotes their knowledge (accurate or otherwise), and which can be relatively easily evaluated by instructors (Kinchin et al., 2000).

2. Methods

2.1 Participants

The study consisted of undergraduate students enrolled in an introductory level course on aquatic toxicology. The course was designed to teach both science majors and non-majors at any year in their undergraduate career. Of the 27 students enrolled, 8 were science majors, 15 were non-science majors, and 4 were undeclared (Table 1). The majority of students were freshmen, but students from all years were enrolled in the course.

This project was reviewed by the UC Santa Cruz Office of Research and granted an exemption from IRB review. Student identities were changed to protect the privacy of individuals who participated in this project.

2.2 Study Design, part I

The aquatic toxicology course met for 70 minutes, three times each week. During the first two weeks of the course, 4 case studies were taught using active learning techniques such as small group work constructing concept maps, small group discussions and just-in-time-teaching (as in Henderson & Rosenthal, 2006). System thinking approaches were used in three of the case studies. Students prepared for class by reading the background to each case; in class, students were presented with more detailed information about the case, given an opportunity to discuss the case in small groups, and then assigned to groups to construct concept maps. These concept maps then served as the basis for group discussions predicting changes to the system which were provided as verbal prompts by the instructor.

On the 7th class meeting, a formative assessment was given. The assessment consisted of 10 multiple choice (MC) questions, 5 constructed response (CR) questions, 1 concept map (CM) to construct individually, and the same CM to construct in assigned groups of 3 – 4 students. The questions pertinent to this study can be found in Appendix 1. All of these questions were designed as transfer questions; students were expected to use knowledge they had learned in previous cases and to apply this in a novel situation, that is, within content that had not been covered previously in the course.

The three MC questions were designed to gauge students' abilities to read and interpret concept maps about a fictitious toxic element (# 1), predict emergent properties of the system (# 2) and identify whether a system was fully depicted (# 3). The alternative answers in these questions were designed to reveal if students held common prior conceptions about atmospheric pollution and systems in general. The constructed response questions asked students to explain their reasoning for how relationships among components and processes would lead to the observed emergent property in question # 3 (# 4) and to predict a temporally emergent property (# 5).

For the CM portion, students were individually prompted to depict a system in which nuclear waste was contaminating the environment. A "word bank" was provided that suggested possible words to use. After completing maps individually, students were assigned to groups to complete the same task but as a group. Individual student CMs were collected prior to group mapping in an effort to encourage thought and discussion of what would belong on the group map; this group work was audio recorded. In addition, groups were asked to address 3 hypothetical scenarios about their system which dealt with predicting changes in processes or relationships. These conversations were only audio recorded due to time constraints, but given more time the same goal could have been accomplished by asking the students to write up their main discussion points for evaluation by the instructor. All concept maps and the discussion of the hypothetical scenarios were evaluated and coded for the presence of prior conceptions and flagged for what looked like misrepresentations of student knowledge or items what were particularly likely to be misinterpretations by the instructor. In addition, notes were made in instances where there was a paucity of information; these were instances of significant components not represented in the work, or everyday terms being used in place of appropriate scientific terminology such as “infest” or “infect” instead of “contaminate” (Table 2).

2.3 Study Design, part II

In order to validate the coding of the concept maps, students were individually interviewed by the instructor seven weeks after this formative assessment. For this portion, 27 of the 28 students participated. Students came to the interviews unaware of what would be discussed. They were verbally reminded of the concept mapping prompt from the formative assessment, then handed a copy of their concept map from the assessment. After a minute of familiarization with their own work, students were asked to talk the interviewer through their map. When pertinent, students were also asked to re-explain portions of their group map.

Using the evaluation notes taken on each individual map and corresponding group map or transcript, the interviewer asked the student to elaborate on their prior conceptions (or on a paucity of information). From the student’s explanations, the interviewer was able to make an informed decision about whether the student’s work had been misinterpreted due to the nature of the concept mapping activity, or if there was truly a prior conception depicted.

2.4 Study Design, part III

In an ancillary study conducted seven months after the work with students, the instructor conducted phone interviews of five faculty members from several different universities. These interviews were conducted to gain insights regarding how to improve small group collaborative work in college settings. Faculty members were selected based on their prior publications and presentations regarding the use of active learning in undergraduate education. Selections from these brief interviews are included in the analysis and discussion sections here, as they were pertinent. Their identities have been concealed, and are referenced as Faculty Member A – E. Interview questions are listed in Appendix 2.

3. Results

The MC questions, by inherent design, were only able to reveal 3 prior conceptions each. The CR questions revealed 11 different prior conceptions, 2 of which were held by 20% or more of the class (Figure 2). Among the individual CM and group CM activities, 11 and 17 prior conceptions, respectively, were identified and validated as such upon follow-up interviewing.

In four instances, interviews revealed prior conceptions that had not been evident from the concept maps. In most cases, these concepts were only tangentially related, which probably explains why they were not revealed in the CMs. For example, student Nate’s explanation of groundwater (below) and those identified in Table 3:

> Interviewer: You said earlier that you didn't know how groundwater moves, so give me your theory on it. How does it, why does it, how does it move?

Nate: OK, so there's sediment and there's water around sediment. I don't understand… is the sediment moving along..? *(pause)* No. The sediment obviously doesn't move. So the water moves independent of the sediment. Are there factors that move the sediment about? *(pause)* No, actually, I have no idea why water moves from one place to another.

Interviewer: What if I was on top of a hill and I poured water on the ground? And it soaked into the ground… where is it going to go?

Nate: Like gravity? Is it going to move? Does the body of water, groundwater, move sporadically? Well no, there are other factors.

The follow-up interviews also revealed nine instances interpreted as prior conceptions that were actually misrepresentations of student knowledge in graphic form, or misinterpretations of knowledge by the instructor. These interviews served as a good reminder that concept maps are not capable of revealing all of students' prior conceptions and are subject to errors of interpretation.

In general, students who were science majors revealed fewer scientifically incorrect prior conceptions (0 – 2, average = 1) than non-science majors (1 – 4, average = 3) in the individual CMs, group discussions and follow-up interviews. Students who had not yet declared their majors each revealed 1 prior conception. This suggests that within this course, the science majors could have served as "more knowledgeable others" to their group members. However, the difference in number of factually incorrect prior conceptions revealed is not considered significant due to the small number of students in this study. There were also several students who participated minimally in the follow-up interview, which left the instructor with the sense that these students were reluctant to communicate and therefore some of their prior conceptions may not have been revealed. This could have been due to cultural norms, comfort with the English language, assessment-related anxiety, etc., but these contexts were not investigated further.

4. Analysis

4.1 Types of conceptions revealed

4.1.1 Multiple Choice and Constructed Response

Multiple choice and CR questions are useful when gauging how students understand specific aspects of a system (Fu et al., 2009). For instance, students can be directed to focus on specific aspects of a system or more broadly on processes and relationships. However, there are limits to the MC method, such as when students regurgitate factually correct information but lack a greater understanding of why that answer is the best one. For this reason, the CR portion was more useful than the MC portion in revealing students' prior conceptions in this study.

Constructed response questions require students to have a deeper understanding of information than MC questions, which promotes students to learning with a different approach (Scouller, 1998). In this study, the CR answers revealed students who were able to select the correct answer on the MC but did not know why it was the correct choice. On MC question # 9 (What would you expect to happen if there were a severe drought one year?), eleven students chose the intended answer "c" (More Sq would end up in the atmosphere the year of the drought).

However, of these eleven students, only one was able to explain their answer with scientific reasoning on the corresponding CR question (# 11: Revisit your answer to question 9. In 2 or 3 sentences, explain the rationale behind your answer choice). Ten students chose the answer “a”, aligning themselves with the prior conception that only wet atmospheric deposition (i.e., rain) was responsible for removing the toxin from the atmosphere. The students who chose other answers (b or d) were able to make logical arguments for why their answers were correct, but overall none of the 27 students were able to attribute a mechanism (dry deposition, dust, etc.) to explain their answer. Many students did little more than restate the MC answer despite the scaffold given to answer the question. However, this question revealed five prior conceptions related to pollution in the atmosphere and demonstrated that a lesson on the atmosphere as a system needed more in-depth coverage.

Given the limited information gained from the MC questions, these types of questions appear to be best used in summative assessments to check for the persistence of such prior conceptions. The CR questions were more useful in understanding students’ prior conceptions, and have utility in both formative and summative assessments.

4.1.2 Concept Maps

Unlike MC and CR questions, the instructor has little control over the construction of a CM. This is a strength because the concept maps reveal a diversity of students’ prior conceptions with regard to both a specific content area and understanding of how interrelated systems function. In MC questions, the only prior conceptions revealed are ones the instructor provides as an answer choice. In CMs, students are nearly unlimited in their abilities to reveal their ideas. Previous research has corroborated this, finding that CMs "measure a very different dimension than multiple choice tests" (Markham et al., 1994).

The majority of prior conceptions of both individual and group maps were related to content knowledge (Figure 3). This was not surprising because this subject (nuclear waste) had not yet been taught in this class. For example, on student Nate's individual concept map (Figure 4), he showed nuclear material as being able to evaporate to the atmosphere in the same way that water evaporates. The remaining prior conceptions identified in the concept maps were related to processes in the system (e.g., unsure about how groundwater moves).

Many of the prior conceptions were held by a large portion of the class, and overall, the CM activity was helpful in pointing out which areas the instructor should focus on. For example, 25 of 27 students believed that nuclear materials were volatile enough to evaporate into the atmosphere from underground reservoirs, and this belief was illustrated on all group CMs. In addition, some prior conceptions were held by a small percentage of students and were not ones the instructor would have thought to address, but were important to address. These included that acid rain is not related to radiation leaks and that ozone and solar radiation are different from nuclear waste radiation.

4.2 Validation with interviews

While CMs are powerful tools in gauging student knowledge, they are not without their drawbacks. One such drawback of CMs is that they are subject to the interpretation of the instructor. In this study, I was the sole evaluator of the concept maps and transcripts of group discussions. This limited the power of these results, but was also an accurate representation of how concept maps are used in most classrooms (i.e., one teacher/grader). As mentioned before, there were also a handful of instances where prior conceptions were misinterpreted. These were in addition to 73 instances that were correctly identified as a misrepresentation of student knowledge (e.g., not connecting components with essential process arrows). In a formative assessment activity designed to gauge students knowledge, this issue is not particularly problematic; the information the instructor gained in this project far outweighed the instances that information was misrepresented or misinterpreted as a prior conception, or vice versa.

Besides prior conceptions and misrepresentations, there were often instances where a paucity of specific content knowledge (e.g., vocabulary) was revealed on the concept maps. In the follow-up interviews, about half of the vernacular terms from the concept maps were no longer used; students pointed to the arrow with the vernacular label but verbalized the scientific vocabulary term. This demonstrated both that at the time of the hybrid assessment students did not have the capability to discuss the system in scientific terms, and that in the weeks following this assessment they had learned or remembered appropriate terminology. In one student’s follow-up interview, she declared “I feel like I know so much more now that I can explain this sort of stuff. Now I have words for things!" Another way to reveal that students had learned content knowledge would have been to administer a post-assessment concept mapping activity in place of the interviews.

4.3 Individual versus Group CMs

I anticipated that group CMs would have fewer incorrect conceptions than individual CMs because students would negotiate during the activity. The group maps themselves did have fewer prior conceptions (5) than the individual CMs (11). However, groups had fewer prior conceptions because students did not offer their ideas to the group for discussion – not because group negotiation led to shared knowledge consistent with scientific evidence. This was determined using the voice recordings from the group map creation, where the most noticeable feature was a lack of conversation. In most groups, one member drew as he or she proposed an idea, and the other group members did not oppose either the idea or what had just been drawn.

Although the map creation lacked in conversation, the three hypothetical prompts did promote discussion. The groups revealed more conceptions (12) when specifically prompted to discuss scenarios about their CMs. In discussing the hypothetical prompt of what would happen with twice as much rain as normal, one group verbalized the conception that rain influences runoff, which leads to rivers and the water can carry nuclear waste to the ocean:

Barbara: There's going to be more runoff so more is going to end up in the ocean than other places.

Cary: More people dead.

Nate: It's logic. There's more runoff more people die.

While their conversation demonstrated scientifically correct knowledge not represented on their CM, it also revealed that they held a prior conception that runoff and/or nuclear material somehow kills (more) people.

As in the above excerpt, most of the audio transcripts of group work revealed more of a cooperative, accepting nature than a collaborative nature among the students; i.e., students proposed information and added it to the group concept map with little or no discussion among fellow students. In this superficial dialogue, the students were talking but not critically evaluating what each other said. There was little to no constructive feedback of each other's ideas. This was highlighted by 5 instances where groups allowed a factually incorrect conception offered by 1 member to persist, even when other group members did not hold the same beliefs (as gauged from their individual CMs). For example, some of Nate's prior conceptions were shared by the group (or not disputed) and re-appeared on the group's concept map (Figures 4, 5). These included the evaporation of nuclear material to the atmosphere and disconnected components such as the sun. In addition, several other prior conceptions not on Nate's individual poster appeared on the group poster: nuclear waste led to acid rain, groundwater became "runoff", and confusing the processes of evaporation and condensation.

It was unclear whether the appearance of individual prior conceptions on group maps was a result of students not caring about the task, or because they did not know how to productively disagree. Roth and Roychoudhury (1993) noted that in their study, unsupervised groups could sometimes let unintended or scientifically incorrect concepts persist in learners and that ideas had the potential to become ingrained if there was no intervention. In the study presented here, the perpetuation of prior conceptions was, perhaps, a major drawback of group concept mapping. It could be overcome by reviewing concept maps with students individually (written feedback), as a group (at the time of co-construction), or as an entire class for widely held prior conceptions.

There were a few instances of groups helping individual members learn, which was one of the anticipated outcomes of having students work collaboratively. During the design of the group concept map (Figure 5), Nate's collaborators addressed one of his prior conceptions:

> Nate: So then there's clouds and sun *(draws)*
>
> Cary: And then condensation.
>
> Nate: Is that precipitation or condensation?
>
> Barbara: Precipitation is rain.
>
> Nate: Is rain? Oh I've been doing it wrong my entire life. I've always done it the other way!
>
> Cary: Well, condensation is from here *(points to air)* due to the sun, and then precipitation *(points in downward motion)*.

However, disagreement like this was rare. Based on the learning theory of social constructivism, I expected to find productive (or unproductive) disagreements in the students' conversations, and was surprised when I did not find many. Despite the group work “looking right” in the classroom it did not produce a noticeably different result than the individual CM activity, suggesting it did not function in the same way as the group learning espoused in the literature. In effect, students were huddled around in small groups, completing a joint task, but the students did not bring “conflict” or “tension” to drive learning (Engestrom, 2011). As a result, the focus of this study into how best to elicit student conceptions was expanded into why individual and group mapping did not reveal significant differences.

4.4 Groups versus Teams

The words *group* and *team* are commonly interchanged, just as the words *collaborative* and *cooperative* learning are too often used synonymously. However, there are substantial differences between students working in a group versus working as a team. Teams are not students who sit physically near other students, nor is it enough for students to just discuss material with one another (Teed et al., 2012). Rather, teams are groups of students who are dependent on each other for overall success. Work by Tuckman (1965) looked at the necessary stages of teamwork: forming, storming, norming and performing. As their names imply, there are key social interactions at each stage of a team working together. Team rapport takes time to develop, and getting to the “performing” stage – where the benefits of collaborative learning are reaped – takes time. Students must get comfortable with one another before this stage is possible. In many ways, the group CM activity was group work and not teamwork.

Using Tuckman's four stages and Johnson et al.'s five essentials to successful group work (1998), there are several things that could improve the CM activity in the future as detailed in Table 4. In brief, group members need to depend on each other for success, and each person needs to participate fully as a team member. Students must be comfortable sharing their own ideas and critiquing those put forward by teammates. Developing a functional team requires time, and two weeks is an unrealistic time period for this. Lastly, students need a formal opportunity to give each other feedback on their social skills and role(s) as a teammate.

In addition to information gleaned from the literature, the faculty interviewed in the third part of this study offered helpful insights. These experts suggested ensuring group heterogeneity in educational background (i.e., at least one science major per group) to avoid issues with students not being able to help teach one another. This suggestion is highly aligned with Vygotsky's concept of a more knowledgeable other helping learners reach new levels of understanding. By ensuring one member of each group is familiar with scientific concepts, the odds are greater that each group will be able to achieve more as a team. In conjunction with the changes in Table 4, each of these relatively simple changes could make the group work I observed function more like teamwork.

To make teamwork most successful, larger social factors which play into collaborative learning also bare evaluation. Each of the interviewed faculty members spoke about student comfort with and expectations of active learning within their department or larger university as a mediating influence on the utility of active learning within their classrooms.

5. Discussion

5.1 Social factors

The social dynamics of a classroom can determine the overall effectiveness of active learning, regardless of how well structured the collaborative learning might be. This dynamic is the product of students' prior experiences, their expectations of what a class should be, and the experience of the instructor.

All five of the faculty members I interviewed mentioned the importance of students' prior experiences with active learning as a factor in the success of teamwork in their courses. Active learning techniques are gaining traction in undergraduate education (e.g., Alberts, 2012; McLaughlin et al., 2010), but it is not uncommon for students to be unfamiliar with these activities (e.g., Knight and Wood, 2005). Three of the faculty members I interviewed described discomfort among students who were required to participate in collaborative learning to succeed in their courses. Initially, students reported disliking active learning. In order to promote successful collaboration among students who are uncomfortable or new to active learning, getting student buy-in is crucial. The faculty I interviewed recommended regularly showing the class statistics of why active learning is a better way to build knowledge (and earn better grades) to help the students see the value of active learning. Another way to promote active learning is to remind students that the skills employers are looking for (e.g., interpersonal skills; Kerr and Runquist, 2005) cannot be learned through a lecture – they must be practiced.

The three interviewed faculty members said it was common for students to change their opinions about active learning after completing their course (10 – 15 weeks). They speculated that students became more socially comfortable with one another over time, diminishing the perceived "risk" of communicating their ideas in class. In my study, student surveys were taken twice, once after the assessment (start of week 3) and again at the end of the course (end of week 10). On the first survey, 70% of the students responded that they felt comfortable participating in the class; only one student said they were not comfortable participating and the remaining 26% reported feeling neutral. At the same time, 64% of the students still preferred learning with a traditional lecture and 53% preferred learning from PowerPoint presentations; 41% of the students reported enjoying learning in small groups. It is interesting to note that students self-reported comfort participating in class, but still preferred traditional classroom practices. Again, two weeks was an insufficient amount of time for students to master their role as active learners and likely contributed to their preference for more familiar instructional methods. At the end of the course, 36% of students reported that they preferred the group work over lecturing, while 24% reported explicitly disliking group learning; 9% of respondents said they had learned more in group activities than in the portions of the class taught with traditional lectures. Because the last 8 weeks of the course were taught mostly with traditional lectures, it was not surprising to me that only a small percentage of the class reported enjoying active learning. Discomfort with active learning likely stemmed from their short and flawed exposure to it, but could also have been a product of larger societal factors.

Universities are diverse places, often culturally, economically, politically, etc. Fostering a supportive environment for students from all backgrounds to feel comfortable in active learning is important because the skills students learn will be crucial in their careers. Active learning techniques such as teamwork can be counter to some cultural norms. Active learning borrows from both individualist and collectivist perspectives, favoring the act of engaging in discussion and arguing with evidence and the interaction of students with one another in team learning (Trumball et al. 2001; LAB 2002). Students who come from Native American, Latin American, African American and Asian backgrounds are often raised with a collectivist perspective (Greenfield et al., 1996; LAB 2002) and can struggle with succeeding in constructivist practices where individualistic characteristics and disagreement with peers and instructors are favored. The ethnic demographic of this class was diverse, with 50% of the students as non-white (32% Asian, 14% Hispanic, and 4% African American); this could explain some of the discomfort with group learning.

Team-based learning is more student-centered than lecture, and it takes both time and maturity to develop the skill of learning in this situation. Anecdotal evidence provided by Faculty Member A in her interview suggested that diversity in family income can play a role in student comfort with active learning. She reported that students from wealthier backgrounds also came from well-funded K-12 schools where active learning was regularly used. By the time these students got to her class, they were familiar with how to interact productively in groups during class. When Faculty Member A moved to a new institution with a large percentage of non-traditional students (adult learners with families, commuters, people working 40 hours per week, low-income families), she found that the student group dynamics were very different, making the team-based learning she employed at her previous institution ineffective. While these students were not incapable of team learning, the time required to get the students to Tuckman's "performing" stage was impractical, so she adopted a different form of team learning where students were given joint tasks only in the laboratory portion of the course.

5.2 Student expectations

The expectations that students have regarding what a class is or should be also influence the success of active learning. Many students enter college, particularly the sciences, with the expectation that their responsibility is minimized to performing well on exam days; normal class days are passive lectures. Where does this student expectation, and often demand, come from? Giddens' structuration theory (Giddens, 1984) in the context of college classrooms suggests that active learning is difficult to implement because:

1. Students expect to learn in a manner similar to their previous learning experiences (often didactic lectures).
2. Instructors teach the same way they were taught.

3. The physical layout of classrooms (amphitheater-style) is not conducive to any other form of teaching.

By teaching with traditional didactic lectures, student and instructor expectations of what learning and teaching look like are continually reinforced.

I propose that successful student-centered approaches to learning are caught in a socially constrained “rut”. By which I mean both teachers and students have traditional expectations of their roles in learning, and changing these expectations is difficult. This change requires a large investment of time, and this rut is best overcome by groups of instructors or whole departments rather than in isolation.

Students who are new to active learning take several weeks (or an entire term) to become comfortable with this form of learning. The more opportunities that students have to practice active learning, the more quickly students will reach Tuckman’s “performing” stage in each class because they will be familiar with what their role is as an active learner. While not impossible for instructors to implement individually, student achievement in active learning classrooms will be limited until the students are able to warm up to the idea of this form of learning. In a 10 week course, students might not get to a point where they are able to fully benefit from active learning until the end of the class. Instructors who continually struggle each term to implement active learning with resistant students and few results are likely to burn out.

Instead, it could be more effective if instructors established a community or practice. By this, I am referring to Lave and Wenger’s definition of community of practice (Smith, 2003; 2009), in which communities are comprised of people mutually interested in promoting active learning in the undergraduate classroom. Through the instructors' practice of shared teaching techniques, the students gain a more consistent and clearer understanding of how to be active learners. Therefore, efforts to improve teaching and learning by groups of colleagues are just as important, if not more so, as the efforts made by individual instructors. Of the faculty members I interviewed, all mentioned that colleagues within their department also use student-centered approaches to teaching and learning. Faculty Member B related that the majority of his department is extremely supportive of active learning, even though a few professors disregard their efforts. In addition to his department, he described "pockets" of faculty scattered throughout the campus that have similar interests in improving teaching and learning. Faculty Member C described a "norm" in moving towards active learning techniques within her University. Faculty Member D said that students have become so used to their physics courses involving active learning that they complained when one professor used the traditional lecture method alone. Faculty Member A contrasted the "culture of teaching" among the faculty at her first institution where students liked team-based learning with her current institution where active learning approaches are less common and team learning was not well received by students. In addition to being talented teachers, part of the successful use of active learning by each faculty member undoubtedly stemmed from colleagues also implementing these instructional methods.

5.3 The role of the instructor

The instructor’s prior teaching experiences and comfort level with teaching can also have a strong influence on the overall success of active learning. One of the interviewed faculty members suggested that nothing works well the first time you try it; you have to tweak your approach and try again. Faculty Member E said, “Perhaps unsurprisingly, faculty go in and try innovative teaching techniques and it doesn’t work.” Two of the faculty pointed out that it is unrealistic for instructors to expect to be able to use active learning properly without formal training. It equates to asking an education specialist to read a chemistry paper and then replicate the experiment in the lab with no formal training. It just won’t work!

Short-term professional development approaches are starting points for helping instructors change their practices, but have been met with limited success in actually transforming teaching practices (Ebert-May et al., 2011). Instead, instructors need to experience intensive student-centered approaches as learners themselves through programs like the National Academies Summer Institutes on Undergraduate Education. By experiencing active learning, instructors are more likely to change their conceptions about what science teaching and learning should look like, are more prepared to implement active learning approaches, and are better able to help their students change their expectations of what learning looks like.

6. Conclusion

6.1 Assessment

Each of the forms of assessment was useful for gauging students' prior conceptions in different ways. MC questions were useful in gauging what common incorrect conceptions the students held. CR questions allowed students to explain their thoughts, and were a useful way to get at what underpinned the students' prior conceptions. The individual CMs were a useful tool to gauge student conceptions in a very broad context around a given topic; the group concept maps revealed much of the same information. On the other hand, the group discussions of hypothetical prompts revealed more prior conceptions about system relationships than either the group or individual maps alone.

As a classroom tool, CMs hold promise at the start of a course or content unit, to allow instructors can gauge what prior conceptions the students are bringing with them to the class, and adjust course lessons as appropriate. In addition, CMs are a way for students to physically represent their mental model and perhaps even confront their own prior conceptions when they *see* that their ideas are not coherent with one another. Paired MC and CR questions are better for formative assessments, because persistent incorrect conceptions and the reasoning for them are made visible, and instructors can re-focus efforts on specific conceptions as needed. While any of these forms of assessment would be useful in summative assessment situations, the free construction of CMs present more challenges in evaluation than the MC or CR questions. Instead, the CMs may be more useful if students are asked to interpret a provided map.

6.2 Active learning

Concept maps also hold great potential as learning tools for team learning activities when implemented properly. As in all active learning that promotes student collaboration, appropriate team skills must be scaffolded and given time to develop. This will ensure a positive learning experience for students, and help re-define student expectations for what learning in the classroom should look like. Successful implementation of active learning is also a function of students' socially constructed expectations of what teaching and learning should look like. Instructors who work with colleagues to change student roles are more likely to see their students reap the full benefits of active learning.

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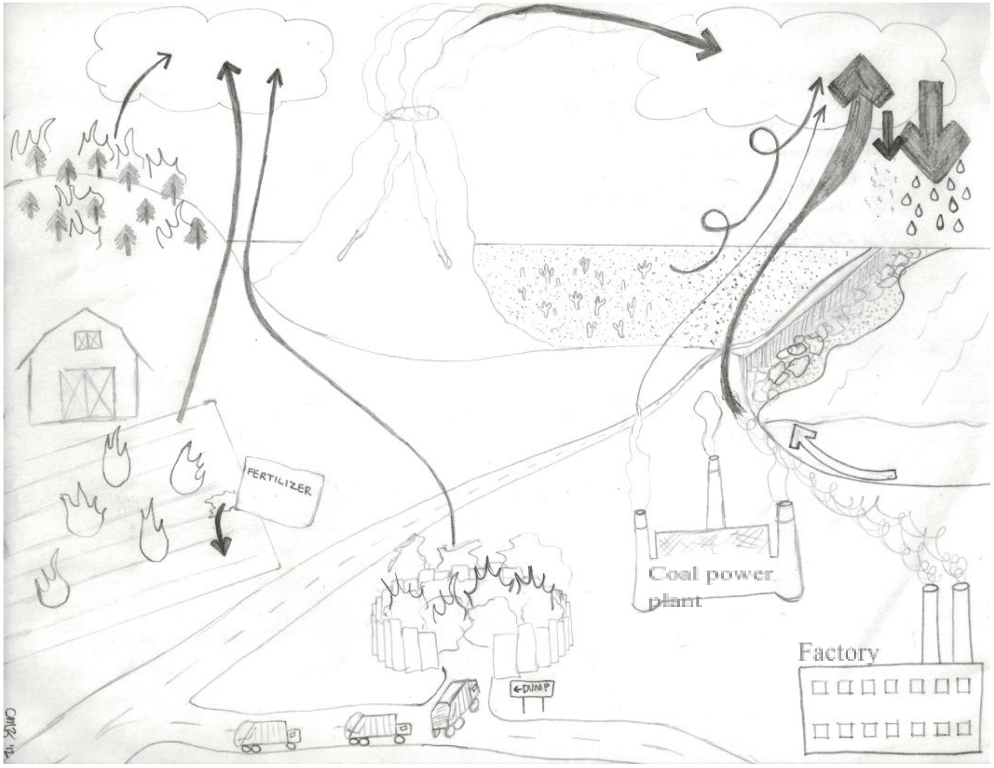
8. Appendix I. Formative assessment

<u>Multiple choice</u>

Use the picture below about the fake toxic element squirrellium (Sq) to answer questions 1 – 3:



Movement of the toxic element squirrellium (Sq). Arrow size represents the magnitude of each process.

1. Which component/process has the greatest impact on Sq movement?

    a. Fertilizer/fertilization

    b. Garbage/waste incineration

    c. Factories/atmospheric emission releases

    d. Volcanoes/ash eruptions

2. What would you expect to happen if there were a severe drought (no rain) one year?
    1. During the drought, all of the squirrellium would end up trapped in the atmosphere.
    2. Squirrellium would build up on farm fields from the fertilizers.
    3. More squirrellium would end up in the atmosphere the year of the drought.
    4. The year after the drought, there would be a lot of squirrellium on the surface of the ocean.
3. This diagram is a complete system.
    1. True: impacts on organisms don't need to be shown in a complete system.
    2. False: no relationships can be inferred from the diagram.
    3. True: each arrow shows all of the possible movements of Sq.
    4. False: not all sources and "sinks" of Sq are accounted for

Short Answer

4. Re-visit your answer to question 9 (What would happen if there was a severe drought). In 2 or 3 sentences, explain the rationale behind your answer choice. (If you get stuck, try thinking of it as "If there were a drought, then (a, b, c, or d) because ______).
5. Revisit the diagram of squirrellium (Sq). If power plants and factories were able to put scrubbers on their smokestacks (to catch all of the Sq), what changes in the diagram would happen by the next day? What changes would happen in 10 years?

1 day:

10 years:

Individual Concept Mapping

Hanford, WA is five miles south of the Columbia River. Here, a nuclear complex known as the "Hanford Site" or "Hanford Nuclear Reservation" is run by the U.S. government. Established in 1943 as part of the Manhattan Project and later used in the Cold War, it produced ~50,000 nuclear weapons. While production has ceased, an estimated 53 million gallons of radioactive liquid waste and 25 million ft^3 of solid waste remains. Much of this waste has been stored in tanks underground, which have begun leaking. Using what you know about the movement of toxins from our class, draw a system map. Incorporate as many components as possible both from your own knowledge and from the "word bank" (on projector).

These will be graded both on the number of components included, connecting processes (labeled arrows), and coherence (if verb label makes sense, arrow points in proper direction). For example:

is a coherent choice.

doesn’t make much sense.

Group Concept Mapping

In your assigned groups, create a concept map using the same prompt (above). When you’ve finished constructing your map, appoint one group member to be your writer, who will take brief notes on the discussion of the following prompts:

With your system mapped out, discuss what components, processes, and relationships would change if:

a. Next year there is twice as much rain as normal.
b. Salmon from the Pacific Ocean swim upstream and spawn nearby in the Columbia River.
c. 10 years from now, humans have revived NASA’s space missions. What are the risks of extracting, packaging, and blasting the nuclear waste into space? Is it worth the risk?

9. Appendix II. Interview questions from part III of the study design.

1. Can you begin by telling me a little history of when you started using collaborative learning and why?
2. When you first started, did it work the way you anticipated? As in, were students readily participating and benefiting from this type of instruction?
3. Did you ever have it not work? Do you ever have a group where it doesn't now that you've gotten it "down"?
4. What are tricks to making it work? What have you tried that worked and didn't work?
5. What other kinds of "experiments" have you done with teaching?
6. What does your classroom look like day to day?
7. Do the other faculty members in your department have a similar instruction style? Are student expectations such that working in an active classroom is the norm?

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Table 1. Participant statistics for the 27 students enrolled in Aquatic Toxicology.

	Major			
Year	Undeclared	Non-science	Science	Total
1	4	9	4	17
2	0	2	2	4
3	0	2	2	4
4	0	2	0	2
Total	4	15	8	27

Table 2. Examples of what was marked as a paucity of information and the proper vocabulary term for the situation.

Paucity of content knowledge (Vernacular term)	Vocabulary term
Assimilate	Flow, seep
Soak up	Evaporate
Runs off	Seeps
Infest, infect	Contaminate
Liquidate	Irrigate

Table 3. Student quotes of prior conceptions not evident from the concept maps, revealed during follow-up interviews.

Student quotes	Prior Conception
Is there a way with [the nuclear waste] in the clouds and the rain where will it affect the lightening that shoots out of it?	Lightening shoots out of clouds; nuclear waste can react like a nuclear bomb
I think plants and trees would get more of their contamination from the soil because the roots are directly in the soil.	Plants take up soil (not water) from the ground
The fish population would die… it's a river. Fish don't live in rivers, they just travel through it.	Fish do not live in rivers

Table 4. Recommendations of changes for future team learning.

	This study	Best practices	Future changes
1	As already noted, interdependence (social norms, discussion, feedback, etc.) was mostly nonexistent among the students in this study. They completed the CMs individually prior to the group work, and this perhaps contributed to their sense that group cooperation or discussion was unnecessary. Each person saw themselves as capable of building a successful CM on their own, and this undermined the investment for reliance on each other.	Group members must depend on each other for success; if there is a way to succeed individually, students will find and use it. Social interdependence theory dictates that, depending on how group interdependence is structured, the results can have positive (cooperative), negative (competition), or nonexistent (individualistic) group outcomes (Johnson & Johnson 1989).	In order to determine if group CMs reveal equally fruitful information as individual CMs, the group prompt could be on the same topic but superficially different from the individual prompt. In this way, students will be more invested in participating in both activities. Group work may also work better if it were done prior to individual work, so that students negotiate with others at the same time they are negotiating with themselves.
2	The infrastructure of the activity was such that individual accountability was minimal. There were no measures in place to prevent one student from doing all or most of the work for the team. Although not obvious, five of the eight groups had "alpha" leaders who were the first person that grabbed a marker and began drawing. This was apparent because the leader's individual map bore a strong similarity to the group map and one member's individual.	There must be some amount of individual accountability, where each student is assessed for their part of the group work. This ensures an "alpha" leader does not do all the work for the team, and every student is motivated to participate (Johnson et al., 1998).	To improve individual accountability in the future, students could have to explain their contributions to the group product, write a short essay on what he or she has learned, or the instructor could warn students that audio recordings of the group work would be factored into the grading, in order to ensure equitable participation among all members.

3	Instances of students correcting each other's prior conceptions were rare, and their dialogue or "cross talk" seemed inhibited. This could have been because the groups were new, and in their "forming" stage still.	Students must promote each other's success in a face-to-face setting (Johnson et al., 1998). This means helping and teaching each other, and in return getting or giving feedback on each other's contributions.	More time is needed to develop a comfort with putting one's own ideas up for critique, and being comfortable enough to disagree with classmates' opinions. This comfort level is hugely important, and isn't something that can be rushed. Two weeks was not enough time.
4	Group work social skills had been previously practiced in this course, but students were assigned to different teams each time and there was no formal feedback provided to encourage students to develop (or further refine) their teammate skills.	The course instructor needs to teach and support the necessary social skills for group work (Johnson et al., 1998). One of the outcomes of this form of learning is a better ability to be a teammate, and this learning must be scaffolded just as any other learning.	By assigning students to permanent teams for the course, group diversity (major, year, gender, etc.) would be ensured and students would have the chance to work through the full set of stages for team development described by Tuckman (1965). To help scaffold the team dynamic, Roth and Roychoudhury (1993) recommend assigning individual students to specific roles at first, to promote participation and the "overall quality of the process".
5	Students were not given the opportunity to give each other feedback on their roles as team members, in part because of the design of this activity as an assessment.	Students must have the opportunity for "group processing", giving each other feedback on their roles as a team member (Johnson et al., 1998). This provides students with the chance to reflect on how to improve their skills in the future.	Feedback would be more appropriate and feasible in consistent teams of students, particularly as an out-of-class assignment.

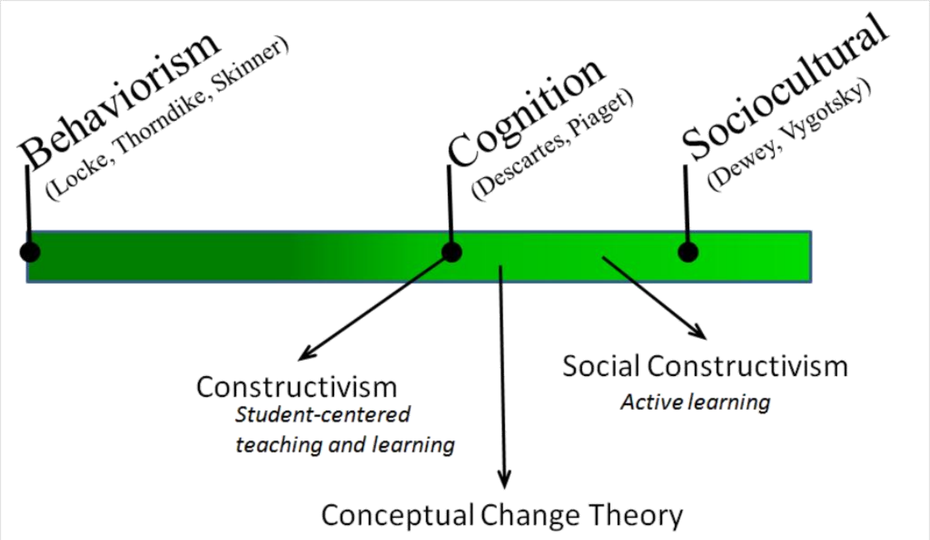

Figure 1. The spectrum of learning theories includes behaviorism, cognition theory, and sociocultural theory. This work employs the latter two theories.

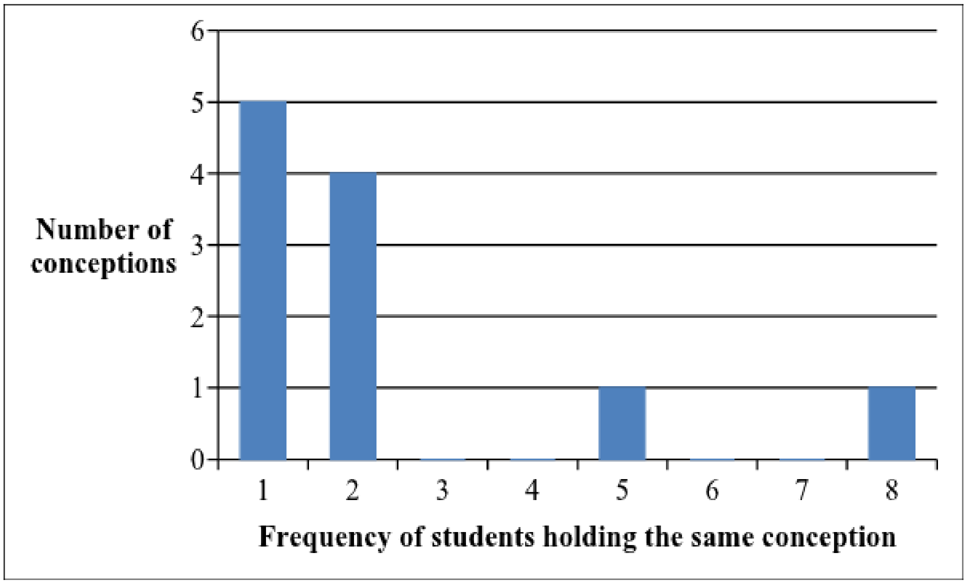

Figure 2. Frequency of prior conceptions on CR portion of the assessment; nine of the prior conceptions were held by just one or two students, but two conceptions were held by 20% or more of the class.

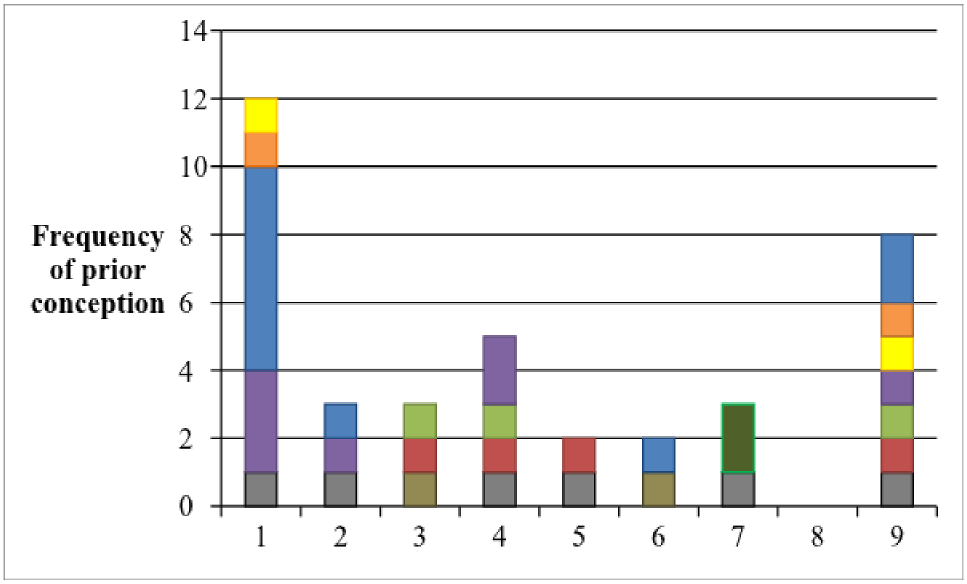

Figure 3. Frequency of the types of prior conceptions relating to content, processes, or relationships. I = individual CM portion, G = group CM portion, D = discussion of hypothetical prompt. The color within each type of prior conception relates to the same conception. For example, within *Content* the purple represents the same conception that appeared in 2 individual maps and 1 group map; this is a different conception from the purple ones represented in the *Process* and *Relationship* categories. Overall, most prior conceptions were related to Content knowledge, and the group discussion revealed more prior conceptions than the construction of the group CM itself.

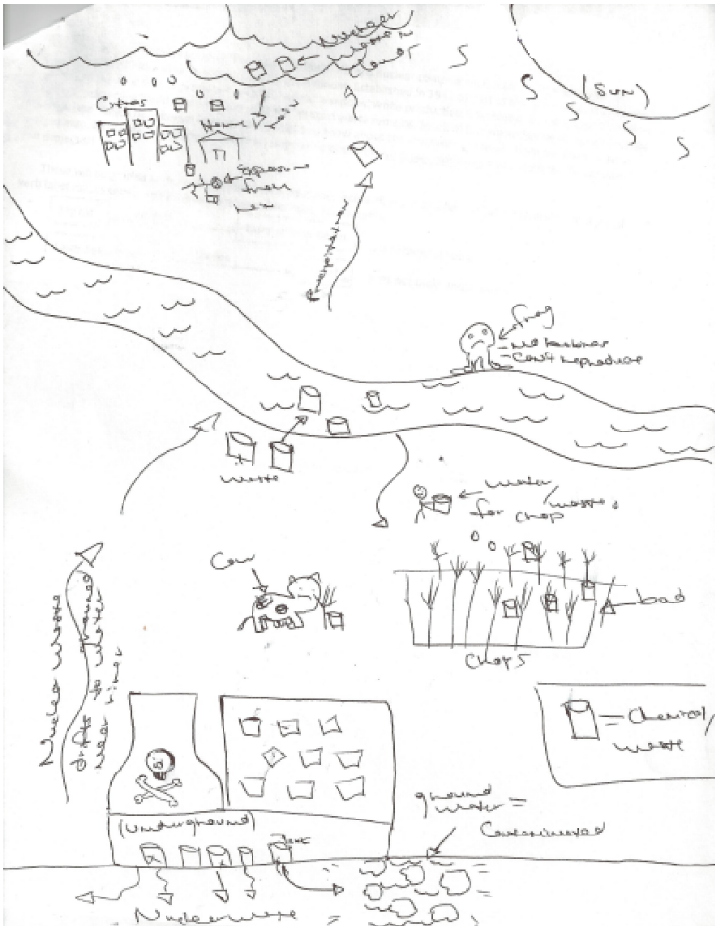

Figure 4. Nate’s individual concept map from the formative assessment.

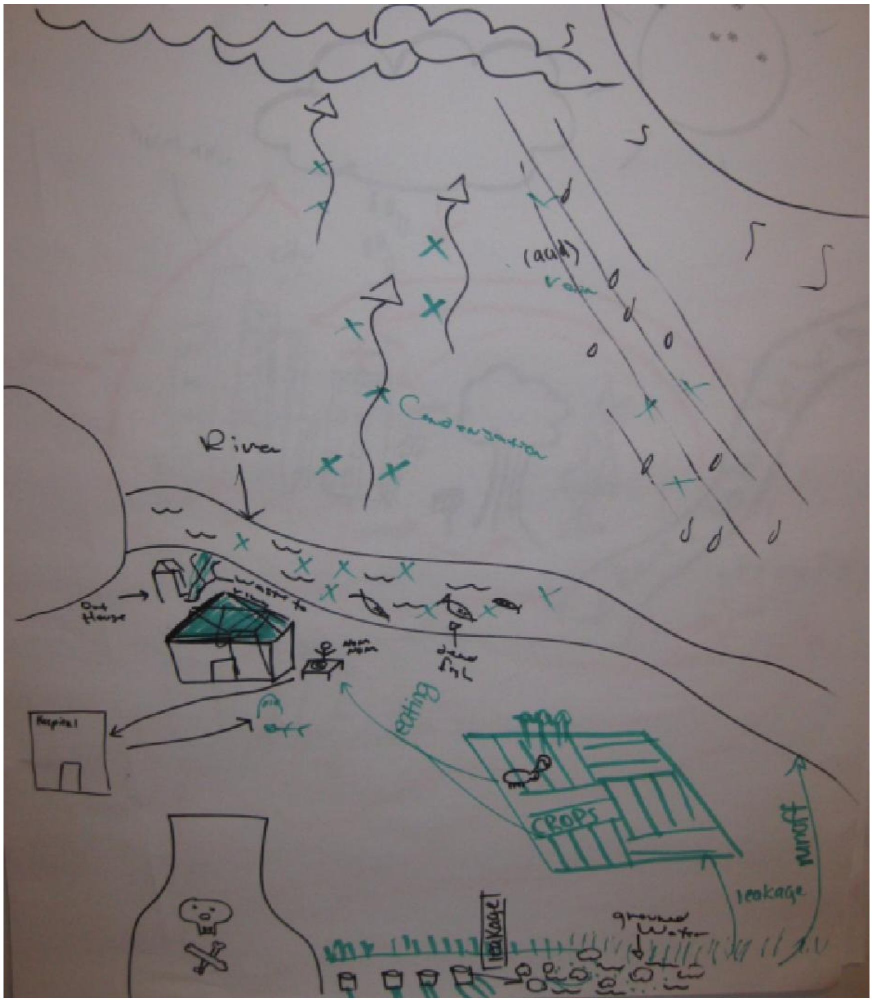

Figure 5. The group concept map Nate participated in creating.

CONCLUSION

The results of this dissertation work both lay the foundation for the rapid processing and analysis of lead (Pb) concentrations and isotopic compositions in seawater as well as establish a baseline for the changing Pb isotopic compositions (PbICs) in the subsurface North Pacific Ocean. These outcomes are important because of the expanding interest in studying Pb contamination in the world ocean through international programs such as GEOTRACES (www.geotraces.org) and because future studies of Pb in the North Pacific will have a metric against which to compare their measurements.

In Chapter 1, the WIGS laboratory's method (Ndung'u et al., 2003) for pre-concentrating seawater and analyzing Pb concentrations on-line showed good agreement (within 8 pmol kg^{-1}) with other methods used by Bill Landing's group at Florida State University and Alan Shiller's group at the University of Southern Mississippi (Zurbrick et al., 2012). The WIGS method for determining Pb concentrations was advantageous to prior methods because it used relatively small quantities of reagents, effectively reducing the reagent blank during sample processing. In addition, automation made this technique faster than other reported methods.

In Chapter 2, a method for the extraction of large volume (50 – 1000 mL) seawater samples was presented (Zurbrick et al., 2013). Similar to the on-line concentration method, these extractions for PbICs had a relatively lower blank (1 – 30 pg Pb) compared with prior organic solvent extraction, co-precipitation, and other resin-based extractions (1 – 6000 pg Pb; Patterson and Settle, 1976; Reimer and Miyazaki, 1992; Miyazaki and Reimer, 1993; Halicz et al., 1994; Wu and Boyle, 1997; Munksgaard et al., 1998; Weiss et al., 2000; Reuer et al., 2003; Wu et al., 2010; Boyle et al., 2012). In addition, the semi-automated method allowed for relatively rapid extractions that produced results comparable to those reported by Ed Boyle's group at the Massachusetts Institute of Technology (Boyle et al., 2012).

In Chapter 3, a baseline of total dissolvable Pb concentrations and PbICs was established in the Northwest Pacific Ocean from samples collected in 2002. A subsurface Pb concentration maxima was documented throughout the central North Pacific, and resulted from the entrainment of Pb in subducted Western Subarctic Gyre surface water. In this subsurface feature, PbICs were consistent with surface waters (Gallon et al., 2011) that had been previously attributed to Chinese industrial emissions. Conversely, abyssal waters were more similar to background PbICs determined from FeMn crusts and benthic sediments by others (Chow and Patterson, 1962; Chow and Tatsumoto, 1964; Kersting, 1995; Ling et al., 1997). These findings were consistent with the expectation that deep water, which is relatively old (~ 1000 years; Matsumoto, 2007), would look different than near-surface waters.

In Chapter 4, dissolved Pb samples were analyzed from the Northwest Pacific Ocean which was revisited in 2009 and 2011 during two GEOTRACES cruises. In the western basin, abyssal water PbICs were similar to surface water PbICs, both of which reflected inputs from Chinese industrial emissions. In contrast, the PbICs in the central North Pacific abyssal waters were similar to values previously reported in

2004 (Wu et al., 2010). The less radiogenic PbICs in the western basin deep water relative to the central North Pacific were attributed to the relatively larger particle export flux there and subsequent rapid isotopic equilibrium between the dissolved and particulate-bound Pb. Using the 2002 work as a baseline, the rate of isotopic change in deep waters was calculated and the future abyssal ocean was projected to be isotopically similar to surface waters in the next several decades.

In Chapter 5, the Pb composition of coastal waters near and off-shore of California was reported. The San Francisco Bay sediments and water were isotopically consistent with historic US gasoline Pb, as previously reported (Ritson et al., 1999; Dunlap et al., 2000). The flushing of the Bay with seawater carried this historic Pb to the continental shelf just off the coast, where it was remobilized into upwelling waters. Calculations showed that surface waters directly above the continental shelf were derived of 31% historic US gasoline Pb and 69% Asian industrial Pb. However, the signature of US Pb diminished as eddies carried this water off-shore and mixed it with relatively greater amounts of Asian industrial Pb which were both deposited to off-shore surface waters and upwelled in waters near-shore.

This work has demonstrated that despite the global phase-out of leaded gasoline, industrial emissions have maintained elevated levels of Pb in the environment. Remobilization of historic US leaded gasoline continues to affect the coast of California, while atmospheric industrial emissions are transported long distances across the entire North Pacific and beyond. With future coal consumption in

China projected to increase another 150% by 2030 (U.S. E.I.A.), Pb contamination of the North Pacific is expected to increase for the next several decades unless strict emissions policies are implemented.

Finally, in a critical reflection of my own teaching, I found the utility of multiple choice questions was best in summative assessments and constructed response questions (short answer) were more powerful in formative assessments. Although the differences between individual and small group concept maps were minimal, implementation of this activity with several small adjustments in the future could eliminate several pitfalls to collaborative learning.

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