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Intercalibration of Cd and Pb concentration measurements in the northwest Pacific Ocean

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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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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 ultrahigh 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 microcolumns 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, 26.0°N, 175.0°W 80 m	FSU	1.7	2.8	BDL	57.8	67.3	55.6
	UCSC	0.4	2.2	1.2	63.8	74.8	69.4
	USM	ND	ND	ND	66.0	80.2	64.8
IOC-4 Station 8, 26.0°N, 175.0°W 170 m	FSU	51.9	52.9	51.1	77.6	76.4	114.6
	UCSC	50.2	53.8	54.2	87.5	85.3	128.4
	USM	ND	ND	ND	89.6	88.6	130.6
IOC-4 Station 8, 26.0°N, 175.0°W 300 m	FSU	145.2	159.4	150.2	65.8	71.6	70.3
	UCSC	164.3	159.8	159.1	77.0	77.8	76.5
	USM	ND	ND	ND	78.7	118.9	78.3
IOC-4 Station 8, 26.0°N, 175.0°W 700 m	FSU	790.6	819.2	851.7	47.1	49.3	48.4
	UCSC	878.8	824.5	898.4	53.3	57.0	54.2
	USM	ND	ND	ND	56.9	58.2	53.6
IOC-4 Station 8, 26.0°N, 175.0°W 900 m	FSU	972.8	935.2	952.2	55.8	48.5	63.0
	UCSC	1008.1	967.4	1019.9	60.2	52.4	69.8
	USM	ND	ND	ND	65.1	60.3	75.0
IOC-4 Station 8, 26.0°N, 175.0°W 1500 m	FSU	978.7	1016.7	922.0	25.8	22.2	22.0
	UCSC	984.8	951.6	964.3	27.8	19.4	22.3
	USM	ND	ND	ND	29.9	24.6	25.8
IOC-4 FISH 20 45.9°N, 158.6°E	FSU	541.4	778.4	576.4	59.2	63.7	60.1
	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 49.8°N, 166.6°E	FSU	655.2	653.8	616.1	45.3	48.1	44.0
	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 39.6°N, 170.6°E	FSU	109.1	174.8	122.9	65.9	72.1	68.8
	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 26.0°N, 175.0°W	FSU	2.5	4.4	2.0	45.6	41.9	42.2
	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 24.9°N, 153.6°W	FSU	2.5	2.9	2.0	29.1	37.1	27.6
	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-

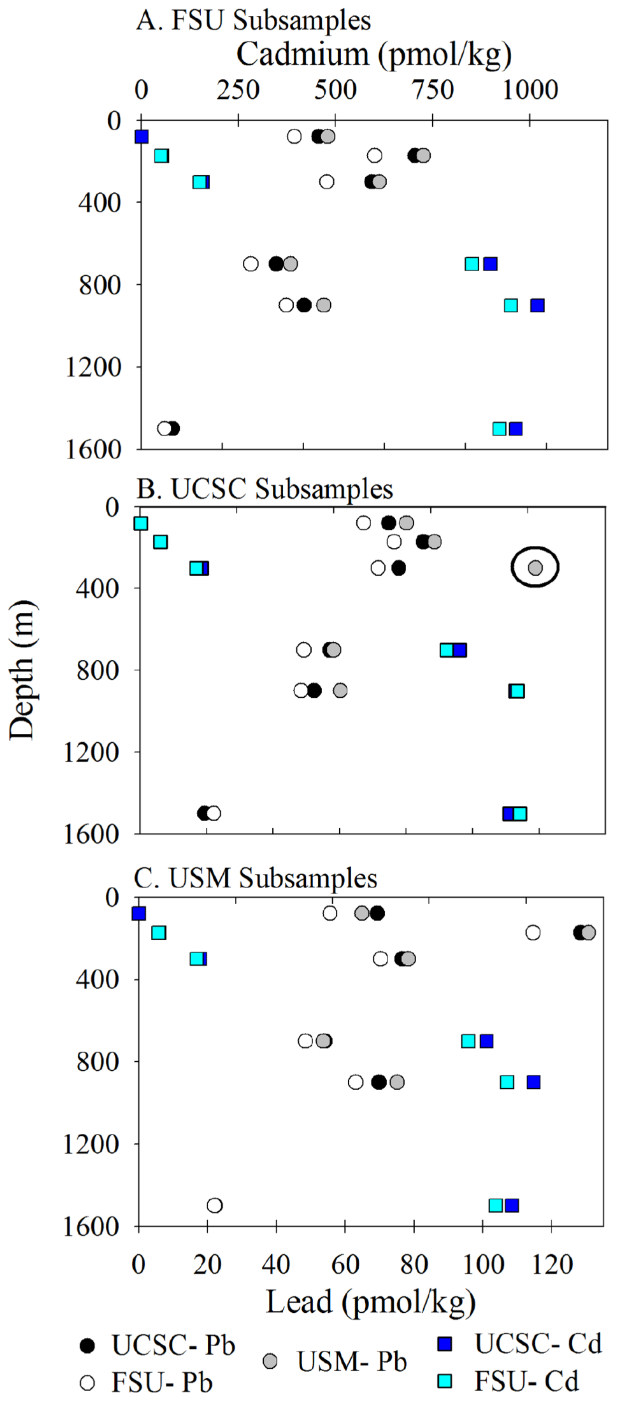

Figure 1. Cadmium and Pb concentrations in IOC-4 Station 8 subsamples from A) FSU, B) UCSC and C) USM. Analyses conducted by FSU, UCSC and USM were in agreement. The data point circled in black (IB) was a sample that leaked during shipping and became contaminated for Pb. Note that the symbol sizes are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

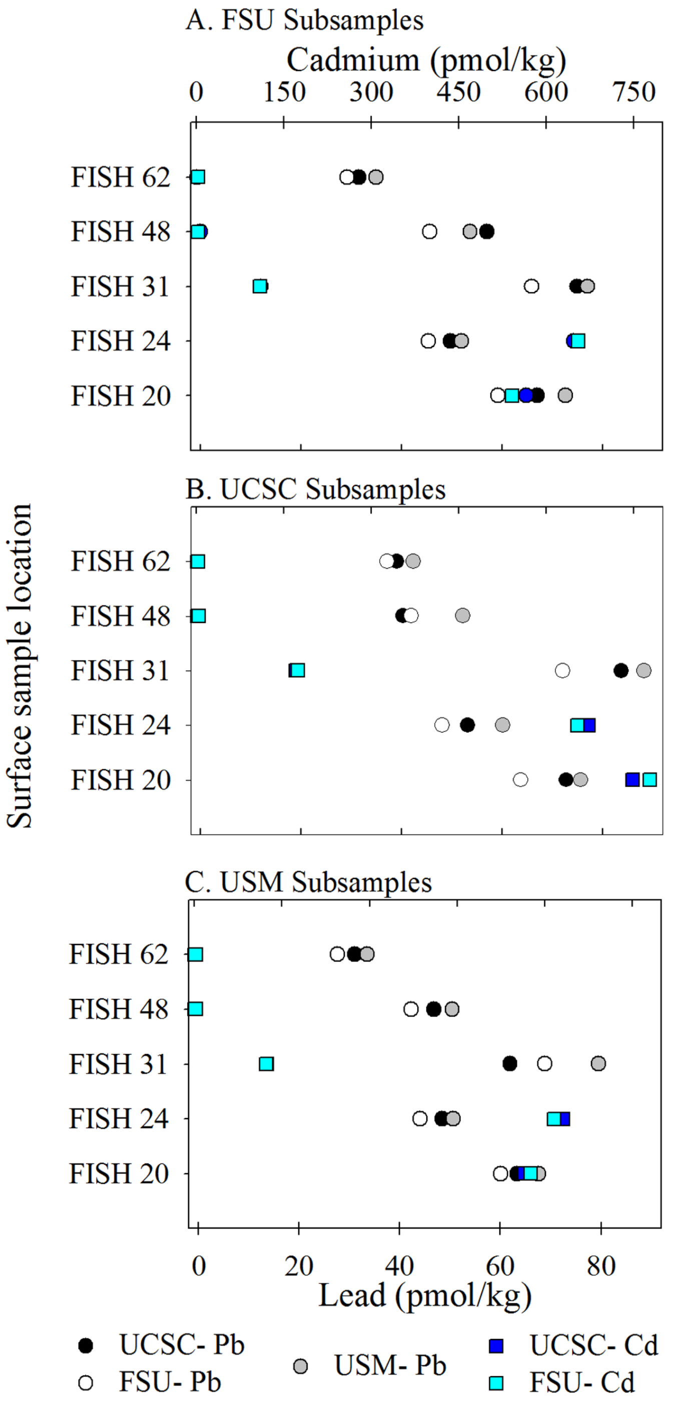

Figure 2. Cadmium and Pb concentrations at five locations in IOC-4 towed-FISH surface water subsamples from A) FSU B) UCSC and C) USM. Analyses conducted by FSU, UCSC and USM were in agreement. For locations see Table 3. Note that the symbol sizes are larger than the analytical error of the measurements.

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.

References

Boyle, E. A., B. A. Bergquist, R. A. Kayser, and N. Mahowald. 2005. Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA: Temporal variability and an intermediate water hydrothermal plume. Geochim. Cosmochim. Acta 69:933-952 [doi:10.1016/j.gca.2004.07.034].

Bruland, K. W., R. P. Franks, G. A. Knauer, and J. H. Martin. 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. Anal. Chim. Acta 105:233-245 [doi:10.1016/S0003-2670(01)83754-5].

———, K. H. Coale, and L. Mart. 1985. Analysis of seawater for dissolved cadmium, copper and lead: an intercomparison of voltammetric and atomic absorption methods. Mar. Chem. 17:285-300 [doi:10.1016/0304-4203(85)90002-7].

———, K. J. Orians, and J. P. Cowen. 1994. Reactive trace metals in the stratified central North Pacific. Geochim. Comsmochim. Acta 58:3171-3182. [doi:10.10160016/7037(94)90044-2].

———, and M. C. Lohan. 2004. Controls of trace metals in seawater, p. 23-47. *In* H. D. Holland and K. K. Turekian [eds.], The oceans and marine geochemistry, vol. 6. Elsevier-Pergamon.

———. 2011. GEOTRACES: Standard and reference materials. <http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials>

Colbert, D., K. S. Johnson, and K. H. Coale. 1998. Determination of cadmium in seawater using automated on-line preconcentration and direct injection graphite furnace atomic absorption spectrometry. Anal. Chim. Acta 377:255-262 [doi:10.1016/S0003-2670(98)00428-0].

Doner, G., and A. Ege. 2005. Determination of copper, cadmium and lead in seawater and mineral water by flame atomic absorption spectrometry after coprecipitation with aluminum hydroxide. Anal. Chim. Acta 547:14-17 [doi:10.1016/j.aca.2005.02.073].

Flegal, A. R., and C. C. Patterson. 1983. Vertical concentration profiles of lead in the Central Pacific at 15°N and 20°S. Earth Planet. Sci. Lett. 64:19-32 [doi:10.1016/0012-821X(83)90049-3].

———, K. Itoh, C. C. Patterson, and C. S. Wong. 1986. Vertical profile of lead isotopic compositions in the north-east Pacific. Nature 321:689-690 [doi:10.1038/321689a0].

Gallon, C., M. A. Ranville, C. H. Conaway, W. M. Landing, C. S. Buck, P. L. Morton, and A. R. Flegal. 2011. Asian industrial lead inputs to the north pacific evidenced by lead concentrations and isotopic compositions in surface waters and aerosols. Environ. Sci. Technol. 45:9874-9882 [doi:10.1021/es2020428].

Johnson, K. S., and others. 2007. Developing standards for dissolved iron in seawater. EOS Trans. 88:131-132 [doi:10.1029/2007EO110003].

Landing, W. M., and others. 1995. Analytical intercomparison results from the 1990 Intergovernmental Oceanographic Commission Open-Ocean Baseline Survey for Trace Metals: Atlantic Ocean. Mar. Chem. 49:253-265 [doi:10.1016/0304-4203(95)00016-K].

Lee, J. M., E. A. Boyle, Y. Echegoyen-Sanz, J. N. Fitzsimmons, R. Zhang, and R. A. Kayser. 2011. Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. Anal. Chim. Acta 686:93-101 [doi:10.1016/j.aca.2010.11.052].

Measures, C. I., G. A. Cutter, W. M. Landing, and R. T. Powell. 2006. Hydrographic observations during the 2002 IOC Contaminant Baseline Survey in the western Pacific Ocean. Geochem. Geophys. Geosyst. 7:Q03M06 [doi:10.1029/2004

GC000855].

Milne, A., W. M. Landing, M. Bizimis, and P. Morton. 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Anal. Chim. Acta 665:200-207 [doi:10.1016/j.aca.2010.03.027].

Ndung'u, K., J. R. Donat, M. Thomas, J. A. Consolvo, and A. R. Flegal. 2001. Intercalibrated lead concentration measurements in the Atlantic Ocean. Deep-Sea Res. II 48:2781-2786 [doi:10.1016/S0967-0645(01)00017-0].

———, R. P. Franks, K.W. Bruland, and A.R. Flegal. 2003. Organic complexation and total dissolved trace metal analysis in estuarine waters: comparison of solvent-extraction graphite furnace atomic absorption spectrometric and chelating resin flow injection inductively coupled plasma-mass spectrometric analysis. Anal. Chim. Acta 481:127-138 [doi:10.1016/S0003-2670(03)00063-1].

Ranville, M. A., and A. R. Flegal. 2005. Silver in the North Pacific Ocean. Geochem. Geophys. Geosyst. 6:Q03M01. [doi:10.1029/2004GC000770].

———, G. A. Cutter, C. S. Buck, W. M. Landing, L. S. Cutter, J. A. Resing, and A. R. Flegal. 2010. Aeolian contamination of Se and Ag in the North Pacific from Asian fossil fuel combustion. Environ. Sci. Technol. 44:1587-1593 [doi:10.1021/es902523m].

Shiller, A. M., and G. R. Bairamadgi. 2006. Dissolved gallium in the Northwest Pacific and the South and Central Atlantic Oceans: Implications for aeolian Fe input and a reconsideration of profiles. Geochem. Geophys. Geosyst. 7:Q08M09 [doi:10.1029/2005GC001118].

Wu, J., and E. A. Boyle. 1997. Low blank preconcentration technique for the determination of lead, copper and cadmium in small-volume seawater samples by isotope dilution ICPMS. Anal. Chem. 69:2464-2470 [doi:10.1021/ac961204u].

———, R. Rember, M. Jin, E. A. Boyle, and A. R. Flegal. 2010. Isotopic evidence for the source of lead in the North Pacific abyssal water. Geochim. Cosmochim. Acta 74:4629-4638 [doi:10.1016/j.gca.2010.05.017].

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