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## Asian Industrial Lead Inputs to the North Pacific Evidenced by Lead Concentrations and Isotopic Compositions in Surface Waters and Aerosols

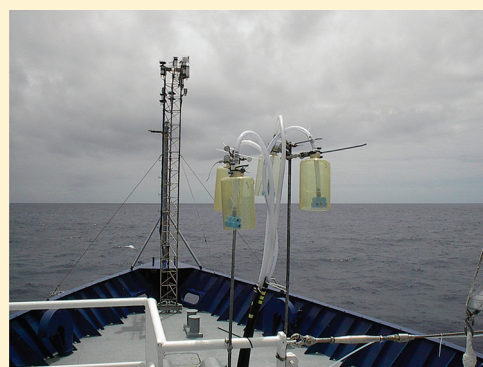
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**ABSTRACT:** Recent trends of atmospheric lead deposition to the North Pacific were investigated with analyses of lead in aerosols and surface waters collected on the fourth Intergovernmental Oceanographic Commission Contaminant Baseline Survey from May to June, 2002. Lead concentrations of the aerosols varied by 2 orders of magnitude ( $0.1\text{--}26.4\text{ pmol/m}^3$ ) due in part to variations in dust deposition during the cruise. The ranges in lead aerosol enrichment factors relative to iron (1–119) and aluminum (3–168) were similar, evidencing the transport of Asian industrial lead aerosols across the North Pacific. The oceanic deposition of some of those aerosols was substantiated by the gradient of lead concentrations of North Pacific waters, which varied 3-fold ( $32.7\text{--}103.5\text{ pmol/kg}$ ), were highest along with the Asian margin of the basin, and decreased eastward. The hypothesized predominance of Asian industrial lead inputs to the North Pacific was further corroborated by the lead isotopic composition of ocean surface waters ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.157\text{--}1.169$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.093\text{--}2.118$ ), which fell within the range of isotopic ratios reported in Asian aerosols that are primarily attributed to Chinese industrial lead emissions.



### INTRODUCTION

The distribution of lead in ocean surface waters in the preceding century was dominated by atmospheric inputs of industrial aerosols, including those from smelting, coal combustion, and leaded gasoline emissions. The latter emissions, which accounted for the majority of those inputs, peaked in the late 1970s and early 1980s.<sup>1,2</sup> After that, the nearly global phase-out of leaded gasoline resulted in a decrease in lead concentrations in North Atlantic surface waters<sup>3</sup> and a corresponding shift in their isotopic composition.<sup>4</sup>

Unfortunately, there has been no corresponding documentation of the impact of the virtual elimination of leaded gasoline on lead concentrations in the North Pacific because there have been very few measurements of lead concentrations, much less lead isotopic compositions, of those waters. For example, lead isotopic compositions have only been measured in two deep vertical profiles in the eastern North Pacific<sup>5,6</sup> and one shallow vertical profile in the California coastal current system.<sup>7</sup> Two of those three data sets are over 20 years old.<sup>5,7</sup>

Moreover, quite a bit has changed since most of the studies on lead in the North Pacific were conducted, including the virtual elimination of leaded gasoline in the US in 1991<sup>8</sup> and China in 2000.<sup>9</sup> As a consequence, coal combustion has become the principal source of eolian lead in China,<sup>10–13</sup> which is now the

world's largest coal consumer.<sup>14</sup> In addition to adversely impacting the air quality in China,<sup>15</sup> its industrial lead aerosols have been observed in Korea,<sup>16</sup> Taiwan,<sup>17</sup> and Japan,<sup>18,19</sup> and it has been proposed that Asian emissions of industrial lead from fossil fuel combustion are now impacting atmospheric lead concentrations in the United States<sup>20–22</sup> and Canada.<sup>23</sup> Consequently, we hypothesized that Asian industrial emissions have also measurably impacted lead levels in North Pacific surface waters, which have recently been found to have elevated levels of other metals associated with Asian fossil fuel combustion.<sup>24</sup>

Here, we present measurements of lead isotopic compositions, along with corresponding lead concentrations, of surface waters in the western and central North Pacific that were collected on the 2002 Intergovernmental Oceanographic Commission Contaminant Baseline Survey (IOC-IV), whose overall purpose was to investigate the effects of the Asian dust deposition on the chemical composition of the North Pacific Ocean.<sup>25</sup> In addition to measurements in seawater, we made complementary analysis of lead concentrations in aerosols that were collected concurrently

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during that survey. These samples, although representing ephemeral atmospheric conditions, provide information on the composition and source of atmospheric depositions to the North Pacific. Together, the two data sets support our hypothesis that lead fluxes to North Pacific surface waters are now predominantly eolian inputs from coal combustion in China.

## EXPERIMENTAL SECTION

Concurrent aerosol and surface water samples were collected across the northwest Pacific during the fourth Intergovernmental Oceanographic Commission Contaminant Baseline Survey (IOC-IV), from May 1 to June 3, 2002. The cruise transect (~15,000 km in length) extended northeast from Osaka Bay, Japan across the Kuroshio Current, into the subarctic Pacific – a high-nutrient low-chlorophyll (HNLC) region, then south and east into the North Pacific Subtropical Gyre.<sup>25</sup>

**Atmospheric Sampling and Analysis.** Aerosol (>0.4  $\mu\text{m}$ ) samples (average of 15 m<sup>3</sup> of filtered air) were collected for approximately 10 h with the aerosol sampling system and protocols detailed by Buck et al.<sup>26</sup> The filters were kept intact for the initial measurements of aluminum and iron by energy-dispersive X-ray fluorescence (EDXRF) at the National Oceanic and Atmospheric Administration Pacific Marine Environmental Laboratory, as described elsewhere.<sup>26</sup> The filters were then digested at the University of California-Santa Cruz (UCSC) with ultrapure (Optima grade, Fisher Scientific), concentrated (10:1) HNO<sub>3</sub> and HClO<sub>4</sub>, which dissolved all of the particulate lead except for a small fraction of lead sequestered in refractory aluminosilicate minerals. The digests were evaporated to near-dryness, the digestion was repeated, and the samples then dissolved up in 1.5 M ultrapure HNO<sub>3</sub> for lead concentration measurements. Those were made with a magnetic-sector high-resolution inductively coupled plasma mass spectrometer (HR ICP-MS; Finnigan Element) at UCSC using a rhenium spike as an internal standard. All lead data were corrected for field and procedural blanks that were processed and analyzed concurrently. Precision, calculated as the % relative standard deviation of replicate analyses ( $n = 6$ ) of a mid-range standard, was <2%.

**Surface Water Sampling and Analysis.** Utilizing a modified bathythermograph or “fish” towed from a boom extended about 8 m from the port aft quarter of the research vessel, unfiltered North Pacific surface waters were obtained from outside the ship’s wake. Water was pumped from the “fish” through Teflon tubing into an onboard trace metal clean laboratory under HEPA (Class 100) filtered air. All samples were collected in acid-cleaned 2 L low-density polyethylene (LPDE) bottles using trace metal clean techniques<sup>27</sup> and transported back to UCSC, where they were acidified to <pH 2 with ultrapure HCl in a HEPA (Class 100) filtered air, trace metal clean laboratory.

Lead concentrations in seawater were measured by HR-ICP-MS at UCSC, after the water was concentrated online, using chelating resin flow injection.<sup>28</sup> Procedural blanks for lead were <6 pmol/kg, precision was <5%, and detection limits were <5 pmol/kg. A recent intercalibration of dissolved lead concentration measurements in seawater was conducted by Zurbrück et al.<sup>29</sup> Replicate samples from the IOC-IV cruise were reanalyzed by UCSC, Florida State University, and by Alan Shiller at the University of Southern Mississippi using a variety of techniques. The analytical agreement between all three laboratories was averaged  $\pm 2\%$  from the mean values on samples ranging from 20 to 130 pM of lead.

Lead isotopic composition measurements (<sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb) of the seawater samples were made by HR-ICP-MS using established procedures<sup>30</sup> after they were concentrated offline.<sup>31</sup> Instrument dead time was monitored during every session and corrected accordingly. Depending on the original lead concentration in the sample, 0.1 to 1 L of seawater was extracted using an ion-exchange resin and recovered in 1 mL of 1.5 N ultrapure quartz-distilled HNO<sub>3</sub> (spiked with 2 nmol/kg of thallium) to a final lead concentration of ~3–16 nmol/kg. Procedural blanks were <0.6 pmol/kg of lead. Measured isotopic ratios were corrected for mass bias using thallium additions according to an exponential function (<sup>205</sup>Tl/<sup>203</sup>Tl = 2.388). Counts of <sup>204</sup>Pb were corrected for isobaric interferences from <sup>204</sup>Hg by monitoring <sup>202</sup>Hg and assuming natural abundances of mercury isotopes (<sup>204</sup>Hg/<sup>202</sup>Hg = 0.2298). Analyses were calibrated with concurrent measurements of NIST SRM 981 Natural Lead (Isotopic). Replicate analyses of the samples ( $n = 2$  to 4) produced data within  $\leq 1$  permil of the average value for <sup>206</sup>Pb/<sup>207</sup>Pb, <sup>208</sup>Pb/<sup>206</sup>Pb, and <sup>206</sup>Pb/<sup>204</sup>Pb. Multiple analyses of the GEOTRACES intercalibration seawater material GDI ( $n = 4$ ) provided standard errors ( $2\sigma$ ) of 0.7 permil for <sup>206</sup>Pb/<sup>207</sup>Pb, 3.1 permil for <sup>208</sup>Pb/<sup>206</sup>Pb, and 30 permil for <sup>206</sup>Pb/<sup>204</sup>Pb. In addition, intercalibration of two seawater samples (GEOTRACES intercalibration materials GSI and GDI) using this setup showed that isotopic composition data were within  $\leq 3$  permil,  $\leq 2$  permil, and  $\leq 11$  permil for <sup>206</sup>Pb/<sup>207</sup>Pb, <sup>208</sup>Pb/<sup>206</sup>Pb, and <sup>206</sup>Pb/<sup>204</sup>Pb, respectively of those measured at MIT.<sup>32</sup>

## RESULTS AND DISCUSSION

**Lead Concentrations of Aerosols.** Concentrations of lead in the aerosols varied by 2 orders of magnitude (0.1–26.4 pmol/m<sup>3</sup>) over the course of the cruise (Table 1). These values were within the range or lower than those (1–40 pmol/m<sup>3</sup>) observed in the autumn of 2002 on a transect in the Pacific Ocean from 125°E–132°E and 26°N–29°N.<sup>33</sup> They were also substantially lower than those in recent reports on lead levels in aerosols collected in mainland China (97–2970 pmol/m<sup>3</sup>)<sup>34,35</sup> and over the China Sea (26–628 pmol/m<sup>3</sup>).<sup>33</sup>

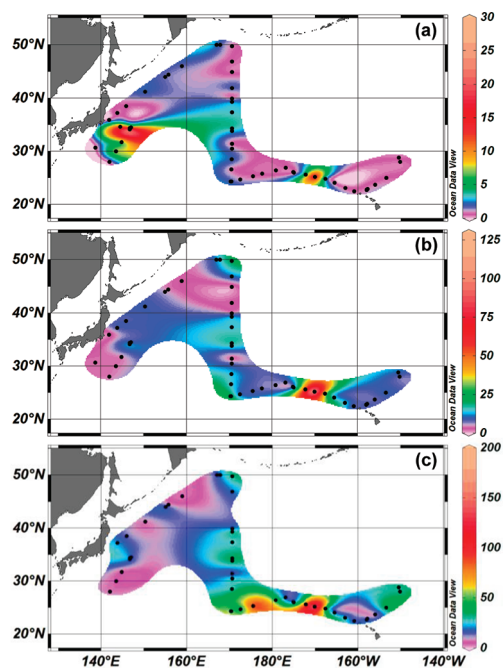
The aerosol lead concentrations corresponded, in part, with variations in dust deposition during the course of the cruise. Those included four periods of distinctly elevated dust levels as reported by Buck et al.,<sup>26</sup> which were characterized by 5-day back-trajectories calculated with The HYbrid Single-Particle Lagrangian Integrated trajectory Model (HYSPLIT, FNL data set).<sup>36,37</sup> (1) The first dust event, recorded as the ship moved from the southeast of Japan toward the northeast at latitudes 29°N, 141°E to 34°N, 147°E, was traced to an air mass that traveled over China, Mongolia, and northern Japan. This event correlated with elevated lead aerosol concentrations, including the highest value (26 pmol/m<sup>3</sup>) measured in the survey. (2) The second dust event, observed from 44°N, 155°E to 50°N, 167°E, corresponded with an increase in lead concentrations up to 2.9 pmol/m<sup>3</sup> and was traced to air masses that passed over Russia and Japan. (3) The third dust event, which occurred while the ship transited from 41°N, 170°E to 34°N, 170°E, brought air masses that had been over the ocean for most of the 5-day period prior to sampling. Aerosol lead concentrations increased up to 3.8 pmol/m<sup>3</sup> during that period, and our data show they increased until the ship reached 24°N a few days after that. (4) The fourth dust event, which occurred northwest of the Hawaiian Islands at 24°N, 158°W,<sup>26</sup> was characterized by relatively small iron and

Table 1. Lead Concentrations and Enrichment Factors in Aerosols<sup>c</sup>

start latitude (°N)	start longitude (°E)	date (UTC)	start time (UTC)	Pb (pmol/m <sup>3</sup> )	EF <sub>Al</sub> (UCC) <sup>a</sup>	EF <sub>Fe</sub> (UCC) <sup>a</sup>	EF <sub>Al</sub> (Loess) <sup>b</sup>	EF <sub>Fe</sub> (Loess) <sup>b</sup>
30.65	138.68	5/2/2002	22:06	0.1	-	4	-	4
28.02	142.02	5/3/2002	21:12	0.7	7	4	5	3
29.98	143.49	5/4/2002	11:04	7.9	6	4	4	4
31.69	144.78	5/4/2002	21:14	5.2	5	4	4	4
34.13	146.67	5/5/2002	11:31	26.4	17	13	13	11
34.46	147.02	5/5/2002	20:57	5.3	7	5	5	4
34.44	146.69	5/6/2002	11:13	8.5	34	14	27	13
34.59	144.50	5/6/2002	21:01	12	-	-	-	-
35.88	141.85	5/8/2002	11:06	0.1	-	1	-	1
37.17	143.83	5/9/2002	21:21	1.2	21	9	17	8
38.49	145.90	5/9/2002	11:02	0.6	13	8	10	7
41.23	150.33	5/10/2002	11:04	2.1	7	9	6	8
44.00	155.00	5/13/2002	11:48	1.5	19	6	15	5
44.38	155.73	5/13/2002	20:20	1.5	6	4	5	4
46.02	158.89	5/13/2002	10:16	1.6	3	3	3	2
50.00	167.00	5/15/2002	20:05	2.9	13	10	10	9
50.00	167.76	5/15/2002	9:56	1.4	22	15	17	14
49.76	170.58	5/16/2002	20:03	0.9	31	21	25	20
46.94	170.58	5/16/2002	10:07	0.5	19	11	14	10
44.90	170.58	5/17/2002	20:09	0.3	-	1	-	1
41.88	170.58	5/17/2002	10:21	1.9	-	3	-	2
39.29	170.57	5/18/2002	10:24	3	32	14	25	12
39.85	170.58	5/18/2002	20:01	0.3	18	3	14	3
37.31	170.58	5/19/2002	20:06	3.1	25	14	19	13
34.33	170.58	5/19/2002	10:02	3.8	34	17	26	16
33.77	170.57	5/20/2002	20:58	2.9	36	16	28	15
31.37	170.58	5/20/2002	10:01	0.5	13	2	10	2
30.50	170.58	5/21/2002	21:46	1.4	27	8	21	7
28.47	170.50	5/21/2002	10:51	2.2	28	14	22	13
26.59	170.42	5/22/2002	20:14	0.8	-	15	-	14
24.25	170.33	5/22/2002	10:05	2.3	40	23	31	21
24.25	170.33	5/23/2002	20:08	2.7	85	34	66	31
24.27	170.42	5/23/2002	9:49	0.7	35	10	27	9
24.70	172.47	5/24/2002	19:16	1.1	33	9	26	8
25.33	175.45	5/24/2002	9:15	0.8	92	9	72	9
25.78	177.62	5/25/2002	18:57	0.4	-	7	-	6
26.44	-179.19	5/25/2002	8:59	0.4	48	7	37	6
26.92	-176.89	5/26/2002	19:00	0.6	17	8	14	7
26.06	-175.10	5/26/2002	9:05	0.5	25	9	20	8
26.00	-175.00	5/26/2002	19:07	0.4	12	6	9	5
25.60	-172.24	5/26/2002	8:12	3.4	67	47	53	43
25.19	-170.12	5/27/2002	18:22	17.6	168	119	131	108
24.76	-167.55	5/27/2002	8:03	1.2	31	25	24	23
24.07	-165.54	5/28/2002	18:03	0.7	18	15	14	14
23.13	-162.98	5/28/2002	7:59	0.7	27	16	21	14
22.74	-158.03	5/29/2002	7:56	0.8	21	9	17	8
22.48	-160.88	5/29/2002	18:10	0.7	13	7	10	7
22.75	-158.00	5/30/2002	18:05	1.1	15	9	12	9
22.87	-157.76	5/30/2002	8:01	0.9	10	7	8	6
23.74	-155.96	5/31/2002	17:05	0.9	7	7	6	6
24.95	-153.44	5/31/2002	7:06	0.6	39	10	30	9
27.99	-150.15	6/1/2002	7:14	0.3	30	7	24	7
28.84	-150.45	6/2/2002	17:04	0.8	32	11	25	10

<sup>a</sup>Reference Upper Continental Crust (UCC) values:<sup>40</sup> Al = 8.04 wt %; Fe = 3.50 wt %; Pb = 20 ppm. <sup>b</sup>Reference Loess values:<sup>48</sup> Al = 6.60 wt %; Fe = 3.34 wt %; Pb = 21 ppm. <sup>c</sup>Dashes indicate samples for which data were either below detection limit or not determined.





**Figure 1.** (a) Lead concentrations ( $\text{pmol}/\text{m}^3$ ) and (b) enrichment factors relative to Al and (c) relative to Fe in aerosols collected during the IOC-IV cruise. Sampling locations are shown as small black dots on both images.

aluminum concentrations compared to the three other dust events and also had a relatively low maximum lead concentration ( $1.1 \text{ pmol}/\text{m}^3$ ) at  $23^\circ\text{N}$ ,  $158^\circ\text{W}$ .

We found two additional occurrences of relatively high lead concentrations. (1) The first, which occurred at  $24^\circ\text{N}$ ,  $170^\circ\text{W}$ , was relatively small ( $\leq 2.7 \text{ pmol}/\text{m}^3$ ). (2) The second, which occurred at  $25^\circ\text{N}$ ,  $170^\circ\text{W}$ , was anomalously high with an abrupt increase in aerosol lead concentrations to  $17.6 \text{ pmol}/\text{m}^3$ . It is not possible to conclusively determine the origin of these lead enriched air masses using 5-day air mass back trajectories, but Asian aerosols may cross the North Pacific within 6–10 days<sup>38</sup> and become entrained in the trade winds and advected back across the North Pacific,<sup>39</sup> as indicated by the following discussion of the lead isotopic composition of those aerosols.

**Lead Enrichment Factors of Aerosols.** We calculated lead enrichment factors (EF) relative to iron ( $[\text{Pb}]/[\text{Fe}]_{\text{sample}}/[\text{Pb}]/[\text{Fe}]_{\text{crust}}$ ) in mole:mole and aluminum ( $[\text{Pb}]/[\text{Al}]_{\text{sample}}/[\text{Pb}]/[\text{Al}]_{\text{crust}}$ ) of the aerosols in order to evaluate the importance of anthropogenic lead inputs in the aerosols. Both of these metals are useful tracers of mineral dust inputs because they are present in the upper continental crust at relatively constant concentrations of about 8% and 3.5%, respectively.<sup>40</sup> An EF close to 1 indicates lead of predominantly crustal origin (i.e., delivered with soil materials), while an EF  $> 5$ –10 indicates anthropogenic sources.<sup>41</sup>

The lead EF values of the aerosols relative to the average upper continental crust composition ranged from 1 to 119, when normalized to iron, and from 3 to 168, when normalized to aluminum (Table 1). Because it can be assumed that most of the natural lead in those aerosols was from Asian dust, we also calculated EFs relative to the elemental composition of this dust. While there is some debate on the sources of Asian dust,<sup>42–45</sup> Chinese Loess plateau, which have the most extensive soil erosion in the world, are a generally accepted and well-characterized source;<sup>46–48</sup>

therefore, we used the elemental composition of this plateau for our calculations. The reference values used for our calculations ( $\text{Al} = 6.6\%$ ;  $\text{Fe} = 3.3\%$ ;  $\text{Pb} = 21 \text{ ppm}$ )<sup>48</sup> are on the lower end of those reported in the literature for aluminum (6.5–8%) and iron (3.4–3.6%) and on higher end for lead (10–20 ppm).<sup>46–48</sup> Consequently, the EF values calculated here are conservatively low estimates of the anthropogenic contributions to the aerosols sampled during the cruise. Those EFs ranged from 1 to 108, when normalized to iron, and from 3 to 131, when normalized to aluminum (Table 1). Therefore, when the lead EFs of the aerosols were normalized to either iron or aluminum concentrations in either their average crustal abundance or Chinese Loess Plateau concentrations, the majority ( $>75\%$ ) of the aerosols had EF values  $>5$ —attesting to the predominance of industrial lead in those aerosols.

It is notable that the aerosols collected during the first dust event that was closest to Asia had the highest lead concentrations ( $0.7$ – $26.4 \text{ pmol}/\text{m}^3$ ) but relatively low EFs (3–17), while aerosols in the central North Pacific had lower lead concentrations but greater EF (Figure 1). These differences in aerosol composition and character can be explained by either mixing of dissimilar sources along the Asian mainland or particle-size sorting during transport. The higher lead concentrations but lower EF along the Asian mainland may be due to the mixing of industrial (Pb-rich) aerosols with weathered crustal material from Chinese desert areas and Loess Plateau that are seasonally introduced into the atmosphere during Kosa events between March and May.<sup>39</sup> While industrial sources of aerosols such as coal plants emit aerosols continuously throughout the year, mineral dust events are episodic. The high lead values ( $17.6 \text{ pmol}/\text{m}^3$ ) and highest enrichment factors (EF = 108–168) observed in the central North Pacific near Hawaii (Figure 1; Table 1) could reflect a mix of air masses that received relatively lower inputs of mineral dust with respect to industrial inputs.

However, since industrial aerosols are found predominantly in the fine particle-size fractions, and the fine fraction might reasonably be predicted to be transported further than coarse (lithogenic) particles, the aerosols found in the central North Pacific could also result from preferential removal of mineral dust (coarse-particle) during transport. Size-fractionated studies of aerosol particles conducted during the IOC IV cruise show that the first major dust event closest to the Asian mainland (May 4–6) showed a maximum in both coarse ( $>2.5 \mu\text{m}$ ) and fine ( $<2.5 \mu\text{m}$ ) size-fractions but was dominated by coarse particles (Mitsuo Uematsu, personal communication) and coincided with the highest concentrations of aerosol Al.<sup>26</sup> However, coarse particle-size fractions fell sharply and remained low in all samples collected east of  $170^\circ\text{E}$ , even when elevated aerosol lead concentrations were observed in the central North Pacific (May 27). While this evidence is not conclusive, it does support the idea that coarser mineral dust particles are preferentially removed during transport compared with fine anthropogenic dust particles, resulting in similarly high aerosol lead concentrations but greater lead EF.

**Lead Concentrations of Surface Waters.** Lead levels in the surface waters ranged from  $32.7$  to  $103.5 \text{ pmol}/\text{kg}$  (Table 2). Since the residence time ( $\sim 2$  years) of lead in those waters is relatively short,<sup>1,54</sup> we were surprised that those levels were so similar to those ( $12$ – $66 \text{ pmol}/\text{kg}$ ) previously measured in the central and eastern regions of the North Pacific over the last three decades<sup>1,2,5,6,55,56</sup>—including the period when leaded gasoline additives were still being used extensively in both North America

Table 2. Lead Concentrations and Isotopic Compositions in Surface Seawaters<sup>c</sup>

latitude (°N)	longitude (°E)	date (UTC)	Pb (pmol/kg)	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>208</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb
28.25	142.19	5/4/2002	90.37	1.161	2.118	18.19
34.28	146.50	5/5/2002	103.48	1.165	2.107	18.16
38.27	145.56	5/9/2002	70.47	1.157	2.115	18.03
41.11	150.14	5/10/2002	89.19	1.161	2.108	18.06
44.00 <sup>a</sup>	155.00	5/11/2002	72.36	1.157	2.114	17.97
45.88	158.61	5/13/2002	75.30	-	-	-
48.70	164.29	5/14/2002	58.00	-	-	-
50.00	167.00	5/14/2002	55.81	1.162	2.099	18.02
49.54	170.58	5/17/2002	84.06	-	-	-
42.09	170.58	5/17/2002	86.78	-	-	-
39.22	170.35	5/17/2002	87.18	1.160	2.109	18.02
37.10	170.58	5/18/2002	87.83	-	-	-
33.46	170.35	5/19/2002	103.52	1.163	2.105	18.20
30.30	170.35	5/20/2002	84.14	1.162	2.106	18.17
28.85	170.51	5/21/2002	57.29	-	-	-
24.15	170.20	5/22/2002	45.00	1.163	2.104	18.16
25.27	175.20	5/24/2002	44.63	1.166	2.099	18.18
26.40	-179.40	5/25/2002	43.46	1.164	2.102	18.12
26.00	-175.00	5/26/2002	47.42	1.164	2.103	18.21
25.67	-172.52	5/27/2002	40.21	-	-	-
23.99	-165.33	5/28/2002	37.64	1.169	2.095	18.23
23.18	-163.15	5/29/2002	32.70	1.167	2.096	18.14
22.45 <sup>b</sup>	-158.00	5/30/2002	32.84	1.166	2.093	18.19
24.86	-153.63	6/1/2002	42.82	-	-	-
27.73	-150.14	6/2/2002	48.49	-	-	-
26.65	-152.06	6/3/2002	59.78	1.164	2.103	18.10
24.56	-153.56	6/3/2002	44.98	1.165	2.099	18.21

<sup>a</sup> KNOT time-station. <sup>b</sup> HOT-ALOHA time-station. <sup>c</sup> Dashes indicate samples that were not analyzed for lead isotopes.

and Asia. For example, the lead concentration of 32.8 pmol/kg at the HOT-ALOHA station (22°N, 148°W) is statistically indistinguishable from the average ( $30.5 \pm 3.1$  pmol/kg) of measurements at that site in 1997–1999.<sup>55</sup> In contrast, the lead levels of our oceanic surface waters are consistently lower than the concentrations (~200–2200 pmol/kg) of dissolved lead measured in the East China Sea.<sup>57</sup> These values, the highest ever reported in the marginal seas and oceanic waters, were attributed by the authors to aeolian inputs of industrial lead from the adjacent Chinese mainland.<sup>57</sup>

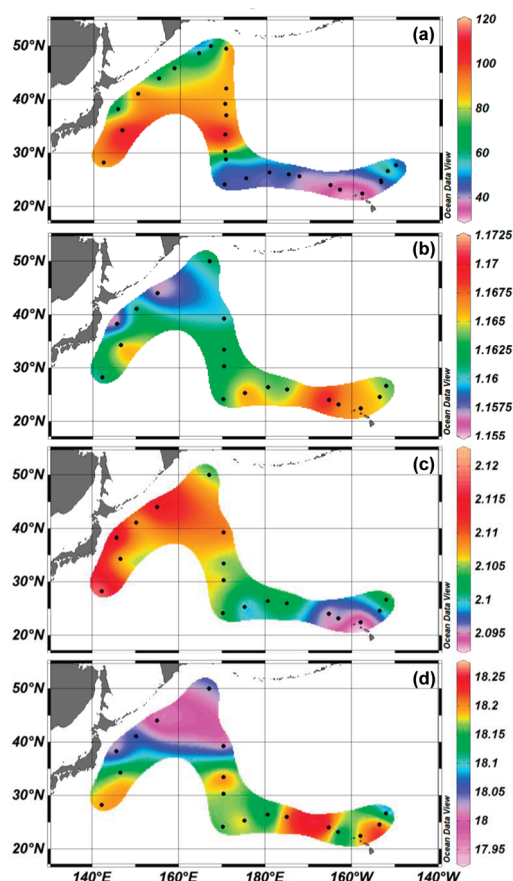
Their proposal that Chinese industrial aerosols accounted for the anomalously high levels of lead in the East China Sea is concordant with the spatial distribution of lead concentrations in our IOC-IV surface seawater, with relatively high values in near shore waters and relatively low values in the most oceanic waters (Figure 2). It is also consistent with the relatively low lead concentrations around 50°N, in the HNLC region of the Western Subarctic Gyre, because that more northerly location is less impacted by Asian industrial aerosols. In addition, the distribution of lead concentrations of those IOC-IV surface water samples parallels that of silver concentrations of aliquots of those samples that were attributed to aeolian fluxes of Asian industrial aerosols associated with high-temperature industrial emissions such as coal combustion and metal smelting.<sup>58</sup>

The aerosol and surface water lead concentrations show some spatial similarities, and there is a loose correlation ( $R^2 = 0.31$ ,  $p < 0.05$ , simple linear regression,  $n = 18$ ) between the two at locations

where they were both collected. That relatively limited correlation is not surprising to us, because the atmospheric residence time (hours to weeks) of lead<sup>59</sup> is short compared to its residence time (~2 years) in those waters.<sup>1,54</sup> Consequently, the surface water concentrations represent an integration and smoothing of short-term variations of atmospheric depositions to the ocean.

**Lead Isotopic Composition in Surface Waters.** Lead isotopic ratios of the surface waters, which varied from 1.157 to 1.169 for <sup>206</sup>Pb/<sup>207</sup>Pb and from 2.093 to 2.118 for <sup>208</sup>Pb/<sup>206</sup>Pb (Table 2), are quite similar to other recent measurements of lead isotopic compositions in the North Pacific. For example, isotopic ratios (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.1603; <sup>208</sup>Pb/<sup>206</sup>Pb = 2.109) of corals collected near Ogasawara Island (27.13°N, 142.20°E) between 1995 and 2001<sup>60</sup> are close to those (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.161; <sup>208</sup>Pb/<sup>206</sup>Pb = 2.118) of surface water we collected near that island (28.25°N, 142.19°E). Similarly, the isotopic ratios (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.157; <sup>208</sup>Pb/<sup>206</sup>Pb = 2.114) of surface waters collected at KNOT (44°N, 155°E) are very close to those (<sup>206</sup>Pb/<sup>207</sup>Pb =  $1.163 \pm 0.001$ ; <sup>208</sup>Pb/<sup>206</sup>Pb =  $2.116 \pm 0.002$ ) that Nagaoka et al.<sup>51</sup> measured in settling particles (770 m) at that station in 2005–2007. In addition, the range of isotopic compositions of surface waters reported by Wu et al.<sup>6</sup> for samples collected along a more eastward transect in 2004 are within the range of our samples.

Lead isotopic ratios of those waters — like their lead concentrations — exhibit spatial variations: <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb ratios increase and <sup>208</sup>Pb/<sup>206</sup>Pb ratios decrease eastward (Figure 2;

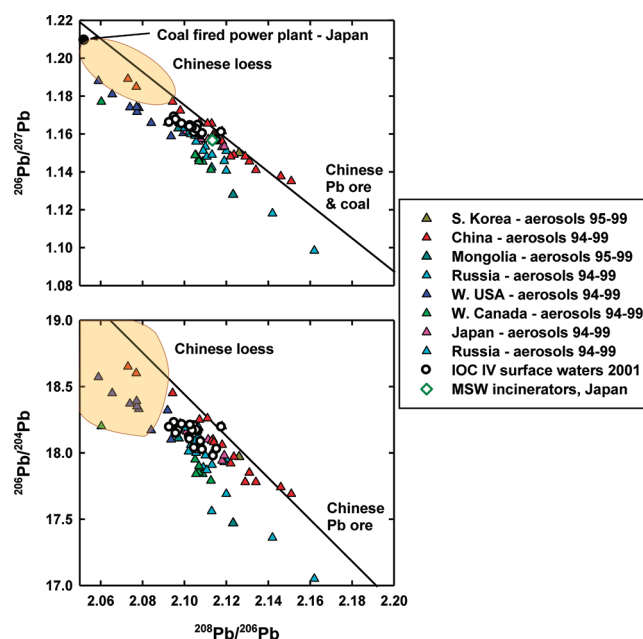


**Figure 2.** (a) Lead concentrations (pmol/kg) and lead isotopic compositions (b)  $^{206}\text{Pb}/^{207}\text{Pb}$ , (c)  $^{208}\text{Pb}/^{206}\text{Pb}$ , and (d)  $^{206}\text{Pb}/^{204}\text{Pb}$  in surface waters collected during the IOC-IV cruise. Sampling locations are shown as small black dots on both images.

Table 2). The gradients are also consistent with those reported by Inoue and Tanimizu,<sup>60</sup> who found higher lead concentrations and isotopic signatures typical of Chinese lead in corals from coastal areas (Hainan and Hong Kong) compared to those of corals further offshore (Ogasawara) in the North Pacific.

The predominantly Asian origin of lead in North Pacific surface waters is further evidenced by plots of the lead isotopic composition ( $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$ ;  $^{206}\text{Pb}/^{204}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$ ) of surface waters sampled during the IOC-IV cruise and those of industrial lead aerosols from circum-Pacific countries (Figure 3). The marked variability of  $^{206}\text{Pb}/^{207}\text{Pb}$ : $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ : $^{208}\text{Pb}/^{206}\text{Pb}$  ratios in different countries reflect differences in the ratios in their lead ores, fossil fuels, and leaded gasoline additives.<sup>20,61,62</sup> Because these isotopic signatures may have changed substantially with time due to changes in human activities and policies (e.g., bans on leaded gasoline, changes in imports, and controls on emissions),<sup>9</sup> we limited our comparison to recent data in the literature.

While the comparison of isotopic ratios is far from definitive, it shows that the lead isotopic compositions of the surface waters sampled are within the range of isotopic ratios measured in Chinese, Japanese, Korean, and to a lesser extent Russian and Mongolian aerosols (Figure 3). In contrast, the seawater ratios are distinct from US and Canadian isotopic signatures. The seawater ratios are also different from those of Chinese Loess,<sup>47,63</sup> even though mineral dust from Chinese plateau is



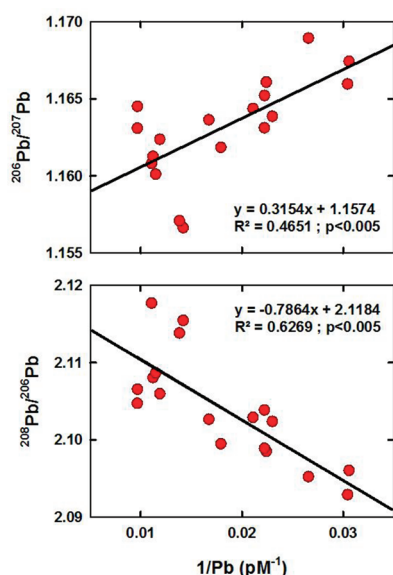
**Figure 3.**  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$  in IOC-IV surface waters in relationship with literature data.<sup>9,13,19,20,47,62,63,65,79,80</sup> The Chinese lead ore and coal lines were obtained from the linear regression ( $R^2 = 0.964\text{--}0.972$ ;  $p < 0.005$ ) of data from Cheng and Hu<sup>9</sup> and references therein.<sup>12,81,82</sup> Chinese Loess domains (yellow shaded area) were extrapolated from literature data for bulk and leachate fractions.<sup>47,63,80</sup>

commonly found in the atmosphere over the North Pacific during the spring.<sup>39</sup>

It is assumed that industrial lead emissions from Japan, which is closest to the IOC-IV transect (excluding the US state of Hawaii), contribute to the lead levels of surface waters collected on the transect. Since Japan started using unleaded gasoline in the mid-1970s and banned leaded gasoline in 1985,<sup>12</sup> most of industrial lead in the urban atmosphere of Japan now originates from the incineration of municipal solid waste (MSW),<sup>12,64</sup> and the isotopic composition of Japanese MSW fly ash<sup>64</sup> is within the range of surface waters collected near the Japanese coast ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.157 \pm 0.003$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.113 \pm 0.007$ , Figure 3).<sup>65</sup> However, the amount ( $\sim 46$  t Pb/yr) of lead released from Japanese MSW combustion is so small compared to other Asian industrial lead emissions (see below) that the impact of those emissions on lead concentrations in most of the North Pacific is considered to be minimal.<sup>51</sup> In addition, lead isotopic compositions of the IOC-IV surface waters are clearly distinct from the typical signature of fly ash from Japanese coal-fired power plants ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.209 \pm 0.003$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.052 \pm 0.006$ ; Figure 3),<sup>65</sup> indicating that emissions from this source are not an important portion of lead in those waters.

Lead isotopic ratios in some of our surface water samples are similar to those measured in aerosols in Russia, Mongolia, and Korea (Figure 3), and previous studies using lead isotopes have documented the transport of atmospheric emissions from these regions to the Sea of Japan<sup>19</sup> and Japan.<sup>66,67</sup> For example, precipitation collected in Japan showed a seasonal trend in lead isotopic composition associated with air masses from northern China and eastern Russia in winter and from the southeast in summer.<sup>66,67</sup> But on a global scale, atmospheric lead inputs from eastern Russia and Mongolia to the North Pacific are considered





**Figure 4.**  $1/\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  in IOC-IV surface waters. The intercept of the regression line with the  $y$  axis ( $1/\text{Pb} \sim 0$ ) provides end-member ratios at infinitely high lead concentrations, hence approximating the signature of the main source of lead in the samples.

to be relatively small, because those regions are much less populated and much less industrialized than China. Atmospheric inputs from South Korea to the North Pacific are also considered to be relatively small, even though it is a highly industrialized country, because its coal consumption is  $\sim 30$  times lower than it is in China.<sup>14</sup>

Moreover, coal consumption in China, which is now the country's largest source of atmospheric lead contamination,<sup>10,12,13,68</sup> is projected to markedly increase for decades to support the country's dramatic industrial and economic expansion. That consumption increased by a factor of 5 between 1980 and 2009 and is predicted to increase by 3.5% every year until 2035. In 2009, Chinese coal consumption alone represented 47% of the world's consumption, with an annual consumption of 3150 Mt of coal.<sup>14</sup>

To put the potential environmental impacts of that amount in perspective, we estimated that the release of industrial lead from coal combustion in China is  $\sim 20,000$  t/year. This estimate was based on reports of the average lead concentration ( $13.6 \pm 6.6 \mu\text{g} \cdot \text{g}^{-1}$ ) of Chinese coal<sup>10</sup> and the reported atmospheric discharge (50%) of lead from Chinese power plants.<sup>69</sup> That amount is more than the estimated amount (18,000 t/year) of atmospheric lead annually deposited in the entire North Pacific in the late 1980s — when leaded gasoline was still being used extensively in most of North America and Asia.<sup>70</sup>

Isotopic compositions of lead in the Chinese atmosphere as well as coal and lead ores span a wide range, but Chinese lead has a unique thorogenic isotopic signature that is characterized by an enrichment in  $^{208}\text{Pb}$ .<sup>9,13</sup> Since the isotopic ratios of our seawater samples fit within these atypical ratios (Figure 3), they indicate that Chinese industrial lead emissions are the predominant source of industrial lead inputs to the North Pacific.

This indication is substantiated by our plot of the linear regression between lead isotopic compositions and inverse of lead concentrations (Figure 4). The intercept of the regression ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.157$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.118$ ), which provides an estimate of the isotopic ratios of the main source of lead in the samples, falls on the line describing lead ore and coal in China.

These findings corroborate previous reports of the long-range transport of Chinese industrial lead aerosols to the China Sea,<sup>33,57,71,72</sup> Korea,<sup>16</sup> Taiwan,<sup>73</sup> the Oki Islands,<sup>74</sup> Japan,<sup>12,18,65–67,75–78</sup> and the North Pacific.<sup>6,51,60</sup> The findings are also consistent with measurements in annually banded corals, which indicated that Chinese industrial lead aerosols supplanted Japanese emissions as the predominant source of lead to the western North Pacific in the mid 1980s, and accounted for  $\sim 60\%$  of lead in surface waters by the mid 1990s.<sup>60</sup> Finally, our data indicate that Chinese industrial lead emissions are now the dominant source of lead inputs to the western and central North Pacific and may account for recent changes in the lead isotopic composition of aerosols in California,<sup>20,21</sup> Alaska,<sup>22</sup> and the Yukon.<sup>23</sup>

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