

## Determination of Lead Sources in Water Samples Using Isotope Ratios

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There is a need to determine the source(s) of lead (Pb) in contaminated drinking water. USEPA regulations (USEPA 1991) call for first-draw, one-liter monitoring of customer taps for the determination of Pb. Often, the assumption is made that Pb contamination in a water sample collected this way is from Pb solder and the tap fixture. It is difficult to distinguish whether Pb is coming from Pb service mains and lines or from household plumbing fixtures and pipes.

In this study, Pb isotope ratios in water and plumbing samples were measured to determine the source(s) of Pb in a particular water sample. Pb has four stable isotopes: <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb. Although <sup>204</sup>Pb is not radiogenic (its concentration has remained constant since the formation of the earth), the remaining three isotopes are. During Pb ore genesis, Pb becomes separated from its parent isotopes resulting in the fixing of the isotope ratios in time. These Pb isotope ratios vary with geographic location, so they can be used as tracers when used in plumbing materials. Pb isotopes are not fractionated during the fabrication of plumbing materials. If a manufacturer of Pb-based plumbing materials bought Pb ores from a specific mine, the finished product will have a characteristic Pb isotope fingerprint that reflects its source.

Numerous investigators have used inductively coupled plasma - mass spectrometry (ICP-MS) to determine Pb isotope ratios in environmental media (Keinonen 1992; Gulson et al. 1995b) human blood (Alexander et al. 1993; Gulson et al. 1995a; Tera et al. 1984), paint (Alexander et al. 1993; Gulson et al. 1995a), deciduous teeth (Alexander et al. 1993), and drinking water (Gulson et al. 1997) but research on the use of isotope ratios to determine sources of Pb in specific drinking water samples has not been done.

It is well established in the literature that Pb can reach drinking water through the dissolution of plumbing materials (Murrell 1990; Schock and Neff 1988; Subramanian et al 1991) and that Pb in water may influence

blood Pb levels in humans (Gulson 1994; Gulson et al 1997; Cosgrove et al 1989). These studies have evaluated total Pb levels in water samples. Although researchers have established that Pb in drinking water emanates from household plumbing rather than source water, definitive data to validate this assumption in areas where source water contamination may be present are lacking.

## **MATERIALS AND METHODS**

Houses to be sampled were selected based on the age of the house, plumbing materials used, and the nature of the service line. Samples were collected from homes whose water had not been used for at least eight hours before sampling. Water samples were collected from the kitchen cold water tap early in the morning as follows. While the water was kept at a slow, steady stream, two 0.015 L "first draw" samples were collected, followed by a 0.125 L sample. The next 0.125 L sample (flush sample) was used only to determine volume, pH, and temperature. Several 0.125 L samples were then collected in series.

Two standards (1.0 and 30.0 ppb Pb) were prepared from a 1,000 ppm Pb stock solution (Inorganic Venture, Red Bank, NJ, USA). The standards were also spiked with thallium concentrated nitric acid. The procedural blank consisted of 10 mL distilled 18 megaohm water, 300 uL nitric acid, and 200 uL (1 ppm) thallium and was used to subtract background Pb contamination from all analyses. Accuracy of the isotope ratio determination was assessed using National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) NIST 981 + thallium, common Pb metal.

Pb isotope ratios and concentrations were determined using a VG PlasmaQuad PQ2+ Turbo ICP-MS (Fisons Instruments, Beverly, MA, USA). Operating conditions were described in detail previously (Hall and Murphy 1993). Detailed descriptions of ICP-MS and applications are described in The Handbook of ICP-MS (Jarvis et al. 1991). The instrument was tuned for optimum sensitivity and precision at Pb-206.

Pb concentrations were determined by summing the area counts per second (ACPS) of Pb-204, Pb-206, Pb-207, and Pb-208 and comparing them to a two point standard calibration curve. The ACPS for both standards and samples were normalized to T1 internal standard. The concentrations of the standards (1.0 and 30.0 ppb) were chosen so that the tap water samples were bracketed by the standards. For Pb concentration analyses, NIST-1643c (trace elements in water) was analyzed to verify the accuracy of the analyses. Within experimental error, the concentrations we determined were within the range of the certified values. Isotope ratios were corrected for mass discrimination

using NIST SRM-981 (common Pb isotopic standard, 25 ug/L) that was spiked with thallium.

## RESULTS AND DISCUSSION

Summary data describing the Pb concentrations in sequentially collected samples are reported in Table 1. One overall pattern in the data is that Pb levels in water samples collected from homes constructed in the 1980's are highest in the first 0.5 L. This indicates that Pb may be leaching from new faucet fixtures in these relatively newly constructed homes. There were no statistical differences in Pb concentrations according to volume of water flushed for water from those homes in which a Pb main was present, indicating that the main is a constant contributor of Pb to the system. Homes constructed in the 1970s showed overall the lowest Pb levels regardless of sample volume with slightly higher levels in the first 0.5 L collected than in flushed water samples.

In Figure 1, the Pb isotope ratios from water samples were plotted against the regression models developed from Pb isotope ratios found in plumbing samples in order to apportion the dominant source(s) of lead in the drinking water samples from two of the nine homes sampled. Shown are the 95% confidence limits of the model. Correlation coefficients for the regression models developed for all nine homes sampled are given in Table 2. The percent contribution of lead from a particular plumbing fixture in a water sample is determined by placement of the water sample on the regression curve. The corresponding graphs in Figure 2 show more clearly the relative contribution of lead from plumbing fixtures to water, using one lead isotope ratio,  $^{206}\text{Pb}/^{208}\text{Pb}$ . Tera et al. (1984) also found linear trends in isotopic composition in children's blood lead values when they plotted them against lead values collected from air filters and so were able to determine the percent contribution of lead in air to children's blood in a similar manner.

In most cases, it was possible to determine the major sources of Pb in a water sample from evaluation of the isotopic composition in the water samples with those from the plumbing fixtures collected from that particular home. For instance, in home DA, it was evident that 100% of the Pb in three water samples was from basement solder, while in other samples, basement solder contributed 40-70% of the lead in the water sample.

It is apparent in the graphs that solder and pipes in the kitchen were responsible overall for the lead appearing in the first 0.5 or so liters of lead coming from both kitchen taps. After two or more liters, the contribution from lead solder in the basement and throughout the house was the primary contributor of lead to water samples and, finally, after flushing

**Table 1.** Lead concentrations ( $\mu\text{g/L}$ ) for water samples collected sequentially from nine homes in NJ.

	LEAD MAIN PRESENT				HOMES BUILT 1970's				HOMES BUILT 1980's			
	0.5 I	1 I	1-2 I	>2 I	0.5 I	1 I	1-2 I	>2 I	0.5 I	1 I	1-2 I	>2 I
Volume												
N	16	23	10	32	8	12	4	11	8	4	5	26
25%	2.7	2.51	1.81	2.28	1.29	0.61	0.23	0.10	2.63	0.78	0.83	0.93
Median	4.37 <sup>a*</sup>	6.77 <sup>a</sup>	2.67 <sup>a</sup>	3.88 <sup>a</sup>	1.86 <sup>a</sup>	0.81 <sup>b</sup>	0.54 <sup>ab</sup>	0.14 <sup>cd</sup>	17.99 <sup>a</sup>	0.92 <sup>ab</sup>	0.92 <sup>ab</sup>	2.45 <sup>b</sup>
75%	48.78	23.04	11.57	5.44	3.02	1.04	1.54	0.90	38.32	6.87	5.16	3.55

\* Medians with the same letter are from statistically identical populations within each of the three categories.

**Table 2.** Regression parameters for plumbing and water Pb isotopic ratios ( $^{206}\text{Pb}/^{208}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$ ) collected from nine homes in NJ.

Home	Year Built	$r^2$	
		Plumbing	Water
DA	1920	0.98	0.53
KH	1920	0.91	0.44
LY	1920	0.61	0.61
GWA	1960	0.95	0.72
KS	1970	0.95	0.40
MZ	1970	0.996	0.65
GWB	1980	0.93	0.63
VM	1980	0.82	0.31
JK	1980	0.92	0.21

greater than 10 liters, contributions from the water meter (if served by a public supplier) or from the holding tank (if on a private well) was evident. Isotopic composition reached equilibrium at this point and up to a maximum of 300 liters flushed. This pattern is in agreement with work conducted by Gulson et al. (1994) where equilibrium was observed after approximately 10 liters of water were flushed through the system.

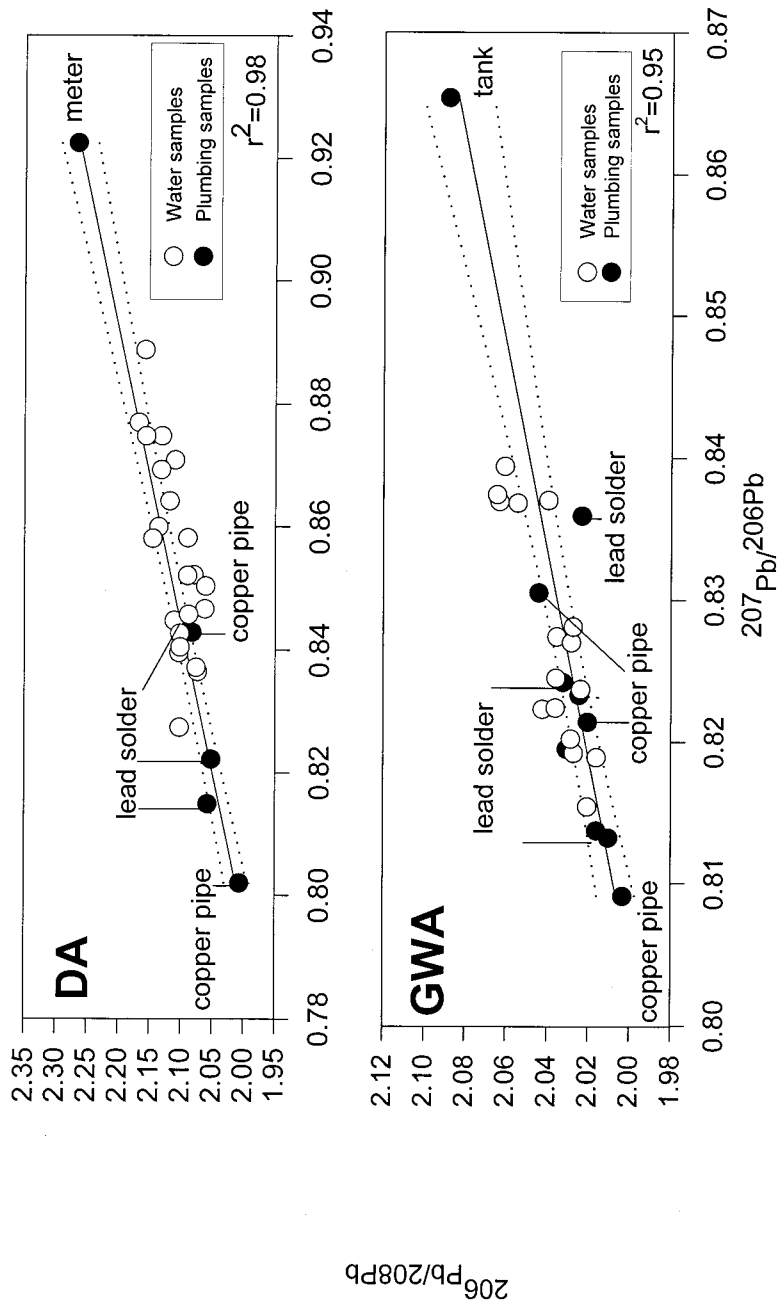
It was impossible to collect samples from inside the kitchen faucet, although it is apparent from the data at some of the homes that this was a major source of lead, in particular, homes constructed in the 1980s. In these homes, the highest lead concentrations measured was in the first 0.015 L of water collected, which corresponds to water in direct contact with the faucet fixture. The isotopic compositions of these samples did not lie directly on the plumbing regression curve. Therefore, it is concluded that the source of the lead in these otherwise lead-free plumbing systems was the kitchen faucet fixture.

One home (DA) was revisited in the summer and sampled again to determine the effect of temperature on lead leaching (all other sampling was conducted in the winter and early spring). The samples collected in the warm weather contained higher lead levels overall than those collected in cold weather but the pattern of leaching was identical in the two sampling events; higher lead concentrations in the first 0.5 L and a decrease with flushing volume.

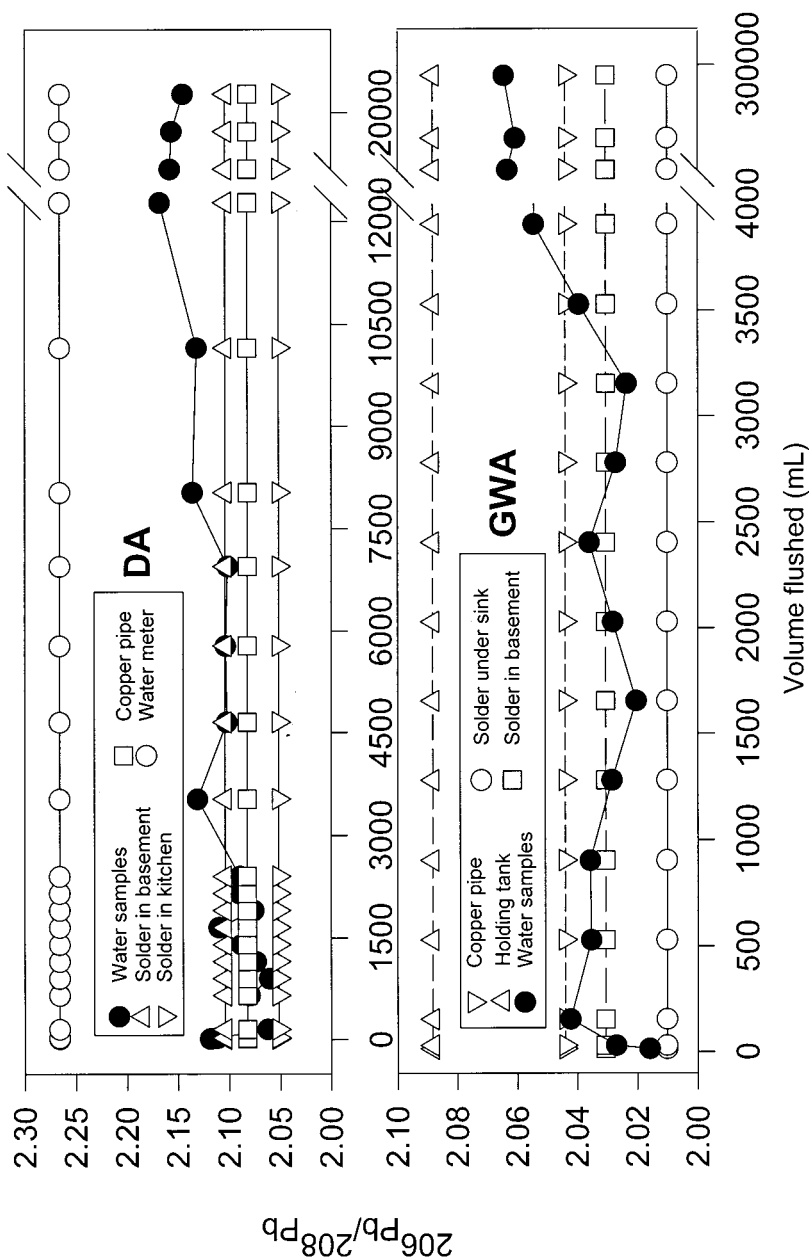
Utilization of ICP-MS for Pb isotope fingerprinting is effective in identifying sources of Pb in tap water. The deviation of some of the water samples' isotopic compositions from the regression curve indicate that additional sources of lead may be contributing to the lead in the water samples. One such source is the kitchen faucet. An interesting result from the study was that copper pipes contributed some amount of lead to the water samples in almost every house. This indicates that buildings having extensive copper plumbing may expect to see Pb in drinking water as a result of leaching of the copper pipe.

Rather than assume that elevated lead levels are coming from service lines, water systems should test further. New faucet fixtures, newly lead soldered joints and new brass fixtures may contribute more lead to tap water samples than service lines and mains. While lead pipes can cause problems in some instances, they are not always the reason for elevated lead levels especially in first volume samples.

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**Figure 1.** Regression models of lead isotope ratios in two homes: DA is served by public surface water and was built in the 1920's; GWA is served by ground water and was built in the 1960s



**Figure 2.** Lead isotope ratios from water and plumbing samples: DA is served by public surface water and was built in the 1920's; GWA is served by ground water and was built in the 1960s

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