Lead Astray

David Bradley

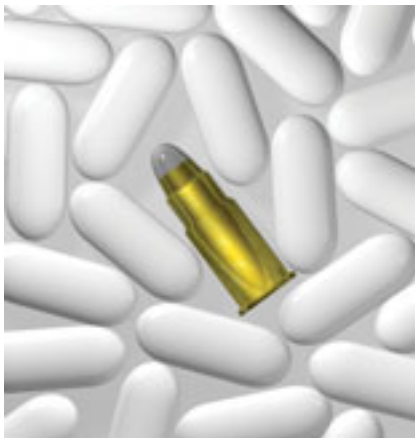
MS finds a smoking gun: Using firearms can be hazardous to the health of the shooter.

The health hazards associated with using firearms are well documented for those on the receiving end, but the people shooting the bullets do not emerge unscathed either, according to one clinical trial. Australian researchers studying dietary calcium supplements found that one of the volunteers in their trial had blood lead levels far higher than the rest of the cohort. They knew that dietary calcium supplements sometimes contained traces of lead contamination. They also knew that most adults have some of the calcium in their skeletons replaced by lead from the environment, and that this lead can enter the bloodstream. But because this research group had been doing criminal forensics work on bullets as well, they recognized telltale signs that their volunteer's elevated lead levels might be related to his gun hobby. Using thermal ionization mass spectrometry (TIMS) to measure lead isotope ratios (an indicator of the lead's geographical origin) in their subject's blood samples, they made a strong case for the connection between bullets and blood lead levels.

Loads of Lead

Brian Gulson of the Graduate School of the Environment (GSE) at Macquarie University (Sydney) and Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) gets all fired up about environmental health. He researches the biokinetics of lead in human pregnancy, toxic metals in mining and urban environments, lead's impact on the environment and people, the sources and pathways of these metals, and remedial action. He is also interested in the dietary intake of toxic metals and in forensic science. "We are uniquely positioned to do this research," he says, "because of the unique lead isotopic signature in the Australian environment and in long-term Australian residents" (see box, "Plumbing the Depths").

Australia has an abundance of geologically old (about 1.7 billion years) major lead deposits that have been used for more than 100 years for industrial purposes, including lead in gasoline manufactured by Associated Octel in the United Kingdom. The old deposits have a unique lead



isotopic signature, or fingerprint, that is markedly different from geologically younger lead deposits (<400 million years), a few smaller ones of which are found in Australia; however, they are more common in other countries, including the United Kingdom and the United States.

The GSE team has recently exploited this lead signature in their research to help them understand the outcome for individuals taking calcium supplements (which sometimes contain traces of lead) and in looking at the mobilization of lead from bone during pregnancy. Because lead and calcium are similar in valency and atomic size, calcium-containing dietary supplements can contain varying quantities of lead impurities. Lead replaces calcium in the skeleton, which is the repository for more than 90% of the lead in the body of a typical adult. The main biomarker for lead is blood, and a value of 100 µg/L is potentially toxic, especially in young children. Taking contaminated calcium supplements could have serious health implications, especially for pregnant women, whose bone tissues are more susceptible to calcium loss, and for their unborn children, who absorb lead via the placenta, leading to potential harmful effects on the brain and growing bones.

Their earlier studies on the mobilization of lead from maternal bone during pregnancy and lactation had offered some worrying insights. For instance, they confirmed that lead is mobilized from skeletal stores faster than usual during pregnancy, and it inevitably reaches the growing fetus. This exposure, Gulson says, has implications for how neurobehavioral disorders are viewed in the young child. Previously, this internally derived source of lead exposure had been largely ignored because there was no way to quantify the amounts of lead released from the bones. "The source of the lead may not just be the more common targets such as old leaded paint or industrial sources, but may include traditional medicines and cosmetics," says Gulson.

Lead Supplement

Gulson's team recently carried out a case control study into the absorption of lead from calcium dietary supplements. They recruited men and women between 21 and 47 years of age and measured their base blood lead concentrations for a couple of months before the supplementation was started. The volunteers were then split into a treatment group receiving a calcium supplement (phosphate–citrate–amino acid), a second group receiving just calcium carbonate, and a control group that received no supplement. Because the isotopic ratios of the blood lead were very different from the lead impurities in the calcium supplements, it was easy to distinguish the source of any increase.

"The method makes use of the fact that there can be considerable variation in the proportions of the four stable isotopes found in naturally occurring lead," explains Gulson. This is because three of the isotopes are the end products of radioactive decay of uranium and thorium. "The ratios of the

Plumbing the Depths

Lead in the environment largely comes from industrial sources that have themselves been derived from a small number of mineral deposits. Most of these deposits have a characteristic isotopic pattern—a signature or fingerprint.

People growing up in a particular environment will take lead with a characteristic signature into their bodies. A proportion of this lead, effectively labeled with this signature, will be incorporated into their skeletons. If an individual relocates to a different environment with a different lead signature, the original signature can still be detected in the individual's blood for many years, because lead is released from the skeleton as part of the normal bone-remodeling process.

The analyst would see a mixture of the signatures from the new and old environments in blood (and urine) samples. Any process that affects the bone-remodeling rate will affect the proportions of the two signatures observed. "For this to be a useful tool, the signature of the environment which labelled the skeleton has to be significantly different from the signature of the new environment," explains Gulson.

A lead signature is usually recorded as the ratio of one isotope to another. The bullet study used the ratios expressed relative to ^{206}Pb, and the most common ratio reported is $^{206}Pb/^{204}Pb$. A complete signature would also need $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$. The accepted "gold" standard for determining lead isotopic ratios is with solid-source thermal ionization mass spectrometry, which is capable of attaining high sensitivity but requires extensive sample preparation and is costly.

Note: For a comparison study of TIMS and ICP-MS, see Inn, K. G. W.; et al. *J. Radioanal. Nucl. Chem.* **2001,** *249,* 121–131 (available at *http://tis.eh.doe.gov/health/marshall/intercomparison.pdf*).

isotopes to one another are related to factors such as the proportion of uranium to thorium and the age of the mineral deposit from which the lead was mined," he adds.

The team could thus estimate how much lead each type of calcium supplement contributed to the blood. They found that the daily lead dose from the supplements was about 3 µg (baseline dietary lead intakes have already been well documented and are generally very low). However, the mean blood lead concentrations showed only minimal changes across all three groups. This, Gulson confirms, is consistent with earlier research that relied on radioactive lead tracers. Importantly, however, the $^{206}Pb/^{204}Pb$ ratio for those taking the calcium carbonate differed from those taking the complex calcium supplement by 0.5%. "That's a significant difference, more than 10 times our experimental errors," says Gulson. He suggests that since calcium carbonate is the most commonly used calcium supplement, it is important to follow up this finding with a more detailed study, especially for children who might get more of their calcium from calcium-fortified cereals and juices than from dairy products.

Criminal Lead

Meanwhile, Gulson's team has also worked on the analysis of lead-rich forensics samples. It was the connection between Gulson's forensics experience and his dietary studies that put him on the trail of another lead issue. The research group had used a combination of high-precision lead isotope measurements with TIMS and SEM commonly known to match exhibits in a murder case, including lead projectiles removed from the crime scene and lead-rich scrapings and particles from spent cartridges, a gun silencer, and particles from the crime scene. They were able to demonstrate that the lead-rich scrapings and the projectiles had the same isotopic composition. They could even pinpoint that the geological source of the lead used in the ammunition projectiles was from Australia, but that the primer was from the United States.

Lead Wait

A male volunteer in one of Gulson's control groups for lead exposure stood out from the crowd, providing the link between the dietary studies and the forensics work. The other volunteers showed very little variation in their blood lead levels, but this 40-year-old man showed unexpected shifts

in the lead concentration readings as well as wild variations in the isotopic ratio of the lead in his blood. According to the researchers, they expected to see a uniform isotopic ratio and lead concentration over the period of sampling in such a volunteer. The baseline, they anticipated, would be the same as they had seen in the control group for their calcium supplements study. The lead concentration and ratios for this man "far exceeded any we have found in several hundred environmentally exposed subjects," they say. You might say that this was the "smoking gun".

It was obvious for the researchers to ask whether this man was a recreational shooter. Gun users are at high risk of lead exposure from ammunition vapors and particulates. Sure enough, he was, and more to the point, he assembled his own ammunition. Moreover, discussion about other potential sources of the lead in his blood narrowed the possibilities to primarily from his shooting.

Fortunately, the man had kept a shooting diary as well as samples of ammunition. The man used various types of ammunition, including solid cast lead manufactured in Australia, copper-jacketed lead rounds, Teflon-coated lead bullets manufactured in Australia, and American-made 0.22-mm-caliber ammunition.

Primary Lead

The team took regular blood samples from the man and found he had chronically elevated plumbum levels. Again, TIMS allowed them to work out the lead isotope ratios in his blood and correlate this with his ammunition. The researchers determined that the lead that constituted about 11% of the primer was probably from the United States, consistent with the purchase source.

The volunteer generally fired 80–200 rounds at a session, either indoors or outdoors. However, researchers found that the type of bullet had the biggest influence on his blood lead. During the initial sampling period from May to August 1999, the man was using cast bullets made from Australian lead, and during this time, the ratio of ^{206}Pb to ^{204}Pb decreased while his blood lead concentration doubled.

Such a doubling has health implications for the police and even recreational shooters, adds Gulson, "especially where people have to practice indoors for much of the year." Although the type of bullet used had the greatest influence on the one test volunteer, some enthusiasts might use nonjacketed bullets outdoors, and the bullets used in most countries use primer that contains lead. Volatilized lead contained in an indoor space could reach higher concentrations than for outdoors. Gulson's group does not know the extent of the difference between indoor and outdoor lead levels, but they expect the effect to be small. Even outdoor shooting poses some level of risk. Other researchers have reported that firearms instructors for the City of Los Angeles working at outdoor ranges were exposed to air lead levels that exceeded the U.S. OSHA lead in air standard of 50 $\mu g/m^3$ after just 12 minutes. Our recreational shooter told Gulson's team that he was typically shooting for at least an hour to an hour and a half.

The man did not use firearms for the subsequent three months, and although the isotopic ratio drifted toward his norm, his blood lead concentration remained constant. This was an unexpected finding, because typically lead from the bloodstream would be sequestered in the skeleton, causing the blood lead levels to decrease over time. There is some possibility that the man continued to make ammunition during this period, even though he was not using it, and that this might have been a continuing source of lead exposure. The man's spring ceasefire saw his blood lead eventually fall to normal levels.

Surely, a healthy argument against bearing arms?

Further Reading

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Brian Gulson's webpage; www.gse.mq.edu.au/Research/staff/brian_gulson.shtml.

Isotopes in Health and the Environment Home Page; www.gse.mq.edu.au/Research/IHE/ihe_index.htm.

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