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Changes in blood lead of a recreational shooter

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Abstract

We have measured the concentration and isotopic composition of lead in blood over a 15-month period for a subject who undertook recreational shooting in outdoor and indoor firing ranges on an irregular basis. We have also measured the isotopic composition in cast lead, Cu-jacketed and Teflon-coated bullets, propellant and primer from which he assembled the cartridges. Blood lead concentration increased from 3.2 to 6.7 μg/dl with use of dominantly cast lead bullets in the outdoor range. In two intervals when no firing was undertaken for 3–4 months, the blood lead concentrations either decreased towards a baseline value in the case where only Cu-jacketed bullets were fired or remained elevated when dominantly cast lead bullets were fired. The propellants contained <2 ppm Pb and contribute negligibly to blood lead. The isotopic composition of the primer used for all bullets was consistent with a source from the US. The bullets were of different materials and made in Australia and the US, with lead from sources of different geological age and hence different isotopic signatures. Variations in blood lead concentration and isotopic composition appear most strongly influenced by the bullets. Although more expensive, the use of Cu-jacketed bullets, non-lead primers and well-ventilated indoor firing ranges would lessen the health impacts of recreational shooting.

Keywords: Bullets; Blood lead; Isotope ratios; Male; Firing range

1. Introduction

It has been recognised for decades that routine use of firearms for occupational purposes may have a deleterious impact on the health of the individual because of the use of lead in the ammunition (Fischbein et al., 1979; Valway et al., 1989; Svensson et al., 1992; Abudhaise et al., 1996; Lofstedt et al., 1999). Of most concern has been where the activity is undertaken indoors as is commonly the case in the Northern Hemisphere. There is limited information, however, from recreational exposures (George et al., 1993; Lofstedt et al., 1999) and of shooting in outdoor environments (Tripathi et al., 1990, 1991; Goldberg et al., 1991) where the dispersion of the lead fumes and particles is considered to be of lesser consequence.

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We have undertaken a study of an individual who was enlisted as a control in an investigation of the uptake of lead in blood during calcium supplementation (Gulson et al., 2001). Unexpectedly, his blood exhibited changes in lead concentration and isotopic composition that were eventually traced to recreational use of firearms.

2. Methods

2.1. Subject

The subject was a male 40 years of age with no occupational exposure to lead. His wife and two of his children had been part of the longitudinal study into mobilisation of lead from maternal bone during pregnancy and lactation (Gulson et al., 1997, 1998), so some control over diet and environmental lead sources was possible.

He assembled his own ammunition and undertook recreational firing with an irregular timetable.

2.2. Cartridge construction

There are three main sources of lead in cartridges.

2.2.1. In this case, there were four types used; three of 9 mm and one of 0.22 calibre

1. Solid cast lead manufactured in Australia.
2. Cu-jacketed lead in which a Cu coating up to 1 mm thick is a electroplated onto a Pb core; these were manufactured in the US.
3. Teflon-coated lead, manufactured in Australia.
4. 0.22 cast lead calibre, manufactured in the US.

2.2.2. Propellant

The propellant for the 9-mm bullets consists of cellulose, nitroglycerin and diphenylamine. This is made in Australia for the 9-mm cartridges and the US for the 0.22 cartridges.

2.2.3. Primer

The primer generally consists of lead styphenate, tetracine, barium nitrate, ground glass and gum arabic. This is made in the US. The weight of the primer was from 17 to 21 mg.

2.3. Bullet sampling

Scrapings with a clean scalpel were taken from the bullets. A weighed amount of the propellant was placed in a clean Teflon container to which a ^{202}Pb spike was added to obtain the lead concentration at the same time as the isotopic composition. A primer cartridge was prised open, a small amount of powder removed and weighed, and spiked with a ^{202}Pb spike.

2.4. Blood sampling

Three venous blood samples of approximately 3-ml capacity were taken at quarterly intervals and another three at 2-month intervals; this was the protocol for the calcium supplements investigation.

2.5. Sample preparation

The bullets, primer and propellant were dissolved in ultra clean nitric acid and the lead separated by anion exchange chromatography, followed by anodic electrodeposition in the case of the bullet and primer. Lead from blood samples was separated as described previously (Gulson et al., 1997, 1998).

2.6. Isotopic measurements

For isotope ratio measurement, fractions of the purified lead samples were loaded onto a zone-refined rhenium filament using the silica gel technique (a mix of dilute phosphoric acid and purified silica gel) and analysed for lead isotope composition (and lead concentrations by isotope dilution) on a thermal ionisation mass spectrometer or TIMS (VG-ISOMASS 54E) run in fully automatic mode. Isotopic ratios were measured as ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{206}Pb/^{204}Pb. Precision estimates on the isotopic ratios have been defined by a repetition of the digestion/lead separation/mass spectrometry stages of the same samples of blood, urine and water. The precisions we allocate our data are $\pm$0.2% (2 σ) on the ^{206}Pb/^{204}Pb ratio, and $\pm$0.1% on the ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios and $\pm$3% for the lead concentrations. Data are normalised to the accepted values of the

Table 1
Diary of events for shooting

Date	Shooting range	Rounds fired	Bullet type used	PbB (μg/dl)
18 May 1999	Outdoor	80	Cast lead 9 mm (silver shadow)	
26 May 1999	Outdoor	80	Cast lead 9 mm (silver shadow)	3.2
24 Jun 1999	Outdoor	130	Mix of cast lead 9 mm (silver shadow) and Cu jacket (30–40 cast lead) (Cu jacket — no sample)	
29 Jun 1999	Outdoor	130	Cu jacket — no sample	
12 Aug 1999	Outdoor	80	Cast lead 9 mm (silver shadow)	
18 Aug 1999	Outdoor	80	Cast lead 9 mm (silver shadow)	
31 Aug 1999				6.7
28 Sep 1999	Outdoor	80	Cast lead 9 mm (silver shadow)	
6 Dec 1999				6.6
21 Dec 1999	Indoor	200	Cu jacket — mix speer	
5 Jan 2000	Indoor	80	Cu jacket — mix speer	
6 Jan 2000	Indoor	80	Cu jacket — mix speer	
1 Feb 2000				5.4
10 Apr 2000				3.8
2 May 2000	Indoor	140	Cu jacket, 0.22 cast lead and TFE-coated mix (~60 speer, ~60 federals, 30–40 Teflon-coated)	
9 May 2000	Indoor	140	Cast lead	
5 Jun 2000	Indoor	200	Cu jacket, 0.22 cast lead and TFE coated mix (~60 speer, ~60 federals, >80 Teflon coated)	6.0
13 Jun 2000	Indoor	140	Cast lead	
15 Jun 2000	Indoor	140	Cast lead	
20 Jun 2000	Indoor	200	Cu jacket, 0.22 cast lead and TFE coated mix (~60 speer, ~60 federals, >80 Teflon coated)	

international standard NBS SRM 981 (National Institute of Standards and Technology, NIST), by applying a correction factor of +0.08% per a.m.u. to allow comparisons between laboratories. A measurement of the environmental lead acquired by the sample throughout the entire preparation analysis procedure was obtained in the form of a lead 'blank' measurement. The amount of contamination detected in blanks was generally around 200 pg for blood. As the blanks contributed negligibly to the lead in the sample, no blank corrections to the data were performed.

3. Results

The 'diary' of firing of the subject is listed in Table 1 and lead isotopic for the ammunition are listed in Table 2. The lead isotopic ratios and blood lead concentrations are represented graphically as a time series in Fig. 1 and are subdivided into three sampling periods delineated by the dashed vertical lines. The blood lead concentrations are listed above each sampling point. The first blood sample of 3.2 μg/dl was obtained on 26 May 1999 and followed a range attendance on the 18 May 1999. Prior to this, there were range visits on 5 January 1999, 8 December 1998 and 10 November 1998. The relatively long break between the January 1999 firing and the time of the first blood sample in May 1999 may explain the relatively low blood lead of 3.2 μg/dl but, because it was taken approximately 1 week after the firing, is probably not the true background (baseline) value for the subject. Nevertheless, a follow-up sampling of blood on 7 June 2001, at least 3 months since the last firing, had a $^{206}Pb/^{204}Pb$ ratio of 17.33 and blood lead concentration of 3.4 μg/dl, consistent with other possible baseline values.

Table 2
Lead isotopic compositions of the different components of the bullets

Sample type	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Pb (ppm)
AP100 propellant	2.2145	0.9529	16.13	1.9
AP70 propellant	2.2136	0.9527	16.13	1.9
Federal 0.22 propellant	2.0698	0.8472	18.42	2.0
Lead cast bullet (silver shadow)	2.1938	0.9333	16.56	nm
Cast lead 0.22 bullet	2.0144	0.8198	19.04	nm
Cu-plated hollow point bullet	2.0180	0.8204	19.10	nm
Cu-plated lead bullet	2.0249	0.8250	18.99	nm
TFE-coated cast lead bullet	2.2042	0.9385	16.45	nm
TFE-coated cast lead bullet	2.1985	0.9381	16.47	nm
TFE-coated lead bullet	2.2032	0.9415	16.38	nm
Primer	2.0269	0.8253	19.01	108 000

nm, not measured.

The expected results for this individual were for uniform isotopic ratios and lead concentrations over the period of sampling, as found in most subjects in the lead in the calcium supplements study (Gulson et al., 2001) and in the isotopic compositions for Australian female control subjects in the pregnancy study (Gulson et al., 1997, 1998).

The isotopic and blood lead variations observed in the subject far exceeded any we have found in several hundred environmentally-exposed subjects which we have monitored longitudinally. Following discussions about his potential sources of exposure, recreational firearm use appeared to be the major contributor. Because of the experiences/expectations of his wife with the research team over a 10-year period of the pregnancy study, he had fortunately kept a diary of his activities as well as ammunition.

The propellant powder for the 9-mm cartridges was manufactured in Australia and had isotopic ratios characteristic of geologically-ancient Australian lead (Gulson, 1986). The propellant for the 0.22 cartridges had an isotopic composition characteristic of geologically young lead such as found in the Mississippi Valley of the US (Doe and Stacey, 1974). However, both propellants contained only approximately 1.9 ppm of lead.

The 9-mm cast lead bullet and two Teflon-coated bullets had low $^{206}Pb/^{204}Pb$ ratios and are consistent with a dominant geologically-old lead source such as found in Australia. The 0.22 cast lead and 9-mm Cu-coated bullets had isotopic compositions with a $^{206}Pb/^{204}Pb$ ratio of approximately 19.0, consistent with a US source. Stupian (1975), Keisch and Callahan (1978) and Andrasko et al. (1993) measured high $^{206}Pb/^{204}Pb$ ratios in US-manufactured Winchester bullets.

The same type of primer, containing approximately 11% Pb, was used for all bullets. The lead isotopic composition of the primer was similar to that in the US bullets.

Assuming simplistically that the two dominant sources of lead are from the bullets and these are manufactured from either geologically-ancient Australian lead or geologically-younger lead from the US, the approximate contributions to blood lead from these two sources can be estimated for different periods from isotopic mixing relationships commonly used in isotope geochemistry (Faure, 1986). In the first interval from 0 to 97 days, during which time the blood lead concentration more than doubled, there was a 31% shift in the blood isotopic composition probably in response to the use of cast lead bullets. In the second interval from 194 to 251 days there was a smaller 18% shift in the isotopic composition probably in response to the firing of Cu-jacketed bullets. In the third interval from 320 to 376 days when a complex mix of bullets was fired, there

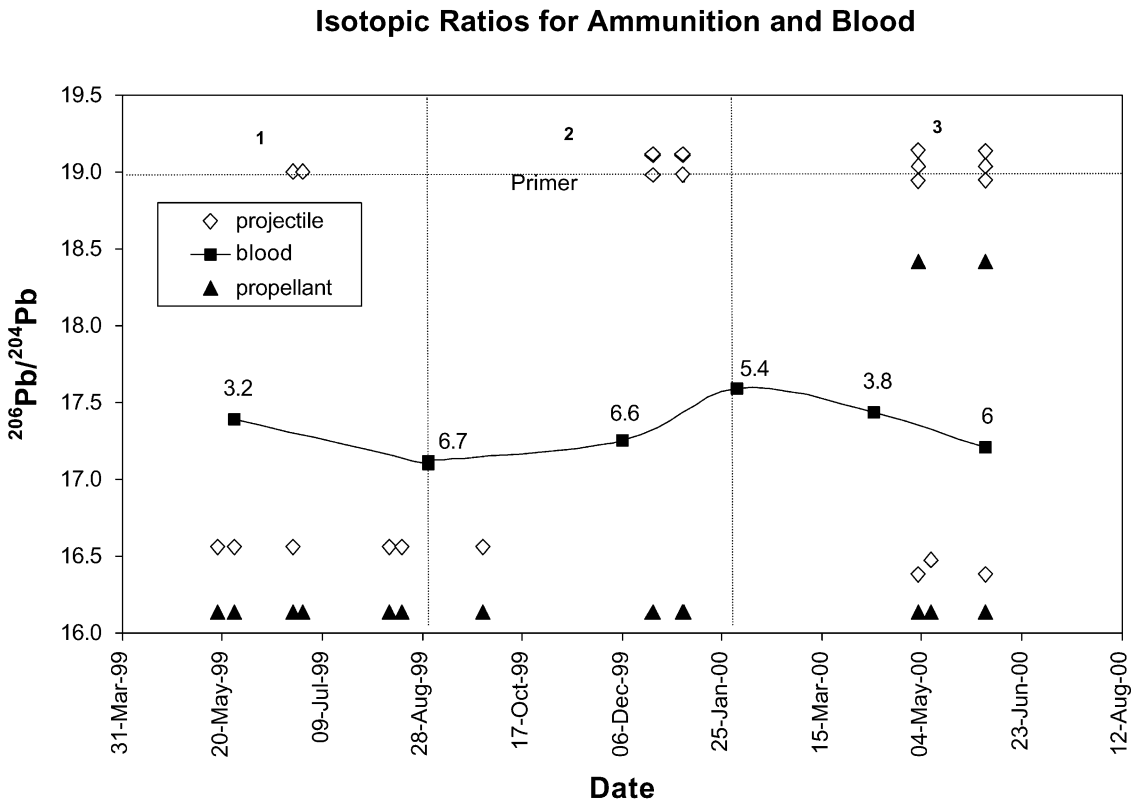

Fig. 1. Time series plot showing variations in blood lead isotopic compositions and concentrations associated with use of ammunition containing lead from different geological sources. Blood lead concentrations in μg/dl are given above the sampling point. The propellant contains <2 ppm Pb. Australian manufactured bullets (projectiles) have low $^{206}Pb/^{204}Pb$ ratios compared with the high values for the US manufactured ones. The vertical dashed lines represent three segments (1, 2, 3) of shooting relative to blood leads. Note the two intervals when no shooting occurred.

was a 25% shift in blood isotopic composition. These shifts attributed to the whole cartridge would be considerably larger if the primer was also taken into consideration in the calculation. As the primer and Cu-jacketed bullets have the same isotopic composition, it is not possible to differentiate between the individual contributions to blood lead from these two sources.

4. Discussion

Previous lead isotopic investigations of firearm use focused on the analysis of the lead bullets (Stupian, 1975; Keisch and Callahan, 1978; Andrasko et al., 1993). Keisch and Callahan (1978) were the only investigators to measure the isotopic composition of primers to compare with hand wipes.

The propellant is considered to contribute minimally to blood lead because of its very low concentration of <2 ppm Pb. In spite of the primer being a potential major contributor with a lead concentration of approximately 11%, it is considered to have a smaller impact on the observed blood lead because the same primer was used in all bullets. In contrast, Svensson et al. (1992) attributed a significant contribution to blood lead concentration from the primer as they found shooters in indoor firing ranges had a lower blood lead if using air-propelled bullets compared with powder-charged ammunition.

The type of bullet is considered to be the dominant influence on blood lead. During the initial sampling period from 18 May 1999 to 31 August 1999 (1 in Fig. 1), the overwhelming dominant bullets used were the cast lead bullets made from Australian lead. Exposure to this type of lead is consistent with the decreased $^{206}Pb/^{204}Pb$ ratios in blood from 17.39 to 17.10 combined with a doubling of the blood lead concentration. This activity was undertaken outdoors. During the next 3 months of no exposure, the blood isotopic composition drifted towards his baseline level, but the blood lead concentration unexpectedly remained the same. The small decrease in blood lead concentration and increase in blood $^{206}Pb/^{204}Pb$ ratio over the second period from December 1999 to 8 February 2000 is attributed to the indoor use of the US manufactured Cu-jacketed bullets with a probable contribution from the primer. It is not possible to differentiate between the contribution from the bullet and primer because they have almost identical isotopic compositions. The period of no-firing from 6 January 2000 to 2 May 2000 witnessed a decrease in lead isotopic composition and blood lead concentration, the latter decrease consistent with the clearance of lead from blood with a half-life of approximately 20 days (Rabinowitz et al., 1976; Chamberlain et al., 1978). The last period of firearms use from 2 May 2000 to June 2000 was carried out indoors and involved a mixture of Australian cast lead (~28%), US Cu-jacketed and 0.22 calibre (~48%) and Teflon-coated ammunition (~24%). The decrease in $^{206}Pb/^{204}Pb$ ratio from 17.44 to 17.21 and almost doubling of blood lead concentration from 3.8 to 6.0 μg/dl are attributed to the cast lead bullets, a non-trivial increase.

The larger contribution to blood lead of the cast lead ammunition compared with Cu-jacketed or Teflon-coated bullets is consistent with observations of the deposits on the barrel after firing. Negligible deposits of lead are observed in the case of the Cu- and Teflon-coated bullets but heavy deposits are found in the barrel, as well as can be seen emitting from the barrel during firing, in the case of the cast lead bullets. Valway et al. (1989), Tripathi et al. (1990, 1991) and Goldberg et al. (1991) found up to a 97% reduction in air lead concentrations and lower blood lead levels in shooting instructors using Cu-jacketed bullets. With such large reductions in air lead concentrations and the stability of Cu-jacketed bullets, it would appear that any changes in blood lead or isotopic composition of the present subject are also influenced by the primer. In the present case, the lead changes in the second period of Cu-jacketed bullets represent a larger contribution from primer compared with cast lead bullets.

There appears to be little difference in effect on blood lead from indoor or outdoor firing. This conclusion was enunciated earlier by Goldberg et al. (1991) for City of Los Angeles instructors participating in uncovered outdoor ranges. For these instructors, Ozonoff (1994) estimated that a firing range instructor would exceed the US OSHA lead in air standard of 50 $\mu g/m^3$ after 12 min. In the present case, the recreational shooter estimated that it took approximately 60–90 min to complete the firing.

The subject undertook no other activities involving lead exposure. One potential lead source apart from firing is in preparation of the ammunition. No visible dust was obvious while reloading the cartridges, and only the bullet and primers were touched with fingers; the subject washed his hands vigorously after the loading. It is possible that there was a contribution due to cleaning the cases before reloading, when a 'tumbler' with nutshell was used to clean the cases, and emptying the tumbler did produce some fine dust. However, the reloading was carried out at periods overlapping those with no shooting so that reloading is not considered a major contributor to blood lead.

Other studies on recreationally-exposed subjects are limited to a New Zealand study (George et al., 1993) and one in Sweden (Lofstedt et al., 1999). In New Zealand, the mean time spent shooting small-bore rifles in indoor ranges was only 70 min/week but the blood lead concentrations were similar to full-time instructors at pistol ranges. The mean red cell concentrations at the end of a 6-month shooting season was >50 μg/dl compared with 33 μg/dl before the start of the following season. The study by Lofstedt et al. (1999) involved Swedish police officers and covered both occupational and recreational exposures of the

subjects so that it was not possible to separate the effect from recreational use. They concluded that exposure from shooting was no longer a health risk because of lead-free ammunition and well-ventilated firing ranges; the blood lead levels in male officers were 5.0 μg/dl and, in female officers, 3.7 μg/dl.

Seasonal changes in blood lead concentration in children are well-documented in the US but less so in adults (Hunter, 1977; Rabinowitz and Needleman, 1982; Hwang and Wang, 1990; Meyer et al., 1992; Johnson et al., 1996; Schell et al., 1997). Manton (1977, 1985) and Manton et al. (2000) observed seasonal changes in blood lead concentration and lead isotopic composition. However, we have not observed any significant seasonal effects on either blood lead concentration or isotopic composition in female adults and children, many of whom have been monitored longitudinally for more than 3 years (Gulson et al., 2000).

In conclusion, exposure to lead from both indoor and outdoor firing ranges on a recreational basis can result in a doubling of the blood lead concentration, in spite of the limited exposure time. The major contribution is from the type of bullet so that jacketed bullets, non-lead primer and good ventilation in indoor ranges should allow for a safer activity.

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