Africa and
The Middle East

Lead isotope tracking of atmospheric response to post-industrial conditions in Yerevan, Armenia

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Abstract

Temporal gradients in environmental lead concentrations and isotopic compositions trace the rapidly shifting transition from high to low industrial emissions in Yerevan, Armenia following the dissolution of the Soviet Union in the early 1990s. Shortly after the breakup, in 1995 and 1996, atmospheric lead concentrations averaged $\sim 0.4\,\mu g\,m^{-3}$ and the combustion of leaded gasoline was the primary source of industrial lead emissions in Yerevan. But by 1998, unleaded gasoline was predominant and atmospheric lead concentrations had decreased by two orders of magnitude to $\leqslant 0.003\,\mu g\,m^{-3}$ because industrial lead emissions from stationary sources had also been radically curtailed. The increased proportion of unleaded gasoline use is clearly seen in comparisons of the isotopic compositions of lead in air and gasoline. In 1998 and 1999, the isotopic composition of atmospheric lead ($1.1605 \leqslant {}^{206}Pb/{}^{207}Pb \leqslant 1.1641$) was comparable to that in soil ($1.1357 \leqslant {}^{206}Pb/{}^{207}Pb \leqslant 1.1649$); and it was markedly different from the average isotopic value of gasoline (${}^{206}Pb/{}^{207}Pb = 1.1407$ in 1998 and 1.1555 in 1999). Binary mixing calculations suggest that 75% of the atmospheric lead in 1998 was derived from re-suspended soil that retains lead from past emissions and 25% was derived from a mixture of present industrial emissions and uncontaminated soil. Anthropogenic lead persists in urban air, albeit at relatively low levels, despite leaded gasoline phase out and stationary emissions curtailment. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Global reductions in atmospheric lead concentrations have been primarily linked to the phase-out of leaded gasoline (US Environmental Protection Agency, 1986; Thomas et al., 1999). This decrease has evoked the proposal that atmospheric lead isotopic compositions are returning to terrestrial values (Shotyk et al., 1998), but until recently the sources of atmospheric lead in air following the elimination of leaded gasoline combustion have not been well documented, especially in urban air (Bollhofer and Rosman, 2000, 2001). Furthermore, few

cities have seen a dramatic reduction in stationary emissions with the simultaneous phase out of leaded gasoline.

One exception is Yerevan, Armenia, where lead emissions from stationary and mobile sources were both curtailed during the 1990s. Stationary source emissions decreased by > 80% in the early 1990s (Fig. 1) (Babayan et al., 1998; Ministry of Nature Protection, 1998b), while emissions from mobile sources reportedly remained high in the first half of the decade due to the continued use of leaded gasoline (COWI, 1998a; Ministry of Nature Protection, 1998b). Subsequent gasoline import data suggest that by 1998 those lead emissions from mobile sources had also decreased sharply due to increased imports of unleaded gasoline from western European

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nations (Table 1). Although recent government reports still identify lead from gasoline emissions as one of the most important environmental health threats in Yerevan (Ministry of Nature Protection, 1998a, b), monitoring for atmospheric lead has not been reported since 1997 (Ministry of Nature Protection, 1998b), and atmospheric lead isotopic compositions have never been measured (A. Gabrielian, pers. comm.).

Consequently, this study focused on quantifying the sources and determining the fate of lead in Yerevan during that transitional period in the past decade. Lead concentrations and stable lead isotope compositions (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) were measured in air, gasoline, soil, and ore deposits in Armenia during the mid to late 1990s, in order to discern the shifting sources of atmospheric lead in Yerevan. Since the lead used in the city at the start of that decade was supplied by the former Soviet distribution network (Y. Poghosian, pers. comm.), these measurements also provide insight into the lead isotopic signatures of past and present emissions from Soviet and Post-Soviet Asia, a poorly constrained component in global studies of atmospheric lead fluxes (Sturges and Barrie, 1989; Hopper et al., 1991; Rosman et al., 1994; Simonetti et al., 1999; Bollhofer and Rosman, 2001) (Fig. 1).

2. Background

2.1. Lead emissions from stationary sources

Following the collapse of the Former Soviet Union (FSU), Armenia's industrial production decreased by about 80% (Ministry of Nature Protection, 1998b; Feyzioglu, 1999). In Yerevan, these reductions occurred at numerous facilities including a lead battery recycling plant, lead crystal and light bulb manufacturing factories, printing factories, and chemical, metallurgical, and electronics plants (Kurkjian, 2000). In the southwest region of Yerevan, there may be industrial emissions that are not accounted for because it is a government facility. However, industrial operations and the associated emissions of air pollutants are still down substantially from 1980 levels (Babayan et al., 1998; Ministry of Nature Protection, 1998b). Based on this continued depression in industrial activity the reported $260\,kg\,yr^{-1}$ of lead emissions from stationary sources in 1995 (Ministry of Nature Protection, 1998b) is tentatively assumed to provide a first order estimate of lead emissions in Yerevan during the latter half of the decade.

2.2. Lead emissions from mobile sources

The atmospheric flux of lead from mobile sources during the mid-1990s in Yerevan can be estimated from

Fig. 1. Republic of Armenia and the surrounding region.

Table 1
Gasoline imports to Armenia, 1996–1998

Country	1996[a]	1997[a]	1998[a]	Maximum estimated lead content[b]	Percent market share of unleaded gasoline
Russia	39.7	84.5	11	0.17–0.37	50
Georgia	24.5	5.1	4.1	0.37	98
Iran	9.7	—	—	0.19	0
Bulgaria	8.7	—	—	0.15	5
Italy	6.9	—	—	0.15	44
Romania	5.6	—	—	0.32	60
Great Britain	4.9	—	59.4	0.15	67
Panama	—	5.1	11	0.82	93
Switzerland	—	2.9	—	0.15	87
Others[c]	—	2.4	14.5	—	—

[a] Percent of total gasoline imports to Armenia (Y. Poghosian, pers. comm.).
[b] COWI (1998a); Lovei (1998); units are $g\,l^{-1}$.
[c] Others may include: Iran, Bulgaria, Italy, Rumania, Great Britain, Japan and Switzerland.
Unleaded gasoline is generally regarded as $[Pb] < 0.026\,g\,l^{-1}$.

government records of the volume of gasoline imported (Table 1) and the reported lead concentrations in the gasoline of supplier nations (COWI, 1998a, b). Those gasoline imports totaled $311,125 \, m^3$ in 1996; and reports indicate all of that gasoline contained lead alkyl additives, although the lead concentration in the imported gasoline was not measured in Armenia (COWI, 1998a). Presumably the lead concentration ranged from 0.15 to $0.37 \, g \, l^{-1}$, based on independent information from some of the gasoline suppliers (COWI, 1998a, b; Davidson, 1998; Lovei, 1998).

Based on these reports, we estimate that in 1996 $> 98\%$ of lead emissions were from the combustion of leaded gasoline. The country's population was officially estimated to have been 3.7 million in 1996 and $\approx 40\%$ of people (and $\approx 40\%$ of vehicles) are located in Yerevan. Accordingly, we estimate that at least $124,450 \, m^3$ of leaded gasoline was consumed in Yerevan in 1996. Assuming the lowest reported lead content ($0.15 \, g \, l^{-1}$) for gasoline imported by Armenia (COWI, 1998a, b) and a 25% retention of that lead within vehicle exhaust systems (Huntzicker et al., 1975), a minimum of $14,000 \, kg$ of lead was emitted from mobile sources in Yerevan in 1996. Since the total emission of lead from stationary sources at that time was $260 \, kg$ (see discussion above), mobile emissions accounted for at least 98% of the atmospheric lead in Armenia in 1996. Therefore, we conservatively estimate that 98% of the lead in soil in Yerevan has accumulated from the deposition of leaded gasoline, a figure consistent with the proportion of atmospheric lead emission coming from gasoline combustion on a global basis during the past 20 years (Nriagu and Pacyna, 1988).

Similar estimates of atmospheric lead emissions for the end of the decade can be calculated using the upper limit for lead concentrations in unleaded gasoline ($0.026 \, g^{-1}$ from Table 1). A conservative estimate yields $3200 \, kg$ of lead emitted in 1998. It is likely that the actual lead emissions from mobile sources are much less because the unleaded gasoline samples measured contained $< 0.1 \times 10^{-3} \, g \, l^{-1}$ of lead.

3. Methods

3.1. Samples

Researchers from the University of California at Santa Cruz (UCSC) and the American University of Armenia (AUA) collected 13 air samples from 1996 to 1999, using trace metal clean techniques (Flegal and Smith, 1995). These samples were collected on acid-clean, 37 mm diameter Teflon® filters (0.45 μm pore size), with a pumping rate of $0.25 \, l \, s^{-1}$ and a sampled air volume ranging from 7 to $21 \, m^3$. The samples were collected at $30 \, m$ above ground level, and, additionally, at $3 \, m$ above ground level in 1999.

At the request of the Armenian Ministry of Nature Protection, which has limited analytical facilities, an additional nine air samples were analyzed at UCSC. These samples were collected from 1995 to 1996 with a pumping rate of $2.4 \, l \, s^{-1}$ and sampled an air volume ranging from 63 to $179 \, m^3$. But the samples were collected on non-acid-cleaned cellulose filters with a pore size of $5 \, \mu m$, 10 times larger than the internationally accepted size of $0.45 \, \mu m$ that is typically used in research on metals in air (Bollhofer et al., 1999; Veron et al., 1999). In addition, before being delivered for analyses, the cellulose filters were not handled in a trace metal clean fashion. Despite the non-standard sampling techniques, we analyzed the samples with the assumption that the amount of contamination in those presumably high lead samples would be relatively small.

Researchers also collected gasoline and soil samples using trace metal clean techniques (Flegal and Smith, 1995). Gasoline samples were collected at sites (16) throughout Yerevan from 1997 to 1999 and aliquots (1 ml) were evaporated in acid-clean Teflon® vials before being transported to UCSC for analysis. Surface (1–2 cm depth) soil samples (24) were collected within $3 \, m$ of the road from uncovered ground (i.e., no vegetation) throughout Yerevan in 1999 and were double bagged in plastic prior to being transported to UCSC for processing and analysis. Ore samples (5) from several locations throughout Armenia were provided by researchers at the Institute of Geosciences of the Armenian National Academy of Sciences.

3.2. Analyses

All of the samples were processed and analyzed in a trace metal clean, HEPA filtered (Class 100) laboratory at UCSC, using high-purity (sub-boiling, quartz double distilled) reagents and high-purity water ($18.3 \, M\Omega \, cm$). Both sets of air filters were leached in $8 \, N \, HNO_3$, evaporated to dryness and reconstituted with $8 \, N \, HNO_3$ and diluted in 10 ml of $1\% \, HNO_3$. Residues from evaporated gasoline samples were dissolved in concentrated HNO_3, evaporated to dryness, reconstituted in $8 \, N \, HNO_3$, and diluted in 10 ml of $1\% \, HNO_3$. Aliquots (0.5 g) of the soil (dried for 3 days at $45°C$) were leached in $6 \, N \, HCl$, centrifuged to separate the leachate, evaporated to dryness, reconstituted in $8 \, N \, HNO_3$, and diluted in 10 ml of $1\% \, HNO_3$ for measurements of their "labile" lead concentrations. Since only isotopic compositions were determined in the lead ores, about 0.02 g of ore was leached in 20 ml of $1\% \, HNO_3$.

Lead concentrations were measured with a Finnigan MAT Element magnetic sector high-resolution inductively coupled plasma source mass spectrometer (ICP-MS). The analyses were made using an external calibration with bismuth added as an internal standard to correct for any instrumental drift or matrix effects

changing the signal intensity. Replicate analyses reproduced the concentration measurements to better than 5% relative standard deviation ($n = 4$). Lead concentrations of procedural blanks (~ 200 ng) were ≈ 1000 times lower than concentrations in the samples.

Lead isotopic compositions were measured with a VG Sector 54 Warp thermal ionization mass spectrometer (TIMS). The analyses were made with aliquots (0.5 ml) that had been purified using Teflon® microcolumns loaded with AG1-X8 75–150 mesh anion exchange resin, flushed with HCl, and eluted with HBr (Flegal et al., 1989, 1993). Mass fractionation corrections were derived from concurrent analyses with a 55 ng ml^{-1} NIST SRM 981 (common lead isotope standard) with the per-atomic mass unit bias correction averaging 0.0011. Average errors (± 2 sigma) for $^{206}Pb/^{204}Pb$ were ± 0.022 for air and gasoline, and ± 0.0013 for soil and ore; $^{206}Pb/^{207}Pb$ errors were ± 0.001 for air and gasoline, and ± 0.00004 for soil and ore; and $^{208}Pb/^{207}Pb$ errors were ± 0.001 for air and gasoline and ± 0.00007 for soil and ore.

4. Results

4.1. Lead concentrations

Atmospheric lead concentrations of samples collected in Yerevan between 1995 and 1999 are presented in Table 2. Samples collected near ground level (3 m) by the Armenian Ministry of Nature Protection in 1995 and 1996 ranged from 0.2 to 0.6 $\mu g\,m^{-3}$. Samples collected (at heights of 3 and 30 m) by UCSC/AUA researchers in 1998 and 1999 are ≈ 1–2 orders of magnitude lower. The latter range from $< 0.04\,\mu g\,m^{-3}$ for samples collected at 3 m to $\leqslant 0.003\,\mu g\,m^{-3}$ for samples collected at 30 m in 1998 and 1999.

Concentrations of lead in gasolines collected in Yerevan between 1997 and 1999 are also presented in Table 2. All of these concentrations are $< 0.1 \times 10^{-3}\,g\,l^{-1}$ of lead. The lead concentration in Armenian gasoline is below the maximum allowable limit ($0.15\,g\,l^{-1}$) in Western Europe.

Concentrations of lead in near-road surface soil samples collected in Yerevan in both April and November 1999 are presented in Table 3. These concentrations range from 46 to 4238 $mg\,kg^{-1}$ (dry weight). The average soil lead concentration of 290 $mg\,kg^{-1}$ ($n = 24$) is 15–30 times higher than the reported natural terrestrial background concentration (10–20 $mg\,kg^{-1}$) in Yerevan's soil, which is the range of concentrations in the mafic lava flows from which the soils are weathered (H. Shahinyan, pers. comm.). This elevated soil concentration average (290 $mg\,kg^{-1}$) is similar to the average soil concentration (240 $mg\,kg^{-1}$) of an investigation of 1035 surface samples collected in Yerevan during 2000–2001 (Dunlap, 2001). Other

studies (Rabinowitz and Wetherill, 1972; Erel et al., 1997; Lankey et al., 1998) have indicated that near-road soil lead is controlled by the deposition of gasoline lead. These soil concentrations are typical of cities where leaded gasoline has been used (Nriagu and Pacyna, 1988; Erel et al., 1997). Moreover, the soil concentration profiles show a gradual decrease in concentration away from the roads further corroborating that mobile emissions were the primary source of lead in the near-road surface soils (Dunlap, 2001).

4.2. Lead isotopic compositions

The lead isotopic compositions for air samples collected in Yerevan in 1995–1996 fall within the range of Yerevan's soil isotopic compositions (Fig. 2). This correspondence is attributed to the historic contamination of the surface soil by prior atmospheric emissions of industrial lead, since it is readily scavenged onto soil particles (Erel et al., 1997). Based on the preceding mass balance calculations in this report, $\sim 98\%$ of the labile lead in that soil was derived from atmospheric emissions from the combustion of leaded gasoline. Stationary emissions from the southwest industrial area ($\sim 6\%$ of total surface area in Yerevan with $^{206}Pb/^{207}Pb < 1.15$) may not be fully accounted for since the amount of historic emissions and the full range of isotopic compositions of lead dispersed from that area are unknown. The estimated predominance of gasoline lead in surface soils may, therefore, be less than our mass balance and isotopic mixing models suggest for that area. Still, the average isotopic composition of surface soils is considered to represent a time-averaged value for gasoline lead throughout the rest of Yerevan.

Assuming that the surface soil lead throughout the non-industrial area of Yerevan (94%) of the city is a binary mixture of past gasoline lead emissions and natural terrestrial lead, plots of 1/[Pb] vs. $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios may be used to estimate the average leaded gasoline isotopic composition. The y-intercepts of these two plots define the average gasoline values ($^{208}Pb/^{207}Pb = 2.442$ and $^{206}Pb/^{207}Pb = 1.157$). This estimate has been substantiated by paired concentration and isotopic composition analyses of blood lead of the inhabitants in Yerevan (Kurkjian and Flegal, 2001). Using the results from the above plots and a background soil concentration of 15 $mg\,kg^{-1}$, a natural end member isotopic composition of $^{208}Pb/^{207}Pb = 2.478$ and $^{206}Pb/^{207}Pb = 1.194$ is yielded.

The lead isotopic compositions for the suite of environmental samples collected in 1998 are plotted in Fig. 3. The lead isotope measurements of individual gasoline samples are averaged to produce a value for the lead composition of gasoline emissions. All of the air isotopic compositions plot at substantially higher $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ values than that of the

Table 2
Lead isotopic compositions and concentrations for air and gasoline in Yerevan, 1995–1999

Sample no.	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	[Pb]
Yerevan air ($\mu g\,m^{-3}$)				
Samples collected by the Ministry of Nature Protection				
MEA1 (5/95)	17.9393 ± 0.0008	1.1513 ± 0.00001	2.4345 ± 0.00004	0.6
MEA2 (6/95)	17.8980 ± 0.0074	1.1486 ± 0.0014	2.4321 ± 0.0014	0.3
MEA3 (7/95)	17.9411 ± 0.0092	1.1517 ± 0.0016	2.4351 ± 0.0016	0.4
ME-A4 (8/95)	17.9061 ± 0.001	1.1495 ± 0.00001	2.4324 ± 0.00004	0.3
MEA5 (9/95)	17.8810 ± 0.024	1.1468 ± 0.0038	2.4325 ± 0.0038	0.4
MEA6 (5/96)	17.9401 ± 0.0068	1.1499 ± 0.0016	2.4347 ± 0.0016	0.5
MEA7 (6/96)	17.9285 ± 0.009	1.1508 ± 0.0016	2.4343 ± 0.0016	0.2
MEA8 (7/96)	17.9439 ± 0.0032	1.1509 ± 0.00002	2.4342 ± 0.00004	0.3
MEA9 (8/96)	17.9106 ± 0.0014	1.1479 ± 0.00004	2.4331 ± 0.0002	0.3
Samples collected by UCSC				
A2 (8/96)	18.0357 ± 0.0166	1.1549 ± 0.0002	2.4390 ± 0.0002	—
A3 (8/96)	17.9450 ± 0.012	1.1515 ± 0.002	2.4344 ± 0.002	—
A4 (8/96)	17.9264 ± 0.084	1.1504 ± 0.002	2.4349 ± 0.002	—
A13 (11/96)	18.0039 ± 0.0068	1.1561 ± 0.00006	2.4371 ± 0.0001	—
A14 (11/96)	18.0753 ± 0.0064	1.1581 ± 0.001	2.4431 ± 0.0002	—
A22 (7/98)	18.0948 ± 0.068	1.1641 ± 0.0008	2.4390 ± 0.0014	0.001
A23 (7/98)	18.4824 ± 0.38	1.1611 ± 0.002	2.4404 ± 0.003	0.001
A24 (11/98)	18.50384 ± 0.002	1.1872 ± 0.00001	2.4720 ± 0.00004	0.003
A25 (11/98)	18.1454 ± 0.10	1.1609 ± 0.0004	2.4420 ± 0.0008	0.002
A27 (1/99)	17.9727 ± 0.04	1.1612 ± 0.0002	2.4391 ± 0.0006	0.001
A28 (2/99)	18.1149 ± 0.02	1.1605 ± 0.0002	2.4417 ± 0.0006	0.002
A30 (10/99)	17.9555 ± 0.004	1.1516 ± 0.00004	2.4253 ± 0.00012	0.039
A31 (11/99)	17.9856 ± 0.008	1.1516 ± 0.0002	2.4334 ± 0.0004	0.037
Gasoline samples ($g\,l^{-1} \times 10^{-3}$)				
September 1997				
G2	18.1724 ± 0.02	1.1655 ± 0.0048	2.4410 ± 0.0048	0.1
G5	17.1061 ± 0.009	1.1052 ± 0.00008	2.3843 ± 0.0002	0.02
G10	18.5395 ± 0.0068	1.1829 ± 0.00008	2.4706 ± 0.00018	0.02
G17	18.1825 ± 0.0048	1.1660 ± 0.00006	2.4414 ± 0.0001	0.1
April 1998				
G22	18.0634 ± 0.12	1.1618 ± 0.01	2.4465 ± 0.001	<0.1
G28	17.7521 ± 0.10	1.1404 ± 0.0006	2.4090 ± 0.0012	<0.1
G29	17.8974 ± 0.002	1.1522 ± 0.0002	2.4213 ± 0.0004	<0.1
G30	17.2059 ± 0.006	1.1084 ± 0.00008	2.3778 ± 0.0001	<0.1
April 1999				
G32	18.0918 ± 0.0028	1.1593 ± 0.00004	2.4445 ± 0.0006	<0.1
G33	17.9779 ± 0.0046	1.1544 ± 0.00006	2.4324 ± 0.00016	<0.1
G34	17.9827 ± 0.008	1.1508 ± 0.001	2.4124 ± 0.0002	<0.1
G35	18.0888 ± 0.0036	1.1587 ± 0.00006	2.4363 ± 0.00012	<0.1
G36	18.0285 ± 0.0082	1.1542 ± 0.0026	2.4399 ± 0.0006	<0.1
G37	—	—	—	0.01
G38	—	—	—	0.004
G40	—	—	—	0.002

Errors shown are ± 2 standard errors on the mean.

gasoline value, and three of those air compositions plot within the range of soil isotopic compositions. The anomalous isotopic composition of the fourth air sample ($^{206}Pb/^{207}Pb = 1.187$) is tentatively attributed to an unidentified source and may correspond to that of a natural terrestrial dust.

The isotopic compositions for the air samples collected at 30 m in 1999 are similar to those collected

Table 3
Lead isotopic compositions and concentrations for soil in Yerevan, 1999. Ore compositions reflect massive sulfide deposits in north and southeast Armenia

Sample no.	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	[Pb] (mg kg^{-1})
Soil				
April 1999				
S1	18.0162 ± 0.0006	1.1545 ± 0.00002	2.4380 ± 0.00004	80
S2	18.0195 ± 0.0017	1.1529 ± 0.00002	2.4373 ± 0.00004	119
S3	18.1054 ± 0.0043	1.1551 ± 0.00006	2.4435 ± 0.0002	110
S4	17.7384 ± 0.0013	1.1357 ± 0.00004	2.4222 ± 0.0001	86
S7	17.9817 ± 0.0010	1.1556 ± 0.00002	2.4381 ± 0.00004	46
S8	18.0259 ± 0.0007	1.1568 ± 0.00004	2.4419 ± 0.00004	89
S9	18.1494 ± 0.0010	1.1598 ± 0.00004	2.4454 ± 0.0001	46
S10	18.1060 ± 0.0009	1.1591 ± 0.00004	2.4446 ± 0.00006	67
S11	18.1664 ± 0.0008	1.1639 ± 0.00002	2.4481 ± 0.00004	56
S13	18.0285 ± 0.0014	1.1542 ± 0.00006	2.4403 ± 0.00008	74
Nov. 1999				
S14	18.0491 ± 0.0012	1.1575 ± 0.00004	2.4350 ± 0.00008	64
S15	18.1306 ± 0.0007	1.1610 ± 0.00004	2.4465 ± 0.00006	82
S16	17.7960 ± 0.0009	1.1422 ± 0.00004	2.4234 ± 0.00006	140
S17	17.8742 ± 0.0013	1.1475 ± 0.00004	2.4271 ± 0.00004	157
S18	17.7604 ± 0.0018	1.1389 ± 0.00004	2.4208 ± 0.00006	256
S19	18.1429 ± 0.0015	1.1613 ± 0.00004	2.4467 ± 0.0001	113
S20	17.8435 ± 0.0015	1.1447 ± 0.00006	2.4258 ± 0.00008	235
S21	18.1248 ± 0.0008	1.1611 ± 0.00002	2.4440 ± 0.00004	60
S22	17.9444 ± 0.0014	1.1517 ± 0.00004	2.4333 ± 0.00006	63
S23	18.0343 ± 0.0011	1.1555 ± 0.00006	2.4390 ± 0.00008	58
S24	18.1488 ± 0.0016	1.1607 ± 0.00004	2.4529 ± 0.00006	203
S25	17.9789 ± 0.0010	1.1537 ± 0.00004	2.4369 ± 0.00008	163
S26	18.2299 ± 0.0013	1.1649 ± 0.00004	2.4461 ± 0.00006	407
S27	18.5765 ± 0.0016	1.1769 ± 0.00006	2.4686 ± 0.0002	4238
Ore				
Ore1	18.2781 ± 0.0005	1.1725 ± 0.00002	2.4621 ± 0.00004	—
Ore2	18.5432 ± 0.0006	1.1887 ± 0.00002	$2.471740.00004$	—
Ore3	18.8885 ± 0.0005	1.2058 ± 0.00002	2.4904 ± 0.00002	—
Ore4	18.2664 ± 0.0006	1.1710 ± 0.00002	2.4614 ± 0.00004	—
Ore5	18.9791 ± 0.0063	1.2057 ± 0.00006	2.4886 ± 0.0002	—

Errors shown are ± 2 standard errors on the mean. Soil concentrations are dry weight.

in 1998 ($^{206}Pb/^{207}Pb \sim 1.161$) and overlap soil values (Fig. 4). The air samples collected near street level (3 m) plot at lower $^{206}Pb/^{207}Pb$ values. The lead isotope measurements of individual gasoline samples are averaged, like 1998, to produce a value for the lead composition of gasoline. The air and gasoline isotopic compositions are decoupled suggesting that a source, other than contemporary gasoline emissions, is dominating the lead signature in air for 1999.

5. Discussion

The overlap of air and soil isotopic compositions and the relatively high atmospheric lead concentrations in 1995–1996 ($\sim 0.4 \mu g\, m^{-3}$) both suggest that the combustion of leaded gasoline was the dominant source of industrial lead emissions in Yerevan during that period. While those atmospheric lead concentrations are circumspect because the sampling techniques may have either undersampled the air (i.e., large filter pore size) or contaminated the samples (i.e., absence of defined trace metal clean techniques), the large volume of air sampled and the relatively high concentrations of lead in the samples minimize those concerns. Moreover, the air concentrations are within the range typical of urban areas where leaded gasoline is consumed (US Environmental Protection Agency, 1986; Thomas et al., 1999), and they are consistent with our mass balance calculations of the predominance (98%) of gasoline lead emissions during that period.
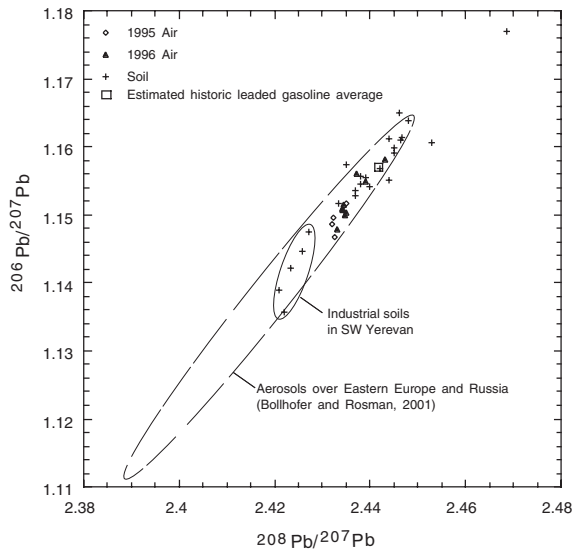
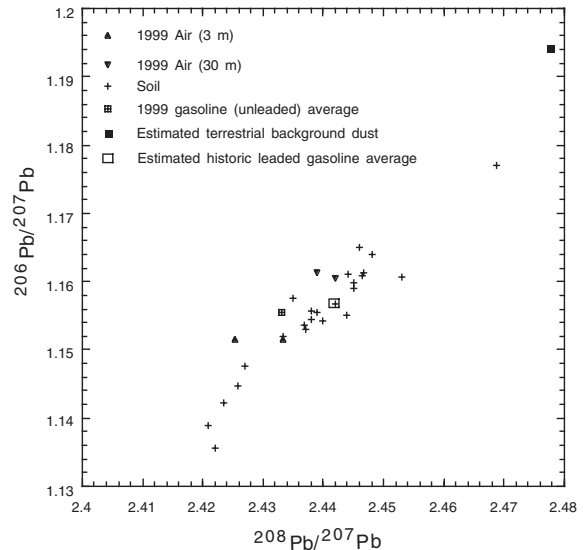Fig. 2. Lead isotopic compositions for air and soil in Yerevan from 1995 to 1996.

Fig. 4. Lead isotopic compositions for air, gasoline, and soil in Yerevan, 1999.
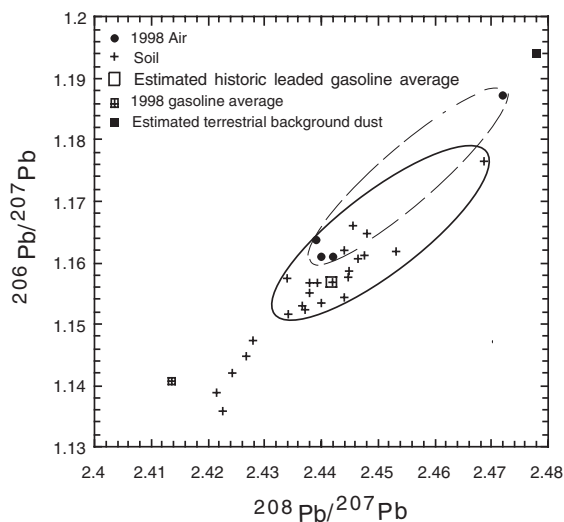

Fig. 3. Lead isotopic compositions for air, gasoline, and soil, in Yerevan, 1998.

Current (1998–1999) atmospheric concentrations of lead are $< 0.04 \, \mu g \, m^{-3}$, an order of magnitude lower than during the time of leaded gasoline combustion. These lower lead levels are indicative of the combustion of unleaded gasoline and also suggest that stationary sources are not contributing a significant lead flux to the atmosphere. Additionally, the atmospheric lead levels are below both the Armenian ($0.3 \, \mu g \, m^{-3}$) and World Health Organization ($0.5 \, \mu g \, m^{-3}$) guidelines for maximum allowable concentration of lead in ambient air (Ministry of Nature Protection, 1998b).

Isotopic compositions of air for 1995 and 1996 in Yerevan fall within the array attributed to Eurasian industrial lead emissions (Fig. 2). These include measurements of lead depositions in Greenland snow cores sources (Rosman et al., 1994), as well as in atmospheric samples (Hopper et al., 1991; Bollhofer and Rosman, 2001). The Yerevan air compositions also fall in the upper range of eastern Europe and Russian regional values (Bollhofer and Rosman, 2001). The similarities in these diverse isotopic composition measurements are consistent with records that indicate that most of the leaded gasoline used in Armenia was imported from the FSU and Eastern Europe during the first half of the 1990s (Table 1).

Similarly, the dramatic shift in isotopic compositions and reduction of atmospheric lead concentrations in 1998 are consistent with records that document the predominance of unleaded gasoline imported from Western Europe during the second half of the decade (Table 1; Fig. 3). All of the gasoline samples measured in 1998 were unleaded and the concentrations of lead in air were two orders of magnitude lower than in 1995–1996 (Table 2). Trace amounts of lead were emitted to the atmosphere by the combustion of unleaded gasoline, but the isotopic composition of the air appears to have a source other than gasoline. This is also illustrated by the decoupling of the lead isotopic compositions in gasoline and air collected in 1998. The overlap of the air and soil isotopic compositions ($^{206}Pb/^{207}Pb \sim 1.16$) suggests that the re-suspension of historically contaminated soils was one of the primary sources of lead to the atmosphere.

As previously noted, the surface soil lead concentrations are on average up to 20 times higher than natural

background levels, and the concentration of total suspended particulate matter (24 h mean concentration) in Yerevan (400–600 μg m^{-3}) is, at times, more than 2-fold higher than the WHO guideline (180 μg m^{-3}) and 8-fold higher than Armenia's maximum permitted concentration of 50 μg m^{-3} (Ministry of Nature Protection, 1998b). Using the average lead concentration in Yerevan's soil, atmospheric lead concentrations in Yerevan may be as high as 0.116 μg m^{-3} during periods of high dust levels. On days when dust levels in the air are 80% lower than 400 μg m^{-3} and when 80% of the dust in Yerevan's air is from sources other than soil (e.g., garbage incineration), the lead from soil alone would still raise the lead concentration in air to 0.005 μg m^{-3}. This input, alone, could account for the maximum level that we measured in 1998 and 1999, but it could not account for the much higher atmospheric lead levels measured in 1995–1996.

One air sample (A24) from 1998 (^{208}Pb/^{207}Pb = 2.4720), plots on the mixing line trending towards the proposed natural endmember of the city's soil (Fig. 3). Although this sample falls within the range of lead in copper ores mined and smelted in Armenia, the smelting occurs on the other side of a mountain range over 100 km north of Yerevan, and lead from the mines has reportedly never been used in Yerevan industry (H. Shahinyan, pers. comm.). Lead for industrial use in the Soviet Union was imported from more lead-rich deposits outside of Armenia. Since the air sample in question was collected on a day when it was raining and wind speed was only 0.51 m s^{-1}, the rain and low wind speed would have suppressed the addition of both city soil dust and anthropogenic emissions to the air. Consequently, the elevated isotope composition on that day is tentatively attributed to advected terrestrial background soil dust.

We, therefore, estimate that 75% of the lead in urban air in 1998 is attributable to past gasoline emissions bound to the city's soil (as represented by the average leaded gasoline isotopic composition), and 25% is attributed to the natural soil-lead in the absence of direct gasoline emissions. The amount of lead in air coming from city soil may approach 100% on days in which dust levels are high.

Isotopic compositions for air samples collected in 1999 at a height of 30 m overlap soil values, consistent with the 1998 samples, and they are also decoupled from the isotopic value of lead measured in unleaded gasoline samples (Fig. 4). The samples taken at 3 m are within the soil field but at lower isotopic values. Although the average gasoline isotope value falls within the range of air values, the amount of lead emitted from unleaded gasoline is very low compared to the calculated lead flux from soil dust (see above). Therefore, we interpret the 3 m air samples (^{206}Pb/^{207}Pb = 1.152) to contain lead from the re-suspension of soil, which may

also be influenced by industrial lead from southwest Yerevan.

6. Conclusion

The lead concentration in Yerevan's air (1998–1999) is at least an order of magnitude lower than during the time of leaded gasoline combustion (1995–1996), and is below applicable guidelines for the maximum allowable concentration of lead in ambient air. This reduction is attributed to the curtailment of both stationary and mobile emissions of lead within the past decade. With the removal of these dominant sources of lead once, the presence of historically contaminated soils now represent a persistent, relatively low level source of atmospheric lead from lingering past emissions. As is the case with air over the European continent (Shotyk et al., 1998; Dunlap et al., 1999), this secondary source of lead exposure may become increasingly important as air quality standards become more stringent over the next decade and stationary source emissions are reduced, especially in developing countries.

Present day lead isotopic compositions in Yerevan's air are controlled by the re-suspension of lead bound to city soil. This soil-bound lead is dominated (98%) by past leaded gasoline emissions. Localized stationary emissions in southwest Yerevan have contributed to soil contamination, but the lead signature in soil throughout the city is predominantly influenced by gasoline lead.

Finally, the range of isotopic compositions of the past industrial emissions bound to Yerevan's soil is $1.1357 \leqslant {}^{206}$Pb/^{207}Pb$\leqslant 1.1649$. This is in the range of industrial lead signatures from other FSU countries that have been, and may still be, actively emitting lead to the atmosphere. This Eurasian lead signature appears to be one of the components in the mixture found in Greenland snow cores as well (Rosman et al., 1994).

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