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Applied Geochemistry xxx (2004) xxx–xxx

Applied Geochemistry

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# Long-range downstream effects of urban runoff and acid mine drainage in the Debed River, Armenia: insights from lead isotope modeling

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Received 4 February 2003; accepted 14 January 2004
Editorial handling by M. Novak

**Abstract**

Lead concentrations and isotopic compositions measured along 80 km of the Debed River in the Republic of Armenia provide new insights into the geochemical and physical controls on riparian Pb transport by allowing comparison of the long-range, downstream impacts of acid mine drainage with runoff from an industrialized city. The modern background Pb concentration in Armenian surface waters is estimated to be ~0.01 μg/L, based on analyses of remote alpine rivers in Armenia. The lead concentration in the Debed River is 8 μg/L (800 times background) after passing through Vanadzor, the second largest industrial city in Armenia; it then decreases to 1 μg/L before the Debed River flows into the Alaverdi mining district. There, the Debed River receives waters from two mining drainage streams with Pb concentrations >3000 μg/L, but those concentrations decrease 3 orders of magnitude to ~3 μg/L by the time the river exits Armenia and flows into the Republic of Georgia.

Isotope mixing plots show shifts in Pb isotope composition as the river flows out of Vanadzor, evidencing the mixture of an average terrestrial Pb composition ($^{206}Pb/^{207}Pb \approx 1.17$; $^{208}Pb/^{207}Pb \approx 2.45$) with past leaded gasoline and other industrial Pb emissions retained in the river's sediments within that region ($^{208}Pb/^{207}Pb \leqslant 2.45$). The isotopic composition again shifts (e.g., $^{208}Pb/^{207}Pb \geqslant 2.46$) as the river passes through the Alaverdi mining district, where isotopic ratios in the water are characteristic of Pb in the area's massive sulfide deposits.

Modeling both downstream elemental concentrations and Pb isotopic compositions further resolves the physical and chemical behavior of the contaminants in the river system. A multi-element model of concentration gradients in the acid mine drainage streams indicates Pb is attenuated by $Al(OH)_3$ precipitation (54% of the loss) and by adsorption onto other particles settling out of the water column (46% of the loss). Modeling of Pb transport in the Debed River indicates the natural outflow of Pb is ~10 kg/a, while the contributions from industrial runoff and acid mine drainage are each ~$10^3$ kg/a, two orders of magnitude greater than the natural flux. Thus, the total annual flux of Pb from the Debed River as it leaves Armenia and flows into Georgia is calculated to be 2500 kg/a. This value is consistent with the average annual Pb flux of 2360 kg/a estimated for the last 20 a. The predicted effects of local climate change over the next 100 a may reduce annual Pb flux by 10–15%, slowing the removal of contaminant Pb and maintaining the two order of magnitude increase over the natural flux.


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doi:10.1016/j.apgeochem.2004.01.024

## 1. Introduction

Recent studies of the effects of acid mine drainage have focused primarily on the geochemical variations that occur within 10 km of mining districts (e.g., Berger et al., 1999; Nordstrom et al., 1999; Benner et al., 2000; Schemel et al., 2000). In these near-source regions, pH shifts and the accompanying precipitation of Fe and Al hydroxides can cause orders of magnitude changes in trace element concentrations (Berger et al., 1999; Schemel et al., 2000). In addition, near-source waters are frequently polluted with mine-derived toxic metals that adversely impact ecosystems in contact with those waters (Lottermoser et al., 1999; Apodaca et al., 2000).

However, the long-range downstream effects of acid mine drainage are much less well studied, especially in comparison to other human impacts on riparian systems. Notably, there is very little information on the long-range transport of contaminant metals and their potentially chronic contamination of rivers downstream from acid mine drainage sites after the rivers cross state and national borders. This paucity of knowledge is especially true in countries with limited resources for environmental monitoring and research, including Armenia.

To understand the magnitude of and geochemical controls on long-range metal transport in such a river impacted by acid mine drainage and urban runoff, the authors measured Pb isotope compositions and major and trace element concentrations in waters along 80 km of the Debed River in Armenia (Fig. 1). The river flows through Vanadzor, the second largest industrial city in Armenia, and then through the Alaverdi mining district (Fig. 2), where open pit mining without waste containment has historically released Cu, Pb, Zn, and other trace metals into the river's tributaries (Vermishev, 1994; Kurkjian, 2000). In addition to sampling the river's waters, Pb isotopic compositions of potential Pb sources in the mining and industrial regions were determined, as well as Pb concentrations in 110 surface water samples from throughout Armenia to provide a context for understanding the impacts of contamination in the Debed River system (Fig. 3).


Fig. 1. Armenia and surrounding region.

These data were used to address several related questions about the origins, long-range transport, and fate of Pb in the river system. The length-scale of downstream impact from both industrial and mining sources was determined from concentration measurements along the Debed River. Lead isotopic compositions provided quantification of the relative contributions of possible sources of Pb to river water, which were not possible with concentration measurements alone. Normalization of those data to other trace metal concentrations evidenced the principal geochemical controls on the behavior of Pb that govern its long-range transport and impact on the river downstream from the study area into neighboring Georgia and ultimately the Caspian Sea.

## 2. Background

The discharge of waste from mining and industry in Armenia, including discharges into the Debed River, has historically been inadequately controlled (Kurkjian, 2000). The river passes through the second largest industrial city in the country, Vanadzor. Then, approximately 40 and 60 km downstream, the river receives acid mine drainage inputs from tributaries flowing through the country's largest Cu mining district centered around the smelter town of Alaverdi (Fig. 2).

The river's drainage basin outside of these industrial and mining regions is dominated by mountainous, undeveloped land. These conditions minimize the influence of other anthropogenic Pb inputs that would complicate the study of the effects of industrial Pb inputs from Vanadzor and Alaverdi. The river system, therefore, provides an excellent setting for comparing the long-range transport of Pb contamination from both urban discharges and acid mine drainage.

As the Debed River passes through Vanadzor upstream of the first sampling point in this study, it flows through Paleogene surface geology and encounters Pb accumulated in the bed sediments from atmospheric deposition, urban runoff, and point source discharges. The high conditional partition coefficient of Pb in sediments ($K_d \geqslant 10^{7.4}$ in river sediments at pH $\sim$ 7) produces strong sediment retention of Pb from past emissions (Benoit, 1995), which have historically been dominated by those from leaded gasoline combustion in Armenia (Kurkjian et al., 2002; Kurkjian and Flegal, 2003). For example, the authors' previous research suggests that in 1996 more than 98% of the Pb emissions in Yerevan, the Armenian capital and industrial center, were from the

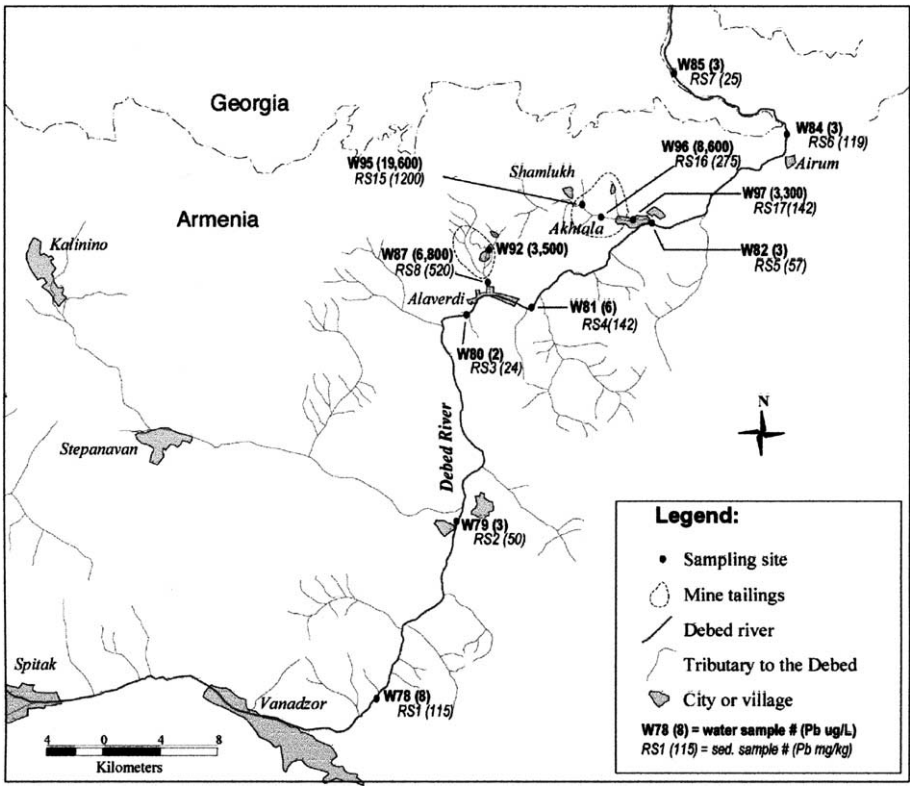


Fig. 2. Alaverdi mining region with sediment and water sample locations.

combustion of leaded gasoline (Kurkjian et al., 2002; Kurkjian and Flegal, 2003). This estimate is consistent with global emission inventories for Pb (Nriagu and Pacyna, 1988) and those in other studies for urban Pb emissions (e.g., Lovei, 1998).

The isotopic composition of leaded gasoline previously emitted in Vanadzor was estimated by comparison to Yerevan because both cities had the same gasoline sources (Kurkjian et al., 2002). Since the average concentration of Pb in near-road soil samples in Yerevan is 290 mg/kg or 15–30 times background concentrations, over 90% of the urban soil Pb in both cities is believed to result from historic atmospheric deposition from leaded gasoline emissions (Kurkjian et al., 2002). This anthropogenic origin has been corroborated by analyses of Pb concentrations in more than 1000 soil samples that showed a consistent decrease in Pb concentrations moving away from roads in Yerevan (C.Dunlap, unpublished data), which is consistent with studies of particle size distributions of Pb emitted from automobiles and deposited near roadways elsewhere (Habibi, 1970; Eldering and Cass, 1996; Lankey et al., 1998). Therefore, the authors infer that the near-road Pb in Vanadzor is similarly dominated by previously consumed leaded gasoline, and the isotopic composition ($^{208}Pb/^{207}Pb = 2.442 \pm 0.003$, 95% confidence on the mean) of this time-averaged soil Pb is used as a proxy for leaded gasoline emissions deposited in the Debed River drainage basin.

After flowing through Vanadzor, the Debed River passes through the Alaverdi mining district (Figs. 2 and 3). Mining and processing of sulfide ores in this district have occurred for centuries, but the rate of ore extraction greatly expanded during 70 a of Soviet occupation (Decaye and Tereshchatova, 2000). At its height, it produced ~50,000 tonnes of Cu/a before being shut down in 1989 for economic, environmental, and political reasons (Levine, 1996; Decaye and Tereshchatova, 2000; Minerals Information Team, 2001). Following the dissolution of the Soviet Union, the Cu mines and smelter were abandoned for nearly a decade, and then re-opened in the late 1990s (Decaye and Tereshchatova, 2000). While production at the mines does not yet approach pre-independence levels, fresh mine tailings are continually being added to those previously deposited along the banks of two tributaries of the Alaverdi and Shamlukh streams, which flow into the Debed River.

Downstream of the mines, the river flows through 30 km of rural farmland, mountains, and undeveloped countryside. There, the regional geology is dominated by Jurasic deposits. The river then flows into Georgia and, ultimately, the Caspian Sea.

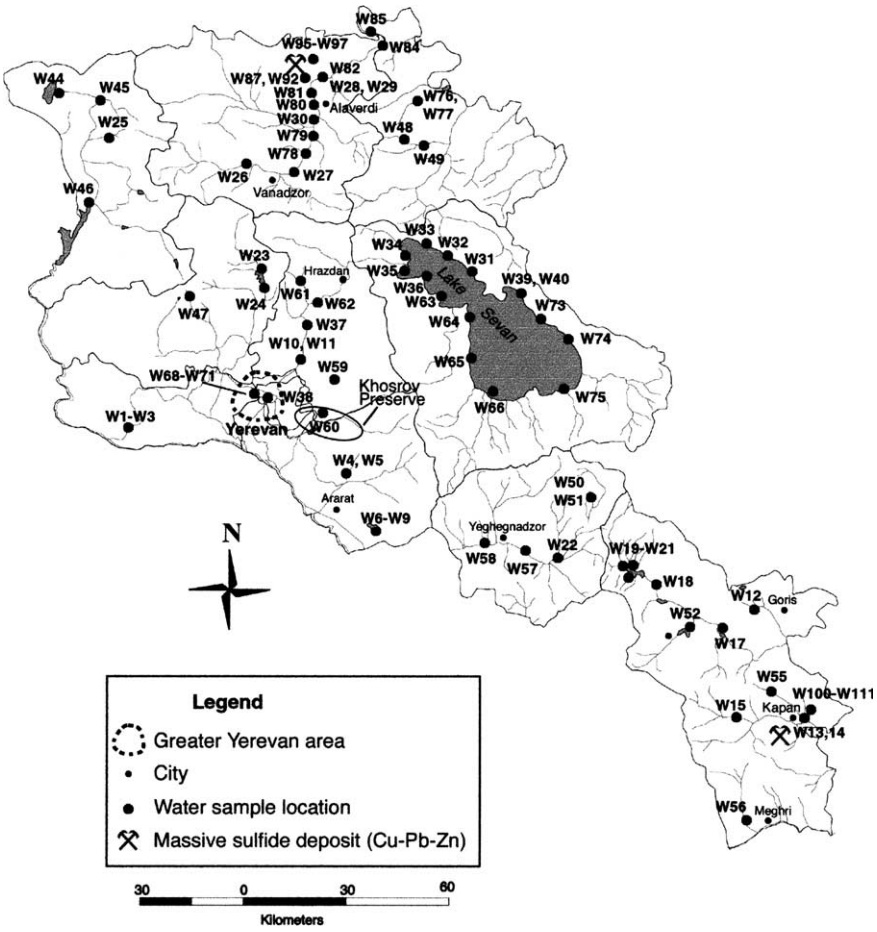


Fig. 3. Surface water sample locations, 1996–1999, Armenia.

As previously noted, there has been little investigation of Pb contamination throughout Armenia, including the Alaverdi mining district (Ministry of Nature Protection, 1998a; Kurkjian, 2000). River water quality has not been regularly assessed during the past 10 a due to Armenia's economic difficulties, and environmental samples in Armenia have never been measured for Pb isotopic compositions (Ministry of Nature Protection, 1998b), prior to the authors' complementary study of urban aerosols and soils (Kurkjian et al., 2002). Consequently, the transport and fate of Pb in Armenia's rivers is poorly understood, and this study provides important insights on contamination both within this region of Armenia and transboundary contamination in the Caucasus.

## 3. Sampling and analytical methods

Four sample sets were collected and analyzed for this study. Water samples were collected from the Debed River and its mining region tributaries, and measured for major and trace element concentrations, Pb isotopic compositions, and ancillary water quality parameters (e.g., pH, temperature, turbidity, and conductivity). To provide a context for interpreting the extent of Pb contamination in the river, a surface water survey was conducted across Armenia with 110 surface water samples collected and analyzed for Pb concentrations. To provide constraints on Pb contributions from the mining source, ore samples were collected from the Alaverdi mining district and analyzed for Pb isotopic composition. And, to gain additional insight into industrial emissions in Vanadzor, two air samples collected there in 1996 were analyzed for Pb isotopic compositions for comparison with those previously collected and analyzed ($n = 22$) in Yerevan (Kurkjian et al., 2002).

More specifically, unfiltered surface water (dissolved and particulate) samples ($n = 110$) were collected throughout Armenia from 1996 to 1999 using trace metal clean techniques (Flegal and Smith, 1995). Of those samples, 16 were collected from the Alaverdi

mining region on two different occasions (4 in November 1996 and 12 in March 1999). Those samples were collected from 3 surface water bodies: (1) the Debed River, before it flows into the mining district; (2) two streams that drain the Cu mines, before they flow into the river; and (3) the river, during and after it flows though the mining district. River sediment was concurrently collected at sites adjacent to the river water sample sites in 1999.

Ore samples from the Alaverdi mining district and air samples from Vanadzor were collected and analyzed for their Pb isotopic compositions. The Institute of Geosciences of the Armenian National Academy of Sciences provided ore samples from two locations in the mining district. Sample "ore-1" is from the Shamlukh Mine and "ore-2" is from the Alaverdi Mine. The air samples were collected in the center of Vanadzor on November 19–20, 1996. Those samples were collected 10 m above street level on acid-cleaned, 37 mm diameter Teflon® filters (0.45 μm pore size), with a pumping rate of 0.25 L/s and a sampled air volumes of 7 and 21 $m^3$.

All of the samples were shipped to the University of California at Santa Cruz (UCSC) for processing and analyses in a trace metal clean, HEPA filtered air (Class 100) laboratory using high-purity acids (Seastar®) and high purity (18.3 MΩ-cm) water (Milli-Q®). The water samples were acidified with concentrated $HNO_3$ to a $pH < 2$, and aliquots (~3 mL) were measured for concentrations. Aliquots (~0.5 g) of sediment were dried for at least 3 days at 50 °C, weighed, and leached in 6 M HCl. The solutions were centrifuged to separate the leachate, evaporated to dryness, and reconstituted in 8 M $HNO_3$.

Both the water and sediment digests were diluted in 1% $HNO_3$ for Pb concentration measurements with a Finnigan MAT Element magnetic sector high-resolution inductively coupled plasma source mass spectrometer (ICP-MS). Elemental analyses were made using an external calibration with a National Research Council of Canada reference material (SLRS-4, riverine water reference material for trace metals). An internal standard ($^{209}Bi$) was added to correct for any instrumental drift in signal intensity. Replicate analyses reproduced the concentration measurements to $\leqslant 5\%$ relative standard deviation (RSD). Lead concentrations of procedural blanks were typically 1000 times lower than the average sample concentrations.

The 1999 Alaverdi water samples were also measured for major cations and trace metal concentrations. Major cation and trace element concentrations from the mining streams and the Debed River were measured on a Perkin–Elmer Optima 4300 DV optical emission spectrometer (OES). Scandium ($^{45}Sc$) was added as an internal standard. The percent recovery ranged from 87% to 106% with the average recovery within ±5%.

For the ore and air samples, only Pb isotopic compositions were determined for use in fingerprinting the industrial sources of Pb. About 0.02 g of ore was leached in 20 mL of 1% $HNO_3$. The air filters were leached in 8 M $HNO_3$, evaporated to dryness, reconstituted in 10 mL of 1% $HNO_3$, processed, and analyzed using the techniques detailed in Kurkjian et al. (2002). Since previous studies have demonstrated that isotopic equilibrium is quickly established between the surfaces of suspended particulates and Pb in the filtered fraction of river waters (Benoit and Hemond, 1991; Dunlap et al., 2000), only unfiltered water samples were collected to study Pb systematics and to calculate the isotopic mass balance.

Lead isotopic compositions in water, sediment, soil, ore, and air were measured with a VG Sector 5430 thermal ionization mass spectrometer (TIMS). The isotopic 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., 1989a; Flegal et al., 1993). Samples were loaded onto Re filaments on silica gel and $H_3PO_4$. Mass fractionation corrections were derived from concurrent analyses with a 55 ng/mL National Institute of Standards and Technology SRM 981 (common Pb isotope standard). Average errors ($\pm 2\sigma$) for $^{206}Pb/^{204}Pb$ were ±0.022 for air and ±0.0013 for soil and ore; $^{206}Pb/^{207}Pb$ errors were ±0.001 for air and ±0.00004 for soil and ore; and $^{208}Pb/^{207}Pb$ errors were ±0.001 for air and ±0.00007 for soil and ore.

## 4. Results

### 4.1. Lead concentrations in surface waters

Lead concentrations measured in 110 surface waters collected throughout Armenia provide an estimate of background Pb concentrations in Armenia's surface waters and context for Pb loading in the Debed River (Fig. 3). Those surface water concentrations fall into 3 categories: (1) remote waters with Pb concentrations <0.01 μg/L; (2) waters passing through populated areas with Pb concentrations from 0.4 to 8 μg/L; and (3) water from acid mine drainage streams (in Alaverdi as detailed in this study, and in Kapan, a southern Armenian mining district) with Pb concentrations >3000 μg/L. The average Pb concentration of rivers in category 2 (the majority of those sampled) was ~1 μg/L, which is taken as a baseline Pb concentration of surface waters in Armenia that pass through populated areas. This baseline concentration is elevated by two orders of magnitude above the Pb concentrations (0.007 μg/L) found in the most remote waters flowing through Khosrov Nature Preserve in central Armenia. In no water samples, outside of the two streams draining mine tailings, was the Pb concentration above the World Health Organization

and United States Environmental Protection Agency's maximum allowable concentration for drinking water of 15 μg/L.

Variations of Pb concentrations measured along the Debed River were used to divide the study area into 3 segments (Fig. 2; Table 1). In the first segment, Pb concentrations decreased as the river flows past Vanadzor into more rural areas. The Pb concentrations in water along this segment decreased from 8 μg/L near Vanadzor to 2 μg/L at the farthest point downstream from Vanadzor before entering the mining district in samples collected in 1999. In the second segment, which is the mixing zone where the Debed River receives water from two tributaries (the Shamlukh and Alaverdi streams) draining the Alaverdi mining district, Pb concentrations in the river ranged from 3 to 6 μg/L, but those within the two tributaries ranged from 19,600 μg/L nearest the mine tailings to 3350 μg/L downstream from tailing piles. In the third segment, which is downstream from the mining district, Pb concentrations appeared relatively constant at ~3 μg/L as the river exits Armenia and flows into Georgia.

Table 1
Pb concentrations (μg/L) and isotopic compositions for surface water, sediment, and ore in Alaverdi, and air in Vanadzor (1996–1999)

| Year collected | Sample no. | | $^{206}Pb/^{204}Pb$ | $^{206}Pb/^{207}Pb$ | $^{208}Pb/^{207}Pb$ |
|---|---|---|---|---|---|
| Water | | [Pb] (μg/L) | | | |
| 1996 | W26 | 0.3 | – | – | – |
| | W27 | 0.3 | – | – | – |
| | W28 | 2.2 | – | – | – |
| | W29 | 1.5 | – | – | – |
| | W30 | 1.3 | – | – | – |
| 1999 | W78 | 7.9 | 18.1277 | 1.1620 | 2.4470 |
| | W79 | 3.4 | 18.1421 | 1.1635 | 2.4474 |
| | W80 | 1.9 | 18.1414 | 1.1648 | 2.4498 |
| | W81 | 5.7 | 18.3329 | 1.1764 | 2.4598 |
| | W82 | 2.6 | 18.2950 | 1.1752 | 2.4584 |
| | W84 | 2.9 | 18.2897 | 1.1739 | 2.4576 |
| | W85 | 2.8 | 18.2739 | 1.1716 | 2.4563 |
| | W87 | 6778 | 18.4933 | 1.1851 | 2.4684 |
| | W92 | 3536 | 18.5152 | 1.1859 | 2.4704 |
| | W95 | 19,594 | 18.5075 | 1.1863 | 2.4696 |
| | W96 | 8602 | 18.4969 | 1.1858 | 2.4691 |
| | W97 | 3350 | 18.5291 | 1.1891 | 2.4707 |
| Sediment | | [Pb] (mg/kg) | | | |
| 1999 | RS1 | 115 | 18.1573 | 1.1625 | 2.4482 |
| | RS2 | 50 | 18.1277 | 1.1615 | 2.4483 |
| | RS3 | 24 | 18.1812 | 1.1678 | 2.4508 |
| | RS4 | 142 | 18.3894 | 1.1802 | 2.4639 |
| | RS5 | 57 | 18.2094 | 1.1685 | 2.4549 |
| | RS6 | 119 | 18.1757 | 1.1652 | 2.4490 |
| | RS7 | 25 | 18.3978 | 1.1748 | 2.4678 |
| | RS8 | 520 | 18.4836 | 1.1850 | 2.4677 |
| | RS15 | 1200 | 18.5526 | 1.1860 | 2.4714 |
| | RS16 | 275 | 18.4990 | 1.1862 | 2.4688 |
| | RS17 | 142 | – | – | – |
| Air | | | | | |
| 1996 | Al | – | 18.0767 | 1.1585 | 2.4424 |
| | A2 | – | 18.0134 | 1.1562 | 2.4382 |
| Ore | | | | | |
| | Ore-1 | – | 18.5432 | 1.1887 | 2.4717 |
| | Ore-2 | – | 18.9791 | 1.2057 | 2.4886 |

Average errors ($\pm 2\sigma$) for $^{206}Pb/^{204}Pb$ were ±0.022 for air and ±0.0013 for soil and ore; $^{206}Pb/^{207}Pb$ errors were ±0.001 for air and ±0.00004 for soil and ore; $^{208}Pb/^{207}Pb$ errors were ±0.001 for air and ±0.00007 for soil and ore.

Table 2
Concentrations (mg/L) of major cations and trace metals in surface waters and field-measured water conditions

| Sample No. | Fe | Mg | Mn | Ca | Al | Na | Sr | Cu | Zn | pH | km | Turbidity (NTU) | Temperature (°C) | Conductivity (mS) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 78 | 1.10 | 11.66 | 0.06 | 51.08 | 1.01 | 23.31 | 0.24 | <0.1 | <0.1 | 6.6 | 0.0 | 110 | 6 | 0.48 |
| 79 | 0.72 | 12.99 | 0.06 | 57.37 | 0.72 | 24.22 | 0.28 | <0.1 | <0.1 | 6.6 | 14.6 | 20 | 6 | 0.47 |
| 80 | 0.61 | 10.41 | 0.04 | 41.51 | 0.63 | 15.94 | 0.22 | <0.1 | <0.1 | 5.9 | 32.6 | 20 | 7 | 0.34 |
| 81 | 0.99 | 10.10 | 0.06 | 39.74 | 0.93 | 15.25 | 0.20 | <0.1 | <0.1 | 6.6 | 38.0 | 20 | 8 | 0.35 |
| 82 | 0.67 | 10.25 | 0.04 | 40.91 | 0.65 | 15.84 | 0.21 | <0.1 | <0.1 | 6.6 | 49.5 | 50 | 8 | 0.35 |
| 84 | 0.74 | 10.33 | 0.04 | 40.04 | 0.71 | 17.32 | 0.20 | <0.1 | <0.1 | 6.6 | 62.6 | 20 | 8 | 0.37 |
| 85 | 0.68 | 11.09 | 0.04 | 43.29 | 0.68 | 19.20 | 0.22 | <0.1 | <0.1 | 6.6 | 73.3 | 20 | 8 | 0.38 |
| 87 | 45.13 | 37.79 | 1.48 | 103.79 | 15.54 | 13.11 | 0.35 | 4.82 | 4.04 | 4.4 | – | 420 | 4 | 0.91 |
| 92 | 0.92 | 23.05 | 0.19 | 125.63 | 0.66 | 17.55 | 0.39 | 0.33 | 5.83 | – | – | – | – | – |
| 95 | 15.29 | 104.43 | 4.41 | 344.06 | 22.97 | 12.11 | 1.02 | 17.61 | 106.86 | 3.6 | 0.0 | 30 | 4 | 2.4 |
| 96 | 42.84 | 22.89 | 1.20 | 73.06 | 15.13 | 7.33 | 0.28 | 7.78 | 11.28 | 4.0 | 1.3 | 350 | 3 | 0.72 |
| 97 | 16.21 | 32.02 | 1.27 | 94.18 | 7.67 | 13.87 | 0.38 | 2.86 | 4.08 | 5.6 | 3.6 | 110 | 5 | 0.73 |

Distance given in km is downstream distance with the first sample on each stream marking the 0 km starting point.

### 4.2. Elemental concentrations in surface waters

Major cation and other trace element concentrations of the Debed River waters and mining stream waters collected in 1999 also exhibited pronounced spatial gradients (Table 2). For example, most elemental concentrations show the most recognizable trends in the Shamlukh stream, where – as with Pb – Al, Cu, and Zn concentrations rapidly decreased downstream towards the confluence with the Debed River (Fig. 2). In contrast, Fe concentrations exhibited an initial increase and then remained relatively constant along the rest of the transect.

### 4.3. Water quality parameters

Other water quality parameters (pH, temperature, turbidity and conductivity) in the Debed River and mining stream samples taken in 1999 were consistent with the elemental data (Table 2). The pH of the Debed River was 6.6 along all segments, while the pH in the Alaverdi and Shamlukh streams ranged from 3.6 to 5.6. Turbidity was highest in the mining district stream waters with one sample from the Alaverdi stream having the highest turbidity: 420 NTU (nephelometric turbidity units). Although turbidity along the river was typically 20 NTU, the sample collected nearest to Vanadzor in segment one had a turbidity of 110 NTU.

### 4.4. Lead concentrations in sediment

Lead concentrations in river sediments paralleled the water concentrations in the Debed River and mining stream samples (Table 1; Fig. 2). The highest concentrations in the river were found in the sample from segment one taken nearest to Vanadzor (RS1 = 115 mg/kg) and in one sample from segment two downstream of the confluence with the Alaverdi mining stream (RS4 = 142 mg/kg). The concentrations of Pb in sediments in the Alaverdi and Shamlukh mining streams ranged from 275 to 1200 mg/kg, and were often markedly higher than those in the river sediments.

### 4.5. Lead isotopic compositions

Pb isotopic compositions in river waters and sediments, mining stream waters and sediments, air from Vanadzor, and ores from the Alaverdi mining district also varied markedly (Table 1; Fig. 4). The $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios in the first segment of the river, where it leaves Vanadzor, were the least radiogenic measured in the study area. In segment two of the river, following input from the Alaverdi mining stream, the isotopic composition of the water increased ($^{208}Pb/^{207}Pb = 2.460$), and then decreased slightly after the input of the Shamlukh stream ($^{208}Pb/^{207}Pb = 2.458$). The

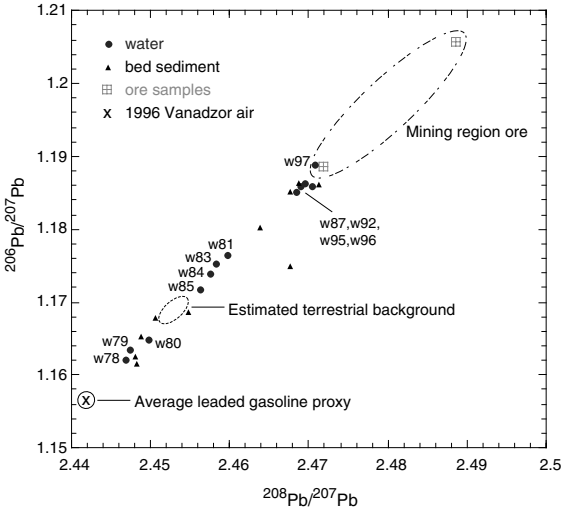


Fig. 4. Lead isotopic compositions for water, sediment, ore, and air.

average isotopic composition of the mining drainage streams was $^{208}Pb/^{207}Pb \approx 2.470$.

The latter ratio contrasted with the average Pb isotopic composition of the air samples collected in Vanadzor ($^{208}Pb/^{207}Pb = 2.440$ and $^{206}Pb/^{207}Pb = 1.157$). These ratios were consistent with those estimated (Kurkjian et al., 2002) for the historic average of leaded gasoline emissions in Yerevan ($^{208}Pb/^{207}Pb = 2.442$ and $^{206}Pb/^{207}Pb = 1.157$). As previously indicated, all of Armenia's gasoline was imported through Yerevan, and distributed throughout Armenia. During the time the air samples were taken in Vanadzor, the gasoline contained Pb alkyl additives with estimated Pb concentrations ranging from 0.15 to 0.37 g/L (COWI, 1998).

## 5. Discussion

### 5.1. Lead concentrations in water

In the first segment of the Debed River, upstream of the mining district, Pb contamination is primarily attributed to past gasoline emissions deposited in and subsequently released from riverbed sediments around and downstream from Vanadzor. In 1996, the average Pb concentration in water collected from the river (0.9 μg/L) is similar to Armenia's countrywide baseline Pb concentration (1.0 μg/L). The higher (2- to 26-fold) Pb levels in this segment of the river collected in 1999 are attributed to higher surface runoff. In contrast to the clear, dry weather during sampling in 1996, sampling in 1999 was during a period when recent spring snow was observed to be melting off and advecting soil into the Debed River. This temporal variation in non-point source discharges of historic atmospheric deposition from the combustion of leaded gasoline in the Debed River in Armenia is consistent with observations of temporal fluxes of industrial Pb in the Sacramento River in California (Steding et al., 2000). Both studies attest to the slow transport of contaminant Pb within a drainage basin.

Similarly, surface waters in the mining district exhibited elevated levels of Pb resulting from increased surface runoff in 1999 compared to 1996. In the Shamlukh stream, Pb concentration increased by nearly a factor of 4000. Snowmelt in the mining district increased both surface runoff and the movement of water through exposed waste piles, leaching and transporting Pb into the two mine drainage streams. The 32% increase in mining production in Alaverdi between 1996 and 1999 (Ministry of Nature Protection, 1998a; Decaye and Tereshchatova, 2000) created fresh tailing piles, further contributing to the effects of surface runoff in 1999.

### 5.2. Modeling lead variation in the Debed River system

An exponential decay equation provides a first-order approximation of the behavior of a non-conservative substance introduced into a river (Thomann and Mueller, 1987)

$$C = C_0 e^{(-Kx)},$$

where $C$ is the concentration of the element at downstream distance $x$, $C_0$ is initial concentration (i.e., at $x = 0$), $K$ is decay rate (per km) and $x$ is downstream distance (km).

The equation describes the exponential decrease in concentration of a substance, asymptotically approaching zero concentration downstream from its place of introduction. The decrease of Pb concentration in river water is controlled by the physical settling-out of sediment carrying adsorbed Pb and by chemical processes that scavenge dissolved Pb (e.g., complexation and precipitation). In the two mining streams, application of the exponential decay model provides insight about the relative importance of the chemical and physical processes controlling downstream changes in the concentrations of Pb and other trace elements.

In the two mining streams, the loss of Al downstream correlates to the loss of Cu and Pb mobilized in the streams. This gradient is consistent with those in numerous reports on acid mine drainage, where the increase of pH downstream causes precipitation of Fe and Al hydroxides that complex and remove trace metals (Anderson and Benjamin, 1990; Berger et al., 1999). The decrease in trace element concentrations in the Alaverdi and Shamlukh streams correlates with that of Al, but not with that of Fe, indicating that scavenging of those trace elements is also dominated by $Al(OH)_3$ precipitation.

The loss of Al in the Shamlukh stream was, therefore, modeled using the exponential decay equation. The decay rate ($K$) that provides the best-fit model for Al is lower than those for Cu and Pb models, suggesting that the precipitation and settling out of Al hydroxides cannot completely account for the downstream loss of Cu and Pb in the mining streams (Fig. 5). The modeled decay rates in the Shamlukh stream for Cu and Pb are almost identical (0.57), while the decay rate for Al (0.31) is 46% lower than those rates. Consequently, in relative terms, the loss of Al appears to account for ~54% of the loss of Cu and Pb downstream and the remaining loss (46%) of those elements is tentatively attributed to adsorption onto other particles settling out of the water column.

Results of the empirical and modeled concentrations for Al, Cu, and Pb in the Shamlukh stream exhibited a similar trend (Fig. 5). However, the water sample collected from the Debed River at the confluence of Shamlukh stream (W82) had consistently lower measured concentrations for each element relative to their modeled value. This disparity is likely the result of dilution within the river that is not accounted for in the model. The difference in water temperature of the Shamlukh stream (5 °C) and the Debed River (8 °C) may also play a role, because the colder stream water

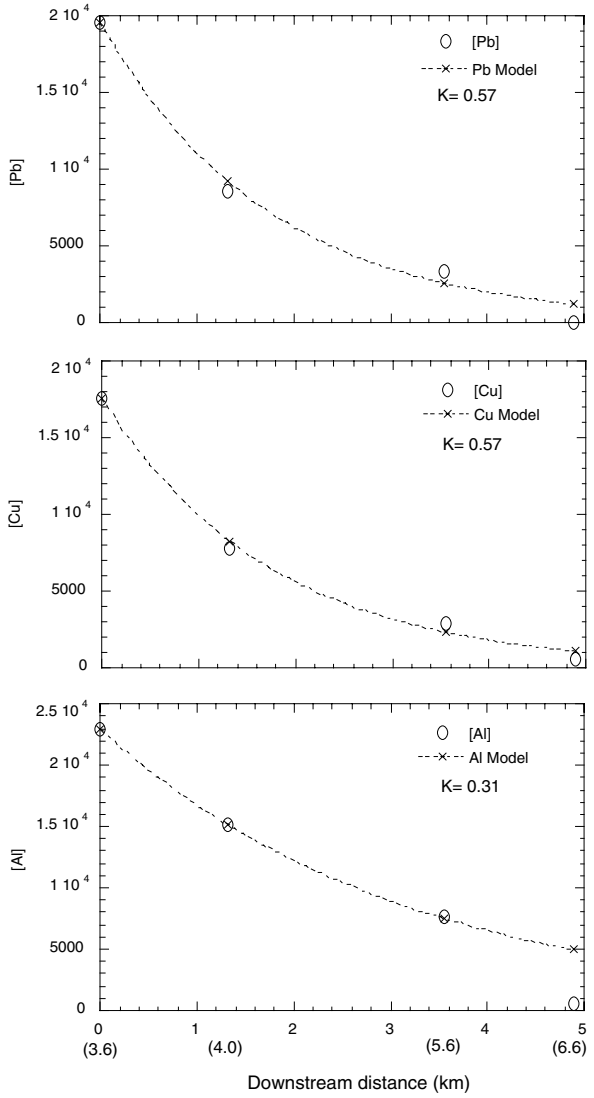


Fig. 5. Distance (km) vs. element concentrations (μg/L) for water samples W95, W96, W97, and W82 for Pb, Cu, and Al in the Shamlukh stream of the Alaverdi mining district. The pH values are shown in parenthesis.

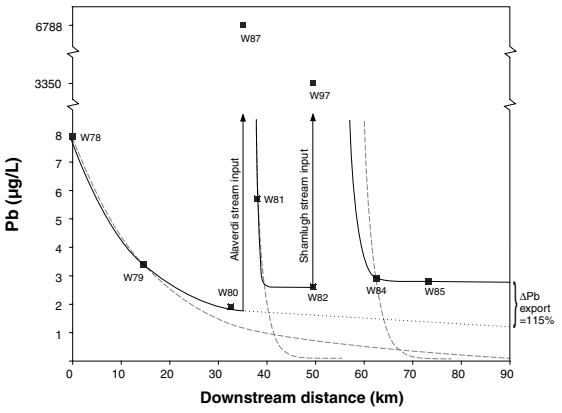


Fig. 6. Trendlines of decay models for Pb concentrations along the Debed River. Dashed lines are the best model fits for a simple decay model with no Pb contribution from river bed sediments. Solid black lines are the best fits for decay models that include a term for Pb flux out of river bed sediments. The black dashed line is the propagation of the solid black line, showing the concentration trend that the Debed River may have followed if the mining district was not present. The calculated increase in Pb concentration in the Debed River due to inputs from the mining district is 115% (see text for full discussion).

presumably forms a wedge of higher density that flows beneath the less dense, warmer surface water in the river, where the samples were collected.

In the absence of pH-induced hydroxide formation in the Debed River, downstream Pb loss appears to be controlled by particle settling (Fig. 6). This is illustrated by an exponential decay model constructed for each of the 3 segments of the river, as previously defined by Pb concentration gradients. In all segments, however, the exponential decay model underestimates the downstream concentrations (dashed curves in Fig. 6).

In order to refine the model and better approximate the river system's behavior, the addition of Pb from an internal source, resuspended bed sediment, was considered. A revised equation is used to include an internal source contribution: $C = C_0 e^{(-Kx)} + I_s$. The latter constant, $I_s$, is the contribution of Pb from bed sediment suspended into the water column.

This revised model (indicated by solid curves) closely fits the observed data trends. In the first segment of the river, the best-fit value for $I_s$ is 1.3 μg/L, indicating that 1.3 μg/L of Pb is contributed to the water column from suspended bed sediment. In the mining district the value of $I_s$ used in the model for the Debed River after the first mining stream input of Pb is 2.6 μg/L, and the value of $I_s$ used to model the behavior of Pb in the river after the second mining stream input is 2.8 μg/L. The higher values of $I_s$ required to model Pb concentrations as the Debed River flows through the mining regions suggest that the acid mine drainage into the river has increased the average Pb concentration in Debed River bed sediments.

The dotted curve in Fig. 6 is a propagation of the modeled trend in Pb concentration for the first segment of the Debed River, disregarding input from the mining region. Comparison of this modeled trend to the actual trend of Pb concentrations in the river as it leaves Armenia provides a measure of the increase in transboundary Pb flux into Georgia due to contamination from the mining district: the measured transbounday flux is 115% greater than the modeled estimate of its value in the absence of the mining drainage inputs. Therefore, the mining district produces a doubling of the amount of contaminant Pb transported into Georgia via the Debed River.

### 5.3. Lead concentrations in sediment

The trend in Pb concentrations in sediment mimics that of Pb in water. The southern-most water (W78) and sediment (RS1) samples collected from the Debed River contained the highest Pb concentrations upstream of the mining district. Sample W78 also had the highest turbidity measurements in the river. Since more than 97% of Pb is bound to particulates in natural waters (Benoit, 1995), this gradient is tentatively attributed to the turbulent resuspension of sediment that has been chronically contaminated by gasoline Pb emitted in Vanadzor.

### 5.4. Lead isotopic compositions in the Debed River system

A plot of [1/Pb] vs. $^{208}Pb/^{207}Pb$ shows two inferred Pb isotopic mixing trends in the Debed River (Fig. 7). The source mixing suggested here confirms the interpretation of the trace element concentration data and modeling. That is, Vanadzor and the Alaverdi mining district contain the two dominant human sources of Pb to the river system: past leaded gasoline emissions retained in soils and mining district Pb. As the Debed River flows north from sample W78, gasoline Pb in the river appears to be diluted (both in concentration and radiogenic Pb composition) by a source that the authors ascribe to average regional terrestrial (crustally derived) Pb. After the river receives discharge from the two mining streams at Alaverdi, the isotopic composition of the water increases from $^{208}Pb/^{207}Pb = 2.45$ (W80) to $^{208}Pb/^{207}Pb = 2.46$, the isotopic composition then begins to return to the inferred average terrestrial isotopic value (and lower Pb concentration) as the Debed River flows out of Armenia.

Fig. 7 indicates what the authors infer to be 3 Pb components in the river water: one component with $^{208}Pb/^{207}Pb \leqslant 2.447$, a second with $^{208}Pb/^{207}Pb > 2.470$, and a third component with intermediate isotopic composition ($^{208}Pb/^{207}Pb \approx 2.453$). The first component

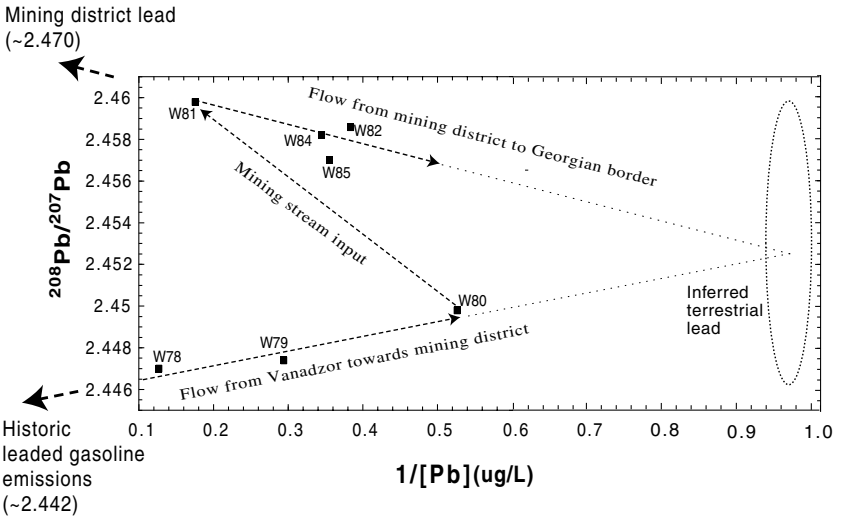


Fig. 7. Binary mixing trends inferred for Pb along the Debed River. The dotted ellipse encloses an estimated range for the isotopic composition of a terrestrial Pb end member. This range of values is suggested by the convergence of two binary mixing lines: (1) as the Debed River leaves Vanadzor (before receiving mine drainage) and (2) as the Debed River leaves the Alaverdi mining district. Derivation of the isotopic composition for historic leaded gasoline emissions and for the mining district are discussed in the text.

corresponds to leaded gasoline isotopic compositions, and the second component corresponds to the composition of Pb in the Alaverdi mining district, as mixed into the two mining streams. The third component is an average terrestrial Pb isotopic value derived from the graphical intersection of the two mixing trends in the river system (Fig. 7). A similar plot constructed for $^{206}Pb/^{207}Pb$ isotopic compositions yields a $^{206}Pb/^{207}Pb$ ratio $\approx$1.167 for this average terrestrial value.

As demonstrated in other systems, Pb isotopic compositions may be used to trace contributions from different anthropogenic and natural sources in the environment (Flegal et al., 1989b; Rosman et al., 1993; Ritson and Flegal, 1994; Veron et al., 1999; Chiaradia and Cupelin, 2000; Bollhofer and Rosman, 2001). Specifically, isotope mixing can be used to quantify contributions from each source when the isotopic signatures of the sources are well constrained (Ritson et al., 1994; Rosman et al., 1998; Chiaradia and Cupelin, 2000; Dunlap et al., 2000; Steding et al., 2000).

However, the estimated average terrestrial isotope composition in the Debed River study area is not sufficiently constrained to allow source component mixing to be precisely quantified. Because the Debed River crosses from Paleogene surface geology near Vanadzor into Jurassic deposits from Alaverdi northwards to the Georgian border, it is likely that the terrestrial Pb isotope composition near Vanadzor differs from that prevailing once the river enters the mining district. The average value that is calculated is therefore insufficient to allow the calculation of percentage contribution from each source in the two binary mixing trends that are observed (Fig. 7). The isotopic compositions are, however, consistent with the concentration data, which suggest that Pb concentrations in the Debed River are dominated by human inputs.

### 5.5. Lead washout and transboundary flux

Transboundary Pb flux from the Debed River is calculated by combining the measured and modeled Pb concentration measurements with annual discharge data for the Debed River (V. Sargsyan, pers. commun.). Three transboundary Pb fluxes can be calculated: the total Pb flux into Georgia, the Pb flux due to gasoline Pb from Vanadzor, and the Pb flux from the Alaverdi mining district. The total transboundary Pb flux for 1999, assuming a constant 2.8 μg/L Pb concentration as measured near the Georgian border, is calculated to be 2526 kg/a. The transboundary Pb flux attributed to Pb originating from Vanadzor can be calculated by using the modeled Pb concentration in the absence of any mining inputs (black dotted curve, Fig. 6). As the Debed river crosses the Georgian border, the model predicts a Pb concentration of 1. 3 μg/L from Vanadzor, corresponding to an annual flux of 1173 kg/a (or 46% of the calculated annual flux). Calculated by difference, the mining district contributes a transboundary Pb flux of 1353 kg/a (or 54% of the total). Consequently, these analyses suggest that the mining district causes an increase in Pb exported into the neighboring country of Georgia by 115% more than the levels upstream of the mining sites in Armenia.

### 5.6. Long-term temporal trends

Lead flux estimates for 1999 as calculated above can be further refined: the Pb concentrations measured in the Debed River in 1996 and 1999 can be used to estimate the variations in transboundary Pb flux from the Debed River over the last 20 a. The 1996 samples were taken during the annual September–February dry season, when lower surface runoff and lower river discharge would be expected to produce yearly lows in Pb flux in the river. In contrast, the 1999 samples were taken during the March–August period when both precipitation and runoff are elevated, as observed on the days when the samples were taken. The data from 1996 to 1999 can, therefore, be used as proxies for low-flow and high-flow Pb flux; they can be combined with monthly discharge data for the last 20 a (V. Sargsyan, pers. commun., 2003) to provide a first-order estimate for yearly and decadal variations in transboundary Pb flux. In making this estimate, the transboundary Pb flux from September to February is taken to be 1.5 ng/L, an estimate of the 1996 (low-flow) Pb concentration as the Debed River crosses the border and flows out of Armenia. During the high-flow season from March to August, the value of 2.8 ng/L, calculated from 1999 data, is taken to represent the high-flow Pb concentration as the river leaves Armenia.

The resulting 20 a record shows that both 1996 and 1999 were typical years for transboundary Pb flux from the Debed River (Fig. 8). Because this estimate implicitly couples Pb flux with precipitation and runoff (as represented in discharge measurements), the relatively dry years of 1985, 1989, and 2000 show the lowest Pb flux in the last two decades, while the very wet year in 1988 shows the highest. The average estimated Pb flux over the 20 a period from 1991 to 2001 is 2360 kg/a. The results of this study are consistent with estimates of the transboundary Pb flux from the river during the last 20 a. However, a predicted consequence of local climate change over the next 100 a in Armenia (Ministry of Nature Protection, 2000) indicates a 10–15% reduction in precipitation, and the associated decrease in surface runoff would slow the process of Pb washout from the river system.

### 5.7. Lead washout from the river system

Because concentrations of Pb in water would be very low in the absence of resuspended sediment, it is the contamination of the river's bed load by mining streams that sustains the elevated flux. The high partition coefficient for Pb in sediment suggests that the sediment will retain mining contamination as the bed load is transported downstream. The effects of mining contamination may persist for tens of kilometers, as a conservative estimate. Inattention to proper containment of the mine tailings has, therefore, produced chronic contamination of the Debed River.

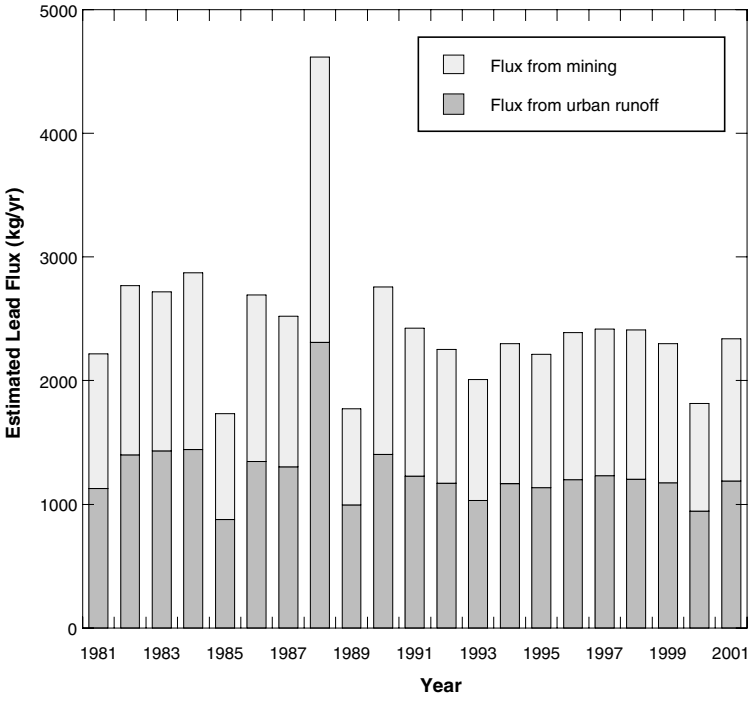


Fig. 8. Estimated annual Pb flux from the Debed River as it exits Armenia and enters Georgia. The natural lead flux is 10 kg/a.

The flushing of Pb from this riverine system is limited by the high partition coefficient ($K_d \geqslant 10^{7.4}$) for Pb in suspended sediments. As observed in rivers elsewhere, transport of these particle-reactive contaminants is a slow process (Dunlap et al., 2000; Steding et al., 2000). With the elimination of Pb sources to the Debed River, washout of the contaminated bed sediments resulting from both the mining activities and the Vanadzor input would likely take decades, if not centuries. However, with the renewed and expanded mining activities in Alaverdi, mining inputs will likely dominate the Pb signature in the segment of river that flows through the mining district, and influence the water and sediment concentrations and compositions even farther downstream.

## 6. Conclusion

Lead concentrations and isotopic compositions of water samples show that the transport of Pb in the Debed River can be modeled as at least a 3-component system. The primary inputs to the river have been chronic contamination from historic emissions of leaded gasoline ($^{208}Pb/^{207}Pb < 2.442$), Pb advected via acid mine drainage from tailings deposits ($^{208}Pb/^{207}Pb \geqslant 2.47$), regional terrestrial background Pb near Vanadzor and Alaverdi (average $^{208}Pb/^{207}Pb \approx 2.453$). An isotopic mixing plot suggests that along the Debed River between Vanadzor and the Alaverdi mining district in the river is dominated by a mixture of past leaded gasoline emissions and Paleogene terrestrial background Pb. However, once the river flows through and exits the Alaverdi mining district, its Pb isotope composition evidences mixing of Jurassic terrestrial background Pb with that from the mine tailings.

The rapid decrease in metal concentrations (e.g., Cu and Pb) in the Shamlukh stream draining the Alaverdi mines is attributed almost equally to co-precipitation with Al hydroxides (54%) and other particulate adsorption and settling (46%). These processes reduce Pb concentration in the water by 83% along a 3.5 km segment of the stream. Despite the rapid attenuation of Pb concentrations in mining stream waters before entering the Debed River, the contribution from the mining district more than doubles the Pb flux in the river as it leaves Armenia. This contamination is attributed to the ongoing advection of uncontained mine tailings into the Debed River, contaminating the bed sediments.

The increase in transboundary Pb flux due to past gasoline emissions and mining operations in northern Armenia will persist for decades, if not centuries. Predicted reductions in precipitation resulting from local climate change will only prolong the process of contaminant Pb washout, and will do little to mitigate the two order of magnitude surplus of anthropogenic Pb flux in the Debed River.

## Acknowledgements

The authors are grateful for the technical assistance provided by Rob Franks and Pete Holden. We also thank Mihran Aslanian, Hrach Shahinian, Vilik Sargsyan, and The Institute of Geosciences of the Armenian National Academy of Sciences for assisting with sample collection and providing background information. This research was supported by the University of California Toxic Substances Research and Teaching Program, NATO Linkage Grant No. 974677, and the Sarkis Acopian Endowment at the American University of Armenia.

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