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Childhood lead poisoning from the smelter in Torreón, México

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ABSTRACT

Lead concentrations and isotopic compositions in blood samples of 34 children (ages 2–17 years) living within a 113 km^2 area of a silver–zinc–lead smelter plant in Torreón, México were compared to those of associated environmental samples (soil, aerosols, and outdoor and indoor dust) to identify the principal source(s) of environmental and human lead contamination in the area. Lead concentrations of soil and outdoor dust ranged 130–12,050 and 150–14,365 $\mu g\ g^{-1}$, respectively. Concentrations were greatest near the smelter, with the highest levels corresponding with the prevailing wind direction, and orders of magnitude above background concentrations of 7.3–33.3 $\mu g\ g^{-1}$. Atmospheric lead depositions in the city varied between 130 and 1350 $\mu g\ m^{-2}\ d^{-1}$, again with highest rates <1 km from the smelter. Blood lead (PbB) concentrations ($11.0 \pm 5.3\ \mu g\ dl^{-1}$) levels in the children ranged 5.0–25.8 $\mu g\ dl^{-1}$, which is 3–14 times higher than the current average ($1.9\ \mu g\ dl^{-1}$) of children (ages 1–5 years) in the US. Lead isotopic ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) of the urban dust and soil (1.200 ± 0.009, 2.467 ± 0.003), aerosols (1.200 ± 0.002, 2.466 ± 0.002), and PbB (1.199 ± 0.001, 2.468 ± 0.002) were indistinguishable from each other, as well as those of the lead ores processed at the smelter (1.199 ± 0.007, 2.473 ± 0.007). Consequently, an elevated PbB concentrations of the children in Torreón, as well as in their environment, are still dominated by industrial emissions from the smelter located within the city, in spite of new controls on atmospheric releases from the facility.

1. Introduction

Although great strides have been made in reducing environmental lead pollution over the past several decades, the metal is still ranked second on the US Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Priority List of Hazardous Substances (http://www.atsdr.cdc.gov/cercla/). Moreover acute environmental lead pollution continues to be a global problem, particularly around mining and smelting operations (Banza et al., 2009; Bao et al., 2009; Fraser, 2009; Gulson et al., 2009; Munksgaard et al., 2010). This is especially true for children in those areas because of their proclivity to ingest lead through pica and to assimilate a relatively greater amount of inhaled and ingested lead than older individuals (NRC, 1993; Moodie et al., 2010).

Moreover the global emission of lead from primary smelting operations is still substantial, in spite of marked reductions in the use of lead in gasoline additives, paint, and many other industrial uses. Based on reports of emission factors (Skeaff and Dubreuil, 1997) and global production for 2003–2008 (USGS, 2010), we estimate the current global atmospheric flux of lead from smelting and refining non-ferrous metals (primary production of Cu, Ni, Pb, and Zn) alone ranges 25,830–30,800 ton y^{-1} (mean = 28,100 ton y^{-1}). The greatest percentage (~30%) of those emissions is in China, where the emission controls of smelters are relatively limited or non-existent as in the case of the infamous secondary smelting of e-waste in Guiyu (Huo et al., 2007).

Lead emissions from mining and smelting in México are an order of magnitude smaller (~3% of global emissions) than those of China, but they are still substantial (832–1012 ton y^{-1}) and most are from one facility, Met-Mex Peñoles S.A. de C.V. (“Met-Mex”) in Torreón. That smelter went into production in 1902 and was operated with little or no environmental controls for a century, measurably elevating blood lead (PbB) concentrations of the children within the city (Albert and Badillo, 1991; Benin et al., 1999; Valdés-Pérezgasga and Cabrera, 1999; García-Vargas et al., 2001; Albalak et al., 2003). In 1999, México's Environmental Protection Agency (Procuraduría Federal de Protección al Medio Ambiente, PROFEPA) mandated corporate efforts to reduce that lead pollution, clean-up the area, and monitor the adjacent environment (Metals and Minerals Latin America, 2000).

This study, therefore, was designed to assess the efficacy of those efforts and to characterize the current level and source of lead contamination in Torreón. We employed both lead concentration

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and stable lead isotopic composition measurements to "fingerprint" sources of natural and industrial lead in environmental samples and humans, as applied in previous studies of lead contamination of children in mining and smelting communities (e.g., Gulson et al., 1994).

2. Methodology

2.1. Study area

Torreón, population ~577,500 (INEGI, 2005), is located in the State of Coahuila in the center of northern México (Fig. 1). Torreón is the largest city of the "La Laguna" region, was built up around the Met-Mex-Peñoles facility. The facility is the largest producer of refined silver (76.0–118.3 millions of ounces y^{-1}) and metallic bismuth (970–1187 ton y^{-1}) in the world and is now (2002–2009) among the largest producers of gold (0.832–1.742 millions of ounces y^{-1}), refined zinc (225.2–368.7 thousands of ton y^{-1}), lead (113.8–142.5 thousands of ton y^{-1}), and cadmium (753–948 ton y^{-1}) at the global level (www.penoles.com.mx). Met-Mex-Peñoles also produces chemicals, including sodium sulfate, magnesium oxide, ammonium and magnesium sulfate, sulfuric acid, oleum, and antimony trioxide.

In 1999, PROFEPA imposed restrictions for environmental violations to the company after studies found that 2500 children of the 2700 tested had unacceptable levels of lead in their blood (García-Vargas et al., 2001). The smelter company was ordered to reduce the emissions of particles in the smelting operations, which was achieved by the installation of a number of air pollution control advices (e.g., electrostatic precipitators, multicyclones, and wet scrubbers) (www.penoles.com.mx). The company was also ordered to implement a remediation program to clean-up the urban environment within 2 km of the plant. This program included a clean-up of dust in at least 20 neighborhoods around the smelter and the relocation of 400 endangered families. About 120 ton of polluted soil and urban dust were removed. In addition, the company implemented a permanent cleaning post-remediation program based on the routine collection of dust and soil and household cleaning around the smelter. A few months later, in 2000, the restrictions were lifted because PROFEPA determined that the company had met 95% of the environmental conditions imposed.

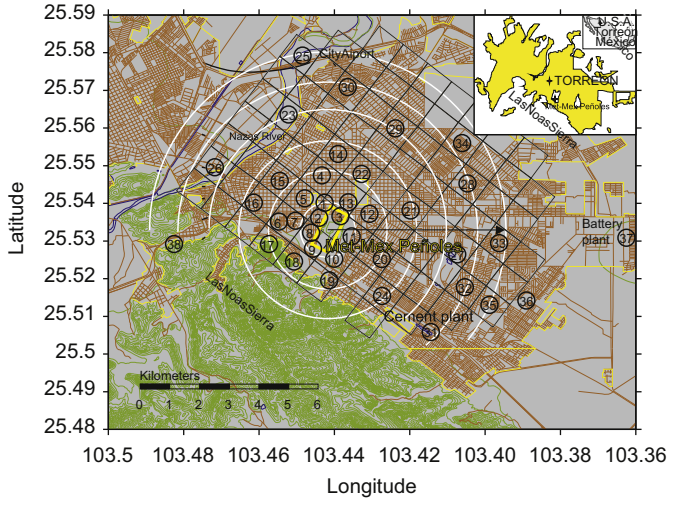

Fig. 1. Study area: Torreón city (NE México). Location of the collection stations (marked with open circles) and the potential Pb sources (Met-Mex Peñoles, Cement and Battery plants and City Airport).

2.2. Study design

Environmental samples (aerosols, soils, and outdoor and indoor dust) were collected with trace metal clean techniques (Flegal and Smith, 1995) in the spring (April, 2005), fall (September, 2005), and winter (February–March, 2006) within a 113 km^2 area surrounding the smelter, along with blood samples of 34 children (ages 2–17 years) living within that area (Fig. 1). Additional samples were collected around a battery manufacturing plant, a cement plant, and the airport, because each of those facilities may account for other sources of lead contamination in Torreón. Other samples of soils and rocks ($n=22$) were collected outside of and upwind from the study area to derive "background" values for lead in the region. Surface (0–2 cm) soils were composites (aliquots of equal amounts from 3 to 5 locations) collected from public gardens and play areas. Outdoor dust was collected with surface swipes (1–2 m^2) from cement tile roofs (ca. 3 m above the street-level) of 39 houses, because dust provides an indirect measure of air pollution integrated over varying time periods (Davis and Gulson, 2005). Indoor dust was collected with established protocols (Lanphear et al., 1999) from window sills in the 22 houses of the children, who lived within the 30 km^2 area surrounding the smelter.

We inspected each of the children's homes to determine whether other sources might be contributing to their lead exposure, and interviewed their parents to determine whether there might be additional sources of lead exposure to the children (Moodie et al., 2010). The interviews included questions about the type and frequency of household cleaning, the last time it occurred, and whether there had been any recent renovations or painting in the dwelling. Since paint may be a source of lead contamination (NRC, 1993), it is notable that none of the children in the study lived in homes with visibly deteriorating or peeling paint.

Aerosols were collected to quantify an atmospheric lead deposition. Acid-cleaned (1 M HNO_3+HCl) acrylic frame plates (1 m^2) were placed 3 m above the ground level and deployed for 8–36 h to collect particulate matter at sites around the Met-Mex facility. The collections were made during dry periods and under stable weather conditions, when wind direction and wind speed represented 60% of the inventoried conditions, based on a 5-year wind rose. Aerosols were also continuously collected over a 14 month period (November 2004–April 2006) at a monitoring station ~1 km northeast of the facility. Those aerosols were collected on acid-cleaned PTFE filters (0.45 μm) placed 3 m above ground level, with a pumping rate of 0.25 l s^{-1} and sampled air volumes of 12–30 m^3.

2.3. Study cohort

The study was limited to children of families living in residential neighborhoods around the smelter, who agreed to participate in the study. A brief questionnaire was completed for each participating child and/or their parents, who provided their written informed consent. Thirty-four (34) children (ages 2–17 years) were included in the study. Their socio-economic backgrounds (e.g., parents' level of education and household income) were similar. Based on interviews, most of those children had been in Torreón since they were *in utero*, and lead concentrations in the children blood (PbB) had previously been measured in ~80% of them. As a consequence of those measurements, four of the children had recently (within a few months to a couple of years) been relocated beyond a 1 km radius of the smelter.

Blood samples (4.5 ml) of the children were collected by medical staff from the Hospital of the University Autonomous of Coahuila (Universidad Autónoma de Coahuila), using trace metal clean techniques and human sampling protocols. Each sample

was placed in a 5 ml test tube containing 0.5 ml of 3.8% sodium citrate solution to prevent coagulation. The samples were immediately refrigerated and shipped overnight (8 h travel time) to a trace metal clean laboratory at the UNAM in Mazatlán, México, where they were refrigerated until they were processed. Aliquots of the blood samples were then transported to another trace metal clean laboratory at the UCSC for additional processing and analyses.

2.4. Analyses

Soil and dust samples were oven dried to a constant weight and sieved (<75 μm) in a trace metal clean laboratory at UNAM. To avoid changes in the physical structure of the soil that could have biased the results, the samples were not ground prior to sieving. To approximate the soil and dust fractions, which is predominantly ingested by children, analyses of lead concentrations and isotopic ratios were limited to smaller (<75 μm) particles, as in the previous studies of soil ingestion and bioavailability (Duggan and Inskip, 1985; Gulson et al., 1995; Calabrese et al., 1996; Mielke et al., 1997; Stanek et al., 1999).

All of the samples were processed and analyzed in HEPA filtered air (Class 1000), trace metal clean laboratories (Flegal and Smith, 1995) using high-purity reagents (trace metal grade) and water (18 MΩ cm; Milli-Q) at UNAM and UCSC. Aliquots of dried, filtered (<75 μm) dust samples were digested with 10 ml concentrated HNO_3:HCl (3:1 v/v) and 2 ml concentrated HF in a block digester at 120 °C for 12 h. Aerosol filters were digested with 10 ml concentrated HNO_3:HCl (3:1 v/v). Approximately 0.3–0.5 g of blood was digested with 5 ml concentrated HNO_3:HCl (3:1 v/v). Digested samples were evaporated to dryness and then dissolved with 1 M HNO_3 for lead concentration measurements.

Lead concentration analyses were made with a Finnigan MAT Element® magnetic sector high-resolution inductively coupled plasma source mass spectrometry (HR-ICP-MS) at UCSC. Accuracy of the analyses was determined with concurrent processing and analyses ($n=6$) of National Institute of Standards and Technology (NIST) standard reference material (SRM) 2584 (indoor dust). Total recovery of lead in the SRM ranged 97–101% with a precision of ±6.0%. The detection limit for lead in blood was <1 μg dl^{-1}. Field and procedural blanks were ≤0.1% of the lowest lead concentrations in aerosols samples.

Lead isotopic compositions were then measured with a Finnegan MAT Neptune® magnetic sector multi-collector, high-resolution inductively coupled plasma source mass spectrometer (MC-ICP-MS) at UCSC. Prior to isotopes analyses, sample solutions were passed through a conditioned AG1×8 anionic resin, using established protocols (Gallon et al., 2008). A thallium standard (NBS 997) was then added to the samples to correct for mass bias correction (Rehkämper and Halliday, 1998). Exponential mass bias correction was made with NIST SRM 997 ($^{205}Tl/^{203}Tl=0.418911$). Replicates of SRM 981 were run at the start of each set of measurements and after every four samples. The measurements were consistent with previous analyses ($n=76$) of an SRM 981 over three years ($^{208}Pb/^{207}Pb$ 2.3686 ± 0.0075, $^{204}Pb/^{207}Pb$ 0.0646 ± 0.0046, $^{206}Pb/^{207}Pb$ 1.0935 ± 0.0028) on the MC-ICP-MS and comparable to their certified values ($^{208}Pb/^{207}Pb$ 2.3685, $^{204}Pb/^{207}Pb$ 0.0646, and $^{206}Pb/^{207}Pb$ 1.0934).

3. Results and discussion

3.1. Environmental samples

Lead concentrations and isotopic compositions of the environmental samples are presented in Table 1. Lead levels in the soils from Torreón ranged 130–12,050 μg g^{-1} (median 374 μg g^{-1}, $n=112$). In contrast, regional background concentrations of lead in soils and bedrocks were two to three orders of magnitude lower, ranging 7.3–33.3 μg g^{-1} (median 10.1 μg g^{-1}, $n=22$). Lead concentrations of outdoor dust ranged 150–14,365 μg g^{-1} (median 880 μg g^{-1}, $n=102$). Levels were highest immediately southeast of the smelter, corresponding with the prevailing wind direction, and systematically decreased with distance from the smelter. Relatively elevated lead concentrations were also found in urban dust collected near the battery plant (942–1110 μg g^{-1}) and cement plant (720–975 μg g^{-1}) compared to those (<200–415 μg g^{-1}) at other sites at similar distances from the smelter. For comparison, the US EPA cleanup goals for lead at CERCLA Superfund sites are 200–500 μg g^{-1} in soils and 400 μg g^{-1} in playground soils (U.S. Environmental Protection Agency, 2001), and lead concentrations in street dust within a 2–4 km radius of the smelter in Torreón were mostly >400 μg g^{-1}.

Table 1
Lead isotopic composition and Pb concentration (±SD) in urban environmental samples from Torreón, México.

Site	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Pb (μg g^{-1})
Street dust				
1 (0.59 km, NW)	18.4755	1.2046	2.4666	3111 ± 229
2 (0.38 km, W)	18.7223	1.2001	2.4626	12,056 ± 188
3 (0.64 km, E)	18.7063	1.1972	2.4733	1125 ± 22.8
4 (1.46 km, NW)	18.9376	1.2139	2.4700	253.1 ± 301
5 (1.0 km, NW)	18.6765	1.2065	2.4678	1710 ± 166
7 (1.21 km, W)	18.6812	1.2012	2.4907	934 ± 71.5
10 (1.41 km, SW)	18.8531	1.2066	2.4734	3565 ± 116
11 (0.64 km, SE)	18.6344	1.1926	2.4633	2435 ± 884
12 (1.79 km, E)	18.8359	1.2055	2.463	754 ± 165
20 (2.56 km, SE)	18.9376	1.2139	2.47	529 ± 98.3
26 (4.1 km, NW)	18.7085	1.2067	2.4549	462.5 ± 48.8
30 (4.62 km, N)	18.7085	1.2067	2.4549	335.1 ± 89.1
33 (7.2 km, SE)	18.8359	1.2055	2.463	174.3 ± 35.2
37 (9.0 km, E)	18.6146	1.2025	2.4674	334.5 ± 2.9
38 (5.13 km, W)	18.8016	1.2033	2.4659	85.1 ± 31.0
Outdoor dust				
1 (0.59 km, NW)	18.7219	1.1982	2.4696	8685 ± 602
2 (0.38 km, W)	18.7359	1.1991	2.4696	14,365 ± 951
3 (0.64 km, E)	18.7391	1.1993	2.4694	5131 ± 272
4 (1.46 km, NW)	18.7266	1.1985	2.4698	827.7 ± 124
5 (1.0 km, NW)	17.8897	1.2004	2.4723	2846 ± 95.4
9 (1.26, SW)	18.7656	1.201	2.4714	2846 ± 95.5
10 (1.41 km, SW)	17.8304	1.1982	2.4773	4170 ± 638
11 (0.64 km, SE)	18.7203	1.1981	2.4686	6641 ± 461
19 (2.31 km, S)	18.7230	1.1964	2.4717	1518 ± 1773
26 (4.10 km, NW)	18.1312	1.2021	2.4704	763.1 ± 27.7
37 (9.0 km, E)	18.8294	1.2032	2.4672	1042 ± 49.9
Indoor dust				
1 (0.59 km, NW)	18.7141	1.1977	2.4684	7539 ± 827
2 (0.38 km, W)	18.7281	1.1986	2.4697	8183 ± 3157
5 (1.0 km, NW)	18.7297	1.1987	2.4695	1902 ± 618
7 (1.21 km, W)	18.7063	1.1972	2.4683	2252 ± 912
9 (1.26, SW)	18.7250	1.1984	2.4694	831 ± 150
36 (7.92 km, E)	18.7203	1.1981	2.4659	258 ± 140
37 (9.0 km, E)	18.8185	1.2025	2.4670	457 ± 119

Lead loadings in indoor dust ranged 214–20,280 μg m^{-2} (median 1902 μg m^{-2}). Again, for comparison, the U.S. Department of Housing and Urban Development health standard for lead in settled dust on window sills of 2690 μg m^{-2} (HUD, 1999), and 7 of the 22 homes sampled in Torreón (<1 km) had indoor dust lead concentrations that were 2–8 times higher than the guideline. The indoor dust lead concentrations decreased with distance from smelter, similar to the geographic gradients of outdoor dust and soil lead concentrations in Torreón.

Outdoor ambient air lead levels in monitoring station (November 2004–April 2006) ranged 0.065–0.705 μg m^{-3}, with an average (x ± sd) of 0.196 ± 0.150 μg m^{-3} (Table 2). Relatively higher

Table 2
Lead isotopic composition and Pb concentration (± SD) in aerosols collected in the urban area from Torreón, México. Collection site located at 1 km NW from the smelter.

Period	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Pb (ng m^{-3})
November 2004–January 2005	18.8078	1.2037	2.4673	164 ± 55.3
November 2005	18.7313	1.1988	2.4643	139 ± 120
December 2005–January 2006	18.7359	1.1991	2.4678	233 ± 206
October 2006	18.7484	1.1999	2.4647	113 ± 97.2
February 2006	18.7219	1.1982	2.4657	22.5 ± 76.5
March 2006	18.7344	1.1990	2.4675	56.1 ± 132

atmospheric lead concentrations were observed in December 2005 (0.583 ± 0.108 μg m^{-3}) and relatively lower concentrations were observed in October 2005 (0.097 ± 0.0224 μg m^{-3}), compared to the other sampling periods. Although a gradient in air lead concentration was expected from the air collecting station towards the smelter plant and on urban environment around, the current concentrations of lead in air were significantly lower to those (geometric mean of 6.1 μg m^{-3}, 1.6–14.9 μg m^{-3}) reported before than sanctions in 1999 (García-Vargas et al., 2001).

Outdoor atmospheric lead deposition varied from 30 to 1350 μg m^{-2} d^{-1}. Highest deposition rates (860–1350 μg m^{-2} d^{-1}) were always < 1 km from the smelter and usually downwind from the facility. Further out, the rates ranged 130–310 μg m^{-2} d^{-1} at 2 km and 31–75 μg m^{-2} d^{-1} at > 4 km from the smelter. In addition, the atmospheric lead concentrations were used to estimate the indoor deposition flux (F) from the dry deposition velocity (V_d). Although large variations in the lead outdoor deposition velocities (0.05–1.3 cm s^{-1}) have been reported (U.S. Environmental Protection Agency (EPA), 2007), we determined that a value of 1.0 cm s^{-1} for the indoor deposition flux (V_d indoor > V_d outdoor) was most appropriate for our study. That value yielded indoor lead fluxes in the air collecting station area ranging 56–609 μg m^{-2} day^{-1} (169 ± 130 μg m^{-2} day^{-1}), with maximum deposition rates > 500 μg m^{-2} day^{-1} during winter. For comparison, even the lower dry deposition fluxes in Torreón were higher than those reported in dense urban areas, such as in Los Angeles (8.9–29 μg m^{-2} d^{-1}) and the maximum values were three orders of magnitude higher than in non-urban sites (1.4 μg m^{-2} d^{-1}) (Sabin et al., 2006).

There were significant correlations ($R \geq 0.75$, $p < 0.01$, Spearman's correlation) between lead concentrations of soil, outdoor dust, and indoor dust with distance to the smelter (Fig. 2a).

3.2. Lead in children blood

Lead concentrations of the children blood (PbB) ranged 5.0–25.8 μg dl^{-1}, with a geometric mean of 9.8 μg dl^{-1} (Fig. 3). Because the small sample size and non-randomized design of the study made it difficult to compare the mean PbB values with other parameters (e.g., age, sex, and location), a bivariate analysis of Kruskal–Wallis and Mann–Whitney was used to evaluate potential differences between PbB in children groups within Torreón.

It was hypothesized that the PbB levels would be highest in children born before than 1997 (> 9 years old), when the phase out of leaded gasoline was completed in México; intermediate in children born between 1998 and 1999 (7–9 years old), before the new emission controls were installed at the smelter; and lowest in the younger children (2–6 years old), born after those controls were operational and the remediation program was completed. Although non-significant ($p > 0.05$) differences were observed among these age groups, children between the ages of 9–11

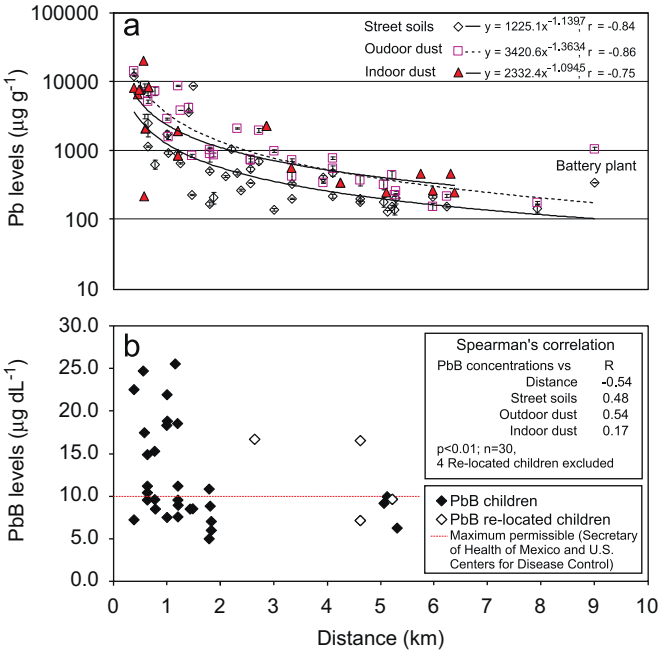

Fig. 2. (a) Lead levels (μg g^{-1}) in environmental proxies (street soil and dust, outdoor and indoor house dust) and (b) blood lead levels (μg dl^{-1}) in children vs. distance from the Met-Mex smelter.

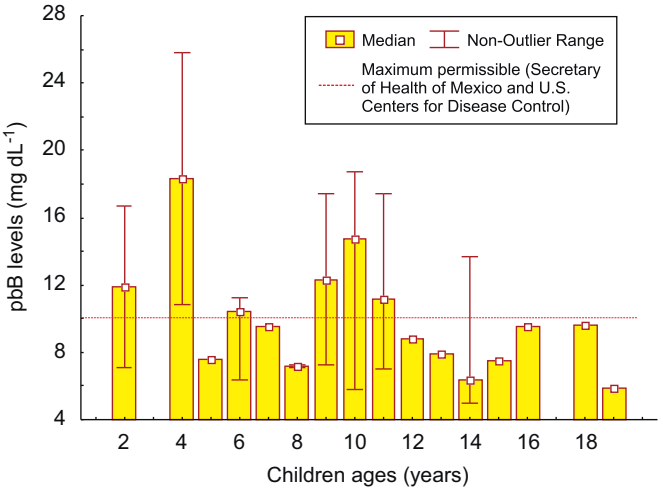

Fig. 3. Blood lead levels (μg dl^{-1}) in children living in the impacted area vs. by ranges of age (N=34).

(n=11) and 2–4 years (n=7) showed higher values than those of the other children. The relatively elevated levels in the older children (9–11 years) are consistent with our hypothesis that they were exposed to greater amounts of lead from smelter emissions and the uses of leaded gasoline in México during their early childhood; and we propose the relatively elevated levels in the younger children (2–4 years) is due to their greater proclivity for pica and other hand-to-mouth behavior that increase their exposure to lead in soil and dust.

No statistically significant ($p > 0.05$) differences were observed between PbB levels of girls (5.2–25.8 μg dl^{-1}) and boys (5.0–25.5 μg dl^{-1}). This coincides with the results of a recent study of PbB levels of children in another mining-smelter community, which found significant gender differences (Moodie et al., 2010).

When we compared between PbB levels of children relocated >1 km (9.7 ± 3.1 μg dl^{-1}) of the smelter and those of children who had always lived <1.0 km (11.9 ± 6.1 μg dl^{-1}) or 1–2 km (10.4 ± 5.7 μg dl^{-1}) from the smelter, no significant differences were found ($p > 0.05$).

3.2.1. Predictors of the PbB levels

Relationships between PbB concentrations in children with distance of the smelter and lead dust (street, outdoor, and indoor) were evaluated with a Spearman rank non-parametric test (Fig. 2b). The correlation ($R = -0.14$) between PbB levels and distance from the smelter was negative, but not significant ($p > 0.01$, $n = 34$). Correlations between PbB levels and street and outdoor dust concentrations ($R \geq 0.48$) were low, but significant ($p < 0.01$). Those positive correlations indicate measurements of lead concentrations in environmental urban could be predictors of the lead exposure and PbB concentrations of children in Torreón, but they would be limited by the high variability of the PbB values measured and the small number of analyzed children. The influence of other parameters (smelter distance, wind direction, age, and sex) on PbB values, which were evaluated by multivariate analysis of variance, showed that proximity to the smelter ($R = -0.54$; $p < 0.01$) was the only other statistically significant risk factor for elevated PbB levels.

Significant relationships have been previously reported between lead concentrations in urban environmental matrices (e.g., soils, outdoor, and indoor dusts) and children's PbB levels (e.g., Burgoon et al., 1995; Mielke et al., 1997; Johnson and Bretsch, 2002). Mathematical models have shown that children's PbB levels could rise 3–7 μg dl^{-1} with their exposure to every 1000 μg g^{-1} of lead in soil or dust, with a probable dose–response relationship of 6.8 μg dl^{-1}/1000 μg g^{-1} (Burgoon et al., 1995). That is consistent with the results of our study which showed elevated levels of lead in dust and soil corresponded with elevated levels (≥ 6.8 μg dl^{-1}) in more than 60% of children sampled. Thus, the ingestion and the inhalation of indoor and outdoor dust and soil are presumed to account for most of the childhood lead poisoning in Torreón.

While this study shows that total lead concentrations in soils and dust provide may be used to predict PbB levels in Torreón, estimation of potential human health risks posed by contaminated dust and soil can be improved by measurements of the lead bioaccessible fraction. Thus, the application of a physiologically-based extraction test (PBET) in the soil and dust samples from Torreón, such as the simulated in vitro gastro-intestinal extraction procedure proposed by Ruby et al. (1993, 1996), is planned for the next phase of investigation of lead pollution in Torreón.

3.3. Lead isotopes

As previously noted, stable lead isotopic compositions are listed with associated lead concentrations in Tables 1 and 2. The Student-Newman–Keuls test was used for comparing isotopic compositions of lead in the urban pollution proxies and PbB with the potential sources of the metal. There was no statistically significant ($p < 0.05$) difference between the average of those isotopic ratios (^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb) for street dust (18.742 ± 0.1256, 1.2021 ± 0.0051, 2.4662 ± 0.006); outdoor dust (18.5285 ± 0.3793, 1.1998 ± 0.0019, 2.4706 ± 0.0031), indoor dust (18.7346 ± 0.0379, 1.1987 ± 0.0017, 2.4683 ± 0.0014), or atmospheric particulate matter (18.7466 ± 0.0312, 1.1998 ± 0.0020, 2.4662 ± 0.0015) in Torreón. No significant differences were observed between groups of environmental samples ($p < 0.05$). We did not measure the isotopic composition of other potential sources of lead contamination in the study area (e.g., aviation gas, batteries, and cement ash), because we did not find significant ($p < 0.05$) differences in the lead isotopic composition of soil and/or dust at sites, where those sources could be important (e.g., airport, battery plant, and cement plant). However that does not preclude the presence of other sources of lead contamination within Torreón.

The range of isotopic ratios in PbB of children from Torreón (18.6403–18.7720, 1.1975–1.2015, and 2.4660–2.4750) was similarly narrow, and their average isotopic ratios were indistinguishable from those of environmental samples collected within the city (Table 3). Moreover all of those environmental and human PbB ratios were comparable to those of Mexican lead ores (^{206}Pb/^{204}Pb = 18.7167–18.8419, ^{206}Pb/^{207}Pb = 1.1960–1.2044, and ^{208}Pb/^{207}Pb = 2.4654–2.4778) processed at the smelter in Torreón (Table 4). In contrast, these isotopic results were significantly different ($p < 0.05$) to the Pb isotopic composition in background rock and soils from rural area (1.1832–1.1921 for ^{206}Pb/^{207}Pb and from 2.4549 to 2.4611 for ^{208}Pb/^{207}Pb). None of the subjects showed lead isotopic ratios in their blood different to the industrial source of lead and no significant ($p < 0.05$) differences were observed in the isotopic results between groups of children.

Fig. 4 is an isotope:isotope (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{207}Pb) plot of the environmental samples and childrens' blood in Torreón. Also included in the figure is (a) the range of lead isotopic compositions ($1.173 \geq ^{206}$Pb/^{207}Pb ≤ 1.191 and $2.440 \geq ^{208}$Pb/^{207}Pb ≤ 2.459)

Table 3
Lead isotopic composition and Pb concentration ($\pm$SD) in blood children living around the Met-Mex complex in Torreón, México.

Site	n	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	Pb (μg dl^{-1})
1 (<0.6 km, W-NW)	6	18.6694 ± 0.0291	1.2005 ± 0.0005	2.4700 ± 0.0004	10.9 ± 5.1
3 (<0.6 km, E)	4	18.7031 ± 0.0079	1.1970 ± 0.0004	2.4658 ± 0.0004	11.0 ± 6.4
5, 8 (0.6–1.0 km, W-NW)	11	18.7641 ± 0.0079	1.2009 ± 0.0005	2.4662 ± 0.0004	12.6 ± 7.0
7 (0.6–1.2 km, W)	6	18.7344 ± 0.0293	1.1990 ± 0.0005	2.4689 ± 0.0005	13.6 ± 7.2
11 (<0.6 km, SE)	3	18.7281 ± 0.0140	1.1986 ± 0.0006	2.4668 ± 0.0004	12.8 ± 2.9

Table 4
Lead isotopic composition and production volume of ore milled from 2004 to 2006 in several of the most important suppliers of the concentrates to Met-Mex Peñoles.

Peñoles mines (100%)	^{204}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	Ore milled (10^6 metric ton): 2004–2006
Proano/Fresnillo	18.8419	1.2040	2.4778	10,119
NAICA	18.7167	1.1960	2.4654	3443
Francisco I. Madero	18.8188	1.2044	2.4766	11,010
Sabinas	18.8188	1.2044	2.4766	4500

From: http://www.penoles.com.mx/penoles/sobre_penoles/perfil/divisiones/minas/.

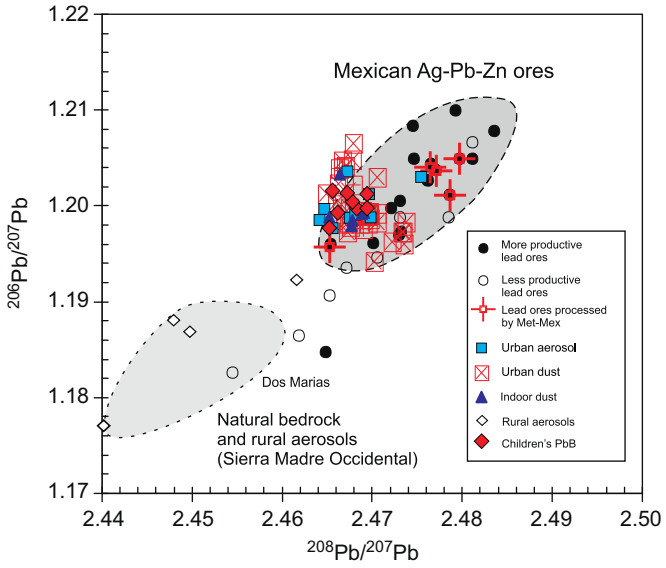

Fig. 4. Lead isotopic compositions ($^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$) of (a) environmental Pb from urban area in Torreón (dust and aerosols), (b) Pb blood in children living around the smelter, along with those of (c) natural lead sources in México (i.e., upper crust from Sierra Madre Occidental, NW México), and (d) Mexican lead ores processed by Met-Mex smelter.

reported for the upper continental crust of the Sierra Madre Occidental in México (SMO) (Cameron et al., 1992; Smith et al., 1996), which was used as the reference for parental bedrock and (b) the range of lead isotopic compositions ($1.186 \geq {}^{206}Pb/^{207}Pb \leq 1.211$ and $2.465 \geq {}^{208}Pb/^{207}Pb \leq 2.484$) of Mexican lead ores (Cumming et al., 1979) processed at the smelter in Torreón (www.penoles.com.mx). These data show that isotopic ratios of lead for all of the environmental samples collected from the urban areas ($<113\ km^2$) around the smelter and for all of the PbB samples collected from children living within that area fall along a line constrained by the lead isotopic compositions of Mexican lead ores and Mexican bedrock. The gradient is most simply explained with a two end-member mixing model: industrial lead ore and natural lead.

Although significant differences in the Pb isotopic exist between lead from natural and industrial origins, it is not possible to distinguish between metal from previous and on-going smelter emissions and previous leaded gasoline combustion emissions. We do not have the definitive information about the origin of lead used in tetraethyl production in México, but we presume that it was mostly derived from the domestic lead ores processed in Met-Mex. This is, in part, because environmental samples in other regions of the country, including some remote areas, where industrial lead contamination was primarily restricted to atmospheric depositions from leaded gasoline emissions, have similar lead isotopic ratios (Soto-Jiménez et al., 2006). It is also notable that the use of the leaded gasoline was eliminated in México in 1997, approximately two years before than the installation of emission controls at the smelter and the associated clean-up of Torreón—and a decade before our samples were collected from that area.

Therefore, we recognize that historic emissions of leaded gasoline combustion probably account for some of the current problems of lead pollution in Torreón; however, the legacy contaminations from leaded gasoline emissions cannot account for the current levels of environmental and human lead contamination in that area. Moreover in spite of the relatively high levels of lead were found in areas immediately surrounding to the battery and cement plants, the potential contributions of those industries to the regional lead pollution also appear to be swamped by those from the smelter.

3.4. Evaluation of the emission reduction and remediation efforts

Quantification of industrial lead emissions by Met-Mex Peñoles is difficult, because non-data on emission factors (ε) are available. However, based on the control emissions technologies applied to the smelting operations at the facility (www.peñoles.-com), we selected the most probable emission factor published in the literature of $0.2\ kg\ ton^{-1}$ for the primary production of lead (Skeaff and Dubreuil, 1997; Pacyna and Pacyna, 2001). Considering the annual primary lead volumes during 2002–2008, we estimated that the lead emissions varied from 27.7 to $31.7\ ton\ y^{-1}$. Before PROFEPA's sanctions in 1999 (e.g., period 1990–1998), the emission rates of lead to the atmosphere in Torreón probably is estimated to have ranged 270–350 to 680–$885\ ton\ y^{-1}$ ($\varepsilon = 2.0$ and $5.0\ kg\ ton^{-1}$, respectively). Thus, a significant decrease of lead emissions ($>95\%$ compared to one decade ago) appears to have been achieved after Met-Mex installed an air pollution control system in response to PROFEPA's Remediation Action Objective.

That reduction in lead and particulate emissions of Met-Mex corresponds with the recent decrease in lead concentrations in the air, and to a lesser extent in soils and urban dust, around the smelter. It is also consistent with the decline in the average PbB levels of children measured for this study compared with previously reported levels ($22.4 \pm 7.8\ \mu g\ dl^{-1}$, <1 km radius) in Torreón (García-Vargas et al., 1999, 2001). These attest to the human health benefits of reducing emissions from the smelter in Torreón, along with the elimination of leaded gasoline in México in 1997.

Yet, our measurements show that nearly half ($\sim 44\%$) of the PbB values of children measured in our study exceed current Mexican and US levels of concern for children ($10\ \mu g\ dl^{-1}$), and that $\sim 15\%$ of those children had PbB levels that were at least 2-fold above that level of concern. Moreover PbB values of children in this study were 3–14 times higher than the most recent (1999–2004) average PbB of $1.9\ \mu g\ dl^{-1}$ of children (aged 1–5 years) in the US (Jones et al., 2009) and 300 to 1600 times higher than the estimated natural PbB level ($0.016\ \mu g\ dl^{-1}$) in humans (Flegal and Smith, 1992). This is a concern because no threshold for sublethal lead toxicity has been identified (NRC, 1993) and new studies continue to lower the concentration, where there are measurable adverse effects of lead (e.g., Jusko et al., 2008). This problem is compounded by announcements that environmental lead emissions from smelting operations have been reduced to safe levels in Torreón, when this and other studies in other mining and smelting communities indicate that is not the case (e.g., Fraser, 2009; Munksgaard et al., 2010).

4. Conclusions

This study provides an independent assessment of the current level of lead pollution in Torreón, México, one of the world's most polluted cities, due emissions from the Ag–Cd–Pb–Zn smelter located within the city. Results demonstrate that recent efforts to control environmental lead pollution originating from the largest smelter in México have been only partially successful. The data show that lead concentrations and stable isotopic composition in environmental samples revealed that pollutant lead is mostly from contemporary emissions from the smelter, in spite of reported reductions in those emissions. PbB concentrations ($5.0–25.8\ \mu g\ dl^{-1}$) of children living in the community had declined 2-fold from the previous levels ($8.4–52.1\ \mu g\ dl^{-1}$), but they were still 3 to 14 times higher than the average PbB of their contemporaries in the US. Unfortunately, this disparity between reported elimination of toxic emissions and the documented

presence of toxic levels of lead in children in this Mexican smelter community is consistent with similar disparities in other smelter cities (e.g., Perú and Australia).

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