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Case Studies

Occupational Exposures to Heavy Metals at a Bolivian Smelter

Dawn Tharr, Column Editor

Reported by Aaron Sussell, Mitchell Singal, and Sherrilyn Wainwright

Introduction

In December 1993 the Pan American Health Organization (PAHO) requested assistance from the Centers for Disease Control and Prevention (CDC) to conduct a pilot study of community exposures to heavy metals, especially arsenic and lead, in Oruro, Bolivia. The request was prompted by community concerns and national media reports about the possibility of community health effects related to the processing of imported waste materials at a smelter operated by the Bolivian government. The wastes were known to contain high concentrations of arsenic, lead, and other heavy metals. In response to the request, the National Center for Environmental Health designed an epidemiologic pilot study to assess community exposures to heavy metals and collaborated with the National Institute for Occupational Safety and Health (NIOSH) to measure community and occupational exposures. CDC investigators joined PAHO and Bolivian public health personnel to conduct a field survey in Bolivia in March 1994. We have previously reported that no significant take-home or community exposures to heavy metals were found in Oruro.[1] Smelter workers, however, were at risk; this case study reports the occupational exposure component of the study.

Due to resource and time constraints, the occupational exposure assessment was limited to monitoring workers in the smelter who were expected to have worst-case exposures to heavy metals. Fifteen workers were sampled to assess their exposures to airborne arsenic, lead, antimony, bismuth, cadmium, iron, tin, and zinc. Settled dust and drinking water samples were collected to evaluate other potential sources of exposure to metals. Because preliminary information indicated that sulfur dioxide exposures might be a significant problem, worker sulfur dioxide exposures were also measured. Biological samples to measure blood lead levels (BLLs) and urine arsenic (UA) concentrations were collected from 15 workers, only 2 of which also participated in the air monitoring.

Background

Smelting at this facility (elevation 3686 m) began in 1971. The facility was the largest smelter in Bolivia and one of the most important smelters in Latin America, employing about 300 workers in the smelting of high grade tin, antimony, lead, and other metals. The plant has three major areas: the high grade smelter, the low grade smelter, and the antimony smelter.

Sulfide ores, such as tannite (Cu_2FeSnS_2) and tealite ($PbZnSnS_2$), are commercially important sources of tin in Bolivia. Bolivian ores often contain relatively high amounts of arsenic in addition to sulfur. The facility also imports and processes tin ores from Peru, as well as waste materials containing commercial quantities of arsenic, lead, tin, and zinc from Peru and other countries.

Bolivian ores are first sent to a roasting furnace to oxidize and volatilize excess arsenic and sulfur. Ores are roasted in cylindrical ovens at 750°C; potentially toxic emissions from this process include sulfur dioxide, carbon monoxide, carbon dioxide, arsenic trioxide, and arsine. The base material still contains about 1 percent sulfur after roasting. Commercial quantities of arsenic are recovered from the process, packaged, and exported from the facility. After roasting, base materials are transported to the high grade tin smelter in another building. The high grade smelting process uses a single reducing stage to obtain high grade tin, with a capacity of 20,000 tons/year. The basic stages of the process are: calcination in floor furnaces, reduction in reverberatory furnaces, slag volatilization in a fuming furnace, and thermo- and electro-refining. Emissions from the high grade furnaces are exhausted to a series of wet scrubbers (for treatment of carbon dioxide and sulfur dioxide) and then to bag house filters or electrostatic precipitators (for treatment of particulate heavy metals).

The low grade smelter, located in a separate building, uses a cyclone furnace for processing low grade metal ores, with a capacity of 10,000 tons/year. The slag from the cyclone furnace is processed in a volatilization furnace, and the volatile powders are later reduced in an electric furnace. Another building houses the antimony smelter, which uses a cyclone-type volatilization furnace to produce up to 4270 tons of metallic antimony and 1000 tons of arsenic trioxide/year. The impure antimony oxides produced are reduced in rotary-type furnaces, and the crude metal is then delivered to reverberatory furnaces to refine them and obtain concentrations of 99.5 to 99.6 percent antimony.

Evaluation Methods

Fifteen first-shift workers, representing 12 job categories, were selected for exposure monitoring. Personal breathing zone (PBZ) air samples were collected during one shift according to NIOSH Method 7300, and analyzed by inductively coupled plasma–atomic emission spectroscopy for arsenic, bismuth, cadmium, iron, lead, antimony, tin, and zinc using Method 7300.[2] Air sampling pumps were calibrated on site with a primary standard (electronic bubble flow meter). Full-shift PBZ exposures to sulfur dioxide were measured using colorimetric diffusion tubes—Dräger® sulfur dioxide 5/a-D (measurement range: 0.7 to 19 ppm for 8 hours). Sulfur dioxide values in ppm-hours were read directly from the tubes at the end of the work shift; the results were corrected for the local average barometric pressure (440 mmHg) and reported in parts per million.

Bulk samples of settled dusts were collected within small areas (about 10 × 10 cm) with clean wooden tongue depressors to a depth of approximately 1 cm, and placed in 20-ml glass vials or sealable plastic bags. A drinking water sample was collected from each of two sources which were used in the cafeteria kitchen. Water

TABLE 1. Personal Exposure Monitoring Results for 15 Workers

Job Title	Arsenic ($\mu g/m^3$)	Cadmium ($\mu g/m^3$)	Lead ($\mu g/m^3$)	Antimony ($\mu g/m^3$)	Sulfur Dioxide (ppm)
High grade furnace operator[A]	26[B]	11	71	7[C]	4.1
Rotary furnace feeder	31	11	83	1[C]	1.1
Roaster feeder	88	0.7	9.3	2[C]	11
Equipment operator helper	0.04[C]	7.8	140	4	1.2
Filter operator	3	180	58	1[C]	6.9
Filter operator	129	16	280	1[C]	31
Filter operator	18	0.5[C]	9.5	4500	12
Discharge operator	12	230	63	1[C]	14
Furnace operator	390	2.5	30	10	8.3
Vessel operator[A]	11	19	43	2[C]	0.5
Mixture operator	55	5.4	37	11	1.2
Metal refiner	9	12	33	2[C]	1.2
Control panel operator	6	0.5[C]	7.4	7[C]	2.4
Dust transporter	7	25	47	2[C]	22
Dust transporter	9	11	46	1[C]	—
Geometric mean	14	8	42	5	4.3
NIOSH REL-TWA	2C[D]	LFL[E]	<100	500	2
OSHA PEL-TWA	10	5	50	500	5

[A]The worker also participated in biological monitoring (Table 2).
[B]Approximate value above the minimum detectable concentration.
[C]None detected. One-half the minimum detectable concentration is reported for statistical purposes.
[D]C = ceiling limit for any 15-minute period.
[E]LFL = lowest feasible level.

was allowed to run from the taps for 5 minutes prior to sampling. The samples were collected in 250-ml high density polyethylene bottles and acidified on site to a pH of less than 2 with concentrated nitric acid. All of the environmental samples (air, dust, and water) were transported to NIOSH and then shipped to a U.S. contract laboratory. The dust and water samples were analyzed according to NIOSH Method 7300 (modified for sample matrix) for arsenic, bismuth, cadmium, lead, iron, antimony, tin, and zinc.[(2)]

Biological sampling for BLLs and UA concentrations were obtained from 15 workers, 2 of which also participated in the air sampling. Blood and urine samples were collected and preserved on site, refrigerated with dry ice, and transported to the CDC for analysis. Blood samples were analyzed for BLL by graphite furnace atomic absorption spectrophotometry (GFAAS) with a sample detection limit of 0.6 $\mu g/L$.[(3)] Samples were analyzed for UA concentration by GFAAS with a sample detection limit of 4.0 $\mu g/L$.[(4)] Creatinine-corrected values for UA samples were determined by analyzing early morning urine samples.

NIOSH investigators met with company officials and observed work practices, hygiene facilities, and engineering controls in the facility. All worker participation in this study was voluntary.

Results

General Considerations and Limitations

A total of 28 workers participated in either air or biological monitoring as part of the NIOSH exposure assessment. Job titles that were monitored were expected to have the highest exposures to heavy metals, but since exposures for only about 10 percent of the exposed workers were monitored, it is not possible to say that the highest exposures were actually measured. Results for metals and sulfur dioxide are expressed as time-weighted averages that generally represent full-shift sampling.

Workers who participated in the biological monitoring worked on all three shifts; they were preselected for the community exposure study based on several criteria, including having young children in their families. Because of time limitations, for air monitoring, NIOSH investigators asked the company to identify 15 first-shift workers who, if possible, had the same job titles as the workers who participated in the biological monitoring. However, for the most part, job titles appeared to be different, but some of these differences may be due to translation errors (Tables 1 and 2). Two workers, the high grade furnace operator and the vessel operator, participated in both biological and air monitoring.

Air Monitoring Results

Hazardous exposures to arsenic, cadmium, lead, and antimony were prevalent among the 15 workers; the results are expressed as time-weighted averages in Table 1. The reported exposures are without regard to respirators that may have been worn. Geometric means and ranges for these exposures were: arsenic, 14 $\mu g/m^3$ (range: none detected [ND] to 390 $\mu g/m^3$); cadmium, 8 $\mu g/m^3$ (range: ND to 230 $\mu g/m^3$); lead, 42 $\mu g/m^3$ (range: 7.4 to 280 $\mu g/m^3$); and antimony, 5 $\mu g/m^3$ (range: ND to 4500 $\mu g/m^3$).

Some of the worker exposures to these metals were very high, particularly to arsenic and cadmium, which are potential occupational carcinogens. Six of the 16

TABLE 2. Biological Monitoring Results for 15 Smelter Workers

Job Title	Years Employed	UA (μg/g creatinine)	BLL (μg/dl)
High grade furnace operator[A]	10	96	42
Furnace control room operator	18	149	18
Chief of roasting point	18	177	26
Chief of antimony smelting point	19	7.7	20
Chief of high grade volatilization point	17	1[B]	54
Low grade crystalization operator	12	119	20
Control room operator	14	60	16
Control room operator	20	101	16
Furnace operator	16	2	13
Vessel operator[A]	17	37	22
Low grade control room operator	11	32	25
First operator	24	78	19
Low grade thermal refining	23	112	18
Low grade thermal refining	28	25[B]	15
Low grade thermal refining	16	206	17
Median	17	78	19

[A]The worker also participated in air monitoring (Table 1).
[B]None detected. Values are the minimum detectable concentrations (adjusted for creatinine).

arsenic exposures measured (38%) were greater than ten times the NIOSH recommended exposure limit (REL) of 2 μg/m^3. The highest measured arsenic exposure, for a discharge operator, was 195 times the NIOSH REL and 39 times the Occupational Safety and Health Administration (OSHA) permissible exposure level (PEL). Three of 15 cadmium exposures were at least five times the OSHA PEL of 5 μg/m^3, and the highest two exposures, for a furnace operator and a filter operator, were 46 and 36 times the OSHA PEL, respectively. Lead-exposure for one filter operator was greater than five times the OSHA PEL of 50 μg/m^3, and another filter operator had an antimony exposure nine times the NIOSH REL of 500 μg/m^3.

None of the worker exposures measured for iron, tin, and zinc were hazardous; all were well below the respective occupational exposure criteria. (There are no criteria for bismuth, but only trace levels were measured.)

Exposures to sulfur dioxide were also a health hazard for most of the workers; the geometric mean was 4.3 ppm (range: <1 to 31 ppm, Table 1). As with the heavy metals, some very high exposures were measured. Five of the 15 workers had sulfur dioxide exposures at least five times the NIOSH REL; the highest exposure, for a filter operator, was 15 times the NIOSH REL.

The severity of the personal exposures to heavy metals and sulfur dioxide indicates that engineering controls were inadequate or lacking in a number of areas. The filter operators were exposed to very high levels of both heavy metals and sulfur dioxide. Their job, handling bag filters and filter dust in bag houses of conventional design, is inherently dusty, and is made hazardous both by the toxic metals in the dust and by gases present in the bag houses.

Other Environmental Sampling

Eight dust samples of process and waste materials were collected in the buildings to assess the potential for worker exposure to heavy metals through direct contact with contaminated surfaces. Settled dust was visible on many of the horizontal surfaces in this building, such as railings and walkways, as well as benches and floors in the locker rooms. The sampling results indicated that the potential for ingestion of metals existed; surfaces throughout the facility had high concentrations of arsenic, lead, and other metals.

The geometric mean concentrations of arsenic and lead in the settled dusts (and one process material) collected throughout the facility were 5210 and 7342 μg/g, respectively. Similar concentrations, 3600 μg/g arsenic and 6300 μg/g lead, were found in dusts on the floor of a clothes changing area.

Results indicated that drinking water sources at the facility were not a significant source of heavy metal exposure. Lead or arsenic were not detected (<3 μg/L arsenic and <2 μg/L lead) in the water source that came from surface water in the nearby mountains. The on-site well water contained 9 μg/L arsenic, a level below the U.S. Environmental Protection Agency maximum contaminant level of 50 μg/L for arsenic in drinking water, and no lead was detected. (Arsenic occurs naturally in Bolivian groundwater supplies.) The concentrations of other metals in drinking water were not of health significance.

Hygiene Facilities and Practices

Inadequate hygiene facilities and practices created a potential for ingestion of heavy metals by the workers and take-home exposures among the workers' families. Although workers were provided changing areas and storage lockers, there was no separation of clean and dirty areas. Two of the three changing areas were locker rooms with adjacent showers; the third was a separate open area without walls or a ceiling. This open area had the heaviest accumulation of settled dust on floors and other surfaces (dust sample results reported above). The workers who used the open changing area reportedly had to walk to and from the showers wrapped in their towels, a journey that necessitated negotiating two flights of stairs through smelter production areas.

On the positive side, the company did provide a clean cafeteria with well-designed hand washing stations. Work clothing (cloth coveralls) was also provided to each worker, although workers did not remove or cover outer clothing before entering the cafeteria.

It is not uncommon for Bolivian workers to chew coca leaves as a stimulant. This practice could result in ingestion of metals, since some of the workers carried the coca in their work coveralls.

Respiratory Protection

While NIOSH investigators did not attempt a complete evaluation of the respiratory protection program at this facility, some serious problems related to respirator use were observed.

The respirators that were provided and used were not adequate. Workers in the job categories evaluated were provided NIOSH-approved half-face air-purifying respirators equipped with combined cartridges for organic vapors/acid gases and high efficiency filters for toxic dusts. The NIOSH-assigned protection factor for this type of respirator used is 10—protective for atmospheres containing up to ten times the exposure limit for the substances of concern.[5] However, airborne exposures to arsenic, cadmium, and sulfur dioxide among the workers sampled clearly exceeded ten times the RELs.

Furthermore, in high exposure areas respirators were not always consistently or properly used. Some of the workers did not wear respirators in areas where dust and fume levels were visibly very high, and supervisors and company officials did not always wear respirators while passing through these areas. Several workers were observed wearing respirators that had pieces of woven cloth stretched over the parts of the rubber facepiece which forms the face-to-facepiece seal. These respirator modifications were presumably made to improve wearer comfort.

Biological Monitoring Results

The 15 workers who participated in biological monitoring had been employed a median of 17 years at the smelter (range: 10 to 24 years; see Table 2).

The median UA concentration was 78 μg/g creatinine, with a range of <1 to 206 μg/g creatinine (Table 2). Nine of the 15 UA levels measured were greater than the American Conference of Governmental Industrial Hygienists (ACGIH) biological exposure index (BEI™) of 50 μg/g creatinine.[6] According to ACGIH, the BEIs represent levels that are likely to be observed at the end of the work week in healthy workers who have an exposure equivalent to the ACGIH threshold limit value. A normal adult UA concentration is less than 30 μg/L (approximately equivalent to micrograms/gram creatinine) in the absence of significant consumption of seafood or drinking water contaminated with arsenic.[7]

The median BLL of the 15 workers monitored was 19 μg/dl, with a range of 13 to 54 μg/dl (Table 2). Four of the workers had BLLs greater than the U.S. Public Health Service goal of 25 μg/dl, and two had a BLL greater than the ACGIH BEI of 30 μg/dl.[6,8]

Discussion and Conclusions

NIOSH investigators concluded that the facility's program to control worker exposures to heavy metals and sulfur dioxide was not adequate. Among the workers included in the study, many of the measured exposures to arsenic, cadmium, lead, and sulfur dioxide were a health hazard. In this limited study it was not possible to determine the relative amounts that smelting waste materials versus raw ores contributed to these exposures. Biological monitoring results, in conjunction with high airborne exposures measured, confirmed that smelter workers were occupationally overexposed to arsenic and lead. Measured exposure levels were compared to occupational exposure criteria developed by NIOSH, the U.S. Public Health Service, ACGIH, and OSHA. Although none of these standards have been adopted by Bolivia, there is no reason to believe that Bolivian workers are more resistant to the effects of toxic substances than workers elsewhere.

This study illustrates the great difficulty of adequately protecting workers in a country that has limited resources and few or no health regulations to protect workers. The health hazard control program observed in the smelter was lacking in several important areas. Smelter engineering controls which have been used in the United States for two decades were not in use. Hygiene facilities were provided to the workers, but they were generally not adequately designed or maintained. Air-purifying respirators were used as the primary means of controlling hazardous occupational exposures. This is undesirable because respirators can be very uncomfortable to wear; wearing them can create additional stress on the workers (particularly at high altitude); and it is difficult to ensure that they are used and maintained properly. All of these problems with respiratory protection were observed in this facility.

Recommendations

The following recommendations were among those offered as measures to reduce the hazardous occupational exposures to heavy metals and sulfur dioxide in the smelter. The company was also provided portions of a previous NIOSH technical report showing examples of engineering controls for smelters.[9]

1. A more thorough assessment of occupational exposures to heavy metals and sulfur dioxide should be conducted. Airborne exposures should be measured over several days to confirm the overexposures measured, determine the amount of daily variation in exposures, and collect additional data (such as real-time data) which can be used to design effective engineering controls.
2. When additional exposure assessment is completed, more specific recommendations for engineering controls and changes in work practices can be provided by a qualified industrial hygienist. NIOSH recommends that exposures to occupational carcinogens (arsenic and cadmium) be reduced to the lowest feasible levels.
3. The respiratory protection program should be improved so that the respirators are used consistently and properly, while providing the maximum possible protection from hazardous exposures to toxic metals and sulfur dioxide. NIOSH-approved, full-facepiece, powered air-purifying respirators with the appropriate combined cartridges should be made available to workers.
4. The design and maintenance of hygiene facilities should be improved, including more frequent cleaning of locker rooms using a vacuum cleaner with a high efficiency particulate air (HEPA) filter, separation of clean and dirty areas, and installation of shoe cleaning machines. As a general rule,

workers should not be allowed to wear work coveralls and other outer clothing into the cafeteria unless the clothing has been HEPA-vacuumed. Respirators should be worn during vacuuming.

5. The importance of good hygiene practices, including not bringing food, tobacco products, or coca into contaminated areas, should be continually reinforced.
6. Ventilation systems for all control rooms should be modified to ensure that uncontaminated outside air is supplied, and that the rooms are maintained under positive air pressure with respect to surrounding production areas to prevent infiltration of air contaminants.
7. A medical surveillance program, including appropriate biological monitoring, should be available to workers exposed to toxic substances, particularly arsenic, cadmium, and lead. The purposes of such a program are (a) to detect overexposures and exposure-related health effects in individual workers and take appropriate corrective action, and (b) to help identify inadequately controlled exposure sources in the work areas included in the surveillance program.

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EDITORIAL NOTE: Aaron Sussell and Mitchell Singal are with the NIOSH Hazard Evaluation and Technical Assistance Branch in Cincinnati, Ohio. Sherrilyn Wainwright (formerly with the National Center for Environmental Health) is with the CDC Epidemiology Program Office, Division of Field Epidemiology (working with the Georgia Department of Human Resources, Atlanta, Georgia). This study would not have been possible without the valuable assistance of the Pan American Health Organization staff in Bolivia, including Luiz Augusto Galvao, Manuel Nasif Issa, and Juan Guillermo Orozco. More detailed information on this evaluation is contained in the Health Hazard Evaluation Report 94-0109-2494, available through NIOSH, Hazard Evaluation and Technical Assistance Branch, 4676 Columbia Parkway (MS R-9), Cincinnati, Ohio 45226; telephone (800) 356-4674; facsimile (513) 533-8573.