

In Vitro Studies Evaluating Leaching of Mercury from Mine Waste Calcine Using Simulated Human Body Fluids

JOHN E. GRAY,^{*,†}
 GEOFFREY S. PLUMLEE,[†]
 SUZETTE A. MORMAN,[†]
 PABLO L. HIGUERAS,[‡] JAMES G. CROCK,[†]
 HEATHER A. LOWERS,[†] AND
 MARK L. WITTEN[§]

U.S. Geological Survey, P.O. Box 25046, MS 973, Denver, Colorado 80225, Universidad de Castilla-La Mancha, Plaza M. Meca 1, 13400 Almadén, Spain, and Department of Pediatrics, University of Arizona, Tucson, Arizona 85724

Received January 12, 2010. Revised manuscript received March 17, 2010. Accepted April 21, 2010.

In vitro bioaccessibility (IVBA) studies were carried out on samples of mercury (Hg) mine-waste calcine (roasted Hg ore) by leaching with simulated human body fluids. The objective was to estimate potential human exposure to Hg due to inhalation of airborne calcine particulates and hand-to-mouth ingestion of Hg-bearing calcines. Mine waste calcines collected from Hg mines at Almadén, Spain, and Terlingua, Texas, contain Hg sulfide, elemental Hg, and soluble Hg compounds, which constitute primary ore or compounds formed during Hg retorting. Elevated leachate Hg concentrations were found during calcine leaching using a simulated gastric fluid (as much as 6200 μg of Hg leached/g sample). Elevated Hg concentrations were also found in calcine leachates using a simulated lung fluid (as much as 9200 μg of Hg leached/g), serum-based fluid (as much as 1600 μg of Hg leached/g), and water of pH 5 (as much as 880 μg of Hg leached/g). The leaching capacity of Hg is controlled by calcine mineralogy; thus, calcines containing soluble Hg compounds contain higher leachate Hg concentrations. Results indicate that ingestion or inhalation of Hg mine-waste calcine may lead to increased Hg concentrations in the human body, especially through the ingestion pathway.

Introduction

Mercury is a heavy metal of environmental concern because elevated concentrations can be toxic to all living organisms. Mercury has no known biological function, and human exposure to Hg is considered undesirable and potentially hazardous (1, 2). Generally, humans and organisms do not easily eliminate Hg, and as a result, Hg tends to concentrate in their tissues (bioaccumulation). When ecosystems are exposed to high Hg concentrations, the highest Hg concentrations are generally found in the highest trophic levels of the food chain, a process called biomagnification. High concentrations of Hg in humans adversely affect the central

nervous system, especially the sensory, visual, and auditory parts that affect coordination (3). In extreme cases, Hg poisoning can lead to death (1, 2, 4). For all organisms, the early stages of development (especially embryos) are the most sensitive to Hg (4, 5).

Consumption of fish and fish products is the primary pathway of Hg uptake in humans (3). However, human exposure to Hg through inhalation and ingestion of particulates originating from Hg mines has not been well studied, although Hg contamination originating from gold mine tailings has been evaluated (6–8). Mine wastes in areas of past Hg mining are especially problematic because these wastes contain highly elevated concentrations of Hg (9–11). The dominant form of Hg ore worldwide is cinnabar (HgS, hexagonal); however, during retorting, cinnabar ore is converted to elemental Hg (Hg⁰), which is the final product of Hg mining (10). Mine waste calcines found at Hg mines are known to contain unconverted cinnabar, but in addition, calcines contain minor metacinnabar (HgS, isometric, metastable relative to cinnabar), elemental Hg⁰, and highly reactive Hg compounds such as Hg chlorides (mercurous and mercuric), oxides, oxychlorides, and sulfates, which are formed during ore retorting (11–14).

Various studies of mine runoff water and laboratory experiments indicate that Hg mine wastes have the capacity to release (leach) significant concentrations of Hg into watersheds downstream from Hg mines (9, 11, 15–18). Leaching experiments of Hg mine wastes using water to simulate storm runoff conditions have shown a high potential to release Hg into aquatic systems surrounding Hg mines (15). Previous research has reported bioaccessibility of Hg using in vitro studies of soil (6, 19, 20), but little is known about the release of Hg into human body fluids during ingestion or inhalation of Hg-bearing mine-waste calcines that are highly enriched in Hg. Throughout the world, mine-waste calcine has been used in road construction for many years, and in addition, recreational areas, homes, farms, and gardens are built on top of calcines or abandoned Hg mines, and towns are on, or are in near proximity to, abandoned Hg mines (9, 10, 14, 15)—all of these practices and situations potentially lead to human ingestion and inhalation of calcine particulates.

The objective of this study was to evaluate leaching of Hg and Hg bioaccessibility when samples of Hg mine-waste calcine were leached with (1) a simulated human gastric fluid, (2) a simulated human lung fluid, (3) a protein-enriched serum-based fluid (RPMI-1640 with fetal bovine serum, developed by Roswell Park Memorial Institute, used for the culture of human normal and neoplastic leukocytes), and (4) deionized water acidified to pH 5.0. Resultant leachates were analyzed for concentrations of Hg. In addition, in vitro cell line experiments were carried out to evaluate effects on cultures of living cells (cell lines) when they are exposed to contaminants, such as high concentrations of Hg. Calcines used in this study were collected from two sites (a) Almadén, Spain, (38° 47', 4° 51'), and (b) Terlingua, Texas (29° 19', 103° 37').

Study Areas

Samples of mine-waste calcine were collected from Almadén, Spain, the world's largest Hg mining district, which has produced over 286 000 000 kg of Hg during more than 2000 years of mining (21). Production from Almadén represents more than 30% of the total known Hg produced worldwide (22, 23). Mining activity at the Almadén mine ceased in May

* Corresponding author phone: (303) 236-2446; fax: (303) 236-3200; e-mail: jgray@usgs.gov.

[†] U.S. Geological Survey.

[‡] Universidad de Castilla-La Mancha.

[§] University of Arizona.