



# Determination of mercury and its fractionation products in samples from legacy use of mercury amalgam in gold processing in Randfontein, South Africa



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## ABSTRACT

This study aimed at determining the levels of total mercury (THg) in tailings dams, soil, sediments and water samples collected in the vicinity of legacy mercury amalgam gold mines. Acid digestion was employed in sample digestion followed by analysis using CVAAS. Tailings dams, community and garden soil, and stream sediments were further investigated for mercury fractions using a five step sequential extraction procedure. The concentrations of THg in tailings dams, community and gardens soil were 0.890–6.755 µg/g, 0.431–0.968 µg/g and 0.471–1.019 µg/g, respectively and the concentrations of THg in the sediments obtained from tailings dams, streams and wetlands were 0.649–1.998 µg/g, 0.604–1.356 µg/g and 0.681–1.356 µg/g, respectively. The concentrations of THg, in aqueous samples obtained from tailings, streams and wetlands were 0.032–0.070 µg/l, 0.004–0.068 µg/l and 0.007–0.012 µg/l, respectively. The sequential extraction procedure showed that most Hg in the tailings dams was largely elemental Hg and Hg bound to sulphur. Soil and sediments were largely dominated by organic bound Hg. Moderate seasonal correlation was observed in tailings dams soil, but weak seasonal correlation in soils collected in the vicinity of tailings. However, a strong seasonal correlation was observed in sediments and water samples. The concentrations of Hg obtained largely existed in organic and sulphate bound Hg and there is elevated potential to methylate Hg.

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## 1. Introduction

Mercury (Hg) is one of the first elements with an in-depth study of its speciation or fractionation products [1]. The presence of Hg in the environment comes from two major sources, namely natural and anthropogenic. Its pristine concentration varies between 0.080 and 0.400 µg kg<sup>-1</sup> in rocks, sediment or soil samples [2]. Native Hg is rare in nature, but it usually appears as complex sulphides with Mn, Zn, Fe, and other metals in the Earth's crust [3]. Global anthropogenic inputs of Hg into the environment were estimated at about 3.2–30 × 10<sup>6</sup> kg year<sup>-1</sup>, whereas global natural Hg emissions were considered to be 3 × 10<sup>6</sup> kg year<sup>-1</sup> [4,5]. The first health

effects of Hg manifested in the early 1950s in Japan after Hg contaminated fish were consumed. Related Hg food poisoning incidences have also been reported in Iraq and Nigata [2]. In view of these incidences, the United Nations through the United Nations Environment Programme (UNEP) endorsed the Minamata Convention on Mercury.

Gold mining is one of the major minerals mined globally and it is one of the major sources via which Hg gets into the environment, particularly when Hg amalgam is used during the recovery of gold from its ores [4]. Hg amalgam was widely used in the past to recover gold from its ores until about 1920 in the Witwatersrand basin, South Africa [5]. This method has since been replaced with the cyanidation process. However, the resulting wastes from the Hg amalgam processes were dumped on next available empty lands. In South Africa, gold mine tailings dams occupies large areas (about six billion cubic meters) and are located near communities which may be affected by Hg released through erosion processes [6]. By

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law, the tailings dams are supposed to be vegetated in order to prevent wind and precipitation erosions. However, pollution still remains in the tailings dams since a number of these dams have not been re-vegetated.

Hg levels in various environmental compartments have been studied in South Africa [7–18]. However, information on Hg concentrations on gold mine tailings dams was non-existent until the studies conducted by Lusilao et al. [5,19,20]. Although the aforementioned studies by Lusilao were on tailings dams and their immediate matrices, the studies did not give much attention to the fractionation of Hg in soils and sediments in communities located in the vicinity of gold mine tailings dams. Furthermore, the aforementioned study [19] used a four-staged fractionation method which is not exhaustive enough to isolate the different fractions. It is pertinent to point out that generally, most studies to date on Hg have not been conducted along with other anions and trace metals. This aspect is extremely important since these parameters have the potential to influence the behaviour, mobility and bioavailability of Hg in the environment.

Therefore, this study aimed at determining THg and its fractions and association with trace metals and anions in order to understand the fate, mobility and distribution of Hg within the legacy amalgam gold mining affected environment. Sequential extraction was used to examine operationally defined fractions of Hg in tailings dams, soil and sediment samples. Furthermore, seasonal distribution of levels of Hg in soil, sediments and water samples collected from gold mine tailings dams and its immediate surrounding areas in Randfontein, South Africa are presented. It is envisaged that this study will provide the benchmark on the fractionation and seasonal variation of Hg within gold mining environment where Hg amalgam was previously used for the extraction of gold from its ores as well as highlight Hg association with other trace metals and anions.

## 2. Materials and methods

### 2.1. Standards, reagents and apparatus

#### 2.1.1. Standards and reagents

All the reagents used were Hg free and were, supplied by Sigma-Aldrich (Germany). Sulphuric acid (95–98%), hydrochloric acid (37%), nitric acid (70%), potassium permanganate ( $\geq 99\%$ , low in Hg), potassium persulphate ( $\geq 99\%$ ), sodium chloride ( $\geq 99\%$ ) and hydroxylamine sulphate (99%) were used throughout the experiments. Aqueous tin chloride prepared from tin (II) chloride dihydrate ( $\geq 98\%$ ) was used to reduce the oxidised Hg to elemental Hg which was subsequently vaporised into the instrument for analysis. To digest the samples for trace metal determination, some of the above mentioned acids (nitric acid, hydrochloric acid) and 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) from SSM Instruments (Pty) Ltd (South Africa) were used. Ultra-pure water prepared in our laboratory using SG Series Compact purchased at Evoqua water technologies (United Kingdom) was used throughout the experiment. Standard solutions of Ag, Al, Au, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Zn standards for AAS supplied by FLUKA Analytical (Switzerland) and Pb standard supplied by MERCK (Germany) were used throughout the experiments. For anions multi-element standard VII (Merck, Germany) and certified multi-anions standard solution PRIMUS (Fluka, Switzerland) containing  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  were used to calibrate the instrument and spiking.

All the glassware used were thoroughly washed with detergent, rinsed with tap water, soaked overnight in 10%  $\text{HNO}_3$ , rinsed three times with de-ionised water and dried in a clean oven at  $\pm 95^\circ\text{C}$  overnight.

### 2.2. Sampling area and sample collection

Randfontein is located South-west of Johannesburg (30 km West), in Gauteng Province South Africa. Some of the major and oldest gold mines in South Africa are located in Randfontein, where majority of the mines that operated before 1920 employed amalgam process as means of extracting gold from its ores. Fig. 1 shows the study area and sampling points.

Twenty five (11 soil, 7 sediments and 7 water) samples were collected from legacy amalgam tailings dams and their surrounding areas in winter (June) and summer (December) periods in 2015. Soil was collected at 5 cm depth (after clearing the debris) using acid-washed stainless steel trowel, placed in Ziploc bag and later in a sampling cooler bag. Water samples were collected by dipping thoroughly acid washed Teflon plastic-container 5 cm below the water surface. The precautions as prescribed by the USEPA Method 7471B and 245.1 for sampling procedures were carefully employed throughout the sampling processes [21,22]. The collected samples were transported to the laboratory and refrigerated until treatment and analysis commenced.

### 2.3. Sample preparation and digestion

Soil and sediment samples were air dried for  $\pm 24$  h. The dried samples were gently macerated to separate the lumps and sieved with a stainless steel sieve of different sizes ranging from 45–630  $\mu\text{m}$ . The fractions were subsequently subjected to particles size analysis using Microtrac S3500. Samples of  $< 45 \mu\text{m}$  were used for all other analysis of soil and sediments. For THg analysis, acid digestion procedures for preparing solid, semisolid and water samples for analysis of Hg using CVAAS as outlined in USEPA methods 7471B and 245.1 were employed, respectively [21,22]. Briefly, macerated, sieved and thoroughly homogenized samples without applying intense force to break large particles were used. A 1 g of soil was weighed and carefully transferred into a 250 ml round bottom flask. Working under the fume hood and treating each sample individually, 10 ml of ultra-pure water was added. This was followed by the addition of 5 ml of aqua regia (3:1). The flasks were then sealed with aluminium foil to prevent any loss of Hg vapour and heated for 2 min at  $95^\circ\text{C}$  in a heating mantle. The mixture was allowed to cool down after which 50 ml of ultra-pure water added. This was followed by the addition of 15 ml of freshly prepared potassium permanganate solution. The set-up was left for 15 min to allow for complete oxidation of Hg. For water samples, 100 ml was used and 8 ml of potassium persulphate added. Thereafter, the flasks were mounted with condensers and were sealed with aluminium foil to prevent any potential loss of Hg vapour. All the flasks were covered with glass wool within the heating chamber to ensure even distribution of the applied heat. The samples were then heated for 3 h, cooled and finally, 6 ml of sodium chloride-hydroxylamine hydrochloride added to reduce excess potassium permanganate. The samples were then made up to the 250 ml mark and kept in the refrigerator until instrumental analysis.

Sequential extraction described by Bloom et al. [23] was used to further investigate the fractions of Hg in soil and sediments. Samples analysed using this technique was frozen to minimize changes on Hg fractions prior to commencing with sample preparations. Briefly, soil samples collected from tailings dams, community, garden and sediments samples were sequentially leached with five extraction solutions shown in Table 1. For each extraction step, 50 ml of the extraction solution was added to 1 g of sample placed in a conical flask, sealed and shaken end-over-end at 250 rpm for  $\pm 24$  h. The obtained decant was centrifuged at 3000 rpm for 15 min, and the aqueous solution was filtered through a Whatman 0.45  $\mu\text{m}$  filter paper. The same extraction solution was used to rinse

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