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RESEARCH NOTE

Mercury and Other Heavy Metals in Groundwater in the Abandoned Mercury Mine in Puerto Princesa City, Philippines

Jessie O. Samaniego*, **Cris Reven L. Gibaga**, **Norman D.S. Mendoza**, **Charles Darwin T. Racadio**, **Alexandria M. Tanciongco**, and **Rasty M. Rastrullo**

Department of Science and Technology – Philippine Nuclear Research Institute
Quezon City 1101 Philippines

A rapid environmental assessment of the abandoned Palawan Quicksilver Mines, Inc. (PQMI) mined-out area and vicinities in Puerto Princesa City, Philippines was conducted from October 2018 to December 2019 to trace the pathways of mercury (Hg) concentration in different media, including groundwater. In this study, existing wells, drilled boreholes, and hand water pumps near the PQMI pit lake were used as sampling wells. Hg and other heavy metals – arsenic (As), barium (Ba), chromium (Cr), manganese (Mn), and nickel (Ni) – were analyzed to determine the concentrations and compared to the international and Philippine standard for drinking water. Results showed that As, Ba, and Hg concentrations in the entire groundwater samples collected from sampling wells have concentrations that are within the international and Philippines standards for drinking water. Groundwater samples from drilled boreholes have the measured Cr, Mn, and Ni concentrations exceed the standards for drinking water. The results further suggest that there is no mixing of groundwater and surface waters within the aquifer.

Keywords: abandoned mine, groundwater, heavy metals, mercury

The abandoned Hg mine in Puerto Princesa City is the only naturally occurring Hg deposit in the Philippines. The Hg ores in this deposit mostly occur in mercury sulfide (cinnabar) hosted by opalite bodies deposited along the fractures and weak zones in the bedrock (Irving 1954; Williams *et al.* 1999). The mine site, operated by PQMI from 1953–1976, is located approximately 3 km west of Honda Bay coast and within the catchment of Tagburos River, which is a local fishery and recreational area (Gray *et al.* 2003). For the past four decades, remediation work has not been carried out at this site, where bare mine waste calcine stockpiles and unvegetated areas can be observed until now. Today, the former open-pit mine is filled with water and included in the list of abandoned and inactive mines in the Philippines, which pose a high risk to human health and the environment and require rehabilitation (Samaniego *et al.* 2019).

Hg emissions from small-scale gold mining areas and abandoned Hg mine site are a major concern in the Philippines as it pollutes the nearby terrestrial and marine ecosystems (Opiso *et al.* 2018; Samaniego and Tanchuling 2018). Tailings and mine wastes from these mining areas, if not checked, may cause groundwater contamination due to the mixing of groundwater with surface waters (lake, river) and rain infiltration within aquifers. In the ongoing study on the tracing of the pathways of Hg contamination in the abandoned PQMI mine area and its vicinities, Hg concentrations in different media – including groundwater

*Corresponding Author: josamaniego@pnri.dost.gov.ph

– were assessed. In the previous report of the study, the measured Hg and other heavy metals concentrations in the surface waters (pit lake, river) were within the Philippines Class C guidelines (DENR 2016) – except for Mn and Ni in pit lake and Fe and Mn in the river, which are high in concentration (Samaniego *et al.* 2019). In the study of Williams and co-authors (1996) in the same area, the aquifer and stream water samples showed no evidence of Hg contamination – with values < 40 ng/L – and concluded that the role of potable water as a source of human Hg exposure is, thus, likely negligible. Aside from the said report, there was no other detailed study on the groundwater contamination brought about by the Hg concentrations from the mine wastes, leachate from the nearby landfill, and seepage from the lake. At present, several households in the area still use water well hand water pumps for their domestic consumption while the local water district supplies water taken from groundwater sources. The objective of this study is to test the groundwater quality in the area in terms of Hg and other heavy metals concentrations in and around the vicinity of the PQMI mined-out area and to compare it with the Philippines and the international standards for drinking water.

Two existing wells (established more than 10 yr ago), eight drilled boreholes (established less than 1 mo), and two hand water pumps (established more than 5 yr ago) were used as groundwater sampling wells for Hg and other heavy metal analyses in this study (Figure 1). Drilled boreholes were established in this study to augment the number of available deep wells in the area that are required to assess the groundwater quality. Each site was chosen and was positioned to be distributed on the study area based on road accessibility, lack of available groundwater well sites, and areas with few permanent structures nearby. Existing wells and hand water pumps are maintained by different private owners and pumping station is operated by the Puerto Princesa Water District. Photos of different sampling wells used in the study are shown in Figures 2a–c.

The groundwater depth of the drilled boreholes and the existing wells were measured using the Water Level Marker (Solinst, Canada). Groundwater sampling was undertaken after purging one well water volume with an electric pump to obtain a representative sample at depth using the Point Source Bailer (Solinst, Canada). Water samples from hand water pumps and water district were

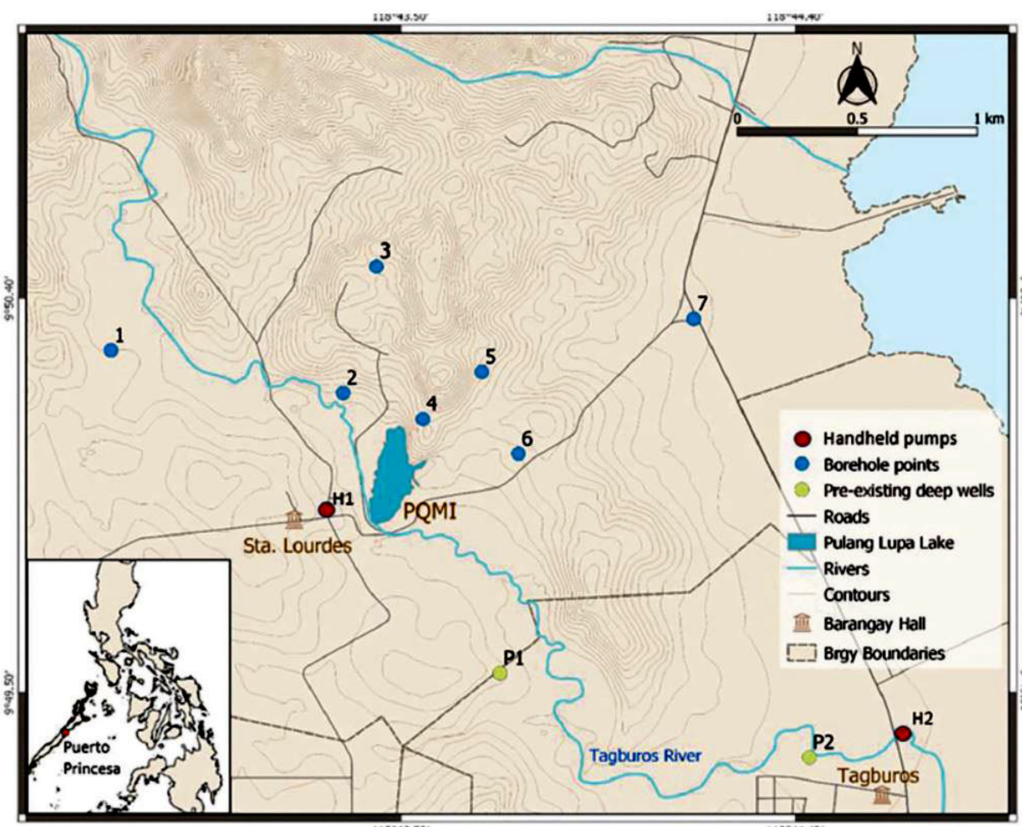

Figure 1. Location map of the drilled boreholes, existing wells, and handheld pumps used as sampling wells.

Figure 2. Photos of sampling wells: a) private-owned existing well, (b) pumping station of Puerto Princesa City Water District, and c) one of the drilled boreholes.

drawn by manual pumping and electric pump, respectively, were poured directly to the acid-washed 1-L high-density polyethylene sampling bottles. All groundwater samples were preserved by acidification using 5 mL HNO_3 and were stored in iced styrofoam containers during transport from site to laboratory. The concentration of Hg and other heavy metals (As, Ba, Cr, Mn, Ni) were determined using Direct Mercury Analyzer DMA-80 evo (Milestone, Italy) and Inductively Coupled Plasma – Optical Emission Spectroscopy (Agilent Technologies, USA), respectively. Detection limit for total Hg (THg), As, Ba, Cr, Mn, and Ni are 0.001 µg/L, 0.008 mg/L, 0.005 mg/L, 0.005 mg/L, 0.003 mg/L, and 0.003 mg/L, respectively.

The THg concentrations of the groundwater samples collected from the drilled boreholes, private wells, and hand water pumps in November and December 2019 sampling campaigns are presented in Table 1. All measured THg concentrations are below the international and Philippines standards for drinking water of 1 µg/L (WHO 2017; DOH 2017). The THg concentrations measured from the groundwater samples from existing wells (P1 and P2) and hand water pumps (H1 and H2) were below the detection limit of 0.001 µg/L. Groundwater samples from the drilled boreholes (1, 2, 3, 6, 7, 8) were collected within 1 mo after the completion of drilling works. Water samples from these boreholes were analyzed to be within the World Health Organization (WHO) and Philippine National Standards for Drinking Water (PNSDW) acceptable level, with a range of 0.011–0.204 µg/L of THg. Most of these current measurements of THg concentrations are still the same with the measured concentrations (< 40 ng/L) two decades ago (Williams *et al.* 1996). The results suggest that the groundwater in the PQMI area is not contaminated by the surface waters and there is no infiltration from the PQMI pit lake. The minimal presence of Hg in the groundwater exhibits the very low solubility potential of the Hg-bearing compounds like the cinnabar.

The naturally occurring heavy metals in the groundwater samples that are of health significance in drinking water were analyzed and compared the results to the WHO standards and PNSDW (Table 1). As was not detected (< 0.008 mg/L) from both drilled boreholes, existing wells, and hand water pumps. Ba concentrations in all groundwater samples are within the WHO and Philippines standards. The concentration of Cr, Mn, and Ni in the groundwater samples from existing wells (P1 and P2) were below the respective detection limit while Cr, Mn, and Ni concentrations in samples from hand water pumps were below the WHO and Philippines standards. Cr in drilled boreholes has a concentration ranging from 0.05–0.3 mg/L, where the majority of the samples were above the limit of 0.05 mg/L. Mn concentrations (0.6–1.4 mg/L) of all groundwater samples from the drilled boreholes were above the PNSDW limit of 0.04 mg/L. Similarly, Ni in groundwater samples (0.3–1.5 mg/L) were above the 0.07 mg/L standards for drinking water.

High concentrations of Cr, Mn, and Ni in the groundwater samples from drilled boreholes came from the naturally dissolved ions and compounds from the ultramafic rocks in the area that host these elements (Vithanage *et al.* 2019). It will take some time that these ions to settle in the bottom of the boreholes and make the groundwater free from the elements as verified in the water quality of existing wells. The anomalous concentration of Cr, Mn, and Ni in the sampling sites brought by the geology of the area. Based on the drill core data from the drilled boreholes, the aquifer consists of unconsolidated materials from ultramafic rock formations of Puerto Princesa City, where cinnabar ore resides and have naturally high concentrations of Cr, Mn, and Ni.

The anomalous concentration of Cr, Mn, and Ni in the area is inherent in the laterite-rich soils and ultramafic bedrock formations of Puerto Princesa City, where the cinnabar ore resides.

Table 1. Hg and other heavy metals concentration of groundwater samples collected from drilled boreholes and existing wells.

Borehole no.	Well depth (m)	THg (µg/L)	As (mg/L)	Ba (mg/L)	Cr (mg/L)	Mn (mg/L)	Ni (mg/L)
1	52.0	0.032	< 0.008	0.05	0.2	1.0	0.3
2	41.0	0.023	< 0.008	0.03	0.2	1.4	1.0
3	30.0	0.016	< 0.008	< 0.005	0.3	0.6	1.1
4	20.0	Dry	Dry	Dry	Dry	Dry	Dry
5	6.0	Dry	Dry	Dry	Dry	Dry	Dry
6	35.0	0.204	< 0.008	0.009	0.05	0.7	0.3
7	50.0	0.011	< 0.008	0.04	0.2	1.2	1.5
8	20.0	0.015	< 0.008	0.1	0.1	0.9	0.7
P1	13.8	<0.001	< 0.008	0.03	< 0.005	< 0.003	< 0.003
P2	55.4	<0.001	< 0.008	< 0.005	< 0.005	< 0.003	< 0.003
H1	–	<0.001	< 0.008	0.008	< 0.005	0.3	0.007
H2	–	<0.001	< 0.008	0.008	< 0.005	0.1	0.01
WHO standard		1.0	0.01	1.3	0.05	–	0.07
PNSDW		1.0	0.01	0.07	0.05	0.4	0.07

Note: Well depth of hand water pumps (H1 and H2) were not measured.
Detection limit for THg, As, Ba, Cr, Mn, and Ni are 0.001 µg/L, 0.008 mg/L, 0.005 mg/L, 0.005 mg/L, 0.003 mg/L, and 0.003 mg/L, respectively.
DMA precision is ± 1%/ng of Hg, while measurement uncertainties of ICP-OES for As, Ba, Cr, Mn, and Ni are ± 0.00009 mg/L, ± 0.00007 mg/L, ± 0.00007 mg/L, ± 0.00010 mg/L, and ± 0.00005 mg/L, respectively.

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