

# Sediment Fixation of Arsenic in the Ash Lagoon of a Coal-Fired Power Plant, Philippines

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**Abstract**—Arsenic in the sediments of the ash lagoons of the coal-fired power plant in Pagbilao, Quezon Province in the Philippines was sequentially extracted to determine its potential for leaching to the groundwater and the adjacent marine environment. Results show that 89% of the As is bound to the quasi-crystalline Fe/Mn oxides and hydroxide matrix in the sediments, whereas, the adsorbed and exchangeable As hosted by the clay minerals, representing those that are easiest to release from the sediment matrix, is below 10% of the acid leachable As. These As in these sediment matrices represent the possible maximum amount of As that can be released and supplied to the groundwater and the adjacent marine environment. Of the 89% reducible As, up to 4% is associated with the easily reducible variety, whereas, the rest is more strongly bonded by the moderately reducible variety. Based on the long-term As content of the lagoon water, the average desorption rate of As is calculated to be very low -- 0.3-0.5% on the average and 0.6% on the maximum. This indicates that As is well-fixed by its sediment matrices in the ash lagoon, attenuating the influx of As into the adjacent groundwater and marine environments.

**Keywords**—Arsenic, natural attenuation, coal-fired power plant, Philippines.

## I. INTRODUCTION

COALS contain pyrite and organics [1,2], the chief mineral sources of As and other heavy metals in coal. Because of its environmental and health significance, As has become a focal metal in coal-combusting plants, alongside Hg and Cd among the heavy metals [3]. In coals, it can be super-concentrated in pyrites and other sulfides, even attaining a maximum concentration of 35,000 parts per million [4]. The heavy metals in coal are liberated during the combustion process and are concentrated in the fly and bottom ashes [2], [5]-[6]. These fly and bottom ashes comprise the bulk of the by-products of coal combustion which are impounded in the ash lagoons of power plants.

This study on the ash lagoon of the 700-MW Pagbilao Power Station, situated southeast of metropolitan Manila (Fig. 1), determines the geochemical behavior and fate of As relative to its possible dispersion toward the immediate groundwater reservoir in the plant site and to the adjacent marine environment. The ash lagoon serves as the repository of combusted coal by-products – fly and bottom ashes, and

can be a major source of heavy metals for these adjacent water bodies.

There are three separate but adjacent ash lagoons inside the power plant. The lowest of the ash lagoon, also the most proximal to the coast, has been adopted by a community of wild migratory birds from mainland Asia and Japan as their temporary sanctuary during winter time, enroute to their southward destination. While this pond is topographically lower than the upper two integrated ash ponds, it may be the most vulnerable among the three lagoons to metal leaching and from surface runoff coming from the neighboring coal yard. Based on the groundwater flow of the area [10], percolating water from the elevated integrated ash lagoons seeps through to this lagoon because it is along the groundwater pathway and because it is situated at a lower elevation.

## II. METHODOLOGY

Sixteen samples were collected from the ash lagoons. Sediments from the lagoon bottom have the bulk consistency of coal ash. Those taken from the subaerially exposed portion of the ash lagoon contain uncombusted coal feed fragments, ash, and detrital clays and minerals.

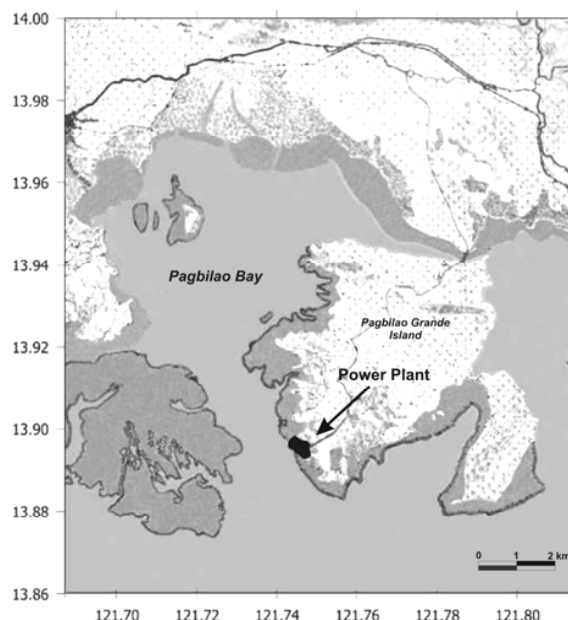


Fig. 1 Location of the power plant at Pagbilao Grande Island in Quezon Province, 115 aerial km southeast of Manila

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The sediment were analyzed for their total leachable As contents following the USEPA Method 3050B on metal leaching in sediments. Six of these sediment samples were also analyzed using the sequential heavy metal extraction procedure of Förstner and Calmano [11].

### III. RESULTS AND DISCUSSION

The As concentrations are compared with the average shale values because of the absence of the geochemical baselines unique to the study area. The use of average shale values as approximate baselines for Philippine sediments proved to be valid as supported by the geochemical studies on the core sediments of Laguna Lake, Manila Bay, and Lingayen Gulf [11].

Note that the concentrations measured represent the total acid leachable concentrations and not the total available concentrations. They represent those metal fractions of the total concentration which are environmentally significant. However, as the As in the sediments is not bonded to just one kind of sediment matrix, the availability of As in the different matrices is also geochemically as well as environmentally variable. Thus, the total leachable concentration may be interpreted only as the maximum amount of potentially and environmentally significant As in the sediments. The contribution of each particulate metal host is provided by the sequentially extracted As.

Sediments from the upper two ash lagoons exhibit similar bulk sediment characteristics. As enrichment in these ash sediments is persistently and almost invariably higher, from 2 to 3.6 times, than its average shale concentration, or from 25.88 – 47.31 mg/kg total acid leachable As. Expectedly, as in most world coals, coal ashes are higher in As than in the uncombusted feed coal [12]. Clay mineral control on As in the sediments is extremely weak, hosting only 3-6% of the total acid leachable As. This may mean that clay minerals are scarce components of the ash sediments. Because this clay mineral-controlled As fraction represents the weakest As bond in the sediments, this can be used to approximate the amount of As that can be easily released from the sediment matrix to the overlying water column of the pond. This means that 0.82-1.63 mg/kg As, based on sample measurement, can be used to approximate the desorbed As contribution of the ash dominated sediment to the overlying pond water.

However, clay is not the only sediment matrix that contributes to metal desorption to the water column. The reducible phases of Mn and Fe oxides and hydroxides also host As, and actually are the more geochemically robust hosts of As in the ash-dominated lagoon sediments. They are associated with 89% of the leachable As in the ash sediments, or correspondingly, 20 - 26 mg/kg As. The reducible Fe and Mn oxides and hydroxides come in two bonding types: those that are easily reducible and those that are moderately reducible. Of this dominant matrix species, only 1 - 4% or 0.26 - 1.17 mg/kg As are bound to the highly amorphous or easily reducible oxides and hydroxides. This means that at least 85% of the As, or those that are relatively strongly bonded to the oxides and hydroxides, is relatively

environmentally inert or is not easily available through natural desorption processes.

The association of As to another sediment matrix, the particulate organic components of the ash sediments, including those associated with sulfide substances, is practically nil. On the other hand, organic matter component may be very scarce in the lagoon's ash sediments, similar to the occurrence of clay minerals. The crystalline components of the lagoon's ash sediments host only up to 7% of the total As. This As fraction can be cited as the most environmentally stable because it is fixed in the mineral lattices.

In the lower ash lagoon, where the migratory wild birds temporarily settle during their southward migration, the total leachable As in the sediments is enriched up to seven times their average shale values (up to 13.0 mg/kg). As, as differentiated by its matrix species, shows that about 63% of its total concentration is related to its affinity with the amorphous Fe/Mn oxides and hydroxides, following a scenario similar to those observed in the two integrated upper lagoons, where 89% of the As is controlled by these phases. Of these, only 9% As is related to the easily reducible variety of Fe and Mn oxides and hydroxides; 54% of the As is hosted by their moderately reducible counterpart.

The organic matter in this lagoon's sediments has a very low As contents, corresponding only to about 1%, or 0.34 mg/kg As. About 20% As is associated with the sediment's crystalline fraction. This translates to a content of 7.73 mg/kg As hosted by the crystalline minerals in the sediments. Surprisingly, organic matter and clay minerals, being known as the geochemically active hosts of heavy metals in the natural system, are the scarce hosts of As in the lagoon sediments, representing only 1% and 6% of the total As.

Based on the As concentrations measured from the sediments of the ash lagoons, As desorption from the sediment matrix to the pond's water and to the groundwater can be described to be relatively very low. The potential amount of As that may be released or desorbed is equivalent to the As concentrations derived from the clay matrix and the easily reducible phases. Although it was found out that the sediments host a high amount of As based on the sequential extraction and total leachable data, As remained strongly fixed in the sediment matrix.

In the two upper integrated lagoons, the As release from their sediment matrix can be qualified to be hardly induced because there is a significantly high amount of As that is bonded to the moderately reducible Fe/Mn oxides and hydroxides. Their release requires substantial acidification of the water column to a very low pH level, which can only be brought about in the site by a human factor. This geochemical scenario is well-supported by the groundwater and pond water monitoring data, that the amount of As released into the receiving bodies of water is very low.

To correlate the lagoon water As load with the metal contents of the sediments provides a testament to the very low As release of the sediments. As plots from a four-year water data with monthly water sampling periods show a dominant As maxima within the concentration range of 0.05 – 0.20 mg/li As and an average at 0.08 mg/li As in the lagoon water. Assuming that there is no As source other than the lagoon

sediments and if the measured sediment concentrations of potentially remobilizable As is taken as, on the average, equal to 26 mg/kg (i.e., concentration range = 19.18 to 31.13 mg/kg As) based on the sequential analysis data, then the averaged As concentration of the integrated lagoon water, 0.93 mg/li (0.20 mg/li As maxima) can be said to be extremely low. This is equivalent to just 0.3-0.5% average desorption from the sediments or to a maximum of 0.6% As desorption. This correlation strongly suggests a geochemically well-constrained As fixation by the metal matrices in the sediments of the ash lagoons and the consequent retardation on the remobilization of As to both the ground and surface waters in the pond and its vicinity.

#### IV. CONCLUSION

Arsenic is clearly sourced from the coal ash and is being fixed by the sediments, specifically by the amorphous Fe/Mn oxides and hydroxides in the sediment matrix. There is a very high preference of As fixation in the more crystalline variety of Fe/Mn oxides and hydroxides than in the more amorphous varieties. Matrix speciation data show that at least 85% of the As are relatively more strongly bonded by these amorphous substances, controlling their low desorption to the water column, and ultimately, their dispersion to the adjacent ground and marine waters. The average desorption rate of As from the sediment matrix to the overlying water column based on the sediment source and the water column data is calculated to be very low -- 0.3-0.5% on the average and 0.6% on the maximum.

#### ACKNOWLEDGMENT

The authors acknowledge Maunsell Philippines and Mirant Philippines for the conduct of the study and thank Mr. Jose Reynato Maliwanag Morente and Mr. Jess Bayrante for their support to publish this paper.

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