Geochemical distribution and behaviour of mercury and arsenic in the Brunei-Muara District, Brunei Darussalam

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Abstract. Both mercury and arsenic are toxic elements which can affect human health and ecosystems negatively. Monoelemental geochemical maps were constructed to identify the spatial distribution of both mercury and arsenic in Brunei Muara District of Brunei Darussalam. This paper is a product of a pilot project aiming at constructing the geochemical atlas of Brunei Darussalam. Extensive field work and sampling enabled us to collect 187 subsoil samples with a sampling density of 1 km². Both mercury and arsenic were analyzed in the fine fraction and the relevant geochemical maps were constructed and correlated with the geological, land use and different vegetation types maps of Brunei Darussalam. Certain anomalies observed on heat maps can be linked to anthropogenic activities in industrial and urbanised areas, as well as to analyze mobility of these elements due to natural phenomena and different types of soils.

1. Introduction
Geochemical mapping is a technique developed to give information on the spatial distribution of chemical elements on the Earth’s surface. These maps are employed in many countries for various purposes such as mineral exploration (e.g. [1]) and environmental monitoring (e.g. [2]). Geochemical mapping can help to monitor possible harmful elements and to assess hazard risks for human health (e.g [3]). A geochemical mapping for the soils of Brunei Darussalam is lacking, therefore understanding natural and/or anthropogenic surface processes and effects in the environment is poor. A series of geochemical maps of Brunei Darussalam could be utilised as an exploration tool for targeting potential mineral resources, as well as for environmental monitoring purposes (including agricultural activities and groundwater quality) to help government and private bodies to make rational decisions in environmental planning and management [4]. Acid sulphate soils occur widely in Brunei Muara [5] and the construction of a geochemical atlas might help to provide a clearer picture of their spatial distribution, as well as their negative effects. Heavy metals and trace elements, like for example, Cd, Zn, Pb, Cu, Hg and others, may contribute to soil contamination with apparent adverse effects and their distribution and behaviour can be monitored with the aid of geochemical atlases. According to Halamic et al. [6], there are several factors, which affect the concentration of heavy metals in soils: (1) the parent material and the process which generates the soil, (2) input of these elements to soil by wind, rain and other processes, and (3) anthropogenic input and deposition of particles into stream systems [7].

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This paper is part of an ongoing project for the construction of the geochemical atlas of Brunei Darussalam and aims to present an example of the distribution and behaviour of two toxic metals, mercury and arsenic in the soils of the country. This work attempts to investigate the origin of these elements in the soil by comparing and correlating their distribution with geological formations, urbanized areas, infrastructure and industrial areas. This work also briefly discusses the statistical approaches to determining the threshold values based on the work of Reimann et al. [8].

2. Study Area

2.1 Geographical location
Brunei Darussalam is located at the northwest of the Borneo Island, SE Asia and includes Brunei-Muara, Tutong, Kuala Belait and Temburong Districts (Fig. 1). Brunei Darussalam has a tropical climate, hence receiving acid rain with an annual rainfall frequently exceeding 2,300 mm [9,10].

2.2 Geological setting
Brunei Darussalam occurs near the junction of three large lithospheric plates controlling the Cenozoic plate-tectonic evolution of Southeast Asia: the continental Eurasian plate to the northwest, the Indian and Australian Plates to the southwest and south respectively and the Pacific Plate to the east. Brunei Darussalam occupies a central position, at the boundary among the northeastern part of Sundaland, the Sulu and Celebes Seas regions to the east and the South China Sea to the NW [11]. Table 1 summarises the different formations outcropping in Brunei Darussalam and their composition and figure 1 shows their spatial distribution.

Table 1. Summary of the geological formations of Brunei Darussalam.

| Formation           | Composition                                                                 |
|---------------------|-----------------------------------------------------------------------------|
| Holocene sediments  | clay and sand in places overlain by peat                                   |
| Pleistocene sediments| clay, sand, gravel and peat                                                |
| Liang Formation     | sand, sandy clay, clay and thin horizons of lignite                        |
| Seria Formation     | sand, soft sandstone, sandy clay, clay and lignite                         |
| Miri Formation      | sandstone, sandy shale, claystone and shale                                |
| Belait Formation    | sandstone, sand shale, clay and lignite                                     |
| Lambir Formation    | sandstone and shale with thin limestone, marl and calcareous sandstone beds|
| Meligan Formation   | massive sandstone, shale and some thin beds of limestone                   |
| Setap Shale Formation| clay, shale and subordinate sandstone                                      |

3. Methodology
A sampling grid was designed with a sample density of 1 sample per km² and so far, 187 subsoil samples (50-75 cm depth) have been collected. Sampling is still ongoing and “holes” still exist in the data hence, this is a preliminary study. The samples were obtained with a hand-held screw-type auger with a bore diameter of 6” and stored in lab-grade sample bags. The samples were screened, carefully cleared of organic materials and homogenized in the Mineralogy, Petrology and Geochemistry Lab, Faculty of Science, UBD. Drying (60 °C), sieving (< 63μm) and geochemical analyses of the fine fraction were performed at Activation Laboratories, Ancaster Ontario, using a combination of 4-acid digestion ICP-MS and INAA. Detection limits for As and Hg are 0.5 ppm and 10 ppb, respectively, and the analytical precision, calculated from replicate analyses, is better than 5%.

The monoelemental As and Hg geochemical maps, as well as the pH spatial map were produced with SAGA GIS 2.3.2 and interpolation was done by adopting the inverse distance weighted (IDW) method (Fig. 2). The grid-cell size chosen for this study was 0.0015 degrees. Two geochemical maps were
produced for each element to illustrate the difference of the threshold values from two different statistical treatments.

![Simplified geological map of Brunei Darussalam](image)

Figure 1. Simplified geological map of Brunei Darussalam. Inset shows Brunei-Muara District (modified after [11]).

Descriptive statistics were calculated and the threshold values were determined with both median + 2 MAD [8] and Tukey boxplot [12] techniques and outliers for each element were defined. The use of two techniques for the identification of the threshold values aims to compare the different datasets produced and to suggest the most suitable threshold values. Median + 2MAD produces a much lower threshold value than Tukey boxplot technique. The determination of outliers is important as these anomalies can help to decode adverse anthropogenic activities for the environment or other natural processes.

Tukey boxplot technique uses the upper whisker or Tukey inner fence (TIF) to define the threshold value, using the equation:

$$TIF = Q3 + 1.5 \times IQR$$

(1)

Where, Q3 is the upper quartile and the IQR denotes the interquartile range (upper quartile – lower quartile). This method allows to identify outliers even if there are none in the dataset (where the max value is less than the TIF) [13], as the outlier is extrapolated within the interquartile range. However, median + 2MAD is still favored by geochemists as this method produces lower threshold values and thus produces more outliers and areas to be investigated further [13].

4. Results

4.1 pH

Figure 2 shows the heatmap of pH in the region of Brunei Muara District. The central and northern parts show higher pH values, whereas the western and southern regions are the more acidic ones. Notably, the whole region contains highly acidic soils, which has a negative effect in several activities.
4.2 Statistical data
The statistical summary and threshold values obtained with TIF and median + 2MAD for As and Hg are shown in Table 2.

|          | Lower Quartile | Median | Upper Quartile | Standard Deviation | TIF | Median + 2MAD | Minimum | Maximum |
|----------|----------------|--------|----------------|-------------------|-----|---------------|---------|---------|
| Hg (ppb) | 10             | 70     | 100            | 52.51             | 235 | 158.38        | 5       | 320     |
| As (ppm) | 11             | 14.8   | 17.3           | 4.93              | 26.75 | 22.41       | 2.4       | 33.7    |

The statistical distribution of the concentrations of Hg and As are shown in boxplot diagrams (Figure 3). Tukey boxplot technique defines a threshold value of 235 ppb and produces one outlier for Hg (Table 2 and Figure 3a) whereas a lower threshold value (158.38 ppb) from the median + 2MAD method returns seven outliers. Three outliers for As and a threshold value of 4.93 ppm are identified with the boxplot (Table 2 and Figure 3b) whereas seven outliers identified when the median + 2MAD threshold value (22.41 ppm) is considered.

4.3 Mercury (Hg)
Figure 4 shows the heat maps for the distribution of Hg in Brunei-Muara District generated using the threshold value obtained from median + 2MAD (a) and Tukey boxplot (b) methods. This paper will focus on the map produced with the median + 2MAD method, which better depicts the relevant geochemical anomalies (outliers; reddish colors in Figure 4a).

According to Mihaljevic [14], regular soils contain 20-150 μg kg⁻¹ (ppb) of mercury, the uppermost value of which nearly coincides with our calculated threshold. The analyzed soil samples of Brunei Muara contain Hg ranging from very low values (below detection limit) up to 320 ppb (Table 1). Three different regions can be recognized in Brunei Muara with distinctive characteristics for the distribution of Hg (Figure 4a). Regions A and B are characterized by the occurrence of positive Hg anomalies and concentrations generally higher than 100 ppb (upper quartile ranges). In contrast, soil in region C shows very low Hg concentrations. Belait and Liang formations outcrop in region A, whereas Belait Formation and recent sediments occur in region B (See Figure 1). Several industrial activities are found around region A, as well whereas heath and secondary forests dominate regions A and B with some agricultural
activities in region B, as well. Region C is mostly occupied with recent sediments and comprises the urban areas of Brunei Muara District.

**Figure 3.** Boxplot plots of (a) Hg (ppb) and (b) As (ppm) from the Brunei Muara District.

**Figure 4.** Distribution of Hg in Brunei Muara District, using threshold values obtained from (a) median + 2MAD and (b) Tukey boxplot.

### 4.4 Arsenic (As)

Figure 5 shows a heat map for the distribution of As in Brunei-Muara District generated using the threshold value obtained with median + 2MAD (a) Tukey boxplot (b) methods. Again the the first method returns more geochemical anomalies, hence the relevant map will be the focus of the present paper.
According to Kabata-Pendias and Pendias [15] As concentrations in most soils range from 1 to 95 mg kg\(^{-1}\) (ppm) with mean values of about 9 ppm. The statistical data of As show that the concentrations of As in Brunei Muara soils range from 2.4 to 33.7 ppm (Table 1). Several positive outliers (with values higher than the threshold of 22.41 ppm) were identified in the area. Three regions can be distinguished (Figure 5a): Regions A and B include most of the positive geochemical anomalies of As. In contrast, very low As concentrations generally occur in region C. Unlike Hg, As shows some anomalous values in the urban area (B in figure 5a). Regions A and B are dominated by the occurrence of Belait, Liang and Seria Formations, as well as the recent deposits whereas Miri and Belait Formations along with recent sediments and Seria Formation occur in region C (see Figure 1). In regions A and C, heath and secondary forests, can be found. Farming activities occur in region C.

**Figure 5.** Distribution of As in Brunei Muara District using threshold values obtained from (a) median + 2 MAD and (b) Tukey boxplot.

### 5. Interpretations

#### 5.1 Mercury (Hg)

Mercury (also known as quicksilver) belongs to the same group of the periodic table with zinc and cadmium. It does not react with acids, such as dilute sulfuric acid or nitric acid but reacts readily when atmospheric hydrogen sulfide or solid sulfur are available. Mercury occurs in the forms of mercuric (Hg\(^{2+}\)), mercurous (Hg\(^{2+}\)), elemental (Hg), or alkalyted forms (methyl/ethyl mercury). Mercurous and mercuric Hg are more stable under oxidizing conditions. When reducing conditions exist, organic or inorganic Hg may be reduced to elemental Hg, which may then be converted to alkalyted forms by biotic or abiotic processes. Mercury is very toxic in its alkalyted forms, which are soluble in water and volatile in air.

Mercury has a natural strong affinity to organic and inorganic coal matter and it can be readily adsorbed in the interlayered spaces of clay minerals, at pH < 5 [16-18]. Therefore, the observed higher concentrations of Hg can be explained from the presence of clays and/or coal seams occurring in Belait and Liang Formations (Table 1).

According to Selin [19], 30% of total mercury emission comes from anthropogenic activities (such as industrial waste, production and manufacturing of metals and chemicals, fossil fuel combustion and traffic activity). Region A in figure 4a includes several industries ranging from car workshops, factories, as well as recycling centres, which may have a contribution in the emission of Hg. Region C shows a low concentration of Hg, which contradicts studies that have shown high concentrations of this element in urban areas. A likely explanation is that the sandy and devoid of organic matter recent sediments do not have the capability to adsorb Hg, therefore it can be easily oxidized and transported in the atmosphere in a volatile form [20].
5.2 Arsenic (As)
Arsenic is a metalloid with several allotropic forms and widely known for its toxic character in groundwater contamination. Inorganic arsenic predominantly exists in trivalent and pentavalent oxidation states. In terms of toxicity, arsenite, As(III) is more toxic than arsenate, As(V), which occurs predominantly in soils.

Arsenic is usually concentrated in clays, lignites, hydrous Fe and Mn oxide, sulphides and phosphates [21,22]. However, clays and lignites do not appear to exert a major control on the concentrations of As in Brunei Muara District because the areas with both positive and negative geochemical anomalies occur in clay-containing formations. This suggests that the distribution of As in Brunei Muara District has mostly an anthropogenic origin. This hypothesis is in line with the anomalous As values occurring mostly in the urbanized areas including various industrial activities.

Regions A and B (Figure 5a) also consist of secondary and heath forests. The soil-organic content is high in these regions due to the presence of decomposing organic matter. Dissolved organic matter contains negative charges, resulting in the competition of adsorption of sites between it and As [23]. Higher levels of organic matter cause As to be more available to the environment, hence increasing its abundance in the soils of regions A and B.

Agricultural activities are mostly concentrated in region C where the soil pH ranges from 3.6 to 3.8. In these pH span, As mobilisation increases as a result of dissolution of Fe oxides contained in the soil, possibly resulting in As to become bioavailable and hence capable to be absorbed by plants [24]. However, further study is needed to confirm this hypothesis. Both areas A and B both have relatively higher pH, which might reduce the solubility of As in soil, thus resulting in the anomalous concentrations of As in both these areas.

6. Conclusions
Preliminary geochemical data helped us to investigate the distribution and behaviour of Hg and As, which are two well-known toxic elements, in the soils of Brunei Muara. The geological setting of the region and particularly the occurrence of clays and lignite seams are well correlated with the distribution of Hg, as this element is strongly adsorbed by them. At least part of mercury is also assigned to anthropogenic impact likely deriving from industrial activities. Arsenic shows a behaviour irrespective of the geology of the area and hence the anomalous amounts are related to anthropogenic impacts. Organic matter promotes the availability of As in the environment whereas low pH is a factor promoting the dissolution and mobility of As.

The proper statistical treatment of data is a critical factor for understanding the distribution and behaviour of chemical elements in soils. Selecting the suitable method is not always an easy task and much effort is required in order to define the threshold values, which are critical for decision-makings. This is an ongoing research project, therefore more data are expected in the near future.

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