Modelling the distribution of arsenic and mercury in urine using chemometric tools

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Abstract: Among the heavy metals and other chemicals that contaminate the immediate environment of all gold mining communities, Arsenic and Mercury compounds are some of the most prevalent, exposing residents to their health risks. This menace is the result of the mining activities, particularly, Artisanal and Small-scale gold mining, in these communities. Among the mining areas in Ghana, Artisanal and small-scale gold mining is a recent activity only in the Eastern Region, particularly in the Aduasena, Afosu, Intronang, Hweakwae, New Abirem, Mamano and Hamlets communities. The objective of this research is to investigate the levels of Arsenic and Mercury in the residents of these seven communities using spectroscopic analysis of their urine samples and to identify which gender and at what age does any resident in a typical Ghanaian mining community stand most endangered by the levels of these contaminants. Samples of first urine void of residents upon waking up in the morning were taken, digested with nitric acid and analysed for the concentrations of Arsenic and Mercury using the Perkin Elmer PinAAcle 900T Graphite Furnace AAS. The spectroscopic analysis of the urine samples showed that more than 20% of the residents had concentrations of Arsenic higher than the (normal) recommended level, with some reaching as high as 221 μg/L for Arsenic and 3.90 μg/L for mercury. Statistical analysis of the results showed that the levels...
of both Arsenic and Mercury seem to increase with increasing age, despite some extremely high concentrations for arsenic in the Aduasena youth between 31 and 40 years. This trend indicates that males were seen to be more at risk from these contaminants, with the youth between 11 and 20 years standing most endangered.

Subjects: Environmental Issues; Research Methods in Environmental Studies; Environmental Policy

Keywords: modeling; distribution; arsenic; mercury; urine; chemometrics

1. Background

1.1. Introduction

From time extending beyond the reach of memory, the scope of our existence on the planet has, to the largest extent, been determined by the state of our natural environment. The exploitation of natural resources, particularly, by environmentally injurious methods has greatly contributed to the dwindling safety of our lives. Primarily, all mineral resources can be categorized into two groups:

(a) Fuel minerals (Pollution issues: Mining) such as coal, petroleum and natural gas.
(b) Non-fuel minerals (Pollution issues: Mining), which are metallic minerals like gold, manganese, bauxite, copper and platinum.

The nonfuel metallic minerals naturally exist with other unwanted materials as ores which are buried under a thick layer of soil or rock known as the overburden (or waste) rock (Guidebook for evaluating mining projects EIA’s, 2010). The overburden rock must be excavated by the appropriate machinery to allow access to the metallic ore deposit. After digging the earth for them, these ores are treated, generally, with chemicals or heat, to produce the metals of interest. The chemicals applied in these treatment processes expose us to countless health hazards, as their wastes are discharged into the environment. The soil, waterbodies, plants and other living organisms become very much susceptible to the adverse impacts of the harmful concentrations of the chemicals and heavy metals released into the environment from these extraction processes. Arsenic is generally found, in high concentrations, in areas where there are gold deposits, and mercury is common in those communities where the treatment of gold or its extraction is mainly done using the amalgamation method.

1.2. Overview of Artisanal and small-scale gold mining in Ghana

Artisanal and small-scale mining refers to the type of mining done by individuals, groups, families or cooperatives with minimal or no mechanization and often in the informal (illegal) sector of the market (Hentschel, Hruschka, & Priester, 2003). Many other parts of the world where it thrives, artisanal and small-scale gold mining (ASGM), popularly called “galamsey” in Ghana usually plays an important role in poverty alleviation for the miners and other residents in the mining communities. Most of those involved in the activities are low-income earners and therefore the trade serves as the most promising income opportunity available.

Besides the seven listed communities in the Eastern Region, other typical communities in the country where “galamsey” operations take place include Tarkwa, Bogoso, Prestea, Kati, Chirano, Konongo and Obuasi. Artisanal gold mining activities began in those seven communities in the Eastern region only recently. In these communities where mining operations are prominent, the large-scale mining sector which is run by well organized, transnational companies, like Newmont in New Abirem, often engage in conflict with the ASGM operators over land and resources. However, the activities of both parties, if registered, are supported by the legal framework of mining operations under the PNDC law. ASGM operators usually prefer concessions where the ore
deposits are very rich and easy to process with the amalgamation method (application of mercury). This situation arises because the small-scale miners lack the sophisticated machinery and processing equipment that would help them to obtain higher yields of gold. Most ASGM activities release mercury to the environment by the disposal of mercury-laden tailings and process water to the ground and waterbodies or atmospheric emissions of mercury vapours from the smelting of gold-mercury amalgam. Since more than one processing technique is available in the processing of the raw ore, the particular method applied in the processing of the ore determines the degree of pollution of the environment by particularly, mercury, from its use and disposal. For instance, the whole ore amalgamation method used in many other countries like Indonesia and Tanzania will definitely put more mercury waste in the environment than in Ghana where the partial gravity-amalgamation method is mostly used (Artisanal Gold Mining). There are a lot of variations in the legalities surrounding the operations of ASGM among the different countries where the trade is practised. Unlike Ghana, where a legal framework is instituted to regularize its activities, ASGM is completely banned in other countries. The legal framework that controls the activities of ASGM in Ghana consists of one called the Small Scale Gold Mining Law—1989, established under the PNDC Law 218 in the year 1989 (Ghana Legal). Despite the continual efforts by the government to legalize the operations of ASGM in Ghana, the proliferation of illegal mining in the country continues to burgeon due to their unwillingness to go through the necessary registration procedures to acquire mine concessions or to obtain the permit to start their operations. According to a report issued the Ghana Chamber of Mines in 2008, only 300 out of between 300,000 and 500,000 miners who were currently in operation by then (Macdonald et al., 2014) (Fatien, Mark, Melanie, & Clint, 2014) had gone through the necessary registration procedure to start a business. This is a sure evidence of the perpetration of illegal mining activities in the country.

1.3. Arsenic

Arsenic is a naturally occurring semi-metallic element commonly found with other organic and inorganic substances in soils, groundwater, surface water, air, and some foods (US EPA). Generally, it is a significant component of all gold deposits, whose content may range from traces to a value greater than 5 mg per gram of the ore. Artisanal mining activities on these deposits produce a significant reduction in the pH of nearby waterbodies which shows a strong evidence of its contamination. Human exposure to high concentrations of inorganic arsenic compounds could be very threatening since they are very poisonous. This usually occurs through drinking groundwater which already contains elevated concentrations of inorganic arsenic, food prepared with this water and food crops irrigated with water from high-arsenic sources (WHO, 2010). A long period of exposure to inorganic arsenic can cause chronic arsenic poisoning, otherwise known as arsenicosis. Arsenicosis is, basically, caused by the ingestion, inhalation or absorption of harmful concentrations of arsenic (from arsenic-containing compounds) (WHO, 2010). It is clear that the most frequent causes of these health impacts are from arsenic contamination of water, affected foods and polluted air. Hence, among the measures to mitigate the risk of exposure, the WHO recommends that occupational exposure of arsenic and its compounds must be kept as low as possible as well as making safe drinking water available for consumption (WHO, 2010). This may be achieved by keeping the arsenic concentration below the recommended 10 μg/l (0.01 mg/L) (Arsenic and Inorganic Arsenic Compounds), especially for places where arsenic contamination is high.

1.4. Mercury

Mercury, a very poisonous heavy metal like arsenic, is a naturally occurring element found in the air, water and land (WHO, 2017). Mercury is the only metallic element that is liquid at room temperature in its pure state, and it is this liquid form which is been used by artisanal miners. During its use, mercury is mixed with the gold-concentrated material forming a gold-mercury amalgam, which is subjected to heating, vaporizing the mercury to obtain the gold. Inhalation of elemental mercury (in the vaporized form), ingestion or dermal exposure of different compounds of mercury can produce neurological and behavioural disorders. This is usually common for occupational exposure in goldmine workers and residents of the surrounding communities of mining areas (Abrefa et al., 2011). Vaporized elemental mercury can be transported in the atmosphere over a long period and get deposited in sediments of lakes, rivers and other waterbodies in
the mining communities. In this case, the elemental mercury where it is transformed into methyl mercury by bacteria in the waterbodies which then bioaccumulates in living organisms in water (WHO, 2007).

Bioaccumulation is said to have occurred when an organism contains a higher concentration of the substance than the environment does. People then become exposed when they eat fish, shellfish or any other seafood that is contaminated with methyl mercury (WHO, 2007). When large amounts of methyl mercury are ingested over several weeks, it can cause damage to the central and peripheral nervous systems (WHO, 2007).

1.5. Heavy metals urine test

According to the American Society for Clinical Chemistry (American Association for Clinical Chemistry, 2013), the presence of heavy metals and other elements can be tested for using blood or urine samples of subjects and sometimes, but scarcely, hair or fingernails. However, the different means employed in the testing do not necessarily test for the same form of the metal. For instance, methyl mercury, which is a highly toxic form of mercury found in fish is can be detected in the blood but not in urine. But, urine is particularly most preferred in testing for arsenic and the inorganic forms of mercury. Methyl mercury is formed from the conversion of elemental and the inorganic forms of mercury upon bioaccumulation, mainly in fish. Since arsenic is considered for testing in this research and there is scarcely any fishing activity in any of the seven mining communities, mercury contamination in the residence is most likely to be, largely, in the inorganic form. Hence, urine analysis is chosen as the basis for the spectroscopic analysis of the two elements. Residents of industrial areas, cities and communities where mining activities are prevalent report a much higher incidence of chronic illnesses than those living in areas where these activities are relatively less. These are usually, from a medical standpoint, attributed to their higher exposure to heavy metal contaminations of water, air and food. When heavy metals get into the human body, they can cause tissue destruction, functional disturbances and a general weakening of the person’s resistance to diseases. Since they do not have any physiological importance, these toxic heavy metals stay in the body, run through the blood and may go through excretion through the kidneys into the urine. Heavy metal urine test, therefore, becomes a useful tool for assessing the retention of heavy metals in the body. Typically, the levels of mercury in urine are the best indicators of recent mercury exposure, especially in the inorganic form. This is the first study about the measurement of Arsenic and Mercury in this area.

2. Methods

2.1. Description of the sampling area

The Eastern Region of Ghana, besides the Ashanti and Northern Territories, was one of the administrative areas, of the country (formally known as Gold Coast) until independence. It has a land area of 19,323 km², constituting 8.1% of the total land area of the country (Statistical Service, 2005) and also shares boundaries with the Greater Accra, Volta, Brong Ahafo, Ashanti and Central regions (GSS, 2013). The Eastern Region is very well known for the mining of bauxite and diamond. However, gold mining in the region is a more recent activity. Newmont is the major large-scale gold mining company operating in the area, located in the Birim North district of the region, with all other gold mining being artisanal and small scale. The region lies between latitudes 6 and 7 degrees North and longitude 1.30 West 0.30 degrees East. The sampling area for this research is displayed in Figure 1, showing Intronang, Hweakwae and Aduasena in the central part of the Abirem North district, while Afosu, New Abirem and Mamano are located on the Eastern part. The rise in mining activities, particularly artisanal mining, has created considerable environmental and health issues in some areas of Birim North district. The region has basically, phyllite and graywacke rocks. However, the geologic and pedologic structure of the Birim North district shown in Figure 1 is mainly birimian type quartz and schist granite. The concentration of Arsenic in quartz vein will make the soil and waterbodies naturally susceptible to Arsenic contaminations. The geologic diversity of the district particularly gives it its various mining potentialities.
2.2. Sampling of human urine
Urine samples were collected from the residents of seven communities in the Birim North district of the Eastern Region on a voluntary basis. The samples were collected into 50-ml Polyethylene sterile urine containers. Before sampling, donors were educated on the significance of the research. This was to change their superstitious beliefs, on what their urine samples could be used for. Urine sample containers were distributed to volunteers and were advised to collect the first urine upon waking up in the morning. Sample bottles were tightly covered with bottle caps, sealed with sellotape and stored in cold ice chest containing ice. The samples were collected in four different batches. The first two batches consisted of 63 samples from New Aembre, 63 from the Hamlets and 56 from Hwewkwew while the next batch consisted of 65 from Afosu, 185 from Intronang, 55 from Aduasena and 44 from Mamano. The samples were transported to the KNUST Chemical Engineering Process Development Laboratory, where they were kept in deep refrigeration prior to analysis.

2.3. Preliminary (open) digestion of urine samples
To ensure conversion of the arsenic and mercury associated with particulates in the urine to a free state that can be determined by the spectroscopic analysis, the samples were taken through Nitric acid digestion as described as follows.

2.4. Apparatus
(a) Hot plate
(b) 150 mL Griffin beakers, acid-washed and rinsed with double distilled water
(c) 100 mL volumetric flasks
(d) Boiling chips

2.5. Reagent
Concentrated analytical grade of Nitric acid.

2.6. Procedure
Each sample container was swirled to ensure thorough mixing of the samples. A volume of 30 mL of this sample was transferred into a 150 mL Griffin beaker. A volume of 5 mL of Conc. HNO₃ was added, coloured, and the content of the beaker was subjected to heating in a microwave digester at different temperature and pressure regimes as shown in the chart below.
2.7. Atomic absorption spectroscopy analytical procedure

Arsenic and Mercury lamps were chosen for the instrument in order to produce wavelengths of lights that can be absorbed by the elements (arsenic and mercury) being analysed for. The digested samples were fed into the sample introduction system of the instrument in which the solution (liquid) was aspirated into the flame produced by the nebulizer. This was done to produce a cloud of atomized species of the sample.

This enables the ions of the arsenic and mercury to absorb the wavelengths of the light produced by their lamps, before reaching the detector. The amount of wavelength of light produced in any case depends on the quantitative measure of the element present in the digested sample. The absorbance values obtained from the analysis were obtained by comparing with calibration curves prepared for known samples.

3. Results and discussion

3.1. Levels of arsenic and mercury in residents

Table 1 shows the basic statistics on the results obtained from the spectroscopic analysis of the urine samples received from all 521 subjects from the seven communities. Of this number, 182 were males and the remaining, which constitute of 65.1% of the total, were females. The youngest subject was a 4-year-old male from the Intronang community with urinary arsenic and mercury levels of 43.05 μg/L and 1.61 μg/L respectively. The eldest subject, on the other hand, was a 51-year-old male from the New Abirem community, with Arsenic and Mercury levels of 64.78 μg/L and 0.83 μg/L in respective orders. From the analysis, the overall mean As concentration was 62.55 μg/L, while that of Hg was 1.02 μg/L with standard deviations of 54.53 μg/L and 1.733 μg/L respectively.

According to the Agency for Toxic Substances and Disease Registry (ATSDR 2007) and the Health Encyclopedia, the normal urinary levels of Arsenic and Mercury in humans are supposed to be less than 100 μg/L (ATSDR, 2007) and 20 μg/L (Health Encyclopaedia) respectively. The data, however, show that a 6-year-old male from Intronang recorded the highest As concentration of 365.0229 μg/L with his Hg level being 13.24 μg/L. Though both levels are high for this subject, the As concentration is far higher than the recommended limit, more than three times as much. The highest Hg concentration, 13.78 μg/L was recorded for an 11-year-old male subject from the same Intronang community which, on the other hand, is considerably lower than the stated limit. Regarding the ATSDR recommendation, 24.5% of the males and 19.7% of the females, in all seven communities, recorded As levels higher than the 100 μg/L bound (ATSDR, 2007). These values, corresponding to 20.5% of the total subjects sampled, are definitely alarming for seven communities where artisanal mining started just recently, compared to the oldest mining town, Tarkwa, and other older ones like Obuasi, Prestea and Bogoso.

3.2. Age-group and gender analysis for As and Hg levels

We analysed the degrees of contaminations of As and Hg with respect to the gender of the residents to determine their levels of risk. The ages of the residents were categorized into the following classes: 1–10, 11–20, 21–30, 31–40 and 41–50. Figure 2 shows a representation of the age-group analysis of the urinary arsenic concentrations of male residents in the seven communities. Clearly, the most obvious observation in Figure 2 is that the male residents of Aduasena in the age range of 31–40 years recorded the highest urinary concentrations of Arsenic (186 μg/L) followed by the 11–20 years group. The age group with the least levels of urinary Arsenic was...
| Community     | Gender | Age range (years) | Arsenic (As) | Mercury (Hg) |
|---------------|--------|-------------------|--------------|--------------|
|               |        | Minimum | Maximum | Mean       | SD    | Minimum | Maximum | Mean    | SD    |
| Aduasena      | Males  | 6-49    | 3.9595  | 186.5163  | 54.1872 | 47.0262 | 0.0995  | 0.8252  | 0.5536 | 0.3536 |
|               | Females| 6-48    | 6.5370  | 212.1396  | 50.9179 | 44.2156 | 0.0386  | 4.7349  | 0.7992  | 0.8829 |
| Afosu         | Males  | 7-45    | 1.4001  | 100.0937  | 37.2673 | 27.8287 | 0.0836  | 1.0527  | 0.4999  | 0.2941 |
|               | Females| 6-50    | 4.0328  | 105.6437  | 33.9540 | 27.8733 | 0.0870  | 5.4555  | 0.8183  | 0.8904 |
| Intronang     | Males  | 4-49    | 23.7035 | 365.0229  | 88.1196 | 67.9192 | 0.0932  | 13.7802 | 2.3480  | 3.9093 |
|               | Females| 6-50    | 6.5832  | 306.5667  | 104.9772| 69.0720 | 0.124   | 8.6696  | 1.4795  | 1.3815 |
| Hweakwae      | Males  | 6-49    | 2.1162  | 218.1631  | 72.5596 | 58.5399 | 0.0998  | 2.4684  | 0.6125  | 0.5321 |
|               | Females| 6-45    | 6.5467  | 154.1605  | 55.8657 | 41.4415 | 0.1753  | 1.7285  | 0.5826  | 0.4208 |
| New Abirem    | Males  | 8-51    | 9.4246  | 168.2856  | 75.5228 | 48.3168 | 0.3141  | 7.3929  | 1.3120  | 1.3332 |
|               | Females| 6-44    | 8.6728  | 177.5921  | 54.4271 | 41.5627 | 0.0811  | 11.8488 | 1.3905  | 2.5077 |
| Mamano        | Males  | 6-44    | 11.862  | 123.7193  | 59.8641 | 43.3174 | 0.1534  | 0.6949  | 0.5718  | 0.5805 |
|               | Females| 6-49    | 2.7642  | 156.9364  | 62.6791 | 44.1474 | 0.035   | 2.3652  | 0.6572  | 0.6879 |
| Hamlets       | Males  | 6-45    | 6.4580  | 200.4183  | 38.9590 | 65.9855 | 0.0557  | 1.6447  | 0.5158  | 0.5824 |
|               | Females| 7-49    | 6.6911  | 221.0776  | 35.3709 | 59.9105 | 0.1758  | 0.7051  | 0.4023  | 0.1588 |
found to be 21–30 years with arsenic levels of 33 μg/L. Figure 2 also shows that residents within the age group of 21–30 years in the Afosu community recorded the highest Arsenic levels. This was followed by an equal level of 33 μg/L for the 31–40 and 41–50 age groups. In the Hamlets, the 21–30 age group recorded the highest mean As level of 77 μg/L. It is also observed that the 41–50 age group recorded the highest As concentration in the Hweakwae community. This was followed by the 11–20 years age group which recorded a mean level of 99 μg/L. The 11–20 age group of the Hamlets recorded the lowest urinary As concentration of 6 μg/L. In Intronang, Mamano, and New Abirem communities, it can be observed that the age group 31–40 years had consistently high average concentrations of urinary Arsenic while the 41–50 years had low levels.

From Figure 3, it can be seen that the male residents of the Intronang community recorded the highest urinary Hg concentration of 5.0 μg/L. This was followed by the 11–20 years and 21–30 age groups recording mean mercury levels of 2.4 μg/L and 2.3 μg/L respectively. In Intronang, the 41–50 age group recorded the least mean concentration of 1.2 μg/L. It can also be observed from Figure 3 that males in the 41–50 age group in the New Abirem community recorded high levels of mercury their urine recording a mean value of 2.5 μg/L. The age groups 1–10 years and 11–20 years also mean values of 1.3 μg/L and 1.3 μg/L respectively.

From Figure 4, it can be observed that the arsenic is very high among the female residents of the Intronang community with the 41–50 age group recording the highest mean value of 150 μg/L. This was followed by 21–30 and 11–20 age groups, also recording mean values of 133 μg/L and 108 μg/L.
respectively. Females in the Hamlets within the age group 21–30 years recorded the least urinary Arsenic levels. They also recorded relatively for all the other age groups, except the 11–20 group, compared to all the other communities.

4. Further analysis
Table 2 shows the correlation matrix for the urinary As concentrations of residents of the seven communities. The correlation matrix reveals that there is a significant correlation of 0.621 between the Hamlets and Afosu community. There is another significant correlation of 0.602 between the Hamlets and New Abirem. Table 3 on the other hand, shows the correlation matrix of mercury concentrations in the urine of the residents in the seven communities. The correlation matrix reveals that there is a significant correlation in the Hg levels in the urine of the inhabitants of the Intronang and New Abirem communities. Again, a positive correlation was observed in the Hg levels of the urine of the residents of the Aduasena and Mamano communities. The correlation in the urinary Hg levels of the residents of Intronang and Hweakwae as well as Aduasena and Hweakwae were also significant with values of 0.695 and 0.626, respectively. Another significant correlation observed in the matrix in Table 3 is that in the urinary Hg concentrations of Intronang and Aduasena having a value of 0.634.
|                | Aduasena | Afosu  | Hamlets | Hweakwae | Intronang | Mamano | New Abirem |
|----------------|----------|--------|---------|----------|-----------|--------|------------|
| Aduasena       | 1        |        |         |          |           |        |            |
| Afosu          | −0.086   | 1      |         |          |           |        |            |
| Hamlets        | 0.268    | 0.621  | 1       |          |           |        |            |
| Hweakwae       | −0.179   | 0.286  | −0.097  | 1        |           |        |            |
| Intrang        | 0.048    | −0.341 | −0.144  | −0.255   | 1         |        |            |
| Mamano         | 0.198    | −0.367 | −0.053  | 0.119    | 0.462     | 1      |            |
| New Abirem     | 0.041    | 0.350  | 0.602   | 0.319    | 0.326     | 0.178  | 1          |
Table 3. Correlation analysis of urinary mercury concentrations of the residents in the seven communities

|                  | Aduasena | Afosu  | Hamlets | Hweakwae | Intronang | Mamano | New Abirem |
|------------------|----------|--------|---------|----------|-----------|--------|------------|
| Aduasena         | 1        |        |         |          |           |        |            |
| Afosu            | 0.330    | 1      |         |          |           |        |            |
| Hamlets          | -0.329   | -0.538 | 1       |          |           |        |            |
| Hweakwae         | 0.626    | -0.221 | -0.373  | 1        |           |        |            |
| Intronang        | 0.634    | -0.342 | 0.082   | 0.695    | 1         |        |            |
| Mamano           | 0.786    | -0.671 | -0.357  | 0.193    | 0.181     | 1      |            |
| New Abirem       | -0.358   | 0.141  | 0.037   | -0.552   | 0.879     | -0.250 | 1          |
| PC's             | PC1      | PC2    | PC3     | PC4      | PC5       | PC6    | PC7        |
| Eigen value      | 6.942    | 1.761  | 0.390   | 0.231    | 0.121     | 0.119  | 0.100      |
| % accounted by PC's | 72.5     | 18.4   | 4.1     | 2.4      | 1.3       | 1.2    | 1.0        |
4.1. Principal component analysis (PCA)
From Table 4. The first principal component has variance 5.408 (equal to the largest eigenvalue) and accounts for 77.26% of the total variance in the data. The second, third up to the seventh principal components have eigenvalues less than 1, hence the first principal component with eigenvalues greater than 1 represents 77.26% of the total variability.

4.2. Eigenanalysis
The principal components are the linear combinations of the original variables that account for the variance in the data. The maximum number of components extracted always equals the number of variables. Two principal components will be retained (PC1 and PC2) since PC1 and PC2 have high eigenvalues of 6.942 and 1.761, respectively, and also both PC's account for the highest variability in the data with PC1 and PC2 accounting for 72.5% and 18.4%, respectively. Hence, the two principal components PC1 and PC2 best explain the high levels of As and Hg of the seven communities and these reasonably summarize the variations in the urinary concentrations of arsenic and mercury of core residents in the communities.

The correlation circle in Figure 6 shows the dimension F1 (factor 1, with the most explained variance) plotted against F2 (factor 2, the second most explained variance). The correlation circle typically depicts three possibilities: the variables are highly correlated when the two red lines are pointing in the same direction, poorly correlated when the perpendicular or orthogonal and negatively correlated when they are pointing in opposite directions. Figure 7 shows a dendrogram plotted for the As and Hg contamination trends in the communities. Figure 7 reveals the levels of similarity between the average urinary concentrations of As and Hg of the residents in the various communities.

The plot clearly shows that the Mamano, Aduasena and Hweakwae communities form one cluster (cluster 1) different from the cluster (cluster 2) formed by the Afosu and the Hamlets communities. However, it can be inferred that the communities in the first cluster join at a higher level of similarity of contamination than those in the second cluster. The Intronang and New Abirem communities are outliers on the dendrogram as they do not form any cluster but are fused (arbitrarily) at rather higher distances.

The dendrogram plotted for the communities in Figure 7 reveals the levels of similarity between the average urinary concentrations of As and Hg of the residents in the various communities. The plot clearly shows that the Mamano, Aduasena and Hweakwae communities form one cluster

| Component | Initial Eigenvalues |
|-----------|---------------------|
|           | Total | % of Variance | Cumulative % |
| PC 1      | 5.408 | 77.261 | 77.261 |
| PC 2      | 0.652 | 9.309 | 86.571 |
| PC 3      | 0.492 | 7.034 | 93.604 |
| PC 4      | 0.244 | 3.490 | 97.095 |
| PC 5      | 0.136 | 1.950 | 99.044 |
| PC 6      | 0.056 | 0.794 | 99.838 |
| PC 7      | 0.011 | 0.162 | 100.000 |

| PC's | PC1 | PC2 | PC3 | PC4 | PC5 | PC6 | PC7 |
|------|-----|-----|-----|-----|-----|-----|-----|
| Eigen value | 6.942 | 1.761 | 0.390 | 0.231 | 0.121 | 0.119 | 0.100 |
| % accounted by PC's | 72.5 | 18.4 | 4.1 | 2.4 | 1.3 | 1.2 | 1.0 |
(cluster 1) different from the cluster (cluster 2) formed by the Afosu and the Hamlets communities. However, it can be inferred that the communities in the first cluster join at a higher level of similarity of contamination than those in the second cluster. The Intronang and New Abirem communities are outliers on the dendrogram as they do not form any cluster but are fused (arbitrarily) at rather higher distances.

4.3. Multivariate tests

Figure 5 shows the output of the Wilks’ Lambda Test (Rao’s approximation) used to test the significance of the urinary concentrations. From the analysis, it was observed that the Wilks’
Lambda test observation and critical value of 0.9027 and 1.7651, respectively, with 12 degrees of freedom. The test produced a p-value of 0.5428, which is greater than the alpha value (significance level) of 0.05. This implies that there is no significant correlation among the urinary levels of Arsenic and Mercury.

The output of Pillai’s Trace in Figure 6 was also used to test the significance of the urinary concentrations. It was revealed that Pillai’s Trace gives a value of 0.0286, and the F observation and critical value were 0.9049 and 1.7651, respectively, with 12 and 748 degrees of freedom. The test gave a p-value of 0.5416 which is greater than the significant level of 0.50. This gives an indication that there is no significant correlation between the urinary levels of the two contaminants.

Table 5 was used to test the significance of the urinary concentrations of the arsenic and mercury in the residents of the seven communities studied. It was observed that there is no significant correlation among the urinary levels of the two contaminants. Table 6 was also another significant test that was conducted on the urinary concentration of arsenic and mercury of the residents of the communities. The test also confirmed that there exist no significant correlation between the urinary levels of the two contaminants.

Table 7 the output of Hotelling-Lawley Trace. From the analysis, it was seen that Hotelling–Lawley Trace gave a value of 0.0291 with the F observation and critical value being 0.9013 and 1.7690,

| Table 5. Wilks’ Lambda test (Rao’s approximation) |
|-----------------|-----------------|
| Wilk’s Lambda   | 0.9716          |
| F (Observation) | 0.9027          |
| F (Critical Value) | 1.7651        |
| Degree of Freedom 1 | 12              |
| Degree of Freedom 2 | 746            |
| P-value          | <0.5428         |
| Significance Level | 0.05         |

| Table 6. Pillai’s trace |
|------------------------|
| Pillai’s Trace         | 0.0286          |
| F (Observed value)     | 0.9049          |
| F (Critical value)     | 1.7651          |
| DF1                    | 12              |
| DF2                    | 748             |
| p-value                | 0.5416          |
| Significance Level     | 0.05            |

| Table 7. Hotelling-Lawley trace |
|---------------------------------|
| Hotelling-Lawley Trace         | 0.0291          |
| F (Observed value)             | 0.9013          |
| F (Critical value)             | 1.7690          |
| DF1                             | 12              |
| DF2                             | 577             |
| p-value                         | 0.5455          |
| Significance Level              | 0.05            |
respectively. The Hotelling–Lawley Trace yielded a p-value of 0.5455 which is greater than 0.05. This result further shows that there is no significant correlation between the urinary levels of As and Hg.

5. Conclusion
It can be concluded that the residents of the Intronang community recorded the highest mean concentration of Arsenic and Mercury in their urine. This was followed by the residents of New Abirem and Aduasena. The inhabitants of the Hamlets recorded the least urinary concentrations for both Arsenic and Mercury. With respect to gender, the male residents of all the communities, generally, recorded relatively higher urinary concentrations of Arsenic than the females. The same conclusion can be drawn in the case of Mercury, in which the males of the Intronang community, recorded the highest, followed by those of New Abirem. This trend particularly deviates from a claim in Clow & Howorth-Brockman (2009), which says that females are more likely to have higher mercury levels than males. This is deviation is due to the fact that the levels of exposure of the two contaminants, for residents of communities with no mining activities are not the same as in a typical community where artisanal gold mining activities take place. Considering the latter, more males are involved in those activities than females and may be affected by the contaminations of these chemicals to a higher degree than females. It can also be concluded, based on the age-group analysis that the 11–20 age group of the residents recorded generally, the highest levels of urinary Arsenic for both males and females. The 11–20 age group also the highest mean concentration of urinary Mercury for the residents of the communities. The Principal Component Analysis further reveals that the urinary concentrations of Arsenic and Mercury of the residents are poorly correlated, indicating that residents with low levels of As and/or Hg may not necessarily have low or high levels of the two contaminants in a well-defined pattern. However, the Arsenic and Mercury contamination trends are more similar for the residents of the Mamano, Aduasena and Hweekwae communities than those of Afosu and the Hamlets. There is, however, scarcely, any interesting similarity in the contamination trends between the Intronang and New Abirem communities. In addition, it was noted that more than 20% of the residents of the seven communities recorded urinary Arsenic concentrations higher than the normal recommended by the ATSDR. The inappropriate disposal of chemical-laden mining wastes, especially by artisanal miners in the environment, is likely to cause leaching of these chemicals, particularly Arsenic and Mercury compounds, into the soil, which easily contaminate underground water and other waterbodies which have many household uses by the residents of such communities in the country. Besides water contamination, Mercury vapours and Arsenic are most likely to be high in the air owing to the very dusty environment of these communities and the smelting of the gold-mercury amalgam. These, among other sources of contaminations, maybe some of the reasons why Arsenic and Mercury levels are very high in the residents of communities where artisanal gold mining goes on in Ghana.

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