Spatial Variability of Trace Metals in Surface and Groundwater Within a Contaminated Mining Environment in Ghana

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Abstract: The aim of the study was to spatially assess the distribution of heavy metals within the catchment of the Tarkwa mining area using interpolation techniques in a geographical information systems environment. Water quality trends for 84 sites in Tarkwa, a mining district in Ghana, were examined for fourteen (14) parameters-pH, conductivity, Total Dissolved Solids (TDS), turbidity, nitrates, sulphates, Chemical Oxygen Demand (COD), total cyanides, arsenic (As), cadmium (Cd), iron (Fe), manganese (Mn), nickel (Ni) and lead (Pb). Kriging was utilized to illustrate the spatial patterns of variables. The results showed that surface and groundwater are contaminated by As, Cd, Fe, Mn and Pb with the average concentrations exceeding World Health Organisation guideline values. The spatial dependence of the heavy metals was assessed using variogram parameters which varied from 320.30 to 4842.25 m. Significant correlations were found among heavy metals, which suggest a common origin. This is confirmed by the cluster analysis which indicated that Fe, As and Pb belonged to one group. The use of geostatistical tools in water quality assessment in this study enhances our understanding of spatial trends.

Key words: Contamination, kriging, mining, spatial interpolation, trace metal

INTRODUCTION

Human and ecological use of in-stream water is a function of ambient water quality. Human modification of land particularly by mining has a far-reaching stress on watershed hydro-geochemistry and consequently water use (Chang, 2007; Chang, 2008). Environmental monitoring programmes are indispensable for our understanding and management of aquatic ecosystems. Prior to our recognition of environmental changes, some idea of baseline variability must be established against which to evaluate gross deviations (Boyer *et al.*, 1997). Due to the adverse effects of anthropogenic actions on surface and groundwater resources, it is fundamentally central to understand spatial as well as temporal patterns in water quality in these systems in an effort to direct management efforts (Boyer *et al.*, 1997).

In Ghana, attention is increasingly being drawn to anthropogenic (particularly mining-induced) influence on water bodies. Gold-mining related contamination of water bodies and biota in Ghana is attracting a growing body of literature (Armah *et al.*, 2010a). Generally, studies on heavy metal contamination in Ghana have either been carried out in water bodies and biota within either mining or non-mining areas; with emphasis on the latter. Within

mining environments such studies have focused on speciation of heavy metals such as mercury (Donkor *et al.*, 2006); and arsenic (Amonoo-Neizer *et al.*, 1993) in different environmental media. Other studies have considered the levels and distribution of heavy metals in either groundwater (Smedley, 1996; Kortatsi *et al.*, 2008; Obiri, 2007) or surface water environments (Armah *et al.*, 2010b; Yidana *et al.*, 2007) or both (Akabzaa *et al.*, 2009; Armah *et al.*, 2010a). Still, others have focused on levels of heavy metals in biota. For example, levels and distribution of mercury in hair (Voegborlo *et al.*, 2010), arsenic, cadmium and mercury in tuber crops (Essumang *et al.*, 2007); and arsenic, cadmium and mercury in fish (Essumang, 2009) have been previously been highlighted. Human health risk assessments (both carcinogenic and non-carcinogenic) arising from heavy metal contamination of water bodies in mining areas have also received considerable attention (Obiri *et al.*, 2006; Obiri *et al.*, 2010a; Obiri *et al.*, 2010b; Essumang, 2009). Most of these studies point to increasing anthropogenic influence on the quality of water within mining communities.

A number of techniques have also been utilised to explore the dynamics of heavy metals within water bodies in mining communities including multivariate statistical

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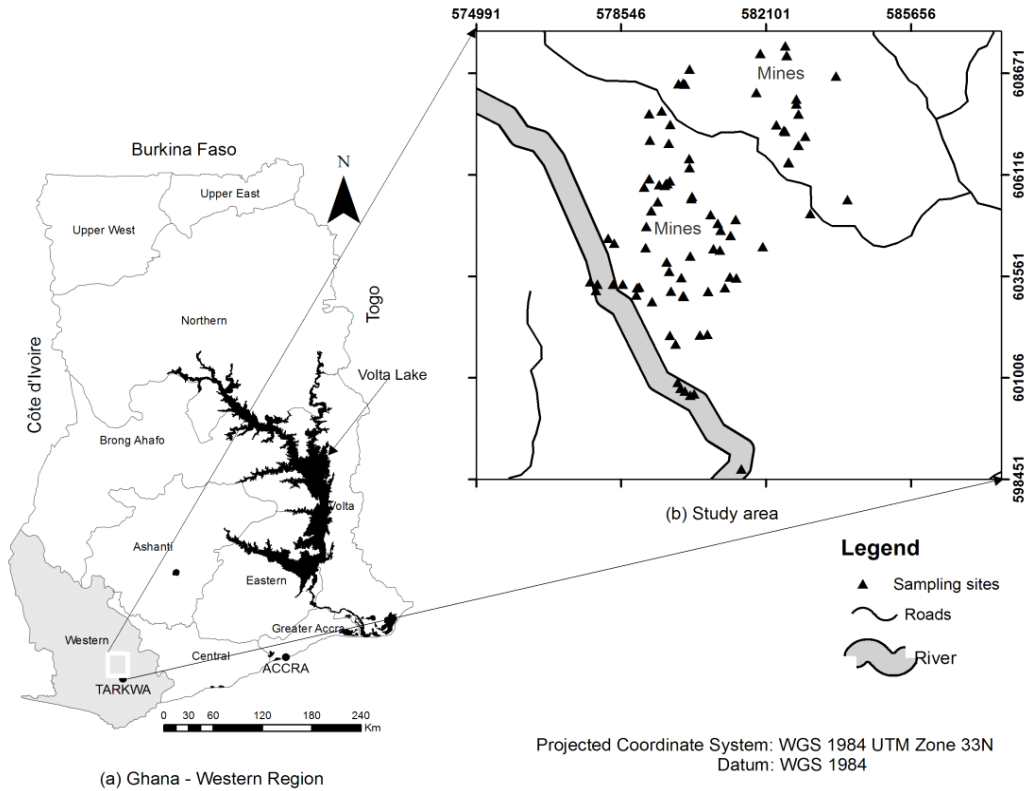
Fig. 1: Location map with (a) the Western Region in Ghana, (b) the study area indicating sampled site within mining areas around Tarkwa and environs

analyses (Armah, 2010a; Armah, 2010b; Yidana *et al.*, 2010; Akabzaa *et al.*, 2009); and spatial modelling (Duker *et al.*, 2006), have been applied to gain more comprehensive insights into heavy metal contamination in mining communities of Ghana.

Multivariate geo-statistics has been applied in quite a few studies to present a more objective account on the source of some heavy metals in contaminated water bodies in mining areas, particularly anchored in the quantitative analysis of the spatial variability of the elements and their interaction at different spatial scales. In Ghana, however, the use of this technique is rather nascent. Consequently, not much work has been done to delineate the spatial aspects of heavy metal contaminants in the aquatic environment of mining communities in Ghana notwithstanding its centrality to effective pollution control and risk mitigation. It is against this background that this study was carried out. Ultimately, a better understanding of spatial patterns in water quality will sharpen our actions and efficiency in our bid to sustain fragile aquatic ecosystems. The context of the research is to correlate aqueous contamination with mineral sources and industrial inputs in order to position drinking water boreholes for public health protection.

The objectives of the study were as follows:
- Provide information on existing levels of some major water quality parameters at selected monitoring stations within the Tarkwa mining area
- Compare the existing levels of water quality parameters and heavy metal concentrations to the World Health Organisation guideline values.
- Spatially assess the distribution of heavy metals within the catchment of the Tarkwa mining area

MATERIALS AND METHODS

Study area: Tarkwa is a town in the southwest of Ghana, located approximately 193 km west of Accra. As of 2005, it was estimated to have a population of 40,397. It is a noted centre of gold and manganese mining. Tarkwa Mine which is a large open-caste gold mine is situated to the North West of the town and Nsuta manganese mine is situated to the East of the town. Tarkwa Mine mines several low grade conglomeratic "reefs" of Tarkwaian type (Kuma and Younger, 2004). These reefs are of mid-Proterozoic age (Kuma and Younger, 2004). Since 2007, Tarkwa Mine has the distinction of being the largest gold mine in Ghana. Approximately 24 tons of gold is

produced annually and 100 million tons of earth is moved to achieve this production rate. The Tarkwa Goldfield was discovered a few years before the Witwatersrand Goldfield in South Africa.

Sampling techniques:

Sample collection: Sampling was carried out at selected locations in Tarkwa from February to April 2010. There was the need to optimise sampling and analysis to ensure the quality of the data. Sampling bottles were washed with detergent and rinsed with 10% hydrochloric acid and double-distilled water prior to sampling. At each of the sampling locations (Fig. 1), the bottles were rinsed with the water to be collected to reduce or completely eliminate any contaminations that might be introduced. Samples from surface water were collected at the subsurface in order to avoid the colloidal layer as this can influence the concentration of certain parameters. For samples from boreholes and taps, the water was allowed to run for some time to purge the system before being sampled. Two 500 mL of water samples were collected at each location into a blackened, clearly labelled plastic bottle. The collected samples were immediately put into ice-chests containing ice cubes (around 4ºC) and conveyed to the laboratory for analysis. This procedure averts microbial growth, flocculation and reduce any adsorption on container surfaces, processes which could affect the results. Internationally accepted and standard laboratory procedures were followed in the analysis of the samples. The samples were collected from surface water bodies (rivers and streams), groundwater (boreholes and wells) and alternate source of water for communities within the Tarkwa mining area. Geo-satellite positioning of all the locations were determined with a Garmin Etrex GPS. A total of Eigty-four (84) water samples were collected during the study. Sampling protocol followed acceptable standards (APHA, 1998). At each sampling location, physicochemical water quality parameters (pH, conductivity, total dissolved solids and turbidity) were measured *in situ*. Water quality parameters measured include nitrates, sulphates, Chemical Oxygen Demand (COD) and total cyanides. Metal concentrations measured included As, Cd, Fe, Mn, Ni and Pb.

Laboratory sample processing: A flame AAS (Atomic Absorption Spectrophotometer) Shimadzu model 6401F was used for analysis of the samples after preparation of appropriate calibration standards. Due to expected low concentrations of the metals in the natural water samples and limited instrument sensitivity, pre-concentration of the water samples was done by evaporating 100 mL of the water to 4 mL on a hot plate. The digestion of the water samples was then achieved by adding 5 mL of 11.1 M HNO_3 and heating on the hot plate for 30 min. Some 10 mL of 16.3 M HCl was added and digestion continued until the solution remained light brown or colourless. The volume was then adjusted to 25 mL with distilled water. Reproducibility and recovery studies were conducted. In the reproducibility studies, 1.0 mg/L standard solutions of each heavy metal were measured (ten times) using flame Shimadzu model 6401F. The percentage of heavy metals recovered in the recovery studies ranged between 93.6 to 99.6% (standard error ±0.005 to 0.560). The standard error is less than 1, which suggests that the analysis methods employed were reproducible.

Data analysis: The descriptive statistics was performed with SPSS version 17.0 for windows (SPSS Inc., Chicago, IL, USA). The distribution of the data was tested for normality by Kolmogorov-Smirnov (K-S) test. For the data severely skewed, a natural logarithmic transformation was applied. Relationships between surface and groundwater properties and metal concentrations were established by using correlation analysis. Cluster Analysis (CA) was carried out to explore the correlations existing among the heavy metals. Using ArcGIS 9.3 ordinary kriging was engaged for geo-statistic interpolation. Kriging - is a series of techniques that allows for the prediction of variable values or multi-variable interactions at locations where no data are obtainable. Thus, by means of the simultaneous equation systems of kriging, point data can be used to create surfaces where each location in the study area is represented by a point estimate of the true value at that point (Scott and Janikas, 2010). Kriging is a best linear unbiased predictor; it provides predictions and estimates of errors at each prediction point. Kriging creates map surfaces and error surfaces, that is, surfaces that represent the confidence level in spatial point estimates. The manner in which kriging is carried out ranges from relatively simple procedures (simple and ordinary kriging as in this case) to complex prediction systems (co-kriging and disjunctive kriging).

Standardized semivariograms were simulated using Surfer 8.0 software and spherical models were selected to fit the semivariograms. The Moran's I, a global measure of spatial autocorrelation (Table 5), was used to identify the degree of spatial dependence on groundwater parameters and heavy metals. The Global Moran's *I* tool computes a single summary value, a *z*-score, describing the degree of spatial concentration or dispersion for the measured variable (Scott and Janikas, 2010). Comparing this summary value indicates whether or not the measured variable is becoming, overall, more dispersed or more concentrated over time (Longley *et al*., 2005). The variogram describes quantitatively how a property changes as the separation between places increases. Its values are estimated from data for a set of separating distances or lags to give the experimental variogram. This may then be modelled by a limited set of mathematical

Table 1: Heavy metal concentration and selected physicochemical properties of surface and groundwater (n=84)

	Heavy Metals						Ground and surface water properties						
	As (mg/L)	Cd (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Pb (mgL)	pH	Electrical Conductivity (uS/cm)	Dissolved Solids (mg/L)	Turbidity (FAU)	Nitrates (mg/L)	Sulphates (mg/L)	COD (mg/L)	Total Cyanides (mg/L)
Min.	0.00	0.00	0.00	0.00	0.00	0.00	4.15	36.00	16.90	5.00	0.02	0.00	0.00	0.00
Max.	0.22	0.28	14.99	15.00	0.02	0.34	11.14	1559.00	718.00	700.00	2.55	563.00	160.00	0.08
Mean	0.04	0.02	1.44	1.00	0.004	0.04	6.86	311.46	152.39	47.98	1.32	96.67	36.73	0.01
SD.	0.041	0.029	2.792	2.283	0.003	0.057	1.255	265.492	127.079	109.29	20.450	127.082	31.771	0.012
Variance	0.002	0.001	7.797	5.212	0.000	0.003	1.574	70485.908	16148.996	11944.820	0.202	16149.930	1009.406	0.000
Skewness	1.74	8.50	3.26	3.71	2.25	4.03	1.25	2.16	2.07	4.19	-0.19	1.59	1.26	4.52
Kurtosis	3.8	575.84	11.49	16.67	8.09	18.27	2.43	6.34	5.62	18.73	0.39	2.56	1.97	23.65
Reference value														
EPA	0.1	0.1	10	-	-	0.1	6 - 9	1500	1000	-	-	1.5	250	1.0
WHO	0.01	0.003	0.3	0.4	0.07	0.01	6.58.5	-	1000	-	-	-	-	-

Table 2: Pearson correlation coefficients of total metal concentrations and selected water properties (n = 84)

	As	Cd	Fe	Mn	Ni	Pb
pH	0.401**	0.275*	0.525**	- 0.217*	0.177	0.527**
Electrical Conductivity	0.363**	0.314**	0.357**	- 0.009	0.226*	0.453**
Dissolved Solids	0.353**	0.314**	0.332**	0.030	0.224*	0.432**
Turbidity	0.332**	0.405**	0.477**	0.005	0.046	0.293**
Nitrates	0.037	0.040	- 0.034	- 0.057	0.052	0.017
Sulphates	0.454**	0.275*	0.626**	- 0.027	0.340**	0.617**
COD	0.219*	- 0.012	0.357**	0.070	0.038	0.186
Cyanides	0.146	- 0.018	0.256*	- 0.018	- 0.041	- 0.010

*: Correlation is significant at the 0.05 level; **: Correlation significant at the 0.01 level

functions. Variogram analysis is based on the principle of intrinsic stationarity, that is, inherent in the nature of spatial effects is that as distance increases between observations on the same variable, variance will increase (Longley *et al.*, 2005). The increasing variance continues with increasing distance until a particular distance is reached when the variance will equal the population variance. The semivariogram is a function represented in a diagram that shows the nature of this increasing function. Given the enormous number of calculations that must be performed, the techniques require large samples and high levels of computer power.

RESULTS

Exploratory data analysis: Descriptive statistics (mean, median, standard deviation, minimum, maximum, skewness and kurtosis) for total concentrations of heavy metals and selected groundwater parameters are reported in Table 1. Among the metals, Fe had the highest mean concentration (1.44 mg/L), while the lowest value was for Ni (0.004 mg/L). The results showed that surface and groundwater in the mining area is contaminated by As, Cd, Fe, Mn and Pb with the average concentrations exceeding WHO guideline values. The study showed that generally selected groundwater properties were within the WHO guideline values. Groundwater pH was also variable ranging from acidic (4.15) to moderately acidic (6.69), with the mean value of 6.86. Dissolved solids concentration ranged from 5 to 718 with average level of 152 mg/L. Cyanides concentration of 0.08 mg/L were recorded in some samples which are slightly above the WHO guideline values.

Correlation analysis: Pearson correlation coefficients (Table 2) calculated for each pair of variables showed interdependence of total metal concentrations and selected water parameters. There were: (1) significant positive correlations between metal concentrations and pH, except Mn and Ni; (2) significant positive correlations between metal concentrations and Electrical Conductivity, except Mn; (3) significant positive correlations between metal concentrations and Dissolved Solids, except Mn; (4) no obvious correlation between metal concentrations and Nitrates; (5) significant positive correlations between As, Fe and COD; (6) no obvious correlation between metal concentrations and cyanides, except Fe.

For correlation among heavy metals (Table 3), there were: (1) significant positive correlations between As and other metals, except Mn; (2) significant positive correlations between Cd and Fe, Pb; (2) significant positive correlations between Fe and Ni, Pb; (3) significant positive correlations between Mn and Ni; (4) significant positive correlations between Ni and Pb. These suggest common sources for these contaminants.

Cluster analysis (CA) (Fig. 2) revealed that, on the basis of the close relations between the heavy metals in water sampling locations Fe, Pb, As, are in one group while Ni, Cd and Mn are in another group.

Geo-statistics and mapping of heavy metals: Figure 4 shows the spatial distribution of heavy metals in sampled water. The spatial dependence of the heavy metals was assessed using variogram parameters. The ranges of the variograms for heavy metals varied from 320.30 to 4842.25 m. The nugget value of less than 0.032 for As, Cd, Mn, Ni and Pb indicated the existence of a strong spatial auto-correlation for these elements. High nugget

Table 3: Correlation coefficients among heavy metals

	As	Cd	Fe	Mn	Ni	Pb
As	1.00					
Cd	0.226*	1.00				
Fe	0.630**	0.243*	1.00			
Mn	- 0.031	- 0.031	- 0.122	1.00		
Ni	0.243*	0.176	0.310**	0.396**	1.00	
Pb	0.609**	0.452**	0.747**	0.001	0.496**	1.00

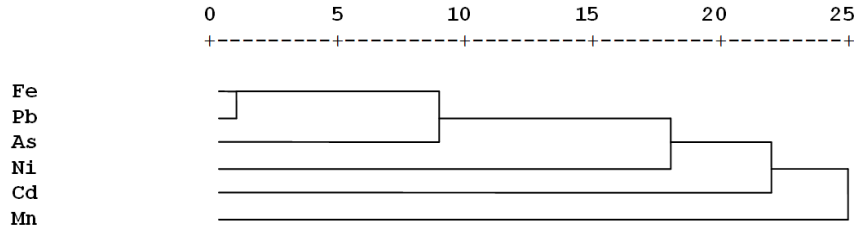*: Correlation is significant at the 0.05 level; **: Correlation significant at the 0.01 level

Fig. 2: Cluster tree of elements using Cluster Analysis (CA) based on Pearson's correlation coefficients

Table 4: Key parameters of the fitted spherical models of heavy metals

	C_0	$C_0 + C_1$	Range (km)
As	0.0010624	0.0013161	1.70272
Cd	0.00055893	0.00042155	4.84225
Fe	5.5641	6.6096	1.88049
Mn	0	8.4695	0.848433
Ni	0	0.000012602	0.320304
Pb	0.00043681	0.0059847	1.86891

Table 5: Moran's I for selected water quality parameters and heavy metals

	Moran's I
pH	0.031997
Electrical conductivity	0.118925
Dissolved solids	0.136991
Turbidity	0.032782
Nitrates	0.015598
COD	- 0.031604
Cyanides	- 0.280371
As	0.097343
Cd	- 0.022676
Fe	0.035458
Mn	0.139381
Ni	0.017391
Pb	0.059609
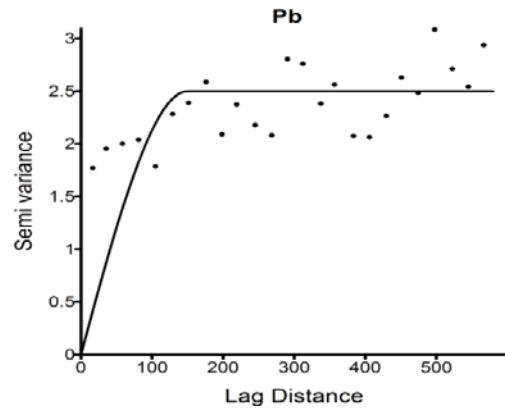
Fig. 3b: Semi-variogram model for Pb
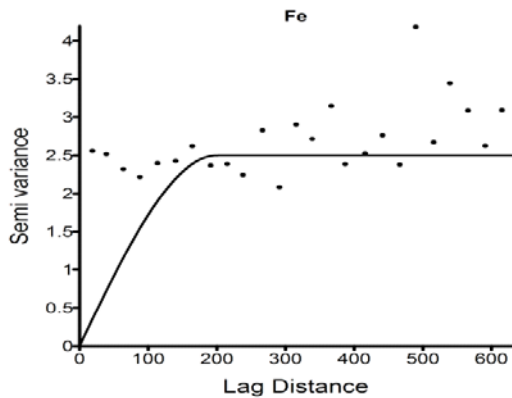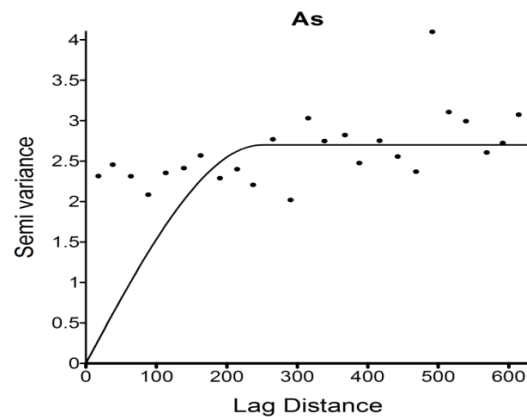

Fig. 3a: Semi-variogram model for Fe

Fig. 3c: Semi-variogram model for As

value that indicated a nugget effect was obtained in semi-variograms for Fe while Fe and Mn had the highest sill values (Table 4). Semivariograms for heavy metal concentrations with experimental values are displayed by dots and the fitted model is exhibited by the solid line (Fig. 3a-f). The degree of spatial dependence on roundwater parameters and heavy metals is shown in Table 5.
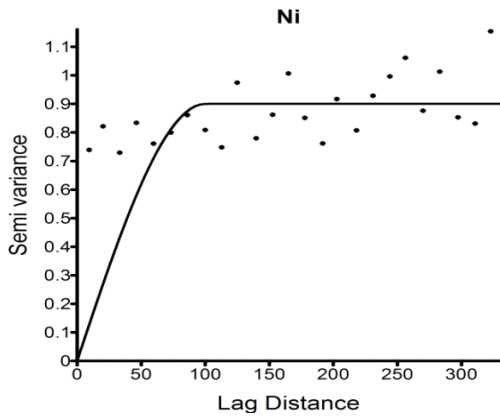
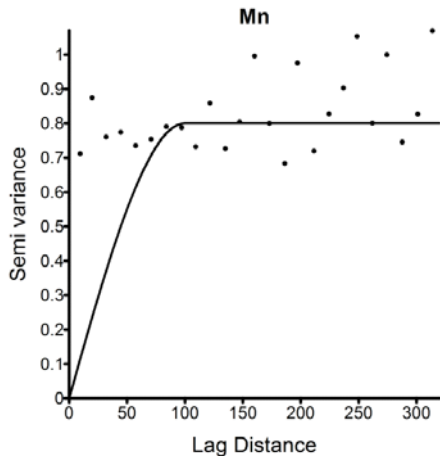Fig. 3d: Semi-variogram model for Ni
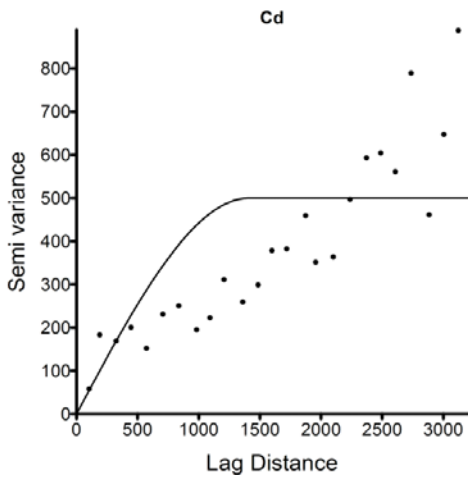

Fig. 3e: Semi-variogram model for Mn
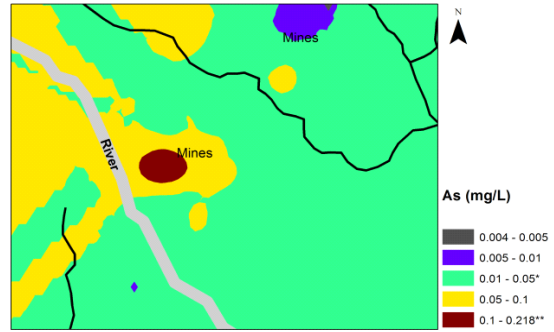

Fig. 3f: Semi-variogram model for Cd

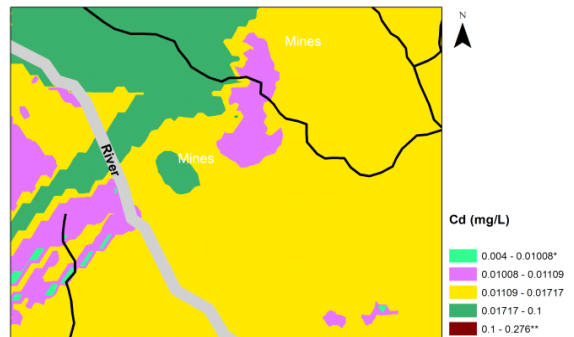Fig. 4a: Interpolation map of As

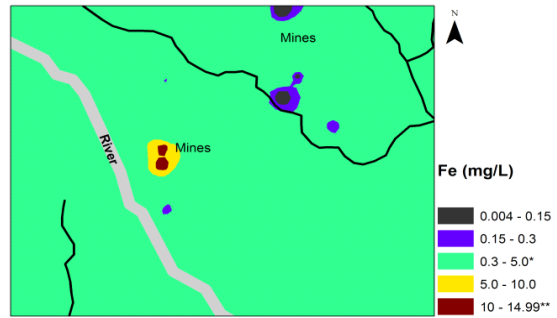Fig. 4b: Interpolation map of Cd

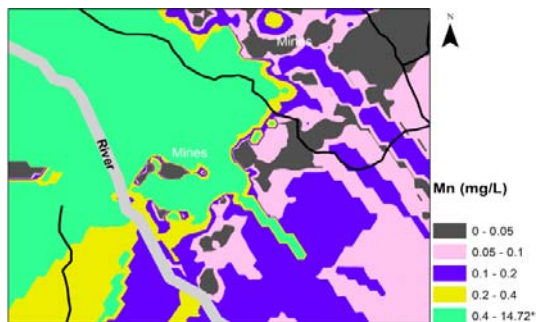Fig. 4c: Interpolation map of Fe

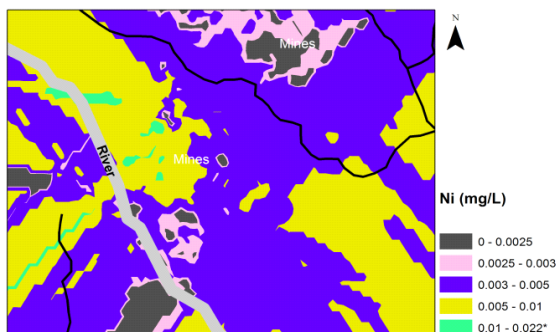Fig. 4d: Interpolation map of Mn
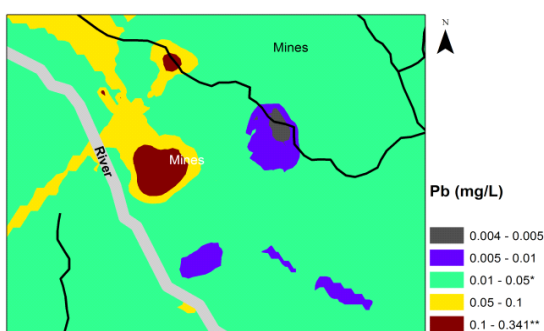
Fig. 4e: Interpolation map of Fe

Fig. 4f: Interpolation map of Pb

DISCUSSION

With the exception of Fe and Mn which show high variance, the semi-variograms show minimal variances for the heavy metals. This is supported by the lower values on the semi-variance axes. This shows there is a trend in the data (as exhibited by the spatial distribution maps), with minimal local, spatially-related variability and minimum noise in the data. The results showed that surface and groundwater in the mining area is contaminated by As, Cd, Fe, Mn and Pb with the average concentrations exceeding WHO guideline values. The geostatistical maps show that the elevated heavy metal concentrations in surface and groundwater originate from the mining activities in the area. Significant correlations were found between heavy metals and physicochemical properties, suggesting interaction and influence of heavy metals on the water properties. More so, significant correlations were found among heavy metals, which suggest a common origin. This is corroborated by the cluster analysis which indicated that Fe, As and Pb belonged to one group while the other heavy metals belonged to another group. The geostatistical maps showed that Fe and Mn had different spatial distribution patterns in the sampled water within the study area. While Mn had its highest concentrations dispersed from the center to the western half, and particularly to the

northwest, Fe had its highest concentrations as pockets over three areas while higher values were fairly distributed over the study area. This nearly uniform distribution of higher concentrations of Fe in the study area may be attributable to the preponderance of Arsenopyrite, which, in turn, explains the significant positive correlation between Fe and As. However, Pb and As showed a significant positive correlation in the cluster analysis, and a close examination of the geostatistical maps reveals that they have similar spatial distribution pattern except that higher concentrations of As appear to be slightly widely dispersed than Pb. This also demonstrates a strong anthropogenic input. Also, even though Pb, Ni and Cd belonged to one group in the cluster analysis, the geostatistical maps showed different spatial distribution patterns. These differences in spatial distribution could be attributed to differences in the behaviour and reactions of these metals in water that affect their mobility . For example, Cd is highly mobile compared to Pb (Alloway, 1995) and may have shorter residence time; a situtation that can affect the oncentration and dispersion of Cd in groundwater. Chemical leaching and precipitation have been found to be the major contributors to heavy metal contamination in soils and sediments (Avil *et al*., 2005) and consequently groundwater. The study area is a rainforest area with very high annual rainfall. Therefore, it can be deduced that chemical leaching, weathering and rainfall may be the major contributory factors to heavy metal contamination of the sampled water in the study area.

It is interesting to note that almost all the heavy metals assessed show a spatial dispersion pattern from the mine at the center to the westward direction, with the eastern part having usually lower values. This dispersion pattern makes the western and particularly the north-western part of the study area a hotspot of heavy metal contamination. In addition, for As, Pb, Fe and Cd, the mine at the centre of the study area constitutes another hotspot. The pattern of dispersion from the centre to the western part can be explained by the topography of the area. The eastern part of the study area had higher elevation values compared to the western portion. As such, both overland and sub-surface transport of heavy metals from the mine area are possible This study shows that GIS and geo-statistics are useful tools for mapping and visualizing the spatial distribution of heavy metal contamination in surface and groundwater.

CONCLUSION

In this study, water quality trends for 84 sites in Tarkwa, a major mining town in Ghana, were examined for fourteen (14) parameters-pH, conductivity, total Dissolved Solids (TDS), turbidity, nitrates, sulphates,

chemical oxygen demand (COD), total cyanides, arsenic (As), cadmium (Cd), iron (Fe), manganese (Mn), nickel (Ni) and lead (Pb). The results showed that water in the mining area is contaminated by As, Cd, Fe, Mn and Pb with the average concentrations exceeding WHO guideline values. The use of the heavy metal contaminated water for drinking can have implications for human exposure to the communities within the catchment of the Tarkwa mining area. The elevated levels of toxic heavy metals in the immediate vicinity of the Tarkwa mines has potential health implications for those living and working in the areas, as well as consequences for the wider environment. The degree of contamination and the different routes of release highlighted by these data demonstrate a lack of adequate controls in the use of hazardous and toxic chemicals within the Tarkwa mining area. With the aid of krigging- a geostatistical tool; spatial dependence of the heavy metals was assessed using variogram parameters; which varied from 320.30 to 4842.25 m. The nugget value of less than 0.032 for As, Cd, Mn, Ni and Pb, points to the existence of a strong spatial auto-correlation for these elements. Significant correlations were found between heavy metals and physicochemical properties, suggesting interaction and influence of heavy metals on the water properties. More so, significant correlations were found among heavy metals, which suggest a common origin. This is corroborated by the cluster analysis which indicated that Fe, As and Pb belonged to one group hile the other heavy metals belonged to another group. The results provide a reference for water use and remediation and control of contamination. The study highlights the importance of incorporating spatial dimensions into water quality assessment in order to deepen our understanding of spatial distribution of heavy metals in surface and groundwater within contaminated environments.

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