Geochemical and chemometric analysis of soils from a data scarce river catchment in West Africa

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Abstract
Metal levels beyond stipulated thresholds are a considerable concern for environmental pollution regulators and public health administrators around the globe. Data is, however, lacking in most regions especially developing countries for practical policy decision making and management. In this study, we obtain 49 high-resolution soil cores from three vertical profiles in the Densu River Basin of Ghana and measured the concentrations of major and trace metals (Ca, K, Fe, Ti, Cr, Cu, V, Ni, and Zn). The aim was to examine and provide data on metal levels to serve as baseline information on mobilization studies for waste management. Geochemical methods for estimation of metal enrichment and accumulation were employed to determine enrichment and pollution, sources, and mobilization of the metals. Hierarchical cluster and principal components analyses were used to examine metal associations and the effects soil physicochemical properties on the metals. The results show spatial variations in metal concentrations within and between individual soil profiles and are attributed to variability in soil formation processes and the locations where samples were collected, respectively. Moderate to high enrichment factors ($EF$) and geo-accumulation ($I_{geo}$) indices were observed for Vanadium (V) and Chromium (Cr) in all soil profiles indicating some level of anthropogenic interference leading to pollution possibly from vehicular and agricultural inputs. The Pourbaix diagrams, however, show that the Cr and V abundances may be natural. Our analysis also show that most of the metals investigated are of natural (i.e., geologic) origin but further investigations are recommended. The combination of field observations and established methods such as geochemical and statistical analyses have aided in extracting beneficial information from the small sample size.

1. Introduction

Soil and groundwater pollution from agricultural activity is becoming an important topic of interest worldwide as a result of the increasing public and regulatory concern on groundwater contamination and its impacts on human health and ecological systems (Kulkarni et al 2009). Elemental analysis of fine-earth (<2 mm) or other particle-size fractions has been useful in the study of soil properties on pedon, landscape, or on ecosystems basis by providing information on geologic properties and parent material uniformity or mineral weathering, composition, and phase quantification (Burt et al 2003). Elemental data from soil analysis have also been useful in providing information in the environmental studies of soil and water, for example, metal contamination through atmospheric deposition or transport in surface water or groundwater (Jones et al 1997, Martens and Suarez (1997), Burt et al 2000, Whatmuff 2002). It has, however, been widely recognized that soil contamination does not only occur on large surfaces but also in depth. Therefore, the characterization of soil state after pollution requires a three-dimensional soil sampling with a large number of samples having to be analyzed.
2. Materials and methods

2.1. Study area

The Densu river basin (figure 1) is a coastal river catchment and covers an area of about 2,490 km². The watershed lies between latitude 5°30′N–6°20′N and longitude 0°10′W–0°35′W in Ghana (Dorm-Adzobu 2007). There are approximately 200 settlements in the basin, and the total population over 600,000, equivalent to 240 peoples per km² (Dorm-Adzobu 2007, Fianko et al. 2010, Adomako et al. 2011). Agriculture in the form of cash crops, and food production is the principal occupation, and this engages nearly 40% of the economically active population (Dorm-Adzobu 2007). There are few light industries in the region and there are proposals to develop engineered sanitary landfills as final disposal sites for municipal solid waste to aid waste collection and management in the greater Accra metropolis.

The basin is underlain by complex geology of Precambrian granite and granodiorite with associated gneiss in most parts. The other formations include rocks of the Upper Birimian that occur at the watershed of the Densu river in the northwest, which consist mainly of metamorphosed lava and tuff, and pyroclastic rocks; the rocks of the Togo series, which underlie the south-eastern part of the basin. The Togo series consists of sedimentary rocks (Forstner and Muller 1981, Einax and Soldt 1998). With such large data sets involved in soil investigations and usually containing many objects and many features, the analysis by univariate statistical methods is complicated and typically insufficient. The collection of massive data is also accompanied by the enormous economic cost of sampling, more labor, and the destruction of the natural environment; methods that may be unsustainable. A simple and more economical alternative is the application of multivariate statistical methods to substantially extract, as much information as possible, from fewer data and a moderate number of samples and reduce the destructive footprints left behind during soil sampling (Sielaff and Einax 2007). The adaptation of the technique is most essential in developing countries, where less money is voted for science research, but pollution activities are on the rise.

Multivariate statistical methods have recently been used for the evaluation of data sets of two-dimensional soil sampling (Krieg and Einax 1994, Zhang et al. 2007). Data sets of individual and single vertical soil profiles sampled in equidistance steps by using cluster analysis, multidimensional variance and discriminant analysis, and factor analysis, have also been evaluated (Bam et al. 2011, Wang et al. 2011) including many others. Multivariate statistical methods provide information about the association of sites and pollutants, identify the relationship between contaminants or other variables that affect the environment, and modeling from large environmental and ecological datasets. Multivariate methods are beneficial in understanding the most influential factors or sources of chemical components. While the technique is useful in qualitative analysis, it lacks the quantitative capacity to determine the degree to which a particular pollutant may be affecting the environment.

Another method of treating such large soil datasets is by geochemical analyses, which provide the quantitative capacity and can be used in assessing the pollution status of soils (Forstner and Muller 1981, Blaser et al. 2000). Geochemical methods such as the index of geo-accumulation ($I_{geo}$) and the metal enrichment factor (EF) analyses have been introduced as quantitative measures to assess metal pollution in aquatic sediments and solid waste materials (Muller et al. 1977). The present-day metal content in soil derived from natural or anthropogenic sources can be assessed by quantifying the enrichment factors (EF) of the soils using a reference element (Ji et al. 2008, Sekabira et al. 2010, Bam et al. 2011). The EF emphasizes the extent of changes in the elemental concentrations of the individual soils relative to the elemental concentration of the samples obtained from the average earth’s crust or local bedrock or soil (Blaser et al. 2000, Bam et al. 2011). EFs have the unique advantage of both indicating the source and the extent of pollution in an environment, thus capable of bridging the gap between multivariate statistics, e.g., Principal component and Cluster analysis (PCA and CA) and $I_{geo}$ evaluations.

In this study, we combined multivariate statistics (e.g., HCA and PCA), and geochemical methods ($I_{geo}$ and EF) to quantify the status of soils obtained from the three vertical profiles from one of the most densely populated river catchment in Ghana, West Africa, and also determine the possible elemental sources. Previous soil study in the catchment (e.g., Bam et al. 2011) explored how to maximize samples from a single soil profile to determine how soil properties control the vertical distribution and geochemical migration of the trace elements. A further investigation and inventory of the background soil properties and metal concentrations over the entire catchment, which comprised granite-granitoid complex and the sedimentary geology, necessitated this study to provide data and status of major and trace elements. The inventory of background of soil properties and metal concentrations are lacking in this region and data obtained in this study is envisaged to be useful for mobilization studies of such elements after industrial or domestic waste disposal.
and their metamorphosed versions (e.g., quartzite, schist, shale, and phyllite) of eroded materials deposited in the basin (Ganyaglo et al. 2011).

The main soil types of the basin include the forest ochrosols (96%), and Savannah ochrosols and lithosols (4%) (Agyili et al. 1993, Dwomo and Asiamah 1993, Asiamah et al. 2000, Bekoe 2005, Ganyaglo 2011). The soils developed over the parent weathered rock of granites of the Birimian formation. The forest soils are mainly found in the northern part of the basin and are slightly leached alkaline soils, which retain nutrients in more significant quantities necessary for cash crops, such as cocoa and coffee cultivation. The Savannah ochrosols are well drained porous soils that are generally deficient in nutrients (Agyili et al. 1993, Asiamah et al. 2000, Bam et al. 2011).

The climatic conditions in the catchment conform to the general conditions that prevail within the middle belt of Ghana. The monthly average temperature is around 26 °C, although some areas record lower figures. Maximum temperatures of between 29 °C and 31 °C are recorded in March and April, and minimum temperatures of 21 °C and 23 °C are experienced in August. Double maxima rainfall is experienced in a year with the primary rainy season starting in April and ending in July whiles the minor seasons begins in September and ends in early November (Dickson and Benneh 1988). The vegetation consists of coastal savannah, thicket, and grassland in the south and moist semi-deciduous forest in the north.

Figure 1. A map of the Densu basin showing the geological terrains, the three profiles locations and river tributaries.
2.2. Sample collection and preparation

A total of 49 fresh single soil cores were collected from three vertical soil profiles (depths 0.25–4.5 m) between 27th June to 3rd of July 2008 at Nkronso, Teacher Mante and Ayikae Doblo in the Densu basin in Ghana (figure 1). The sites were selected based on human settlement, agricultural and industrial activities, topography, and geology to help evaluate the extent of pollution at the north, middle, and the south (downstream) portions of the basin. Nkronso is the northern portion of the river catchment, which is generally a highland, while Teacher Mante and Ayikae Doblo are in the middle and the southern areas, respectively with progressive declining relief. The soil cores from the three vertical profiles (figure 2) were labeled after the sites as NK (NK1, NK2, ... NK18) for samples obtained from Nkronso, TM (TM1, TM2, ..., TM16) for Teacher Mante, and AD (AD1, AD2, ... AD15) in the case of Ayikae Doblo. Details of soil collection procedure and sample treatments have been reported in Bam et al. (2011).

The soil cores were collected using a plastic trowel and placed in Ziploc® bags. The bags were immediately sealed at the mouth to avoid soil water evaporation. Soil color (figure 2) was determined in situ using the Munsell soil color chart. The soil sampling followed the standard guide for environmental purposes (ASTM D5730−04 2004). The soil cores were transported to the National and Environmental Chemistry Research Centre laboratory of the Ghana Atomic Energy Commission, Accra, and kept under the temperature of 4 °C until moisture content analysis.

About 50 g of each fresh single moist soil sample was dried in an oven at 105 °C for 1 day to determine soil gravimetric water content (Bam et al. 2011).

The samples for trace and major element analysis were air-dried at 29 °C in a dust-free place for 14 days and disaggregated using agate mortar and pestle at the Ghana reactor-1 center of the Ghana Atomic Energy Commission. The samples were then passed through a >2 mm sieve and pulverized to obtain homogenized samples that were less than a 100 μm fraction (Bam et al. 2011).

2.3. Soil pH and Eh measurement

Soil pH and Eh measurements were done following the method described by Blakemore et al. (1987) and used in Bam et al. (2011). A soil solution (1:5) was prepared by adding 25.0 ml of de-ionized distilled water to 5.0 g each of the fresh soil samples. The pH and Eh measurements were taken using an Ion Selective Electrode, Ion 6 (Eutech Instruments Pte Ltd/ Oakton Instruments, USA). The Ion Selective Electrode meter was calibrated using pH buffers and Sn solution. Standard protocols in the manual were duly followed to obtain reliable pH and Eh results. Prior to the pH meter electrode calibration, the electrode used was first soaked in a pH 4 buffer solution for about 1 h. It was then rinsed with de-ionized water and the electrode calibrate with National Institute of Standards and Technology (NIST) pH buffers of pH 4.01, 7.00 and 10.01. After calibration, the pH electrode was rinsed with de-ionized water and wiped with dry clean tissue paper. The electrodes were then dipped into the soil suspension and the pH reading was taken after each reading stabilized. After each reading, the electrode was well rinsed with de-ionised water before subsequent reading was taken.
For the E_{47} measurements, a multi-point ion calibration was performed using a 1.0 ppm, 10.0 ppm and 100.0 ppm standard solution of Sn (Teknolab AB, Sweden). The electrodes were then rinsed with deionised water and wiped with tissue papers. The E_{47} readings were taken in similar manner as the pH (Bam 2009).

2.4. Sample analysis by energy dispersive-x-ray fluorescence (ED-XRF)

The total elemental concentrations of the 49 soils were determined by energy dispersive-x-ray fluorescence (ED-XRF) irradiation technique. Details of the method are described as follows (Bam et al 2011, Cesareo et al 2005): A 5.0 g aliquot of each of the pulverized sample was pressed at a pressure of 15 tons into 32 mm diameter pellet. The pellets were packed into sample holders and in-turns placed on the low-energy x-ray excitation source for 10 min irradiation. The low-energy x-rays, which has a maximum power of 3.0 kW (60 kV and 50 mA) for energy dispersive x-ray fluorescence excitation, were produced from Compact 3K5 x-ray Generator (Ital IS Structures, Italy). Each sample was irradiated at 0.8 kW (40 kV and 20 mA) with Mo secondary target as the anode (Bam et al 2011, Cesareo et al 2005). The x-ray fluorescence (Kα and Lα) lines detection and counting was done with a Si(Li) detector (Canberra, model SL30165, Canada), which has an energy resolution of 160 eV for Mn Kα energy peak at 5.895 keV, and was coupled to a preamplifier and amplifier operating at −500 V (Aboh and Ofosu 2005). The fluorescence lines were analyzed in Accuspec multichannel analyzer card, and the resultant fluorescent x-ray lines were stored in a computer. The analyses of the complex spectra were performed by an AXIL software, which is based on iterative non-linear least square fit of the frequencies to Gaussian–shape. The Quantitative Analysis of Environmental Samples (QAES) software (Kump 1993) was used to analyze and quantify the elemental concentrations resulting from the line intensities (pure Kα and Lα lines) of the measured for each element (Aboh and Ofosu 2005). The concentrations of metals in the reference materials, IAEA Soil 7 (Austria) (IAEA Analytical Quality Control Services (AQCS) 1999) and Estuarine Sediment 1646a (NIST, USA), which were prepared and irradiated as the samples were generally within 10% of the certified values. We reported the detection limits compared with certified values are reported in table 1. All x-ray fluorescence analysis was carried out at the Nuclear Physics Department of the Ghana Atomic Energy Commission.

2.5. Data analysis

Data analysis was carried out using SPSS v. 16 and Statsoft STATISTICA v. 8 statistical packages. To examine the relationships between soil properties and major and trace element concentrations, the data matrix of sample cores (n = 49) and parameters (n = 12) was subjected to R-mode HCA and PCA analyses to find groupings or patterns, and the influence of parameters within a multivariate space, and hence identifying the effect of soil physicochemical properties on them. The HCA is an unsupervised pattern recognition technique that uncovers the fundamental structure or underlying behavior of data (Vega et al 1998, Venugopal et al 2009). This analysis used the Ward’s method and the squared Euclidean distances for grouping of similar observations into respective discrete classes or groups to maximize within-group similarity and minimize among-group similarity according to a decided objective criteria (in this case the cutting level of the dendrogram is at 15). We obtained principal factors for the PCA by reducing the dimensionality of the data set from the number of geochemical parameters measured to a smaller set of significant underlying factors (e.g., the variance, orthogonal linear combinations that maximize the total variance). Although not substantially different from the HCA, PCA has been used as an alternative method to confirm results obtained through HCA (Bam et al 2011, Wang et al 2011) and combined approach has been used widely to reveal the correlation structure of variables (in geochemical data sets) allowing interpretation of geological processes affecting soil geochemical data (Kaiser 1966, Davis 1986, Lucho-Constantino et al 2004, Wang et al 2011). The overview of the most representative variable projections for the distinguishing of existing proximity and oppositions (Kaiser 1966, Davis 1986). Soil core pollution status was obtained by geochemical examinations using the EF and Igeo calculation methods. E_{47}-pH diagrams were used to predict chemical forms of metal ions in solution. The E_{47}-pH diagrams were constructed using the chemical speciation modeling software: Hydra/Medusa in SPANA (Ingrι et al 1967, Eriksson 1979). Hydra contains the hydrochemical database with logK data at 25 °C for most chemical speciesto defined chemical system of interest. Medusa creates the desired diagrams for visualization (Puigdomenech 2015, https://www.kth.se/che/medusa).

3. Results and discussion

3.1. Major and trace metal concentrations in soil profiles

The Figure 3 is a box-whisker plot summarizing the minimum, maximum, median, and average orders of values of the trace and major element concentrations variations in the Densu river basin and those of the upper continental crust, granite and topsoil (20 cm) in literature. The data for the statistical summary is in appendix. The average concentration of trace elements found in soils of the three profiles were significantly different from
Table 1. EDXRF analytical detection limits indicated by decimal places) and recommended values of soil standards used in this work.

| Standard name                  | Analytical results | Element | K<sup>a</sup> | Ca<sup>b</sup> | Fe<sup>c</sup> | Ti | V<sup>d</sup> | Cr<sup>e</sup> | Ni<sup>f</sup> | Cu<sup>f</sup> | Zn<sup>f</sup> |
|--------------------------------|-------------------|---------|---------------|---------------|---------------|----|-------------|--------------|--------------|---------------|---------------|
| NIST SRM-1646a (Estuarine Sediment) | This work         |         | 0.67          | 0.456         | 1.743         | 0.556 | 47.62      | 63.9         | 21.8         | 7.9           | 45.57         |
| ± Range                        |                   |         | 0.034         | 0.022         | 0.087         | 0.028 | 0.52       | 2.5          | 0.5          | 0.4           | 3.16          |
| Recommended value             |                   |         | 0.864         | 0.519         | 2.008         | 0.456 | 44.84      | 40.9         | 23<sup>g</sup> | 10.01         | 48.9          |
| ± Range                        |                   |         | 0.016         | 0.02          | 0.039         | 0.021 | 0.76       | 1.9          | 0.34         | 1.6           |               |
| IAEA SOIL-7 (Austria)         | This work         |         | 1.34          | 22.75         | 3.28          | 4583.29 | 68.84      | 123.89       | <22.9        | 14.30         | 104.21        |
| ± Range                        |                   |         | 0.42          | 6.74          | 0.9           | 1373.16 | 16.56      | —            | —            | 2.70          | 31.26         |
| Recommended/information value |                   |         | 1.21          | 1.63          | 25.7          | 3000   | 66         | 60           | 26           | 11            | 104           |
| ± Range                        |                   |         | 1.31–1.27     | 1.57–1.74     | 25.2–26.3     | 2.6–3.7<sup>h</sup> | 59–73      | 49–74        | 21–37        | 9–13          | 101–113       |

<sup>a</sup> Noncertified values by the issuing agency.

<sup>b</sup> Values in mg/kg.

<sup>c</sup> Values in cg/kg.

<sup>d</sup> Values in mg/kg.

<sup>e</sup> Values in mg/kg.

<sup>f</sup> Values in mg/kg.

<sup>g</sup> Values in mg/kg.

<sup>h</sup> Values in mg/kg.
the average values for the upper continental crust, the granite, and the topsoil for the elements Ca, Ti, V, Cr, Cu and Ni. Ca and Ti values were generally lower than the values reported for the Earth crust and topsoil. V, Cr, Cu and Ni values were also slightly higher than the average values reported in granites. The variability in metal concentrations between profiles and the average recorded upper continental crust, the granite, and topsoil are attributed to the natural variability associated with soils and soil surface activities influenced by land-use change and climate and meteorological impact on the soil formation processes. The samples from the site AD had substantially higher average and variable concentrations than those of the sites NK and TM. The AD profile is also associated with the lowest topography in the basin which receives deposits from rainfall runoffs from the upper part of the basin. The observed values for V and Cr, are above the 1997 and 2007 recommended values for soil quality required for agricultural, industrial or commercial use in Canada and many other European countries (e.g., CCME 2007, Ministry of the Environment—MEF, Finland 2007, Tóth et al 2016). The distribution of the major and trace elements in each profile is shown in figure 3. The concentration increase in trace metal levels near the soil surface in the three vertical profiles and the subsequent sharp decrease to a plateau down a vertical soil profile is considered as signals for pollution (Golchert et al 1991, Dineseu et al 1998, Candeias et al 2010). For all the metals investigated, there was no clear pattern recognizable to describe such elemental distribution (the graphs in figure 4). We, however, see some increments in Ca, Cr, and V concentrations within the 1 m depth below ground but these concentrations decrease afterward. Earlier studies elsewhere on pollution patterns (e.g., Candeias et al 2014) indicate that trace metal concentration increases near the soil surface in the vertic soil surface. The observed values for V and Cr in particular are above the 1997 and 2007 recommended values of soil quality for the protection of environmental and human health in Canada and many other European countries (e.g., CCME 2007, Ministry of the Environment—MEF, Finland 2007, Tóth et al 2016).

3.2. Soil water, chemistry and Pourbaix (EH-pH) diagrams
In Figure 5, we showed the variations in soil physicochemical properties with depth. The volumetric soil moisture contents determined ranged between 6.3% and 29.2% indicative of low porosity and partially dry soil. Generally, the moisture content increased down the profiles because evaporation is limited to the upper layers of the soil.

For all the three vertical soil profiles, the pH values varied between 5.0–7.99 pH units and this suggests a weak acid to moderately alkaline soils. pH ranges of 4–8, 5–7 and 7–9, have been reported for normal soils in the temperate, humid and arid environments, respectively (Brady 1984, Alloway 1995). We observed some variations in pH values with depth among the three soil profiles. Several mechanisms exist to buffer pH to varying extents among them are weathering processes, cation exchange reactions and dissolution of minerals (Bache 1979, Wild 1988, Borregaard and Elberling 2004). Soil pH usually increases with depth in humid regions where bases, Ca, K and or Na are leached down the profile, and can decrease with depth in arid environments where evaporation causes salts to accumulate in the surface horizon (Alloway 1995). We speculate that the
Figure 4. The vertical distribution of K, Ca, Ti, Fe, Cr, V, Ni, Cu, and Zn in the three vertical soil profiles in the Densu river basin, Ghana.

Figure 5. The vertical distribution of Eh, pH and moisture content in the three vertical soil profiles.
dissolution of base cations might be a plausible reason for the variations observed in our soils considering the high concentration of these metals in our soils. However, even with these buffering mechanisms, soil pH can differ significantly due to localized variations within the soil. Typically, diurnal and seasonal fluctuations have been observed in soil pH at different parts of a field because of the changes associated with water and soil formation processes (e.g., Rengel 2002, Rengel 2011). Soil pH also depends on the salt concentration (ionic strength) of the aqueous phase of the soil-water suspension used for the determination because salt cations affect the equilibrium between adsorbed and dissolved H\(^+\) ions (Schofield and Taylor 1955, Alloway 1995, Borggaard and Elberling 2004). We did not use cation solution for soil suspension and therefore could not examine or attribute the effect of such a medium on our soils. The general view is that these variable pH values could have some impact on how soluble ions and trace elements are mobilized and transported both horizontally and vertically in our soil.

In addition to the above stated views on the variation of pH in soils, Sposito and Page (1985) further observed that soil pH is also affected by the changes in soil redox potentials. Under reduction conditions soil pH generally increase and oxidation conditions bring about a decrease. The redox potentials (E\(_{H_4}\)) of the soils ranged between −84.9 mV to 27.5 mV and these indicate anaerobic soils with moderate to strong reduction property. Large positive values of E\(_{H_4}\) favour the existence of oxidized species and low or negative values are associated with reduced species (Sposito and Page 1985). Aqueous free electron activity (H\(^+\)), precipitation and dehydration processes result in the changing redox conditions. The changes may also alter salt-ion equilibrium leading to the the formation of the various oxides as well as determining which form of the element will be available in solution (Lindsay 1979, Wild 1988, Sheppard et al 2000). Soil E\(_{H_4}\) mainly affects the elements Fe although V, Cr and Cu can also be affected (Sposito 1983). We modelled pH variability on cation dissolution using the pH - E\(_{H_4}\) ranges observed in this study (Figure 6). In Figure 7, we reproduced the ion species in solution for the Cr, V and Fe. Figure 6 shows that except for the iron (III) species (Figure 6b), the solubility of the various forms of the elements Cr, V, Cu, Ni and Ti will remain either constant or decrease with increasing pH. The modelled predicted

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**Figure 6.** Ionic solubility diagrams for the trace and major ions in the soil soils of the Densu catchment.
solubilities \((\log S - \text{pH})\), indicate that the metals are generally less soluble under slightly acidic to alkaline \((\text{pH} \sim 6 \text{ to } 8)\) and this imply they may be less susceptible to leaching in these soils.

The E_{41}pH diagrams in Figures 7(a)–(c) illustrate the effect of changing pH and redox potential on the ionic species of V, Cr and Fe in soil. The diagrams indicate what form of a given ion/species is likely to be soluble/present under the given conditions of pH and E_{41} in natural environments (Bass Becking et al. 1960). The E_{41}pH diagrams show that the likely V chemical phases are the V(II), V(III) and V(V). Chromium and Iron are mostly Cr(II) and Cr(III), and Fe(III), respectively. These ions come in the form of hydroxyl or oxides and occurs naturally in soils.

### 3.3. Multivariate statistical analysis

**3.3.1. Hierarchical cluster analysis (HCA)**

The figure 8 shows the CA results. The rescale distance combined cluster axis represents the degree of association between groups of variables; the lower the rescaled distance value, the more significant the association (Jolly et al. 2018). Three clusters were identified by the rescaled distance of 15. In cluster 1, Fe and V are highly correlated with each other and so are Ni and Zn. Second, there is an association of all these elements with Ti and Cr. Reasons for the clustering of these elements can be linked to their origin or contamination sources, as shown in the PCA results (figure 9). In the second cluster (cluster 2), Ca and pH are highly correlated with each other and also there is an association with K. The relationship between Ca, K and pH shows that for the soils under the study, the variability in the soil pH can (or is) influenced by the concentrations of K and Ca. The result is similar.
to the observations by Maskall and Thornton (1996) for vertical soil profiles obtained from wildlife reserves in Kenya. Cluster 3 shows some moderate (large scale) correlation between Eh and MC while having an association with Cu. The mobility and bioavailability of Cu ions may be influenced by Eh conditions, and similarly, Eh may be influenced by soil moisture content.

3.3.2. Principal component analysis (PCA)

For this study, PCs were extracted from the analysis of matrix relating the variables of Fe, V, Zn, Ni, Cu, Cr, K, Ca, Ti, pH, MC, and Eh in 49 soil samples. The factor loadings for each variable, variance, explained, and cumulative variance of principal components (table 2) is obtained by PCA using the elemental concentrations and the physicochemical properties of the soil samples.
Table 2. Four principal and rotated principal components as analyzed for the soil properties and element concentrations. Varimax rotation with Kaiser (1965) normalization is applied. Significant correlations in bold.

| Variable | Principal component | Rotated Principal component |
|----------|---------------------|----------------------------|
|          | 1       | 2       | 3       | 4       | 1       | 2       | 3       | 4       |
| K        | −0.15   | −0.43   | −0.72   | 0.22    | 0.01    | 0.11    | −0.86   | −0.16   |
| Ca       | 0.72    | −0.33   | −0.02   | −0.16   | 0.66    | 0.59    | 0.01    | −0.21   |
| Ti       | 0.70    | 0.45    | −0.07   | 0.30    | 0.65    | −0.17   | 0.1     | 0.56    |
| Fe       | 0.90    | 0.04    | −0.35   | −0.14   | 0.97    | 0.02    | −0.07   | −0.01   |
| V        | 0.86    | 0.18    | −0.26   | −0.07   | 0.91    | −0.06   | 0.02    | 0.12    |
| Cr       | 0.57    | 0.08    | 0.56    | −0.40   | 0.43    | 0.19    | 0.76    | −0.08   |
| Ni       | 0.90    | 0.11    | 0.08    | −0.16   | 0.85    | 0.12    | 0.35    | 0.10    |
| Cu       | 0.22    | 0.42    | 0.24    | 0.79    | 0.03    | −0.03   | 0.06    | 0.95    |
| Zn       | 0.84    | 0.18    | 0.24    | 0.19    | 0.69    | 0.19    | 0.34    | 0.46    |
| E$\text{Ei}$ | −0.26   | 0.86    | −0.35   | −0.23   | −0.02   | −0.99   | 0.02    | 0.01    |
| MC       | −0.51   | 0.28    | 0.66    | −0.09   | −0.64   | −0.14   | 0.59    | 0.07    |
| pH       | 0.25    | −0.85   | 0.37    | 0.23    | 0       | 0.99    | −0.01   | −0.01   |
| Eigen value | 4.85  | 2.47    | 1.85    | 1.15    | 4.43    | 2.46    | 1.90    | 1.53    |
| Variance (%) | 40.43 | 20.61   | 15.38   | 9.57    | 36.94   | 20.46   | 15.82   | 12.77   |
| Cumulative variance (%) | 40.43 | 61.04   | 76.42   | 85.99   | 36.94   | 57.4    | 73.22   | 85.99   |

Four principal components were considered in the factor analysis, accounting for 85.99% of the total variance of the data. It is worth highlighting that the first three components describe 76.42% of such variance. Loading factors $>0.5$ are shown in large bold/italic characters, for enhanced reading.

The first principal component (PC1), explaining 40.43% of the total variance, defines two groups of variables: major elements Fe and Ti and the associated trace elements V, Zn, Cr and Ni positively related, in opposition to the soil physicochemical property MC. This loading is attributed to mixed sources as weathering of the soil chemical transformation processes (Brady 1979, Brady 1984, Alloway 1995). The second component (PC2) explains 20.61% of the total variance, with high and moderate negative loadings for pH and Ca, respectively and strong loading for E$\text{Ei}$. This suggests an inversely relationship between pH, Ca and E$\text{Ei}$. The group reveals a source effect which can be natural alterations in soil chemical transformation processes (Brady 1979, Brady 1984, Alloway 1995). The third component (PC3), which describes 15.38% of the variance, has a high negative factor loading for K and moderate positive loading factors for Cr and Zn. This has been attributed to the weathering of lithophile (K feldspars and plagioclase) and the effect of leaching of soil minerals in the case of K (Shotyk 1996, Blaser et al 2000, Borgaard and Elberling 2004). Surface runoff of road exhaust and industrial burning of fossil fuels debris could account for Cr.

The moderate loading of the soil moisture content here re-emphasized the importance of water in the concentration of both K and Cr in this group. The fourth component, (PC4), accounts for 9.57% of the total variance, has a positive factor loading for Cu only. This suggests that there is little relationship between Cu and the other elements or soil properties. Indeed, the concentration of Cu is higher than average but well within the acceptable limits in soils (CCME 2007). We attributed this group to the application of sewage sludge from the treatment of soil and also the use of Cu based fungicides and fertilizers. The compounds formed as a result of these can be tightly bound to soils and are able to form insoluble precipitates in solution under strongly reducing and pH which are mildly acidic to alkaline (Lindsay 1979, Alloway 1995).

All variables have been explained by at least one of the four principal components.

In figure 9, graphical projections of the PCA results disclose the position of the 12 selected variables’ coordinates, representing the correlation coefficients between the variables, in the different factorial plans. Three groups of the variables can be identified in the three factorial plans.

In the first factorial plan (PC1 / PC2), the selected variables can be separated into three groups (figure 9(a)). A first group (group 1—Fe, Ti, V, Ni, Cu, Ca, and Zn) with positive loadings in PC1 reveals an association of elements strongly correlated. The elements Fe, Zn, Cu, Cr, and V are related to contamination from anthropogenic sources such as fuel combustion, wear and tear from vehicle tires and the use of primary cells, and in the case of Ti, the local geology. This, however, must be investigated further to determine the extent (or lack thereof) of any anthropogenic source of contamination actually occurring in the catchment. The second group (figure 9(b)) is a high correlation group of variables comprising of MC, E$\text{Ei}$ and K. This group suggests the influence of the moisture content (MC) on the concentration of the base cation K and the subsequent effect on E$\text{Ei}$ of the soil. The relationship could be due to leaching of dissolved K, and the creation of anaerobic conditions.
in the soil should moisture content increase or decrease. The relationship between Cr and pH is demonstrated in group 3 (figure 9(c)). This association represents the influence of pH conditions on the mobility/bioavailability of the variable. In the second factorial plan (PC1/PC3), the association of Cr, Zn, Ni, Ti, V, Fe, Ca, Cu, MC, EH and pH variables has been outlined as in PC1/PC2 groups 1, 2 and 3. The third factorial plan (PC1/PC4), is again dominated by the association of Cr, Ca, Cu, Ti, Zn, V, Fe, Ni, V, Mg, EH, and pH. These results likely show same/ mixed origin or controlling factors of the elements studied in the soils of the three profiles.

The PCA projected groups confirmed the associations suggested by the HCA—mixed sources (natural background and vehicular activities), chemical relativities, and agricultural activities.

3.4. Enrichment factor (EF) and index of geo-accumulation (Igeo)

The extent of soil contamination was assessed using an enrichment factor (EF) as the multivariate methods (PCA, and CA) are unable to specify the levels of pollution. The EF has the advantage of putting all elements on a common scale, representing the appropriate departure of each element in a sample from the reference composition (Bam 2009, Berth 2003), in this case, the average upper crust values. In EF calculations, element concentrations are double normalized when generating an enrichment factor. The first normalization is to a major component of the fine-grained fraction of the soil. A widely used element to normalize the metals in soil is Zr. Zr mainly originates from natural lithogenic sources (rock weathering of mineral zircon) and has no significant anthropogenic source (Blaser et al 2000). The second normalization is the ratio relative to reference material:

\[
EF = \frac{(X/Zr)_{sample}}{(X/Zr)_{reference}}
\]

where X/Zr is the ratio of the metal of concern (X) to the Zr. As reference values, we used the average (X/Zr) ratio in the upper continental crust or rock value (Zr = 165 (or Zr = 180 mg kg\(^{-1}\)) for granite formation; Taylor 1964). The sample Zr value used were those reported in Bam (2009, 2011) for Potroase in the Densu basin, which averaged 163 mg kg\(^{-1}\). The EF values for the studied metals shown in table 3 were interpreted after Berth (2003).

Table 3 presents the percentage of the sample (%) according to calculated EF values among the three profiles. The results showed low EF values for K, Ca, Fe, Ti, Ni, Cu, and Zn, indicating no or minor enrichment for these metals in the three profiles. It should be noted that Cr and V had higher EF values compared to the other minerals with moderate to moderately severe enrichment. Accordingly, it is of particular importance to investigate Cr and V geochemical behavior in soils in these areas.

The ‘index of geo-accumulation,’ Igeo, like the metal enrichment factor, was introduced as a quantitative measure of metal pollution in aquatic sediments and solid waste materials and can also be used in assessing pollution status of soils. The index of geo-accumulation, Igeo, is calculated according to the following expression
Table 4. Muller’s classification for geo-accumulation index (Igeo) (Li et al. 2008).

| Index class | Igeo | designation of soil quality |
|-------------|------|----------------------------|
| > 5         | 6    | extremely contaminated     |
| 5–4         | 5    | strongly/extremely contaminated |
| 3–4         | 4    | strongly contaminated      |
| 2–3         | 3    | moderately/strongly contaminated |
| 1–2         | 2    | moderately contaminated     |
| 0–1         | 1    | uncontaminated/moderately contaminated |
| < 0–0       | 0    | uncontaminated              |

Table 5. Calculated geo-accumulation indices (Igeo) for the metals insoils.

| Sample | Element | K | Ca | Ti | Fe | V  | Cr  | Ni  | Cu | Zn |
|--------|---------|---|----|----|----|----|-----|-----|----|----|
| AD     | Min     | 2.60 | 4.58 | 1.74 | 1.93 | 0.08 | 0.07 | -2.67 | -3.21 | -1.98 |
| Max    | 0.46    | -0.86 | 0.36 | 0.95 | 2.34 | 2.90 | 1.55 | 0.99 | 2.21 |
| Average | -0.97    | 1.77 | -0.20 | 0.16 | 1.62 | 2.03 | 0.15 | -0.71 | 0.79 |
| Std Dev | -1.40    | -2.44 | -1.68 | -0.83 | 0.28 | 1.09 | -0.06 | -0.82 | 0.66 |
| Number  | 15      | 15  | 15  | 15  | 15  | 15  | 15  | 15  | 15  |
| NK     | Min     | -2.40 | -5.88 | -0.69 | -1.00 | 0.12 | -0.34 | -2.54 | -2.14 | -1.30 |
| Max    | -1.06   | -3.70 | 0.18 | 0.89 | 2.00 | 1.40 | -0.97 | 2.59 | 1.50 |
| Average | -1.56    | -4.43 | -0.37 | -0.32 | 0.96 | 0.83 | -1.71 | 0.33 | 0.18 |
| Std Dev | -3.77   | -5.76 | -2.91 | -1.57 | -0.49 | -1.22 | -3.23 | 0.47 | -0.90 |
| Number  | 18      | 18  | 18  | 18  | 18  | 18  | 18  | 18  | 18  |
| TM     | Min     | -1.45 | -5.69 | -0.73 | -0.88 | -0.36 | -0.25 | -2.42 | -1.85 | 2.34 |
| Max    | 0.07    | -1.59 | 0.64 | 0.58 | 2.18 | 1.39 | 0.68 | 1.38 | 2.04 |
| Average | -0.50   | -2.58 | 0.02 | -0.16 | 1.39 | 0.49 | -0.76 | -0.24 | 0.50 |
| Std Dev | -2.12   | -3.56 | -1.88 | -1.59 | -0.04 | -0.96 | -1.03 | -0.44 | 0.34 |
| Number  | 16      | 16  | 16  | 16  | 16  | 16  | 16  | 16  | 16  |

(Sekabira et al. 2010, Batayneh et al. 2014, Nowrouzi and Pourkhabbaz 2014):

\[
I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)
\]

where \(C_n\) is concentration of the element ‘n’ in a fraction of the soil (<2 μm), and \(B_n\) is the represents the geochemical background of the element ‘n’ and here we used the average upper continental crustal value of the elements since there was no measured pre-civilization soil values for the area. Factor 1.5 is introduced to include possible variations of the background values which are due to lithologic variability.

Thus the ‘index of geoaccumulation’ is a measure which compares present-day metal concentration with pre-civilization background values.

Although seven \(I_{geo}\) classes were established by Muller et al. (1977) based on the numerical value of the index, table 4, each step from one class to the next higher class averages a doubling of concentrations. The highest class (Class 6) reflects at least 100—fold enrichment above the background values.

The results of \(I_{geo}\) values are tabulated in table 5. According to the Muller (1977) scale, among the 9 metals investigated, the \(I_{geo}\) of V were ranked from uncontaminated to moderately contaminated for the three profiles in the order NK < TM < AD. EF values for Cr ranged from uncontaminated to strongly contaminated for soil samples obtained from NK and AD, respectively. It is notable that profile AD has a maximum average of 1.62 (moderately contaminated) for V and 2.03 (moderately to strongly contaminated) for Cr, compared to 0.96 in profile AD and 1.39 in TM for V and 0.83 and 0.49 respectively for Cr in both profiles. These findings are in good agreement with the results obtained from EF classification.

Generally, the largest man-made sources of chromium emissions to the environment are chemical manufacturing, the combustion of fossil fuels from automobiles and waste incineration (Lin and Ho 2007). Waste incineration, vehicular activity and agricultural inputs are some of the major human activities in this
basin and increased the concentration of trace elements. Chromium and its compounds may be associated with cancer and genetic damage. Excessive exposure may affect the unborn child, kidney, liver, lung, digestive system, nose and skin (World Health Organization 2004). Vanadium source in the area is mainly from exhaust smoke from the combustion of petrol and gasoline by automobiles.

4. Conclusions

Analysis of the major and trace metals (Ca, K, Fe, Ti, Cr, Cu, V, Ni and Zn) from the three profiles indicated that profile AD (downstream of the basin) had significantly higher concentrations of trace metals investigated than profiles NK and TM in the uppermost and the middle portions of the basin. This was followed by profiles TM and NK respectively, indicating that the effect of pollution in the basin is most intense in the lower portions and less in the upper regions of the basin. Principal component analysis and cluster analysis results allowed for the discrimination of Ti, Ni, Zn, Cr and V from Ca, pH, and also from E44, MC and Cu and this has led to three sources of the metals in the basin- natural background, agricultural, and vehicular activities. Even though enormous values of enrichment factor (EF) and geo-accumulation index ($I_{geo}$) was reported for V and Cr in this study, this does not suggest vehicular activities, industrial and agricultural inputs are contributing to soil pollution in the basin because their forms suggest geologic origin. This needs further investigations using more suitable instruments because EDXRF is not particularly great in analysis some trace metals and such analysis should be accompanied with the advanced isotope tracer study. The study also reveals that although there has been a growing perception of massive pollution in the basin, most of the metals investigated are of natural geologic origin. However, a more complementary study analyzing the organic and inorganic components of the soil by integrating the soil criteria, $EF$, and $I_{geo}$ should be considered to provide a more representative assessment of contamination in the basin using the data presented in this study as a baseline.

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Table A1. Statistical summary of metal concentrations (mg/kg) in the cores of the three profiles: AD, NK and TM and the soil physicochemical parameters of $E_\text{H}$ (mV), pH in pH units and volumetric moisture content%.

|       | K   | Ca  | Ti   | Fe   | V    | Cr   | Ni   | Cu   | Zn   | MC  | pH  | $E_\text{H}$ |
|-------|-----|-----|------|------|------|------|------|------|------|-----|-----|-------------|
| **AD** ($N = 15$) |     |     |      |      |      |      |      |      |      |     |     |             |
| Min   | 5173.0 | 2595.0 | 2568.3 | 22170.0 | 212.9 | 143.3 | 17.7 | 8.9  | 26.6 | 6.3 | 6.0 | −84.9       |
| Max   | 43200.0 | 34370.0 | 11000.0 | 163280.0 | 1020.4 | 1123.5 | 329.3 | 164.0 | 487.4 | 17.6 | 7.9 | 21.8       |
| Total | 239845.0 | 273307.0 | 110000.0 | 1413745.0 | 9346.3 | 9181.8 | 1889.1 | 757.9 | 2730.6 | —    | —    | —           |
| Average | 16000.0 | 18200.0 | 7456.0 | 94200.0 | 623.0 | 612.0 | 125.0 | 50.5 | 182.0 | 10.1 | 7.1 | −42.1       |
| Std Dev. | 11915.9 | 11504.6 | 2664.5 | 46800.6 | 245.2 | 318.7 | 107.6 | 46.6 | 165.5 | 3.6  | 0.7  | 38.2        |
| **NK** ($N = 18$) |     |     |      |      |      |      |      |      |      |     |     |             |
| Min   | 5936.1 | 1060.2 | 5283.7 | 42100.0 | 220.0 | 118.6 | 19.4 | 34.9 | 42.7 | 14.9 | 6.0 | −78.9       |
| Max   | 15050.0 | 4794.2 | 9699.2 | 157000.0 | 808.4 | 394.7 | 57.5 | 496.8 | 297.5 | 29.2 | 7.8 | 27.5       |
| Total | 191000.0 | 52000.0 | 119000.0 | 1220000.0 | 7100.0 | 4795.0 | 617.0 | 1869.4 | 2134.8 | —    | —    | —           |
| Average | 10640.0 | 2890.0 | 6620.0 | 67700.0 | 394.0 | 266.0 | 34.3 | 103.9 | 119.0 | 25.4 | 6.9 | −25.5       |
| Std Dev. | 2301.2 | 1146.7 | 1137.1 | 28513.1 | 143.7 | 64.4 | 12.0 | 114.6 | 56.1  | 4.9  | 0.5 | 28.9        |
| **TM** ($N = 16$) |     |     |      |      |      |      |      |      |      |     |     |             |
| Min   | 11500.0 | 1208.0 | 5160.0 | 45900.0 | 157.0 | 126.4 | 21.0 | 22.9 | 533.4 | 6.6  | 6.1 | −66.3       |
| Max   | 32800.0 | 20720.0 | 13290.0 | 126000.0 | 917.4 | 393.0 | 180.7 | 214.1 | 430.5 | 20.4 | 7.6 | 15.9       |
| Total | 354000.0 | 167000.0 | 139000.0 | 1210000.0 | 8451.0 | 3381.0 | 1063.2 | 1121.3 | 2371.7 | —    | —    | —           |
| Average | 22100.0 | 10400.0 | 8690.0 | 75700.0 | 528.0 | 211.0 | 66.5 | 70.1 | 148.0 | 13.5 | 6.9 | −25.3       |
| Std Dev. | 7192.3 | 5281.1 | 2320.9 | 28081.3 | 195.8 | 77.0 | 55.1 | 60.8 | 132.8 | 4.5  | 0.4 | 25.8        |
| *Crust* | 20900.0 | 41500.0 | 5700.0 | 56300.0 | 135.0 | 100.0 | 75.0 | 55.0 | 70.0  | —    | —    | —           |
| *Granite* | 33400.0 | 15800.0 | 2300.0 | 27000.0 | 20.0  | 4.0  | 0.5  | 10.0 | 40.0  | —    | —    | —           |
| *Soil* | 15000.0 | 24000.0 | 2900.0 | 26000.0 | —     | —    | —    | 25.0 | 60.0  | —    | —    | —           |

*a Taylor (1964).  
*b Borggaard and Elberling (2004).*
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