Trace Elements in Rainfall Collected around Menengai Area Kenya

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ABSTRACT

Trace element concentrations were measured in precipitation collected from five sites in the Menengai geothermal area, central Kenyan rift region: two sites in the Centre of the caldera (Menengai Well 2, MW2 and Mlima Punda, MPA), two at the caldera edge, at Laydown Meteorological station (MTS) and Menengai Viewpoint (MVPT), and one in the northern part outside the caldera at Rigogo (RIGO), between November 2011 and June 2012. The concentrations at these sites were compared with precipitation collected at a control station 30 km from study area at Egerton University Meteorological station. All samples were analyzed for trace metals (Al, Cd, Cr, Cu, Zn, Ni, Pb, Mn, B, As, Se and Mo). The majority of the rain samples collected had pH values higher than 6.2. The mean, median and mode pH was 6.58. High values of pH were attributed to the neutralization by natural alkaline local dusts which contain large fractions of calcite. Concentrations of measured trace elements species were within similar concentration range as those reported for other sites worldwide. Sources of the trace elements were also assessed based on enrichment factor method. The trace elements of anthropogenic origins (Hg, Zn, As, Se, Mo and Cd) were highly enriched with respect to crustal composition indicating the influence of anthropogenic input for these metals. The concentrations of trace metals that were determined in the rainwater samples were relatively low compared to World Health Organization drinking water quality guidelines hence potable for domestic use through rainwater harvesting.

1 INTRODUCTION

Rainwater chemistry has been the subject of intense research for the last two decades due to increased awareness of environmental problems caused by acid rain. Concerns about air pollution have emerged to be significant social and scientific issues in developing countries due to rapid economic development and consequent increase in energy consumption. The southern area of China has become the third region in the world seriously affected by acid rain during the past several decades following Northeast America (Galloway et al., 1976; Khwaja and Husain, 1990; Heuer et al., 2000; Ito et al., 2002) and Central Europe (Almamani et al., 1998; Marquardt et al., 2001; Topcu et al., 2002). Rainwater compositions play an important role in scavenging soluble components from the atmosphere and helping understand the relative contributions of different sources of atmospheric pollutants. Various sources of the dissolved components in rainwater can generally be divided into three groups: (a) sea salt aerosols; (b) terrestrial aerosols (soil dust, biological emissions); and (c) anthropogenic inputs (industry, agriculture and fertilizers, combustion of fossil fuels) (Negrel and Roy, 1998). Concentrations of many compounds present in the atmosphere have been significantly affected by human activities such as industry, agriculture, burning of vegetation and fossil fuel (Negrel and Roy, 1998). Quantification of these changes and their effect on terrestrial and aquatic ecosystems is important because of their potential adverse effects (Nriagu and Davidson, 1986).

Rainwater functions as a major sink for both gaseous and particulate matter including trace metals in the atmosphere and therefore plays an important role in controlling the concentrations of these species. The chemical composition of atmospheric depositions is the signature of numerous physical and chemical mechanisms of aerosol and precursor emissions, transport, chemical reactions, and removal processes. Therefore, the chemistry of wet depositions can provide insights into temporal evolution of atmospheric pollution, and be used as a pertinent indicator to evaluate natural process versus anthropogenic influences. This is because rainwater compositions play an important role in scavenging soluble components from the atmosphere and helping understand the relative contributions of different sources of atmospheric pollutants (Tang et al., 2005; Özsoy et al., 2008; Yang et al., 2011). Scavenging of the atmospheric pollutants by rain affects the chemical composition and the pH of rainwater. The degree of acidity in rainwater depends on the neutralization effects of certain components such as ammonia and calcium carbonate and/or hydroxide on the acidic ions present in the water (Kulshreshta et al., 1995a, b).

Determination of rainwater composition reveals the relative importance of the different sources/types of gases and particulate matter present in the atmosphere. Determination of background concentration levels of these pollutant in precipitation becomes useful tools in diagnosis where possible environmental impact caused in a specific zone is required and, establishing a comparison when reference laws or standards of non-criteria pollutants are not available. Commonly, these values are established for remote areas with a minimal anthropogenic influence, by this way, it is possible to accomplish a diagnosis of impact caused by non criteria pollutants. In fact, research on precipitation chemical composition of probably impacted zones, allow us to identify, first if there is an acidity problem, and second, to identify the main sources contributing to this acidity by means of correlation between elements, local meteorology and anthropogenic sources. Therefore, to assess the impact from geochemical and anthropogenic sources (human activity, volcanic activity, and crustal) on chemical composition of rainwater in a specific region, knowledge of the background levels of wet deposition is critical for new project areas.

Precipitation is an efficient pathway for removing the gases and particles from the atmosphere. It also plays a significant role in controlling the concentration of these species. Incorporation of S and N oxides in wet deposition is particularly important as they are precursors of major acids (H$_2$SO$_4$ and HNO$_3$) (Voldner et al., 1986; Minoura and Iwasaka, 1996). Therefore, precipitation chemistry measurements play a critical role in defining both the level of acid deposition and the state of some important biogeochemical cycles of the earth-atmosphere system (Moody et al., 1991). Precipitation composition thus is an integral
measurement and helps to understand the relative importance of the different sources of these materials (gases and particles). Because of this concern, precipitation chemistry in both rural-continental and urban areas has been the subject of intense research in the last two decades (Smirnioudi and Siskos, 1992; Samara et al., 1992; Sanusi et al., 1996; Raper and Lee, 1996).

An important feature of the environmental assessment studies is the identification of all possible sources (biogenic, geochemical, natural, and anthropogenic) to determine their relative contribution to the rainwater chemistry. Human activities have an important effect on global and regional cycles of most of elements (Nriagu and Pacina, 1988); however, geochemical sources may also have an important effect (Duca et al., 1991). For this reason, it is essential to discuss the origin of major elements to identify their main sources. A method commonly used by geochemists to relate an element in rainwater with its geochemical source, involves the use of a tracer derived from the specific reference source. Therefore, to assess the enrichment of an element relative to its source, it is necessary to define the excess (fraction with an origin different from reference source) in terms of an enrichment factor (EF). Chemicals present in the atmosphere influence the chemical characteristics of rainwater whereas the material deposited by the rain affects soil, surface water and vegetation.

At present, there are more than 1000 stations conducting precipitation chemistry measurements around the world. All these working stations may be categorised into Global, Regional and Local Networks. Global Networks (Global precipitation chemistry project) sites, collect precipitation at remote areas and provide worldwide information on the background concentration of air pollutants and long range transport of trace substances in the atmosphere while the regional networks in Europe, North America and various other countries aim at documenting the spatial patterns and long-term trends in deposition of acidic materials. A large number of local networks are operated in several countries, which address specific scientific questions, abatement strategies and pollution issues. Data on the chemistry of precipitation in remote areas offer a large potential for clarifying the effects of urban, industrial and agricultural emissions, and to understand the processes that control the chemical composition of the atmosphere in remote regions and the natural biogeochemical cycles.

With regard to mercury wet deposition monitoring around the world, there are currently, over 102 Mercury Deposition Network (MDN) sites in North America of which 92 sites are in the United States, 8 sites in Canada and 2 sites in Mexico. Mercury wet deposition is currently being monitored at these sites (National Atmospheric Deposition Program, 2007). Estimating mercury wet deposition fluxes is important for better understanding the influence of atmospheric mercury on mercury biogeochemical cycling and it’s potentially adverse effects in aquatic ecosystem (Harris et al., 2007; Gray 2006).

In Kenya studies on wet deposition fluxes of airborne chemicals are limited. In 2008 decisions were made to develop the Menengai area for harnessing geothermal energy (). As an important part of an environmental assessment study in Menengai area, precipitation concentrations for mercury, major and trace elements plus wet deposition fluxes of THg were measured from November 2011 to June 2012 at 5 sites. Mercury was of major interest because geothermal power plants have received increasing attention as regards the mobilisation of mercury to the environment. Mercury as a trace element that may be present in the geothermal fluid, and is, due to high volatility, transferred mainly into the vapour phase alongside other non-condensable gases (Robertson et al., 1977; Vitolo and Seggiani, 2002). Since the non-condensable gases present in the geothermal fluid are generally characterized by a reducing behaviour, mercury is prevalently emitted as elemental mercury (Hg) (Robertson et al., 1977; Vitolo and Seggiani, 2002). Mercury (Hg) is a persistent, hazardous air pollutant and bioaccumulative neurotoxin. Atmospheric deposition is widely recognized as a dominant mechanism by which Hg enters terrestrial and aquatic ecosystems (Landis and Keele, 2002; Hammerschmidt and Fitzgerald, 2006) where, uponconversion to the organic form methylmercury, it can bioaccumulate within the food chain (Schoeder and Munthe, 1998). Mercury in the atmosphere exists in three major forms: elemental mercury (Hg\(^0\)), reactive gaseous divalent mercury (RGM) and particulate mercury (PHg). PHg can be formed by physical adsorption of Hg\(^0\)) to atmospheric particulate matter in aqueous phase as the secondary particulate mercury (Wen 2006). Hg\(^0\) represents more than 95% of the total amount and due to its low solubility in water, Hg\(^0\) must first be oxidized before it is efficiently deposited by atmospheric wet and dry depositional processes (Lindberg et al., 2001). Therefore, mercury in precipitation mainly comes from the scavenging of PHg and RGM in air (Guentzel et al., 2001). Most of the mercury in atmospheric wet deposition is in ionic form and less than one percent of the total mercury is in MeHg form (Mason et al., 1997), and therefore atmospheric deposition of MeHg is generally thought to be a minor contributor to MeHg contamination in aquatic ecosystem (Mason et al., 2000). In the aquatic environment, inorganic mercury can be methylated by microorganisms to methylmercury and accumulated in the tissues of organisms. It is the ingestion of methylmercury via fish consumption that poses the greatest risk of exposure to the general public and, therefore, has the greatest potential for adverse environmental and human health effects. This mercury transformation has been summarized by Mason et al., 1994.

On the other hand, Nakuru and Menengai’s water resources depend mostly on rainwater for groundwater recharge; therefore rainwater quality is an important factor. The same is true for the residents who depend on rainwater harvesting for domestic use due to water scarcity in the project area and high fluoride content in groundwater sources that leads to community environmental health problems such dental fluorosis. Due to this reason, understanding the rain chemistry in the Menengai geothermal project area was considered necessary e.g. in assessing potential geothermal influence on the THg concentration in the rain, but Hg is a chemical constituent in geothermal steam that sometimes is emitted into the atmosphere. For other trace elements in precipitation, it is vital to establish the baseline rainwater quality, preclude the current geothermal well drilling activities being undertaken in the area with regard to trace element concentration levels in the precipitation and establish a yard stick for future reference when geothermal development in the area progresses to geothermal power plant generation.

The present paper provides an analysis of rain water collected in the Menengai area and nearby Nakuru, a provincial capital of Rift valley Province, Kenya. The Menengai geothermal area is a green field (an area of geothermal development at exploratory drilling and well discharge stage) with no geothermal power generation yet taking place. The field is however currently undergoing geothermal exploratory well drilling and discharge testing. The geothermal area is surrounded by agricultural fields and deciduous trees. Nakuru town, located south of the geothermal area has several industries including battery manufacturing, soap and cooking fat processing units, maize flour milling, milk processing, chemicals and engineering, and quarrying, all using common fuels like
wood and oil. Emissions from these industries include CO, SO\textsubscript{2}, NO\textsubscript{x} gases and particulate matter. In addition, the population of Nakuru town (473,280 people) and the surrounding area (1495.3 km\textsuperscript{2}) has witnessed increased vehicular density.

In 2011-2012, Geothermal Development Company Limited initiated a precipitation monitoring program in and around the Menengai area to evaluate the magnitude as well as temporal trends and, if feasible, to identify sources of toxics substances. As an important part of the study, precipitation concentrations for trace elements were measured from November 2011 to June 2012 at 5 sites in and near the Menengai caldera and at two control sites. This study also provides the first baseline information on the status of mercury and other trace elements in precipitation around Menengai geothermal area. The results are compared with those in other regions and countries and the possible sources contributing to observed chemical composition are discussed. The study will significantly contribute to the very limited knowledge available on precipitation chemistry and rainwater quality for domestic use in the Menengai area.

2 MATERIALS AND METHOD

2.1 Site description

Menengai Caldera geothermal area is one of many geothermal fields in the Kenyan Rift Valley. The caldera is located in the Rift Valley Province, in larger Nakuru District (at 35° 28’, 35°36’E, and 0°13’, 1°10’S), which is one of the eighteen larger districts of the Rift Valley Province (Figure 1) The larger Nakuru district has recently been subdivided administratively, placing a large section of Menengai caldera in the Rongai and Nakuru North districts. The Menengai caldera lies north of Lake Nakuru and forms the northern divide of the lakes’ catchment basin (Figure 1). The caldera is the remnant of a volcano that erupted about 200,000 years ago with the last eruption occurring around 1,400 years ago. It rises to a maximum height of 2,278 masl and covers an area of 90 km\textsuperscript{2}. With a diameter of 12 km, it is the second largest in Africa after Ngorongoro in Tanzania. Rainfall has been recorded for the last 32 years (1980-2011) near the Menengai caldera, i.e. at Nakuru Meteorological Station (Station ID 9036261), co-ordinate 36°6.243'E, 0°16.23'S which is about 1.5 km outside the Menengai caldera edge (Figure 1). The annual rainfall ranges from 500-1450 mm with an average of 948.2 mm. The rain falls mainly in two periods, the long-rains season in March to June and the short-rains season is in October/November. The dry season usually lasts from December to February often bringing strong winds in the caldera with frequent fire outbreaks. Average monthly temperatures range from 15°C-21°C over the year.

2.2 Precipitation Sampler and Sampling Procedure

Precipitation samples were collected from within and around the Menengai caldera geothermal field a rural area approximately 175 km to the North of the capital of Kenya, Nairobi. Precipitation sampling locations were set up in five different areas. The Menengai caldera area had four sampling sites, one at Menengai geothermal well number 2 (MW-02), one at Mlima Punda area (MPA), one at Menengai View point area (MVPT) and another site at Menengai Weather station (MTS) (Figure 1). Except for Nakuru town/municipality located just south of the caldera the surrounding area is essentially rural, consisting of open areas with scattered houses at distances varying from 100 to 200 m and agricultural fields.

The other sampling sites were situated some distance away from the Menengai caldera, one at Rigogo approximate 6 km north of the caldera, one at the Kericho High School (KRC) approximately 140 km west of Menengai, one at the Egerton University (EU) in Nakuru approximately 30 km southwest of Menengai and one at Kinangop (KINGGO) approximately 110 km southeast of Menengai. For this study, we used site EU as a reference point as it had more rainfall events compared to far away sites like KRC and KINGGO. These three sites are located in rural areas, remote from heavy industrial activities and significant population centers. There was some light industrial activity in the vicinity of the MW-02, MPA and MTS sites, mainly geothermal well drilling and well discharge testing. The sampling sites at EU, MTS and MPA are equipped with meteorological monitoring equipment (manual and/or automatic weather stations).

Event-based bulk precipitation samples were collected using improvised precipitation samplers mounted on the top of a 1.5 m sampling platform located at the sampling sites (Figure 2). Event based sampling was used due to the fact that they could help establish any correlation between variables being considered and activities in the study area. The decision to deploy precipitation collectors was based on the weekly rainfall forecast from the Kenya Meteorological and direct observation of the prevailing weather conditions in the project study area. The purpose of the 1.5 m platform was to limit the influence of locally generated soil splash during rainfall. The samplers consisted of four polyethylene terephthalate (PET) components: (1) a funnel - 15 cm diameter at the top, (2) a connecting tube, acting as a capillary to prevent the diffusion of the precipitation sample as well as the volatilization of volatile elements from sample, (3) a sampling bottle/jar (500 ml volume), and a plastic enclosure inform of a colorless plastic bucket (Figure 2).

Before deploying all components of the sampler were acid cleaned to prevent possible contamination. Cleaning was conducted according to trace metal cleaning protocols. All funnels, tubes and bottles were cleaned rigorously by dipping in dilute acid (0.1N HNO\textsubscript{3}), rinsing with ultrapure deionized water and then placed in separate plastic bags, stored in plastic boxes until use. The bulk deposition sampling funnel was left uncovered for the entire deployment period. The funnels with a 176 cm\textsuperscript{2} collection area are commercially available and are equipped with a fine mesh filtering disk to prevent leaves and insects falling into the sample. The receiving bottles/jars were further shielded from UV radiation during deployment by the colourless plastic buckets.

Samples were collected on event based basis, and the sampling components were cleaned after every sampling before redeployment for subsequent sampling during the entire sample period from December 2011 to end of June 2012. At the same time, the precipitation samples were collected immediately after each rainfall event within a 24 hr period i.e. at 0900 hrs when the sun is not too warm, thus preventing sample evaporation. Samples collected at each site were immediately filtered (using disposable Syringes Filters (CA) with 0.20µm pore size membrane Grade - 25 CS020AS and pressure limit 0.51 mpa) and poured into two 100 ml PET bottles, then transported to the laboratory and stored in a refrigerator until analysis. One full 100 ml PET bottle was used for trace/major elements analysis while the other sample was analysed for physico-chemical parameters such as pH and conductivity. Although we recognize that there may have been evaporative losses after sampling, we assumed losses to be insignificant. A total of 70 rainwater samples were collected during the study period.

3
Figure 1: A map showing the location of the Menengai caldera and (above) the locations of the precipitation monitoring sites: Menengai geothermal well (MW-02); Mlima Punda area (MPA); Menengai View point area (MVPT); Menengai Weather station (MTS); Rigogo (RIGGO); Kericho High School (KRC); Egerton University (EU); Kinangop (KINGGO) and Nakuru Meteorogical station (NMTS). The respective site coordinates are also provided.

Figure 2: Precipitation chemistry sampling apparatus. Sampling platform top measuring 30cmx30cm and a stand of 1.5m above the ground
2.3 Analytical Methods
The pH, Temperature, TDS and Conductivity values of the collected samples were measured for unacidified samples using the Hanna HI 255 pH, Conductivity/Temperatures Meter equipped with a combination glass electrode using a reference (KCl and glass electrodes standardized with a pH of 4.0 and 10.0 reference buffers before pH determination). Unacidified samples were also analyzed for Cl and SO$_4^{2-}$ by UV-visible spectrophotometry using a UV- Shimadzu1800.

Inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Model Elan-6000) was used to analyze trace metals. Detection limits for the respective parameters were <0.01 µg/L for Hg and Cd, <0.1 µg/L for Ni, Se ad Ba, <0.02 µg/L for As, <0.03 µg/L for Mo, <0.05 µg/L for Cr, <0.08 µg/L for Pb, <0.4 µg/L for Cu, <0.7 µg/L for Zn, <1.0 µg/L for Al, and < 10.0 µg/L for B. While detection limits for the respective major elements were <0.3mg/L for Ca, <0.2 mg/L for Na, <0.02 mg/L for K, <0.01 mg/L for Mg and < 1.0 µg/L for Al. The samples were analyzed at the Geochemistry Laboratory Facility of British Geological Survey (BGS), (Nottingham, United Kingdom) for THg, trace and major metals.

2.4 Quality Control and Assurance
Precautions were taken to avoid contamination of samples in both field and laboratory, and to ensure the reliability of our determinations. Prior to installation, the funnel and collection bottles were carefully cleaned and dried in a clean laboratory. An analysis of blanks (deionized water) passed through the funnel to the collection bottles showed that there was negligible contamination. After each precipitation event the collection bottles were removed and replaced with others that had undergone the washing procedure.

2.5 Statistical Analysis
ANOVA test was used as a data analysis tool to compare differences of means between different sampling sites and months (groups) especially comparing precipitation samples between control station (EU) and Menengai area sampling sites during the study. Pearson product-moment correlation coefficient, also known as $r$, $R$, or Pearson's $r$, a measure of the strength and direction of the linear relationship was also used to as a measure of the degree of linear dependence between trace and major elements concentrations in Menengai area precipitation.

3 RESULTS
3.1 Precipitation pH and Conductivity
The pH of the rainwater ranged from 5.89 to 7.17 (average 6.58 with a 95% Confidence Limit of 0.065), which is higher than the pH of typical natural rainwater (5.6) (Seinfeld and Pandis, 2006) (Table 1). With only 1% of the precipitation recorded can be categorized as slightly alkaline (5.6-6.0). Samples with very alkaline (>7.0) of about 24% was observed, indicating the presence of strong influence of precipitation by CaCO$_3$ basic species, notably Ca$^{2+}$. These results indicate a strong influence of alkaline soil dust on rainwater in the Menengai area resulting in Mean and Median pH of 6.58, slightly much higher than pH 5.6 of normal rainwater (Charlson and Rhode, 1982). Statistical analysis revealed no spatial (P value = 0.950114) and temporal (P value = 0.524773) variation in the pH of the rain samples.

<table>
<thead>
<tr>
<th>pH</th>
<th>Frequency</th>
<th>Percentage composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6.2</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>6.4</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>6.6</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>6.8</td>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td>7.2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Conductivity in Menengai area ranged from 3.49 to 59.5 µS/cm, with an average value of 16.79 µS/cm. For sampling site further away from Menengai area, the conductivity ranged from 4.26 to 27.5 µS/cm, 3.26 to 5.14 µS/cm and 6.33 µS/cm for Egerton University (EU), Kericho High School (KRC) and Kinangop (KINAGGO) sites respectively. The average precipitation conductivity for Egerton University (EU) that had more precipitation events samples far away site Kericho High School (KRC) and Kinangop (KINAGGO) was 11.54 µS/cm. There was no spatial (P value = 0.369056) and temporal (P value = 0.118249) variability in conductivity values of the rain samples.

3.4 Trace element concentration in the precipitation
The summary statistics of concentrations of the 13 trace elements determined in the 57 rainwater samples is presented in Table 2. There was no significant variation in trace element concentration across the five precipitation sampling sites and the control site EU for Al, Hg, Mn, Zn, Cd except for As (p value = 0.03) that had high maximum concentrations. Site MPA has highest average As concentration of 0.38 µg/L over the monitoring period. Significant trace element concentration variation evident across the months for Mn (p value = 2.8E-07), As (p value = 0.0023), Zn (p value = 0.003), Cd (p value = 0.0008), and Mo (p value = 0.01). The variation of concentration of these metals can be explained by the scavenging of pollutants. The variation in the concentrations of...
trace metals between different rainfall events could be related to the source of pollutant emissions. The high concentrations of metals were measured in rainfalls after periods of dryness in April 2012, while low concentrations of metals were measured when rain continued for several days. Gratz et al. (2009) study also observed that the highest concentrations were typically observed with low precipitation amounts, suggesting that most trace elements are removed during the onset of precipitation, and additional precipitation acted to dilute samples throughout the remainder of the event.

### Table 2: Levels of trace elements concentration in rainwater (µg/L) around Menengai geothermal field

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Mean</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>36.79</td>
<td>10.17</td>
<td>0.09</td>
<td>456.25*</td>
<td>57</td>
</tr>
<tr>
<td>Hg</td>
<td>0.16</td>
<td>0.16</td>
<td>0.06</td>
<td>0.45</td>
<td>57</td>
</tr>
<tr>
<td>B</td>
<td>29.19</td>
<td>29.33</td>
<td>0.6</td>
<td>171.5</td>
<td>57</td>
</tr>
<tr>
<td>Cr</td>
<td>0.26</td>
<td>0.18</td>
<td>0.003</td>
<td>1.13</td>
<td>57</td>
</tr>
<tr>
<td>Mn</td>
<td>19.72</td>
<td>6.39</td>
<td>0.05</td>
<td>374.63**</td>
<td>57</td>
</tr>
<tr>
<td>Ni</td>
<td>0.49</td>
<td>0.35</td>
<td>0.1</td>
<td>1.94</td>
<td>57</td>
</tr>
<tr>
<td>Cu</td>
<td>1.27</td>
<td>0.76</td>
<td>0.05</td>
<td>6.92</td>
<td>57</td>
</tr>
<tr>
<td>Zn</td>
<td>9304.51</td>
<td>42.56</td>
<td>4.28</td>
<td>116046***</td>
<td>57</td>
</tr>
<tr>
<td>As</td>
<td>0.18</td>
<td>0.1</td>
<td>0.001</td>
<td>1.58****</td>
<td>57</td>
</tr>
<tr>
<td>Se</td>
<td>0.11</td>
<td>0.08</td>
<td>0.03</td>
<td>0.38</td>
<td>57</td>
</tr>
<tr>
<td>Mo</td>
<td>0.18</td>
<td>0.09</td>
<td>0.001</td>
<td>1.3</td>
<td>57</td>
</tr>
<tr>
<td>Cd</td>
<td>4.34</td>
<td>0.01</td>
<td>0.002</td>
<td>50.29</td>
<td>57</td>
</tr>
<tr>
<td>Pb</td>
<td>0.31</td>
<td>0.22</td>
<td>0.01</td>
<td>0.9</td>
<td>57</td>
</tr>
</tbody>
</table>

*MPA had highest maxima with Al at 3 other different sites range being 121.2-300 µg/L. ** One sample at site RIGGO had this maxima with all other samples at other site being <100 µg/L. *** All sites had highest Zn maxima. **** Site MPA has 2 samples with range 1.44-1.58 µg/L.

#### 3.6 Trace Element Enrichment Factor Calculation

In the absence of anthropogenic sources, observed concentrations of metals and ions should be explained by natural sources. However, emissions from the various man-made sources have drastically increased concentrations of metals in our environment. Enrichment factors (EF) are normally applied to identify the origin of an element in precipitation (Keene et al., 1986; Ahmed et al., 1990; Singer et al., 1993; Okay et al., 2002; Safai et al., 2004; Zhang et al., 2007). Enrichment factors (EF) can be calculated to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material. Enrichment factors (Duce et al., 1975) are very good indicators of natural or anthropogenic pollution (Taylor and McLennan, 1985). Therefore we decided to calculate EF for the elements and ions measured in this study thereby obtaining a measure of enrichment levels in and around the Menengai geothermal area. EF values that surpass contamination levels might also be very informative, e.g. in identifying potential sources of the element in question. Al and Ca are two typical lithophilic elements normally used as reference elements for continental crust. Since there was measurement of both Al and Ca elements in the rainwater samples, Ca and Al were chosen as reference elements for major and trace elements respectively to determine their continental origin for this study (Safai et al., 2004; Das et al., 2005; Zhang et al., 2007). Using Ca$^{2+}$ and Al as reference element for soil source, enrichment factors were calculated as shown in equation 1 (Safai et al., 2004; Das et al., 2005; Zhang et al., 2007):

$$EF_{soil} = \frac{\left[ X/Ca^{2+} \right]_{rainwater}}{\left[ X/Ca^{2+} or Al \right]_{soil}}$$

where X was the concentration of the target element, X/Ca or Al ratio was from crust composition (Taylor, 1964). Mason’s (1966) compilation for crustal abundances was used in crustal enrichment factor calculation. Al and Ca were used to calculate EF for trace and major elements respectively. All concentrations were used for EF calculations.

Based on the hypothesis that crustal material is the only source of Al and Ca, a value of EF, near 1 for an element indicates that crustal material is a major source of this particular element. However, EF values in the range of 1-10 are considered to be not enriched due to the differences between chemical composition of local soil and reference crustal composition as per Mason’s (1966) compilation. Elements of EF, between 10 and 100 are considered moderately enriched, indicating greater concentrations of a particular element in the rainwater than would be expected from the crustal material. Finally, EF greater than 100 show highly enriched conditions, indicating a severe contamination due to human activities (Duce et al., 1975). Table 3 shows the calculated enrichment factors of trace and major elements in rainwater samples around Menengai area.

#### 3.7 Pearson Correlation coefficients of measured elements

Pearson’s correlation was applied to the total element concentration analyzed during the study. This was performed to distinguish the possible common sources of the constituents. The matrix correlations are shown in Table 4 for both trace and major elements; the significant correlations are marked in bold letters. Common correlating element groups are: Cr-Hg-Al, Ni-Al-Cr, Se-Cr-Mn-As, Mo-Hg-Cr-Mn-Se, Pb-Al-Cr-Ni, and Cd-Zn. Two trace elements with strong correlation can be selected from these measurement
data: Cd-Zn (correlation coefficient 0.95). Probably, the above-mentioned groups are typical of the entire Menengai area indicating their origin from similar sources caused by long-range transfer of air masses. It is also important to note that no correlation was observed among the trace metals and the $SO_4^{2-}$.

### Table 3: Enrichment factors of measured trace elements in precipitation in relation to crustal composition

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>This Study - Mean (ppm)</th>
<th>Earth Crust (ppm)</th>
<th>Enrichment Factor (EF)</th>
<th>Sample Size (n=57)</th>
<th>Size</th>
</tr>
</thead>
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<tr>
<td>Al</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>57</td>
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</tr>
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<tr>
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<td>4861.65</td>
<td>57</td>
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<tr>
<td>Cd</td>
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</tbody>
</table>

### Table 4: Pearson’s correlation among the trace and major metals measured in precipitation around Menengai area.

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<tr>
<th></th>
<th>Hg</th>
<th>Al</th>
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<th>Mn</th>
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<th>As</th>
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<td>0.47</td>
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<tr>
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</table>

### 4. DISCUSSION

#### 4.1 Precipitation pH and Conductivity

In view of the rainfall events sampled around Menengai area, there is no rainwater acidification in Menengai area unlike areas such as Mangdang Mountain in eastern China (Mean pH of 4.8 and 80% of precipitation events having a pH<5.6, Cheng et al., 2011); Beijing, China (Mean pH 5.12 and pH range 4.02-7.62; Xu and Han, 2009); Loess plateau, northwest China (Mean pH 7.7 and pH range 6.82-8.28; Xu et al., 2009); Guangzhou, south China (Mean pH 4.49 and pH range 3.52-6.28; Cao et al., 2009); eastern Uttar Pradesh, India (Mean pH 6.3 and pH range 6.1-6.8, Tiwari et al., 2006); Danum Valley, Malaysia (Mean pH 5.17 and pH range 4.89-5.90; Sumari et al., 2009); a mining area in Ghana (Mean pH 4.67 and pH range 4.0-5.6; Akoto et al., 2011); on the summit of an active volcano Mt Etna, Italy (pH range 2.45-5.7; Aiuppa et al., 2006); but similar to that in northeastern Mexico with mean pH of 6.58 (Lara et al., 2010). Statistical analysis also revealed no spatial and temporal variation in the pH of the rain samples around Menengai area. The pH of natural precipitation is controlled by dissolved CO$_2$, due to the interaction between water
droplets and carbon dioxide. Precipitation pH is modified by the addition of both acidic and alkaline components (Topçu et al., 2002; Singh and Mondal, 2008).

Conductivity of precipitation in the Menengai area was much higher than the range and average conductivity of the precipitation in areas such as at the global atmospheric watch station in Danum Valley Malaysia (Range 3-21 µS/cm; Mean 8.0 µS/cm; Sumari et al., 2004) but lower than that in areas such as Mining region in Ghana (Range 7.15-59.6 µS/cm; Akoto et al., 2011); Zhejiang and Loess plateau, Northwest China (Range 13-257 µS/cm; Xu and Han, 2009; Xu et al., 2009). Precipitation conductivity is mainly contributed by water-soluble ions, the value being related to the total sum of anions and cations in the rainwater. Low precipitation conductivity is an indicator of good atmospheric environmental quality.

4.2 Trace element concentration in the precipitation and worldwide comparison

In the Menengai area, significant trace and major element concentration variation was evident across the sampling months (March-June 2012) for As, Cd, Zn, Mn, Mo, Mg, K and Ca. The variation of concentration of these elements can be explained by the scavenging of pollutants. The variation in the concentrations of trace and major elements between different rainfall events could be related to the source of pollutant emissions. The high element concentrations were measured in rainfalls after periods of dryness in April 2012, while low concentrations of elements were measured when rain continued for several days. Graz et al 2009 study also observed that the highest concentrations were typically observed with low precipitation amounts, suggesting that most trace and major elements are removed during the onset of precipitation, and additional precipitation acted to dilute samples throughout the remainder of the event. SO$_4^{2-}$, Ca, Na and K were the dominant species accounting for 98% of the total species, which were similar to the results in similar studies in China (Zhang et al., 2007). SO$_4^{2-}$ was the highest concentration anion and constituted approximately 50.0% of the major species which can be attributed to fossil fuel consumption in automobiles and industries as no correlation existed with other major crustal elements.

Galloway et al. (1982) and Jickells and Knap (1984) summarized trace metals concentrations in precipitations collected worldwide and Bermuda respectively, Dasch and Wolff (1989), Baeyens et al. (1990), Kaya and Tuncel (1997), Ayodele and Abubakar (1998), Freydiere et al. (1998), Takeda et al. (2000), Kanellopoulou (2001), Al-Momani (2003), Deboudt et al. (2004) and Migliavacca et al. (2004) summarized more recent values for those elements commonly analyzed in precipitation. For the most part, our data were in good agreement with the preceeding cited authors, with few exceptions. The concentration of Cd, Cu, Zn, Mn and Al were higher than those reported Kano, Nigeria (Ayodele and Abubakar, 1998), Bermuda (Jickells and Knap, 1984), Hiroshima-Japan (Takeda et al., 2000) and Northern Jordan (Al-Momani, 2003). Zn and Mn concentration was higher in Menengai precipitation compared to all reviewed literature. However, concentrations of some measured species were lower than those reported by other authors. For example, Cd concentration was much lower than levels reported in North Sea (Baeyens et al., 1990). Menengai precipitation Cr concentration was lower than those reported for North Jordan (Al-Momani, 2003), Ankara Turkey (Kaya & Tuncel, 1997) and in worldwide review (Galloway et al. 1982). Cu and Ni concentration in the precipitation was lower than those reported for Intertropical Africa (Freydiere et al., 1998), North Sea (Baeyens et al., 1990), Northern Jordan(Al-Momani, 2003), Athens Greece (Kanellopoulou, 2001), South Brazil (Migliavacca et al., 2004) and in worldwide review (Galloway et al. 1982). Pb and Al concentration in Menengai precipitation was much lower than all other areas cited in the reviewed literature.

4.3 Trace Element Enrichment in Precipitation

Enrichment factors (EF) are normally applied to identify the origin of an element in precipitation (Keene et al., 1986; Ahmed et al., 1990; Singer et al., 1993; Okay et al., 2002; Safai et al., 2004; Zhang et al., 2007). Enrichment factors (EF) can be calculated to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material. Enrichment factors (Duce et al., 1975) are very good indicators of natural or anthropogenic pollution (Taylor and McLennan, 1985). It is possible to explain this high trace metal enrichment in precipitation of Menengai area compared to other areas. These trace elements may be derived from soil as materials blown from the ground, volcanic degassing, industrial and domestic pollution. In this area, the most important emission sources could be the industrial zones of Nakuru town, situated at the north-east, upwind from the study, which seems to indicate that the transport of contaminants may come from the industrial activities of Nakuru town, (Pacyna, 1994). The sources of the trace metals could be from the numerous industries located in Nakuru. They include animal feed processing plants, dairy/food processing plant, cooking oil and soap manufacturing plants, hide and skins tanneries, fuel oil-fired industrial boilers, vehicles motor assembly, paint plants, cleaning products manufacturing, dry and wet battery production and disposal plant and disposal of lead batteries and many others industries that may contribute to the emissions of heavy metals.

Trace elements Al and Cr were not enriched to higher than 10 indicating that they have mainly originated from the airborne dust. Although Cr can also have a significant contribution from anthropogenic sources.

The elements B, Mn, Ni, Cu and Pb are moderately enriched compared to the mean crustal composition indicating the presence of other sources contributing to these elements. The potential sources could be particles from automobile emissions, vehicle wear, and road dust as they contain significant concentrations of Cu, Pb and Zn (Shahin et al., 2000; Rose et al., 2001; Weckwerth, 2001; Martuzevicius et al., 2004). Nickel and Mn may also be released from oil-fired furnaces and ferroalloys (Szefer and Szefer, 1986). Where there is consumption of Li, Co and Ni for use in rechargeable cells, it may imply that Ni in the used cells are not recycled or recovered hence its potential to contaminate the environment. As a result of the wide uses of copper and lead products, they were present in all the rainwater sampled. Environmental contamination by Pb is widespread, the major anthropogenic source of this element being the combustion of leaded gasoline (Dimuchowski and Bytnierowicz, 1995; Ghauri et al., 1994). Although its use has been discontinued in some countries, the use of tetra alkyl lead compound as antiknock additive remains the largest application of organolead compounds. Vehicular emissions of tetraalkyllead are subject to atmospheric breakdown to trialkyl- and dialkylead and all the three forms are scavenged from the atmosphere by rainfall (Hewitt and Harrison, 1986).

The high values of EFc found for Hg, Zn, As, Se and Cd show that these metals in rainwater are non-crustal, because elements such Cd and Hg are associated with fine particles (<1 µm), which are generated as high-temperature combustion condensates and infected by smokestacks into the boundary layer (Lindberg, 1982; Scudlark et al., 1994). As for Cd emissions, it is known that in
motor vehicles several of their components are Cd alloys, manufacturing and disposal of Cd batteries and the wear of vehicles tires could also be a source of Cd in precipitation. Natural sources of these elements (besides soils) are volcanoes (Hinckley et al., 1999), wild forest fires (Chankina et al., 2001; Dennis et al., 2002) and/or biogenic sources (Beauford et al., 1975; Hong et al., 1996). Local emissions and long-range transport are considered to be the source of the enriched elements. Na, Mg and K had an EF of less 1 suggesting major influence of crustal source.

4.4 Correlation coefficients of measured elements

In the Menengai area, Cd-Zn (correlation coefficient 0.95) was revealed as trace element group with strong correlation from the precipitation measurement data. It is also important to note that no correlation was observed among the trace metals and the SO\textsubscript{4}\textsuperscript{2-}. Halstead et al. (2000) also found that Cd and Zn were enriched in rainwater relative to crustal material and significant contribution of this element was suggested. Although correlation between species are frequently used to know about the sources of pollutants, it is necessary to be cautious in the interpretation of correlation coefficients in rainwater data, because the concentration may vary by scavenging of particles from the atmosphere. Scavenging of elements from the atmosphere by rain depends on sizes and hydrosopic properties of particles with which elements are associated (Galloway et al., 1993). Therefore, elements which are emitted from totally different sources may show correlations due to similar physical properties of particles that carry them. However, source information can be extracted from correlation data bearing these uncertainties in mind.

4.5 Suitability of Precipitation Chemistry for Potable Rainwater harvesting in the area

The Kenya (e.g. Menengai area) just like other2 parts of world is currently undergoing water crises and rainwater harvesting can augment water supply in all sectors. Rainwater harvesting increases food production and hence forms the foundation of many development projects that promote agriculture and land management (Lundgren, 1993; Humi and Tato, 1992; WOCAT, 1997). For instance, rainwater harvesting reduces women's burden of collecting water for domestic use, leaving time for other productive activities. It also gives opportunity for the girl child to attend school and provides a relatively safe and clean source of drinking water, minimizing incidences of water borne diseases (Baron and Rockstrom 2003).

Although rainwater harvesting is widespread in the project area and many parts of the world, its quality has been an issue that is given relatively little importance. This should not be the case especially if this water is to be included in integrated water resources management. The harvesting of rainwater can either be directly from the atmosphere - in which case the quality is influenced by the atmospheric conditions, or via runoff in which case the quality becomes a major issue of concern and quality parameters like pH, Al, Hg, B, Cr, Mn, Ni, Cu, Zn, As, Se, Mo, Cd, and Pb that were investigated in study are reported on the suitability of the rainwater human use as per the World Health Organization Drinking Water Quality Guidelines (Figure 3, WHO, 1998).

The results indicate that except for Cd, the quality of rainwater around Menengai area conforms to World Health Organization drinking water quality guidelines and hence acceptable as an alternative source of water for industrial - and - for domestic use. With Menengai area precipitation being potable, harvesting rainwater will go a long way in providing water for areas whose other sources are too distant or too costly, or where sinking wells are not practical because of unfavourable geology or excessive drilling costs. The potential for developing new water supplies by means of rainwater harvesting is in the project area is thus tremendous and harvesting is practically suited to supplying water for small villages, schools, households, livestock and wildlife in the area.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Comparison of Trace element concentration in rainwater around Menengai area and recommended World Health Organization drinking water quality guideline.}
\end{figure}

5. CONCLUSIONS

Trace element concentrations were measured in precipitation collected from five sites in the Menengai geothermal area and a control station 30 km from study area at Egerton University Meteorological station.in central Kenya from November 2011 and June 2012. All samples were analyzed for trace elements Al, Hg, Cd, Cr, Cu, Zn, Ni, Pb, Mn, B, As, Se and Mo. The majority of the rain samples collected had pH values higher than 6.2. The mean, median and mode pH was 6.58. High values of pH were attributed to the neutralization by natural alkaline local dusts which contain large fractions of calcite. Concentrations of measured trace elements species were within similar concentration range as those reported for other sites worldwide. Elements of anthropogenic origins (Hg, Zn, As, Se, Mo and Cd) were highly enriched with respect to crustal composition indicating the influence of anthropogenic input for these metals. The concentrations of trace metals that were determined in the rainwater samples
were relatively low compared to World Health Organization drinking water quality guidelines hence potable for domestic use through rainwater harvesting thus precluding any effects of current exploratory geothermal drilling and well discharge testing in the Menengai geothermal area.

ACKNOWLEDGEMENTS
This study was funded by Geothermal Development Company through its Environmental Monitoring Programs Fund. Sincere thanks go to Henry (Environmental Technologist), Geothermal Development Company, Environment and Central Rift Department for helping with bulk precipitation sampling.

REFERENCES


