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Heavy Metal Concentration in the Urban Environment of Addis Ababa, Ethiopia

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This work assesses the issue of whether the measured concentrations of heavy metals in soil, rocks, surface and ground waters in Addis Ababa can be related to anthropogenic contamination or natural weathering of rocks. Heavy metal analyses of rocks, soils, streams, springs and boreholes have been carried out to identify the presence of potentially harmful solutes. The maximum concentration of total chromium measured is 269 ppm in the northern, industry-free zone of Addis Ababa in the B_2-horizon of soil profile (cambisol). The Ni/Cr ratio in the rocks is higher than soils, which could indicate the presence of high concentrations of Cr in soils is from weathering processes. A comparative study of different samples collected from various parts of the city indicates that the chemical composition of the hydrothermally affected volcanic rocks plays an important role in increasing heavy metal concentration in the study area. The fresh country rocks contain relatively low concentrations of heavy metals, as shown by background values. The statistical evaluation indicates that the hydrothermally altered rocks contain far higher mean heavy metal concentrations than the fresh acidic rocks (background values). Consequently, soils derived from altered rocks are enriched with respect to heavy metals. From this study it was possible to observe that the rock and soil outcrops of Addis Ababa are anomalously rich in heavy metals derived from hydrothermal activity. Therefore, heavy metal concentrations in the surrounding rocks and soils are related to geogenic sources whereas anthropogenic contribution as a cause of these concentrations is minor.

Keywords Addis Ababa, heavy metals, soils, hydrothermal activity, industrial effluent

Introduction

In various parts of urban environments of the world work has been done on the heavy metal contamination of soils and water environments. Some prominent works are Chen *et al.* (1997), Wilcke *et al.* (1998), Madrid *et al.* (2002), Chirenje *et al.* (2004), and Markiewicz-Patkowska *et al.* (2005) that have taken into consideration industrial contamination. Due to rapid population and industrial growth in the city of Addis Ababa, the city's environment is susceptible to pollution.

To investigate the state of environmental pollution of Addis Ababa, the capital of Ethiopia with a population of 3.5 million, prior studies (Bekele, 1999; Alemayehu, 2001) have focused on the pollution of water resources through uncontrolled waste disposal. These studies have concentrated on organic pollution generated from industries that allow effluent to be discharged into rivers. According to the results obtained, the industries mainly

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Table 1
Metal concentrations in some river water samples from Addis Ababa

Sample	Zn ppb	Ni ppb	Cu ppb	Cr ppb	Pb ppb	Cd ppb	Co ppb
R1	13.1	0.72	0.77	1.18	8.79	<0.1	<0.1
R2	3.47	1.02	1.17	1.49	4.95	<0.1	0.37
R3	2.89	0.68	0.59	0.68	4.01	<0.1	0.12
R4	<0.1	4.8	<0.1	14	<0.1	<0.1	4.04
R5	54.2	<0.1	<0.1	5.8	7.9	<0.1	<0.1
R6	0.23	<0.1	<0.1	<0.1	90.8	<0.1	1.56
Mean ($\bar{X}$)	14.74	1.81	1.52	4.63	23.29	—	1.51
St. deviation (σ)	22.60	1.73	1.55	5.03	33.80	—	1.57
$\bar{X} + 2\sigma$	59.94	5.27	4.63	14.69	90.89	—	4.64
$\bar{X} - 2\sigma$	−30.48	−1.66	−1.58	−5.43	−44.31	—	−1.63

release effluent with a high Biological Oxygen Demanding (BOD) and minor chemicals (Alemayehu *et al.,* 2005). Previous work, most prominently Itana (1998), focused on analysis of heavy metal concentrations in soils and vegetables in the Akaki area (southern part of the city). This work is critically reviewed in the present study and deals with the industrial sources only. However, the distribution and source of heavy metals in different parts of the city is poorly understood.

Various industries in the city use a large number of chemicals including ZnO, $ZnCl_2$, $ZnSO_4$, Cr_2O_7, Cr_2 $(SO_2)_3$, $CuSO_4$ and Pb in one or more steps to process their products. The heavy metals that could be expected in the effluents are therefore Zn, Cu, Cr and Pb. These have been confirmed through the presence of trace amounts of heavy metals in some streams in the city (Table 1). Alemayehu (2001) indicated that some streams in the city contain total chromium as high as 14 ppb derived mainly from tanning industries. Nickel, on the other hand, was detected in a spring located in the northern sector of the city where there is no industrial activity. Since heavy metals are less mobile and are controlled by particular pH/redox condition, the spatial coverage will be limited around the pollutant centers or passage lines. Due to high heavy metal concentrations obtained in the northern sector of the city (Alemayehu, 2001) where there are no industries, the current research attempts to identify the source of heavy metals in the soil profiles of the city.

Geological Setting

The Addis Ababa region is constituted by Oligo-Miocene (27-5.3 Ma, represented by Alaji rhyolites and Entoto silics) and Pliocene (5.3-1.6 Ma, represented by Addis Ababa basalts, Wochacha and Yerer trachytes and basalts) volcanic rocks with minor amounts of Quaternary alluvial sediments (Girmay and Assefa, 1989). Distinct volcanic centers of Plio-Pleistocene age include Mt. Wochacha (3385 meters above sea level, m a.s.l), Mt. Yerer (3100 m a.s.l), and Mt. Furi (2839 m a.s.l). The northern part of the region is made up of Cenozoic basaltic lavas and felsic flows. The main lithologic units are basalts, rhyolites, trachytes and trachybasaltic lava flows and welded tuffs (Figure 1). The Entoto Silicis (rhyolitic and trachytic lava flows, unwelded tuffs and ignimbrites) constitute the northern part of the city. The basaltic lava flows mainly occupy the central and southern part of the city. The northeast trending Filwoha fault separates the basaltic lavas from the strongly welded trachytic tuffs.

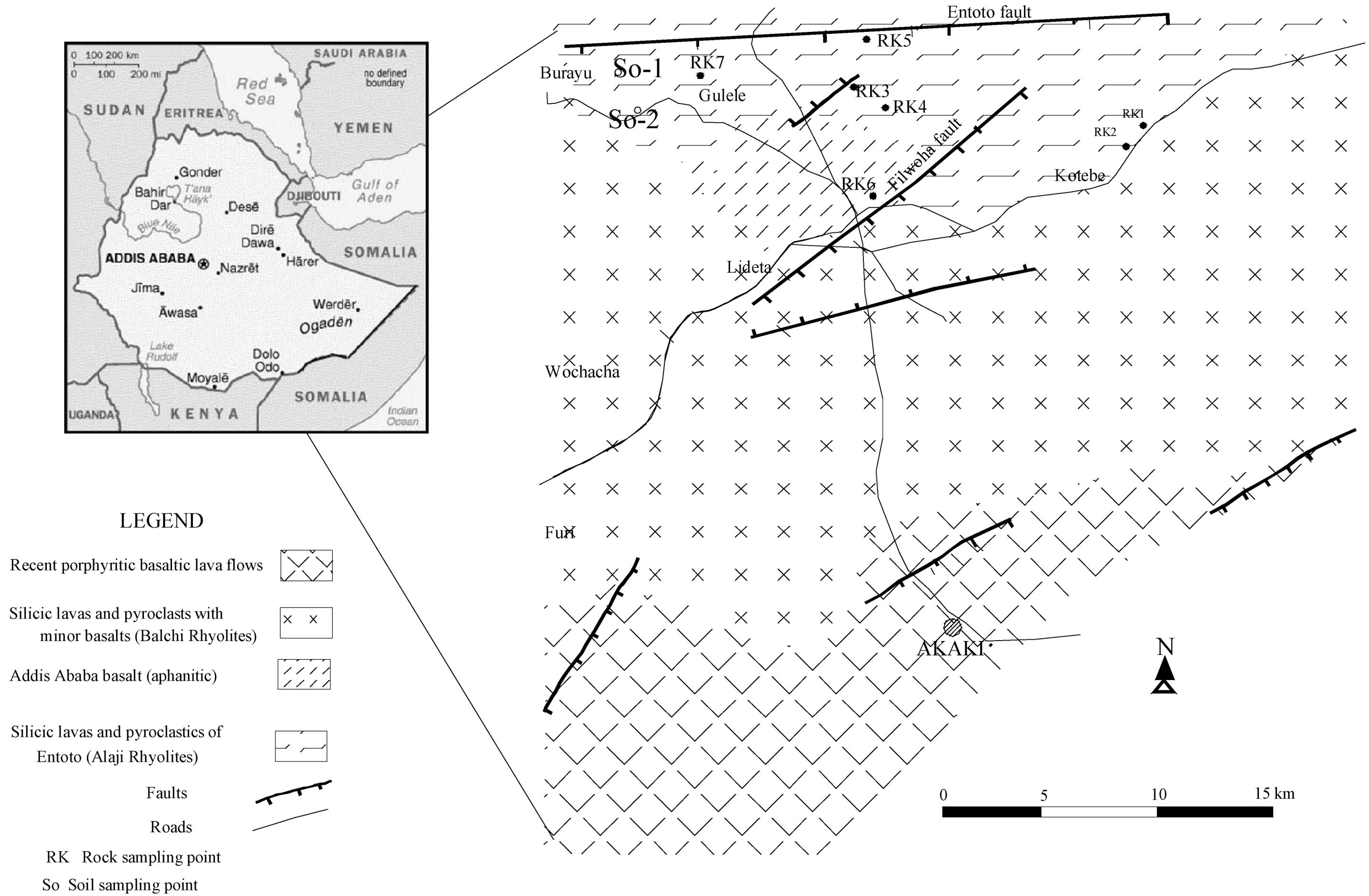

Figure 1. Simplified geological map of Addis Ababa area with rock and soil sampling points.

The younger volcanics represent central volcanic sources at for example the Wochacha, Furi and Yerer volcanic centers. These cover different sectors of the city and constitute various lithologic units including ignimbrites and basaltic lava flows.

The major faulting events in the area occurred during the Oligocene (Entoto fault) and early Pliocene (Filwoha fault) (Mohr, 1983; Zanettin, 1993). There is prominent graben structure in the city center where Meskel square is located. The rocks underlying the city and its environs were altered by intensive hydrothermal activity during the period 6.4–5 million years (Girmay, 1985), resulting in the characteristic reddish color of the residual soils. Kaolin deposits found in many parts of the city are particularly good evidence of hydrothermal activity on rhyolitic lava flows. Moreover, the active thermal center at Filwoha, whose activity could probably have diminished with time to its present position, is excellent evidence of such hydrothermal activity where the faults could have acted as conduits for supersaturated fluid with respect to heavy metals from the lower crust or upper mantle in an acidic steam media.

From a pedological point of view, the southern part of the city is mainly covered by vertisol while the northern, western and eastern parts of the city are covered by cambisols.

Method

In order to properly quantify the concentrations of heavy metals in soils, rocks and water points, a sampling plan was designed according to the presumed causes, i.e. natural or man made sources, to represent the entire city. A total of 25 samples were collected for analysis. The locations of the sampling points are given in Figures 1 and 2.

The water samples were collected with 50 ml polyethylene plastic bottles, while the rock samples were collected from both unaltered and altered zones in selected outcrops. Water samples were filtered through a 0.45 μm pore-size membrane filter and acidified with ultra-pure HNO_3. The filtered and acidified water samples were transported to the laboratory in leak-proof Polyethylene bottles for heavy metals analysis.

The soil samples were collected from pits with a maximum depth of 2 meters (B_2 horizon) and a few samples were taken from road sections. The soil and rock samples were dried, ground, and sieved through a <63 μm Teflon sieve. In the laboratory, samples were disaggregated using a Milestone MLS 1200 microwave oven. Sub-samples of 0.2 g of soils were placed inside Teflon vessels with 3 ml HF, 2 ml HNO_3, and 1ml $HClO_4$. These were then microwaved using three stages of power with time settings of 30% power for 10 minutes, 45% power for 15 minutes followed by 30% power for 5 minutes. The residue from each vessel was transferred into evaporating dishes and dried on a hot plate at 150°C. Thereafter 2 ml HNO_3 plus water were added and the content dried by heating. The resulting residue was finally treated with 1 ml HNO_3 plus water, covered, and gently warmed for 15 min. This solution was rinsed into a 100 ml volumetric flask and diluted to volume after addition of 100 ppb of rhodium and rhenium as internal standards. The analysis was done using ICP-MS spectrometry. Final results were given as the average of three readings.

For the current work the sampling and analytical procedures for heavy metals described in Siegel (2002) were strictly followed. For quality control purposes, a few duplicate samples were digested and analyzed and the error was generally less than 12%. The determination of heavy metal concentrations was performed using a Perkin Elmer Sciex Elan model 5000 inductively coupled Plasma Mass Spectrometer (ICP-MS) at the University of Cagliari, Italy. The instrumental detection limit was 0.1 ppb.

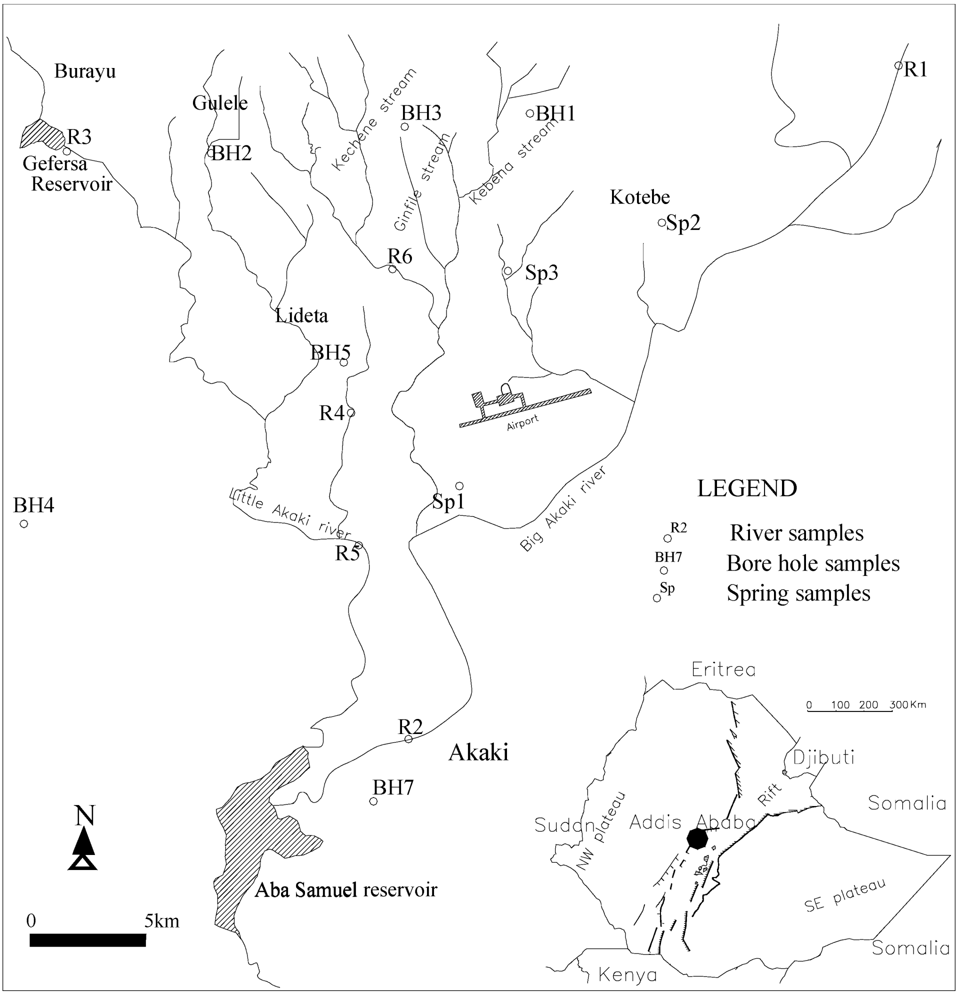

Figure 2. River, spring and bore bole sampling points

Results and Discussion

The sampling localities for the samples are given in Figures 1 and 2, and the analytical results are presented in Tables 1 to 6. Some of the samples that were collected from rivers contain industrial effluents (samples R2, R4 and R5 in Table 1). With the exception of the rivers that receive industrial effluents, most of the rivers contain quite low heavy metal concentrations. The heavy metal concentration in unaltered crustal rocks of the region with similar geological history is given in Table 7. These values are used as background values.

The total heavy metal concentrations obtained from the analysis indicate the increase of heavy metals in boreholes compared with springs from the same formation. This is believed to be due to longer residence times of the groundwater abstracted from the boreholes. Whether a particular metal goes into solution during weathering depends on the intensity of chemical weathering (Drever, 1997) and the chemical strength of the particular water to dissolve the heavy metal. This can occur due to long residence times and a high degree of water-rock interaction. It is also important to note that even though several sampled

Table 2
Metal concentrations in some spring water samples from Addis Ababa

Sample	Zn ppb	Ni ppb	Cu ppb	Cr ppb	Pb ppb	Cd ppb	Co ppb
Sp1	0.87	0.53	0.62	0.94	15.5	<0.1	<0.1
Sp2	8.06	0.92	0.76	1.21	4.31	<0.1	0.12
Sp3	9.35	0.49	0.45	0.3	8.33	<0.1	<0.1
$\bar{X}$	6.09	0.65	0.61	0.82	9.38	—	—
σ	3.73	0.19	0.13	0.38	4.63	—	—
$\bar{X}+2\sigma$	13.55	1.03	0.86	1.58	18.64	—	—
$\bar{X}-2\sigma$	−1.37	0.26	0.36	0.05	0.12	—	—

Table 3
Metal concentrations in some borehole water samples from Addis Ababa

Sample	Zn ppb	Ni ppb	Cu ppb	Cr ppb	Pb ppb	Cd ppb	Co ppb
BH1	16.6	0.68	0.61	0.52	56.2	0.2	0.12
BH2	41.8	0.7	0.89	0.95	33.1	<0.1	<0.1
BH3	23.3	0.57	0.7	0.69	25.1	<0.1	<0.1
BH4	85.8	0.31	0.44	0.86	8.98	<0.1	<0.1
BH5	62.4	0.98	1.82	0.51	5.22	<0.1	<0.1
BH6	146	0.52	0.96	1.44	8.79	<0.1	<0.1
BH7	20.5	0.51	0.56	1.8	4.66	<0.1	<0.1
$\bar{X}$	56.63	0.61	0.85	0.97	20.29	—	—
σ	43.28	0.19	0.43	0.45	17.76	—	—
$\bar{X}+2\sigma$	143.18	1.00	1.71	1.87	55.82	—	—
$\bar{X}-2\sigma$	−29.92	0.22	−0.003	0.07	−15.23	—	—

Table 4
Metal concentration in soils at Akaki, south (After Itana, 1998)

Sample	Zn ppm	Ni ppm	Cu ppm	Cr ppm	Pb ppm	Cd ppm	Co ppm
S-1	115.3	46.41	31.19	81.83	9.11	0.104	26.40
S-2	132.84	69.61	40.74	108.51	9.10	0.188	35.25
S-3	142.20	62.2	39.88	111.87	8.43	0.183	34.61
S-4	137.14	53.23	34.83	116.01	13.06	0.173	44.37
S-5	153.16	48.74	33.02	81.02	17.02	0.163	43.92
*$\bar{X}$	136.13	56.04	35.93	99.85	11.34	0.162	36.91
*σ	12.43	8.67	3.77	15.23	3.28	0.030	6.68
*$\bar{X}+2\sigma$	160.99	73.38	43.46	130.31	17.90	0.223	50.28
*$\bar{X}-2\sigma$	111.27	38.69	28.40	69.39	4.79	0.102	23.54

*Calculated for this work.

Table 5
Metal concentration in soils (cambisols) from Burayu area (north)

Sample	Ni ppm	Cu ppm	Zn ppm	As ppm	Rb ppm	Pb ppm	Ba ppm	Cd ppm	Cr ppm
So-1	20.0	7.0	165.0	14.0	108.0	5.0	495.0	0.050	50.0
So-2	93.0	51.0	117.0	10.0	74.0	20.0	365.0	0.050	269.0
$\bar{X}$	56.5	29.0	141.0	12.0	91.0	12.5	430.0	0.050	159.5
σ	36.5	22.0	24.0	2.0	17.0	7.5	65.0	0	109.5
$\bar{X} + 2\sigma$	129.5	73.0	189.0	16.0	125.0	27.5	560.0	0.050	378.5
$\bar{X} - 2\sigma$	-16.50	−15.0	93.0	8.0	57.0	−2.5	300.0	0.050	−59.50

springs (Samples 2, 3 in Table 2) and boreholes (samples 1, 2, 3, 6 in Table 3) are located in non-industrial areas, the heavy metal content is in the same order as those in the industrial areas, indicating that industrial effluents are not the main controlling factor for the observed concentrations.

In the soil analyses results (Tables 4 and 5) it is clearly seen that the metal concentrations are found in toxic levels. It is important to note that Ni and Cr are compatible elements in lower crustal and mantle rocks (Taylor and McLennan, 1985). Table 7 indicates that unaltered rhyolitic rocks that outcrop in the same geological settings contain relatively small concentrations of Ni and Cr when compared to the hydrothermally altered rocks (Table 6). Therefore, heavy metal input from secondary sources is presumed into the rocks that outcrop in Addis Ababa.

According to Siegel (2002), the concentration for potentially toxic metals $>\bar{X} \pm 2\sigma$ (values of mean plus/minus two standard deviations) is attributed to natural (mineralization) and/or man-made sources. The statistical evaluation performed in the study area showed high values of mean and $\bar{X} \pm 2\sigma$ for rocks and soils as compared with the background values and they gave rise to low values for rivers, springs and boreholes. The$\bar{X}-2\sigma$ values show wide variation for Burayu soils and rock samples which could be due to an error in sampling or non uniform distribution of metals in soils and rocks. The results indicate that a geogenic source from deeper crust or mantle in the form of hydrothermal activity seems

Table 6
Metal concentration in the hydrothermally altered rhyolitic lava flows (acidic rocks)

Sample	Zn ppm	Ni ppm	Cu ppm	Cr ppm	Pb ppm	Cd ppm	Zr ppm	Co ppm
RK1	225.0	25.0	21.0	10.0	107.0	0.300	728.0	12.0
RK2	156.0	13.0	24.0	64.0	98.0	0.100	467.0	40.0
RK3	80.0	27.0	25.0	22.0	405.0	0.020	976.0	26.0
RK4	36.0	17.0	25.0	20.0	165.0	0.040	938.0	5.0
RK5	125.0	8.0	19.0	23.0	202.0	0.020	14.0	49.0
RK6	425.0	54.0	10.0	15.0	74.0	0.400	107.0	18.0
RK7	530.0	15.0	18.0	44.0	581.0	0.200	484.0	16.0
$\bar{X}$	225.29	22.71	20.29	28.29	223.14	0.154	531.0	23.71
σ	170.94	14.17	4.95	17.60	175.52	0.139	349.61	14.58
$\bar{X} + 2\sigma$	567.15	51.05	30.18	63.49	584.19	0.433	1230.22	52.89
$\bar{X} - 2\sigma$	−116.58	−5.62	10.39	−6.92	−117.90	−0.124	−168.20	−5.46

Table 7
Heavy metal concentration in crustal and mantle derived rocks around Addis Ababa used as background values (Source: [1]Ayalew *et al.*, 2002; [2]Gasparon *et al.*, 1993; [3]Peccerillo *et al.*, 2003; [3] Pik *et al.*, 1999)

Locality and rock type	Cr ppm	Average Cr (ppm)	Ni ppm	Average Ni (ppm)
Jima rhyolite[1]	0.2–3.7	1.95	0.6–2.8	1.7
Bede Gebabe rhyolite[2] (Debre Zeit)	1–4	2.5	3–10	6.5
Ziquala rhyolite[2] (Debre Zeit)	2–15	8.5	2–10	6
Gedemsa rhyolite[3]	1–4	2.5	10–19	14.5
$\bar{X}$		3.86		7.18
σ		2.69		4.62
$\bar{X} + 2\sigma$		9.24		16.42
$\bar{X} - 2\sigma$		−1.52		2.06

to be responsible for the heavy metal concentrations. This could indicate that the rivers affected by the industrial effluents may not have adequate capacity to impact on the heavy metal content of the surrounding soils as indicated in Tables 4 and 5.

The volcanic rocks of the study area are rich in heavy metals (Ni and Cr) compared to average crustal derived rocks of the surrounding area. The rock samples that were considered for the current work are hydrothermally altered rocks. The Entoto and Filwoha faults could act as conduits for supersaturated fluid with heavy metals from the lower crust or upper mantle. The reddish color of the altered rocks and the clay deposits provides evidence of hydrothermal activity. The presence of secondary minerals depends to a large extent on the nature and type of original rock and the extent to which leaching has progressed. These processes can also be affected by soil fixation or concentration.

Since the heavy metal concentrations in rivers and boreholes are detected in ppb, the ratios in Table 8 are not comparable. However, the Ni/Cr ratio of rocks is somewhat higher than the soils. This indicates that Cr is retained in the soils after leaching from rocks. Ni enriched in the soils with respect to Cd as seem from the elevated ratio Ni/Cd ratio (Table 8).

All outcropping rocks contain high concentrations of heavy metals (Figure 3). This is attributed to hydrothermal activity related to the deep crustal tectonic discontinuities in the area. On the variation diagram (Figure 3) two clusters could be observed where one cluster consists of soils and rocks with high heavy metal concentrations and the other cluster

Table 8
Metal ratios calculated from data in Tables 1, 3, 4, 5 and 6

	Ni/Co	Ni/Cd	Ni/Cr
Rivers	2	18	0.4
Boreholes	5	3	0.6
Soils (Akaki)	2	346	0.6
Soils (Burayu)	—	565	0.4
Rocks	1	142	0.8

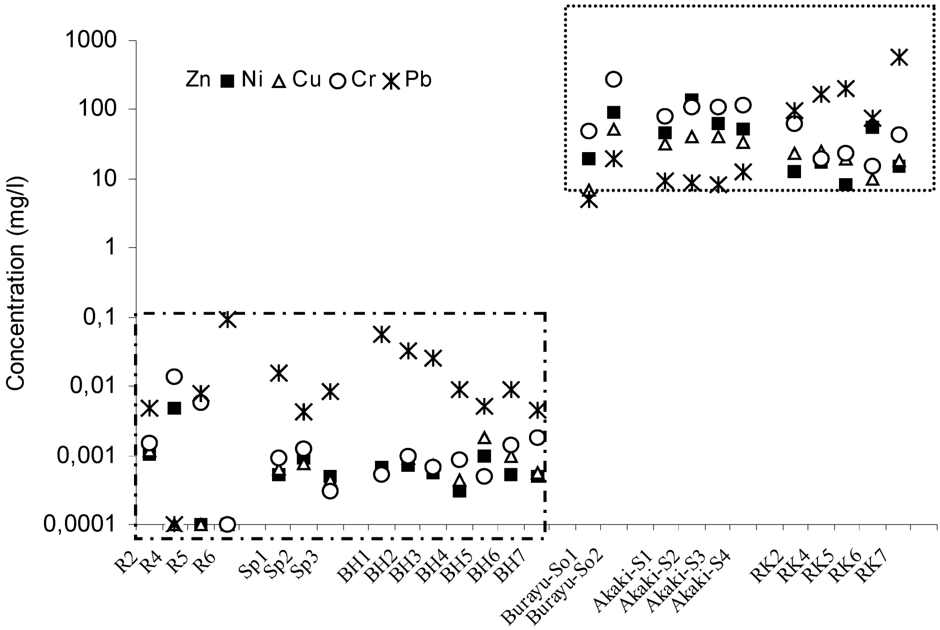

Figure 3. Comparison of heavy metals in streams, springs, boreholes, soils and rocks (R = stream samples, Sp = spring samples, BH = borehole samples, RK = rock samples, Burayu and Akaki are localities in the northern and southern sector of the city where soil samples were collected).

includes rivers, springs and boreholes with lower concentrations of heavy metals. There is a similarity in the enrichment of Pb, Cu, Ni and Zn in the northern and southern parts of the city. The Cr concentration is elevated in the soils collected from the north, due to weathering of hydrothermally altered rocks (Figure 4). As Pb is concerned, almost all samples cluster together, although, the Pb concentration is lower in the soils than the surrounding rock (Figure 5).

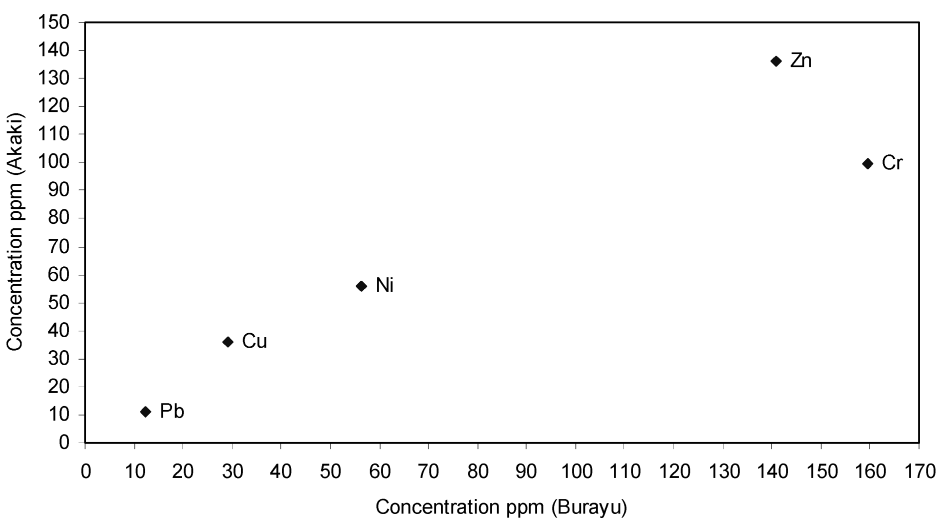

Figure 4. Comparison of heavy metals from Burayu and Akaki soils (Addis Ababa).

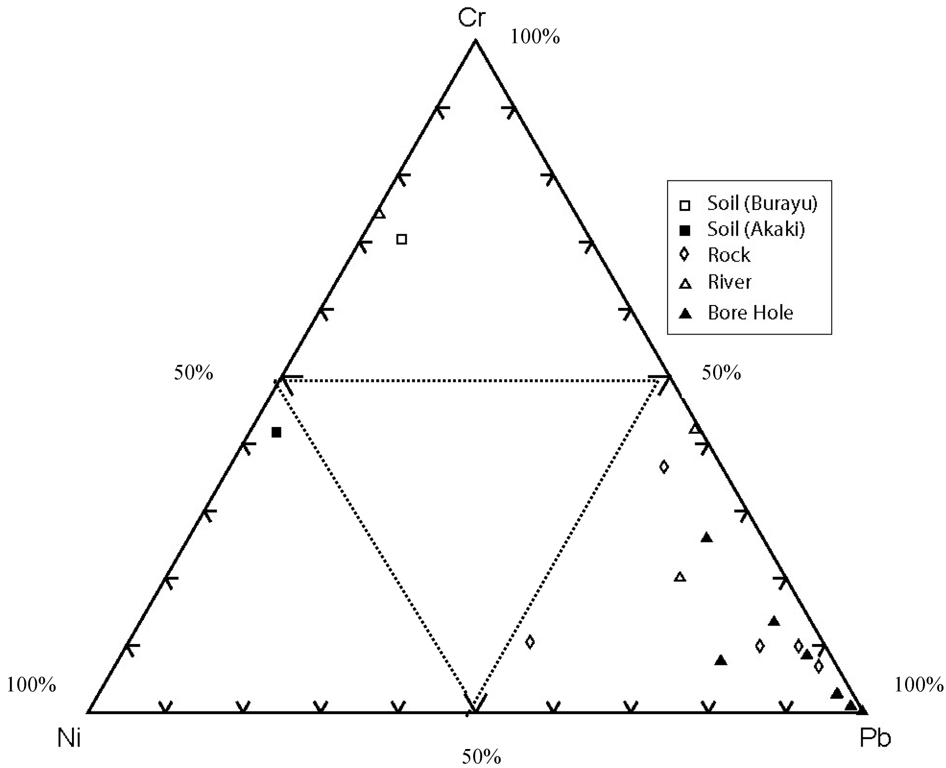

Figure 5. Triangular plot that shows clustering of samples in high lead quadrant.

Due to elevation differences in the city (1200 m elevation difference between the northern and southern parts of the city), it is also important to assume that the soils that are found in the topographically lower southern part of the city could partially be the result of erosion from the topographically higher northern sector of the city. It is also clear that vegetables grown on such soils could extract heavy metals (Page, 1981; Kabata-Pendias and Pendias, 1992; Drever, 1997), which have been generated from rock weathering, and consequently contain anomalous concentrations of metals.

Conclusion

The results of the study indicate that, when one considers the city of Addis Ababa, the outcropping rocks play an important role in releasing heavy metals into soils and that the industrial contribution may be minor, at least in the northern part of the city. Deep crustal faulting at Entoto and Filwoha could be responsible for the emergence of heavy metal-laden solutions from the lower and middle crust to the surface, in the presence of acidic media. Therefore, it could be concluded that around the city of Addis Ababa, heavy metals in the rocks and soils have geogenic sources with minor anthropogenic input. Currently, anthropogenic sources appear to be a minor contributor the the observed heavy metal concentrations in the city.

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