Environmental Research 109 (2009) 745–752

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo ☆

Célestin Lubaba Nkulu Banza [a], Tim S. Nawrot [b], Vincent Haufroid [c], Sophie Decrée [d,e], Thierry De Putter [e], Erik Smolders [f], Benjamin Ilunga Kabyla [a], Oscar Numbi Luboya [a], Augustin Ndala Ilunga [a], Alain Mwanza Mutombo [a], Benoit Nemery [b,*]

[a] Unité de Toxicologie et Environnement, Ecole de Santé Publique, Université de Lubumbashi, Democratic Republic of Congo
[b] Occupational & Environmental Medicine, Unit of Lung Toxicology, Katholieke Universiteit Leuven, Herestraat 49 (O&N 706), B-3000 Leuven, Belgium
[c] Industrial Toxicology and Occupational Medicine Unit, Université catholique de Louvain, Brussels, Belgium
[d] Geology Department, Royal Museum for Central Africa, Tervuren, Belgium
[e] Geology Department, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium
[f] Division of Soil and Water Management, K.U. Leuven, Belgium

ARTICLE INFO

Article history:
Received 5 September 2008
Received in revised form
17 April 2009
Accepted 27 April 2009
Available online 31 May 2009

Keywords:
Mining
Metals
Biomonitoring
Environmental pollution
Africa
Environmental justice
Children
Cobalt
Arsenic
Uranium

ABSTRACT

Background and objectives: The human health impact of the historic and current mining and processing of non-ferrous metals in the African Copperbelt is not known. This study assessed the exposure to metals in the population of Katanga, in the south east of the Democratic Republic of Congo, using biomonitoring.
Methods: Seventeen metals (including Cd, Co, Cu, Pb, U) and non-metals (including As) were measured by ICP-MS in urine spot samples from 351 subjects (32% women), aged 2–74 yr (mean 33 yr). Forty subjects (controls) lived 400 km outside the mining area; 311 subjects lived in the mining area, either very close (<3 km) ($n = 179$; 6 communities) or moderately close (3–10 km) ($n = 132$; 4 communities) to mines or smelting plants.
Results: For all metals (except Ni) urinary concentrations were significantly higher in subjects from the mining area than in control subjects. In subjects living very close to mines or smelting plants, the geometric means (25th–75th percentile) of urinary concentrations, expressed as μg/g creatinine, were 17.8 (10.9–29.0) for As, 0.75 (0.38–1.16) for Cd, 15.7 (5.27–43.2) for Co, 17.1 (8.44–43.2) for Cu, 3.17 (1.47–5.49) for Pb and 0.028 (0.013–0.065) for U, these values being significantly higher than those of subjects living 3–10 km from mines or industrial operations. Urinary Co concentrations were markedly elevated, exceeding 15 μg/g creatinine in 53% of the subjects, and even 87% of children (<14 yr), living very close to the mining areas. Urinary As was also high (79% above 10 μg/g creatinine in subjects living very close to the mining areas). Compared with background values from the US general population, subjects living very close to areas of mining or refining had 4-, 43-, 5- and 4-fold higher urinary concentrations of Cd, Co, Pb and U, respectively.
Conclusions: This first biomonitoring study of metal exposure in the African Copperbelt reveals a substantial exposure to several metals, especially in children. The urinary Co concentrations found in this population are the highest ever reported for a general population. The pathways of exposure and health significance of these findings need to be further investigated.

☆ *Funding sources*: No specific funds were received for conducting this study.
B. Nemery is grateful to Dr. Koichi Honma for his invitation and financial support to participate in a Symposium on Occupational and Environmental Disease in Lubumbashi (February 2006).
C. Banza received a bursary from the Belgian Technical Cooperation (BTC) for a two-months training visit in Belgium (2006).
T.S. Nawrot is a post-doctoral fellow of the Flemish Scientific Fund (FWO Vlaanderen).
The research by S. Decrée and Th. De Putter on copper and cobalt ores in the Katanga is supported by the Belgian Ministry of Foreign Affairs (TDP) and the Belgian Ministry of Science Policy—BELSPO (SD).
* Corresponding author.
E-mail address: ben.nemery@med.kuleuven.be (B. Nemery).

0013-9351/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.envres.2009.04.012

1. Introduction

The province of Katanga, in the south east of the Democratic Republic of Congo (see Map, Fig. 1), has been a place of intensive mining activities for centuries. In the colonial period, the mining of copper (Cu) and cobalt (Co), as well as of uranium (U), represented one of the Belgian Congo's main sources of revenue (Vellut, 1985). After Congo's independence (in 1960), mining activities and metal processing continued by the state-owned Gécamines. In the 1980s Zaire/Congo produced about 6% of the world's total production of Cu and 40% of the world's total refined Co (Prasad, 1989). There were both open pits and underground mines, with washing plants and concentrators, thus generating large mine tailings. Copper and cobalt were refined in several hydrometallurgical plants and smelters, which also produced zinc (Zn), arsenic (As) and cadmium (Cd) as by-products (Prasad, 1989). These activities have increased again in recent years, largely because of the need of copper and other metals for the industrial development of fast-growing economies in Asia (Global Witness, 2004, 2006). Artisanal and semi-clandestine/illegal miners have also been intensively exploiting, handling and smuggling Cu and Co secondary ores, in surface deposits. Among these ores is heterogenite [CoO(OH)], most often exploited as an earthy and powdery/dusty black product ("terre noire"). Artisanal mining has become widespread in Katanga in the last years, with tens of thousands of young people (including children) working as "diggers" ("creuseurs") in poorly regulated and often dangerous working conditions (Global Witness, 2004, 2006). Metal furnaces have been recently built, often in close vicinity of residential areas with little regard for environmental issues.

International bodies, such as WHO and UNEP, have stressed the importance of environmental health issues for developing countries (Gopalan, 2003). Ensuring environmental sustainability is one of the goals of the UN Millennium Project (Sachs and McArthur, 2005). Although environmental risks for developing countries are mainly viewed in terms of the degradation of natural systems, global warming or risks of infection, man-made pollution is also of serious concern (Melnick et al., 2005). Thus, air pollution affects an ever growing fraction of people living in urban environments in developing countries (Romieu et al., 2002). Industrial pollution is another specific issue. Nowadays, this problem, like many environmental risks, is experienced disproportionately in developing countries, while research on this is still conducted mainly in developed countries, where the risks to the populations have often been reduced by legislation and technical measures.

The adverse environmental impact of mines and metallurgical plants has been documented in numerous studies from various countries (Audry et al., 2004; Baker et al., 1977; Diaz-Barriga et al., 1993; Kligerman et al., 2001; Lacatusu et al., 1996; Liu et al., 2005; Rybicka, 1996). However, in Africa, little research has been conducted on the topic of metal pollution. A comprehensive review (Nriagu, 1992) stated that "[mining] operations rely on pollution prone technologies and the controls on the discharge of pollutants from African mines and smelters are lax or non-existent. The net result is that the air, water, soils and vegetation near the mining centers of Africa tend to be severely contaminated with toxic metals." However, neither historical nor actual data on environmental contamination by metals are available for the Katanga mining area.

Human exposure to many metals can be assessed by measuring metal concentrations in urine. Depending on the toxicokinetics of the metal, ongoing or previous exposure can be estimated with urinary metal concentrations (Lauwerys and Hoet, 1993). The objective of this study was to evaluate human exposure to metals in the population living in selected areas of Katanga. We found relatively high levels of toxic metals in urine, especially in children. For some metals (especially Co) maximal tolerable levels for occupational exposures were often exceeded, even in people not exposed through their work.

2. Materials and methods

2.1. Study group

The study was approved by the Academic Board of the School of Public Health at the University of Lubumbashi. In this

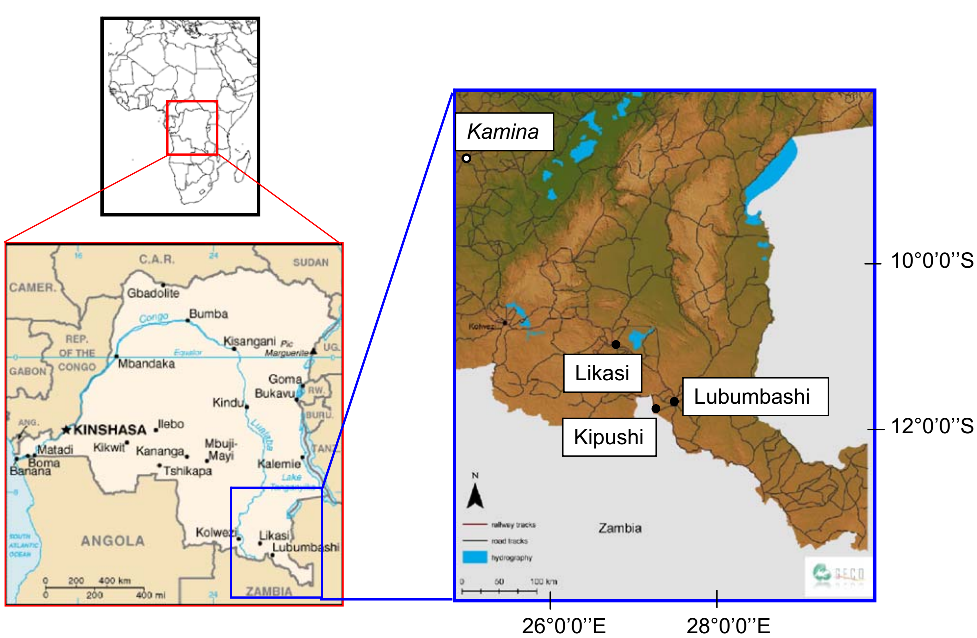

Fig. 1. Maps of Africa (left above), the Democratic Republic of Congo (left under) and part of the Katanga province (right). The Copperbelt stretches along both sides of the border between Zambia and the D.R. Congo. The study took place in southern Katanga in different areas of Lubumbashi (capital), Likasi and Kipushi. Kamina where there is no mining or metal industry was chosen as a control area.

essentially exploratory study, the sampling of subjects was not performed according to a predefined strategy that would provide an epidemiologically valid representation of the exposure of the population of the area. Rather, the choice of study areas was based on anticipated degrees of high or low exposure, as well as on pragmatic considerations, such as accessibility. In these areas, local residents were simply approached, usually at their home or when passing by, and asked (after receiving background explanation about the study) if they (or their children) were willing to provide urine samples and respond to a simple questionnaire (demographic information, smoking, present and past occupation). An attempt was made to recruit participants of both sexes and various ages. Positive responses were obtained from more than 95% of those approached. The samples were obtained between February 2006 (during a visit of B.N. to Lubumbashi) and March 2007 over a number of brief campaigns. In each area the samples were collected during a half or a whole day, generally by C.B. with the help from colleagues or representatives of local authorities. Fig. 2 shows photographs taken during the first field campaigns. Samples from one area with only few participants (Kasumbalesa mine) were excluded. Seven samples from persons with missing demographic information, as well as a few subjects with insufficient urine for analysis were excluded, thus leaving 351 subjects for analysis.

These subjects came from 6 areas situated very close (<3 km) to mines or industrial activities [Lubumbashi (Penga-Penga, $n = 21$; Tshamilemba, $n = 24$; Kawama, $n = 35$), Likasi (Panda, $n = 43$; Shituru: $n = 42$), Kipushi (GCM and Betty, $n = 14$)], 4 areas where exposure was supposed to be less intense because they were located more than 3 km (but less than 10 km) from mines or smelters [Lubumbashi (Hewa Bora, $n = 31$; Katuba, $n = 38$), Kingandu ($n = 36$), Kasumbalesa village ($n = 27$)] and the town of Kamina ($n = 40$), located about 400 km North-west of Lubumbashi. The latter location was chosen as a control area after analyses had revealed high values of metals (especially Co) in urine, even in subjects from the areas with supposedly low exposure.

Sterile polystyrene containers (40 mL) with screw caps (Plastiques-Gosselin, Hazebrouck, France) were used for the

Fig. 2. Upper panel: satellite view of the Tshamilemba district in Lubumbashi next to a metal processing plant [http://wikimapia.org/#y=-11676778&x=27487278&z=13&m=s (accessed April 16, 2009)]. The green color in the right upper corner reflects the presence of copper. The photographs show a general view of the area (left) and a house with a family of whom several members provided a urine sample (right) with the factory wall in the background. Lower panel: satellite view of the GCM district in Kipushi [http://wikimapia.org/#lat=-11.7679024&lon=27.246201&z=16&l=0&m=s (accessed April 16, 2009)]. The photographs show two views of manifestly polluted water originating from a metal factory (left) flowing through the residential area. Photographs taken in February 2006 by B.N.

collection of urine. Participants were instructed to avoid contamination of the urine by the hands. After collection, the samples were generally stored in a cool box, and then in a refrigerator until transportation to Belgium, using commercial flights. A large number of samples were not kept cold during several days while in transit in Kinshasa.

2.2. Analysis of urinary metals

The samples were all analyzed in the Laboratory of the Industrial Toxicology and Occupational Medicine Unit (Université catholique de Louvain, Belgium) without knowledge of their exact provenance in relation to exposure (blind analysis). In all urine samples, 17 metals or metalloids (all called "metals" hereafter) were quantified by means of inductively coupled argon plasma mass spectrometry (ICP-MS) with an Agilent 7500 ce instrument. Briefly, urine specimens (500 μl) were diluted quantitatively (1+9) with a HNO_3 1%, HCl 0.5% solution containing Sc, Ge, Rh and Ir as internal standards. Sb, Al, Cd, Pb, Mo, Te, Sn and U were analyzed using no-gas mode while helium mode was selected to quantify As, Cu, Co, Cr, Mn, Ni, Se, V and Zn. Using this validated method, the laboratory has obtained successful results in external quality assessment schemes organized by the Institute for Occupational, Environmental and Social Medicine of the University of Erlangen, Germany (G-EQUAS program), and by the Institut National de Santé Publique, Québec (PCI and QMEQUAS programs). Creatinine was determined using a Beckman Synchron LX 20 analyser (Beckman Coulter GmbH, Krefeld, Germany). In the first 39 samples, arsenic was also determined by hydride generation followed by atomic fluorescence spectrometry to differentiate inorganic As and its methylated metabolites from organic As (Heilier et al., 2005).

2.3. Statistical analysis

The SAS software package, version 9.1 (SAS Institute Inc., Cary, NC) was used for database management and statistical analysis. Values below the limit of detection were assigned a value at half the detection limit. Non-normally distributed data (all metals) were logarithmically transformed; we report these data as geometric mean and interquartile range (IQR). Means and proportions were compared using the standard normal z-test and chi-square or Fisher exact test, respectively. Our statistical methods also included stepwise multiple regression, terminating when all p values for variables to enter and stay in the models were 0.15. The covariates considered as possible determinants of the urinary metals were sex, age (linear and squared terms), current smoking, occupational exposure and design variables coding for the places of residence. The various residential areas were aggregated into a group of 6 residential areas very close (<3 km) to mining or refining sites, a group of 4 residential areas located moderately close (3 to 10 km) to the nearest mining or refining sites, and a control area (Kamina). Differences in the urinary excretion of metals among the 11 residential areas (as well as among the three larger groups of residential locations) were analyzed by analysis of covariance as implemented in the SAS system by PROC GLM with adjustments for gender, age (age and age squared), current smoking (yes/no) and past or current occupational exposure (yes/no). These potentially important covariates were forced into the models irrespective of their statistical significance. Finally, we applied multiple logistic regression analysis to study the determinants of having urinary metal values above the occupational limit values for Co.

3. Results

3.1. Characteristics of the participants

Nearly one third (32%) of the 351 participants were female. The median age was 32 yr (range 2–74 yr), and the total sample included 47 children below the age of 14 yr (13%). Among men, there were 62 smokers (26%) and their median daily tobacco consumption was 6 cigarettes (IQR 4–10); only one woman reported smoking. One hundred and twelve male subjects (47%), including three children aged below 12, and five women (5%) reported working or having worked as mine diggers or in the metal refining industry. The gender and age distributions and the prevalences of smoking differed across the 11 residential areas. Table 1 presents the subject characteristics when the areas were grouped into three categories (control, moderately close and very close to mining or refining sites). The proportion of women was similar across the exposure classes, but age was substantially lower in the control area (mean age of 23 yr) than in the other two categories (30 and 35 yr), because the subjects in that control area were mainly university students recruited during a teaching visit of C.B. in Kamina. The proportion of subjects with a past or current occupational exposure was highest (43%) in the areas very close to the mining or refining activities, but this proportion was also considerable (30%) in the areas at a higher distance from these operations.

3.2. Urinary metals in the whole population and determining variables

Table 2 presents the geometric means (with the IQR, and the proportion of values below the detection limits) for the urinary concentrations of each of the 17 metals in the control area and in areas very close or moderately close to the mining activities. To account for the differences in demographic characteristics between these three areas, all statistical analyses were done after adjustments for sex, age, current smoking and reported occupational exposures. In the control area (Kamina), many subjects had values below the limits of detection for several

Table 1
Demographic and other characteristics of 351 residents of 11 different areas in Katanga, grouped according to proximity to mining or metal refining operations.

	Control area (Kamina) ($n = 40$)	Residential areas 3–10 km from mining and refining ($n = 132$)	Residential areas <3 km from mining and refining ($n = 179$)
Age, years[a]	22.8 (3.6) [10–33]	29.8 (16.2) [2–67]	35.2 (15.8) [3–74]
Children below age 14 years, n (percentage)	1 (2.5)	23 (17)	23 (13)
Women, n (percentage)	12 (30)	46 (35)	54 (30)
Smokers, n (percentage)	1 (2.5)	16 (12)	45 (25)
Past or current occupational exposure, n (percentage)	0	39 (30)	78 (43)
Current occupational exposure, n (percentage)	0	25 (19)	54 (30)

[a] Mean (SD) [range].

metals and the mean concentrations were significantly lower than those found in southern Katanga for all metals, except Ni.

Table 3 shows the partial R^2 values for the regression of each metal with gender (male/female), age (linear and squared term), residence (11 separate areas, including the control area), smoking (yes/no) and past or current occupational exposure (yes/no), as well as the total R^2 values when all these variables were considered together. These regression analyses indicate that residence area was the factor most strongly associated with urinary metal excretion: this variable was significantly related with the urinary concentrations of all the metals (except Ni), with values of partial R^2 ranging between 0.05 (Te) and 0.52 (Co). Age (linear and squared term) also independently influenced the values of all 17 metals, but with values of partial R^2 ranging between 0.03 and 0.1 only. The urinary Cd concentration was positively correlated with age, while urinary concentrations of all other metals were higher at younger ages. Gender independently influenced the variance of 7 metals, with females having higher values than males, but partial R^2 were low (0.03 at most). Reported (past or current) occupational exposure independently influenced the variance for three metals only (Al, Cu, Pb), again with very low partial R^2 (0.02 at most). Smoking did not significantly influence the urinary concentrations of any of the metals studied. When the same analyses were done with the residential areas grouped into 3 categories (very close, moderately close and control area), the same conclusions were reached, but total R^2 and partial R^2 for the area effects became smaller (e.g. partial R^2 for area reduced to 0.32 for Co, 0.31 for U, 0.20 for As), and there were minimal differences for the other factors (not shown).

Table 2 shows that for As, Cu, Co, Cr, Se, Sn and U, the urinary values in the subjects from areas very close (<3 km) to mining and smelting sites were significantly higher than those of people living farther away (3 to 10 km) from such sites. Quantitatively, the differences were most pronounced for Co (2.8-fold), As (1.7-fold) and U (1.6-fold) (based on adjusted means).

The reported associations did not change when concentrations of metals were expressed as μg/L, or after exclusion of highly diluted ($n = 17$) or highly concentrated ($n = 43$) urine samples, defined as urinary creatinine levels below 0.3 g/L or above 3.0 g/L, respectively (ACGIH, 2006) (data not shown).

3.3. *Determinants of urinary Co, As and Cd values above the occupational limit*

According to the American Conference of Governmental Industrial Hygienists (ACGIH) the Biological Exposure Index (BEI) for urinary Co excretion is 15 μg/L (ACGIH, 2006), but we considered a value of 15 μg/g creatinine. In the control area, none of the participants exceeded this value, while 11% and 53% of the subjects residing moderately close and very close to pollution sites, respectively, exceeded this occupational limit value. In areas closest to mining and smelting sites, 87% ($n = 23$) of the children (age below 14 yr) had Co levels exceeding 15 μg/g creatinine. Multiple logistic regression (after exclusion of the control group) revealed that the odds ratio (O.R.) for exceeding this value was 12.2 (95% CI: 5.8 to 25.3; $p<0.0001$) for those living very close (<3 km) compared with those living >3 km away from the mining/refining activities; in this same multiple logistic regression, the O.R. was 7.5 (95%CI: 3.2 to 18.0; $p<0.0001$) for children younger than 14 yr, and 3.2 for women (95% CI: 1.6–6.3; $p<0.001$), while reported past or current occupational exposure [O.R. 1.1 (95% CI: 0.5 to 2.2; $p = 0.91$)] and smoking [O.R. 1.90 (95% CI: 0.85 to 4.0; $p = 0.12$)] were not significantly associated with exceeding this limit value.

Urinary As was higher than 35 μg/g creatinine – the occupational BEI being 35 μg/L (ACGIH, 2006) – in 22% of the subjects

Table 2
Geometric means of urinary metal concentrations (μg/g creatinine) in 351 residents of 11 different areas in Katanga, grouped according to proximity to mining or metal refining operations.

	Control area (Kamina) ($n = 40$)	Residential areas 3–10 km from mining and refining ($n = 132$)	Residential areas <3 km from mining and refining ($n = 179$)	Overall p	Reference values according to NHANES[a]
Aluminum (Al)	3.96 (2.21–7.92) [25%]	15.8 (7.29–29.2)[b] [3%]	12.4 (6.05–20.7)[b] [2%]	<0.0001	
Antimony (Sb)	0.04 (0.02–0.09) [18%]	0.09 (0.04–0.14)[b] [2%]	0.07 (0.04–0.10)[b] [1%]	0.015	0.13 (0.17)[d]
Arsenic[c] (As)	3.15 (1.99–4.64)	10.8 (5.13–26.0)[b]	17.8 (10.9–29.0)[b,e]	<0.0001	8.24 (14.1)[f]
Cadmium (Cd)	0.18 (0.14–0.27)	0.70 (0.40–0.11)[b]	0.75 (0.38–1.16)[b]	<0.0001	0.20 (0.40)[d]
Chrome (Cr)	0.09 (0.06–0.12) [3%]	0.14 (0.09–0.21)[b] [7%]	0.17 (0.10–0.24)[b,e] [2%]	<0.0001	0.12 (0.23)[g]
Cobalt (Co)	1.34 (0.74–2.19)	5.72 (3.25–9.14)[b]	15.7 (5.27–43.2)[b,e]	<0.0001	0.36 (0.52)[d]
Copper (Cu)	5.89 (4.62–8.60)	12.8 (8.43–19.0)[b]	17.1 (8.44–28.2)[b,e]	<0.0001	
Lead (Pb)	1.28 (0.93–2.01)	2.93 (1.64–4.95)[b]	3.17 (1.47–5.49)[b]	<0.0001	0.64 (1.11)[d]
Manganese (Mn)	0.07 (0.02–0.19) [38%]	0.40 (0.11–1.09)[b] [4%]	0.32 (0.05–1.87)[b] [11%]	<0.0001	0.48 (1.16)[g]
Molybdenum (Mo)	52.7 (36.8–75.6)	84.5 (54.0–143.6)[b]	75.2 (46.8–126.7)[b]	0.009	42.5 (62.0)[d]
Nickel (Ni)	3.11 (2.05–4.41)	3.06 (2.01–4.95)	3.27 (1.90–4.87)	0.79	
Selenium (Se)	7.86 (6.31–9.43)	13.5 (10.9–17.1)[b]	17.4 (13.3–20.6)[b,e]	<0.0001	
Tellurium (Te)	0.08 (0.07–0.09) [5%]	0.10 (0.09–0.11)[b] [2%]	0.09 (0.07–0.12)[b]	0.08	
Tin (Sn)	0.05 (0.02–0.10) [25%]	0.06 (0.03–0.11)[b] [27%]	0.08 (0.04–0.16)[b,e] [15%]	0.004	
Uranium (U)	0.003 (0.002–0.005) [83%]	0.018 (0.010–0.029)[b] [5%]	0.028 (0.013–0.065)[b,e] [6%]	<0.0001	0.008 (0.014)[d]
Vanadium (V)	0.09 (0.06–0.13) [42%]	0.21 (0.13–0.33)[b] [7%]	0.22 (0.13–0.34)[b] [5%]	<0.0001	
Zinc (Zn)	224 (147–368)	312 (225–447)[b]	306 (199–473)[b]	0.049	

Data are geometric means (25th–75th percentile). p-values adjusted by general linear models for sex, age (age and age squared), current smoking and occupational exposure. Values in square brackets [ ] indicate percentages of samples below the limit of detection. The limits of detection are 0.015 μg/L for Sb, 1.57 μg/L for Al, 0.061 μg/L for Cr, 0.046 μg/L for Mn, 0.030 μg/L for Te, 0.032 μg/L for Sn, 0.008 μg/L for U and 0.12 μg/L for V.

[a] US National Health and Nutrition Examination Survey: geometric means (75th percentile).

[b] Indicates significant difference from control.

[c] Total As .

[d] Data from CDC (2005) [values for total population of survey years 2001–2002].

[e] Indicates significant difference between residence <3 km and residence >3 km.

[f] Data from Caldwell et al. (2009).

[g] Data from Paschal et al. (1998).

living very close compared with 19% and 0% of the subjects living moderately close and far away from mining and refining, respectively. Corresponding percentages were 79%, 48% and 10% when taking 10 μg/g creatinine as an upper limit for non-occupationally exposed people (Offergelt et al., 1992).

Nine subjects had values of urinary Cd above 5 μg/g creatinine – the occupational BEI being 5 μg/L (ACGIH, 2006) – and 22 subjects had values of urinary Cd above 2 μg/g creatinine, all of whom lived in the exposed areas.

4. Discussion

According to the Blacksmith Institute, the African Copperbelt, on the border between Zambia and the Democratic Republic of Congo, belongs to the top ten of the most polluted areas worldwide (The Blacksmith Institute, 2008), presumably on the basis of soil pollution data obtained in Zambia (Tembo et al., 2006). No pollution data have been published for southern Katanga, but it is likely that the environmental contamination is similar or even larger as a result of the past unstable political situation and the resulting climate of unregulated exploitation of minerals that has prevailed for many years in the D.R. Congo (Rackley, 2006). As far as we know, no data are available regarding the human exposure to metals in this polluted area. We chose to use the most convenient approach to assess human exposure, i.e., measuring the concentrations of metals in spot samples of urine (Lauwerys and Hoet, 1993). Our strategy for this exploratory study was to obtain urinary samples from a few hundred persons of various ages and sexes living in representative areas of presumably high and low pollution. Admittedly, this pragmatic approach does not provide us with an epidemiologically accurate picture of the human exposure to metals in the province, but the data obtained from these convenience samples are unlikely to have been substantially biased.

In subjects from Kamina, a town some 400 km away from the African Copperbelt and without local mining and metal refining activities, the urinary concentrations of metals were generally similar to reference values obtained in general populations of the USA (CDC, 2005; Paschal et al., 1998), except for urinary Co which was higher than the baseline values of the CDC (Table 1). The mean urinary concentrations of all the studied metals (except Ni) proved to be higher in people living in southern Katanga, than in the control area. The differences were most pronounced for Co, Pb, Cd and U, with 11-, 2-, 3- and 7-fold higher mean urinary concentrations, respectively, in southern Katanga compared to the control area.

The highest excesses (Co, U) likely reflect the predominance of these elements (together with Cu) in the Copperbelt. Furthermore, Co and U are characterized by a high intrinsic mobility (as Co^{2+} and UO_2^{2+}) in surface environments, including surface waters. Pb and Cd are less mobile and/or more readily adsorbed and trapped onto iron oxides in the soils (Bradl, 2004).

Within subjects from southern Katanga, we found higher values of several urinary metals (As, Cr, Co, Cu, Se, Sn, U) among those living very close (<3 km) to mining or smelting operations than those living somewhat farther away (3–10 km). Co, As and U are typically associated with heterogenite ore, which contains up to ~60% Co, together with 199 ppm As and 270 ppm U [average values from 12 heterogenite samples (Decrée et al. unpublished observations)]. As heterogenite is often found as "cobalt caps" on the mines (Gauthier and Deliens, 1999), and thus forms Co-rich soils, this ore is a major contributor of trace elements in the pedosphere/biosphere, where people are living and working, especially in the artisanal mining sector. This probably explains the high concentrations of Co and its associated elements in the urine from southern Katanga residents.

The single most important factor determining the variability in urinary excretion of metals consisted of area of residence (Table 3). Thus, residence area explained 52% of the variance for Co–U when the 11 different areas were considered in the analysis. Lower values (e.g. 32% for Co) were obtained when the 11 areas were grouped into three broader categories defined according to their proximity to mines and smelters. This indicates that area-specific factors (such as type of industrial operation in the vicinity, prevailing winds) were important for determining exposure, but these specific factors could not be analyzed with the available information.

The urinary Co concentrations found in this population are the highest ever reported for a general population, with 87% of the children living very close to the mining or refining sites exceeding even the occupational limit value of 15 μg/L (ACGIH, 2006). In the control area (Kamina) the cobalt levels were much lower but still 2- to 4-fold above baseline levels reported in Japan (Ohashi et al., 2006) or the US (CDC, 2005). We have no definitive explanation for these high Co levels in the control area. In an independent study done in 220 subjects from Kinshasa (D.R. Congo's capital) the geometric mean value of Co–U was 0.38 μg/g creatinine, as measured in the same laboratory (Haufroid et al. unpublished data). Thus the high control values of Co–U found here are unlikely due to analytical errors and could be related to higher cobalt levels in soils or in food.

In non-polluted areas, cobalt exposure is mainly from food sources, including cobalamin (vitamin B-12). Cobalt is excreted for the most part and rapidly in the urine (Barceloux, 1999). The high values of urinary Co found here in children living in the vicinity of mining or refining are probably due to the fact that children explore their environment by hand and mouth and thus dose themselves with metals from house dust and contaminated soil. The higher values of urinary Co (and other metals) observed among the children are unlikely due to the lower creatinine concentrations also found in children, because the values remain higher, even without correction for creatinine (data not shown).

Table 3
Explained variance of urinary metal concentrations among 351 residents of Katanga.

Metals	Partial R^2				Total R^2
	Sex	Age	Area	Work exposure	
Aluminum (Al)	0.03	0.06	0.23	0.01	0.33
Antimony (Sb)	0.01 ($p = 0.08$)	0.05	0.09	–	0.15
Arsenic (As)	–	0.03	0.50	–	0.53
Cadmium (Cd)	0.02	0.09	0.36	–	0.47
Chrome (Cr)	0.01	0.10	0.13	–	0.24
Cobalt (Co)	0.01	0.04	0.52	–	0.57
Copper (Cu)	0.01	0.06	0.31	0.02	0.40
Lead (Pb)	–	0.07	0.30	0.01	0.38
Manganese (Mn)	0.01 ($p = 0.06$)	0.03	0.33	–	0.37
Molybdenum (Mo)	–	0.04	0.07	–	0.11
Nickel (Ni)	0.01	0.08	–	–	0.09
Selenium (Se)	–	0.04	0.31	–	0.35
Tellurium (Te)	0.03	0.07	0.05	–	0.15
Tin (Sn)	–	0.09	0.09	–	0.18
Uranium (U)	–	0.03	0.44	–	0.47
Vanadium (V)	0.01 ($p = 0.07$)	0.07	0.25	–	0.33
Zinc (Zn)	–	0.04	0.10	–	0.14

R^2 = explained variance (i.e. the square of the correlation coefficient). The covariates considered as possible determinants of the metals were sex, age (linear and squared terms), current smoking (yes/no), past or current occupational exposure (yes/no) and design variables coding for the area of residence (in total 11 areas). Results are given for those variables that were correlated, and only when the regression was significant ($p < 0.05$) or suggestive ($p < 0.1$). Smoking status was not significant for any of the metals.

The toxicity of Co has been mainly studied in occupational settings. Cobalt has the capacity to stimulate erythropoietin production and it has been used medically for the treatment of anemia (Barceloux, 1999). Excessive erythrocytosis was recently linked with high serum Co levels in residents of a mining community (Jefferson et al., 2002). Cobalt has the potential to damage the heart, as was shown in several outbreaks of cardiomyopathy among heavy drinkers of beer to which cobalt had been added (Alexander, 1972; Kesteloot et al., 1968; Morin and Daniel, 1967). Cobalt is also toxic for the thyroid (Prescott et al., 1992). Cobalt is a well-established sensitizer that can cause allergic contact dermatitis and (occupational) asthma (Nemery, 1990). Cobalt is the main culprit in hard-metal lung disease, a rare interstitial lung disease (Nemery et al., 2001). Experimental studies have shown plausible pathways to explain the toxicity of cobalt, including oxidative stress and modified activity of transcription factors (De Boeck et al., 2003a, b; Nemery et al., 1993). Cobalt ions are potent inducers of hypoxia-inducible factor (Semenza, 2000). However, the possible consequences of these effects on individuals with high environmental or dietary exposure to cobalt remain to be investigated.

The urinary excretion of Cd reflects life-time exposure (Jarup et al., 1998). The mean Cd level in residents of southern Katanga was 4 times higher than in NHANES (CDC, 2005). However, our values were generally lower than those reported in 10,753 Japanese women (Ezaki et al., 2003) or a population living in a polluted area due to zinc refining and smelting of Belgium, where mean Cd–U was approximately 1 μg/g creatinine (Nawrot et al., 2006). Values of Cd–U above 1 μg/g creatinine are associated with renal tubular dysfunction (Ezaki et al., 2003; Staessen et al., 1994), higher excretion of calcium (Staessen et al., 1991), a lower bone mineral density with higher risk of fractures (Staessen et al., 1999) and a higher risk of lung cancer (Nawrot et al., 2006). Here, the 75th percentile value of Cd–U among subjects living in the vicinity of mining or refining approaches the values associated with these reported clinical effects on bone and lung.

Arsenic is an established human carcinogen and has numerous other adverse health effects (Carlson-Lynch et al., 1994). In our survey, a relatively high As–U value – compared to recent data from NHANES (Caldwell et al., 2009) – was found in subjects living closest to mining/refining (18 μg/g creatinine). However, this value is not as high as the levels reported for Bangladesh (77 μg/g creatinine) and other areas with As contamination of tube-wells (Lindberg et al., 2008). Seafood is known to contain large quantities of organic As. However, separate measurements of inorganic As and its methylated metabolites in our first 39 urine samples showed almost identical values to those of total As obtained by ICP-MS (not shown), thus indicating that As intake via consumption of seafood is low to nonexistent in this inland area of Africa.

After absorption, soluble U is predominantly distributed to the kidneys and bone (CDC, 2005). Approximately half of the U is eliminated in urine within the first 24 h after exposure. Radioactive exposure risk from natural uranium is considered to be low, but this has not been studied in the present circumstances where uranium-containing ores are dug, stored, transported and processed with little or no regard for radiation safety. Tubular kidney dysfunction, the primary toxic effect due to chronic uranium exposure, is unlikely to occur below 0.002 μg/g creatinine (Bijlsma et al., 2008). In a study of 446 Gulf War veterans who were concerned about past exposure to depleted U, the geometric mean urinary U concentration was 0.011 μg/L (McDiarmid et al., 2004), compared with 0.028 μg/g creatinine in our study in subjects living in the vicinity of mining or refining.

Our study has several limitations, the most important of which is the fact that we studied a convenience sample of the population. Although the overall response rate was high (>95%) and we tried to recruit representative residents of the different communities chosen for the study, this convenience sample is certainly not representative for the entire population of the different areas, let alone the whole of southern Katanga. Nevertheless, the data show beyond any doubt that there is a substantial exposure to a variety of metals among those living near sources with presumed, but often visible pollution by mining and smelting operations. Our findings suggest that basic environmental regulations within (and near) the industrial sites could have a dramatic effect on the observed contamination, and thus point to the urgent need to adopt and implement such regulations. Taking into account demographic and other factors such as past or present occupational exposures, we found residential area to be consistently the most important predictor of the concentrations of metals in the urine. Smoking was not an important factor, although it is known to affect urinary values of many metals (Lauwerys and Hoet, 1993), most notably cadmium, but this was presumably due to the low tobacco consumption in the few smokers of this population. Occupation also did not appear as an important factor, probably because there were not so many current workers in the studied population.

The extremely high levels for Co and the high levels of other toxic metals in the urine of these subjects from the general population of Katanga confirm that they are significantly exposed to these metals through their environment. The exact routes of exposure – through the air, the diet (staple foods, specific vegetables, meat or fish), and/or the soil and suspended dust – remain to be established. The higher concentrations of metals found in the urine of children suggest that ingestion of contaminated dust is an important route. Epidemiologic studies are being initiated to investigate the health effects of these exposures in various segments of the population of Katanga.

Acknowledgments

We gratefully acknowledge the assistance of MULEKA Kimpanga Célestin, MUNDONGO Tshamba Henri, LUBOYA Mulenda Job, KONA Musau Pétronie, KASAMBA Ilunga Eric during the field surveys, and of Francine UWAMBAYINEMA for performing the analyses of urinary metals. We thank those who transported samples from Lubumbashi to Belgium. We thank Dr. Johan LAVREAU (RMCA, Tervuren) for contributing information on the geography and geology of Katanga.

References

Alexander, C.S., 1972. Cobalt-beer cardiomyopathy. A clinical and pathologic study of twenty-eight cases. Am. J. Med. 53, 395–417.

American Conference of Governmental Industrial Hygienists (ACGIH), 2006. 2006 TLVs® and BEIs®. Threshold Limit Values for Chemical Substances and Physical Agents. Biological Exposure Indices. ACGIH, Cincinnati, OH.

Audry, S., Schafer, J., Blanc, G., Jouanneau, J.M., 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environ. Pollut. 132, 413–426.

Baker, E.L., Hayes, C.G., Landrigan, P.J., Handke, J.L., Leger, R.T., Housworth, W.J., Harrington, J.M., 1977. Nationwide survey of heavy-metal absorption in children living near primary copper, lead, and zinc smelters. Am. J. Epidemiol. 106, 261–273.

Barceloux, D.G., 1999. Cobalt. Clin. Toxicol. 37, 206–216.

Bijlsma, J.A., Slottje, P., Huizink, A.C., Twisk, J.W., van der Voet, G.B., de Wolff, F.A., Vanhaecke, F., Moens, L., Smid, T., 2008. Urinary uranium and kidney function parameters in professional assistance workers in the Epidemiological Study Air Disaster in Amsterdam (ESADA). Nephrol. Dial. Transplant. 23, 249–255.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. 277, 1–18.

Caldwell, K.L., Jones, R.L., Verdon, C.P., Jarrett, J.M., Caudill, S.P., Osterloh, J.D., 2009. Levels of urinary total and speciated arsenic in the US population: National Health and Nutrition Examination Survey 2003–2004. J. Expo. Sci. Environ. Epidemiol. 19, 59–68.

Carlson-Lynch, H., Beck, B.D., Boardman, P.D., 1994. Arsenic risk assessment. Environ. Health Perspect. 102, 354–356.
Centers for Disease Control and Prevention (CDC), 2005. Third National Report on Human Exposure to Environmental Chemicals. NCEH 05-0570, Atlanta, GA, 21 August 2008, pp. 1–467. http://www.cdc.gov/exposurereport/pdf/thirdreport.pdf (accessed April 16, 2009).
De Boeck, M., Hoet, P., Nemery, B., Kirsch-Volders, M., Lison, D., 2003a. In vivo genotoxicity of hard metal dust: induction of micronuclei in rat type II epithelial lung cells. Carcinogenesis 24, 1793–1800.
De Boeck, M., Kirsch-Volders, M., Lison, D., 2003b. Cobalt and antimony: genotoxicity and carcinogenicity. Mutat. Res. 533, 135–152.
Diaz-Barriga, F., Santos, M.A., Mejia, J.J., Batres, L., Yanez, L., Carrizales, L., Vera, E., del Razo, L.M., Cebrian, M.E., 1993. Arsenic and cadmium exposure in children living near a smelter complex in San Luis Potosi, Mexico. Environ. Res. 62, 242–250.
Ezaki, T., Tsukahara, T., Moriguchi, J., Furuki, K., Fukui, Y., Ukai, H., Okamoto, S., Sakurai, H., Honda, S., Ikeda, M., 2003. Analysis for threshold levels of cadmium in urine that induce tubular dysfunction among women in non-polluted areas in Japan. Int. Arch. Occup. Environ. Health 76, 197–204.
Gauthier, G., Deliens, M., 1999. Cobalt minerals of the Katanga Crescent, Congo. Mineral. Rec. 30, 255–267.
Global Witness, 2004. Rush and Ruin. The Devastating Mineral Trade in Southern Katanga, DRC. Washington DC, Global Witness Publishing Inc, pp. 1–31. 〈http://www.globalwitness.org/media_library_detail.php/125/en/rush_and_ruin〉 (accessed April 16, 2009).
Global Witness, 2006. Digging in Corruption. Fraud, Abuse and Exploitation in Katanga's Copper and Cobalt Mines. Washington DC, Global Witness Publishing Inc, pp. 1–56. 〈http://www.globalwitness.org/media_library_detail.php/154/en/digging_in_corruption〉 (accessed April 16, 2009).
Gopalan, H.N., 2003. Environmental health in developing countries: an overview of the problems and capacities. Environ. Health Perspect. 111, A446–A447.
Heilier, J.F., Buchet, J.P., Haufroid, V., Lison, D., 2005. Comparison of atomic absorption and fluorescence spectroscopic methods for the routine determination of urinary arsenic. Int. Arch. Occup. Environ. Health 78, 51–59.
Jarup, L., Berglund, M., Elinder, C.G., Nordberg, G., Vahter, M., 1998. Health effects of cadmium exposure – a review of the literature and a risk estimate. Scand. J. Work Environ. Health 24 (Suppl 1), 1–51.
Jefferson, J.A., Escudero, E., Hurtado, M.E., Pando, J., Tapia, R., Swenson, E.R., Prchal, J., Schreiner, G.F., Schoene, R.B., Hurtado, A., Johnson, R.J., 2002. Excessive erythrocytosis, chronic mountain sickness, and serum cobalt levels. Lancet 359, 407–408.
Kesteloot, H., Roelandt, J., Willems, J., Claes, J.H., Joossens, J.V., 1968. An enquiry into the role of cobalt in the heart disease of chronic beer drinkers. Circulation 37, 854–864.
Kligerman, D.C., La Rovere, E.L., Costa, M.A., 2001. Management challenges on small-scale gold mining activities in Brazil. Environ. Res. 87, 181–198.
Lacatusu, R., Rauta, C., Carstea, S., Ghelase, I., 1996. Soil–plant–man relationships in heavy metal polluted areas in Romania. Appl. Geochem. 11, 105–107.
Lauwerys, R., Hoet, P., 1993. Industrial Chemical Exposure. Guidelines for Biological Monitoring, second ed. Lewis Publishers, Boca Raton, FL.
Lindberg, A.L., Ekstrom, E.C., Nermell, B., Rahman, M., Lonnerdal, B., Persson, L.A., Vahter, M., 2008. Gender and age differences in the metabolism of inorganic arsenic in a highly exposed population in Bangladesh. Environ. Res. 106, 110–120.
Liu, H., Probst, A., Liao, B., 2005. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Sci. Total Environ. 339, 153–166.
McDiarmid, M.A., Squibb, K., Engelhardt, S.M., 2004. Biologic monitoring for urinary uranium in Gulf War I veterans. Health Phys. 87, 51–56.
Melnick, D.J., Kakabadse Navarro, Y., McNeely, J., Schmidt-Traub, G., Sears, R.R., 2005. The Millennium Project: the positive health implications of improved environmental sustainability. Lancet 365, 723–725.
Morin, Y., Daniel, P., 1967. Quebec beer-drinkers' cardiomyopathy: etiological considerations. CMAJ 97, 926–928.
Nawrot, T., Plusquin, M., Hogervorst, J., Roels, H.A., Celis, H., Thijs, L., Vangronsveld, J., Van Hecke, E., Staessen, J.A., 2006. Environmental exposure to cadmium and risk of cancer: a prospective population-based study. Lancet Oncol. 7, 119–126.
Nemery, B., 1990. Metal toxicity and the respiratory tract. Eur. Respir. J. 3, 202–219.
Nemery, B., Lewis, C.P.L., Demedts, M., 1993. Cobalt and possible oxidant-mediated toxicity. Sci. Total Environ. 150, 57–64.
Nemery, B., Verbeken, E.K., Demedts, M., 2001. Giant cell interstitial pneumonia (hard metal lung disease, cobalt lung). Semin. Respir. Crit. Care Med. 22, 435–447.
Nriagu, J.O., 1992. Toxic metal pollution in Africa. Sci. Total Environ. 121, 1–37.
Offergelt, J.A., Roels, H., Buchet, J.P., Boeckx, M., Lauwerys, R., 1992. Relation between airborne arsenic trioxide and urinary excretion of inorganic arsenic and its methylated metabolites. Br. J. Ind. Med. 49, 387–393.
Ohashi, F., Fukui, Y., Takada, S., Moriguchi, J., Ezaki, T., Ikeda, M., 2006. Reference values for cobalt, copper, manganese, and nickel in urine among women of the general population in Japan. Int. Arch. Occup. Environ. Health 80, 117–126.
Paschal, D.C., Ting, B.G., Morrow, J.C., Pirkle, J.L., Jackson, R.J., Sampson, E.J., Miller, D.T., Caldwell, K.L., 1998. Trace metals in urine of United States residents: reference range concentrations. Environ. Res. 76, 53–59.
Prasad, M.S., 1989. Production of copper and cobalt at Gecamines, Zaire. Miner. Eng. 2, 521–541.
Prescott, E., Netterstrom, B., Faber, J., Hegedus, L., Suadicani, P., Christensen, J.M., 1992. Effect of occupational exposure to cobalt blue dyes on the thyroid volume and function of female plate painters. Scand. J. Work Environ. Health 18, 101–104.
Rackley, E.B., 2006. Democratic Republic of the Congo: undoing government by predation. Disasters 30, 417–432.
Romieu, I., Samet, J.M., Smith, K.R., Bruce, N., 2002. Outdoor air pollution and acute respiratory infections among children in developing countries. J. Occup. Environ. Med. 44, 640–649.
Rybicka, E.H., 1996. Impact of mining and metallurgical industries on the environment in Poland. Appl. Geochem. 11, 3–9.
Sachs, J.D., McArthur, J.W., 2005. The Millennium Project: a plan for meeting the Millennium Development Goals. Lancet 365, 347–353.
Semenza, G.L., 2000. HIF-1: mediator of physiological and pathophysiological responses to hypoxia. J. Appl. Physiol. 88, 1474–1480.
Staessen, J., Amery, A., Bernard, A., Bruaux, P., Buchet, J.P., Claeys, F., de Plaen, P., Ducoffre, G., Fagard, R., Lauwerys, R.R., Lijnen, P., Nick, L., Saint-Remy, A., Roels, H., Rondia, D., Sartor, F., Thijs, L., 1991. Effects of exposure to cadmium on calcium metabolism: a population study. Br. J. Ind. Med. 48, 710–714.
Staessen, J.A., Lauwerys, R.R., Ide, G., Roels, H.A., Vyncke, G., Amery, A., 1994. Renal function and historical environmental cadmium pollution from zinc smelters. Lancet 343, 1523–1527.
Staessen, J.A., Roels, H.A., Emelianov, D., Kuznetsova, T., Vangronsveld, J., 1999. Environmental exposure to cadmium, forearm bone density, and risk of fractures: prospective population study. Lancet 353, 1140–1144.
Tembo, B.D., Sichilongo, K., Cernak, J., 2006. Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia. Chemosphere 63, 497–501.
The Blacksmith Institute. 2008. World's Most Polluted Places 2007. 〈http://www.blacksmithinstitute.org/〉 and 〈http://www.worstpolluted.org/〉 (accessed April 16, 2009).
Vellut, J.L., 1985. Mining in the Belgian Congo. Longman History of Central Africa (II), 74–92.