

Levels of selected trace elements observed in the Kinshasa's waters.

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Abstract

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Background levels of urinary trace elements of toxicological or industrial importance have been reported for Kinshasa's population. The information on the probable sources of trace element exposures is however still scarce. The objective of this study was to investigate background levels of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V and Zn in different environmental medias of Kinshasa. Several samples of drinking, surface and ground waters were collected throughout 24 administrative entities of Kinshasa and 18 trace elements were analyzed using inductively coupled argon plasma mass spectrometry (ICP-MS). The concentrations for As, Ba, Cd, Co, Cr, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V and Zn were lower than the WHO drinking water guidelines or the typical levels. However, the median concentration of Al was higher in ground water (614.3 vs 100 µg/L) and drinking water (382.1 vs 200 µg/L) than these reference limits. Data from the present study constitutes background levels for these trace elements, including essential and ubiquitous toxic elements. This database will be useful for comparison purposes in future studies. The main concerns emerging from this study were Al exposure in drinking and ground waters. The importance of regular monitoring in the Kinshasa's environment is required.

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INTRODUCTION

Trace elements are ubiquitous in the environment. Element presence occurs in both natural and anthropogenic forms. While usually natural forms are present at relative low concentrations, in recent years a number of anthropogenic sources such as dumping of waste, smelter stacks, waste incineration, vehicle exhausts, fertilizers, agricultural waste, and sewage sludges have implied notable contributions to the increase of environmental metal concentrations [MARKUS and MCBRATNEY, 1996; BILOS *et al.*, 2001; HLAVAY *et al.*, 2001; KOCH and ROTARD, 2001].

With the development of mining, smelting and other industrial activities, trace elements are increasingly being found in the environment which can pose severe threats to human and environmental health. Pollution by trace elements (such as cadmium (Cd), lead (Pb), etc.) affects the quality of the atmosphere and the soil

as well as water bodies and threatens the health and life of animals and human beings by way of the food chain. It is known that low trace elements are essential for life [e.g. aluminum (Al), copper (Cu), cobalt (Co), selenium (Se), zinc (Zn)], yet in excess they may also be toxic. Others trace elements (e.g. Cd, Pb, U) are not required for routine functioning of the human body and can be toxic even at low concentration [WILLIAMS *et al.* 2000; JARUP 2003; SHARMA and AGRAWAL 2005; CDC 2009; HEALTH CANADA 2010].

Through a study carried out to assess the exposure to trace elements in urine of the Kinshasa's population (Democratic Republic of Congo - DRC), Tuakuila *et al.* [2012] showed elevated levels of Al, As, Cd, Pb and Hg as compared to other databases. But few data exists concerning different sources of trace element exposures in Kinshasa. The present study aim at filling that gap and its main objective was to investigate background

levels of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V and Zn in the Kinshasa's environment.

MATERIAL ET METHODS

Sample collection in Kinshasa

A total of 100 drinking water samples were collected according to the European guidelines from certain residences throughout 24 administrative entities of Kinshasa and, that is, after flushing followed by 30-min stagnation [HOEKSTRA *et al.* 2009].

Hundred groundwater samples were collected from certain residences throughout 24 administrative entities of Kinshasa in 500 mL plastic bottles (washed three times with the sample water prior to collection).

Fifty surface water samples were collected from 4 rivers (Bumbu, Kalamu, Nd'jili and Yolo) of Kinshasa in 500 mL plastic bottles (washed three times with the sample water prior to collection), 20 mL of it filtered through a 0.45 µm syringe filter (Sartorius Minisart, non-pyrogenic CE) and stored in a 20 mL polypropylene vial.

Data collection was completed during January 2011.

Element analysis

The water samples were kept at 4 °C, acidified to pH <2 (concentrated Aristar HNO₃) and left to equilibrate

for at least 3 days before element analysis [ROSSITER *et al.* 2010].

All samples were transported in a box to be analysed at the Louvain Centre for Toxicology and Applied Pharmacology (LTAP, Brussels, Belgium). Eighteen elements (Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V, and Zn) were quantified by inductively coupled argon plasma mass spectrometry (ICP-MS Agilent 7500 ce).

Briefly, 0.50 mL sample was diluted with 4.50 mL of diluent (1% v/v HNO₃, 0.5% v/v HCl and 50 ppb Sc, Ge, Rh, and Ir as internal standards (IS)). Matrix-matched calibrators were prepared by adding 0.05 mL of a calibration standard into 0.45 mL of acid (1% v/v HNO₃ and 0.5% v/v HCl) and 4.5 mL of diluent. Both acids, HCl and HNO₃, were of suprapur quality and were purchased from Merck (ref 1.00318.1000 and 1.00441.1000). Among the eighteen elements measured by ICP-MS, Al (m/z 27), Se (m/z 78), Mo (m/z 96), Sb (m/z 121), Sn (m/z 118), Cd (m/z 111), Ba (m/z 137), Pb (m/z 208), Tl (m/z 205) and U (m/z 238) were analysed using the standard mode without using the collision cell. The remaining elements, V (m/z 51), Mn (m/z 55), Co (m/z 59), Cr (m/z 52), Cu (m/z 63), Ni (m/z 60), Zn (m/z 66), and As (m/z 75) were analyzed using helium as collision gas. The method used for the determination of 22 trace elements in drinking water, including the 18 measured trace elements in the present study, is ISO15189 certified. Laboratory blanks were prepared by using nanopur water and treating it in the same way as the samples.

Table 1. Distribution of measured trace elements in drinking water. The minimum, mean, maximum and median values are given along with the WHO guideline values.

Parameter	Unit	N	LD	Mean	Min	Q1	Med	Q3	Max	WHO guideline
Al	µg/L	100	1.57	387.8	2.4	151.5	382.1	602.7	943.8	100-200 ^a
As	µg/L	100	0.07	<LD	<LD	<LD	<LD	<LD	1.9	10
Ba	µg/L	100	0.14	24.1	1.6	16.5	21.3	25.0	305.1	-
Cd	µg/L	100	0.01	<LD	<LD	<LD	<LD	<LD	0.43	3
Co	µg/L	100	0.02	0.07	0.03	0.03	0.06	0.09	0.36	-
Cr	µg/L	100	0.06	0.18	<LD	0.12	0.15	0.18	1.72	50
Cu	µg/L	100	0.14	6.4	0.2	1.0	1.8	3.6	246.9	-
Mn	µg/L	100	0.05	16.3	0.1	11.7	16.3	26.9	56.5	400
Mo	µg/L	100	0.05	<LD	<LD	<LD	<LD	<LD	2.42	-
Ni	µg/L	100	0.28	<LD	<LD	<LD	0.32	0.56	12.44	20
Pb	µg/L	100	0.03	1.0	0.05	0.2	0.4	0.8	21.1	10
Sb	µg/L	100	0.01	<LD	<LD	<LD	<LD	<LD	0.31	-
Se	µg/L	100	0.71	<LD	<LD	<LD	<LD	<LD	<LD	10
Sn	µg/L	100	0.03	<LD	<LD	<LD	<LD	<LD	0.89	-
Tl	µg/L	100	0.07	<LD	<LD	<LD	<LD	<LD	<LD	-
U	µg/L	100	0.005	<LD	<LD	<LD	<LD	<LD	0.50	15
V	µg/L	100	0.12	0.4	<LD	<LD	<LD	0.5	1.6	-
Zn	µg/L	100	0.60	105.4	0.9	14.6	35.8	94.5	1446.2	3000

a: recommendation based on aesthetic considerations such as taste and color; LD=limit of quantification; Min= minimum value; Max= maximum value; Q1 – 25th percentile, Med = Median – 50th percentile, Q3 – 75th percentile; AM= arithmetic mean

Table 2. Distribution of measured trace elements in surface water. The minimum, mean, maximum and median values are given along with the typical levels found in the literature.

Parameter	Unit	N	LD	Mean	Min	Q1	Med	Q3	Max	Typical levels ^a
Al	µg/L	50	1.57	127.07	0.36	9.76	15.85	59.21	1107.00	<100
As	µg/L	50	0.07	0.45	0.12	0.29	0.43	0.57	1.12	<10
Ba	µg/L	50	0.14	20.44	9.25	11.31	19.23	24.86	39.85	<380
Cd	µg/L	50	0.01	0.04	0.005	0.01	0.02	0.04	0.29	<10
Co	µg/L	50	0.02	0.21	0.01	0.11	0.19	0.25	0.55	<1
Cr	µg/L	50	0.06	0.44	0.14	0.33	0.43	0.60	0.91	<30
Cu	µg/L	50	0.14	2.25	0.07	0.82	1.19	2.22	12.87	<1000
Mn	µg/L	50	0.05	31.68	1.21	6.21	17.76	45.50	133.30	<50
Mo	µg/L	50	0.05	<LD	<LD	<LD	<LD	<LD	0.83	-
Ni	µg/L	50	0.28	<LD	<LD	<LD	<LD	<LD	1.78	<10
Pb	µg/L	50	0.03	9.93	0.03	0.16	0.36	1.29	183.10	<1
Sb	µg/L	50	0.01	0.34	<LD	0.26	0.30	0.41	0.86	-
Se	µg/L	50	0.71	0.41	0.20	0.34	0.38	0.49	0.82	-
Sn	µg/L	50	0.03	<LD	<LD	<LD	<LD	<LD	<LD	<2
Tl	µg/L	50	0.07	<LD	<LD	<LD	<LD	<LD	0.09	<10
U	µg/L	50	0.005	0.021	0.005	0.014	0.018	0.028	0.062	-
V	µg/L	50	0.12	1.18	0.67	0.92	1.17	1.39	1.88	-
Zn	µg/L	50	0.60	22.23	2.35	4.49	8.17	24.47	125.9	<50

a: Williams et al. 2000; LD=limit of detection; Min= minimum value; Max= maximum value; Q1 – 25th percentile, Med = Median – 50th percentile, Q3 – 75th percentile; AM= arithmetic mean

Table 3. Distribution of measured trace elements in groundwater. The minimum, mean, maximum and median values are given along with the typical levels found in the literature.

Parameter	Unit	N	LD	Mean	Min	Q1	Med	Q3	Max	Typical levels ^a
Al	µg/L	100	1.57	706.18	23.25	185.60	614.35	907.50	2807.00	<100
As	µg/L	100	0.07	0.07	0.03	0.04	0.05	0.08	0.66	<10
Ba	µg/L	100	0.14	44.71	13.19	23.64	35.71	52.62	124.40	<380
Cd	µg/L	100	0.01	0.08	0.01	0.05	0.07	0.09	0.29	<10
Co	µg/L	100	0.02	0.31	0.14	0.21	0.27	0.37	0.74	<1
Cr	µg/L	100	0.06	0.15	0.03	0.05	0.09	0.40	0.56	<30
Cu	µg/L	100	0.14	1.49	0.07	0.08	0.40	1.92	12.19	<1000
Mn	µg/L	100	0.05	47.99	7.15	25.05	42.90	63.77	138.40	<50
Mo	µg/L	100	0.05	<LD	<LD	<LD	<LD	<LD	<LD	-
Ni	µg/L	100	0.28	0.59	0.03	0.15	0.33	0.79	3.39	<10
Pb	µg/L	100	0.03	0.07	0.02	0.03	0.05	0.09	0.25	<1
Sb	µg/L	100	0.01	0.04	0.005	0.007	0.02	0.03	0.68	-
Se	µg/L	100	0.71	0.58	0.25	0.46	0.58	0.70	0.83	-
Sn	µg/L	100	0.03	<LD	<LD	<LD	<LD	<LD	<LD	<2
Tl	µg/L	100	0.07	0.97	0.14	0.36	0.95	1.35	2.61	<10
U	µg/L	100	0.005	0.013	0.005	0.005	0.008	0.014	0.071	-
V	µg/L	100	0.12	0.33	<LD	0.12	0.24	0.42	1.54	-
Zn	µg/L	100	0.60	271.25	2.89	5.82	18.47	45.74	3611.00	<50

a: Williams et al. 2000; LD=limit of detection; Min= minimum value; Max= maximum value; Q1 – 25th percentile, Med = Median – 50th percentile, Q3 – 75th percentile; AM= arithmetic mean

Statistical analysis

The SAS software package, version 9.2 (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.

RESULTS AND DISCUSSION

The results from the trace element analysis (mean, minimum, lower inter-quartile range (Q1), median, higher inter-quartile range (Q3) and maximum values) are displayed in *Tables 1, 2, and 3*. The number of samples analysed (N) and the guidelines or typical

levels in the different environmental medias are also presented.

The first biomonitoring study carried out to assess the exposure to trace elements in urine showed elevated levels of Al, As, Cd, Pb and Hg as compared to other databases. But data on environmental exposure to these elements in Kinshasa are scarce [TUAKUILA *et al.* 2012]. The present study originated from that observation and its main objective was to investigate background levels of Al, As, Ba, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sn, Tl, U, V and Zn in the different environmental medias of Kinshasa. The data from the present study constitutes background levels for 18 trace

elements. Only the parameters of particular toxicological relevance will be discussed here below.

Trace elements in waters

As can be seen in *Tables 1, 2* and *3*, several water samples contain median concentrations of trace elements below or in the range of the reference limits. The concentrations for As, Ba, Cd, Co, Cr, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V and Zn were lower than the WHO drinking water guidelines or the typical levels. However, the median concentration of Al was higher in ground water (614.3 µg/L) and drinking water (382.1 µg/L) than these reference limits.

The occurrence of trace elements in ground water is affected both by hydrochemical factors like mineral composition of the rocks, soil characteristics as well as by anthropogenic activities [KOCH and ROTARD, 2001; NADAL *et al.*, 2004]. Exceeded median Al level found in ground water [median concentration (Q1 – Q3)] 614.3 µg/L (184.6 – 907.5 µg/L) and 2807.0 µg/L as a maximum may be influenced by mineral composition of the Kinshasa soils which contain clay (clay is composed of various minerals among which a high proportion of alumina) or bauxite.

The presence of Al in water for domestic supplies is due either to the addition of Al salts as coagulants or is caused by low pH value of either surface or ground water. Al salts (e.g. Al sulphate: alum) are traditionally used in drinking water treatment plants to remove turbidity, color and dissolved substances via coagulation processes. Several studies have shown that a portion of alum added to the water is not removed and remains as residual Al in the treated water [MILLER *et al.* 1984, LETTERMANN and DRISCOLL 1988, WHO 1998, CECH and MONTERA 2000]. Al toxicity in general population is known to occur in at least two specific situations: neurological diseases (including amyotrophic lateral sclerosis, dementia associated with Parkinson's disease and Alzheimer's disease) [Van der VOET *et al.*, 1999] and osteomalacia or metabolic bone disease (in dialysis patients) [SUAREZ-FERNANDEZ *et al.*, 1999; KAUSZ *et al.*, 1999]. Cerebral disfunction was reported in people exposed to drinking water that had been contaminated with Al sulphate [ALTMANN *et al.*, 1999]. In the addendum to the guidelines published in 1998, considering the beneficial effects of Al as a coagulant in water treatment as well as health concerns about Al, a practical level was derived based on optimization of the coagulation process in drinking water plants using Al based coagulants, to minimize Al levels in the finished water. Thus 100 µg/l (for large treatment facilities) is suggested as the achievable concentration, whereas 200 µg/l or less is a practical level for the small facilities. Seventy per cent (70%) of the samples measured were above the recommended

guideline value, several more than two-fold, with a median concentration (Q1 – Q3) at 382.1 µg/L (151.5 – 602.7 µg/L) and 943.8 µg/L as a maximum. It could be explained by the presence of "Sediment-related degradation of water quality in DRC and excessive turbidity levels have necessitated the use of increasing quantities of coagulant agents, mainly Al sulfate, to precipitate the sediment particulate possibly resulting in elevated residual aluminum in treated water [UNEP, 2011]. Tuakuila *et al.* [2012] also found higher Al concentrations in drinking water: 76% of samples (n = 36) exceeded the WHO recommended level with a mean of 207 µg/L.

Trace elements found in this study were in various concentrations in drinking, surface and ground waters. It is important to remember that these levels may vary considerably, depending on whether the site of interest is rural, urban, or near a concentrated source of the metal, such as an ore deposit or hazardous waste facility. Thus, the levels reported in the *Tables 1, 2* and *3* are only approximations or ranges for comparative purposes, and should not be seen as reflective of levels to be expected in all areas.

CONCLUSION

The data from the present study constitutes background levels for 18 trace elements in different environmental medias, including essential and ubiquitous toxic elements. This database will be useful for comparison purposes in future studies. The main concerns emerging from this study were Al exposure in drinking and ground waters. The importance of regular monitoring in the Kinshasa's environment is required.

The major limitation should be considered in evaluating present results. With regard to sample collection, selection of water samples did not follow rigid sampling strategy (such as random sampling) but by chance, which was practically inevitable under present survey conditions.

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RESUME

Niveaux de quelques éléments en trace observés dans les eaux de Kinshasa

Les niveaux de base des éléments en trace ayant une importance toxicologique et industrielle ont été rapportés dans les urines de la population de Kinshasa.

L'information sur les sources probables de l'exposition à ces éléments est, cependant, encore moins disponible. L'objectif de cette étude était d'investiguer les niveaux de base de Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V et Zn dans les différents milieux environnementaux de Kinshasa. Plusieurs échantillons d'eau souterraine, de boisson et de surface ont été collectés dans les 24 communes de Kinshasa et 18 éléments en trace ont été analysés en utilisant le couplage inductif à plasma à argon couplé à la spectrométrie de masse (ICP-MS). Les concentrations en As, Ba, Cd, Co, Cr, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, U, V et Zn ont été plus faibles par rapport aux valeurs guides de l'OMS ou aux valeurs typiques. Cependant, la concentration médiane en Al a été très élevée dans l'eau souterraine (614,3 vs 100 µg/L) et l'eau de boisson (382,1 vs 200 µg/L) que ces valeurs limites. Les données de cette étude constituent des niveaux de base pour les éléments en trace, incluant les éléments essentiels et toxiques ubiquitaires. Cette base de données sera utile pour la comparaison dans les études ultérieures. La principale préoccupation émergeant de cette étude était l'exposition en Al dans les échantillons d'eau souterraine et de boisson. L'importance d'une surveillance régulière de l'environnement de Kinshasa est exigée.

Mots clés : *Éléments en trace, Valeurs typiques, Exposition environnementale, Surveillance, Kinshasa*

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