Geochemistry and risk assessment of street dust in Luanda, Angola: A tropical urban environment

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A total of 92 samples of street dust were collected in Luanda, Angola, were sieved below 100 μm, and analysed by ICP-MS for 35 elements after an aqua-regia digestion. The concentration and spatial heterogeneity of trace elements in the street dust of Luanda are generally lower than in most industrialized cities in the Northern hemisphere. These observations reveal a predominantly "natural" origin for the street dust in Luanda, which is also manifested in that some geochemical processes that occur in natural soils are preserved in street dust: the separation of uranium from thorium, and the retention of the former by carbonate materials, or the high correlation between arsenic and vanadium due to their common mode of adsorption on solid particles in the form of oxyanions. The only distinct anthropogenic fingerprint in the composition of Luanda's street dust is the association Pb–Cd–Sb–Cu (and to a lesser extent, Ba–Cr–Zn). The use of risk assessment strategies has proved helpful in identifying the routes of exposure to street dust and the trace elements therein of most concern in terms of potential adverse health effects. In Luanda the highest levels of risk seem to be associated (a) with the presence of As and Pb in the street dust and (b) with the route of ingestion of dust particles, for all the elements included in the study except Hg, for which inhalation of vapours presents a slightly higher risk than ingestion. However, given the large uncertainties associated with the estimates of toxicity values and exposure factors, and the absence of site-specific biometric factors, these results should be regarded as preliminary and further research should be undertaken before any definite conclusions regarding potential health effects are drawn.

1. Introduction

Solid particles that accumulate on outdoor, impervious materials in urban environments are collectively referred to as "street dust". The two main sources of street dust, and consequently of the trace elements found therein, are deposition of previously suspended particles (atmospheric aerosol) and displaced urban soil. Additionally, the emissions from several point-sources (vehicular traffic, heating systems, building deterioration, construction and renovation, corrosion of galvanized metal structures, etc.) contribute directly to the street-dust load in their proximity (Harrison, 1979; Hopke et al., 1980; Schwar et al., 1988). Street dust does not remain deposited in place for long. It is easily resuspended back into the atmospheric aerosol, to which it contributes a significant amount of trace elements (Maxwell and Nelson, 1978), or precipitation washes it

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away becoming an important component of the suspended and dissolved solids in street run-off and in receiving water bodies (Vermette et al., 1991, and references therein).

The ultimate reason behind the large body of research on street dust that has accumulated in the last three decades—at least in the developed regions of the world—is the concern over the potential effects of exposure to this material through inhalation, ingestion and dermal contact. Numerous studies have tried to ascertain various aspects of this problem, both for house and street dust: amount and size of dust particles in the home/outdoor environment, rate of deposition onto household /urban surfaces, rate of transfer to the human organism, sources and chemical composition of house/ street dust, behavioural effects on children living in urban areas with high levels of toxic chemicals, etc. (Day et al., 1975; Harrison, 1979; Fergusson et al., 1986; Davies et al., 1987; Fergusson and Kim, 1991; Akhter and Madany, 1993; Edwards et al., 1998; Gulson et al., 1998). The fact that different investigations often arrive at inconclusive and sometimes contradictory results only reflect the enormous difficulties involved in evaluating all the factors previously mentioned for a material whose properties are highly variable in time and space, and for which even the choice of a sampling procedure can pose a serious problem (Archer and Barrat, 1976; Bris et al., 1999). Probably, the most difficult question regarding the potential adverse health effects of street dust is the quantitative evaluation of the rates of exposure. These have only been extensively researched for children and hand-to-mouth activity during games and for the habit of "pica", i.e. mouthing of non-food objects (Biggins and Harrison, 1980, and references therein; Rundle et al., 1985; Watt et al., 1993). For example, Evans et al. (1992) refer to a model in which children are assumed to ingest 60 mg day^{-1} of dirt, and where 30% of the ingested lead is bioavailable (other researchers, like Claeys et al., 1993, place this figure at 50%). With exceptions like those just discussed, most studies have either established an inferred link between elevated concentrations of toxic elements in street dust and the observed incidence of a given effect in a population, or have directly equated risk with predominance of bioavailable or mobile chemical species, as determined in sequential or selective extraction protocols (Banerjee, 2003; Robertson et al., 2003). Some authors have tried a more direct approach, assessing the ecotoxicological significance of trace elements in street dust by means of bioassays (Wang et al., 1998).

Risk assessment strategies constitute an alternative approach to evaluate the potential health effects of trace elements in street dust. These strategies are based on the separate assessment of (a) the toxicity of the chemicals included in the analysis by exposure route (i.e., inhalation, ingestion, and dermal contact), and (b) the levels of exposure to those chemicals for the potential receptors. For non-carcinogenic toxicants, a range of exposures from zero to some finite value (reference dose or acceptable/tolerable daily intake) are assumed to be tolerated by the organism with essentially no chance of expression of the toxic effect. If the daily dose to which a receptor is exposed exceeds the corresponding reference dose, the receptor is considered to be potentially at risk. On the other hand, there is no level of exposure to a genotoxic carcinogen that does not pose a small but finite probability of generating a carcinogenic response. Risk to the exposed individual is measured as the product of the lifetime-average daily dose times a "slope factor", defined as the incremental probability of developing cancer during a lifetime due to chronic exposure to a unit dose of contaminant. This probability must not exceed a subjective level of risk (in the range 10^{-4}–10^{-6}) deemed acceptable by the corresponding regulatory authorities. Risk assessment tools have been extensively employed by regulatory authorities to define soil screening levels or soil guideline values. However, only a few research studies have attempted to use these same tools to evaluate the risk from exposure to toxic elements and radionuclides in urban environments (Boyd et al., 1999; Crick et al., 1987; Nadal et al., 2004).

This paper presents the main findings of a study carried out in Luanda (Angola), during the dry months of August and September 2002 with two purposes: to discuss the differences in the geochemical nature between street dust in a tropical environment and that found in cities of developed regions; and to evaluate, by means of risk assessment strategies, the potential adverse health effects of the exposure of children living in Luanda to street dust.

1.1. Description of the study area

Luanda, the capital city of Angola, is located on the inner side and to the South of the Bay of Luanda, on the Atlantic coast of Africa (Fig. 1). The climate is tropical (average temperature and precipitation: 26 °C and 350–400 mm yr^{-1}, respectively) with two seasons: the warm and rainy season which lasts 8–9 months, and the dry and relatively cold season, known locally as "cacimbo", which extends between June and September. The population of Luanda has grown rapidly in the last 10 years and had reached approximately 2.5 million at the time of this study. Luanda's commercial and residential centre occupies the inner part of the city around the harbour. It is surrounded by a succession of residential districts which are, in turn, encircled by the "muceques" or "shanty-towns" in the outskirts of Luanda. An industrial belt, which includes an oil refinery, a cement plant, a zinc smelter, and an iron foundry, extends outside the muceques, from North to East. Two geologic formations occur predominantly in
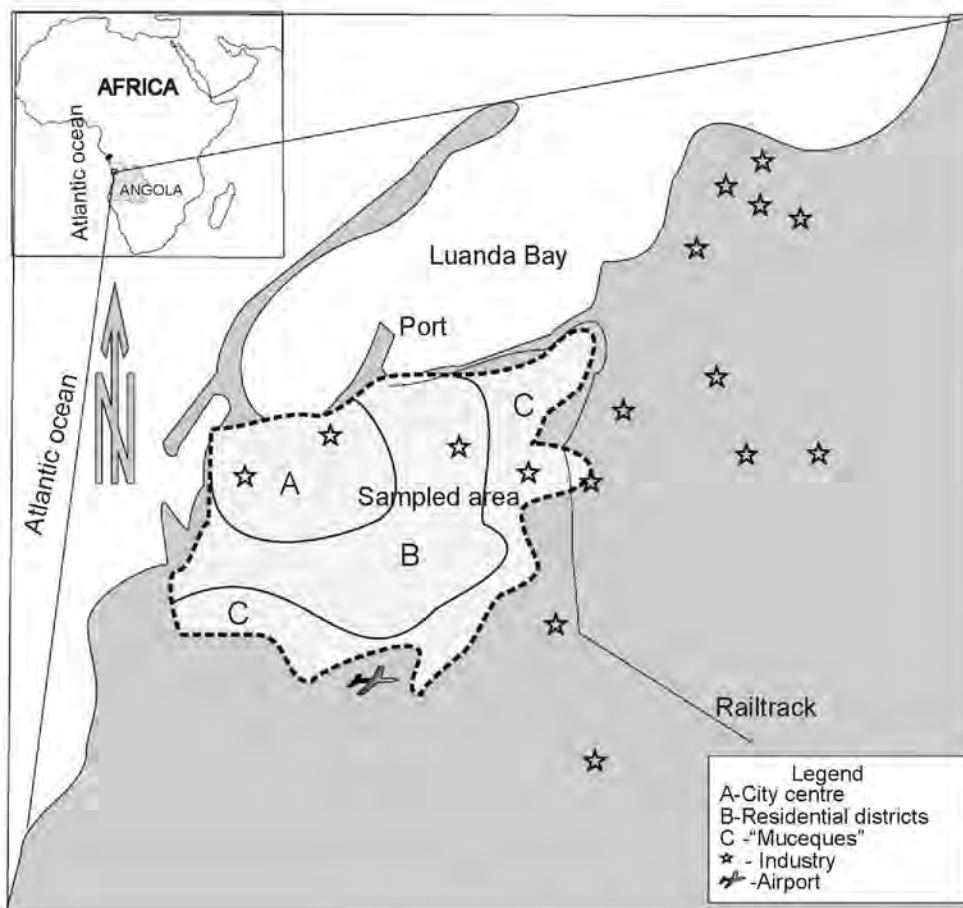
Fig. 1. Location of study area.

and around the city. The "Luanda" formation, which covers most of the low parts of the city and the coastline, is representative of a transitional (marine-fluvial) environment. It is characterized by complex lithological variations, incorporating ferruginous sands with coarse quartz grains, clay-coated fine sand, various types of marl, shell limestone, and grey-greenish clays. The "Quelo" or "red sands" formation predominates in the higher parts of the city. In these areas, an iron-rich, sandy red soil has developed from the underlying sediments of Neogean age. These "red sands" are composed primarily of fine and medium-sized quartz grains, small amounts of kaolinite and illite, and relatively high contents of hematite and goethite which form coatings on quartz grains and, occasionally, ferruginous nodules.

2. Materials and methods

A total of 92 samples of street dust were collected under stable weather conditions in the cold and dry season during the months of August and September 2002. An area covering most of Luanda's city centre and some residential districts around it (Fig. 1) was divided into 0.25 km square units. A sampling point within each unit was selected at random, and approximately 300 g of the dust particles that had accumulated on impervious surfaces (road, pavement, gutter) within a 5-m radius circle around the selected sampling point were collected with a plastic dust pan and brush, and were transferred to an air-tight polyethylene bag for transport to the laboratory. The samples were left to dry at room temperature for five days and were subsequently sieved, in all-plastic sieving sets, through a 2 mm, a 500 and a 100 μm mesh. The fraction below 100 μm was reduced by repeated quartering until a 0.5 g sample was obtained.

Street dust was operationally defined in this study as those particles of outdoor urban material with diameters below 100 μm because they are easily resuspended (as opposed to bigger particles which move mainly by "saltation" and "creep") (Nicholson, 1988; Sehmel, 1980) and can be inhaled through the nose or mouth during breathing. Exposure to dust particles has

traditionally been evaluated for particulate matter with aerodynamic diameters below 10 μm (PM_{10}), and the fine particles within this fraction ($PM_{2.5}$) have been associated with the greatest risks to human health because they are more likely to be toxic and can be breathed more deeply into the lungs (Zhou et al., 2003). However, the equations used as sampling criteria for the inhalable fraction (IF) of particulate matter are applicable up to aerodynamic diameters less than or equal to 100 μm, and there is evidence that the size range of inhalable particles with systemic toxicity that could pose a health risk should be extended even further (Kennedy and Hinds, 2002, and references therein).

The 0.5 g analytical samples were digested with 3 mL of a 2:2:2 mixture of $HCl–HNO_3–H_2O$ at 95 °C for 1 h and diluted to 10 mL with distilled water (Ordoñez et al., 2003). The content of 35 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, Tl, U, V, W and Zn), was determined by inductively coupled plasma–

mass spectrometry (ICP–MS). Quality controls involved analysis of 11 blind duplicates and 3 control standards. For all the elements (except Bi, 12%, and Au, 26%), the mean difference within pairs of duplicates did not exceed 10%, with an average value of 4.5%. A summary of the analytical results is presented in Table 1, where Au has been excluded because of poor repeatability (see discussion above), and S, Tl and W have been omitted because 30% or more of all observations fell below the detection limit (for the rest of the elements, observations below the detection limit were assigned a value of half the detection limit). Additionally, carbonate and organic matter content, and pH were determined in 27 samples. The pH was measured in 1 (sample, w): 2.5 (distilled water, v) mixtures, CO_3^{2-} was determined by back titration of excess HCl with NaOH, and organic carbon was evaluated by oxidation with hot K-dichromate and titration of excess dichromate with ferrous ammonium sulphate.

Table 1
Summary of analytical results (μg g^{-1})

Element	Mean	Median	StDev	Coeff. variat.	Min	Max
Ag	0.58	0.3	0.78	1.34	0.1	5.5
Al	4839	4700	1208	0.25	2800	8800
As	5	4.9	0.92	0.18	3.5	7.8
B	7.9	8	2.1	0.27	3	16
Ba	131	121	42	0.32	68	363
Bi	0.17	0.1	0.18	1.06	0.1	1.6
Ca	80,601	79,150	17,804	0.22	43,300	131,000
Cd	1.1	1.1	0.47	0.43	0.7	4
Co	2.9	2.7	0.86	0.30	1.9	7
Cr	26	26	4.4	0.17	17	37
Cu	42	39	15	0.36	18	118
Fe	11,572	11,100	2360	0.20	8000	20,100
Ga	1.4	1	0.54	0.39	1	3
Hg	0.13	0.11	0.09	0.69	0.03	0.57
K	1363	1300	368	0.27	500	2600
La	6.9	7	1.3	0.19	5	11
Mg	4485	4150	1600	0.36	2000	9300
Mn	258	238	92	0.36	157	728
Mo	2	1.9	0.63	0.32	1.2	6.3
Na	1395	1205	809	0.58	210	6340
Ni	10	9.7	3.3	0.33	6.2	32
P	1218	1180	352	0.29	580	2210
Pb	351	306	237	0.68	74	1856
Sb	3.4	2.8	3.8	1.12	1.1	37
Sc	1.3	1.3	0.31	0.24	0.7	2.4
Sr	172	172	35	0.20	91	268
Th	1.7	1.7	0.36	0.21	0.8	2.6
Ti	107	100	21	0.20	70	180
U	0.97	1	0.19	0.20	0.5	1.5
V	20	20	4	0.20	13	30
Zn	317	271	177	0.56	142	1412

3. Results and discussion

Although direct comparisons among the results of different investigations are complicated by the disparity in sampling protocols, particle size retained for analysis, sample digestion procedures, and the nature and intensity of emission sources, the levels of trace elements in the street dust of Luanda are generally lower than those determined in other cities in developed countries (Table 2). The only significant exception is Pb, the concentration of which is similar if not higher than in those cities used for comparison. This fact probably indicates that traffic is a relevant source of Pb in the street dust of Luanda where, unlike in more developed regions, leaded gasoline is still in use. The concentrations of trace elements in street dust are also remarkably homogeneous across the city as revealed by the low coefficients of variation for most elements (Table 1), including many that have historically been associated with typically anthropogenic—and highly variable—emission sources. Both facts suggest that natural sources dominate the composition of street dust in Luanda, with

the industrial facilities located to the North of the city contributing little to its load of trace elements, probably because they are quite distant from the study area and because the prevalent wind directions (from sea to land and vice versa) carry their emissions eastwards and westwards but not to the South.

The results of a factor analysis of the log-transformed data (to approximate normality, Table 3) seem to corroborate this idea. Five factors were extracted which together account for 71% of the total variance. Of them, only Factor 2 appears to be associated with a clear anthropogenic influence. Factor 1, with high loadings of Sc, Al, Ga, V, Th, Co and La, seems to represent the silicate matrix of the natural material in the street dust of Luanda, and is probably related to the contribution of soil particles of the "red sands" formation. As it was just remarked, Factor 2 appears to be the only one directly linked with non-natural sources. The association of Pb, Cd, Sb and Cu, and with lower loadings, Mo, Fe, Ni, Ba, Cr, Bi, Zn and Co suggests that Factor 2 represents a complex mixture of urban influences: traffic, characterized by Pb–Cu–Ba–Zn (De Miguel et al., 1997;

Table 2
Mean concentration of trace elements ($\mu g\,g^{-1}$) in street dust in several cities (last two columns show particle size—in μm—retained for analysis and the protocol used to digest the samples, respectively)

City	Ag	B	Ba	Fe	Cd	Cu	Cr	Pb	Zn	$\dot{\varnothing}$ (μm)	Digestion
Avilés[a]	1.31	9.57	361	42,200	22.3	183	41.6	514	4829	<2000*	$HCl + HNO_3$
Bahrain[b]					72		144.4	697.2	151.8	<595	$HCl + HNO_3$
Birmingham[c]					1.6	466.9		48	534	<63	$HClO_4 + HNO_3 + H_2SO_4$
Bursa[d]					3.1			210	57	<200	$HCl + HNO_3$
Coventry[c]					0.9	226.4		47.1	385	<63	$HClO_4 + HNO_3 + H_2SO_4$
Delhi[e]					18.94	512.28	4816.94	597.63	365.92	<500	$HClO_4 + HNO_3 + HF$
Kuala Lumpur[f]			1790		2.96	35.5		2466	344	<63	Σ sequential
London[g]				26,000	3.5	155		1030	680	<500*	$HCl + HNO_3$
Luanda	0.59	7.89	131.3	11,572	1.15	41.78	25.65	351.3	316.6	<100	$HCl + HNO_3$
Madrid[h]				19,300		188	61	1927	476	<100	$HNO_3 + HClO_4 + HF$
Manchester[i]				8767		113		265	653	<1000	HNO_3
Oslo[h]			526	51,452	1.4	123		180	412	<100	$HNO_3 + HClO_4 + HF$
Ottawa[j]	0.20			25,660	0.6	188	59	68	184	100–250	$HF + HClO_4$
Seoul[k]					3	101		245	296	<2000	$HCl + HNO_3$
Taejon[l]						57		52	214	<180	$HCl + HNO_3$

[a]Ordoñez et al. (2003)
[b]Akhter and Madany (1993)
[c]Charlesworth et al. (2003)
[d]Arslan (2001)
[e]Banerjee (2003)
[f]Ramlan and Badri (1989)
[g]Schwar et al. (1988)
[h]De Miguel et al. (1997)
[i]Robertson et al. (2003)
[j]Rasmussen et al. (2000)
[k]Chon et al. (1995)
[l]Kim et al. (1998)
[*]Sample was ground prior to digestion.

Table 3
Factor analysis (extraction method: maximum likelihood; rotation: Varimax) of the natural logarithms of the analytical results (for clarity, factor loadings below 0.3 have been omitted, and factor loadings above 0.600 are shown in bold)

Variable	Factor1	Factor2	Factor3	Factor4	Factor5	Communality
LnSc	**0.901**					0.884
LnAl	**0.788**			−0.339	−0.331	0.903
LnGa	**0.781**					0.693
LnV	**0.777**		−0.356			0.909
LnTh	**0.770**					0.698
LnCo	**0.732**	0.411		−0.383		0.858
LnLa	**0.695**		−0.477			0.760
LnCr	0.482	0.463			−0.413	0.730
LnPb		**0.830**				0.777
LnCd		**0.784**				0.717
LnSb		**0.705**				0.568
LnCu		**0.683**				0.588
LnMo	0.446	0.586				0.650
LnFe	0.523	0.535		−0.446		0.819
LnNi	0.337	0.500		−0.350		0.584
LnBa		0.488	−0.450			0.598
LnBi		0.458				0.339
LnCa			**−0.945**			0.977
LnSr			**−0.893**			0.916
LnU			**−0.862**			0.832
LnMg			**−0.818**			0.758
LnAs	0.507	0.363	−0.532		−0.435	0.868
LnNa				**−0.835**		0.745
LnK	0.370			**−0.761**	−0.346	0.862
LnMn		0.331		−0.553		0.471
LnZn	0.367	0.413		−0.551		0.620
LnB	0.327			−0.474	−0.403	0.596
LnTi			−0.359		**−0.678**	0.711
LnP				−0.550	**−0.602**	0.748
LnHg				−0.356	−0.507	0.428
LnAg					−0.471	0.280
Variance	6.090	4.810	4.618	3.683	2.684	21.886
% Var	19.6	15.5	14.9	11.9	8.7	70.6

Stigliani and Anderberg, 1991; Kowalczyk et al., 1978, 1982; Drew, 1975; Friedlander, 1973); uncontrolled incineration of wastes, a widespread practice in Luanda, which could supply significant amounts of Zn, Cd, Sb and Pb (Wadge and Hutton, 1985; Pacyna, 1983; Kowalczyk et al., 1978, 1982); and paint flakes from deteriorating old facades or recently redecorated walls, contributing high concentrations of Pb and Cd (Fergusson and Kim, 1991; Schwar et al., 1988; Davies et al., 1987; Rundle and Duggan, 1986). Variables Ca, Sr, U and Mg are grouped in Factor 3. Although CO_3^{2-} content has not been included in the Factor Analysis, the high correlation coefficients between this variable and those grouped in the third factor ($\rho_{Ca-CO_3} = 0.876$, $\rho_{Sr-CO_3} = 0.817$, $\rho_{U-CO_3} = 0.866$, $\rho_{Mg-CO_3} = 0.714$; all significant at $P = 0.01$, two-sided test) support the hypothesis that this elemental association (Ca–Sr–Mg)

represents the "carbonate" component of the natural matrix of Luanda's street dust. This natural component is probably associated with the influence of the more carbonate-rich facies (marl and limestone) of the Luanda formation. The inclusion of U in this group (as opposed to Th, included in Factor 1) is discussed below. Factor 4 is defined by Na and K and, to a lesser extent, Mn, Zn, P, B and Fe. This combination of variables is probably related to the influence of the marine aerosol (Kowalczyk et al., 1978) and the corrosive action of sea spray on the metal structures (roofs, window ledges, gates, etc.) of Luanda's urban landscape. Lastly, no clear explanation has been found for Factor 5, in which Ti is grouped with elements that show similar or higher loadings on other factors (i.e. P, As and Cr) and with Hg and Ag which (as their low communalities suggest) would form individual factors of

their own if the number of factors extracted were increased.

Probably because natural sources dominate the composition of street dust in Luanda, some of the geochemical processes that take place in soils are also revealed in street dust. A good example of this fact is the separation of U and Th between the "silicate" and "carbonate" natural factors (Table 3). Both elements have similar electron configurations and occur in nature in the tetravalent oxidation state, while their ions have similar radii and can substitute extensively for each other. Under oxidising conditions, however, uranium forms the uranyl ion (UO_2^{2+}, oxidation state $+6$) whose compounds are soluble in water. Therefore, under the conditions that prevail in the outcrops of "red sands" and in street dust, uranium behaves as a mobile element and can be separated from thorium, which exists only in the tetravalent oxidation state and whose compounds are generally insoluble. This phenomenon, i.e. separation of Uranium from Thorium, has also been observed in earlier studies of street dust (De Miguel et al., 1997). Three possible mechanisms can be put forward to explain the subsequent strong association of uranium and a carbonate matrix. In the presence of carbonate ions, U^{6+} could theoretically precipitate as UO_2CO_3, and be, therefore, effectively retained in the parent geologic material (uranium concentrations are higher in the "Luanda formation" than in the "red sands") and in the street dust ultimately derived from it. However, the range of pH and Eh values in which UO_2CO_3 is stable is quite narrow, and it is more likely that U^{6+} would form the stable aqueous carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Gabriel et al., 1998; Krauskopf and Bird, 1995). Although retention of these complexes on a solid matrix is possible in the form of ternary iron oxide–U(VI)–carbonato complexes (Bargar et al., 2000), the most probable mechanism of uranium fixation to the carbonate material is coprecipitation with calcium carbonate, which would explain the high correlation of uranium with both Ca and CO_3^{2-}. This process was investigated by Abdelouas et al. (1998) who concluded that uranium is effectively removed from solution through coprecipitation with calcite and aragonite at relatively high temperatures (24 °C) and, correspondingly, low calcium carbonate solubility.

A second example of a natural geochemical processes reproduced in street dust concerns arsenic and vanadium. The concentrations of both elements in the street dust of Luanda are strongly correlated ($\rho = 0.813$, significant at $P = 0.01$, two-sided test) and this association seems to arise from a similar adsorption behaviour. In natural soils, arsenic and vanadium occur primarily in their pentavalent state forming oxyanions (i.e. arsenates and vanadates) (Adriano, 1986). These oxyanions can bind to natural organic matter and can also be strongly adsorbed on mineral surfaces by a ligand-exchange mechanism, in which an OH or OH_2^+ surface group is displaced by an O of the oxyanion to form an inner-sphere complex (White, 1997). Once so chemisorbed, As and V are not likely to be desorbed again (Kabata-Pendias and Pendias, 1992) and their common mode of accumulation in the soil, and consequently their correlation, is preserved as these natural soil particles are transported and deposited within the city limits to become part of street dust.

3.1. Exposure and risk assessment

The model used in this study to calculate the exposure of children to the elemental toxicants in street dust is based on those developed by the US Environmental Protection Agency (US Environmental Protection Agency, 1996) and the Dutch National Institute of Public Health and Environmental Protection (van den Berg, 1995) for the definition of guidelines or screening levels of contaminants in soils in urban exposure scenarios. The following assumptions underlie the model applied in Luanda:

(a) Children are exposed to street dust through three main pathways: ingestion of dust particles, inhalation of dust particles, and dermal contact with dust particles;

(b) Intake rates and particle emission and volatilization factors for street dust can be approximated by those developed for soil;

(c) Biometric and exposure parameters of a child in Luanda are similar to those of a US or Dutch child;

(d) The overall non-cancer risk experienced by a child can be computed for each element by summing the individual risks calculated for each exposure pathway. For As, the only carcinogen for all three exposure modes considered in the model (Cd, Co, Cr and Ni are considered carcinogens only through inhalation), the aggregate risk is calculated by summing the individual cancer risks across all exposure pathways (US Environmental Protection Agency, 1989);

(e) Except for mercury, the only volatile element, inhalation refers to the intake of particles under 100 μm via mouth and nose. Inhalation-specific toxicity data are available only for Al, As, B, Ba, Cd, Co, Cr, Mn and Ni. For the other eleven elements included in the risk analysis, the toxicity values considered for the inhalation route are the corresponding oral reference doses and slope factors, on the assumption that, after inhalation, the absorption of the particle-bound toxicants will result in similar health effects as if the particles had been ingested (Van den Berg, 1995; Naturvårdsverket, 1996);

(f) Although exposure duration has been set at 6 years, chronic reference doses are appropriate to evaluate non-carcinogenic risk.

(g) For carcinogens, exposure to street dust is quantified as a lifetime average daily dose, i.e. the weighted average of the exposure experienced by an individual as a child and as an adult.

Exposure is expressed in terms of a daily dose and is calculated separately for each element and for each exposure pathway. Specifically, the doses contacted through ingestion and inhalation of particles, and the dose absorbed through the skin have been calculated as shown in Eqs. (1)–(3) (adapted from US Environmental Protection Agency, 1996). For mercury, the only element of those included in the study with a significant vapour pressure at ambient temperatures, an additional route of exposure, i.e. inhalation of vapours, has been considered (Eq. (4)).

Dose contacted through ingestion of street dust particles:

$$D_{ing}(\text{mg kg}^{-1}\,\text{day}^{-1})$$
$$= C(\text{mg kg}^{-1}) \times \frac{\text{Ing}\,R \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}. \qquad (1)$$

Dose contacted through inhalation of street dust particles:

$$D_{inh}(\text{mg kg}^{-1}\,\text{day}^{-1}) = C(\text{mg kg}^{-1}) \times \frac{\text{Inh}\,R \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}}. \qquad (2)$$

Dose absorbed through dermal contact with street dust particles:

$$D_{dermal}(\text{mg kg}^{-1}\,\text{day}^{-1})$$
$$= C(\text{mg kg}^{-1}) \times \frac{\text{SA} \times \text{SL} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6}. \qquad (3)$$

Dose contacted through inhalation of vapours (for mercury only):

$$D_{vapour}(\text{mg kg}^{-1}\,\text{day}^{-1}) = C(\text{mg kg}^{-1}) \times \frac{\text{Inh}\,R \times \text{EF} \times \text{ED}}{\text{VF} \times \text{BW} \times \text{AT}}, \qquad (4)$$

where C is the concentration of trace element in street dust ("exposure point concentration"), Ing R the ingestion rate. In this study, Ing $R = 200\,\text{mg day}^{-1}$ (US Environmental Protection Agency, 2001), Inh R the inhalation rate. In this study, Inh $R = 7.6\,\text{m}^3\,\text{day}^{-1}$ (Van den Berg, 1995), EF the exposure frequency. In this study, EF $= 180\,\text{day yr}^{-1}$ (site specific), ED the exposure duration. In this study, ED $= 6\,\text{yr}$ (site specific), SA the exposed skin area. In this study, SA $= 2800\,\text{cm}^2$ (US Environmental Protection Agency, 2001), SL the skin adherence factor. In this study, SL $= 0.2\,\text{mg cm}^{-2}\,\text{day}^{-1}$ (US Environmental Protection

Agency, 2001), ABS the dermal absorption factor (unitless). In this study, ABS $= 0.001$ for all elements except arsenic. For arsenic, ABS $= 0.03$ (US Department of Energy, 2004), PEF the particle emission factor. In this study, PEF $= 1.36 \times 10^9\,\text{m}^3\,\text{kg}^{-1}$ (US Environmental Protection Agency, 2001), VF the volatilization factor. In this study, for elemental Hg, VF $= 32675.6\,\text{m}^3\,\text{kg}^{-1}$ (US Environmental Protection Agency, 2001), BW the average body weight. In this study, BW $= 15\,\text{kg}$ (US Environmental Protection Agency, 1989) and AT the averaging time. For non-carcinogens, AT (days) $= \text{ED} \times 365$; for carcinogens, AT (days) $= 70 \times 365 = 25550$.

For carcinogens, the lifetime average daily dose (LADD) used in the assessment of cancer risk has been calculated as a weighted average for each exposure route as shown in Eq. (5).

Calculation of the lifetime average daily dose for carcinogens:

$$\text{LADD}(\text{mg kg}^{-1}\,\text{day}^{-1})$$
$$= \frac{C(\text{mg kg}^{-1}) \times \text{EF}}{\text{AT}}$$
$$\times \left(\frac{\text{CR}_{child} \times \text{ED}_{child}}{\text{BW}_{child}} + \frac{\text{CR}_{adult} \times \text{ED}_{adult}}{\text{BW}_{adult}} \right), \qquad (5)$$

where all the acronyms denote the same variables as in Eqs. (1)–(4), except:

CR is the contact (or absorption) rate (i.e. ingestion [CR $=$ Ing R], inhalation [CR $=$ Inh R] and dermal absorption [CR $=$ SA $\times$ SL $\times$ ABS] rates).

In this study, Ing $R_{adult} = 100\,\text{mg day}^{-1}$; Inh $R_{adult} = 20\,\text{m}^3\,\text{day}^{-1}$; SA$_{adult} = 5700\,\text{cm}^2$; SL$_{adult} = 0.07\,\text{mg cm}^{-2}\,\text{day}^{-1}$; BW$_{adult} = 70\,\text{kg}$ and ED$_{adult} = 24\,\text{yr}$ (US Environmental Protection Agency, 1996 and 2001).

The concentration term, C (exposure-point concentration), in Eqs. (1)–(5) that, combined with the values for the exposure factors shown above, is considered to yield an estimate of the "reasonable maximum exposure" (US Environmental Protection Agency, 1989) is the upper limit of the 95% confidence interval for the mean (95% UCL). Since the concentration of most elements in the 92 samples approximate log-normal distributions, the 95% UCL has been calculated as in Eq. (6) (US Environmental Protection Agency, 1996).

Calculation of the exposure-point concentration term for log-transformed data:

$$C_{95\%\text{UCL}} = \exp\left\{ \bar{X} + 0.5 \times s^2 + \frac{s \times H}{\sqrt{n-1}} \right\}, \qquad (6)$$

where $\bar{X}$ is the arithmetic mean of the log-transformed data, s the standard deviation of the log-transformed data, H the H-statistic (Gilbert, 1987) and n the number of samples.

Table 4
Hazard quotient and risk for each element and exposure pathway

Element	C (95% UCL)	Oral RfD	Dermal RfD	Inhal. RfD	Oral SF	Dermal SF	Inhal. SF	HQ_{ing} $(Risk_{ing})$	HQ_{inh} $(Risk_{inh})$	HQ_{dermal} $(Risk_{dermal})$	HQ_{vapour}	$HI = \Sigma HQ_i$	RISK
Ag	6.30E−01	5.00E−03	9.00E−04					8.29E−04	2.32E−08	1.29E−05		8.42E−04	
Al	5.06E+03	1.00E+00	1.00E−01	1.43E−03				3.33E−02	6.50E−04	9.32E−04		3.49E−02	
As-non canc.	5.20E+00	3.00E−04	1.23E−04					1.13E−01	3.16E−06	2.32E−02		1.36E−01	
As-cancer	5.20E+00				1.50E+00	3.66E+00	1.51E+01	6.24E−06	4.00E−09	1.44E−06			7.69E−06
B	8.30E+00	2.00E−01	1.80E−01	5.71E−03				2.72E−04	2.66E−07	8.45E−07		2.73E−04	
Ba	1.38E+02	7.00E−02	4.90E−03	1.43E−04				1.30E−02	1.77E−04	5.18E−04		1.37E−02	
Cd-non canc.	1.20E+00	1.00E−03	1.00E−05					7.91E−03	2.21E−07	2.21E−03		1.01E−02	
Cd-cancer							6.30E+00		3.89E−10				3.89E−10
Co-non canc.	3.10E+00	2.00E−02	1.60E−02	5.71E−06				1.00E−03	9.82E−05	3.51E−06		1.11E−03	
Co-cancer							9.80E+00		1.53E−09				1.53E−09
Cr-non canc.	2.60E+01	3.00E−03	6.00E−05	2.86E−05				5.80E−02	1.70E−04	8.12E−03		6.63E−02	
Cr-cancer							4.20E+01		5.70E−08				5.70E−08
Cu	4.40E+01	4.00E−02	1.20E−02					7.23E−03	2.02E−07	6.75E−05		7.30E−03	
Hg	1.40E−01	3.00E−04	2.10E−05	8.57E−05				3.15E−03	8.79E−08	1.26E−04	1.28E-02	1.61E−02	
Mn	2.70E+02	4.60E−02	1.84E−03	1.43E−05				3.86E−02	3.47E−03	2.70E−03		4.48E−02	
Mo	2.10E+00	5.00E−03	1.90E−03					2.79E−03	7.80E−08	2.06E−05		2.81E−03	
Ni-non canc.	1.10E+01	2.00E−02	5.40E−03					3.52E−03	9.83E−05	3.65E−05		3.55E−03	
Ni-cancer							8.40E−01		4.61E−10				4.61E−10
Pb	3.78E+02	3.50E−03	5.25E−04					7.10E−01	1.98E−05	1.32E−02		7.23E−01	
Sb	3.50E+00	4.00E−04	8.00E−06					5.77E−02	1.61E−06	8.08E−03		6.58E−02	
Sr	1.78E+02	6.00E−01	1.20E−01					1.95E−03	5.46E−08	2.73E−05		1.98E−03	
U	1.00E+00	6.00E−04	5.10E−04					1.10E−02	3.08E−07	3.63E−05		1.10E−02	
V	2.10E+01	7.00E−03	7.00E−05					1.98E−02	5.53E−07	5.54E−03		2.53E−02	
Zn	3.33E+02	3.00E−01	6.00E−02					7.30E−03	2.04E−07	1.02E−04		7.40E−03	

The doses thus calculated for each element and exposure pathway are subsequently divided by the corresponding reference dose to yield a hazard quotient (HQ) (or non-cancer risk), whereas for carcinogens the dose is multiplied by the corresponding slope factor to produce a level of cancer risk. The toxicity values used in the analysis were taken from the US Department of Energy's RAIS compilation (US Department of Energy, 2004). The only exception is Pb whose reference doses have been derived from the WHO's (1993) Guidelines for Drinking Water Quality. Toxicity values for dermal absorption have been used as calculated in RAIS: oral reference doses are multiplied, and slope factors divided, by a gastrointestinal absorption factor to yield the corresponding dermal values. The elements selected for the quantitative risk assessment (Table 4) are those which present a toxicological profile for a chemical form of the element that may realistically occur in street dust.

The results of the risk assessment are shown in Table 4. Ingestion of dust particles appears to be the route of exposure to street dust that results in a higher risk for all elements, except Hg, followed by dermal contact. Given that street dust particles are less cohesive and more easily resuspended than soil grains, the particle emission factor used in the model, which has been developed for contaminated soils, may underestimate the concentration of trace elements in inhaled air. However, except for those elements with inhalation-specific reference doses and/or slope factors, it is unlikely that this exposure route would represent a higher risk than ingestion even for a higher, street dust-specific PEF since the HQ contributed by inhalation is four to five orders of magnitude lower than the corresponding ingestion value. Mercury is the only element for which inhalation (of vapours) seems to pose the highest risk due to the significant vapour pressure of Hg at ambient temperature. The results of the risk assessment also indicate that two elements, As and Pb, drive the risk derived from exposure to street dust. Arsenic, as a carcinogen that can cause lung and skin cancer, is the trace element of most concern. The level of cancer risk associated with exposure to this element in street dust (i.e. 7.69×10^{-6}) falls within the range of threshold values (10^{-4}–10^{-6}) above which environmental and regulatory agencies consider the risk unacceptable. Regarding non-cancer effects, Pb and As exhibit Hazard Indexes larger than 0.1. The HI of Pb (i.e. 0.72), which if contacted by children in large enough doses can trigger neurological and developmental disorders, is particularly close to the "safe" level of HI = 1.

4. Conclusions

The proportion of particles of a natural origin in the street dust of Luanda appears to be higher than in most cities of the northern hemisphere due to absence of significant industrial emission sources and of fossil fuel burning for domestic heating. A first consequence of this fact is the lower concentration of most trace elements and their more homogeneous spatial distribution in the street dust of Luanda than in the urban environments of more developed countries. A second consequence is that the behaviour of trace elements in street dust is governed by some of the same geochemical processes that affect the resuspended and displaced particles of natural soil from which it has mostly originated. Two examples of this are the separation of uranium, in its hexavalent form, from thorium and its subsequent association with carbonate materials, and the strong correlation of As and V that arises from their common mode of adsorption on solid materials as oxyanions.

The results of the risk assessment for the exposure of Luandan children to street dust are affected by a significant degree of uncertainty, associated mainly with the estimates of toxicity values and exposure parameters. This fact precludes the use of the results of this exercise to confirm or discard the presence of unacceptable levels of risk, and underscores the need for further research into site—and street dust-specific exposure and transport factors that would help to reduce the currently considerable uncertainty associated with risk calculations. Even with this limitation, risk assessment has proved to be a relevant tool to identify the trace elements and exposure pathways of most concern. In Luanda, it appears that the exposure pathway which results in the highest levels of risk for children exposed to street dust is ingestion of this material, and that two elements—As and Pb—are of most concern regarding the potential occurrence of health effects.

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