ARTICLE

Chemical Characterization and Human Health Risk Assessment Analysis of Cd, Cr, Fe, Mn and Zn Contents in Street Dust from Different Urban Sites in Minas Gerais State, Southeastern Brazil

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Health risk assessment of different metals (Cd, Cr, Fe, Mn and Zn) was evaluated in 12 street dust samples (SD) collected in Juiz de Fora and Congonhas cities, Southeast Brazil, from May to July 2017. Quartz, hematite, magnesium

and aluminum silicate were found in Congonhas' samples, while quartz, hematite, andaluzite, diopside, dolomite and calcite phases have been found in Juiz de Fora's samples. The main elements observed in the samples were Al, Fe, O and Si, elements such as Ca, K, Mg, Na and Ti were found in minor concentrations. The major mineral phases observed in SD samples by MLA were iron oxides and hydroxides, quartz, clay compounds and many phases containing the Al element, which are in accordance with the XRD analysis characterization. Analytes were detected in the following order: Fe > Zn > Mn > Cr > Cd, except for Mn > Zn in the Congonhas samples. The Zn contents found in some samples were higher than prevention value for industrial areas (2000 mg kg⁻¹). The metals Cd (56 to 90%) and Zn (37 to 59%) showed high gastrointestinal bioaccessibility. The Cr and Fe analytes presented low solubility ranging from 10 to 18% and from 8 to 10%, respectively. It was verified that Cd and Zn presented non-carcinogenic risk through dermal, ingestion and inhalation contact for the most samples studied. However, non-carcinogenic risk factor (HQ) obtained for Zn in all samples collected were greater than the limit set by USEPA. No carcinogenic risk was observed for Cd and Cr in the investigated samples.

Cite: Lourdes, A. M. F. O.; Cuin, A.; Delbem, I. D.; Campos, N. S.; Sousa, R. A.; Ciminelli, V. S. T.; Silva, J. C. J. Chemical Characterization and Human Health Risk Assessment Analysis of Cd, Cr, Fe, Mn And Zn Contents in Street Dust from Different Urban Sites in Minas Gerais State, Southeastern Brazil. *Braz. J. Anal. Chem.*, 2020, 7 (26), pp 36–50. doi: 10.30744/brjac.2179-3425.AR-34-2019

Received 31 October 2019, Revised 10 February 2020, Accepted 5 March 2020, Available online 31 March 2020.

Keywords: Trace elements, Street dust, Human health risk, Bioaccessibility.

INTRODUCTION

Street dust can be used as an indicator of environmental pollution. It is one of the main pathways of the plant, animal, and human exposure to toxic elements [1]. Street dust is defined as a complex matrix containing particles of different sources such as vehicles exhaust, organic materials, soil, deposited atmospheric particulate matter, etc., which can be a source of metallic elements [1-3].

Street dust also offers risk to human health due to the easy mobility of its particles, which may lead to human exposure through digestive, dermal, and inhalation [4]. Among the adverse effects, it can be mentioned the irritation of the upper respiratory tract, respiratory diseases such as lung cancer, acute respiratory infections, and also cardiac diseases [5].

Some studies have shown that trace elements, such as, As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn can be found in street dust samples (SD), which can be a point of concern since exposure to high levels of some of these elements can cause chronic poisoning [2,6]. In summer periods, the atmospheric concentrations are usually lower due to the leaching caused by the rains, and in the winter there is a higher concentration of pollutants due to the intense dry season [2,3]. In this sense, it is important the development of studies regarding the chemical characterization, including both mineral and trace elements composition, of this kind of samples from urban areas around the world.

Several techniques can be used to characterize atmospheric pollutants, such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Atomic Absorption Spectrometry (AAS). These techniques provide relevant information regarding the mineral phases, morphology and the elemental chemical composition of the investigated samples. Recently, the technique of mineral liberation analysis (MLA) has been used to measure the composition and texture of the minerals [7-10]. Although there are a large number of papers using these techniques [11-15], their using together in order to obtaining SD information may be new, especially when applied to bioaccessibility studies.

Bioaccessibility may be defined as the quantity of a compound that is available for absorption when dissolved in body fluids, such as gastrointestinal and pulmonary. Then, bioaccessibility assays with street dust samples can be used to estimate urban pollution and its possible effects on human health [4]. The metallic bioaccessible fractions are also used to estimate these effects through health-risk models [16,17]. These calculations involve the determination of the exposed amount of pollutants as well as estimating factors for carcinogenic and non-carcinogenic risks, for example [2].

In Brazil, there are few works regarding the characterization of street dust sample [7,8,18]. Furthermore, there are no studies available concerning the chemical characterization of street dust from Brazil's southeastern cities associated with bioaccessibility assays. Thus, the goals of this work were the chemical characterization of urban dust samples from Juiz de Fora and Congonhas cities, in the Minas Gerais State, Brazil, and the evaluation of the potential health risks associated with its exposure.

MATERIALS AND METHODS

Studied Area

The studies were carried out with four samples collected in two different cities of Minas Gerais State, Brazil. Juiz de Fora is located in Zona da Mata, Minas Gerais State, at 43°20'40" west longitude and 21°41'20" south latitude. It has a total area of 1,435.749 km² with a population of approximately 560,000 inhabitants and approximately 242,000 vehicles. The city is located in a mountainous region, with altitudes ranging from 467 m to 1104 m and the climate is tropical high-altitude [19,20]. According to Environmental Company of the State of São Paulo [21] the 75% of air pollution in urban centers is due to the vehicles. Thus, an increase of vehicle traffic can affect air quality due to higher pollutants emission in the atmosphere. Mining-related activities emit atmospheric particulate matter (APM) for nearby areas, and air quality

impacts are a concern, as local soil, mineral dust, heavy equipment emissions and combustion sources and resuspension of particulate matter (PM) may all contribute to PM in surrounding areas [22]. High metal content in APM was observed by Mimura et al. [18] near a zinc mining industry, established in Juiz de Fora since 1980. The second city, Congonhas, is located in the macro region of Planning I in Minas Gerais state (20°29'59" south latitude and 43°51'59" west longitude). The city presents a total area of 306.45 km² with a terrain elevation varying from 800-1000 m. The annual mean temperature is 20.9 °C and the climate is humid subtropical. The estimated population of Congonhas in 2018 was about 54,200 inhabitants [20, 23]. United Nations Educational, Scientific and Cultural Organization (UNESCO) [25] recognize Congonhas as a World Cultural Heritage. The famous Sanctuary of "Bom Jesus de Matozinhos" was built in the 19th century on Baroque style. The atmospheric pollution resulting from fossil fuels burning and intense mining activities has been caused progressive corrosion of the statues over the years. The mining-metallurgical industry is the base of Congonhas' economy, and some researchers estimate that an amount of 120 tons of iron ore dust/mon is deposited on the city's public roads. As a result, this deposition in addition to the health problems, affect the integrity of humanity's historical heritages located in Congonhas [23].

Sample Collection

Street dust samples (SD) were collected in the following sampling sites: Juiz de Fora site 1-JF: Igrejinha district (latitude: 21°42'30.67"S, longitude: 43°29'8.90" W, altitude: 713 m) that is a region close to an industrial area; Juiz de Fora site 2-JF: (latitude: 21°46'10.34" S, longitude: 43°21'50.82" W, altitude: 935 m) at the meteorological station of the Federal University of Juiz de Fora, a region with mild traffic and high altitude. Congonhas site 1-CON: São Vicente village (latitude: 20°51'0792" S, longitude: 43.847277"), in the historical center; Congonhas site 2-CON: Federal Institute of Minas Gerais (latitude: 20.485256" S, longitude: 43.843066" W) near to the BR 040 federal highway that connects Brasília, the capital of Brazil, to Rio de Janeiro and shows an intense vehicle traffic. Samples were collected by sweeping 1 m² of a paved surface using plastic brooms and shovels at each of the collection site from May to July 2017, totalizing 12 samples. The contents were stored in plastic bags and transferred to the laboratory. Materials such as stones, branches and leaves were removed and the samples were sieved to a particle size less than 63 µm using a stainless steel sieve [26-28]. Areas with distinct characteristics were chosen in order to clearly demonstrate their influence on the samples investigated.

Instrumentation

A Thermo Scientific atomic absorption spectrometer with double atomization (flame and graphite furnace), model SOLAAR M5 (Waltham, MA, USA), equipped with a deuterium lamp as background corrector was employed for all element determinations. Flame Atomic Absorption Spectrometry (F AAS) was used to determine the contents of Cr, Fe, Mn and Zn while Cd and Cr pulmonary fractions were determined by graphite furnace atomic spectrometry (GF AAS). Hollow cathode lamps of the analytes were employed as radiation sources (Cd: 228.8 nm; Cr: 357.8 nm; Fe: 248.3 nm; Mn: 279.5 nm; Zn: 213.9 nm) and resolution of 0.5 nm for all analytes. For the F AAS, the gas mixture N₂O/C₂H₂ (Cr) and air/C₂H₂ (Cr, Fe, Mn, and Zn) have been used. The fuel flow rate were 4.2 L min⁻¹ (Cr), 1.1 L min⁻¹ (Fe) and 1.1 L min⁻¹ (Mn and Zn). For GF AAS determinations, 99.99% purity argon was used as purge gas (0.2 L min⁻¹). The gas flow was stopped during atomization. The optimized pyrolysis temperatures were 300 and 1600 °C while atomization temperatures were 1000 and 2600 °C, for Cd and Cr, respectively. All measurements were performed in triplicate.

An ultrasound bath Unique Ultrasonic Cleaner, model USC 2800A, with a frequency of 40 kHz, power of 150 W and with time and temperature control was employed to extraction procedures (total and gastrointestinal contents). The samples were accurately weighted in an analytical balance (ME 204, Mettler Toledo, Columbus, OH, USA) and a metabolic bath (SOLAB, model Dubnoff SL-157/22) were used to bioaccessible essays.

The mineral phases of the samples were identified by X-Ray Diffraction (XRD) using a diffractometer

(D8 Advance - Vinci, Bruker). Morphological information was obtained by Scanning Electron Microscopy (SEM) and microanalysis of the samples were done using an Energy Dispersive X-Ray Spectrometer, EDX (Hitachi TM 3000) spectrophotometer. For the Mineral Liberation Analyzes (MLA), a FEV Quanta 650 model SEM-FEG equipped with two Bruker Quanta X-Flash 5010 EDS analyzers and the MLA software package version 3.1.1.283 was used. These analyzes were done at the Microscopy Center of the Federal University of Minas Gerais (CM-UFMG). For each of the particles detected in the images, EDS spectra were collected considering a range of pixels pre-defined by the system operator. The particles were classified by comparing the spectra acquired during measurements with those belonging to a mineral reference list. In this study, the ford analysis or grain-based X-ray mapping (GXMAP) measurement method was applied to identify the phases (minerals or not) present in the sample. In this type of measurement, a series of images is collected. The X-ray mapping is employed within a range of grayness intensities stipulated by the operator [24]. The SEM and MLA instrumental operating parameters are showed in the Table I.

Table I. Related parameters to SEM and to MLA

SEM Parameters	Values	MLA Parameters	Values
Voltage (kV)	25	Scan Speed	8
Working distance (mm)	11	Resolution	500 x 500
Spot size	5	Pixel size ($\mu\text{m}/\text{px}$)	0.60
Brightness	79.6	Acquisition time (ms)	10
Contrast	22.9	GXMAP BSE trigger	18-255
BSE calibration	Cu 245	Minimum grain size (px)	4
		GXMAP X-ray step (px)	6

Reagents and Solutions

All reagents used were analytical grade chemical reagents. The standards used for the construction of the analytical curves were prepared from stock solutions of Fe and Mn (Merck), Cd, Cr and Zn (Qhemis) with concentration of 1000 mg L^{-1} . The standards were prepared in acid medium ($1.0\% \text{ v/v HNO}_3$). The concentrations of the standards used in the construction of the analytical curves ranged from 0.5 to 3.0 mg L^{-1} and 1.0 to $8.0 \mu\text{g L}^{-1}$ (Cr), 0.5 to 16.0 mg L^{-1} (Fe), 0.1 to 4.0 mg L^{-1} (Mn), 0.25 to 2.0 mg L^{-1} (Zn), and 0.5 to $4.0 \mu\text{g L}^{-1}$ (Cd). The reagents used in the extraction procedures were HCl $37\% \text{ v/v}$ (Vetec), HNO_3 $65\% \text{ w/v}$ (Vetec, Cosmos, Rio de Janeiro - Brazil) and H_2O_2 $30\% \text{ v/v}$ (Isofar, Duque de Caxias, Brazil), NaHCO_3 (Isofar, Duque de Caxias, Brazil), Pepsin (Sigma Aldrich, St. Louis, MO, USA), Pancreatin (Sigma Aldrich, St. Louis, MO, USA), Bile (Sigma Aldrich, St. Louis, MO, USA), MgCl_2 , NaCl, Na_2HPO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, St. Louis, MO, USA), $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (Isofar, Duque de Caxias, Brazil), KCl, NaHCO_3 , Na_2SO_4 (Isofar, Duque de Caxias, Brazil). Used glassware were decontaminated in acid bath ($10\% \text{ v/v HNO}_3$) for 24 hours and rinsed at least three times with deionized water before use. All solutions were prepared with purified water at $18.2 \text{ M}\Omega$ in Elga Purelab Option-Q system.

Sample Preparation for AAS determination

Method 1: Extraction using ultrasonic bath (Total contents)

Total metallic contents were determined in SD samples after an ultrasound extraction according to the method developed by Mimura et al. [18]. For this, 100 mg of SD samples were mixed with 5 mL of aqua regia in 50 mL flasks. This mixture was placed in the ultrasonic bath for 10 min at room temperature ($\pm 25^\circ\text{C}$). The obtained extracts were filtered, centrifuged and transferred quantitatively into volumetric flasks. The volume was completed with deionized water to 50 mL .

Method 2: Procedure for in vitro gastrointestinal digestion

The bioaccessible fractions of the analytes were determined based on the method from Campos et al. [29]. For this, 100 mg of SD samples were mixed with 3.50 mL of 0.01 mol L⁻¹ HCl solution. The pH was adjusted to 2.0 with a 1 mol L⁻¹ HCl solution and 400 µL of pepsin solution (6% w/v) was added. The mixtures were incubated in a metabolic bath with mild agitation (level 5) for 2 hours at 37 °C. Next, the pH of the solutions were adjusted to 7.0 by drop wise additions of NaHCO₃ 1 mol L⁻¹ solution and 700 µL of pancreatin (0.4 w/v) and bile salts (2.5% w/v) were added. The mixtures were incubated again for more 2 hours under the same heating and conditions described above. After this procedure, the obtained extracts were cooled to room temperature to inhibit the enzymatic activity and filtered on common paper filter. The filtered solutions (called chyme) were then centrifuged at 2000 rpm for 15 minutes and then filtered through 0.45 µm Milipore® membrane filters.

To the determination of the bioaccessible fractions, the chyme solutions were submitted to an ultrasound-assisted extraction. For this, 5.00 mL of the extracts were mixed with 3.00 mL of HNO₃ and 1 mL of H₂O₂. Then, the mixture was placed in the ultrasonic bath for 1 h at 65°C. After that, the volume was brought to 20 mL with deionized water. The bioaccessibility was calculated by dividing the gastrointestinal soluble contents of the analytes by total content determined by Method 1 and expressed in percentage.

Method 3: Procedure for in vitro pulmonary bioaccessibility

The Gamble method [30] was employed to determine pulmonary bioaccessible fractions. Details about the composition of the synthetic pulmonary fluid used can be reached in Table II. Approximately 1.0 g of SD samples were mixed with 20 mL of this solution at pH = 7.4. Next, the mixtures were incubated in a metabolic bath with mild agitation (level 5) for 24 hours at 37 °C. After this, the solutions were centrifuged for 15 minutes at 2,500 rpm and the soluble part was filtered through a 0.45 µm Milipore® membrane filter and stored in plastic flasks (acidified with 2% nitric acid) at refrigeration (10 °C) until the analysis. In this case, the analytes contents were determined by direct analysis and no sample preparation steps were necessary. Only sample dilution for analyte adjustment in the analytical curves used.

Table II. Composition of Gamble solution employed to pulmonary bioaccessibility experiments

Salt	Concentration (g L ⁻¹)
MgCl ₂	0.095
NaCl	6.019
KCl	0.298
Na ₂ HPO ₄	0.126
Na ₂ SO ₄	0.063
CaCl ₂ .2H ₂ O	0.368
C ₂ H ₃ O ₂ Na	0.574
NaHCO ₃	2.604
C ₆ H ₅ Na ₃ O ₇ .2H ₂ O	0.097

Analysis by MLA, SEM and MEV

For the other techniques used, it was not necessary samples pretreatment, so the direct analysis was done.

Health-risk assessment

Health-risk models, including carcinogenic (CR) and non-carcinogenic risk ratio (HQ) ones, from USEPA [16,17] were used to investigate the levels of the elements determined in the samples collected in this study. These estimating factors were calculated according to equations 1 to 4, as follow:

$$CDI_{ingestion} = \frac{C \times IngR}{BW} \times \frac{EF \times ED}{AT} \times CF \quad \text{Equation 1}$$

$$EC_{inhalation} = C \times \left(\frac{ET \times EF \times ED}{ATn} \right) \quad \text{Equation 2}$$

$$DAD_{dermal} = \frac{C \times SA \times AF \times ABS}{BW} \times \frac{EF \times ED}{AT} \times CF \quad \text{Equation 3}$$

$$HQ = \frac{CDI_{ingestion}}{RfDo} = \frac{EC}{RfCi \times 1000 \mu g m g^{-1}} = \frac{DAD}{RfDo \times GIABS} \quad \text{Equation 4}$$

$$CR = CDI_{ingestion} \times SFo = IUR \times EC = DAD \times \frac{SFo}{GIABS} \quad \text{Equation 5}$$

Where C is the element concentration (mg kg⁻¹) in SD samples. The concentrations obtained after the total extraction of the gastric fraction were used for determination of the ingestion parameter (CDI). The inhalation parameter (EC) values were obtained after the extraction of the pulmonary fraction. IngR is the ingestion rate (the default values for the ingestion exposure of soil/dust used were 200 mg day⁻¹ for children and 100 mg day⁻¹ for adults); EF: exposure frequency (180 days year⁻¹ in this study); ED: exposure period (6 years for children and 24 years for adults); BW: the average body weight (15 kg for children and 70 kg for adults); AT: average in time (for non-carcinogens, AT = EDx365 days; for carcinogens, AT = 70x365 = 25,550 days); CF: conversion factor (10⁻⁶ kg mg⁻¹); SA: surface area of the skin in contacts with the airborne particulates (3300 cm² for adults and 2800 cm² for children); AF: skin adherence factor for the airborne particulates (0.2 mg cm⁻² for both adults and children); ABS: dermal absorption factor (0.001 for Cd; no values were available for other elements; therefore, 1.0% was used in the present study); ET: exposure time (hours/day); ATn: average time (for non-carcinogens, AT = ED x 365 days x 24 hours/day; for carcinogens, ATn = 70 year x 365 days/year x 24 h). All parameters used in the calculation of CDI, DAD and EC were found in reports published by the USEPA during different periods [16]. For the calculations of HQ and CR it was used the parameter RfDo that is the oral reference dose (mg kg⁻¹day⁻¹); RfCi as inhalation reference concentrations (mg m⁻³); SFo as oral slope factor ((mg kg⁻¹day⁻¹)⁻¹); GIABS as gastrointestinal absorption factor; IUR as inhalation unit risk ((mg m⁻³)⁻¹).

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The XRD technique was used to map the main minerals present in the investigated samples. The obtained diffractograms (Figure 1) were compared with the Crystallography Open Database standard (COD) files. In the samples from Congonhas sampling sites, the identified minerals were quartz (SiO₂), hematite (Fe₂O₃), magnesium (MgO₃Si) and aluminum silicate (Al₂O₅Si). Thus, the main elements found in

this type of sample were Si, Fe, O, Al and Mg. These mineralogical data show the same profile found by Queiroz et al. [7] for samples of atmospheric particulate material from Belo Horizonte (Minas Gerais State). For Juiz de Fora samples, the identified phases were quartz (SiO_2), hematite (Fe_2O_3), andaluzite ($\text{Al}_2\text{O}_3\text{Si}$), magnesium silicate (MgO_3Si), periclase (MgO) and lime (CaO). It can be seen that both the SD and APM have common majority constituents indicating common origin.

Figure 1. X- ray diffraction of SD samples collected in May 2017 (a) Congonhas-Site 1 (b) Juiz de Fora-Site.

Scanning Electron Microscopy (SEM) and Energy Scattering X-ray Spectroscopy (EDS)

The SD samples from Congonhas presented particle size distribution from 36 to 125 μm while SD samples from Juiz de Fora showed particle size varying from 32 to 156 μm (Figure 2). In general, the particle size distribution for both cities did not show significant differences, probably due to the origins of the particles emissions, such as constructions, industrial activities and burning of fossil fuels, which is similar for both regions.

The investigated samples presented particles (rounded and cylindrical) with characteristic of biological origin, which include pollen, spores, bacteria and viruses [29]. Rough and schistose particles are irregularly shaped groups and were observed as individual particles or as small particles nucleated onto larger particles forming agglomerates. The observed characteristics reflect the minerals found in the soil, and may be associated with natural source [32]. Additionally, in the samples from Juiz de Fora it was observed crystalline-form particles that are characteristic of natural and marine origin [33-34]. According to the literature [35] particles smaller than 100 μm can penetrate the respiratory tract while particles smaller than 10 μm (PM_{10}) can penetrate in the nasal and oral cavities and penetrate into the larynx, while particles smaller than 2.5 μm ($\text{PM}_{2.5}$) can penetrate even deeper into the respiratory system reaching the lungs (bronchi and alveoli), these particles are also known as thoracic particles. In the present study particles with those characteristics were found in all investigated samples.

Figure 2. Image obtained by SEM for SD samples collected in Juiz de Fora and Congonhas in May 2017. Magnification: x 200 (a) Site 1-JF; (b) Site 2-JF; (c) Site 1-Con; (d) Site 2-Con.

Figure 2. Image obtained by SEM for SD samples collected in Juiz de Fora and Congonhas in May 2017. Magnification: x 200 (a) Site 1-JF; (b) Site 2-JF; (c) Site 1-Con; (d) Site 2-Con. (Continuation)

Regarding EDS results (Figure 3 and Table III), the SD samples from the two cities presented Al, Fe, O and Si in their main constitution. Elements such as Ca, K, Mg, Na and Ti were also found in the samples, but their contents were less than 3% (w/w). The presence of Na in the samples collected in Juiz de Fora may be an indicative of the marine contribution, which is explained by the relative proximity of the studied area with the sea, as observed by Mimura et al. [18]. The EDS data are in agreement with those observed in XRD, and the presence of Fe and Al oxides are in agreement with data reported in literature [36–37].

Figure 3. EDS spectra obtained for SD samples collected in May 2017 in Juiz de Fora (a) Site 1; (b) Site 2; and Congonhas (c) Site 1; (d) Site 2.

Table III. Composition of SD samples collected in May 2017 obtained by EDS (% w/w)

Site	Analytes (% w/w)			
	Al	Fe	O	Si
P1-Juiz de Fora	2.3	2.2	64.4	18.4
P2-Juiz de Fora	7.3	0.3	60.9	14.3
P1-Congonhas	8.2	13.4	64.7	8.5
P2-Congonhas	5.9	21.3	66.4	5.0

Mineral Liberation Analysis (MLA)

The major mineral phases observed in SD samples by MLA (defined as > 1% wt) are Fe oxides and hydroxides, quartz, clay compounds and many phases containing the Al element, which are in accordance with the XRD analysis characterization. According to these results, Fe is mainly bonded to phases with oxides while Mn was observed in association with the group of pyroxenes found in many igneous and metamorphic rocks (Table IV).

Table IV. Mineral phases (% by weight) in SD samples

Phases	Samples			
	P1 – Con.	P2 – Con.	P1 – JF	P2 – JF
Fe Oxides/Hydroxides	78.05	72.25	4.71	10.99
Quartz	13.55	17.27	22.10	46.20
Andesine	<1%	1.26	15.18	10.78
Andratite	<1%	<1%	<1%	1.25
Calcite with Fe	1.34	1.10	<1%	<1%
Albite	<1%	<1%	<1%	1.68
Orthoclase	<1%	0.85	2.75	6.10
Siderite	<1%	<1%	<1%	1.18
Hornblende	<1%	<1%	2.35	2.92
Ilmenite	<1%	<1%	3.07	2.15
Pyroxenes	^a ND	^a ND	2.27	1.32
Vesuvianite	<1%	<1%	<1%	1.22
Biotite	<1%	<1%	1.63	<1%
Clay Minerals	<1%	<1%	33.45	5.77
^b Mixture	<1%	<1%	<1%	<1%
Total	100.0	100.0	100	100.0
Total Particles	6457	7157	8140	16132

^aNot determined; ^bAl, Si, P, S, Cl, Ca, Ti, Mn, Fe, Zn and O.

The pyroxenes are silicon and aluminum oxides with Ca, Na, Fe, Li, Mg, Mn, Zn substituting Si and Al. The general formula is $XY(Si, Al)_2O_6$, where X represents Ca, Na, Fe, Mg, Mn, Zn and Li; and Y represents smaller ions, such as Al, Cr, Co, Fe^{3+} , Mg, Mn, Sn, Ti and V. Chromium appeared mainly in FeOOH

0.12 (P1) and 0.59 (P2) for samples from Juiz de Fora, and 0.54 (P1) and 0.43 (P2) for Congonhas samples. Zn appeared mainly connected to mixtures with other compounds. The Cd probably due to its low concentration was not observed in the MLA analysis. The MLA tool allows the quantitative analysis of single particles of large number of grains. The total number of particles varied from 6,457 to 16,132, which provides good statistics in both cases. The difference observed was due to the larger number of particles that will be analyzed in the samples with a finer particle size distribution.

Health-risk assessment

Regarding total contents (Table V), Fe was the most abundant trace element found in SD samples from Juiz de Fora followed by Zn > Mn > Cr > Cd. For Congonhas SD samples the observed order was Fe > Mn > Zn > Cr > Cd. According to the Brazilian legislation [38] Site 1 (Juiz de Fora) showed both Cd and Cr contents above VP (prevention value – limit value of a substance in soil that cause no changes in its characteristics) for these elements (Cd: 1.3 mg kg⁻¹ and Cr: 75 mg kg⁻¹) which needs attention. Values for Cr were also found above allowed in locations 2 and 3. On the other hand, the Zn contents found in the samples from Sites 1-JF and 1-CON were higher than VP values for industrial areas (2000 mg kg⁻¹). These results are probably due to the influence of industrial activities, such as mining and metallurgy, on the study area. Mimura et al. observed similar behavior in rainwater [40] and atmospheric particulate matter [18].

Table V. Metal contents obtained by F AAS and GF AAS for a resuspended dust sample by ultrasonic bath extraction (mg kg⁻¹) (mean ± standard deviation, n = 3)

Month	Site	Analyte				
		^a Cd	^b Cr	^b Fe	^b Mn	^b Zn
May	P1-JF	1.84 ± 0.07	65.6 ± 3.6	54164 ± 217	1148 ± 60	10638 ± 57
	P2-JF	0.0587 ± 0.0023	28.2 ± 0.8	32313 ± 174	767 ± 59	545 ± 3.09
	P1-Con	0.0948 ± 0.0087	141 ± 7.3	53286 ± 181	2087 ± 85	2450 ± 17
	P2-Con	0.0468 ± 0.0024	48.8 ± 4.1	35424 ± 33	855 ± 13	153 ± 13
June	P1-JF	1.31 ± 0.03	92.4 ± 5.0	60281 ± 842	1490 ± 130	13091 ± 13
	P2-JF	0.0380 ± 0.0009	58.4 ± 2.48	39227 ± 59	880 ± 13	365 ± 17
	P1-Con	0.0229 ± 0.0006	74.8 ± 6.95	52094 ± 529	2974 ± 67	1365 ± 44
	P2-Con	0.0465 ± 0.0017	50.39 ± 3.59	23276 ± 117	3128 ± 15	278 ± 12
July	P1-JF	2.21 ± 0.34	98.2 ± 1.1	54149 ± 90	817 ± 4	10948 ± 60
	P2-JF	0.0569 ± 0.0002	82.2 ± 1.9	42955 ± 111	607 ± 5	640 ± 12
	P1-Con	0.0994 ± 0.001	36.7 ± 3.1	58940 ± 54	1097 ± 21	873 ± 63
	P2-Con	0.195 ± 0.001	46.3 ± 1.3	48055 ± 907	2800 ± 24	449 ± 60

^aµg kg⁻¹ / ^bmg kg⁻¹

The extracted contents of the metallic elements after *in vitro* gastrointestinal digestion are showed in Figure 4. The bioaccessible fraction levels were smaller than total contents showing that investigated trace elements were partially soluble in gastrointestinal tract. The metals Cd (56 to 90%) and Zn (37 to 59%) showed high gastrointestinal bioaccessibility while others, such as, Mn (19 to 35%), presented moderate solubility. The Cr and Fe analytes presented low solubility ranged from 10 to 18% and from 8 to 10%, respectively. The same behavior was observed by Xi Hun et al. [4] in APM from Nanjing (China).

Figure 4. Gastrointestinal bioaccessible contents of Cd, Cr, Fe, Mn and Zn in SD samples from Juiz de Fora (JF) and Congonhas (Con) (mean of 12 samples expressed in %, RSD < 5%, n = 3 readings).

The results obtained after *in vitro* pulmonary bioaccessibility are shown in Figure 5. A lower solubility in synthetic pulmonary fluids was observed for all samples collected, with extractions minor above 50%. The Zn concentration in the pulmonary bioaccessible fractions varied in the range of 5 to 35% while the Cd concentration ranged from 8 to 26%. For Cr, Mn and Fe the concentration values ranged from 0.33 to 0.60, 0.34 to 1.1 and 0.21 to 2.0% respectively.

Figure 5. Pulmonary bioaccessible contents of Cd, Cr, Fe, Mn and Zn in SD samples from Juiz de Fora (JF) and Congonhas (Con) (mean of 12 samples expressed in %, RSD < 5%, n = 3 readings).

Carcinogenic (CR) and non-carcinogenic risk ratio (HQ) were calculated and the results are presented in Tables VI – VIII. For dermal contact risk, (Table VI) HQ values for Cd, Cr, Fe and Mn were lower than reference value (1) for adults and children in all samples collected (USEPA 2013). These results indicate no health-risk associated to dermal contact with the SD samples analyzed in this study. For Zn, HQ values for Site P1-JF were higher than one indicating health risk. Dermal contact with zinc compounds can cause skin irritation which may be an absorption pathway for those compounds into the bloodstream [5]. CR values were determined by Cd and Cr due to their carcinogenic classification according the International Agency

for Research on Cancer (IARC). For children the highest CR values found were 4.14×10^{-6} (Cd) and 5.0×10^{-4} (Cr) while for adults the CR values were 4.1×10^{-6} (Cd) and 7.7×10^{-5} (Cr). These results are considered acceptable since they are below 10^{-4} [16].

Table VII shows HQ and CR values for ingestion through gastrointestinal tract for Cd, Cr, Fe and Mn. All HQ values are below the set limit for adults and children. However, HQ values calculated for Zn in Sites P1 (32 for children and 14 for adults) and P2 (1.7 for children) from Juiz de Fora were higher than 1 indicating health risk. Ingestion of zinc compounds can cause nausea, diarrhea and intestinal irritation [5]. The maximum CR obtained for Cd and Cr were classified as acceptable for all points since its values were 1.4×10^{-5} (Cd) and 4.1×10^{-6} (Cr) for children, and 6.1×10^{-6} (Cd) and 1.8×10^{-5} (Cr) for adults.

Finally, the health risk assessment through inhalation was estimated by CR and HQ calculations which results are shown in Table VIII. Regarding CR calculations for Cd and Cr the highest values were 5.28×10^{-5} (Cd) and 9.2×10^{-8} (Cr) for adults and 1.3×10^{-5} (Cd) and 2.3×10^{-8} (Cr) for children, these values can be considered acceptable showing no carcinogenic risk. For Site 1-JF the values of HQ obtained for Fe were equal to 2.93 also indicating non-carcinogenic health risk. Additionally, for Cd and Zn, all HQ values for samples from both cities were higher than set limit indicating great health human risk. It demonstrates that remediation studies are needed for the studied regions because Cd is not desirable at any level for humans, as it plays no role in our body, and Zn can be harmful in large quantities.

Table VI. Values of non-carcinogenic risk (HQ) and carcinogenic risk (CR) dermal contact of analytes

Classification	Analyte	Samples							
		P1-JF		P2-JF		P1-Con.		P2-Con.	
		CR	HQ	CR	HQ	CR	HQ	CR	HQ
Children	Cd	1.0×10^{-6}	1.7×10^{-4}	3.0×10^{-8}	4.8×10^{-6}	5.5×10^{-8}	8.7×10^{-6}	2.0×10^{-7}	3.1×10^{-5}
	Cr	5.0×10^{-4}	2.0×10^{-1}	1.7×10^{-4}	1.1×10^{-1}	3.0×10^{-4}	2.0×10^{-1}	1.3×10^{-4}	8.4×10^{-2}
	Fe ^a	-	1.1×10^{-5}	-	6.5×10^{-6}	-	1.1×10^{-5}	-	4.7×10^{-6}
	Mn ^a	-	7.5×10^{-4}	-	4.0×10^{-4}	-	1.6×10^{-3}	-	1.5×10^{-3}
	Zn ^a	-	3.5	-	1.6×10^{-1}	-	4.8×10^{-1}	-	2.6×10^{-1}
Adults	Cd	4.1×10^{-6}	6.58×10^{-5}	1.2×10^{-7}	1.9×10^{-5}	5.5×10^{-8}	1.30×10^{-4}	2.0×10^{-7}	1.81×10^{-4}
	Cr	7.6×10^{-5}	5.9×10^{-2}	4.4×10^{-6}	2.9×10^{-2}	7.7×10^{-5}	5.1×10^{-2}	3.2×10^{-5}	2.1×10^{-2}
	Fe ^a	-	2.8×10^{-2}	-	1.6×10^{-6}	-	2.8×10^{-6}	-	1.2×10^{-6}
	Mn ^a	-	1.9×10^{-4}	-	1.2×10^{-4}	-	3.9×10^{-4}	-	3.7×10^{-4}
	Zn ^a	-	8.9×10^{-1}	-	4.0×10^{-2}	-	1.2×10^{-1}	-	6.6×10^{-2}

^aThere is no reference value

Table VII. Non-carcinogenic risk (HQ) and Carcinogenic risk (CR) values for the gastric fraction of the analytes

Type	Analytes	Samples			
		P1-JF	P2-JF	P1-Con.	P2-Con.
Children	Cd ^a	2.25×10^{-3}	7.5×10^{-5}	3.3×10^{-4}	3.72×10^{-4}
	Cd ^b	1.4×10^{-5}	4.7×10^{-7}	2.0×10^{-6}	2.3×10^{-6}
	Cr ^a	2.54×10^{-3}	6.5×10^{-6}	3.3×10^{-4}	3.7×10^{-3}
	Cr ^b	1.6×10^{-6}	4.1×10^{-6}	2.1×10^{-6}	2.3×10^{-6}
	Fe ^a	4.7×10^{-3}	4.0×10^{-3}	8.2×10^{-7}	2.6×10^{-7}
	Mn ^a	5.7×10^{-4}	4.1×10^{-4}	4.7×10^{-7}	5.3×10^{-7}
	Zn ^a	32	1.7	1.9×10^{-3}	1.2×10^{-3}

Table VII. Non-carcinogenic risk (HQ) and Carcinogenic risk (CR) values for the gastric fraction of the analytes (Cont.)

Type	Analytes	Samples			
		P1-JF	P2-JF	P1-Con.	P2-Con.
Adults	Cd ^a	9.6×10^{-4}	3.2×10^{-5}	1.30×10^{-4}	1.81×10^{-4}
	Cd ^b	6.1×10^{-6}	2.0×10^{-7}	8.22×10^{-7}	1.14×10^{-6}
	Cr ^a	1.1×10^{-3}	2.8×10^{-3}	1.3×10^{-4}	1.8×10^{-4}
	Cr ^b	1.6×10^{-6}	1.8×10^{-6}	8.2×10^{-7}	1.1×10^{-6}
	Fe ^a	1.1×10^{-2}	9.4×10^{-3}	4.7×10^{-7}	5.3×10^{-7}
	Mn ^a	3.1×10^{-2}	2.8×10^{-2}	2.2×10^{-1}	1.3×10^{-1}
	Zn ^a	14	7.2×10^{-1}	4.3×10^{-4}	6.0×10^{-4}

^aHQ and ^bCR

Table VIII. Non-carcinogenic risk (HQ) and Carcinogenic risk (CR) values for the lung fraction of the analytes

Type	Analytes	Samples			
		P1-JF	P2-JF	P1-Con.	P2-Con.
HQ (Adults/ Children)	Cd	2.0	7.7	4.5	4.2
	Cr	3.6×10^{-2}	2.0×10^{-1}	2.0×10^{-1}	2.5×10^{-1}
	Fe	2.93	1.1×10^{-1}	6.5×10^{-2}	7.0×10^{-2}
	Mn	3.14×10^{-2}	2.8×10^{-2}	2.2×10^{-1}	1.33×10^{-1}
	Zn	8320	786	1170	757
CR (Children)	Cd	1.3×10^{-5}	4.98×10^{-7}	2.9×10^{-7}	2.7×10^{-7}
	Cr	2.3×10^{-8}	1.5×10^{-8}	1.3×10^{-8}	1.6×10^{-8}
CR (Adults)	Cd	5.28×10^{-5}	2.0×10^{-6}	1.2×10^{-6}	1.1×10^{-6}
	Cr	9.2×10^{-8}	5.8×10^{-8}	5.2×10^{-8}	6.5×10^{-8}

CONCLUSION

This work describes the characterization of street dust samples from two southeastern Brazilian cities (Juiz de Fora and Congonhas) using different instrumental techniques such as F AAS, GF AAS, XRD, SEM-EDX and MLA. According to the results the street dust samples contained different minerals such as quartz hematite and clay. Additionally, the analyzed samples showed particles size below 100 μm , which can penetrate respiratory tract. Regarding health risk assessment, it was verified that Cd and Zn presented non-carcinogenic risk through dermal, ingestion or inhalation for the most samples studied. This behavior was also observed for Fe in samples from Site 1 of Juiz de Fora. Additionally, non-carcinogenic risk factor (HQ) obtained for Zn in all samples collected are greater than the set limit of USEPA, which suggests attention of Brazilian authorities as well. On the other hand, carcinogenic risk factor (CR) obtained for Cd and Cr in all collected samples are considered acceptable showing no carcinogenic risk through contact with street dust samples.

Acknowledgements

The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais), "Rede Mineira de Química", INCT Acqua (Instituto Nacional de Ciência e Tecnologia: Recursos Minerais, Água e Biodiversidade e Mineração), and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for financial support. The authors also thank the "Centro de Microscopia da Universidade Federal de Minas Gerais" for technical support.

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