Geoquimica, mineralogia e biodisponibilidade oral de chumbo, zinco e antimónio em poeiras domésticas recolhidas em habitações da cidade de Estarreja

Geochemistry, mineralogy and oral bioaccessibility of lead, zin and antimony in house dust collected from households in the city of Estarreja

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Resumo: Um estudo focado em elementos potencialmente tóxicos (EPTs) em poeiras recolhidas em dezanove habitações da cidade industrial de Estarreja, foi realizado para fins de estudos de avaliação da exposição humana. Este trabalho em particular tem como objetivo investigar a influência da mineralogia e geoquímica da poeira na bioacessibilidade oral de TEPs selecionados, estimada pelo Unified BARGE Method. Concentrações pseudo-totais e bioacessíveis de elementos maiores e traços foram determinadas por ICP – MS.. A composição mineral das amostras de poeira interior e exterior foi determinada por difração de raios X. Os resultados mostram que a composição química das poeiras discrimina completamente entre as amostras de poeira interior e exterior. O modelo de análise discriminante indica que sódio, magnésio, cádmio e ferro são as variáveis mais importantes na discriminação. . A mineralogia é dominada por um conjunto de minerais que ocorre na maioria das amostras: calcite, quartzo e fesdspatos, com micas em menor quantidade. Minerais do grupo da serpentina, como a lizardite, sais e óxidos-hidróxidos ocorrem nalgumas amostras, frequentemente em quantidades vestigiais. Os fatores de enriquecimento indicam que o zinco e o antimónio são os EPTs de maior preocupação. No entanto, algumas concentrações anómalas em amostras de poeira doméstica contribuíram para que o chumbo fosse também incluído no estudo. Os resultados dos testes de bioacessibilidade variam entre EPTs. Embora o chumbo e o zinco estejam marcadamente bioacessíveis, o antimónio ocorre principalmente em formas insolúveis, o que pode ser explicado pela diferente distribuição da fase sólida dos três elementos. Embora a poeira interior seja muito enriquecida em antimónio, uma possível exposição através da ingestão de poeira é significativamente reduzida pela baixa biodisponibilidade oral mostrada pelo EPT.

Palavras-chave : poeira doméstica, biogeoquimica, mineralogia, elementos potencialmente tóxicos, exposição humana.

Abstract: A pilot survey, focusing on potentially toxic elements (PTE) in house dust collected from nineteen households from the industrial city of Estarreja, was carried out for purposes of human exposure assessment studies. This study aims at investigating the influence of the dust mineralogy and geochemistry on the oral bioaccessibility of chosen PTEs, as estimated by the Unified BARGE method Pseudo-total and bioaccessible concentrations of major and trace elements were determined by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The mineral composition of indoor and paired outdoor dust samples was determined by means of X-ray diffraction analysis. The results show that the chemical composition of the dust samples discriminates completely between indoor and outdoor dust samples. The stepwise multiple discriminant analysis model obtained indicates that sodium, magnesium, cadmium, and iron are the most important variables in the discrimination. The mineralogy is dominated by calcite, quartz, and feldspars, with minor phyllosilicates, comprising a set of phases that occur in most samples. Minerals of the serpentine group (e.g., lizardite), soluble salts and oxides-hydroxides were identified in some samples, usually in trace amounts. The Enrichment Factors indicate that zinc and antimony are the PTEs of the greatest concern. However, due to a few anomalous concentrations found in some house dust samples, lead was further included in the study. The results of the bioaccessibility testing vary between PTEs. While lead and zinc are markedly bioaccessible, antimony mostly occurs in insoluble forms, which can be explained by the distinct solid phase distribution of the three elements. Although Sb is highly enriched in the indoor dust, a potential exposure through dust ingestion is significantly decreased by the low oral bioaccessibility shown by the PTE.

Keywords: house dust, biogeochemistry, mineralogy, potentially toxic elements, human exposure

1. Introduction

An increasing number of associations are being reported between air particulates at the home environment and a broad number of adverse health outcomes. There is, therefore, a necessity to identify and characterise the hazards associated with indoor dust to develop ways of reducing the associated risks and make our homes safer. This paper follows on from earlier research undertaken to assess indoor dust ingestion as a potential exposure pathway to potentially toxic elements (PTEs) in the home environment.

2. Methods

2.1. The study area

Estarreja is a coastal municipality located in the centre of Portugal that extends over an area of 108.2 km^2 and has an estimated resident population of 26 555 inhabitants (CCDR 2011).

The climate is Mediterranean temperate (type Csb according to the K¨oppen–Geiger climate classification system), characterised by dry and warm summers, with average annual temperatures of 14.9ºC and an average annual rainfall of 1048 mm. Main wind directions are N–NW, driven by humid tropical air masses moving to the east, especially in the summer, and E–SE during winter (Figueiredo et al. 2013).

The municipality encompasses one of the most important industrial complexes of the country, known as the chemical complex of Estarreja (CCE). Since the 1950s, the complex has produced a variety of organic and inorganic compounds, such as fertilizers from sulphide ores, nitric acid, aniline, nitrobenzene, chlorate compounds from rock salt, polyurethanes and others.

Data available for the study area from the QualAr database, the Portuguese online database for air quality monitoring, show that during sample collection, only PM_{10} levels (daily average) were occasionally above the 50 µg m^{-3} limit value established by the European Commission (EC) 2008/50 Framework Directive for air quality parameters and pollutants. Other monitored air pollutants such as sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) were below the legislated limits.

2.2. Household dust sampling

In this study, the term household dust encompasses dust samples collected from indoor and outdoor areas of the house (henceforth identifed as indoor dust and outdoor dust, respectively). Although indoor dust ingestion was the exposure pathway of interest, both indoor and outdoor areas were sampled to assess differences in the geochemistry of the paired dust samples, which can provide relevant information for a better understanding of sources, mobility, and fate of the PTEs.

A composite indoor dust sample was collected in each home using a vacuum sampler as earlier described (Reis et al. 2015). Outdoor dust was collected from different areas outside the house such as patios, garden paths and driveways, using a small dust pan and a broom. The <150 mm particle size fraction of the dust was obtained by dry sieving. Although the <250 µm particle size fraction is usually recommended for the ingestion route, several studies have been indicating that above 150 µm the indoor dust is composed mainly of exterior soil (Bierkens et al. 2011). However, since humans are most likely to ingest PTEs that are adhered to soil particles 34–40 µm in diameter (Siciliano et al., 2010), a sub-set of indoor dust samples were sived into the < 38 µm to assess potential differences in the mineralogy of the dust.

2.3. Chemical and mineralogical determinations

A subset of dust samples (n= 8) was subjected to the Unified BARGE Method to estimate the oral bioaccessibility of the PTEs in the indoor dust (Wragg et al., 2011).

The determination of pseudo-total and bioaccessible concentrations was carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

The mineral composition of indoor and paired outdoor dust samples was determined by means of X-ray diffraction analysis using an Philips X'Pert MPD, equipped with an automatic divergence

slit, a CuKa (k = 1.5405 A˚) radiation (20 mA and 40 kV), and a Ni filter.

2.4. Statistical Techniques

Univariate and bivariate statistics, as well as distribution plots, were examined for all variables. Differences between groups were tested using the Mann–Whitney U, being the results interpreted based either on rank differences or group median differences. A probability of 0.05 or lower was regarded as significant in testing the null hypothesis of no differences in concentrations/mineralogy across the home environments. Boxplots and the Shapiro–Wilk test were used to check whether the variables under study had a normal distribution. The results indicated that most variables were not normally distributed, within a 95% significance level. Hence, the chemical data were log-transformed prior to the multivariate analysis.

Stepwise linear discriminant analysis was applied to the chemical dataset to identify the elements providing the best separation between indoor and outdoor dust samples. Linear discriminant analysis (LDA) is a multivariate technique of data analysis used to determine how well two or more groups of samples can be classified into pre-defined groups based on a particular characteristic. In this study, the characteristic of interest was the location (indoor *versus* outdoor).

3. Results and discussion

3.1. Geochemistry and mineralogy of the house dust

Elements such as lithium (Li), beryllium (Be), aluminium (Al), scandium (Sc), vanadium (V), manganese (Mn), iron (Fe), gallium (Ga), arsenic (As), rubidium (Rb), yttrium (Y), cesium (Cs), thalium (Tl), thorium (Th), and uranium (U) have significantly higher concentrations outdoors. These elements were associated with natural sources in an earlier study (Reis et al. 2018). As opposite, Au, W, Sb, Sn, Cd, Ag, Zn Cu, Ni, Cr, Bi, K, Na, and B have significantly higher concentrations in the indoor dust, indicating potential indoor sources for some of the PTEs.

A stepwise MDA model was used to classify samples as IN (indoor) or OUT (outdoor) based on each sample's chemical composition. The number of discriminant functions estimated is one less than the number of groups being classified (Davis 1986). For the analysis of two groups of dust, IN and OUT, one discriminant function was estimated. The Wilks' lambda test ($p < 0.005$) and leave-one-out cross-validation were the methods used to evaluate the ability of the stepwise MDA model to classify samples into the two dust categories. The results show that all samples were correctly classified as In or OUT. Hence, the chemical composition of the dust samples discriminates absolutely between indoor and outdoor dust samples. The stepwise MDA model obtained indicates that Na, Mg, Cd and Fe are the more important variables in the discrimination.

Identified minerals include calcite, quartz, feldspars, and phyllosilicates (mainly micas). Calcite is the dominant phase followed by quartz. Both are ubiquitous in indoor and outdoor samples. It is noteworthy the occurrence of minerals of the serpentine group, such as lizardite, brucite and chrysotile. However, these minerals, as well as Fe-oxyhydroxides (e.g., goethite, lepidocrocite), gibbsite, and soluble salts are rare and some of them occur in trace amounts. Nevertheless, such minor phases could have a key role for discriminating indoor and outdoor dust. Moreover, the serpentine group deserves further detailed research, due to potential health risk associated with its fibrous habit.

3.2. Assessment of potential exposure through indoor dust ingestion

In this study, the enrichment factor (EF) was used as screening tool to identify PTEs of most concern for the health of the inhabitants. EFs > 10 are usually deemed indicators of a non-crustal source for the elements (unnaturally enriched in the sample media), while elements of crustal origin have EFs < 10 (natural geochemical background). Li et al. (2016) further specify that an EF > 100 indicates an anomalous enrichment of the element in the sampled media. The calculated

enrichment factor shows that elements such as boron (B), bismuth (Bi), calcium (Ca), copper (Cu), As, selenium (Se), molybdenum (Mo), cadmium (Cd), tin (Sn), tungsten (W), lead (Pb), and mercury (Hg) are enriched (10 < EF < 100), while zinc (Zn) and antimony (Sb) are anomalously enriched in the household dust (EF > 100). Hence, Zn and Sb were considered the PTEs of the greatest concern, and the elements were studied with further detail. However, due to a few anomalous concentrations found in some house dust samples, Pb was further included in the study.

Table 1 shows some summary statistics for PTEs concentrations in the indoor dust collected from the Estarreja residences. Concentrations of Pb, Zn, and Sb are about two times higher in indoor dust than in outdoor dust samples. However, differences in concentrations are statistically significant only for Zn (U= 90, p= 0.014) and Sb (U= 70, p= 0.002).

Table 1 – Summary statistics of Pb, Zn, and Sb concentrations (mg kg^{-1}) in indoor dust samples (n= 19) and the ratio between indoor and outdoor concentrations.

Element	Ratio	Mean	Range
Pb	1.6	174	53-1180
Zn	1.9	1349	582-5210
Sb	2.0	6.9	1.2 – 8.9

On average, 84% of total Zn, 60% of total Pb, and 13% of total Sb contents in indoor dust samples were extracted by the gastric solutions of the UBM procedure. This result suggests that, while Zn and Pb are mostly associated with labile fractions of the dust, Sb occurs in insoluble dust phases. Furthermore, although Sb is highly enriched in the indoor dust, a potential exposure through dust ingestion is significantly decreased by the low oral bioaccessibility shown by the PTE. Interesting, is that, on a previous study from the authors that has investigated relationships between the chemical composition of the dust and PTE concentrations in toenails of the residents, the performed MDA model shows that indoor dust Zn and Sb contents are good predictors of toenail Zn.

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