

The relationship between soil geochemistry and the bioaccessibility of trace elements in playground soil

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Abstract A total of 32 samples of surficial soil were collected from 16 playground areas in Madrid (Spain), in order to investigate the importance of the geochemistry of the soil on subsequent bioaccessibility of trace elements. The in vitro bioaccessibility of As, Co, Cr, Cu, Ni, Pb and Zn was evaluated by means of two extraction processes that simulate the gastric environment and one that reproduces a gastric + intestinal digestion sequence. The results of the in vitro bioaccessibility were compared against aqua regia extractions (“total” concentration), and it was found that total concentrations of As, Cu, Pb and Zn were double those of bioaccessible values, whilst that of Cr was ten times higher. Whereas the results of the gastric + intestinal extraction were affected by a high uncertainty, both gastric methods offered very similar and consistent results, with bioaccessibilities following the order: As = Cu = Pb = Zn > Co > Ni > Cr, and ranging from 63 to 7 %. Selected soil

properties including pH, organic matter, Fe and CaCO₃ content were determined to assess their influence on trace element bioaccessibility, and it was found that Cu, Pb and Zn were predominantly bound to organic matter and, to a lesser extent, Fe oxides. The former fraction was readily accessible in the gastric solution, whereas Fe oxides seemed to recapture negatively charged chloride complexes of these elements in the gastric solution, lowering their bioaccessibility. The homogeneous pH of the playground soils included in the study does not influence trace element bioaccessibility to any significant extent except for Cr, where the very low gastric accessibility seems to be related to the strongly pH-dependent formation of complexes with organic matter. The results for As, which have been previously described and discussed in detail in Mingot et al. (Chemosphere 84: 1386–1391, 2011), indicate a high gastric bioaccessibility for this element as a consequence of its strong association with calcium carbonate and the ease with which these bonds are broken in the gastric solution. The calculation of risk assessments are therefore dependant on the methodology used and the specific environment they address. This has impacts on management strategies formulated to ensure that the most vulnerable of society, children, can live and play without adverse consequences to their health.

Keywords Bioaccessibility · Trace elements · Playground · Risk · Children · Urban

Introduction

Children are exposed to toxic trace elements via a variety of means including ingestion with food and drink, inhalation of contaminated suspended particulates in the ambient air, direct ingestion of indoor dust in the home and school as well as outdoor street dust and soil from urban gardens. In those countries with a mild enough climate and where many of the population live in high rise buildings, children will make extensive use of formal play areas with an additional exposure pathway, that of any contaminated material deposited on outdoor playgrounds (for example, suspended particles in the urban aerosol, compost fertilised soil from adjacent gardens and lawns, miscellaneous litter). There have been several studies using risk assessments to consider the relevance of this exposure, concluding that ingestion of soil particles contributes most to overall risk (Dudka and Miller 1999). However, the use of such risk assessments raises problems; in that, the oral toxicity reference values commonly used (e.g. IRIS database, USEPA 2011) often owe their derivation to studies of human or animal populations in which the hazardous elements were administered in a soluble form (e.g. arsenic in drinking water: Tseng et al. 1968; Tseng 1977; chromium in drinking water: Zhang and Li 1987). This has led to values of 100 % bioaccessibility (defined as the fraction of the trace element content which is dissolved in the gastro-intestinal tract and is available for transport across the intestinal lumen) and hence an over estimate of potential risk. However, contaminants found in association with soils are not 100 % bioaccessible since they are not in solution but are bound to particulates in a variety of ways and depending on which the element will be released in the gastrointestinal tract to different extents. Therefore, whilst risk assessments based on the toxicity of soluble doses provide a more conservative protective evaluation, the use of bioaccessible concentrations offers a more realistic assessment of risk.

There are many *in vitro* studies of the bioaccessibility of trace elements in urban soils (Ljung et al. 2007; Madrid et al. 2008; Poggio et al. 2009; Rasmussen et al. 2008; Roussel et al. 2010). However, the results are variable and sometimes contradictory, and hence, there is little agreement. This is a reflection of the many and complex factors influencing the

bioaccessibility of elements in a sample, including the geochemical specificity of the element of concern, its anthropogenic or natural origin, the granulometry and mineralogy of the sample, its organic carbon content, mode of retention, and so on. This variability of results also reflects the lack of standardisation of analytical methodologies used and certain difficulties associated with some techniques, in particular those attempting to reproduce conditions prevalent in both the human gastric and intestinal environments. Analytical difficulties associated with emulating these conditions include the need for long extraction times with large numbers of unstable reactants yielding concentrations near or below the detection limit. These problems have led to the development of simplified analytical protocols which address gastric-only conditions (e.g. Ruby et al. 1999) rather than methods seeking to replicate complete mouth–gastric–intestinal pathways (e.g. Oomen et al. 2003). The present paper follows on from the earlier work of Mingot et al. (2011), utilising both the two simplified standard protocols they used to evaluate trace element gastric bioaccessibility and the one which mimics the mouth–gastric–intestinal digestion pathway. Thus, the main aim of this study is an investigation of the influence of selected soil properties on the bioaccessibility of trace elements and hence, their potential impacts on children's health in urban environments.

Materials and methods

Two samples of approximately 500 g of surficial (1–2 cm) playground soil were collected in 16 playground sites within the municipality of Madrid with a plastic dust pan and brush and transferred to polyethylene bags for transport to the laboratory. The samples were oven dried at 45 °C for 48 h and then sieved, in all-plastic sieving sets, through 2-mm, 500- μ m and 100- μ m mesh. Details of the study sites and sample material are given in De Miguel et al. (2007). The fraction below 100 μ m was thoroughly homogenised and repeatedly quartered before four analytical samples were obtained. The remaining material was stored for determination of soil physicochemical properties and for use as an alternative sample if required.

The analytical samples were subjected to four different extraction protocols:

1. The RIVM (Rijksinstituut voor Volksgezondheid en Milieu, Dutch Institute for Public Health and the Environment) method (Oomen et al. 2003) which simulates the digestive process in mouth, stomach and intestine: 9 mL of artificial saliva was added to 0.6 g of soil in centrifuge tubes and the mixture rotated for 5 min at 37 °C. Subsequently, 13.5 ml of gastric juice was added and the mixture rotated for 4 h at 37 °C. Afterwards, 36 ml of intestinal juices (27 ml of duodenal juices and 9 ml of bile) were added and the mixture rotated for 3 h and 30 min at 37 °C. The mixture was centrifuged for 5 min at 3,000 grav in order to separate the solid (pellets) and the liquid (chyme) fractions. 0.9 ml of chyme was diluted with 8.1 ml of HNO₃ 2 % for analysis. Details of the composition of artificial saliva, gastric juice and intestinal juices are presented in Oomen et al. (2003).
2. A simplified bioaccessibility extraction test (SBET) as described by Madrid et al. (2008): 0.5 g of soil was mixed with 50 ml of glycine 0.4 M at pH = 1.5 adjusted with HCl, for 1 h at 37 °C. The mixture was centrifuged and the supernatant filtered using Whatman paper number 2.
3. A modified version of the European Standard Toy Safety Protocol EN-71 (European Committee for Standardization 1995) proposed by Rasmussen et al. (2008): 0.05 g of soil was mixed with 50 ml of HCl 0.07 M (pH = 1.5 adjusted with HCl) for 1 h at 37 °C. The mixture was left standing for an hour and then centrifuged and the supernatant filtered using Whatman paper number 2; and
4. An aqua regia extraction protocol, whose results were used as the reference to establish the bioaccessible ratio (i.e. per cent bioaccessibility) of trace elements: 0.5 g of soil was digested for 1 h in a hot water bath (>95 °C) with a 2:2:2 mixture of HCl, HNO₃ and H₂O. After cooling, the solution was made up to 10 mL with 5 % HCl. The concentration of trace and major elements was determined by inductively coupled plasma-mass spectrometry (ICP-MS). Method detection limits were 0.1 mg Kg⁻¹ for Co, Cu, Ni and Pb, 0.5 mg Kg⁻¹ for As and 1 mg Kg⁻¹ for Cr and Zn.

Quality controls consisted of five sample triplicates and one blank triplicate for each batch of 32 samples as well as analysis in triplicate of certified reference

material STD DS6 (Acme Analytical Laboratories), for the aqua regia extraction, and in duplicate of certified reference material WEPAL ISE 987 (Wageningen University), for the rest of the determinations (including physicochemical properties). The relative standard deviation of the replicates was below 10 % for all elements. Average recovery rates for the aqua regia extraction ranged from 96.7 % for Pb to 99.8 % for Cu. The WEPAL ISE 987 reference material is not certified for bioaccessible concentrations, but it was nonetheless extracted and analysed according to the three protocols previously described. Bioaccessibility ratios, relative to the aqua regia certified values, were consistent with those obtained in this study and ranged between 9 % (RIVM), 4 % (SBET) and 10 % (HCl extraction) for Cr, and 74 % (RIVM), 77 % (SBET) and 89 % (HCl extraction) for As.

The determination of the physico-chemical properties was carried out in duplicate on the <100 µm size fraction: Soil pH and electrical conductivity were measured in 1:2 and 1:5 soil/water extracts, respectively, oxidisable organic matter content was determined using the Walkley–Black method (Walkley 1935), calcium carbonate was determined with the calcimeter Bernard method (Allison and Moodie 1965), and cation exchange capacity was evaluated with 1 N ammonium acetate (Bower et al. 1952). Analyses of the WEPAL ISE 987 standard yielded results that were 116, 102 and 90 % of the certified values for oxidisable organic matter, pH and calcium carbonate, respectively.

Statistical analyses were carried out using R (R Development Core Team 2004).

Results and discussion

Tables 1 and 2 show descriptive statistics for all analysed parameters. Aqua regia concentrations of As, Co and Ni in Madrid playgrounds are similar to regional background values, Cr and Pb concentrations are 50 % higher, and Cu and Zn duplicate their baseline levels (De Miguel et al. 2002). With a relative standard deviation of 4 %, samples exhibited a very uniform basic pH of approximately 8.5; oxidisable organic matter (OM) was more variable and generally low with 78 % of the results <3 %. Total Fe and Ca contents show median values of 1 and 1.3 %, respectively, with

Table 1 Results of aqua regia concentrations (mg Kg⁻¹) and bioaccessibility (as % of aqua regia-extractable concentration) following three extraction tests

Extraction	Element	No. samples	Mean	Median	Std. Dev.	Rel. Std. Dev. (%)	Max.	Min.
Aqua regia	As	32	6.8	6.4	1.6	23	12	4.4
	Co	32	3.8	3.8	0.85	23	5.4	2.3
	Cr	32	23	20	10	45	53	9.9
	Cu	32	21	19	11	50	58	8.7
	Ni	32	8.2	8.1	3.0	36	18	4
	Pb	32	26	22	15	55	66	10
	Zn	32	82	66	49	60	282	33
HCl	As	31	54	53	9.3	17	75	37
	Co	31	29	31	9.7	33	43	13
	Cr	31	7.8	7.2	4.1	53	19	2.8
	Cu	31	52	52	29	56	116	7.3
	Ni	31	20	19	11	54	50	6.4
	Pb	31	53	53	16	31	82	25
	Zn	31	48	45	18	38	82	21
SBET	As	32	62	64	13	20	87	39
	Co	32	26	25	6.4	24	39	14
	Cr	32	6.4	4.8	4.3	67	18	2.0
	Cu	32	46	46	8.9	19	66	30
	Ni	32	20	17	7.5	38	37	9.1
	Pb	32	59	56	15	26	95	38
	Zn	32	47	48	14	30	92	25
RIVM	As	32	43	42	6.6	16	59	33
	Co	32	63	63	12	19	85	43
	Cr	31	40	39	18	45	81	5.0
	Cu	29	61	61	23	37	99	25
	Ni	–	–	–	–	–	–	–
	Pb	24	57	62	30	53	103	4.0
	Zn	32	46	46	12	26	69	25

CaCO₃ ranging from 1.7 to 7.2 %, with a median value of 2.6 %. Compared to similar studies of urban soils which report soil properties, the samples from Madrid playgrounds are OM- and Fe-deficient and have a significantly higher pH (e.g. Juhasz et al. 2007; Ljung et al. 2007; Poggio et al. 2009; Rasmussen et al. 2008; Roussel et al. 2010; Yang et al. 2002).

Assuming constant variance of residuals and zero bioaccessibility at zero total concentration, the percentage of gastric and gastric + intestinal bioaccessibility was established as the slope of a linear regression intercepting the origin of SBET, HCl and RIVM concentrations versus the total concentrations of each element. The bioaccessibility ratios thus estimated for As, Co, Cr, Cu, Ni, Pb and Zn and for

the three extraction methods are shown in Table 3 (“slope”) except for RIVM Ni, which was removed since a third of all results were below the detection limit. Correlations between bioaccessible and total concentrations were highly significant for all elements except HCl Ni (*p* value: 0.21) and SBET Cr (*p* value: 0.02) and quite robust as indicated by the confidence intervals of the linear regressions (Table 3).

As shown in Table 3, the results of SBET and HCl bioaccessibility percentages were almost identical for all elements (relative differences between the results of both methods are <15 %), except for As (19.6 %) and Cr (31.6 %). Arsenic, Cu, Pb and Zn have similar gastric bioaccessibility percentages of between 48 and 63 %. Cobalt and Ni exhibit bioaccessibilities that are

Table 2 Soil properties and concentration of major elements in samples from playground surface soil

	No. samples	Mean	Median	Std. Dev.	Rel. Std. Dev. (%)	Max.	Min.
Fe (%)	32	1.03	1.00	0.23	22	1.43	0.66
Ca (%)	32	2.10	1.35	1.91	91	8.53	0.47
P (%)	32	0.068	0.056	0.045	66	0.254	0.038
Mg (%)	32	0.32	0.32	0.09	28	0.63	0.16
Ti (%)	32	0.023	0.022	0.006	28	0.042	0.012
Al (%)	32	0.84	0.78	0.23	27	1.31	0.45
Na (%)	32	0.013	0.010	0.007	56	0.033	0.006
K (%)	32	0.24	0.21	0.08	33	0.42	0.14
Mn (%)	32	0.028	0.027	0.008	29	0.048	0.015
Organic matter (%)	31*	2.32	2.02	1.59	68	8.22	0.47
pH	32	8.54	8.58	0.30	4	9.00	7.92
CaCO ₃ (%)	28*	2.95	2.60	1.42	48	7.21	1.66
CEC (cmol Kg ⁻¹)	29*	12.2	10.6	5.5	45	19.9	4.7
Elect. Cond. (μS cm ⁻¹)	32	146	139	63	43	364	25

* The mass of <100 μm fraction was not large enough to complete all physico-chemical determinations

Table 3 Linear regression (assuming constant variance of residuals and zero bioaccessibility at zero total concentration) of SBET-, HCl- and RIVM- concentrations versus the aqua regia concentrations of each element (%)

	As	Co	Cr	Cu	Ni	Pb	Zn
RIVM							
Slope	42	64	42	67	–	69	55
Confidence interval	39–44	59–68	37–47	61–73	–	60–79	51–59
SBET							
Slope	63	26	6.2	47	18	59	56
Confidence interval	58–68	23–28	4.4–8.1	45–49	15–20	54–64	51–60
HCl							
Slope	52	28	8.5	55	18	57	61
Confidence interval	49–55	25–32	6.8–10	44–66	14–22	50–63	53–69

half and a third of those values, with Cr showing the lowest percentage at around 7%. Although it is difficult to compare these results with those of other studies elsewhere due to the large variability in extraction protocols, type of soil and grain size considered (Table 4), the indicated order of gastric bioaccessibility, that is, As = Cu = Pb = Zn > Co > Ni > Cr, remains remarkably similar.

However, the results of gastric + intestinal bioaccessibility followed the order Co = Cu = Pb > Zn = As = Cr and were consistently higher in this study than in those included in Table 4 except for As. Although this fact could be attributed to the CaCO₃ rich nature of Madrid playground soils (see discussion

below), it must be acknowledged that estimates of the RIVM method are not as reliable as those of the simplified, gastric protocols. This is not only because of the large number of unstable reactants involved in the extraction sequence but mostly because of the high (approximately tenfold) dilution. This can bring the analytical determinations near or below the detection limit if the soil is not highly contaminated as is the case in this study. A paired *t* test of the results confirmed that As exhibited RIVM concentrations significantly lower than those in the SBET and HCl protocols, whilst Co, Cr and Cu showed the opposite behaviour (for Pb and Zn, the difference was not significant). These results are not easily reconciled with the fact

Table 4 Comparison of gastric and gastric + intestinal bioaccessibility of trace elements in soil

Study	As		Cr		Cu		Ni		Pb		Zn		Extraction method	Soil use/type	Particle size
	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)			
<i>Gastric</i>															
Yang et al. (2002)	44	5.4–100											5	As-spiked	<250 µm
Juhasz et al. (2007)	34	6–89											5	Contaminated	<250 µm
Ellickson et al. (2001)	70	(±8.3)							76	(±11)			3	NIST standard	<74 µm
Madrid et al. (2008)			2.6	1–6	44	39–57	12	8–14	53	46–60	40	34–43	6	Urban (Torino)	<50 µm
Madrid et al. (2008)			9	4–16	20	13–24	60	34–86	39	30–51	55	32–83	6	Urban (Seville)	<50 µm
Rasmussen et al. (2008)					32	(±10)	17	(±7)			29	(±16)	11	Urban	<150 µm
Gbefa et al. (2011)			7		14	–	8	–	5	–	12	–	8	BCR-Sewage sludge	–
Poggio et al. (2009)					17	(±1.4)	4	(±0.2)	18	(±1.2)	43	(±8.2)	6,7	Agricultural	<2 mm
Poggio et al. (2009)				–	15	(±3.6)	16	(±2.0)	20	(±3.2)	4	(±0.4)	6,7	Urban	<2 mm
Roussel et al. (2010)									62	33–76	47	17–85	1,2	Urban contaminated	<250 µm
Luo et al. (2012)					17	(±19)			61	(±52)	68	(±71)	12	Urban	<150 µm
Farmer et al. (2011)									52	(±13)			13	Urban	<250 µm
Pelfrene et al. (2012)									58		35		14	Contaminated	<250 µm
This study—SBET	62	(±12.6)	6.4	(±4.2)	46	(±8.9)	20	(±7.5)	59	(±15.0)	47	(±14.0)	6	Playground	<100 µm
This study—HCl	53	(±9.1)	7.7	(±4.1)	47	(±21)	20	(±11)	52	(±16.5)	48	(±18.37)	10	Playground	<100 µm
<i>Gastric + intestinal</i>															
Ljung et al. (2007)	16	–	4.2				3.9	–	4.2	–			1	Playground	<50 µm
Ellickson et al. (2001)	65	(±5.2)							11	(±2.3)			3	NIST standard	<74 µm
Carrizales et al. (2006)	46	39–66							32	16–34			4,5	Contaminated	<50 µm

Table 4 continued

Study	As		Cr		Cu		Ni		Pb		Zn		Extraction method	Soil use/type	Particle size
	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)	Mean	Range (SD)			
Hamel et al. (1998)	67	(±8)											3	Standard	<74 µm
Hamel et al. (1999)	41	(±2)	34	(±14)					39	(±14)			3	Residential	<125 µm
Gbefa et al. (2011)			8	–	9	–	6	–	7	–	5	–	8	BCR-Sewage sludge	–
Poggio et al. (2009)					31	(±3.0)	8	(±0.4)	5	(±0.4)	27	(±4.6)	6,7	Agricultural	<2 mm
Poggio et al. (2009)					4	(±0.2)	27	(±6.7)	8	(±0.5)	21	(±6.1)	6,7	Urban	<2 mm
Roussel et al. (2010)									32	14–63	23	8–47	1,2	Urban contaminated	<250 µm
Farmer et al. (2011)									22	(±9)			13	Urban	<250 µm
Pelfrene et al. (2012)									20		10		14	Contaminated	<250 µm
This study—RIVM	43	(±6.6)	40	(±18)	61	(±22.5)			57	(±30)	46	(±12)	1	Playground	<100 µm

1: Oomen et al. (2003)

2: Oomen et al. (2006)

3: Hamel et al. (1998, 1999)

4: Ruby et al. (1993)

5: Ruby et al. (1996)

6: Ruby et al. (1999)

7: Ruby (2004)

8: Dean (2010), Cave et al. (2002)

9: Juhasz et al. (2007)

10: Rasmussen et al. (2008)

11: European Committee for Standardization (1995)

12: Drexler and Brattin (2007)

13: Broadway et al. (2010)

14: Roussel et al. (2010)

that raising the pH in the intestinal phase should cause: (a) partial precipitation and enhanced adsorption on mineral colloids and higher absorption in organic matter of cations (i.e. reduced bioaccessibility); and (b) desorption of As, the only trace element that should be present as an anion in the acidic gastric environment, from mineral surfaces and polar groups in organic matter as their density of positive charge decreases (i.e. increased bioaccessibility). Other authors have reported similarly unexpected results for Cu and Ni (Poggio et al. 2009) and have attributed the observed behaviour to the high affinity of the first two elements for glycine, and to metal binding competition between glycine and carbonates. For the weakly alkaline soils in this study, it is more likely that, as the pH is raised in the intestinal phase of the extraction procedure, there is competition with, and displacement of metal cations from available binding sites by the Ca ions previously released from calcium carbonate in the gastric stage. These arguments should be regarded with caution since, as was mentioned before, the reliability of the results of the RIVM procedure is questionable for uncontaminated soils, for which the analytical determinations often fall near the limit of detection of the method.

The influence of soil properties on the bioaccessibility of trace elements was evaluated by means of multiple linear regressions of: (a) the soil concentration of those elements extracted with the RIVM, SBET and HCl methods; and (b) the bioaccessibility ratios (i.e. RIVM:aqua regia, SBET:aqua regia and HCl:aqua regia) on a sub-set of predictor variables selected from the whole set of soil properties, including concentrations of major elements, using a Bayesian information criterion (BIC) analysis (Mingot et al. 2011).

The multiple linear regressions of gastric bioaccessibility ratios on soil properties reveal that SBET extractable Co, Ni and Pb are positively and significantly influenced by the organic matter content of the soil, whilst in the case of the HCl extraction, organic matter seems to influence significantly the bioaccessibility of Cr, Ni and Zn. Coupled with a strong positive correlation between organic matter and total (i.e. aqua regia) concentrations of these elements (except Cr), this fact seems to indicate that as expected, soil organic matter effectively binds cations and that these cations become readily available in the strongly acidic environment of the SBET and HCl extracts. In the case of Cr, binding to organic matter

does not seem to be a very efficient retention mechanism (indicated by a very weak correlation with aqua regia Cr concentrations). The little Cr that is fixed by the polar groups of natural organic matter is again easily released in the gastric environment, as revealed by the highly significant correlation coefficients between SBET and HCl bioaccessible concentrations and organic matter and corroborated by the significant influence of organic matter in the linear model for the SBET:aqua regia bioaccessibility ratio.

The influence of pH on the bioaccessible concentrations of trace elements in Madrid playground soil is not as critical as in other studies. This is very likely a consequence of the very low variability of pH in the samples collected in Madrid. Nevertheless, the gastric bioaccessibility of Cr, and to a lesser extent Ni, especially as estimated in the SBET, does seem to be strongly controlled by soil pH, both in absolute terms and relative to the total Cr concentration in the soil. Chromium is present in urban soil mostly as residual minerals (Poggio et al. 2009), most likely mixed Cr³⁺ and Fe³⁺ oxides (Kabata-Pendias and Pendias 1992). As previously discussed, a small fraction, however, is retained in the form of organic complexes, which readily release Cr in the gastric solution, hence the highly significant correlation coefficient between organic matter and bioaccessible Cr. The role that soil pH plays as a controlling factor of Cr bioaccessibility is probably related to the redox behaviour of this element in alkaline soils. At pH values around 8.5, small deviations towards higher values would promote the occurrence of Cr in soluble Cr⁶⁺ forms that would be removed from the surficial soil matrix. Correspondingly, small drops in pH in the presence of organic matter would facilitate the formation of those Cr(III) complexes previously discussed which constitute the bioaccessible fraction of this element.

Total Fe is positively correlated with the aqua regia concentration of all trace elements analysed except Cr, a fact that lends support to the idea that a fraction of the Fe oxides in the weakly alkaline soils of Madrid retain a negative surface charge at pH 8.5 and act as a retention medium for cations. In terms of gastric bioaccessibility, the multiple linear regressions show that the bioaccessibility ratios of all trace elements decrease as the concentration of Fe increases in the sample (and once the influence of the other variables have been discounted). This could be a consequence of the formation of very stable metal chloride complexes

in the Cl^- -rich, acidic solution used to simulate the gastric environment. These complexes carry overall negative charge and would be removed from solution and fixed to the positive surface charges developed by the Fe oxides at this low pH (Adriano 2001) therefore lowering the bioaccessibility of metal ions.

As opposed to cations, the behaviour of As seems to be mainly controlled by the Ca content of the soil (Mingot et al. 2011). Most of the total load of As in Madrid's samples appears to be bound to carbonate surfaces and maybe also present as Ca As precipitates. This As is readily dissolved and made bioaccessible in the low-pH gastric extracts, hence the high values of HCl As and specially SBET As. Organic matter does not contribute significantly to the overall As content in the playground soil of Madrid but the small fraction of As bound to humic substances most likely through Ca bridges is released in the gastric and gastro-intestinal environments (Mingot et al. 2011). Conversely, the little As bound to the Fe oxides in Madrid's playgrounds is not released during the gastric extraction, as manifested in the significant, negative partial correlation between all three modes of bioaccessible As and Fe.

Conclusions

The gastric bioaccessibility of trace elements in the playground soils included in this study follows the order: $\text{As} = \text{Cu} = \text{Pb} = \text{Zn} > \text{Co} > \text{Ni} > \text{Cr}$. In terms of the implications for risk assessment, in which aqua regia or "total" concentrations are generally used, comparison with bioaccessibility values reveals that total concentrations for As, Cu, Pb, and Zn in the soil was double, whereas that for Cr was more than one order of magnitude higher. The results of the SBET and the HCl protocols are very similar for most metals. Gastric bioaccessibility can be estimated by either method without any appreciable difference except for As, for which SBET concentrations are significantly higher, and for Cr, which shows the opposite behaviour.

The RIVM method reveals that the gastric + intestinal bioaccessibilities of the trace elements analysed follow the order: $\text{Co} = \text{Cu} = \text{Pb} > \text{Zn} = \text{Cr} = \text{As}$ are higher than the corresponding gastric values for Co, Cu and Cr, and higher than the results arrived at by other researchers (see Table 4) except for As. These unexpected high values of gastric + intestinal bioaccessibility could be explained by the preferential binding of

previously released Ca ions and displacement of trace elements from exchange sites in the intestinal phase of the extraction protocol. The RIVM method is complex, involving a large number of unstable reactants and high dilutions, and its results in this study should be interpreted with caution. Despite these complications, relative to gastric-only extraction procedures, the RIVM method or later adaptations thereof (the Unified BARGE Method, Wragg et al. 2011) should yield results that more closely approximate *in vivo* bioaccessibilities.

Different soil properties seem to dictate the behaviour of the different elements in terms of their bioaccessibility. In weakly alkaline, organic matter and Fe deficient, urban soils Cu, Pb and Zn are predominantly bound to organic matter and, to a lesser extent, Fe oxides. Whereas the fraction of those elements originally associated with soil organic matter is readily accessible in the gastric solution, Fe oxides seem to recapture and therefore lower the bioaccessibility of Cu, Pb and Zn in the form of negatively charged chloride complexes of these elements. Chromium is present primarily in the residual fraction of playground soil and therefore very little is bioaccessible, the small percentage of which is associated with soil organic matter. The occurrence of these organo-metallic complexes seems to be strongly pH dependent, and the amount of Cr thus retained appears to increase significantly with only minor pH reductions. Arsenic presents a very different behaviour from that of the other trace elements, in that it is most likely associated with calcium carbonate. The high bioaccessibility of As is a consequence of the ease with which its bonds to carbonate surfaces are broken under the strongly acidic conditions of the gastric solution.

The results of this study clearly demonstrate the influence of soil properties on the bioaccessibility of trace elements in playground soil and highlight the need to determine and understand these properties in order to properly interpret variations of bioaccessibility among different elements and different soils. As a consequence, the modes of retention in the soil and release in the gastric solution that have been discussed for Madrid playgrounds may not be directly applied to other environments and other extraction protocols.

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