Antimony-polluted soils risks assessment with special concern around speciation and bioaccessibility aspects

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INERIS, PARC ALATA BP2, 60 550 Verneuil en Halatte (France)

E-mail contact: karine.tack@ineris.fr

1. Introduction

Antimony is potentially toxic at very low concentrations and has no biological functions. Toxicity of Sb is strongly linked to its speciation. For instance Sb (III) was shown to be ten times more toxic than the form (V). For Sb contaminated soils, the exposure assessment of Humans is a crucial step. The exposure will depend on both the media (soil, water or air) from which the Humans are exposed and the route of exposure (inhalation, ingestion, dermal contact). In the case of polluted soils, direct ingestion is considered as the major exposure route. In this case, the total concentration is commonly characterized. However it does not reflect the actual concentration that is absorbed through the gastro-intestinal (GI) tract, i.e. the bioavailable concentration. The bioaccessibility research group of Europe (BARGE group) set an *in vitro* model (UBM test) to determine the fraction of pollutant potentially extractable during digestive processes, i.e. the bioaccessible fraction. Aims of this study were to combine bioaccessibility and speciation measurements to improve the human health risk assessment of Sb contaminated soils. If the concern of speciation as another tool for polluted matrixes characterization is growing (1), only few literature exists around pollutants speciation during the digestive processes (2, 3). This research is devoted to the study of antimony species evolution during the UBM test, and aim to integrate this approach to polluted soil risks assessment.

2. Materials and methods

Six soils were used in this study: two certified reference materials (IAEA-356 obtained from the international atomic energy agency), PACS-2 obtained from national research council of Canada), two reference materials (IPL1 and MIX1 obtained from the Pasteur Institute of Lille in France), and two industrial soils named Soil-A and Soil-B sampled from a mining site (Glendinning, Scotland). Bioaccessibility measurements were performed using the Unified Barge Method (UBM) (2, 4). This procedure simulates the chemical digestive process taking place in mouth (five minutes), stomach (1 hour) and small intestine (4 hours) compartments within synthetic digestive fluids. The temperature in maintained at 37°C and the UBM test is applied to 0.6 g of soil. After the complete digestion procedure, samples were centrifuged at 3 000 g for 5 minutes. The supernatant was then sampled and analyzed for total Sb and Sb species. Sb species analyses were carried out within 24 hours following the test by HPLC-ICP-MS according to Zheng et al (5), while total Sb analyses were performed by ICP-MS within the week following the test after having conditioned samples with 2% HNO_3 according to AFNOR protocol (6). The UBM test was engaged on soil samples and on Sb-species spiked solutions at different concentrations. All experiments were conducted in triplicates.

3. Results and discussion

3.1. Bioaccessible antimony species from polluted soils

When applied on polluted soil samples, the amount of bioaccessible antimony was not shown to be correlated to the initial concentration of total Sb in the soil. Even if low bioaccessibilities were measured in real polluted soil samples, this information should be strongly considered. Indeed, for the soil A, for example, with the lowest bioaccessible percentage of Sb, the concentration of SbV reached 166±1 µg/L in the gastric juice and 4681±22 µg/L in the gastro-intestinal juice, while it was around 19.3±0.4 µg/L and 53.9±7.8 µg/L for SbIII respectively for the same fluids. These values were translated as the accessible dose for organism absorption via the soil ingestion (Table 1). The concentration of bioaccessible antimony measured with the UBM test can allow calculating the average daily accessible dose (ADAD) for absorption. 10 kg was used as the reference to the official minimal weight of a 1 year child (7), that represents the worst scenario in case of soil ingestion by a 1 year old child. In this context, the toxicological reference values for total antimony can be used as reference values to appreciate the risk associated to children exposure to such kind of polluted soils due to the fact that no toxicological reference value exits for Sb(III) nor Sb(V).

Soil	SoilA	SoilB	SoilA	SoilB
Digestive phase	Gastric		Gastro-intestinal	
RfD (µg/kg/d) (USEPA)			0.4	
ADI (µg/kg/d) (WHO)			6	
SbV (µg/kg)	0.37	10.5	6.54	69.0
SbIII (µg/kg)	0.04	0.03	0.32	1.34
Total Sb (µg/kg)	0.56	9.97	8.46	74.0

Table 1: Comparison of bioaccessible antimony concentration expressed as the interne dose accessible to a 10 kg child in case of soil ingestion to toxicological reference values (µg.kg^{-1}) (RfD = reference dose and ADI = acceptable daily intake)

3.2. Stability of Sb species in simulated digestive media for bioaccessibility measurements

SbV specie was measured in the UBM fluids, while some SbIII was transformed in SbV when the UBM test was applied on S bIII-spiked solutions. This transformation seemed to take place during the entire gastro-intestinal phase while no changes were observed during the single gastric phase. The part of SbIII transformed to SbV appeared to be dependant of the initial SbIII concentration in digestive fluids and could vary from 93% to 3% respectively for initial SbIII at 85 and 42 000 µg/L (Figure 1). A maximal concentration of SbIII transformed in SbV appeared around 550 µg/L in the gastro-intestinal fluid. The kinetic was fast (30 minutes) in the gastro-intestinal juice.

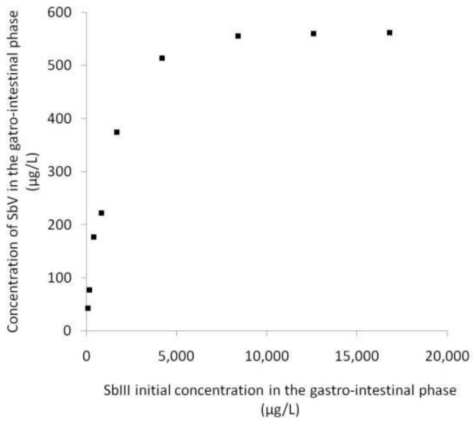

Figure 1: SbV concentrations measured in the gastro-intestinal fluid after the digestion of SbIII-spiked solutions

4. Conclusions

The UBM test is a quite fast and very simple *in vitro* test to express metallic pollutant bioaccessibility in case of soil ingestion. This test seems well appropriate for polluted soil characterization in terms of risks assessment. When coupled to speciation analysis, it offers a deaper understanding of real pollutant species that infants can be exposed to.

5. References

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