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Using bioaccessibility testing in health risk assessment as a decision support tool for appropriate redevelopment of former mining sites: a French case study

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Abstract

In many countries, remediation is required when a site poses a risk to human health and/or the environment. In this context, risk assessment methodologies usually rely on the total contaminant concentrations measured on site without considering chemicals bioavailability. Such approach is actually irrelevant when considering former or abandoned mining sites characterised with high concentrations of heavy metals in soils as it often results in an overestimation of risks, leading to heavy, lengthy and costly remediation works.

The case study was the site of a cassiterite mining exploitation that ended in 1957. At the present time, 3.7 million cubic meter of tailings and waste rocks, with rather high arsenic and other heavy metals concentrations, remain on the site. Beside these residues, and issues associated with the acid mining drainage, there is still great concern with the frequentation by the public of this site. Effectively, because of its astonishing shape, it is highly visited by a wide range of population (local and national). It offers a unique opportunity for sport and leisure activities (e.g.: mountain bike, walking, trail, horse riding) in a relatively flat region. Therefore, this site represents an opportunity of tourism and economic development for the municipality.

The aim of this study was to assess the compatibility of these uses with the soils quality, given that they are especially highly concentrated in arsenic. Ingestion is one of the major routes of soil exposure, by children especially. However, data from literature indicate that the bioaccessible fraction of arsenic for human soil ingestion can vary from 2 to 90%. Therefore, it is relevant to carry out site specific tests.

Bioaccessibility tests were carried out on 10 soil samples collected on site, following the Unified BARGE (BioAccessibility Research Groupe of Europe) Method (UBM). This in vitro method simulates the human digestive procedure using synthetic digestive fluids. Results indicate that the bioaccessibility of arsenic on this site ranges between 5 and 50 %, averaging out at 17%.

The human health risk assessment at this specific site integrated these bioaccessibility results so that health risk quantifications are more relevant, accurate and closer to reality. In this case study, we show that using standard highly conservative approach and more accurate approaches lead to rather different results in terms of possible uses.

Using this approach, appropriate solution for redeveloping the site balancing health and environment protection requirements with tourism and economic issues will be available.

Keywords: *arsenic, bioaccessibility, human health risk assessment, cassiterite, redevelopment*

1 Introduction

In many countries, remediation is required when a site poses a risk to human health and/or the environment. If most of threshold or regulatory values are available on (drinking) water or air quality, no threshold value is available on soil quality in France. In order to assess if soil quality is compatible with the uses, human health

risk assessment (HHRA) is the only available tool. On former or abandoned mining sites, ingestion is one of the major routes of soil exposure to heavy metals contamination, by children especially. Current approaches are usually largely conservative and exposure is currently assessed using the total soil concentration of individual contaminants.

Such approaches lead to important safety margins, and thus could be considered as less appropriate when considering former or abandoned mining sites characterised with moderate to high concentrations of heavy metals in soils resulting of both natural and anthropogenic activities. Moreover, several *in vivo* studies, using diverse animals, such as monkeys, juvenile swine, rabbits, and rodents, have demonstrated that only a fraction of a contaminant, the bioavailable fraction, is absorbed following oral administration (Denys et al., 2012).

The BioAccessibility Research Groupe of Europe (BARGE) has developed an *in vitro* test, the Unified BARGE Method (UBM), to measure the bioaccessibility of soil contaminants. This method was subjected to an *in vivo* validation and provides a robust tool for use in risk assessment of As, Cd and Pb (Denys et al., 2012).

In this paper, we present a case study of an old mining site where remain tailings and waste rocks with moderate to high arsenic concentrations. This site is widely frequented by the population and the aim of the study was to assess the compatibility of the uses with the soil quality. The bioaccessibility testing were used in health risk assessment.

The aim is to obtain a quantification more relevant, accurate and closer to reality in order to define appropriate solution for redeveloping the site balancing health and environment protection requirements with tourism and economic issues.

2 Methodology

2.1 Field site description

The studied site is an old mining exploitation of cassiterite (SnO_2) located to the west of France. The main exploitation was conducted between 1952 and 1957 by open pit mining. The cassiterite deposit is related to quartz veins in schists. It contains also sulphide minerals as arsenopyrite. At the present time, 3.7 million cubic meter of tailings and waste rocks remain on the site with high arsenic concentrations, as shown on Figure 1.



Figure 1 Aerial view of the site (tailings (left) and waste rocks (right) deposits, water-filled open pit)

Because of its astonishing shape, the site is highly visited by a wide range of population (local and national). It offers unique opportunity for sport and leisure activities in a relatively flat region. Several uses have been noted, some developed by the municipality, others that have developed over time, such as mountain bike, horse riding, walking, trail, picnic. Associations often organise trail, mountain bike and BMX competitions on the site. It represents a good opportunity of tourism and economic development for the municipality.

However, arsenic concentrations in soils constitute a potential risk to human health and therefore require assessment.



Figure 2 Examples of uses identified on the site

2.2 Soils characterization

On site investigations were carried out in order to characterize arsenic concentrations in subsoils. The depth sampled were determined according the identified uses. At the tailings disposal site, the main route of exposure identified is the ingestion of soil and dust from superficial horizons. Thus, investigations concerned the horizon from 0 to 5 cm deep.

177 measures using an X-Ray Fluorescence portable (pXRF) analyser were carried out. Due to the relative homogeneity of materials, the sampling plan followed a systematic grid of 50 m. This allows a statistical analyse of results and a good representativeness of average exposure concentrations and arsenic occurrence.

10 samples were collected on site to analyse metallic trace elements in laboratory for soil characterization and site-specific linear correlation with the field analyser. The samples were selected to ensure a spatial representativeness of the site as well as a representativeness of encountered concentrations with the field analyser (selection from the lower, middle and upper range of concentrations measured at the site). Bioaccessibility testing were performed on these samples following the Unified BARGE Method (in accordance with ISO/DIS 17924).

2.3 UBM procedure

Unified BARGE Method is an in vitro method for simulating the human digestive procedure. Digestive fluids are synthetic fluids used in the UBM test to simulate the fluids present in human digestive system: saliva, gastric fluid, duodenal fluid and bile. The current procedure describes a method for simulating the human gastro-intestinal tract through 3 different compartments: mouth (5 minutes), stomach (1 hour), and small intestine (4 hours). Figure 3 shows the schematic diagram of the UBM methodology. Each sample follows two separate tests:

- The gastric phase is a digestive extract collected after 1 hour agitation with saliva and gastric fluids.
- The gastro-intestinal phase is a digestive extract collected after 1 hour agitation with saliva and gastric fluid followed by 4 hours agitation with duodenal fluid and bile.

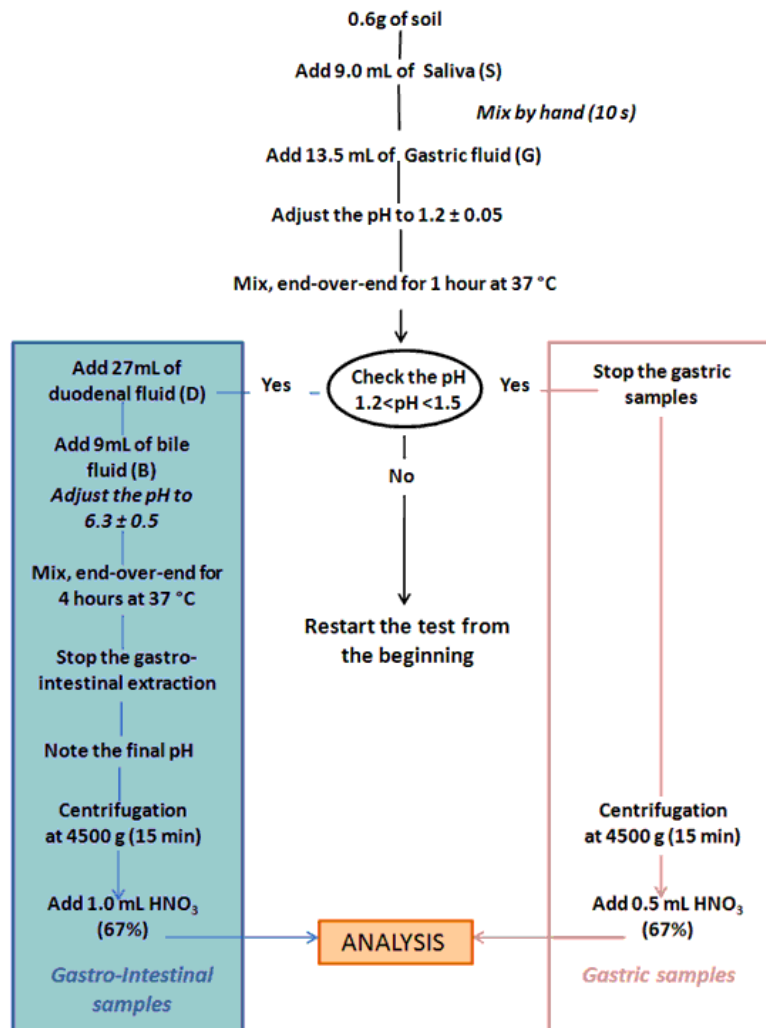


Figure 3 Schematic diagram of the UBM methodology (<http://www.bgs.ac.uk/barge/ubm.html>)

This method was applied on the 10 collected samples in duplicate. Blank and reference materials (NIST 2710a) also followed the complete procedure.

2.4 Human Health Risk Assessment (HHRA)

Human health risk assessment, regarding exposure to chemical substances, is performed following these different steps:

- Hazard identification - Hazard Identification is the process of determining whether exposure to a substance can cause an increase in the incidence of specific adverse health effects (e.g., cancer, birth defects) and whether the adverse health effect is likely to occur in humans.
- Dose-Response assessment - A dose-response relationship describes how the likelihood and severity of adverse health effects (the responses) evolve with the amount and condition of exposure to an agent (the administered dose).

- Exposure assessment - Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposure to a substance in the environment.
- Risk characterization - Risk characterization is the result of the risk assessment process. It aggregates the data collected in previous steps in order to quantify risk levels for human health and their acceptability with regard to standard comparison thresholds. This step also includes the evaluation of the assumptions and uncertainties that may still exist in the assessment.

This paper will not describe “Hazard identification” and “Dose-response assessment” steps.

2.4.1 Exposure assessment

Based on observations made and developments noted on the site, several areas of homogeneous use were defined, as shown in Figure 4 and Table 1. The observations supporting these scenarios were made during many site visits occurring within or out of school holiday periods during the last 3 years.

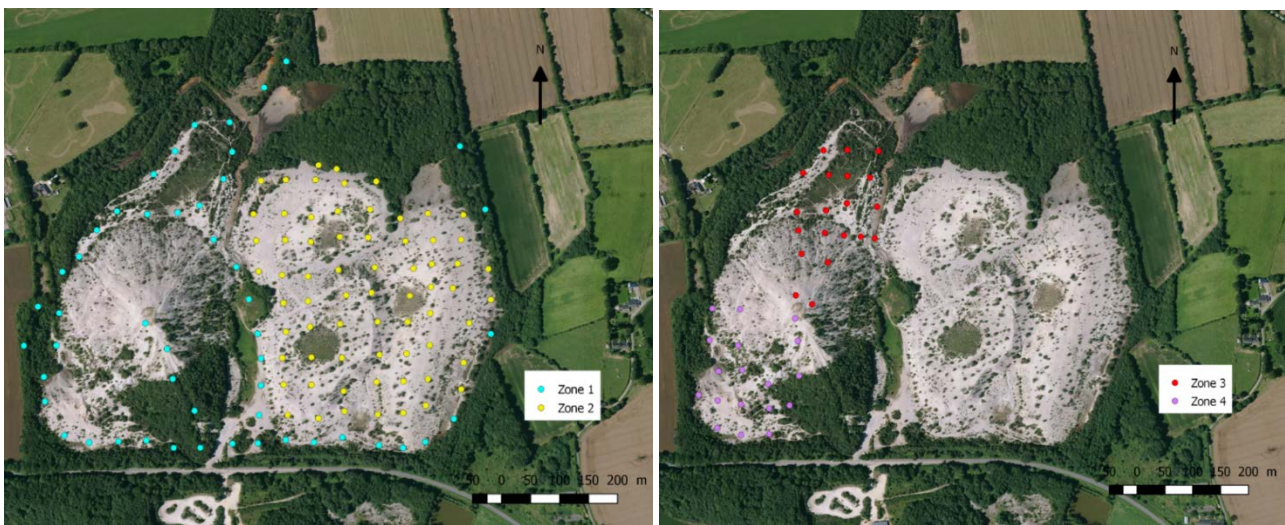


Figure 4 Localisation of selected data for the different scenarios of exposure

Zone	Uses	Receptors	Exposure routes
Zone 1	Walking, running	Child, Adult, Child becoming adult	Soil/dust ingestion Dust inhalation
Zone 2	Walking, running	Child, Adult, Child becoming adult	Soil/dust ingestion Dust inhalation
	Mountain bike, horse riding	Adult (6 to 70)	
	BMX	Adult (15 to 50)	
Zone 3	BMX	Adult (15 to 50)	Soil/dust ingestion Dust inhalation
Zone 4	Mountain bike	Adult (15 to 50)	Soil/dust ingestion Dust inhalation

Table 1 Exposure scenarios defined for HHRA

It is assumed that only adults between 15 and 50 years old engaged in “extreme” sport activities.

2.4.2 Risk characterisation

Potential non-cancer risk for individual contaminants are expressed as Hazard Quotient (HQ). HQs are calculated as the ratio of the estimated daily intake of each contaminant to the corresponding route-specific reference dose (RfD - tolerable daily intake or tolerable concentration).

$$HQ = ADD / RfD \quad (1)$$

where:

HQ: hazard quotient

ADD: average daily dose

RfD: reference dose

When the average daily dose estimated from site-associated soil contaminants exceeds the protective RfD, the HQ exceeds one. Such risk levels are therefore considered as unacceptable.

Risk characterization of carcinogenic substances consists in calculating the Incremental Lifetime Cancer Risk (ILCR). ILCR is expressed as an estimated upper-bound probability of additional lifetime cancer risk due to exposure to site-related contaminants. The upper-bound estimate of excess risk related to each contaminant is calculated by multiplying the lifetime average daily dose (LADD) estimated for that contaminant by its corresponding route-specific cancer slope factor.

$$ILCR = LADD \times CSF \quad (2)$$

where:

ILCR: Incremental Lifetime Cancer Risk

LADD: Lifetime average daily dose

CSF: Cancer slope factor

For non-threshold contaminants, acceptable incremental risk levels in Europe are defined that vary from 1.10^{-4} (The Netherlands) to 1.10^{-6} (Italy), while 10^{-5} is adopted by the large majority of country including France (Carlou, 2007). In this case study, ILCR has to be under 10^{-5} to be acceptable ($ILCR < 10^{-5}$).

2.4.3 Integration of bioaccessibility into risk characterisation

Absolute bioavailability is the fraction of a substance present in ingested soil that reaches the systemic circulation (blood stream). But determine bioavailability is not easily achievable due to both experimental issues linked to blood sampling and to analytical limitations.

Whereas, absolute bioaccessibility is the fraction of substance in soil or soil material that is liberated in (human) gastrointestinal juices and thus available for absorption (ISO/DIS 17924, 2016). So, bioaccessibility is the maximal fraction of a substance that can reach the systemic circulation.

The ingested matrix containing the toxic substance has an influence on the dose-response relationship of the substance. In order to integrate this parameter in risk calculation, the corrective factor is the relative bioavailability (INERIS and InVS, 2012). This variable is defined as the ratio of absolute bioavailability of the substance in the soil matrix to absolute bioavailability of the element in the matrix used to develop the Reference Toxicity Value (RTV as RfD or CSF).

Caboche (2009) and INERIS and InVS (2012) retain the equality of the absorbed fraction of As present in contaminated soil and the absorbed fraction of As present in drinking water (reference matrix for the establishment of the RTVs). In addition, Oomen et al. (2006) indicate that the metabolism of absorbed arsenic does not depend on the matrix in which the element was in the gastrointestinal tract. Finally, the absolute bioavailability of arsenic in water, the reference matrix for RTVs, is close to 100% (INERIS and InVS, 2012). Then, the relative bioavailability of arsenic is set equal to the absolute bioaccessibility of arsenic in soil.

It is thus possible to integrate absolute bioaccessibility of arsenic from the UBM test in risk calculation for exposure by ingestion as shown in equations below:

$$HQ = ADD \times BA_{As \text{ absolute soil}} / RfD \quad (3)$$

Where:

HQ: hazard quotient

ADD: average daily dose

$BA_{As \text{ absolute soil}}$: Absolute bioaccessibility of arsenic (= relative biodisponibility)

RfD: reference dose

$$ILCR = LADD \times BA_{As \text{ absolute soil}} \times CSF \quad (4)$$

where:

ILCR: Incremental Lifetime Cancer Risk

LADD: Lifetime average daily dose

$BA_{As \text{ absolute soil}}$: Absolute bioaccessibility of arsenic (= relative biodisponibility)

CSF: Cancer slope factor

3 Data

3.1 Soil characterisation

Following EPA Method 6200 (EPA, 2007), a strong correlation ($r > 0.8$) must be established between the in situ XRF measurements and the arsenic concentrations measured in the laboratory to be used as a definitive characterisation tool. This method also specifies that one of every 20 XRF samples should be collected and submitted for laboratory analysis. 10 samples were collected and analysed out of the 177-pXRF measures. Figure 5 shows the correlation between in situ XRF arsenic and laboratory arsenic concentrations.

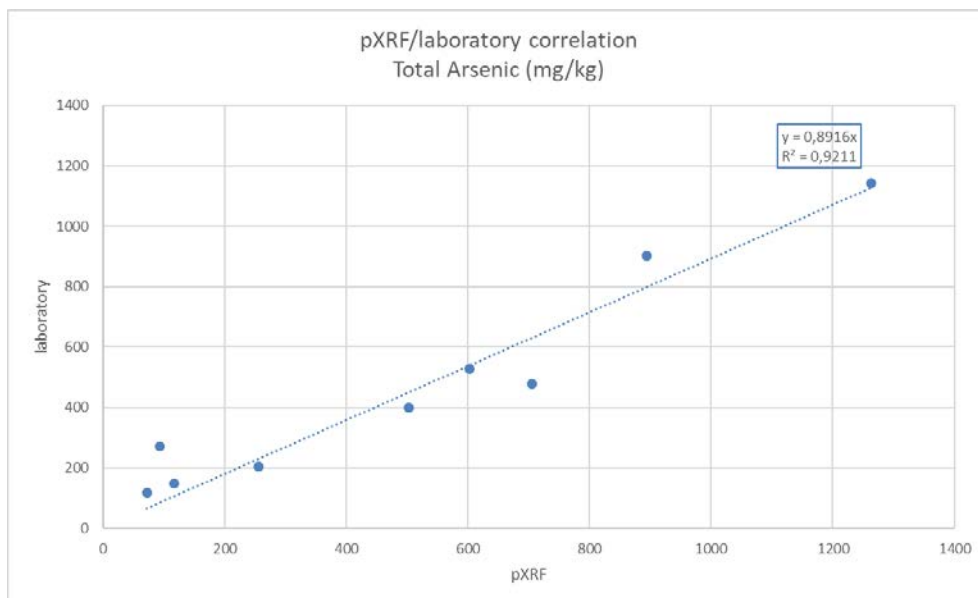


Figure 5 In situ XRF total concentration versus laboratory total arsenic concentration

A strong correlation ($R^2 = 0.92$) is shown between the pXRF arsenic measurements and the laboratory total arsenic concentrations. The equation mentioned on the Figure 5 was used to convert the pXRF measurements to laboratory equivalent arsenic concentrations at the site.

Figure 6 shows the arsenic concentrations repartition on the site. Arsenic concentrations in tailings and waste rocks on site range between 20 and 1,400 mg/kg, with 67 % of concentrations between 100 and 600 mg/kg, while the local geochemical background is around 100 mg/kg. The highest concentrations are encountered on the tailings deposit, while they are close to the local geochemical background (100 mg/kg) on the north part of the site

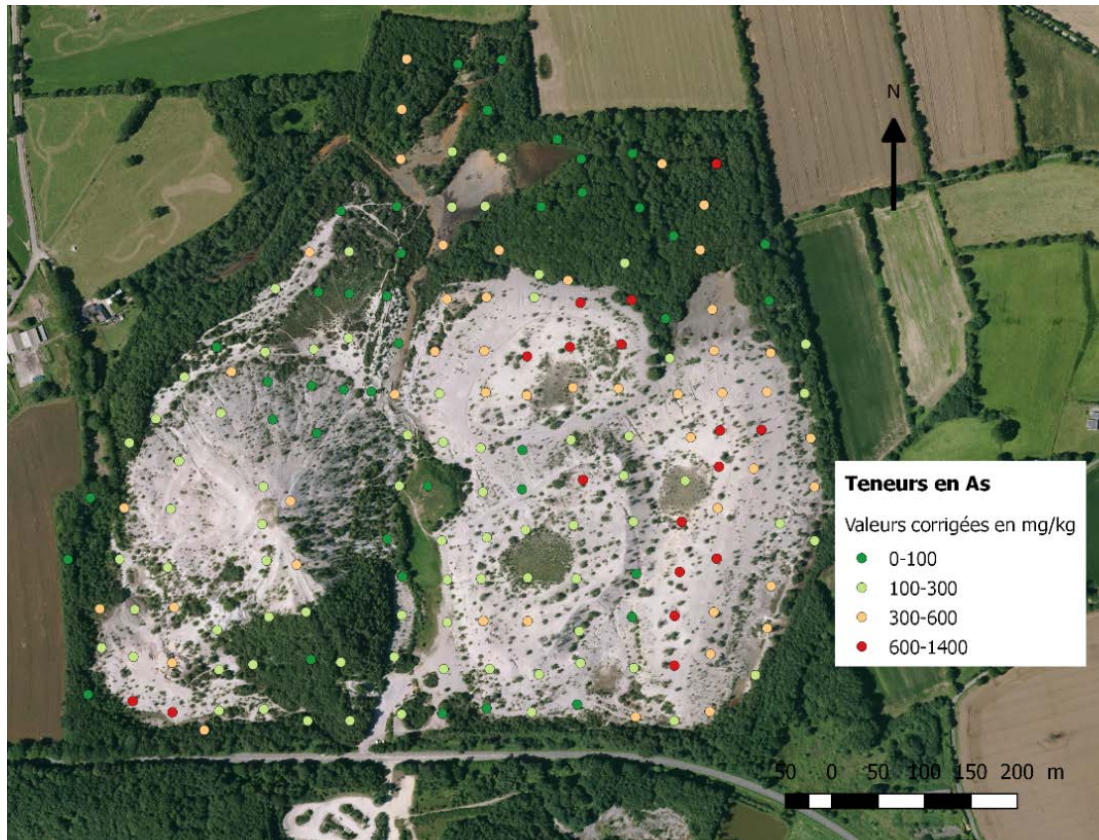


Figure 6 Total arsenic concentrations map

Given the large amount of data, chosen concentrations for HHRA is the average concentration calculated in each zone, as shown in Table 2. In a conservative approach, if the amount of data is not relevant, the maximal encountered concentration is selected leading to an overestimation of risk.

Zone	Number of analyses	Range of encountered concentrations	Selected concentration (average)	Standard deviation
Zone 1	51	26 - 1,031	199	175
Zone 2	77	46 - 1,138	368	253
Zone 3	20	26 - 417	151	123
Zone 4	18	115 - 1,031	282	234

Table 2 Selected arsenic concentrations on the different zones of exposure

3.2 Bioaccessibility

Results on the blank allow validating the absence of contamination related to the procedure that could affect the estimation of arsenic bioaccessibility in the samples.

Results on the reference material (NIST 2710a) reflect a good repeatability of the results and are consistent with all previous results obtained by the laboratory.

Figure 7 shows the results of absolute, gastric and gastrointestinal bioaccessibility in the 10 samples analysed (average, minimum and maximum of the 2 replicates per sample).

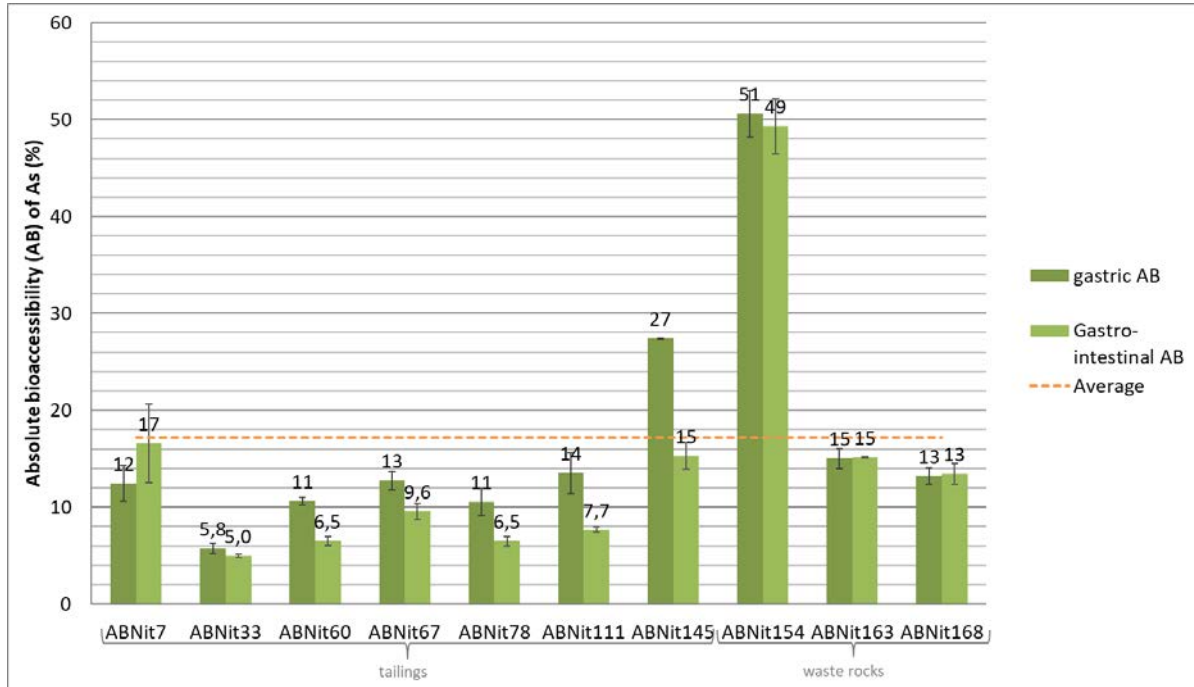


Figure 7 Bioaccessibility testing results

This figure shows a low variability of the results between the replicates of each sample.

Absolute gastric bioaccessibility is superior to gastrointestinal bioaccessibility for 6 samples and relatively similar for the other 4 samples. The gastric bioaccessibility measured on a waste rocks sample (51 % on ABNit154 for 537 mg/kg in soil) is higher than that measured on all the other samples (6 to 27 %). Despite this high value, gastric bioaccessibility in waste rocks is not significantly different than those in tailings (non-parametric Mann-Whitney test: $p=0.11$; significance of difference for $p<0.05$). Therefore, waste rock and tailings were considered to have similar arsenic gastric bioaccessibility, averaging at 17.2 %.

4 Results

Calculations of risk characterisation were performed with site specific parameters when they were available. Potential risks, calculated on the basis of the average concentrations and bioaccessibility of soils, are summarised in the Table 3 below.

Zone	Uses	Receptors	ILCR	HQ	Conclusion
Zone 1	Walking, running	Adult (6 to 70)	5,1E-06	1,2E-01	<u>Compatible</u>
		Child (2 to 6)	4,9E-06	4,7E-01	
		Child becoming adult (2 to 30)	8,6E-06	4,7E-01	
Zone 2	Walking, running	Adult (6 to 70)	9,4E-06	1,8E-01	<u>Not compatible</u>
		Child (2 to 6)	9,1E-06	7,2E-01	
		Child becoming adult (2 to 30)	1,6E-05	7,2E-01	
	Mountain bike, horse riding	Adult (6 to 70)	2,7E-05	4,6E-01	
	BMX	Adult (15 to 50)	3,2E-05	6,6E-01	
Zone 3	BMX	Adult (15 to 50)	1,3E-05	5,2E-01	<u>Not compatible</u>
Zone 4	Mountain bike	Adult (15 to 50)	2,5E-05	5,7E-01	<u>Not compatible</u>

Table 3 Results of risks characterisation

Results above show that HQ is less than 1 for all the considered zones and scenarios. But ILCR is higher than the threshold value (10^{-5}) on zone 2, 3 and 4 for all the considered scenarios.

For the scenario “walking and running” on zone 2, the contribution of risk is the high arsenic concentration, where for others scenarios (mountain bike, BMX, etc.) on zones 2, 3 and 4, the major contribution of risk is the high ingestion rate selected due to these activities that generate a lot of dust.

5 Conclusion

Results show that one zone of the site is compatible with a tourist and leisure use despite the high arsenic concentrations encountered. It would not have been possible to draw such conclusion without a good screening of arsenic occurrence and bioaccessibility testings. Indeed, this method allow a better representativeness of human exposure by a risk quantification more accurate and closer to the reality while remaining conservative.

Site improvements will be proposed to the municipality in order to better control the uses on the site, and to ensure health and environment protection:

- In zone 1, since risk levels are close to the acceptability threshold, it could be wise for example to reduce direct contact of the walkers with soil by consolidating the paths and areas with specific attractive structures (bench, viewpoint indicators) with non-erodible safe soil materials. We could also recommend the removal of the picnic area, where As concentration is higher than the average concentration of the area, or the substitution of the topsoil with safe previously controlled soil. These simple dispositions should be sufficient to enable a safe leisure development and public frequentation of zone 1.
- However, specific dispositions should be implemented to prevent public access to zones 2 to 4. Moreover, the improvement of the trail marking could also help to limit the access to these zones.

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