DELIVERABLE IX

ACTION B.4

Protocol for the management

of As-polluted sites.

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INTRODUCTION

In this document, a brief and concrete perspective on the problem of soil remediation in As-polluted soils will be introduced. The synthesis presented is based on the data, field experiences, and related topics obtained all along the development of the I+DARTS project, although collateral information, the existing literature, and previous studies are also in the inception of this document. The privileged information reported in I+DARTS implies that this guide is more focused in As-polluted soils typical for industrial or mining sites, although a number of them are usually polluted not only by As but for some other heavy metals and metalloids.

Arsenic (As) is predominantly present in the environment, and particularly in soils, in inorganic forms, more than in organic species, being the more habitual trivalent (arsenite) and pentavalent (arsenate); it is also frequent as sulfides such as arsenopyrite or As-rich pyrite. It can be released by naturally occurring processes such as volcanic eruptions and weathering of sulfide minerals. As previously announced, As is often incorrectly included between the group of heavy metals, given that in many polluted sites appear together with copper, mercury, lead and other metals usually included in the same category. However, As is a metalloid of complex geochemical behavior, and therefore its fate along the environmental compartments is different than that of the heavy metals, therefore it is better classified when included in a list of metalloids of concern that would also contain antimony and selenium.

As pop ups naturally in the geosphere, hydrosphere and even in the biosphere, and it can be easily transferred within natural spheres from volcanic eruptions, rocks weathering and fires. On the other hand, man-made products such as paintings, dyes, pesticides and others may include As in their compositions. In this context, the main inputs of As release in the environment are associated with mining and metallurgy works on metallic sulfides (for instance gold mining), with the agricultural use of chemicals containing As, with the production of paper and cement, and with the combustion of waste, coal or oil products.

As is toxic, being capable of substituting phosphorus in essential molecules for life. It is cataloged as a poisonous and carcinogenic element. Organic arsenic variants although very toxic are not usual in soils. Trivalent As has higher toxicity than the pentavalent.

In order to delimit the strategy to be followed when facing the problem of As-polluted soils, a classic approach based on the three usual steps of site remediation will be followed in this document: Site investigation, risk assessment and selection of remediation technologies.

1. - Site investigation.

The usual methodology to describe a heavy metal(loid)s polluted sites is based on quantitative analytics. However the proposal herein established includes not only total contents of the potential contaminants but an environmental forensics approach. Environmental forensics (EF) is dedicated to describe the significance and distribution of pollution but also to identifying former industrial practices and weathering processes associated with the current pollution in the study sites. In this regard, forensics approaches seek for signatures, and/or molecular-markers in order to identify distinctive features of site- or source-specific contamination. In addition, this requires complementary historical information associated with former industrial activities, a correct conceptual model about the geology, and hydrology/hydrogeology of the sites. In contrast, conventional characterisation studies are generally focused only on regulatory limits and the analysis of how much contaminant is present and not on providing information on the source of the contamination.

An EF approach in an As-polluted site could comprise an initial screening of possible sources of pollution (usually solid waste inappropriately disposed), possible affection of surficial water (specially water run-off after heavy rain) and groundwater, and even plants (rhizosphere zone). In fact, knowledge about the mechanisms that regulate the release, mobility, and natural attenuation of contaminants is critical to diminish environmental risks. For instance, the mobility and bioavailability of elements such as As largely depend on their chemical speciation, the predominant grain-sizes and the nature of the soil.

In As-polluted soils it is especially relevant the evaluation of contaminant bioavailability, not only for characterization scopes but for gaining information in order to develop risk assessment and selection of remediation technologies. Within the different analytical possibilities, sequential extraction methods and particularly the Tessier method are

appropriate[1], although other possibilities can be considered (see Table 1). Chemical speciation also cooperates to support conclusions about potential toxicity, although in most of cases only As (III) and As (V) are the only species found, even sometimes only As (V) is present specially in oxic environments or in oxidized waste.

As abovementioned, As-pollution is frequently linked to the presence of accompanying contaminants such as heavy metals (Hg, Cu, Zn, Pb, Cd, etc.) or metalloids (Sb, Se). The correlation between contents of these trace elements or even others can be very helpful to identify sources of pollution and to improve the conceptual model of an specific site. As a consequence, multielemental analyses and subsequent statistics (principal components and similar methods) are recommended.

In other matters, grain-size characterization of polluted soil is another interesting tool. In this sense, not only textural classification should be required but an effective in order to identify grain-size fractions in which the As and other potential contaminants are predominant. A supplementary study using microscopy devices (electronic, optical or microprobe systems) can be also a necessary complement especially in former mining areas where minerals, waste (both mining and metallurgy) can be found.

On the whole, although it is always possible to reduce the characterization step to a simple accumulation of total content determination many other tools are nowadays available (Table 1). In fact, a multi-faceted environmental forensic approach[2] demonstrates that it is possible to carefully unravel tangled evidence resulting from single or multiple soil pollution sources, and this approach would foster more effective risk assessment and site remediation procedures.

Table 1: Analytical approaches to As-polluted soils.

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[1] *Discussed and compared with others in Zimmermann and Weindorf, 2010. International Journal of Analytical Chemistry, Article ID 387803, http://dx.doi.org/10.1155/2010/387803*

[2] *Practical examples of this methodology can be found in the following I+DARTS derived publications: Gallego et al (2015). Comprehensive waste characterization and organic pollution co-occurrence in a Hg and As mining and metallurgy brownfield. Journal of Hazardous Materials, 300, 561-571. Gallego et al (2016). Insights into a 20-ha multi-contaminated brownfield megasite: An environmental forensics approach. Science of the Total Environment, 563-564, 683-692.*

Method/analytical technique	Results foreseen	Comments
As total contents by ICP or similar	As level in the study soil to be compared with soil threshold levels	Basic data required for site investigation
Multilemental analysis by ICP	Contents of trace elements of concern	Basic data required for site investigation
Chemical speciation (usually HPLC + ICP)	As(III), As(V) and organic species	Useful for mobility and toxicity studies
Sequential extraction (several digestions + ICP)	Distribution in bioavailable, mobile and immobile fractions	Useful for mobility, bioavailability and toxicity studies. Useful for feasibility studies of immobilization, bio and phytoremediation technologies
Specific digestion procedures (in vitro "gastric" digestion + ICP)	Relative bioavailability (RBA)	Useful for mobility, bioavailability and toxicity studies. Useful for feasibility studies of immobilization, bio and phytoremediation technologies
General grain-size (Bouyoucos or pipette methods, laser diffraction)	Percentage of silts and clays	Useful for toxicity assessment. It helps to predict As behavior.
Grain-size (wet sieving + ICP)	As-content in different grain-size fractions.	Useful for toxicity assessment. It helps to predict As behavior and to identify sources of pollution. Useful for feasibility studies of soil washing.
Mineralogy (general by DRX or optical microscope)	Main minerals and textures.	Basic data required for site investigation
Mineralogy (specific by SEM or microprobe)	As-minerals (quantitative)	It helps to predict As behavior and to identify sources of pollution.

2. - Risk assessment.

The necessity of risk-assessment is usually determined by the presence of As (or other contaminants) contents above soil screening levels (SSLs) also known as soil threshold levels. SSLs have been usually calculated by means of wide geochemical studies to determine natural backgrounds. In fact, current geochemical backgrounds for As (and other elements) may be elevated relative to levels occurring naturally as a result of industrialization, diffuse pollution, or other factors. Understanding and distinguish among those naturally occurring levels and current background levels (i.e., natural and anthropogenic sources included), and contributions to specific activities of concern, is truly necessary depending on the purpose of the risk assessment. In this context, in some countries/regions risk-based methodologies were used to determine SSLs in the last two decades (in those cases we can name them as RBSSLs – Risk-Based SSLs-).

Irrespective of SSLs determination, when focusing on a site-specific case clean up remediation levels obtained using toxicological considerations through risk assessment are usually very strict, given that As is a renowned carcinogen. This implies noticeable problems for risk management that maybe partially accomplished using data obtained in the methodologies described in the section above. In fact, site-specific human health risks are usually carried out by adapting an internationally recognized methodology (e.g. US EPA risk assessment method). These risks are characterized separately for carcinogenic and non-carcinogenic effects depending on current or future land use patterns (i.e.; residential, industrial, recreational and other uses –crops, cattle-) and thus facilitate the calculation of clean-up levels needed for remedial/corrective actions or to assist other risk management decisions (e.g., changing the land use pattern). Therefore, the final established RBRLs (Risk-based Remediation Levels) will be then applied together with the different possible land uses to obtain a matrix in which costs and remedial actions should be evaluated in order to satisfy the RBRLs and the hypothetic land uses. The problem with As is that most of times the RBRLs obtained are very low (below 20 ppm), and therefore the remedial actions are very expensive and most of the best and sustainable technologies cannot be applied.

For all the above, when dealing with inorganic (metal(oid)s) pollutants and especially with arsenic, it is important to take into account the implications of the bio-availability,

bioaccessibility and other concepts involved in risk assessment and clean-up goals. For instance, bioavailability is defined as the extent to which bioaccessible[3] metals cross biological membranes, expressed as a fraction of the total amount of metal the organism is proximately exposed to (at the sorption surface) during a given time and under defined conditions. Related to hazard, at equally toxic comparable levels for two substances the one with the higher intrinsic bioavailability would pose the greatest risk for either human health or ecological risk assessment.

Therefore, using site-specific bioavailability data to make adjustments to exposure estimates or toxicity values appear to be appropriate in order not to under or overestimate hazard risks. However, in the absence of reliable site-specific data, the default assumption is that the bioavailability of the contaminant is the same in the exposure medium at the site (e.g., soil, water, etc.) as in the exposure medium used to derive the toxicity value. As regards As, default assumption for assessing risks is that the bioavailability of arsenic in soil is the same as the bioavailability of arsenic dissolved in water; i.e., relative bioavailability (RBA) of arsenic (all forms) in soil compared to water-soluble arsenic is assumed to be 1. This assumption will obviously result in an overestimate of the true risk if the bioavailability of arsenic in soil is less than that of arsenic in water.

For human health risk assessment purposes, relative bioavailability is important because we are most often interested in knowing the extent to which the absolute bioavailability[4] of a chemical increases or decreases in different exposure compartments (e.g., food vs. water vs. soil) or with the physical or chemical form(s) of the chemical to which humans are exposed[5]. All things considered the EPA recommended that default RBA values should not be used when site-specific assessments are performed, as underestimate or overestimate risk may occur. However, most of times a default value of 60% is used, recognizing that the this is an estimate that is not likely to be exceeded at most sites and is preferable to the

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[3] *Bioaccessibility refers to the amount of environmentally available metal that actually interacts with the organism's contact surface and is potentially available for absorption.*

[4] *Absolute bioavailability (ABA) is defined as the ratio of the amount of arsenic absorbed to the amount ingested. This ratio is also referred to as the oral absorption fraction.*

[5] *U.S. EPA, OSWER 9200.1-113, 58 pp, 2012.*

assumption of an RBA equal to 100%. RBA development of site-specific could be derived in many different ways. Surely the more straight option is the application of an in vitro model of the SBRC's[6] test also recommended by the EPA; this provides a strong statistical comparison to As relative bioavailability (RBA) determined using in vivo models.

This sort of derivations allows obtaining an accurate RBA value to site-specific environmental conditions needed to perform a more reliable risk assessment. In this case, software based on risk corrective actions (RBCA) allows modifying the value of 0.6 established by default, as abovementioned, by the actual value calculated by the bioaccessibility test in the gastric phase (SRBC).

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[6] *Bradham et al., 2015. Independent Data Validation of an in Vitro Method for the Prediction of the Relative Bioavailability of Arsenic in Contaminated Soils. Environmental Science & Technology 9, 6312-6318.*

3. - Remediation technologies.

From the point of view of eliminating soil contaminants, this guide suggest with priority different cutting-edge technologies of decontamination in accordance with the Article 7 (point 3) of the Spanish Royal Decree 9 / 2005 (lit.): "*The recovery of contaminated soil will be carried out using the best techniques available ... The recovery actions should ensure that permanent solutions materialize, prioritizing, to the extent possible, in situ treatment techniques that avoid waste generation, transfer and disposal*". This is in coherence with the recommendations of the EU Soil Thematic Strategy: "*The recovery is raised to a level of functionality consistent with current and future applications, also considering the financial implication*".

In this sense, the latest best practice examples in Europe have followed these approaches and are based on the use of in situ & green technologies as much as possible[7]. The same can be said about the main trends (sustainable remediation) promoted by the two principal European land contamination stakeholder networks, the Common Forum on Contaminated Land (Common Forum, www.commonforum.eu/) and the Network for Industrially Contaminated Land in Europe (NICOLE, www.nicole.org/).

Following the preceding considerations, and specifically focusing on As-pollution, the current approaches should be based on efficient and sustainable in situ technologies. In this context, as exposed in the previous sections, it is not usual a soil only affected by As given that it is often accompanied by other elements (heavy metals and metalloids) thereby implying a multicomponent pollution that will be taken into account in the next paragraphs as a paradigmatic situation.

From a technical point of view, and once ruled out unsustainable and old solutions such as transport plus disposal option and confinement alternatives, the possible approaches can be divided into three groups:

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[7] *See for instance JRC, 2015. Remediated sites and brownfields. Success stories in Europe; http://publications.jrc.ec.europa.eu/repository/bitstream/JRC98077/lbna27530enn.pdf*

3.1 Mobilization and (phyto)extraction.

These are based on the recovery (extraction) of, as much as possible, of the total amount of contaminants. The most recommended option, for moderate or low levels of pollution, if the conditions of the soil are appropriate could be **phytoextraction**, but it requires the presence in the area of potential autochthonous phytoextractors or the adaptation to the local environment of well-known hyper accumulators. An ideal plant for use in phytoextraction must tolerate high concentrations of metal, be fast-growing, produce large biomass and accumulate high metal concentration mainly in the aboveground. It is also very important that the plants are well adapted to soil and climatic conditions of the area. If, in addition, there are forest species, the benefits are even greater, since mycorrhizal colonization of roots allows them to adapt better and grow in poor soils generating more biomass.

An additional requirement for phytoremediation is the presence of an enough quantity of contaminants in the bioavailable fractions (or at least in mobile fractions)[8]. Mobility can be also improved by means of the application of additional strategies:

- The first one consists on the use of hybrid technologies: i) **Bioaugmentation** (enhanced-phytoremediation) thereby combining microbes and plants to improve conditions in the rhizosphere, an example of combination of enhanced-phytoremediation is given in Figure 1; or, ii) **Electrokinetic**[9] to facilitate the movement of ions.

- The second one is based on the addition of amendments able to "desorb" the contaminants such as EDTA (not recommendable giving its toxicity), citric acid or others.

Other non-biological approaches within the extraction ones could be soil flushing o chemical extractions using biodegradable products but they are much less sustainable than phytoextraction.

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[8] *Usually bioavailable fractions include the first two fractions of the sequential extraction (Tessier methodology), and mobile fractions the third and fourth. The only immobile fraction is the fifth one (residual).*
[9] *Electrokinetic by itself is another option for extracting contaminants but real-scale treatments are scarce and feasibility studies usually unsatisfactory.*
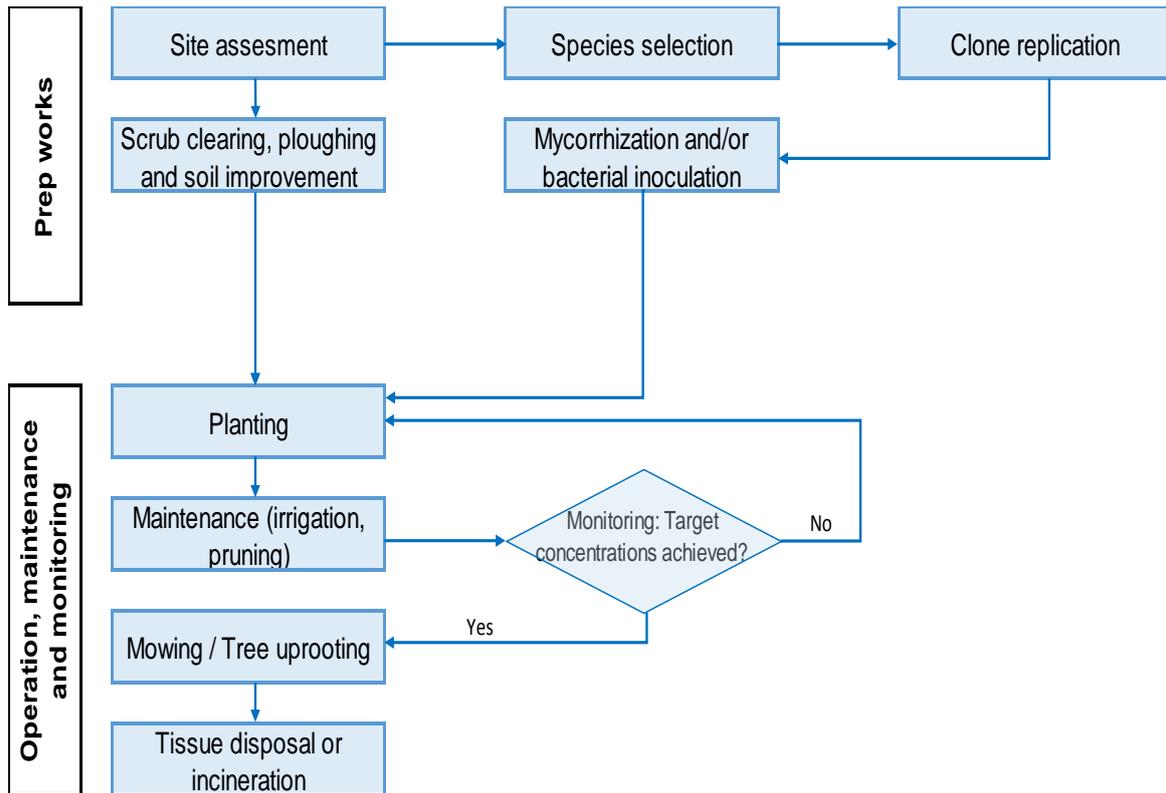
Figure 1: Flow-chart of a possible enhanced-phytoremediation treatment.

3.2 Immobilization.

In situ fixation strategies involve the addition of chemical amendments to the soil matrix to "fix" contaminants by inducing a targeted chemical reaction or process that renders the contaminant immobile and/or non-bioavailable (in this situation, bioavailability refers to the fractional uptake of As in soil into human or ecological receptors). These strategies are similar to in situ solidification/stabilization technologies, which typically involve the use of binding reagents to both induce chemical reactions to immobilize contaminants and enmesh the contaminants within a solidified bulk matrix. Solidification/stabilization treatment can substantially alter the soil properties, such as increasing the soil volume, reducing the soil permeability, and increasing soil pH.

In situ fixation, on the other hand, involves the use of specific chemical amendments to induce chemical reactions that provide for long-term immobilization of the contaminant without substantially altering the soil properties. The objective of this approach is just the opposite of that explained in the preceding section: the immobilization in "inert" residual fractions of as much arsenic as possible, thus minimizing the leachability and the bioavailability and, as a consequence, the environmental risk in general terms. The most important problem for this tactic is most of the national laws and risk assessment methodologies do not explicitly consider the bioavailable fractions for the use of SSL or in the calculation of risks. In fact, although many scientific evidences suggest changes, it is still well-established the use of total concentrations as the main criteria. Therefore the application of immobilization techniques, require not only a good performance but a specific acceptance by the environmental authorities.

From the technical point of view, the most usual alternatives for immobilization in the case of As-pollute soils are the following:

- Amendments addition; usually iron or iron-derived products although many other possibilities including organic products have been used. In fact, a range of products can be used to immobilize metal(loid)s in soil such as organic amendments, by-products from iron and aluminum industry, biochar, coal or bio-fuel fly ashes, gypsum and lime-rich industrial by-products, phosphate compounds, etc. [10]

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[10] For a detailed discussion, see Bolan et al. 2014. Remediation of heavy metal(loid)s contaminated soils - to mobilize or to immobilize? Journal of Hazardous Materials, 266, 141-166.

- **Nanoremediation**, although it could be considered a subgroup included in the preceding one, is taking more importance in the last years and it is probably the technology with a higher room of improvement. Within the different types of "nanocompounds" available, nanoparticles of zero-valent iron (nZVI) are the only realistic option at the present moment. nZVI introduces a significantly increased available reactive surface areas (very high surface area to weight ratio) compared to larger sized ZVI particles, thereby resulting in higher reactivity rates than micron scale ZVI when normalized to mass, which consequently enhances contaminant degradation reactions. Therefore, the use of nZVI to remediate soil and groundwater has increased within the last years, and the use of nZVI has been effective for degrading organic pollutants such as chlorinated organic compounds, and for immobilizing metal(loid)s specially in groundwater, but also in soils.

- **Phytostabilization**, which is based on the ability of some plants to immobilize metal(loids) within the rhizosphere. High adaptability of spontaneous species with multiple metal/metalloid tolerance has been widely reported to serve as potential candidates for phytostabilization of the contaminated sites. Arsenic phytostabilization with indigenous tolerant species with low translocation capacity is advantageous for heavily contaminated sites with high levels of arsenic and other toxic metals. Amendments such as iron oxides, phosphate, organic matter, N-fixation legume and mycorrhizal inoculation are important for plant survival in hostile environment and serve as core strategies to facilitate the success of phytostabilization.

3.3   Excavation and elimination.

These are on-site strategies that require soil excavation and treatment with physic-chemical and thermal treatments. In these guidelines we explicitly exclude ex situ techniques that require the transport of the polluted soils to treatment plants or disposal sites, therefore only technologies available in mobile plants are included.

A first option to treat, for example, a concurrent contamination of arsenic and mercury, could be a thermal desorption[11]; however the secondary impacts of this technology and a possible partial efficiency for arsenic are important disadvantages.

Another option is **soil washing** by means of a combination of physic-chemical technologies including grain-size, gravimetric or magnetic separation together with the use of flotation of chemical extraction approaches (see Figure 2). Soil washing is very versatile and it can be very efficient in sites where a high volume of polluted soil has to be treated. Unfortunately there are only a very few examples of real-scale application for soils affected with arsenic.

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[11] https://clu-in.org/download/Citizens/a_citizens_guide_to_thermal_desorption.pdf
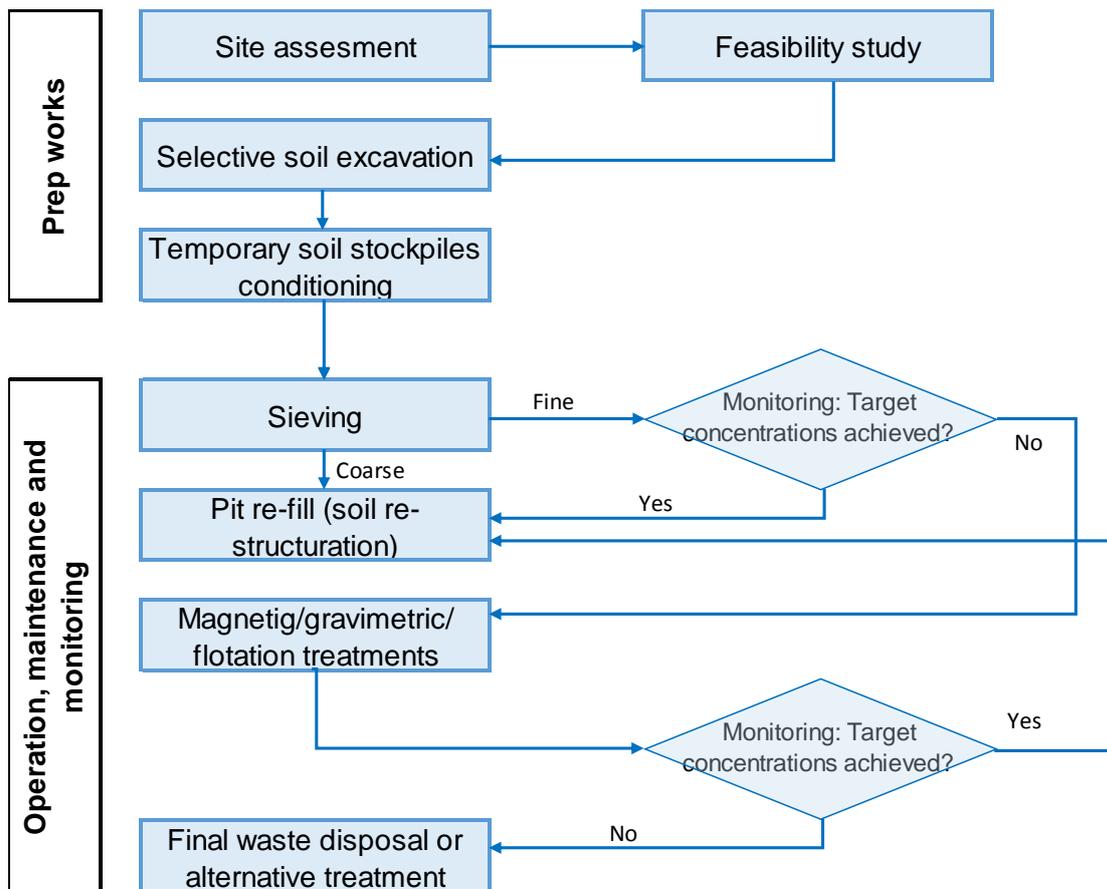
Figure 2: Flow-chart of a possible soil washing treatment.

3.4 Criteria for technology selection.

At any circumstance, and previously to the selection of one of the technologies described above, three main approaches should be considered:

- A detailed knowledge of the site-specific chemistry of As (and accompanying contaminants) should be acquired. In this sense, it is recommended the application of some of the methods indicated in Table 1 (especially those useful to estimate to bioavailability). In this context it must be highlighted how the additional costs suffered in a scrupulous investigation phase usually report higher savings in the remediation step. The effect of these approaches in the use of several technologies has been addressed in I+DARTS as summarized in Table 2.

Table 2: Summary of the main factor affecting remediation technologies when a dynamic risk assessment is applied.

Technology	Reduction of total As concentration in soil	Transformation As(III) vs. As (V)	Reduction of As bioavailability in soil	Effects in environmental risks	Secondary impact (see also action C3)
Phytoextraction	Yes, but very slow	Only to favour plant absorption in the rhizosphere	Yes	Reduction by means of lower bioavailability and decrease of total concentrations	Low
Bioremediation (enhanced phytoremediation)	Yes, but very slow	Improved, only to favour plant absorption	Yes	Reduction by means of lower bioavailability and decrease of total concentrations	Low
Phytostabilization	No	No	Yes	Reduction by means of lower bioavailability	Very low
Electrokinetic	Yes	Not observed	Yes	Reduction by means of decrease of total concentrations	Medium
Soil washing	Yes	No	No	Reduction by means of decrease of total concentrations	Medium-high
Nanoremediation	No	No, possible reduction not observed	Yes	Reduction by means of lower bioavailability	Low (nZVI effects are not significant)

- Lab-scale and pilot-scale tests are also very recommendable if time and potential costs are acceptable. The possibility to compare different technologies or different variants within the same technologies will always facilitate a better approach for the final selection. This affects both immobilization technologies (checking different amendments, plants, etc.) and extraction technologies (for instance, feasibility studies for soil washing as indicated in Figure 2).

- It must be taken into account the generation of possible subproducts or waste as a consequence for the application of a specific technology. This may suppose sometimes an additional cost to be accounted (wastewater generated in soil washing, incineration of phytoextracting plants, etc.) or even an opportunity to diminish the treatment costs. For the latter, it is often possible the utilization of phytoextracting or phytostabilizing plants with high growth rates useful for producing valuable biomass or even biofuels; in the same sense, high metal-content residues of soil washing (usually fine-grained fractions) can be a potential source of metal recovery.

All things together, in I+DARTS, potential cost of future real-scale treatments was evaluated using a 1-Ha normalized hypothetical parcel, with common conditions of As levels, depth of affection and other factors. This facilitated the achievement of comparable data between the different technologies being applied in the demonstration works. A summary of the results obtained with this approach is shown in Table 3:

Table 3: Estimated costs of real-scale application of the technologies tested in I+DARTS

Technology	Cost calculated (following I+DARTS conclusions)	Cost (average estimation for Spain) [(*)]	Cost (international sources) [(*)]	Comments
Phytoextraction	70- 90 €/m^3	60 €/m^3	50 -100 €/m^3	
Bioremediation (enhanced phytoremediation)	80- 100 €/m^3	60 – 80 €/m^3	40 -120 €/m^3	Data of other sources than I+DARTS based on hydrocarbon remediation
Phytostabilization	30 – 40 €/m^3	40 €/m^3	20 – 50 €/m^3	
Electrokinetic	100 – 120 €/m^3	200 €/m^3	150 €/m^3	
Soil washing	130 – 150 €/m^3	150 – 170 €/m^3	80 -200	High cost of infrastructure, increasing yield and decreasing costs with high volumes of soil
Nanoremediation	100 - 150 €/m^3	No data available	No data available	Data available only for groundwater remediation

(*) Based on different sources

4. - Conclusion.

Arsenic is a usual contaminant of soil with harmful effects and many difficulties to be addressed and remediated. Arsenic polluted-sites require important efforts further than conventional approaches (quantification of contamination and excavation & disposal) to achieve a sustainable remediation.

As regards the characterization step, environmental forensic including bioavailability determinations should be considered, in order to make more effective subsequent risk assessment and site remediation procedures.

Site-specific approaches are necessary for the remediation of arsenic-polluted areas. Two of the three main strategies possible (immobilization, mobilization and extraction) apply green-technologies mainly based on phytoremediation easily combinable with amendments or complementary approaches. On the contrary, if physic-chemical technologies are required, soil washing is a versatile option given the high number of variants and supplementary technologies to be combined. Therefore, at any case, specific successful treatments would always incorporate hybrid technologies.