DELIVERABLE IX

ACTIONS C1, C2, C3

Monitoring actions

0. - INTRODUCTION

The monitoring tasks carried out within the project (Actions C1, C2 and C3) have been useful to evaluate economic, environmental (secondary impacts) and soil uses features related to the technologies applied. In this document the main outcomes obtained and the methodologies followed in each one of them are described.

1. Action C.1. Efficiency Analysis of Proposed Remediation Technologies.

1.1 Dynamic risk assessment.

This action was directly derived of the decisions taken in action B1 (Risk Assessment) and also of the cost of the technologies applied in B3. Regarding risk assessment, as stated above, cooperation with IETU was scheduled for this task (a meeting was celebrated in Poland in July 2014 as a continuation of their cooperation in the project initiated in 2013), the methodology that was applied is the following:

- Results for risk analyses obtained in Action B1 were considered a baseline, although some additional data regarding plant contamination and possible consumption by cattle had to be considered (at Olicio site).
- Different scenarios contemplated include not only soil uses but the advanced chemistry of the contaminants; in this sense chemical speciation -for instance As(III) and As (V) proportions were calculated-, and sequential extraction procedures (Tessier) were tested to effectively evaluate real risks. In fact, knowledge about the mechanisms that regulate the release, mobility, and natural attenuation of contaminants is critical to diminish environmental risks. The mobility and bioavailability of elements such as arsenic largely depend on their chemical speciation, and not all forms are equally toxic; arsenite compounds (As(III)) are considered slightly more toxic than arsenate (As(V)).
- The effects of the technologies cannot be considered only in terms of As concentration reduction, it has to be taken into account that some of them (e.g. phytostabilization, nanoremediation) are centred on immobilization and not in extraction or elimination of the contaminants. In this sense, SSL (Soil Screening Level) or RBSSL (Risk Based Soil Screening Level) are essentially risk assessment calculations performed in reverse (i.e., solving for soil concentration based on a specified degree of risk or hazard) taking also into account natural backgrounds. Thus these levels in fact impose a threshold for several chemical elements from which a soil would require a site-specific risk assessment. This value changes usually in terms of the use of the soil; i.e. industrial, residential, recreational and other uses (natural soils, such as agricultural or forests) as happens in our case. In this context, bioavailability and toxicity data of the potential contaminants should be considered to refine the bulk data of total concentrations

As a summary of the results Tables 1 and 2, presents the main conclusions of this type of approach:

Table 1: 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)

Table 2: Application of the criteria exposed in Table 1 merged with data obtained in the study sites and with an "extrapolation" of results and knowledge acquired to real-scale treatments.

Technology	***NITRASTUR***		
	Feasibility	***Effects on risk management***	***Main advantages/ constraints***
Phytoextraction	Feasible, although slow. Faster when considered phytoextraction and phytostabilization effects together.	Moderate reduction	Bioavailable fractions are minority
Bioremediation (enhanced phytoremediation)	Feasible, it improves phytoextraction yields.	Moderate reduction	Bioavailable fractions increased by bacterial action
Phytostabilization	Feasible, especially in areas with low risks.	Slow reduction, only if bioavailable fractions considered	Current law promotes total contents as the main reference
Electrokinetic	Feasible, although combination with other technologies should be attempted	Moderate reduction	Only lab tests were made.
Soil washing	Very feasible, high yields	Quick reduction	Requires excavation, high costs (see table 3). Possible metal recovery would reduce costs.
Nanoremediation	Not useful for soil (too much extension), possible for groundwater (by means or permeable Barriers)	Moderate reduction	Very local effect, high costs.

Table 2 (cont.)

Technology	***EL TERRONAL***		
	Feasibility	***Effects on risk management***	***Main advantages/ constraints***
Phytoextraction	Low feasibility, very slow.	Low reduction	Very high As-contents although bioavailable fractions are also high
Bioremediation (enhanced phytoremediation)	Low feasibility, it improves slightly phytoextraction yields.	Low reduction	Very high As-contents although bioavailable fractions are also high
Phytostabilization	Feasible only as a complement to other technologies. Appropriate to reduce As-bioavailability	Slow reduction, only if bioavailable fractions considered	Very high As-contents Current law promotes total contents as the main reference
Electrokinetic	Feasible, although combination with other technologies should be attempted	Low reduction	Generates wastewater with high load of As and Hg. Not enough data for real-scale estimation
Soil washing	Not feasible	-	Very high As-contents
Nanoremediation	Feasible only as a complement to other technologies. Very quick reduction of As-bioavailability	Moderate reduction only if bioavailable fractions considered	High costs. Other less expensive immobilization alternatives should be tested.

Table 2 (cont.)

Technology	***OLICIO***		
	Feasibility	***Effects on risk management***	***Main advantages/ constraints***
Phytoextraction	Not feasible.	-	Very low As-bioavailable contents
Bioremediation (enhanced phytoremediation)	Not feasible.	-	Very low As-bioavailable contents
Phytostabilization	Very feasible as revealed by the natural attenuation process	Slow reduction, only if bioavailable fractions considered	Moderate-low initial As-contents. Current law promotes total contents as the main reference
Electrokinetic	Not feasible	-	Very low As mobility
Soil washing	Feasible	Quick reduction	Requires excavation. Low volume of soil affected (implies high cost per ton).
Nanoremediation	Feasible	Moderate reduction only if bioavailable fractions considered	High costs, although low volumes of soil are affected. Useful to consolidate immobilization.

Finally, methodologies followed for the analytical approaches followed in this issue (sequential extraction and chemical speciation) are briefly described below:

Given that knowledge of the mechanisms that regulate the release and mobility of contaminants is essential to evaluate the potential risks, a sequential extraction methodology was performed for selected samples. In brief, extracts with reagents of increasing strengths were attained on 2.5-g soil samples and the following fractions were obtained:

- Exchangeable: 2.5 g of dried waste was weighed and transferred to 50-mL centrifuge tubes, to which 25 mL of $MgCl_2$ (1 M, pH 7) was added. The tubes were vigorously shaken at room temperature for 1 h and then centrifuged at 13,000 rpm for 30 min.

The supernatant was passed through a Whatman filter paper (no. 542) and made up to 25 mL.

- Carbonate-bound: The residue from the exchangeable fraction was mixed with 25 mL of CH_3COONa/CH_3COOH buffer (1 M, pH 5); the tubes were shaken at room temperature for 5 h and then centrifuged and treated under the same conditions described above.
- Fe-Mn oxide-bound: The residue from the carbonate fraction was mixed with 25 mL of $NH_2OH.HCl$ (0.04 M in acetic acid 25%); the tubes were shaken at 96ºC in a water bath for 6 h and then centrifuged and treated under the same conditions described above.
- Organic matter-bound: The residue from Fe/Mn oxide-bound fraction was mixed with 5 mL of 30% H_2O_2 and 3 mL of 0.01 M HNO_3; the tubes were shaken at 85ºC in a water bath for 5 h, followed by the addition of 2 mL of 30% H_2O_2 and 1 h at 85ºC in a water bath. Finally, 15 mL of 1 M NH_4NO_3 was added and followed by 10 min of shaking at room temperature. The tubes were then centrifuged and treated under the same conditions described above.
- Residual fraction: The residue from the organic matter-bound fraction was air-dried and ground with an agate mortar. 0.250 g of the ground residue was leached by means of an 'Aqua regia' digestion (HCl + HNO_3) in an Anton Paar 3000 microwave. This fraction and the preceding liquid ones were analysed for heavy metal(loid) content by means of ICP-MS, as detailed in section 2.3.1

On the other hand; As, Hg, and Cr speciation were also evaluated in order to identify the proportion of As (III), Hg (organic), and Cr (VI), more toxic than As (V), Hg (inorganic) and Cr (III) respectively. The species were separated and subsequently quantified in a 1260 Infinity HPLC coupled to a 7700 ICPMS (Agilent Technologies).

1.2 Costs of real-scale treatments.

Regarding economic considerations, cost of future real-scale treatments was evaluated in the second semester of 2015 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

Is must be taken into account that data included in the preceding table are only an approximation. In fact, a method that can effectively allocate remediation funds is necessary because of the high cost of remediation and the usual insufficiency of funds. Decision-making on the application of remediation alternatives is a crucial step after a comprehensive analysis and assessment of contaminants has been conducted. However, available case studies are insufficient, resulting in incomplete essential parameters. Correct decision-making is achieved with enhanced experience and knowledge on the consequences of the decision. These experience and knowledge should be derived from real cases and unfortunately the number of those in Spain is very low.

In addition, the adopted remediation strategy will impact on the cost of the remediation. The amount of remediation, and therefore cost, is very sensitive to the level at which remediation targets are set and to a wide range of other variables. It is not unusual on one scheme, for several contractors to propose different remediation strategies and techniques to suit their operational capability, experience and preference. This may result in a range of costs for the site remediation. The current market conditions should be considered as this may have an impact on the remediation costs due to contractor availability.

2. Action C.2. Socio-Economic effects of LIFE I+DARTS.

This action was mainly focus on the possible future developments to be made in the study sites after a partial or full decontamination. Therefore, it was related with the analysis of the land uses and urban/spatial planning. Different tasks to complete the scheduled objectives were accomplished:

- Meetings with local administration as explained in Action A2.
- Meetings with land owners in order to know their future plans.
- Sites classification in brownfield terminology and prospective of their future uses.

I+DARTS project was mainly located in Langreo and Mieres (Asturias, Spain), two cities characterized by a recent past of local economy highly dependent on heavy industry and mining, which are suffering nowadays notable effects of depopulation and unemployment. The affection of the environmental quality as a consequence of the past and current industrial activities not only conditions the urban planning of the city, but also implies human health risks (as happens in Nitrastur and El Terronal) and it has deteriorated local development, citizens´ sense of place/belonging and hope for new opportunities that revitalize their social and economic fabric. Taking this into account, citizens and other local participants/stakeholders constituted a target audience of the project. Finally, it is expected that current citizen´s satisfaction about their environment at the beginning of the project (environmental quality perception of inhabitants) will increase if finally the demonstration sites are redeveloped.

This was associated with the analysis of the legal situation of the sites in the context of spatial and urban planning conditions in these areas. In this sense, the experts in land planning within the UNIOVI team carefully analysed the current situation (owners, uses, etc.) of the lands under study. In addition, when characterization studies and risk assessment (actions A3 and B1) were close to their end, several contacts with local authorities were done to know their future ideas for land planning affecting the sites studied; in this context, frequent meetings with land owners and local authorities have been carried out all along the project with special relevance to the contacts established with the Langreo city council in order to study in detail the situation of Nitrastur. These activities were leaded by the UNIOVI team but with a main contribution of the PRAS participants in the project.

The situation of the three sites can be summarized as follows[1]:

- Nitrastur: The environmental problem of this area has hindered its incorporation to the urban planning of Langreo, although there is a special planning for the area still inactive. The result is the presence of barrier effect between two of the main populated areas of the

[1] A more detailed description of these issues was presented in Deliverable III annexed to the mid-term report.

city, what it was fostered by the existence of main roads, railway lines and a main river delimiting a great part of the brownfield. In a first approach, the possible future uses of the parcel are recreative, residential or partially industrial. After frequent meetings of information exchange with local administration, land owners and, neighbourhood associations (Langreo), the approach finally proposed is the following: Taking into account the absence of urbanistic interest (Langreo is a shrinking city, especially after the economic crisis 2008-2013), the absence of industrial interests (the abundance of empty industrial soil in Asturias is high) and the site location (it is generating a barrier effect between two of the main populated areas of the city), the most appropriate future use after remediation for the most affected areas of the site could be recreational. In this sense there are some interesting examples in other European areas of the transformation of these sorts of sites into a free gardened space where the main elements of industrial heritage (in Nitrastur, at least three buildings) are preserved.

- El Terronal: It is located in a peri-urban area quite degraded, and nowadays isolated of possible growth axes of the city of Mieres. In fact, the surroundings have been transformed in a cuasi-rural area without significant economic activities, in addition the recent construction of a motorway implied on one side the encapsulation of a part of the spoil heaps and on the other side the erection of a second physical barrier also conditioning the valley topography. There is no urban planning in Mieres since 1985 and therefore the uncertainty about this area is the present situation. Our main conclusion is that the only option to reach a reasonable cleaning objective in this area is the preservation of industrial use, even if no installation of future industrial activities is foreseen. In addition, the problematical is not only restricted to El Terronal parcel; as a result of the industrial abandonment the surroundings suffered effects of depopulation and rising unemployment, together with the affection of the environmental quality. At the same time, both natural and urban soils in this zone have been subjected to an increase in PTEs concentrations as a result of the atmospheric emissions of industry and mining for more than a century (diffuse anthropogenic pollution).

- Olicio: It is located in the municipality of Cangas de Onís (Asturias, Northern Spain), very close to the “Picos de Europa” National Park; therefore the interest of this area is linked to special environmental requirements. This site was included in the 2000s in the Spanish national inventory of polluted soils, and it is very representative of many other sites (mainly spoil heaps and soils affected) situated in mountain areas within northern Spain. Mining exploitation of Hg ores such as cinnabar took place in Olicio between the 1950s and 1970s, and finished abruptly after the crash in Hg prices (mid 1970s). Since then, the site was abandoned and the area was covered by spontaneous vegetation whereas a minor stream flows through the site as a vestige of a small valley that was used to dispose most of the waste generated in the Hg mining and metallurgical activities. Currently Cattle (cows) and agriculture are the main activities in the area. The location of this site far from touristic attractions or main roads in a rural area favoured the traditional uses, and any future planning (including hypothetical remediation works) should capture this local context. It is not foreseen any change in the soil use if this area and therefore an effective demonstration of the absence of environmental risk should be required after remediation.

3. Action C.3. Environmental Impact Assessment (Secondary Impacts).

A similar procedure to that explained in action C.1 for evaluation of remediation costs was designed to evaluate secondary impacts using a 1-Ha normalized hypothetical parcel. This was done to facilitate the achievement of comparable data between the different technologies being applied in the demonstration works. The main results are shown in a matrix/table in deliverable X (annexed to this final report). The aspects taken into account have been:

- The *in situ* or *on site* characteristics of the technology.
- The necessity or absence of preparatory works, the area occupied and the complementary operations needed during implementation
- Energy, chemicals and water consumption
- Liquid effluents and waste generation
- Restoration of soil functions and CO_2 mitigation

As it could be expected, the results for green technologies are more favourable from the point of view of secondary impacts as summarized in Table 4 (see pages below:

IMPACT	TECHNOLOGY					
	Phytoextraction	**Bioremediation (enhanced Phytoextraction)**	**Phytoestabilization**	**Soil washing**	**Electrokinetic**	**Nanoremediation**
In-situ / On-site	In-situ	In-situ	In-situ	On-site	In-situ	In-situ
Preparatory works (prior to remediation)	Access control, ploughing	Access control, ploughing	Access control, ploughing	Selective soil excavation, access control	Access control, electrode planting	Access control, ploughing
Area occupied	Limited to remediation area	Limited to remediation area	Limited to remediation area	Remediated (excavated) area + Soil washing plant + Soil temporary stockpiles	Remediation area + auxiliar facilities (100 m2)	Limited to remediation area
Complementary operations (during or after remediation)	Planting, soil improvement, irrigation, pruning, harvesting	Planting, soil improvement, irrigation, pruning, harvesting, bioaugmentation	Planting, soil improvement, pruning, irrigation	Stockpile conditioning + Excavation pit restoration (soil re-structuring and re-placement)	Water pumping, excavation of soil in the anode area	Tilling
Energy consumption	Low	Low, although preparation of cultures is required	Very low	Yes, high	Yes, low although depends on electric potential	Low
Chemicals consumption	Soil amendments	Soil amendments	Soil amendments	Surfactants / Chelanting agents	Electrode solution	Nanoparticles
Water consumption	Irrigation (50 l/m2 twice a year)	Irrigation (50 l/m2 twice a year)	Irrigation (50 l/m2 twice a year)	Yes for wet sieving (How much?)	Yes (How much?)	Very low
Liquid efluent	No	No	No	Yes (sludge)	Yes (water)	No
Waste generation	Yes (phytoaccumulated vegetal tissue)	Yes (phytoaccumulated vegetal tissue)	No	Yes (Concentrated contaminated soil)	Yes (wasted electrode solution and contaminated water)	No

Soil function restoration (aside from decontamination)	Yes	Yes	Yes	No	No	Yes
CO_2 mitigation	Yes	Yes	Yes	No	No	No
Other secondary impacts	Habitat restoration (+) Long term land occupation (+/-) Animal exposure to plant intake (-) Soil amendments side effects (heavy metals mobilization) (-) Good social acceptance (Green technology) (+)	Habitat restoration (+) Long term land occupation (+/-) Animal exposure to plant intake (-) Soil amendments side effects (heavy metals mobilization) (-) Good social acceptance (Green technology), although bioaugmentation can be questioned (+/-)	Habitat restoration (+) Long term land occupation (+/-) Animal exposure to plant intake (-) Soil amendments side effects (heavy metals mobilization) (-) Good social acceptance (Green technology) (+)	Soil properties alteration (-) Short term land occupation (+)	Soil properties alteration (-) Short term land occupation (+) Circulating water can have side effects (heavy metals mobilization to groundwater) (-)	Soil properties alteration (+/-) Short term land occupation (+) Possible secondary effects of nanoparticles (-)