European Union Network for the Implementation
and Enforcement of Environmental Law

Annex 1

Soil Washing – Case studies

IMPEL Project no. 2021 /08 WG6

1. Your contact details - CASE STUDY: SW n.1

1.1. Name and Surname	Alessandro Teani
1.2. Country/Jurisdiction	Italy
1.3. Organisation	Ambienthesis S.p.A., now Greenthesis S.p.A.
1.4. Position	CTO
1.5. Duties	
1.6. Email address	Alessandro.teani@greenthesisgroup.com
1.7. Phone number	+ 39 335 62 01 002

2. Site background

2.1 History of the site

The concerned area subject to the remediation is located near Milan, Italy. It’s an old industrial site used before for the steel and metallurgical production activities.

The area is divided into sections and is bout 1,290,000 m^2, approximately.

Only the area near the railroad will be subject to the remediation activities and is bout 400.000 m^2, approximately.

2.2 Geological setting

The area of interest is flat, about 140 m above sea level. The soil is composed by gravelly-sandy and sandy alluvial deposits.

The aquifer is at a depth of 30 meters below ground surface.

The first meter of the superficial soil contains slag and other residues mixed with the soil.

2.3 Contaminants of concern

The major part of contaminants is composed by hydrocarbons (light and heavy) and metals (Zn, Cd, Pb, Cr).

The range of contamination is between 100 and 20,000 mg/kg for hydrocarbons and between 300 and 7000 mg/kg for metals.

During the excavations, residues of materials with asbestos were also found, as well as bombs left over from the war, and other waste that was managed separately and safely.

2.4 Regulatory framework

The intervention on the site is developed according to the project approved by the Italian Ministry of the Environment. The soils had to be treated with soil washing in order to allow the recovery of the fractions conforming to the future uses of the residential areas. The non-recoverable fractions that did not comply with the limits of use were sent to landfills. Some portions of land have been subjected to preliminary screening before being subjected to soil washing. Demolition residues were also subjected to volumetric reduction treatment for on-site recovery.

The remediation objectives were measured in relation to the contamination threshold concentrations allowed by Italian law for sites for future residential use, as well as in relation to the eluate for monitoring the quality of the groundwater.

3. Pilot-scale application in field

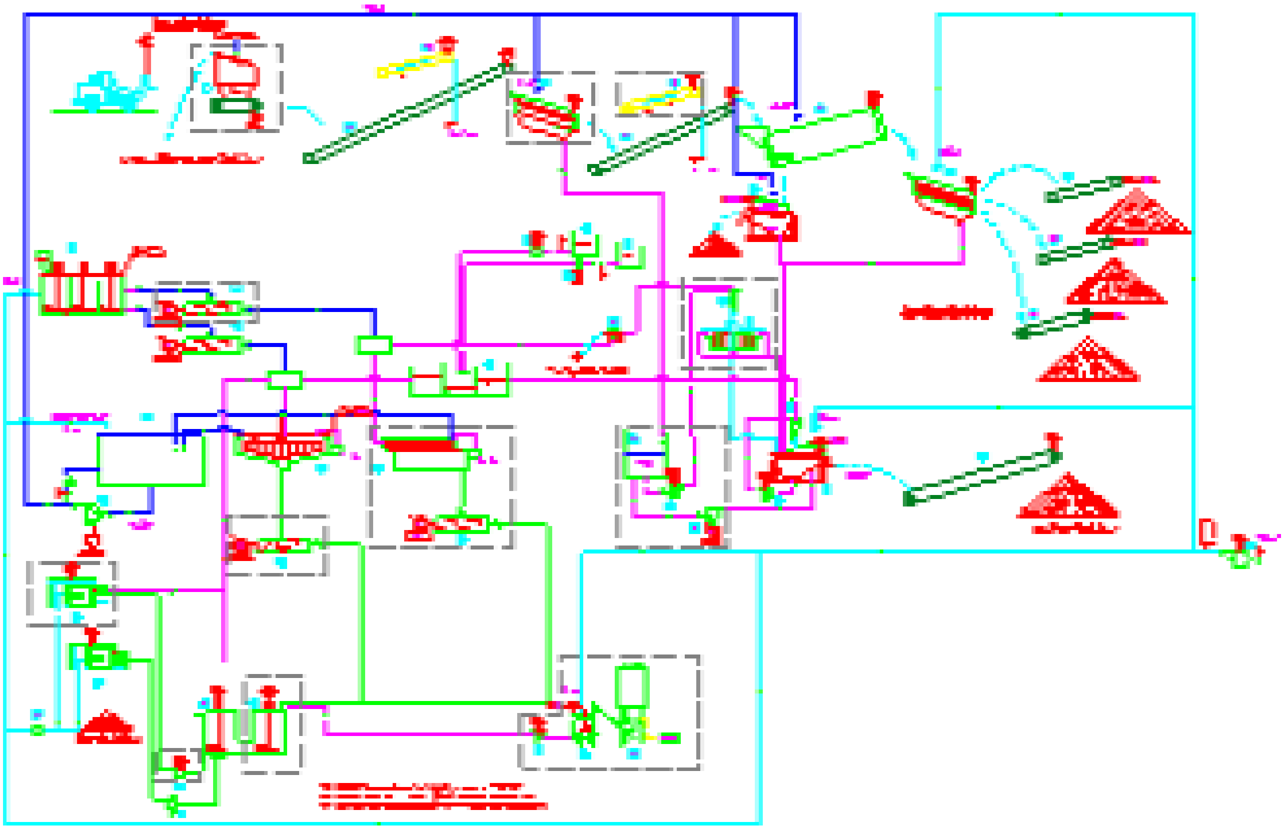
3.1 Soil washing system

There’s no pilot-scale application. Only full scale application based on the lab test of the tender.

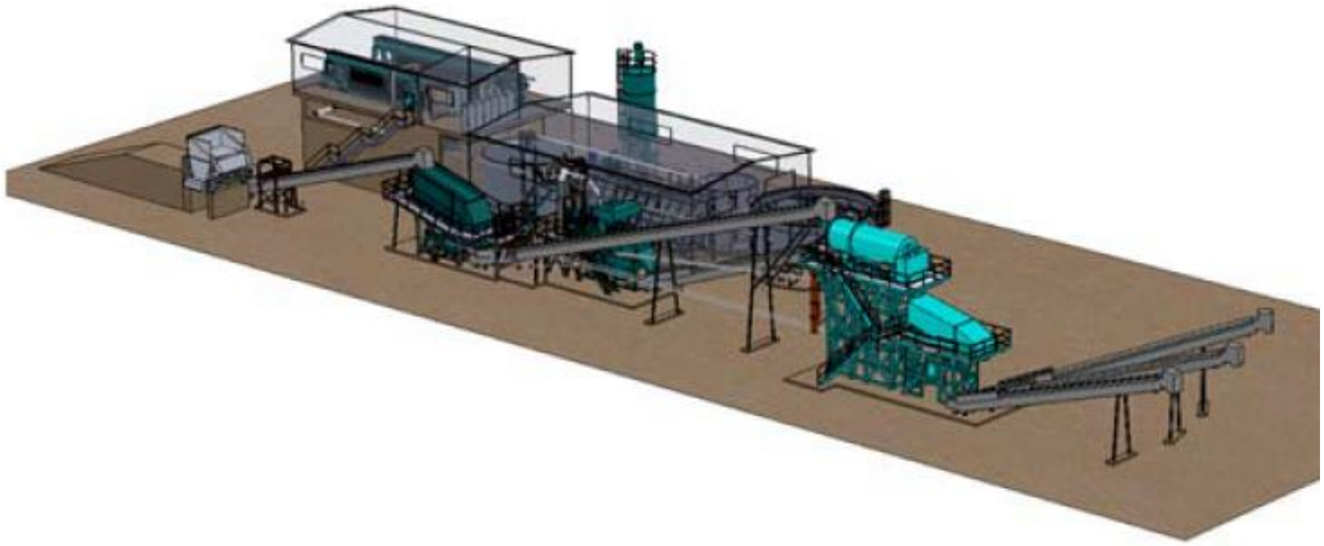
4. Full-scale application

4.1 Soil washing system

The plant is composed of few modular compenents, transportable and positionable on a flat waterproofed ground.



There is an overhead loading hopper, followed by a series of wet screens, capable of selecting the different cuts of sand and gravel, a drum washing, a series of hydrocyclones and the water treatment circuit with two filter presses for extraction of the sludge.



The plant can treat about 130 tons/h, in relation to the characteristics of the incoming materials.

4.2 Feasibility study

The most present contaminants were heavy metals and TPH. The contamination level was between some ppm to 10.000 ppm.

Some hot spot were characterized by the presence of persistent contaminants (PCBs) with a concentration of 100 ppm, approximatively.

The process is performed without the use of particular additives. Only water was used, extracted from the active barrier to protect the groundwater and introduced into the washing plant.

Particular attention was paid to the granulometric aspects and to the very heterogeneous composition of the first most superficial layer which also collected residual anthropic fractions of the production process of the industrial plant.

The structure of the plant has been initially perfected and adapted to improve efficiency precisely in relation to the site-specific aspects mentioned above.

4.3 Water Treatment

The sludge and water are treated in the Waste Water Treatment & sludge dewatering section of the plant. The WWTP is fully automatic in operation by using Thickeners & Filter Press.

The process is composed by a closed cycle, therefore the plant was optimized through the insertion of a water purification section, sand filters and activated carbon filters.

The treatment was carried out without discharges of liquid effluents, with recharge of clean water for about 60-70 l / ton of treated soil.


AMBIENTHESIS
AMBIENTHESIS


AMBIENTHESIS

4.4 Control parameters

The effectiveness of the treatment is related to granulometry of incoming materials, the type and quantity of contaminants.

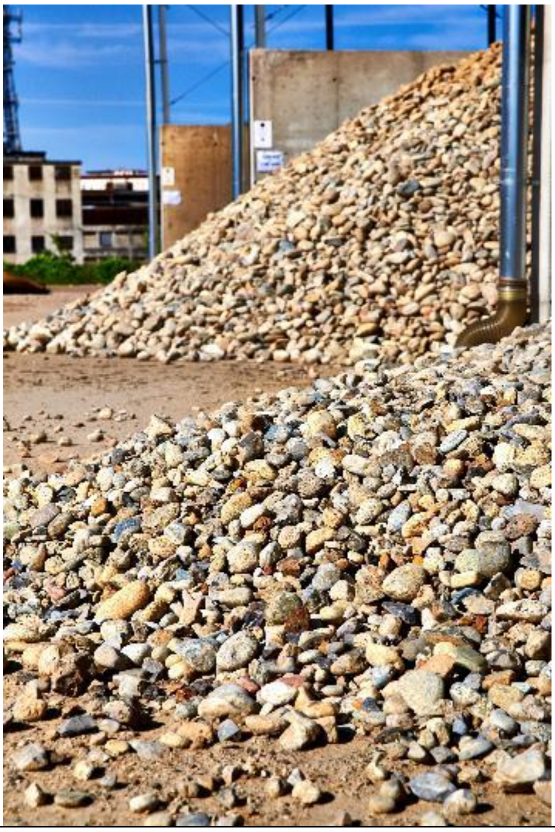
With regard to the particle size, the treatment was applied to materials with silt and clay values <25%.

With regard to the type of contamination, the treatment was applied to organic contamination (hydrocarbons) with concentration <5000 ppm, in some cases also to hazardous waste. The treatment of metal contamination is less effective as in the anthropogenic fractions they are also found in the coarser fractions coming out of the treatment.

In any case, the material entering the plant was subjected to analytical verification (granulometric and contamination content) for batches of approximately 1000 cubic meters.

The treated materials were accumulated and also analytically verified, to check their compliance with the target limits (limits of residential sites).

In addition to the individual batches treated, the overall mass balance of the process was also checked, comparing the transfer of contamination to the individual outgoing fractions.



5. Results

5.1 Removal rate

Although it is possible to add chemicals to the washing solutions in order to improve the removal effectiveness, in this case the process was carried out with the use of clean water only, no additives were added.

The operation was carried out with a liquid / solid ratio of an average equal to 3.

In relation to the content of silts and clays, the hourly production remained between 30 and 70 tons / hour. However, the production is reduced with the increasing of the fine fractions.

75.000 tons of contaminated soil were treated per year, recovering about 75% of the output materials produced.

The contamination abatement efficiency has proved to be excellent in the case of organic contaminants (> 90%), lower in the case of inorganic contaminants.

In this case the inorganics contamiants will be found in the final treated soil.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

The procedures envisaged by the approved project do not contemplate long-term checks on the processed material. Instead, checks were carried out on elution, in order to safeguard the groundwater where the material was relocated.

All the recovered materials met the conditions envisaged for the protection of the groundwater, guaranteeing levels of contamination in the eluates compatible with the contamination limits envisaged for the groundwater.

7. Additional information

7.1 Lesson learnt

The intervention carried out allowed to highlight the following success and limits of the process:

- particle size distribution of the matrix being treated (more clay and silts means less efficiency and sustainability of process).
- the anthropogenic fractions.

We can say that:

- organic contamination can be treated with good results
- the process can works without water discharges
- In absence of particular contaminants, the process proves effectiveness even without the application of additives
- Prior to application on an industrial scale, it is convenient to acquire information on contamination, particle sizes, availability and cost of the landfill where the unrecovered fractions are to be delivered.

If adequate space and time are available in the reclamation sites, the application of soil washing can undoubtedly allow the saving of considerable economic resources and the recovery of land otherwise destined for disposal.

7.2 Additional information

The installation of a plant with capacity of treatment equal 50 tons / hour requires an average surface area of 1 hectare, to have the spaces for maneuvering and accumulating materials. It is possible to conduct the treatment H24, operating on average with 4 operators and two work vehicles. An average of 1 day of orindary maintenance every week is to be foreseen.

Treatment costs are between € 20 and € 50/ton, approximatively,excluding the disposal of waste in landfills. To consider separately the costs of procurement and installation of the plant.

7.3 Training need

Running a soil washing plant requires experience in the geological, chemical and mechanical fields. The management of the process is completely automatic and can be carried out, even remotely, by a process engineer. A supervisor must be present on site, able to coordinate 1 maintenance technician and 2-3 operators.

It is important to have a collaboration with chemists able to evaluate the quality of incoming and processed materials, to allow free sapce in the storage areas and operational continuity.

7.4 Additional remarks

Applying soil washing treatments to reclamation sites is very different from applying the same technology to fixed plants. In remediation sites, the quality of the metarials to be treated is usually not programmable and / or selectable. It must be managed and processed in real time. Often the technical characteristics of the plant are also defined specifically for the site, therefore it is essential to have qualified personnel who know how to better manage the situation, as well as to have characterization data as reliable as possible.

It is important to ensure an organization and documentary availability such as to allow the best traceability of flows, from the origin of the excavation to the recovery location.

1. Your contact details - CASE STUDY: SW n.2

1.1. Name and Surname*	Dr. Benjamin Faigle
1.2. Country/Jurisdiction	Germany
1.3. Organisation	Züblin Umwelttechnik GmbH
1.4. Position	Deputy Manager R&D
1.5. Duties	In-situ methods, PFAS remediation
1.6. Email address	benjamin.faigle@zueblin.de
1.7. Phone number	Tel. +49 (0)7145 9324-249

2. Site background

2.1 History of the site

The German city of Ingolstadt is conveniently located between the Bavarian cities of Nuremberg, Regensburg, Munich and Augsburg, and was thus selected as the place to erect five oil refineries in 1960. After construction began in 1962, the oil refinerey ERIAG (“Erdölraffinerie Ingolstadt AG”) began its operation on this specific site in 1964, and commenced in operation until 2008, when decomissioning of the operational site began.

Figure 1: Areal view of the site of the former oil refinerey. Copyright: AUDI AG

The main tank fields and processing plants and chimneys were dismantled from 2010-2013, and 75ha out of a total of 105ha of land was aquired by IN-Campus GmbH, a Joint venture of AUDI AG and the City of Ingolstadt.

Thorough investigations into contamination at the site were conducted beginning in 2007. These primarily involved exploratory investigations and detailed investigations in multiple stages with downstream remediation investigations. After the site was acquired by IN-Campus GmbH, investigations were stepped up and an analysis carried out focusing on its later use as a research and technology campus.

A total of over 1,200 exploratory drilling operations and digs were carried out and tests conducted at over 250 groundwater control points over the years. Three groups of contaminants have been identified: Petroleum-derived hydrocarbons (C10 - C40) can be found from groundwater level down to dephts of up to 8 m below the groundwater level. Volatile aliphatic (C5 – C9) and aromatic hydrocarbons (BTEX) are present in the groundwater as well es in the unsaturated zone. And Polyfluoroalkyl substances (PFAS) are observed in the upper layer of the soil and in the groundwater.

In 2016, a remediation contract got approval, and remediation efforts began.

In 2017, a consortium of companies ZÜBLIN Umwelttechnik GmbH, Geiger Umweltsanierung GmbH, Wilhelm Geiger GmbH & Co. KG und Strabag Umwelttechnik GmbH was attributed with the remediation of the main area of 50 hectares.

2.2 Geological setting

The site is located next to the river Danube and abandoned meanders. Therefore, the soil consists of former fluvial deposits, which means it is largely sandy gravel with small content of fine material, so the soil is appropriate for the treatment method of soil washing.

The groundwater table lies around 1-3m below Surface level, and is mainly goverend by the level of the river danube, which is controlled by dams. Due to the soils high permeability, the natural flow velocity of the grundwater is very high and lies between 2 and 6 meters per day. Approximately 6-8m below groundwater level, a dense layer is adressed as the base of the first aquifer.

2.3 Contaminants of concern

The input material featured the following range of contaminants:

- TPH (BDL – 10,000 mg/kg)
- C5-C9 (BDL – 1,000 mg/kg)
- BTEX (BDL – 500 mg/kg)
- PFAS (BDL – 20 µg/l) with main compound PFOS

2.4 Regulatory framework

- A general remediation strategy was developed that acknowledges the sites future usage as an industrial site. An integral part of this strategy was the method of soil washing, with the potential to reuse the clean output fractions on site.
- The soil treatment plant was designed and permitted exclusively for on-site treatment of contaminated soil originating from the former refinery site in Ingolstadt.
- Treatment targets for the washing process and the output fraction is defined by the remediation plan for the former refinery site as criteria for backfill soil
- The soil washing plant plant is permitted acc. to German Legislation BImSchG “Bundes-Immissionschutzgesetz”. The permit includes all attendant facilities such as the treatment facilities for the washing fluid, the legal framework for material flow (clearance of material before and after soil washing) as well as safety precautions for the workforce on the site.

3. Pilot-scale application in field

3.1 Soil washing system

- Pilot tests were carried out in a company-owned soil washing plant in Germany, involving 100 t of contaminated soil.
- As the pilot system was able to produce soil without relevant PFAS contamination, the pilot test showed that the contaminated material is washable on a scale larger than typical laboratory tests. The main contaminant sink was the washing water; hence an elaborate treatment procedure for the washing fluid is essential.

3.2 Feasibility study

General Parameters

- Integrated remediation concept setting feasible conditions for the treated soil to be reused as backfill soil on the site
- Suitable contaminant inventory
- Average grain size distribution curve suitable for washing process
- Coarse soil characteristics simplifies the technical treatment steps for soil washing
- As the filter cake needs to be disposed of, a low clay contend of the soil is economically beneficial.
- Large soil quantities requiring treatment to allow the installation of an on-site treatment facility
- Space requirements for on-site treatment fulfilled

Minimum requirements in regards of soil quality:

- Detailed preliminary investigation in regards of contaminant inventory and soil quantities
- Representative grain size distribution curves from relevant contaminated soil zones (e.g. at different depth intervalls)
- Detailed description of the soil incl. e.g. content of organics, non soil fraction like debris and other waste, existence of aggomerations etc.

3.3 Water Treatment

- Granulated activated carbon
- Reactivation of used activated carbon off-site

3.4 Control parameters

The following prerequisites are essential for the pilot test:

- Representative selection of soil for the pilot test
- Setup and execution of a detailed monitoring programme

During the pilot test, the following degrees of freedom should be investigated:

- Test run at different performance levels
- Test run involving different potential treatment steps

The feasibility full scale can then be determined by means of:

- Evaluation of the treatment efficiency for an outlook on the overall project
- Design of a mass balance and mass flow, depending on necessary projected treatment steps
- Definition of feasible disposal procedures and reuse strategy for the resulting output depending on the expected material quality per output stream. Here, the expected output mass balance comes into play.

4. Full-scale application

4.1 Soil washing system

Overview

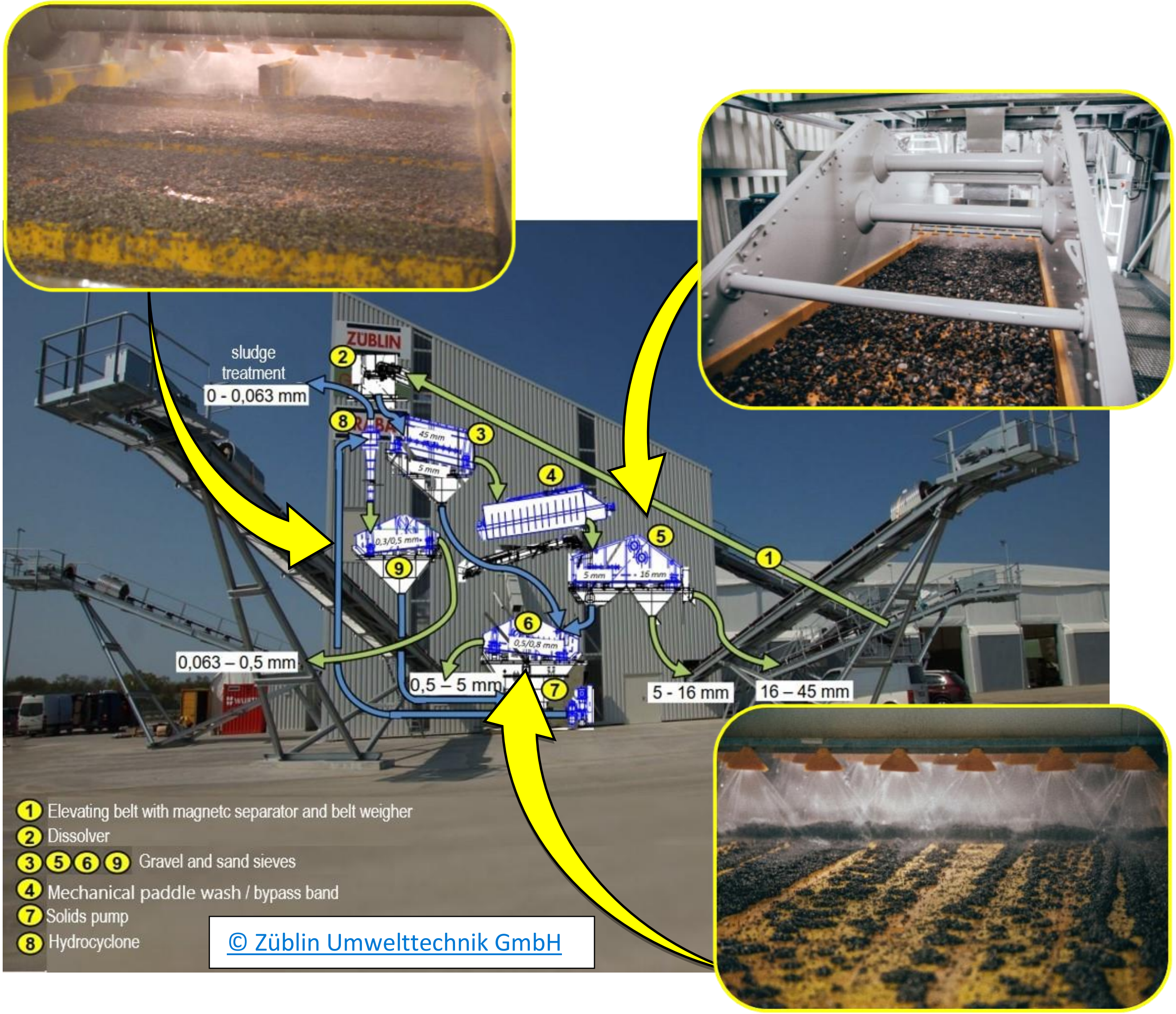
- In the period from 2018-2021, a total of 150,000t of soil mainly contaminated with PFAS and an additional of 280,000t of material with hydrocarbons have been successfully washed and reused on the site. Overall, a total of 430,000 t of contaminated material has been washed in this project.
- From the remediation areas, the excavated material is transported onto a sealed area comprising over 25,000m2, and therein into an enclosed unloading area equipped with off-gas treatment. An encased conveyor belt feeds the contaminated material into the soil washing plant (Figure 2).

Figure 2: Areal view of the soil washing plant (front), sludge treatment facility (left hand side) and the reception hall (in the back). Copyright: ARGE AUDI IN-Campus GbR.

The core-unit for soil washing

- The feeding station is located in the receiving hall to prevent emissions of dust and volatile substances. An encased conveyor belt transports the contaminated material upwards to the uppermost point of the washing tower.
- The rather coarse fraction from the first classifying screen enters a powerscrub logwasher to break up loamy bulbs.

- The material then passes several vibrating screens of different sizes, where the material is washed with the washing fluid applied with various spray bars
- The fine sands are washed and seperated from the process water in the hydrocyclone.
- Washing fluid is recirculated in a closed cycle, which is both environmently friendly and cost-saving
- Only pure water but no additives like tensides and the like are used



© Züblin Umwelttechnik GmbH

Figure 3: Treatment steps of the soil washing plant.

4.2 Feasibility study

- The plant was designed and customized for the project. As such, treatment targets were reached after the first treatment cycle.
- The single treatment steps are described in Chapter 0.1 (solid matter) and 0.3 (sludge and water).

4.3 Water Treatment

Figure 4: Areal view of the sludge treatment plant, Copyright: ARGE AUDI IN-Campus GbR.

Washing fluid is recirculated in a closed cycle

- The process water is rich with sediments and is processed in a sludge treatment plant with a capacity of 400 m3/h (**Error! Reference source not found.**). The slurry water originating from the hydrocyclone is homogenised and pumped to the flocculation step, after wich separation is achieved by baffle plate thickeners. The seperated clear water is still loaded with contaminants, so the water is transferred to large buffer basins for further treatment.
- After separation, the sludge is dewatered by a fully automated filter press (**Error! Reference source not found.**). The filter cake constitutes the sink for the contaminants. As the filter cake gets disposed on landfills at high costs, especially if PFAS are involved, it is economically reasonable to reduce the water content as low as possible to values below 30 %.

Figure 5: Chamber press, the small picture shows the filter cake, Copyright: ARGE AUDI IN-Campus GbR.

- After the sludge treatment, the clear water is transferred to its final treatment step, the water treatment plant (**Error! Reference source not found.**).

Figure 6: Water management using large basins to reduce the capacity of the water treatment plan, Copyright: ARGE AUDI IN-Campus GbR.

The water treatment units purifies approximately 140 m^3/h of clear water, removing the dissolved contaminants with sand filters and activated carbon. Depending on the contaminations at hand, different types of activated carbon are employed to optimize the adsorption capacity.

A share of the washing fluid is lost by adhesion to the output soil, and needs to be replenished with fresh water (external supply).

4.4 Control parameters

A thorough monitoring programm for the output material is essential to establish the reliability in the washing process. The monitoring has to be performed by an independent external expert, who is then responsible for correctuly and regularly sampling, analytics and clearance of each output batch, see Chapter 0.
The target values depend on local regulatory requirements and the project-specific range of contaminants involved.

An additional analytical monitoring programm by the operator of the soil washing facitily is only recommended, for the supervision and establishment of the operation parameters.

For the sludge and water treatment, the typical control parameters such samples for settling time for the quantification of the flocculation agents, fluid levels in buffer tanks or pressure drops in filter are relevant for a safe and uninterrupted operation of the treatment facilities. As these are not special to the process of soil washing, their detailed description is omitted in the report.

In this project, only purified groundwater but no washing supplements have been employed.

5. Results

5.1 Removal rate

The output soil quality after treatment was as follows:

- TPH (BDL - <100 mg/kg)
- C5-C9 (BDL – 1 mg/kg)
- BTEX (BDL – 1 mg/kg)
- PFAS (BDL – 0.1 µg/l) with main compound PFOS

In this project, no washing supplements have been employed, the target values could be achieved with proper operation conditions (high volume of washing water, appropriate flow input material).

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

- The Output of the soil washing plant was stockpiled by means of a frontloader.
- Output fractions “sand” and “gravel” were stockpiled separately
- After target pile size of 500 m3 was reached , sampling acc. to relevant regulation was performed by an independent external consultant
- Long term monitoring is not required

7. Additional information

7.1 Lesson learnt

The project was succesfully completed in 2021, one finds that:

- Soil wasihing turned out to be a very effective technology for the given contaminant inventory
- Over the duration of several years, the treatment procedure was stable and reliable
- Low energy consumption and CO2-footprint compared to alternative solutions (e.g. thermal deorption or off-site disposal on landfills)
- Competitive price under the given site conditions

Over the duration of plant operation, the relevant mass fluxes were monitored to prepare a conaminant mass balance, see the following figures. As the concentrations measured are not totally precise, the depicted values are not corrected in order to gain round sums, but are kept as they were as an inidicator of the accurateness of the flow chart.

Owing to their physical properties, PFAS tend to the water phase and do not adhere to the solid fraction. Therefore, the main sink for PFAS-removal is the activated carbon at the end of the water treatment, see **Error! Reference source not found.**.

Hydrocarbons in contrast remain attached to solid particles and are concentrated in the filter cake, see **Error! Reference source not found.**.

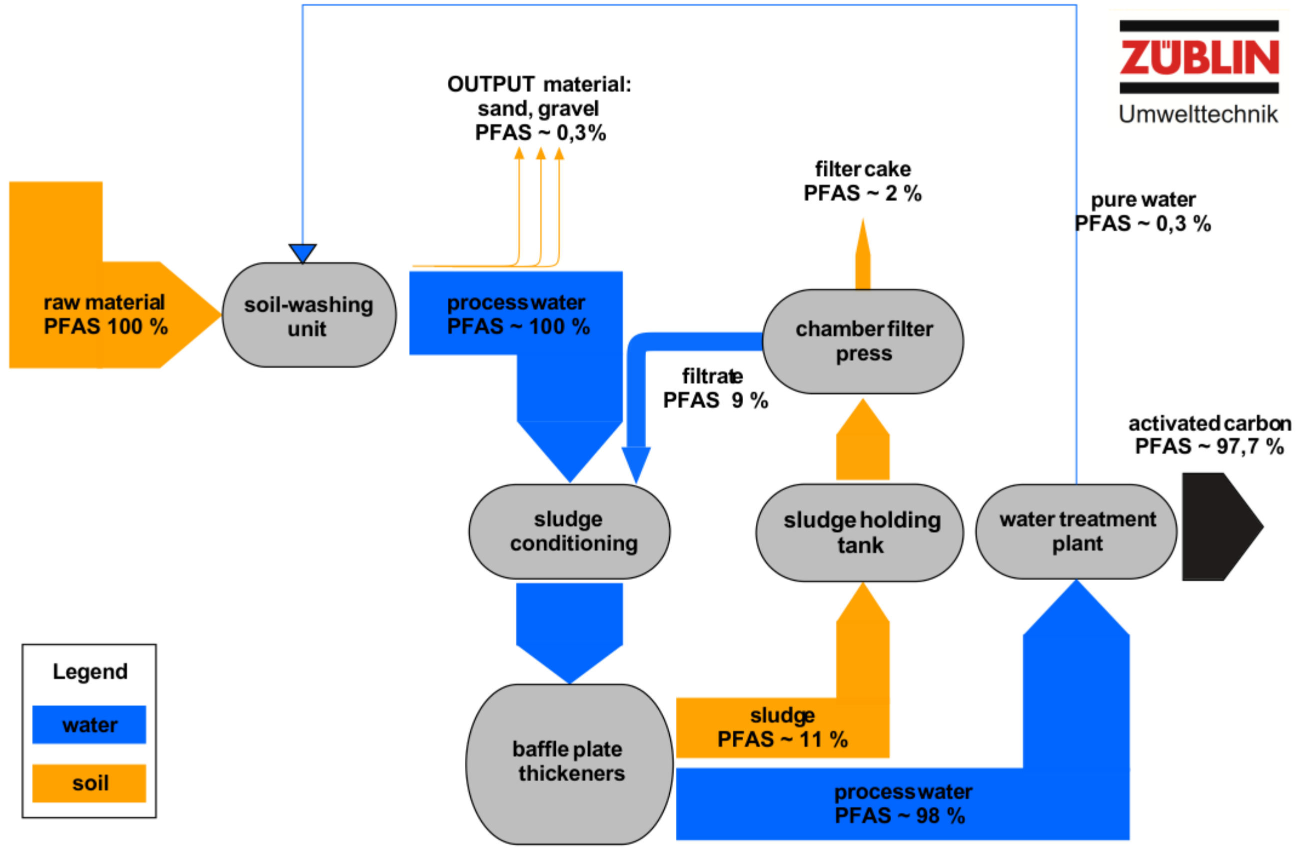
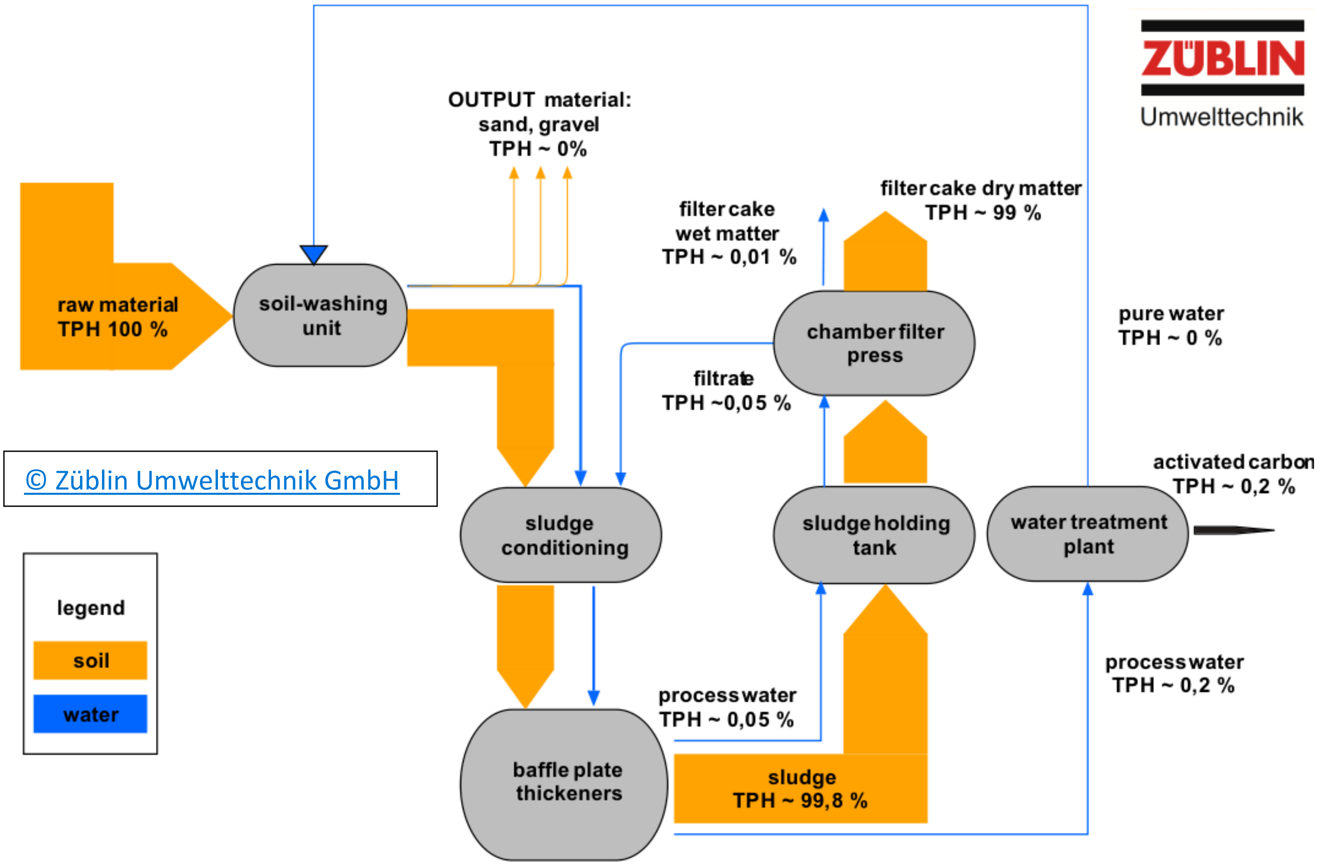


Figure 7: Contaminant sink for the removal of PFAS: water path and activated carbon.



© Züblin Umwelttechnik GmbH

Figure 8: Contaminant sink for the removal of longchained petroleum hydrocarbons (TPH): the solid fraction of the filter cake.

7.2 Additional information

During the operation of the soil washing plant, it was used as a testing facility for many other remediation sites for washing tests under field-scale conditions. Typically, between 200-500 t of contaminated material was investigated. In all cases, even material deemed hardly washable because of certain criteria (too high content of recycling material; low percentage of coarse gravel; relatively large fine fraction; etc.) have been succesfully washed. Therfore, one should refrain from defining hard criteria alloted with the soil structure for declaring a material to be washable or not.
Wether soil washing is an economically feasible method may be a tough decision, which can be answered if a pilot test investigates the limits and potential of the washing procedure, see chapter 0.4. In many cases, however, a soil-washing strategy can be developed without a pilot test.

7.3 Training need

Especially with recent contaminants without long-lasting remediation experience such as PFAS, there is a tendency to doubt that soil-washing of large quantities of contaminated material can be reliably successful and economically attractive. To overcome these doubts, site visits to existing project might be a useful instrument to acknowledge that there is a technical solution apart from disposal in landfills.

Basic requirements and site conditions of the soil washing technology is described in this report. As the success of the washing procedure depends on a variety of operation parameters, specialists should be consulted. For pilot tests or a feasibility study for a specific project, competetnt companies with a wide range of longterm experience should be involved in the decisionmaking. As every project provides its own unique challenges, one should be critical from generalising statements such as “soil-washing is not possible for the given materal”.

Glossary of Terms

Term **(alphabetical order)**	**Definition**
BDL	Concentration which is below the detection limit.
BTEX	Benzene, toluene, ethylbenzene and xylenes
C5-C9	Volatile hydrocarbons with a chainlength of five to nine.
CHC	Chlorinated aliphatic hydrocarbons
PAH	Polycyclic aromatic hydrocarbons
PFAS	Per- and polyfluoroalkyl substances (PFASs) are synthetic organofluorine chemical compounds that have multiple fluorine atoms attached to an alkyl chain.
TPH	Total petroleum hydrocarbons
VOC	Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature

1. Your contact details - CASE STUDY: SW n.3

1.1. Name and Surname*	Massimiliano Confalonieri Beatrice Melillo Paola Canepa
1.2. Country/Jurisdiction	Lombardy Region (Italy)
1.3. Organisation	Environmental Protection Agency
1.4. Position	
1.5. Duties	
1.6. Email address	m.confalonieri@arpalombardia.it b.melillo@arpalombardia.it p.canepa@arpalombardia.it
1.7. Phone number	

2. Site background

2.1 History of the site

The contaminated site is located in the south east of Milan (about 5.5 km from the center of the city) and it covers 641.000 m^2. Since 1910, in these area, there was a chemical industry (Montedison Spa) that produced fertilizers (e.g. Rogor); the industrial plant operated until the 1970s.

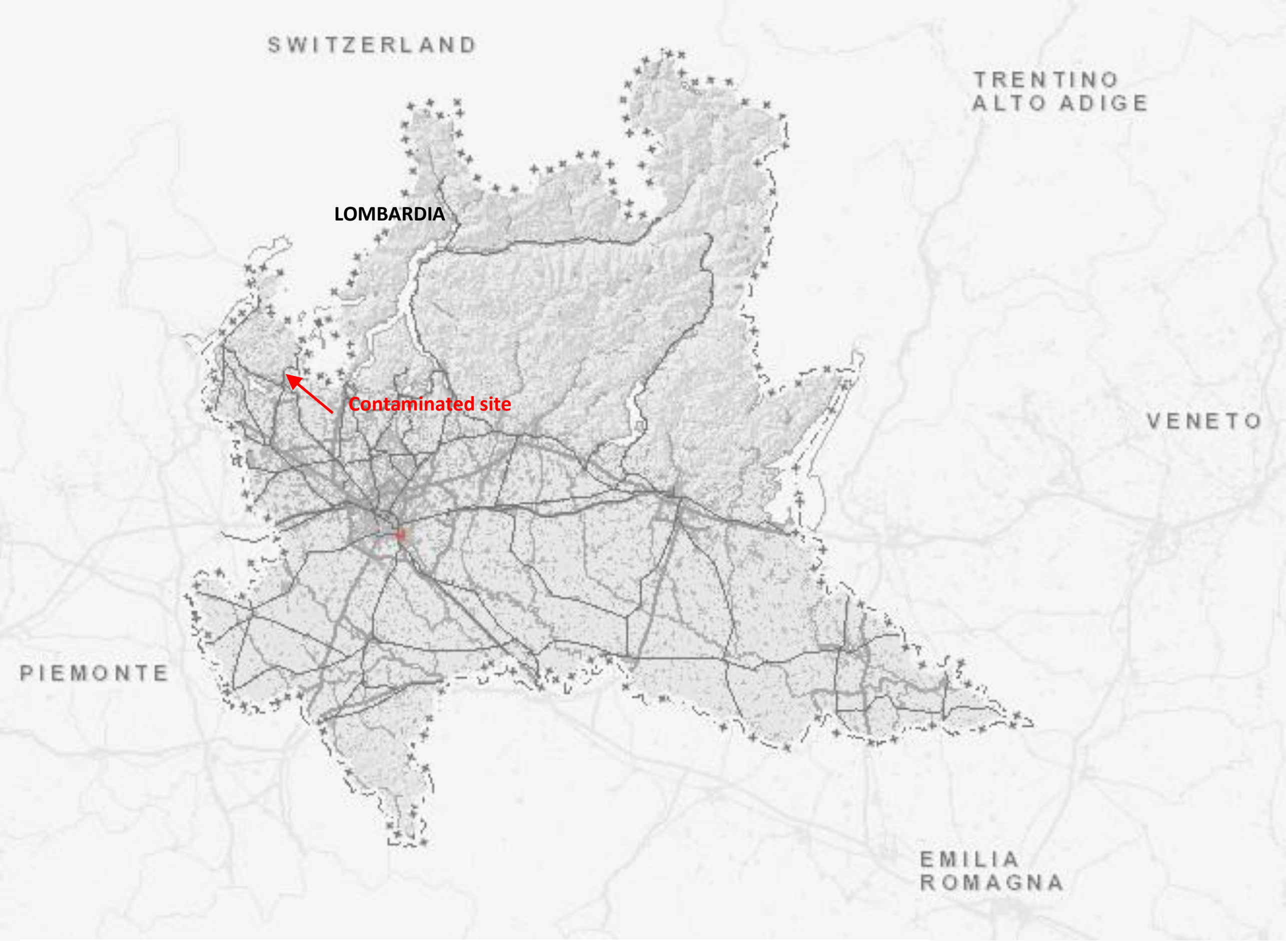


Figure 9 - Location of the contaminated site within the Lombardy region

This area (the so-called "North Area") corresponds to a part of a large urban redevelopment project ("Montecity-Rogoredo" Integrated Intervention Program), started in 2005. The project covers an area of about 1.100.000 m^2; it is aimed at re-qualifying a large abandoned industrial area previously occupied by the Montedison plants to the north and the Redaelli steel mills to the south. The area is located in a strategic point of the city as it is between the Milano - Rogoredo station (the station through which the high-speed railway line passes), the eastern Milan ring road and the Linate airport.

Figure 10 - Location of the contaminated site (in red) with respect to the city center and Milan Linate airport

Figure 11 - Location of the contaminated site (in red), with respect to the railway station and the eastern ring road of Milan

2.2 Geological setting

The area is characterized by a “backfill” layer (a mixed layer of variable grain size soil and anthropic materials, e.g. fragments of brick and firebrick, concrete, fewer slag) located above natural terrain consisting of gravels and sands. The thickness of the “backfill” layer varies from some tens of centimeters to a few meters.

The depth to ground water is between 4,5 e 8,5 meters below ground surface.

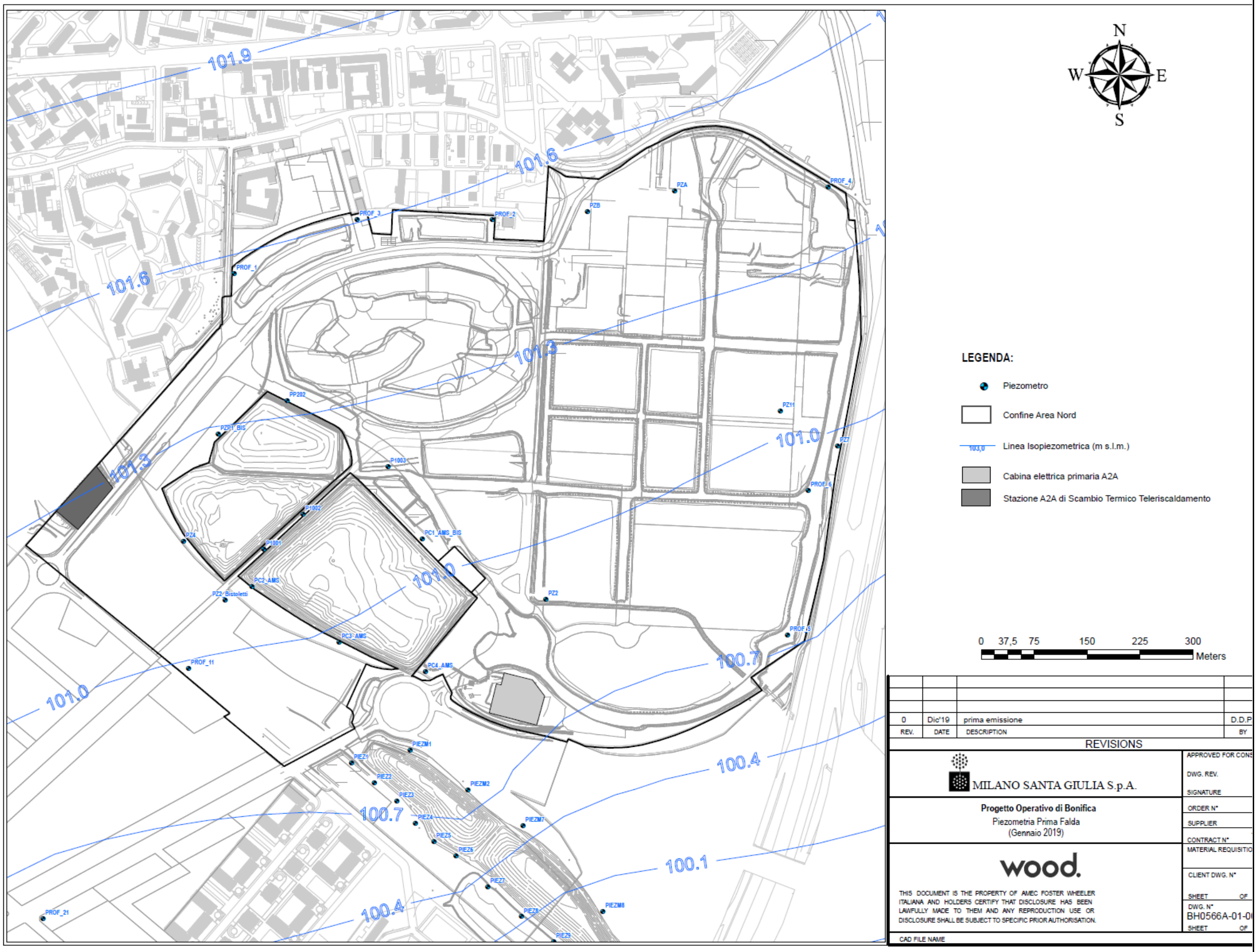


Figure 12 – Water table (January 2019)

Locally, at an average depth of 6 m from the ground level, there is a layer of sandy-clayey silt; the maximum observed thickness of the clay lens is 2,6 meters. A perched water table is located above this clay lens.

Figure 13 - Location and thickness of the silt lens

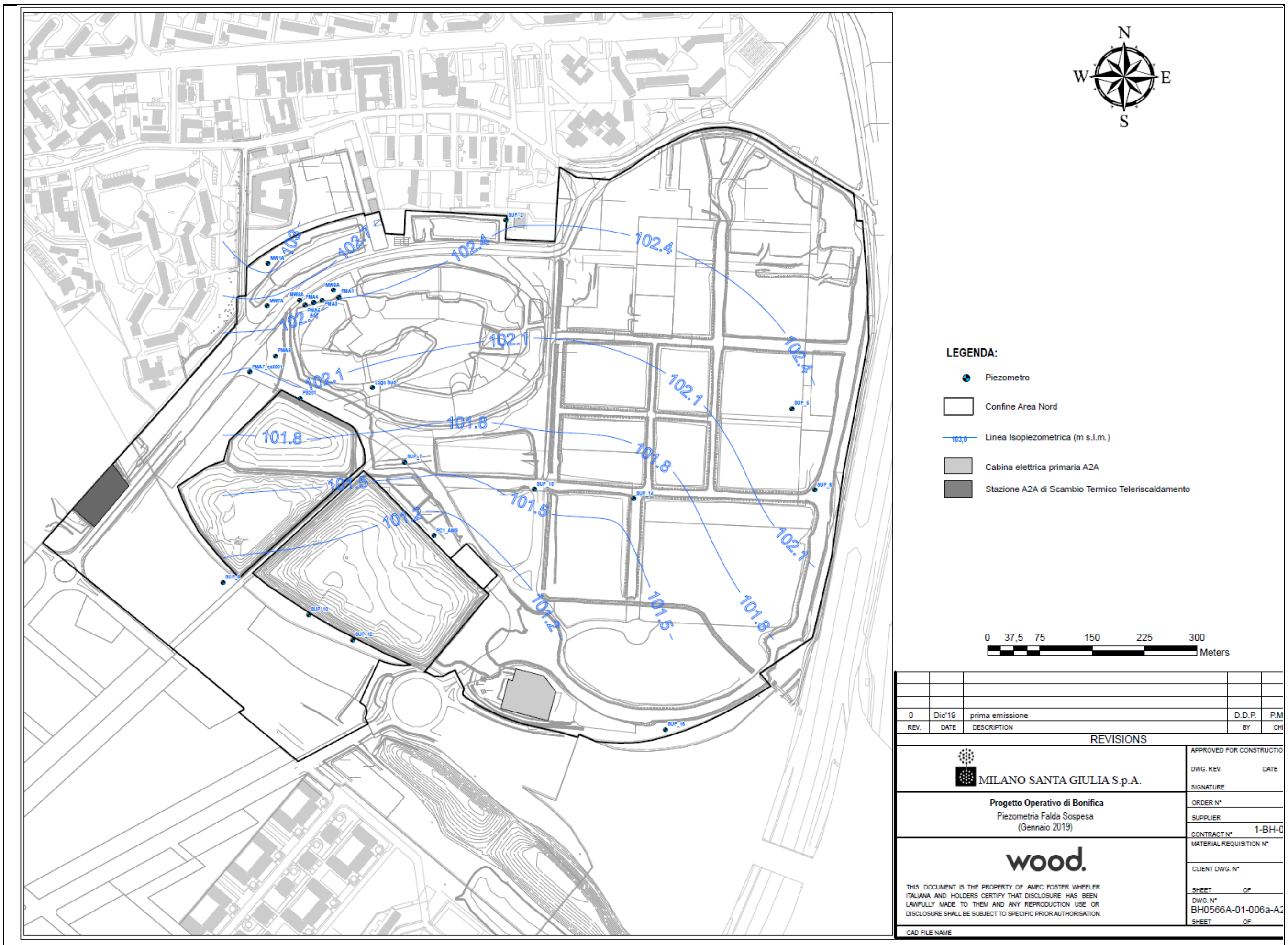


Figure 14 - perched water table (January 2019)

2.3 Contaminants of concern

Backfill material and soil:

- Metals (mainly Zinc, spread throughout the area, and secondly As, Cd, Cr tot, Pb, Cu e Hg)
- BTEX
- PAH (Polyciclic Aromatic Hydrocarbons), PCBs.
- Chlorinated Solvents and Chlorobenzenes (mainly Hexachlorobenzene)
- Pesticides (mainly DDT, DDD and DDE)
- Light Hydrocarbons (C< 12) and Heavy Hydrocarbons (C>12)

Most of the samples that exceed the legal limit concentration, for one or more parameters, are backfill material samples.

Groundwater: Organic halogen compounds, Metals and Pesticides.

2.4 Regulatory framework

The contaminated site covers 641.000 m^2; about 65% of this area (about 408.000 m^2) is intended for residential use and about 35% (about 233.000 m^2) is intended for commercial use. According to the intended use of the area, the concentration of contaminants was compared with the legal limits referred to in Legislative Decree 152/06 and subsequent amendments, part IV, title V, annex 5, table 1 - Column A or B; the comparison shows that most of the samples that exceed the legal limit concentration, for one or more parameters, are backfill material samples.

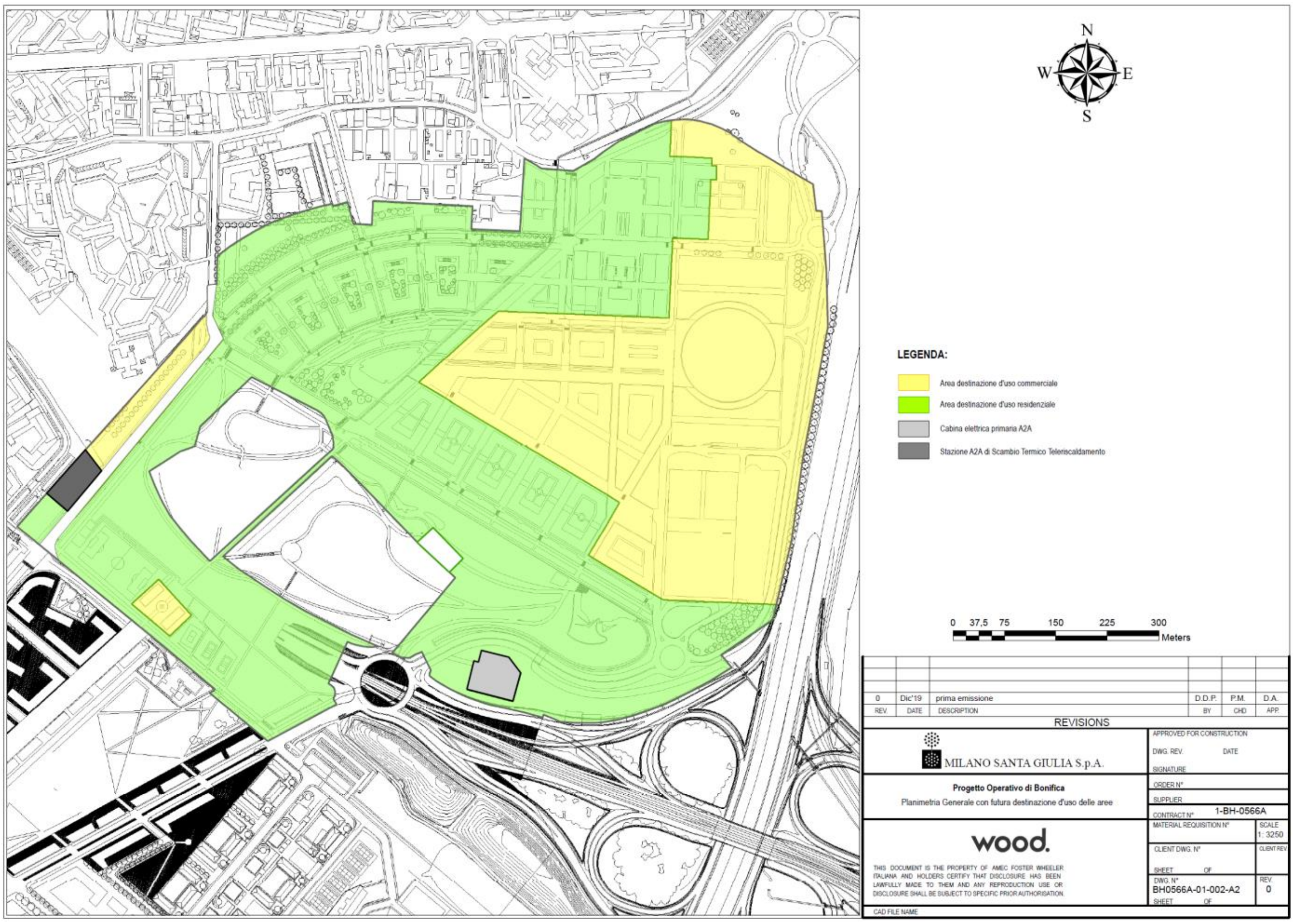


Figure 15 – Intended use of the site: residential (in green) or commercial use (in yellow)

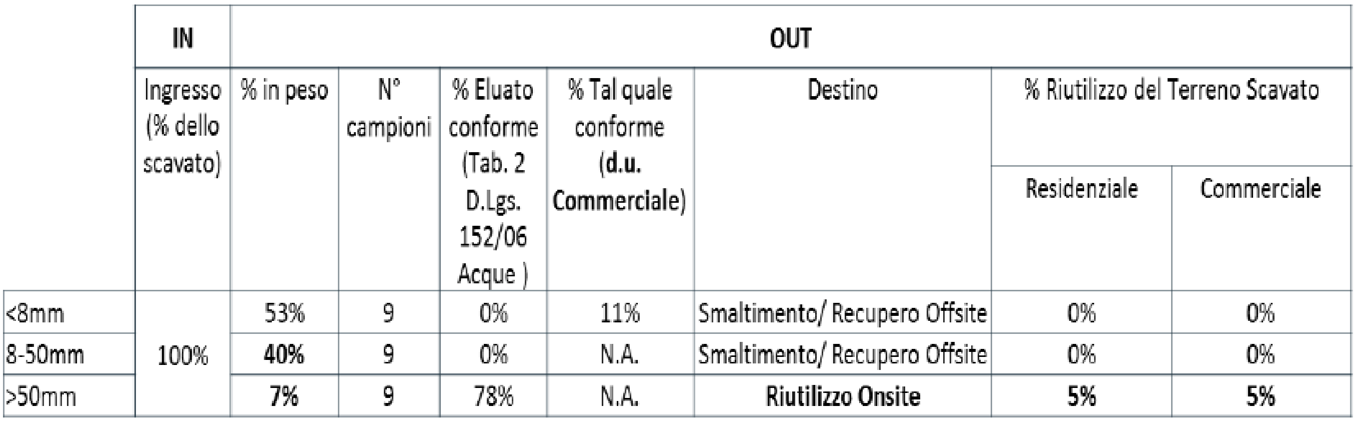
The remediation objectives for the this site were calculated with the Risk Analysis; for some Metals (Cd, Pb, Cu and Zn) the maximum concentration detected on site (Cmax) was taken as the remediation objective. The remediation target for the excavated material (soil and fill materials) that will be reused on site is the legal limits referred to in Legislative Decree 152/06 and subsequent amendments, part IV, title V, annex 5, table 1 - Column A or B, according to the intended use.

3. Pilot-scale application in field

3.1 Soil washing system

The pilot test was conducted on about 310 m^3 of material and involved two phases:

1. Soil screening (on-site) with a mobile soil screener: the soil was separated in pebbles (Ø > 50 mm), coarse and medium gravel (8 mm < Ø < 50 mm) and finer fractions of soil (Ø < 8 mm, that is fine gravel, sand, silt and clay). Each particle size fraction was weighed to define the particle size distribution. An average sample of each particle size fraction was subjected to chemical analysis to evaluate its qualitative status. The fine materials (Ø < 8 mm, about 53% of the escavated material) have been sent to a suitable authorized disposal or recovery plant.



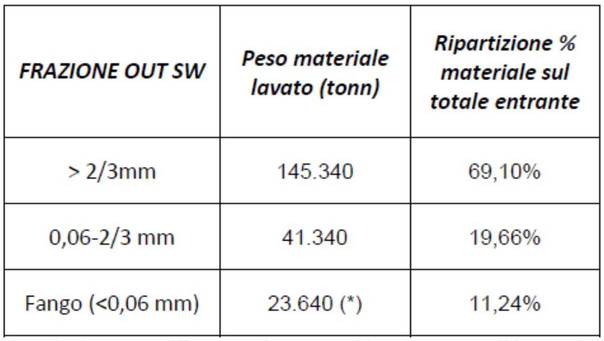
	IN	OUT						
	Ingresso (% dello scavato)	% in peso	N° campioni	% Eluato conforme (Tab. 2 D.Lgs. 152/06 Acque)	% Tal quale conforme (**d.u. Commerciale**)	Destino	% Riutilizzo del Terreno Scavato	
							Residenziale	Commerciale
<8mm	100%	53%	9	0%	11%	Smaltimento/ Recupero Offsite	0%	0%
8-50mm		**40%**	9	0%	N.A.	Smaltimento/ Recupero Offsite	0%	0%
>50mm		**7%**	9	78%	N.A.	**Riutilizzo Onsite**	**5%**	**5%**

Figure 16 - Quality of the excavated material after on site screening

2. Crushing and washing (off site) at an authorized Soil Washing plant: only the coarser fractions of soil (Ø > 8 mm, 47% of the escavated material ~ 210.320 tons) were washed (material treatment flow: about 20 t/h). Only water was used for washing.

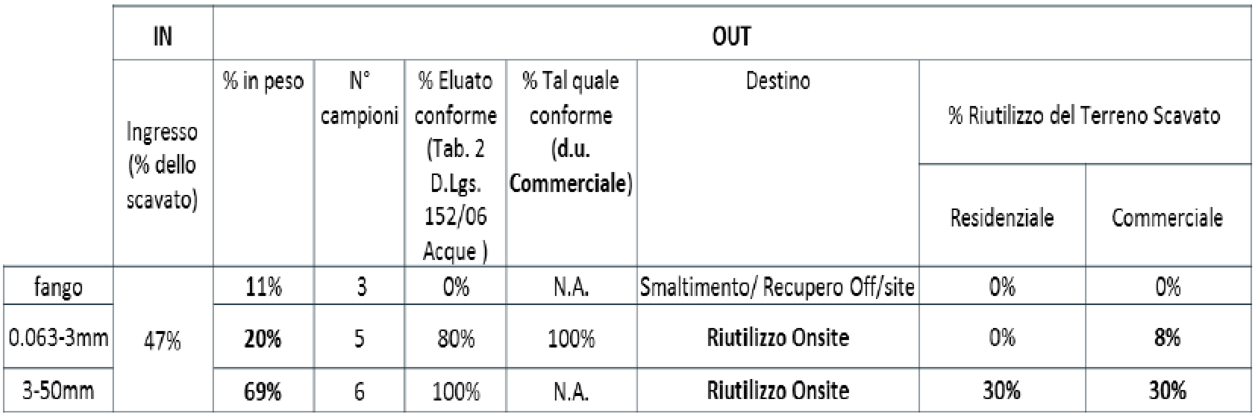
The plant that was used for the pilot test consists of a jaw crusher, a star screener equipped with an iron remover, an aggregate scrubber, a horizontal wet vibrating screener, n. 2 hydrocyclones, a vibrating dryer and a water treatment system.

In the following table, particle size distribution of the washed material (210.320 tons of material) is indicated:



FRAZIONE OUT SW	*Peso materiale lavato (tonn)*	*Ripartizione % materiale sul totale entrante*
> 2/3mm	145.340	69,10%
0,06-2/3 mm	41.340	19,66%
Fango (<0,06 mm)	23.640 (*)	11,24%

The fine material (0,06 -2/3 mm) resulting from the washing treatment derives from the primary crushing and removal of the particulate adhering to the coarse material.



	IN	OUT						
	Ingresso (% dello scavato)	% in peso	N° campioni	% Eluato conforme (Tab. 2 D.Lgs. 152/06 Acque)	% Tal quale conforme **(d.u. Commerciale)**	Destino	% Riutilizzo del Terreno Scavato	
							Residenziale	Commerciale
fango	47%	11%	3	0%	N.A.	Smaltimento/ Recupero Off/site	0%	0%
0.063-3mm		**20%**	5	80%	100%	**Riutilizzo Onsite**	0%	**8%**
3-50mm		**69%**	6	100%	N.A.	**Riutilizzo Onsite**	**30%**	**30%**

Crushing and washing of the coarser (Ø > 8 mm) fractions of soil (about 47% of the total excavated material) produced little sludge to dispose of (about 11%) and washed materials (about 89%); 20% of these materials are made up of sand and 69% of gravel. The washed material was subjected to chemical analyses to assess its compliance with legal limits: 38% of the excavated material is suitable for reuse in commercial areas and 30% in residential area.

3.2 Feasibility study

Based on the experience of Amec Foster Wheeler Italiana srl, Soil Washing does not give satisfactory results if it is applied to soils with a percentage of fine materials (Ø < 0,06 mm) greater than 20%. Generally speaking, the higher the percentage of sand and coarse material, the more effective the washing process will be.

3.3 Water Treatment

The soil washing tests were performed in an authorized plant outside the contaminated site, therefore the wastewater treatment plant is not described in the remediation plan.

3.4 Control parameters

To assess the removal efficiency, the contaminants of concern are measured at the output of any washing cycle.

4. Full-scale application

4.1 Soil washing system

The soil washing facility was started up in early March 2022; the information below comes from the remediation project of the area and describes the plant as planned and not after its construction.

The soil washing facility includes:

- **Pre – Screening**: large materials (Ø> 50 mm), such as construction debris, pieces of rock, pebbles, are removed by a vibrating screen equipped with an iron remover. These materials are generally not contaminated and so on they are sent to the crushing section to recovery on site;
- **Aggregate scrubbing**: the material is loaded at the lower end of an inclined tank and it is transported to the upper end by two rotating shafts, equipped with blades to facilitate the disintegration of it. Silt and clay are removed by the water added to the top of the tank. Impurities and light substances flow out with the water at the lower end of the tank. The pH of the water can be modified to facilitate the solubilization of inorganic compounds, mainly metals;
- **Screening**: the coarse material (2 mm <Ø <50 mm) passes from the top of the scrubber onto a vibrating screener which separates the residual fine material. The coarse material is then further washed to remove the last fine fractions (Ø <2 mm, sand, silt, clay) and it accumulates at the base of the vibrating screener;
- **Sand recovery**: the water containing the fine material is collected in a tank downstream of the vibrating screener, then it is pumped into a hydrocyclone. In the hydrocyclone, the centrifugal force separates the water with silt and clay from the sand; the water with silt and clay flow upwards of the hydrocyclone while the sand comes out from the bottom of it. The wet sand passes through a dispenser that corrects the density of the mixture (60% - 80% of solids) and enters the attrition cells. These cells, thanks to the mixing blades, remove the clay particles and any contaminants on the sand particles. The sands coming from the attrition cells is dried with a vibro dryer. The dry sand mixed with the treated coarse material is transported to the storage platforms.

The Soil Washing plant can process about 200 t/h of material. Actually, the washing is carried out only with water; if the removal of inorganic compounds from the treated material will not be efficient, pH conditioners will be added (strong acids and bases, typically HCl and NaOH).

4.2 Feasibility study

The concentration of contaminants in the material to be treated is just above the legal limit, therefore it is assumed that a single wash is sufficient to obtain a material that complies with the legal limits. After the first washing cycle, the treated material will be subjected to a chemical analysis; if it still does not comply with the legal limits, a second washing cycle will be performed.

4.3 Water Treatment

The soil washing facility was started up in early March 2022; the information below comes from the remediation project of the area and describes the water treatment plant as planned and not after its construction.

About 350-400 m^3/h of water to be treated will derive from the Soil Washing plant.

The water treatment plant includes:

- **sedimentation tanks**: the sludge is concentrated, i.e. the silt and clay fall to the bottom of the tank thanks to the addition of a flocculant. The resulting sludge is transferred to a homogenization silo, while the clarified water is returned to the soil washing plant;
- **sludge homogenization silos**: in the silos the sludge is constantly mixed to avoid sedimentation and to maintain the density suitable for the subsequent treatment in the filter press. Milk of lime can be added to improve sludge drainage capacity;
- **filter press**: the filter presses further reduce the water content in the homogenized sludge, which is now ready to be sent to the Stabilization / Solidification plant;
- **chemical-physical treatment of water**: the water from the filter presses (about 15-20 m^3/h) is transferred to a treatment plant where any dissolved contamination is eliminated by adding additives; the treated water can be used again in the Soil Washing process.

4.4 Control parameters

To assess the removal efficiency, the contaminants of concern are measured at the output of any washing cycle.

1. Contact details - CASE STUDY: SW n.4

1.1. Name and Surname	Prof. Dr. Domen Lestan
1.2. Country/Jurisdiction	Slovenia
1.3. Organisation	Envit Ltd.
1.4. Position	Assistant assistant manager & CTO of Envit Ltd.
1.5. Duties	Full professor at Biotechnical Faculty, University of Ljubljana
1.6. Email address	info@envit.si domen.lestan@bf.uni-lj.si
1.7. Phone number	+386 59 924 819

2. Site background

2.1 History of the site

In the Meza valley in Slovenia, lead - zinc ore has been exploited and processed for more than 300 years. At the end of the 20th century, the Meža River was considered a stream with the highest concentrations of heavy metals in Slovenia. When the mine and processing plants ceased to operate, the direct transfer of heavy metals into the environment has strongly decreased. However, the deposits of poor ore and wastes from ore processing have remained as an indirect source of heavy metal pollution. From those places heavy metals have been washed out into the nearby streams, and carried into the Meža River (Fux, J., & Gosar, M. (2007). Lead and other heavy metals in stream sediments in the area of Meža valley. *Geologija*, *50*(2), 347–360. https://doi.org/10.5474/geologija.2007.025).

Figure 1: Depiched area of demonstration site 35 x 35 m in Meza Valley, Slovenia.

2.2 Geological setting

Figure 2: Pasture soil from the upper 30 cm soil layer. Soil was calcareous, contaminated with Pb, Zn and Cd by floods of Meza River.

pH ($CaCl_2$)	***7.28***
Org. matter (%)	*5.3*
C/N	*10.7*
P_2O_5 (mg 100 g^{-1})	*7.5*
K_2O (mg 100 g^{-1})	*4.8*
$CaCO_3$ (%)	*21*
Sand (%)	*59.2*
Silt (%)	*32.3*
Clay (%)	*8.5*
CEC($mmol_c$/100g)	*18.48*

***Figure 3*:** Standard pedological properties of soil.

2.3 Contaminants of concern

Pseudo total concnetrations of contaminated soils with Pb, Zn (upper 30 cm layer), flooded by Meza River.

1. Pb 1734 ± 78
2. Zn 3313 ±178
3. Cd 24 ± 1

In situ investigations using a portable X-ray fluorescence spectrophotometer (XRF, see below ***Figure 4***) showed a strong concentration gradient of Pb contamination from the riverbank.

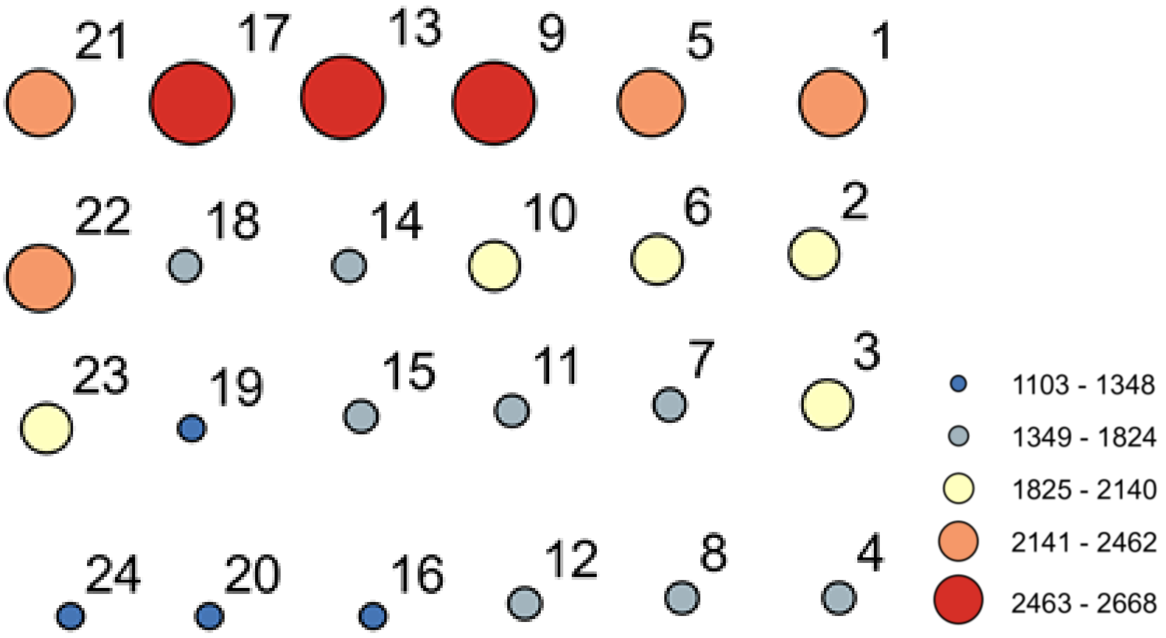


Figure 4: Average soil Pb concentration (0-30 cm, mg kg^{-1}) in site 35m x 35m.

2.4 Regulatory framework

In decree on limit values, alert thresholds and critical levels of dangerous substances into the soil (Uradni list RS, št. 68/96 in 41/04 – ZVO-1) from Slovenia, this soil are contaminated beacause concentration of all three toxic elements (Pb, Zn and Cd) are exceding legislation value for non-contaminated soil (Pb > 100, Zn ≥ 300 and Cd ≥ 2 mg kg^{-1}). Plants that are grown on that soil are also exceding legislation value which are set by COMMISSION REGULATION (EC) No 1881/2006 Setting maximum levels for certain contaminants in foodstuffs.

3. Pilot-scale application in field

3.1 Soil washing system

Washing solution is made by 100 mM EDTA (65% of calcium form, 20% of acid form, 15 % of sodium form). Soil/water ratio is 1:1. Soil are after filtration in filter press 3 times rinsed with recylcled solution from previous batch and at the end with fresh water Fresh water was added to the system to compensate for the losses of process water: due to the moisture difference between the soil entering and leaving the process, water lost with the wet solid wastes, and the hydration of the quicklime (*Figure 5*).

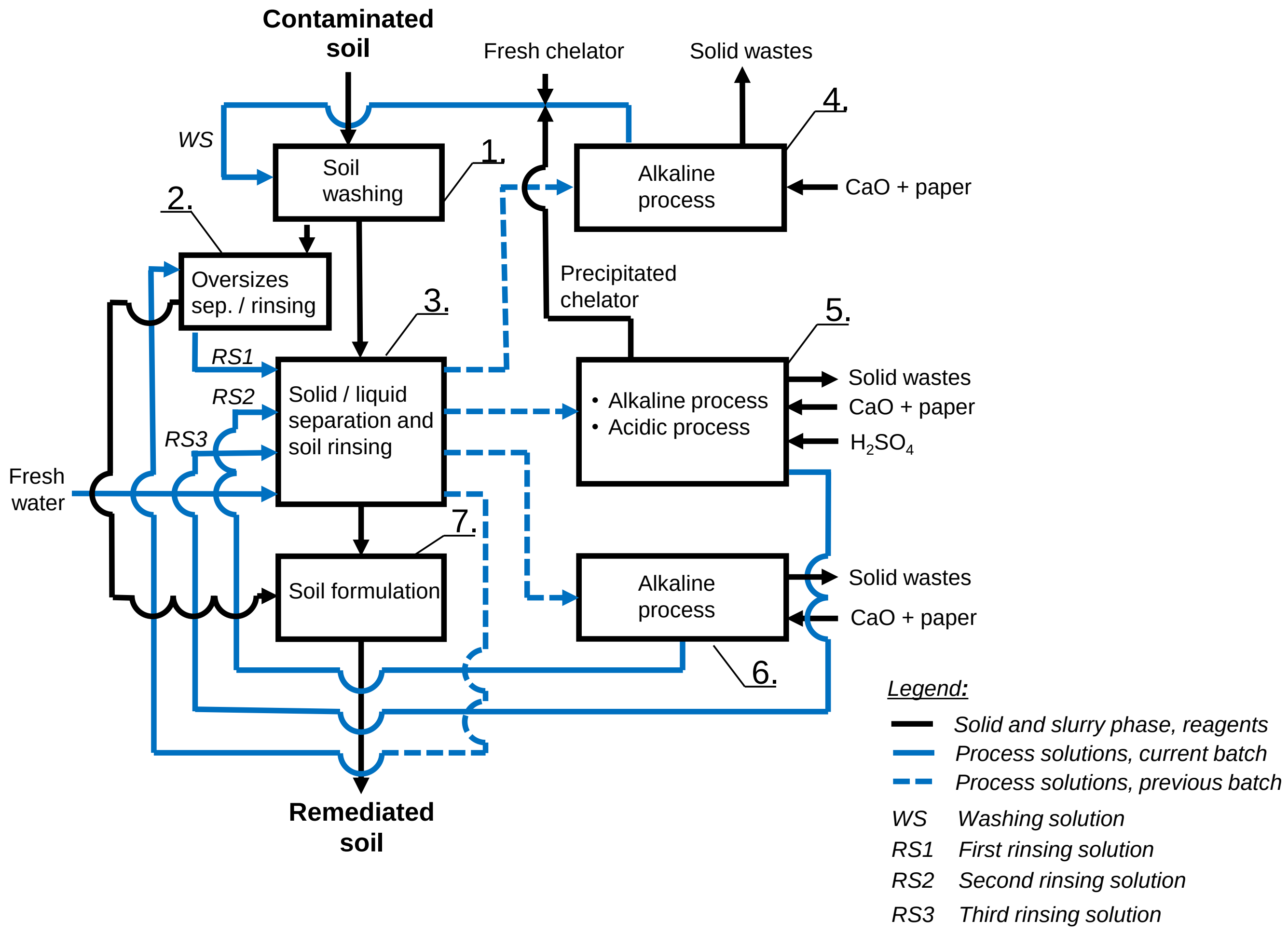


Figure 5: The flowchart of ReSoil® soil remediation process with material mass flows per batch.

The used RS1 (uRS1) from the previous batch is not treated; it issued directly as RS1 in the current batch. The used WS (uWS), used RS2 (uRS2), and used RS3 (uRS3) are treated by alkalinization with quicklime (CaO, pH > 12, 30 min) to remove toxic metals and recycle the chelator in the form of Ca salt (steps 4, 5, 6). The uWS, uRS3 and uRS2 are treated with waste paper for alkaline adsorption of toxic metals. The waste paper is applied into the uRS2 in step 6 and separated from the solution (RS2) by a filter press after 10 min of adsorption reaction. The paper from step 6 is reused in the same way, first in step 5 and then in step 4. Solid waste: hydrated lime from step 4, 5, 6 and the final paper enriched with toxic metals from step 4 is removed from the process solutions by filtration and disposed of safely. The uRS1 is acidified to pH 2 in step 5 by adding 96% H_2SO_4 to precipitate and recover (120 min reaction time) the remaining chelator in acidic form by filter press. The recycled WS is then prepared by adding acidic and fresh chelator to compensate for the loss of chelator in the process: the chelator is removed with the waste and bound to ZVI in the soil solid phase.

ReSoil® is designed as a close loop process (circular economy), everything is designed to have no negative impact on the environment, everything is emission free (no leakage, no gaseous emissions, only solid waste). ReSoil® enables dual action: removal of heavy metals by EDTA and auxiliary extractants & immobilization of residual pollutants by zero-valent Fe (ZVI) and auxiliary adsorbents.

Figure 6: Scheme of ReSoil® system.

3.2 Feasibility study

Fraction share of toxic elements are presented in ***Figure 7.***

Pb is mainly bound to carbonates and organic matter fraction, Zn is mainly bound to residual and organic matter fraction, Cd is mainly bound to carbonates and organic matter fraction. Soil washing was able to remove toxic metals from more labile fraction. Toxic metals which are strong bound to soil particels are not mobile and therefore do not pose a treat for environment and human. With remedation we where able to reduced Pb, Zn and Cd for 68%, 28% and 50%.

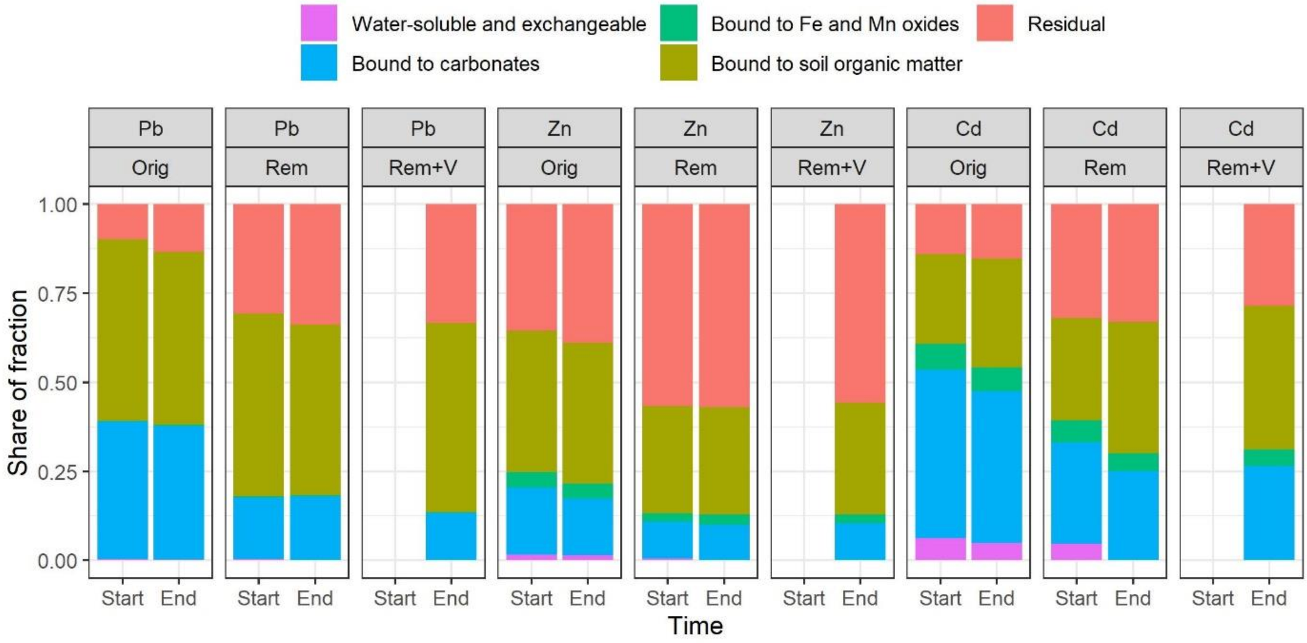


Figure 7: Share of heavy metal fractionation.

The important parameter is difference between stability of EDTA-toxic metals complex and stability of chemicals form of toxic metals present in soil. The toxic metals which could not be removed by ReSoil® process are biological and chemical unattainable. Most of toxic metals after remediation is present in soil as soil minerals, which are inert and non-toxic.

Important parameter is also soil functionality and purpose to use soil as plant substrat after remediation:

Common biological indicators of soil quality (***Figure 8***) were used to assess soil functioning. Most of microbialactivity in soil was similar then in original or recovered in 1 year of gardening. The results of our experiments clearly show that functional arbuscular mycorrhiza can be established without inoculations in remediated soils under environmental conditions. Soil washing has minor effect on standrad soil pedological properties (***Figure 8***).

	Calcareous soil	
	Original	*Remediated*
pH ($CaCl_2$)	*7.28*	*7.67*
Org. matter (%)	*5.3*	*5.6*
C/N	*10.7*	*11.9*
P_2O_5 (mg 100 g^{-1})	*7.5*	*11.1*
K_2O (mg 100 g^{-1})	*4.8*	*6.3*
$CaCO_3$ (%)	*21*	*19*
Sand (%)	*59.2*	*37.2*
Silt (%)	*32.3*	*51.9*
Clay (%)	*8.5*	*10.9*
CEC(mmol$_c$/100g)	*18.48*	*18.23*

Figure 8: Standard pedological analysis of soil.

3.3 Water Treatment

ReSoil® soil washing process does not produce waste water. All solution which are used are recyled in a closed process loop.

3.4 Control parameters

Field monitoring and sampling program that will adequately monitor the effectiveness of the treatment in three dimensions.

- Leaching of EDTA and metal complex from remediated soil.
- Checking soil rinsing efficiency in large filter press.

4. Full-scale application

4.1 Soil washing system

In ReSoil® (***Figure 9)*** the soil is excavated and grid sieved to remove oversize material.

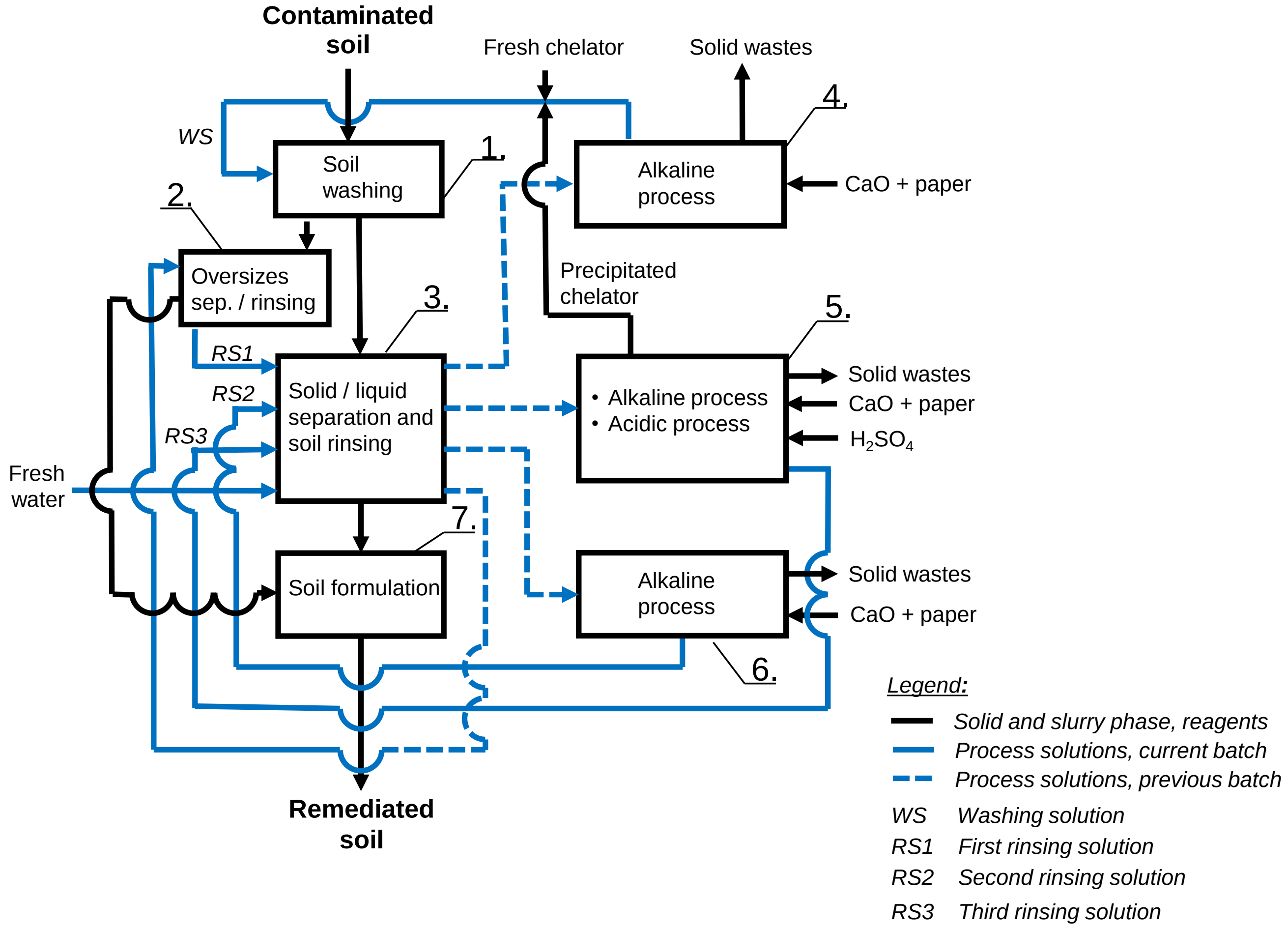
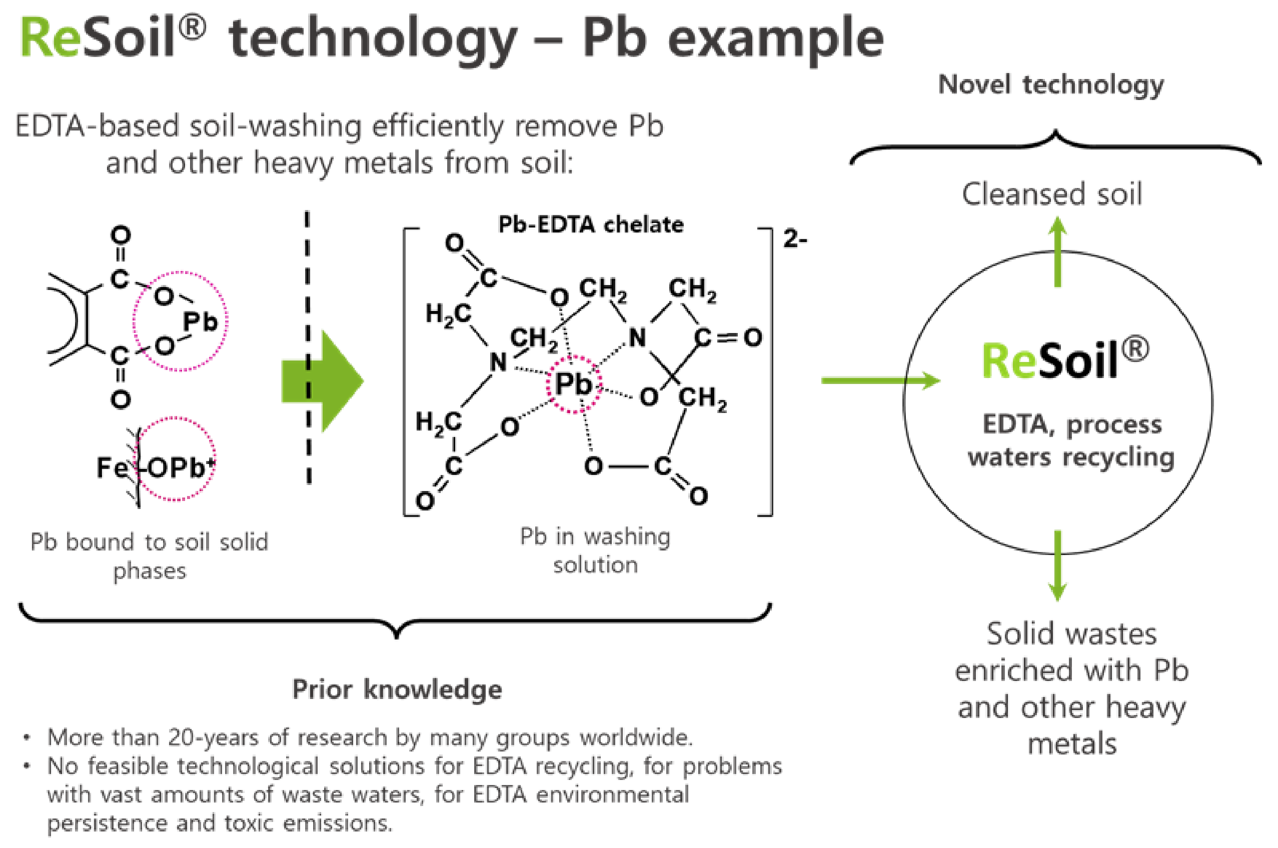


Figure 9: The flowchart of ReSoil® soil remediation process with material mass flows per batch.

Soil is washed in mixer to remove Pb and other toxic metals (Zn, Cd). Washing solution contain ethylenediamine tetraacetate (EDTA), as washing agent. The mechanisms of contaminants removal are explained bellow (*Figure 10*).



ReSoil® technology – Pb example

EDTA-based soil-washing efficiently remove Pb and other heavy metals from soil:

Pb bound to soil solid phases

Pb in washing solution

Prior knowledge

- More than 20-years of research by many groups worldwide.
- No feasible technological solutions for EDTA recycling, for problems with vast amounts of waste waters, for EDTA environmental persistence and toxic emissions.

Novel technology

Cleansed soil

ReSoil®

EDTA, process waters recycling

Solid wastes enriched with Pb and other heavy metals

Figure 10: Example of successful Pb removal with ReSoil® technology.

In a downstream process, the washed soil will be rinsed in a filter press with three consecutive rinsing solutions recycled from the previous batch and with fresh water to compensate for water losses (Figure 2).

Washing solution is made by EDTA (65% of calcium form, 20% of acid form, 15 % of sodium form). Soil/water ratio is 1:1. Soil are after filtration in filter press 3 times rinsed with recylcled solution from previous batch and at the end with fresh water. Fresh water was added to the system to compensate for the losses of process water (***Figure 12***): due to the moisture difference between the soil entering and leaving the process, water lost with the wet solid wastes, and the hydration of the quicklime.

Figure 12: Stationary ReSoil® facility with capacity of 6 t/day constructed under LIFE+ programme.

The flowchart of ReSoil® soil remediation process did not change between pilot and full-scale application. The used RS1 (uRS1) from the previous batch is not treated; it issued directly as RS1 in the current batch. The used WS (uWS), used RS2 (uRS2), and used RS3 (uRS3) are treated by alkalinization with quicklime (CaO, $pH > 12$, 30 min) to remove toxic metals and recycle the chelator in the form of Ca salt (steps 4, 5, 6). The uWS, uRS3 and uRS2 are treated with waste paper for alkaline adsorption of toxic metals. The waste paper is applied into the uRS2 in step 6 and separated from the solution (RS2) by a filter press after 10 min of adsorption reaction. The paper from step 6 is reused in the same way, first in step 5 and then in step 4. Solid waste: hydrated lime from step 4, 5, 6 and the final paper enriched with toxic metals from step 4 is removed from the process solutions by filtration and disposed of safely. The uRS1 is acidified to pH 2 in step 5 by adding 96% H2SO4 to precipitate and recover (120 min reaction time) the remaining chelator in acidic form by filter press. The recycled WS is then prepared by adding acidic and fresh chelator to compensate for the loss of chelator in the process: the chelator is

removed with the waste and bound to ZVI in the soil solid phase.
Process is made in closed cycle loop (described above). In demonstrational plant (***Figure 10***) we are able remediated 1 ton of soil per day, with possibility to work 6 ton per day.

4.2 Feasibility study

The feasibility of ReSoil® novel soil remediation technology can be made in small scale. Only 1kg of soil is needed to make pre-treatment experiement to check efficiency of EDTA (concnetration selection of EDTA).

4.3 Water Treatment

ReSoil® soil washing process does not produce waste water. All solution which are used are recyled in a closed process loop.

4.4 Control parameters

To assess the removal efficiency, the contaminants of concern are measured at the output of any washing cycle. Remediated soil water extraction test is used for assessing soil leaching suitability, by mesuring toxic metals and EDTA concentration in extracts.

5. Results

5.1 Removal rate

The average concentrations of toxic metals were 1854.0 ± 69.4 mg/kg Pb, 3833.2 ± 77.8 mg/kg Zn and 21.2 ± 0.7 mg/kg Cd in the original soil and 545.1 ± 9.6 mg/kg Pb, 2743.4 ± 69.4 mg/kg Zn and 9.9 ± 0.2 mg/kg Cd in the remediated soil. On average, remediation reduced the concentration of Pb, Zn and Cd by 71, 28 and 54%, respectively. Zn removal was characterized by lower extractability, likely due to the predominant Zn association with non-labile soil fractions.

Most of the Pb in original soil was in carbonate, organic, and residual fractions. Washing with EDTA removed on average 86% of Pb from the carbonate fraction and 69% of Pb from the organic fraction. For this reason, the share of Pb in the residual fraction increased, although the total Pb concentration in the residual fraction decreased slightly. EDTA was apparently able to extract a small amount of Pb from the solid matrix of soil minerals as well. Up to 40% of the Zn in original soil was present in the residual fraction. This high proportion of highly non-labile Zn explains the low extractability with EDTA. Nevertheless, EDTA efficiently reduced the water-soluble and exchangeable fraction of Zn by 75%. Zn was also removed from the carbonate, oxide and organic soil fractions by 60%, 59% and 44%, respectively.

Most of Cd was present in the carbonate and organic soil fraction. However, compared to Pb and Zn, Cd was more evenly distributed among the fractions. Similar to Pb and Zn, remediation efficiently removed 67% of Cd from the water-soluble and exchangeable fractions. In addition, 70%, 59% and 44% of the Cd was removed from the carbonate, oxide and organic fractions, respectively.

Overall, the sequential extraction results suggest that most of the toxic metals remaining in the soil after ReSoil® were allocated in no labile soil fractions, making them less accessible and hazardous.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

We conducted raised (demonstrational) bed experiments (***Figure 13***). Demonstrational beds filled with homogenised remediated soil are constructed as lysimeters with drainage system for collection / sampling of soil leachates. The purpose of lysimeter beds was to demonstrate through monitoring that ReSoil® process does not produce toxic emissions / leachates e.g. prevents emissions into environment. Fast growing, all season plant species e.g. buckwheat were used. Lysimeters are installed in beds for easy to sample leachate collection: toxic metals and EDTA in leachates were measured.

We monitored different parameters as:

- leaching of toxic metals and EDTA
- soil physical properties
- soil biological properties (microbial activity and mycorhizae)
- plant growth and toxic metal accumulation

Figure 13: Vegetable garden with remediated soil as a concept of post treatment asn/or longterm monitoring. The growth of leek, lettuce and carrots is depicted.

7. Additional information

7.1 Lesson learnt

1) methodology and procedures

Procedure was very effective, there was no problems with recylcling solutions. Selected equipment in ReSoil demonstration on large scale worked well. There is some room for improvement of reduction dangereous waste after solutions recycling.

2) technical aspects

Because of strong concentration gradient it is important to good mixed soil before treatment to get consistent performance of remediation process.

3) legislative, organizational aspects

Legislative is only made for whole toxic metals concentration in soil. However, after ReSoil® remedation soil with toxic metals concentration above legislative limits are safe beacause all potentional mobile fraction of toxic metals were removed. From organizational aspect we can say that it is very important to use right dissemination of the procedures when presenting innovative rememdiation technology to the lay public. If local people are scared of your process (soil washing with EDTA) it is hard to work and cooperate in that environment.

7.2 Additional information

Toxic metal fractionation, more mobile fraction better success of remediation.

Glossary of Terms

Term (alphabetical order)	**Definition**
ZVI (Fe^0)	Zero valent iron
EDTA	ethylenediamine tetraacetate
H_2SO_4	Sulfuric acid
CaO	Quick lime

1. Your contact details - CASE STUDY: SW n.5

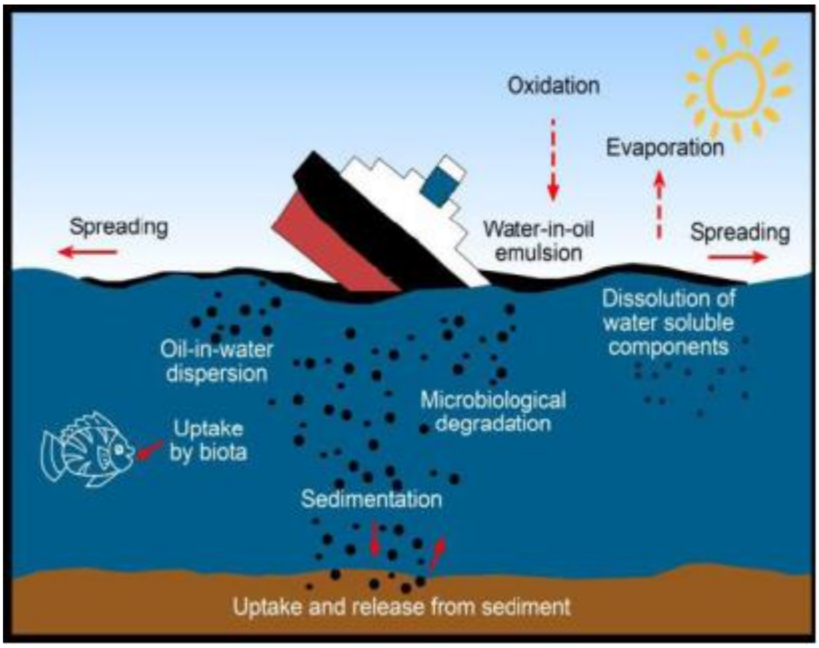
1.1. *Name and Surname**	Alessia Arelli
1.2. *Country/Jurisdiction*	Italy
1.3. *Organisation*	DICAM, University of Bologna - Italy
1.4. *Position*	Official - Soil Protection Department - Geological Survey of Italy - ISPRA - Italian National Institute for Environmental Protection and Research
1.5. *Duties*	PhD student (2013 – 2015) – DICAM, University of Bologna - Italy
1.6. *Email address*	Alessia.arelli@isprambiente.it
1.7. Phone number	0039-3406262512

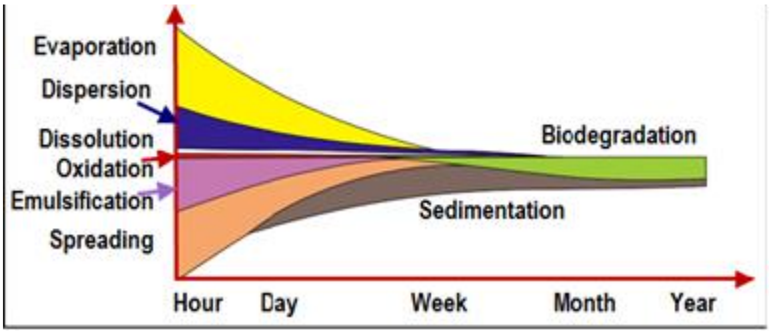
2. Site background

2.1 History of the site

- **Oil spills**

Hydrocarbons contamination of coastal environments due to accidental oil spills and activities related to the petrochemical industry is of high concern. Ocean contamination is due by several sources including the river releases, natural resource exploitation over the oil spills pollution by ships and oil tankers [1]. Was estimated that every year nearly 4 million tons of oil are globally spilled in the sea [2] determining a strong impact on the coastal environment.





[1] Fingas M (2011) Introduction to Oil Chemistry and Properties. In: Fingas M (ed) Oil Spill Science and Technology, DOI:10.1016/B978-1-85617-943-0.10003-6
[2] Cohen MA (2013) Water Pollution from Oil Spills. In: Encyclopedia of Energy, Natural Resource and Environmental Economics, DOI:1016/B978-0-12-375067- 9.00094-2

2.2 Geological setting

- **Beach sand contamination**

A beach sand collected from the shore near Ravenna (northern Italy) was used. From the screening of the sands (<2mm) the matrix was classified as sand, based on the USDA classification. The organic carbon content was estimated <1% (determination of organic carbon with the Sprinter-Klee method), given in agreement with the sandy matrix; and the pH ≈7.2 (potentiometric method). The sand was contaminated in the laboratory with IFO180 (Intermediate Fuel Oil 180) marine fuel by Shell, a mixture of 98% of residual oil and 2% of distillate oil obtained from the heavy and medium fractions of crude oil. Briefly, IFO180 fuel was dissolved at 40 g/L in hexane: dichloromethane (1:20). Different volumes of the fuel solution were then added to the sand and thoroughly mixed, followed by complete solvent evaporation and weathering of oil hydrocarbons, to obtain sand samples contaminated at different final concentrations in the range 0.5 - 20 g/kg.

2.3 Contaminants of concern

- **IFO180, marine fuel, by Shell is regulated from ISO8217.**

IFO180 is composed of 80-92% by high viscosity residues and 5-20% by distillates (IMO, http://www.imo.org/). The chemical composition of the residue is quite variable, usually IFO180 is characterized by long chains of aliphatic hydrocarbons from C10 to C40, cycloalkanes and aromatics. These constitute the non-polar fraction. Furthermore, the refining residue contains asphaltenes, present in the solid state and slightly hydrophobic. Resins and asphaltenes also consist of heterocyclic compounds with sulphur, nitrogen and oxygen representing the polar and heaviest fraction of IFO180. There are also traces of metals (vanadium). In IFO180 there are polycyclic aromatic hydrocarbons (PAHs), typically 1.5%, and traces of benzo [a] pyrene at 0.2% (Material Safety Data Sheet Fuel Oil, Tesoro 2012). Due to the high viscosity of IFO180, this product is suitably pre-treated, the sample untreated is dissolved in a hexane solution: dichloromethane (1:20) overnight, under a hood; in this way the product is treatable and loses the most volatile fraction of hydrocarbons, simulating the natural weathering process that undergoes an oil stain when it is released into the sea and reaches the coasts.

2.4 Regulatory framework

The surfactant aided ex situ washing technology has been proposed for cleaning up oil-contaminated sands; however, while the use of synthetic commercial surfactants at concentrations well above their critical micelles concentrations (CMCs) has been shown to effectively remove hydrophobic pollutants from contaminated soils [3], the environmental compatibility of such remediation practice is limited due to the toxicity, recalcitrance and persistence of such synthetic surfactants in the washed soil. The opportunity to use cheap, non-toxic, and biodegradable pollutant-mobilizing agents in this process has been previously investigated for soils contaminated by polycyclic aromatic hydrocarbons [3], petroleum hydrocarbons [4,5] and chlorinated aromatics [6,7]. So, in this context was tested the effectiveness of biogenic, non toxic and biodegradable pollutant-mobilizing agents or surfactants in the washing of oil-contaminated beach sands. this approach is allowed by the Italian law which promotes the use of bio-sustainable substances in contaminated sites remediation

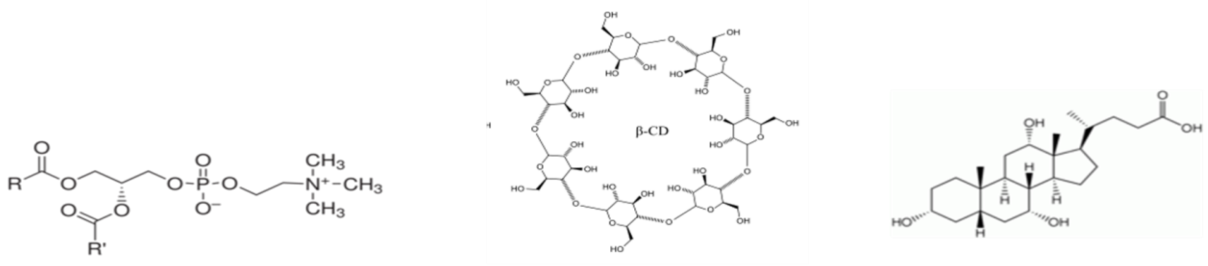
[3] Von Lau E, Gan S, Ng HK, Poh PE (2014). Extraction agents for the removal of polycyclic aromatic hydrocarbons (PAHs) from soil in soil washing technologies. Environ Pollut 184:640.
[4] Singh AK, Cameotraet SS (2013). Efficiency of lipopeptide biosurfactants in removal of petroleum hydrocarbons and heavy metals from contaminated soil. Environ Sci Pollut Res 20:7367.
[5] Hernández-Espriú A, Sánchez-León E, Martínez-Santos P, Torres LG (2013). Remediation of a diesel-contaminated soil from a pipeline accidental spill: enhanced biodegradation and soil washing processes using natural gums and surfactants. J Soils Sediments 13:152.
[6] Berselli S, Benitez E, Fedi S, Zannoni D, Medici A, Marchetti L, Fava F (2006). Development and Assessment of an Innovative Soil-Washing Process Based on the use of Cholic Acid-Derivatives as Pollutant-Mobilizing Agents. Biotechnology and Bioengineering 93:761
[7] Berselli S, Milone G, Canepa P, Di Gioia D, Fava F (2004). Effects of Cyclodextrins, Humic Substances, and Rhamnolipids on the Washing of a Historically Contaminated Soil and on the Aerobic Bioremediation of the Resulting Effluents. Biotechnology and Bioengineering 88:11.

3. Pilot-scale application in field

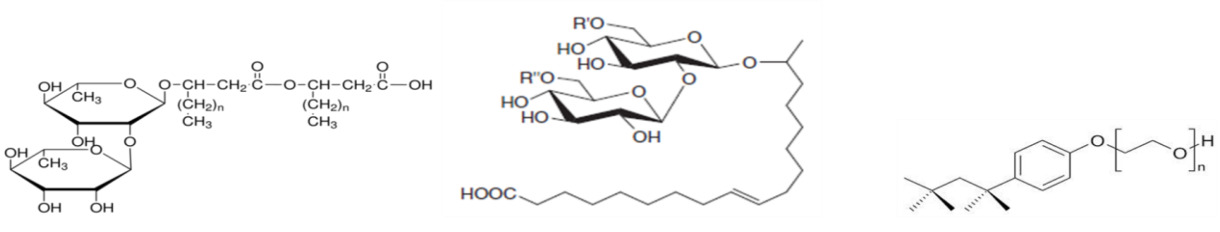
3.1 Soil washing system

- **Biosurfactant and mobilizing agents investigated in sand washing**

A number of biogenic mobilized agents commercially available at low cost were used in washing tests, namely: two soy lecithin commercial products: SOLEC™ F (SL-1) by Solae Italia s.r.l. and TEXTROL™ F (SL-2) having hydrophobic/lipophilic balances of 7 and 4, respectively; a more hydrophilic (hydroxypropyl-β-cylodextrin, HPB-CD) and a more hydrophobic (randomly methylated β-cylodextrin, RAMEB) technical grade cyclodextrins mixture, both provided by Amaizo-Cerestar (USA); four commercial cleaning products based on plant extracts (SuperSolv Safety Solvent, SC1000, Aircraft Cleaner, OmniBrite Acid Cleaner, all provided by BioBased Europe) and bovine bile acids (BB), provided by ICE srl, Italy, that mainly contains cholic acid. In addition, three microbial surfactants were employed, namely rhamnolipids (RL) sophorolipids (SR) and surfactin (SF). Finally, the synthetic surfactant Triton X-100 (TX) was used as reference, given its high hydrocarbons removal efficiency in the washing of soils contaminated by petroleum hydrocarbons.



Soy Lecithin β-cyclodextrins Cholic acid



Rhamnolipids Sophorolipids Triton X100

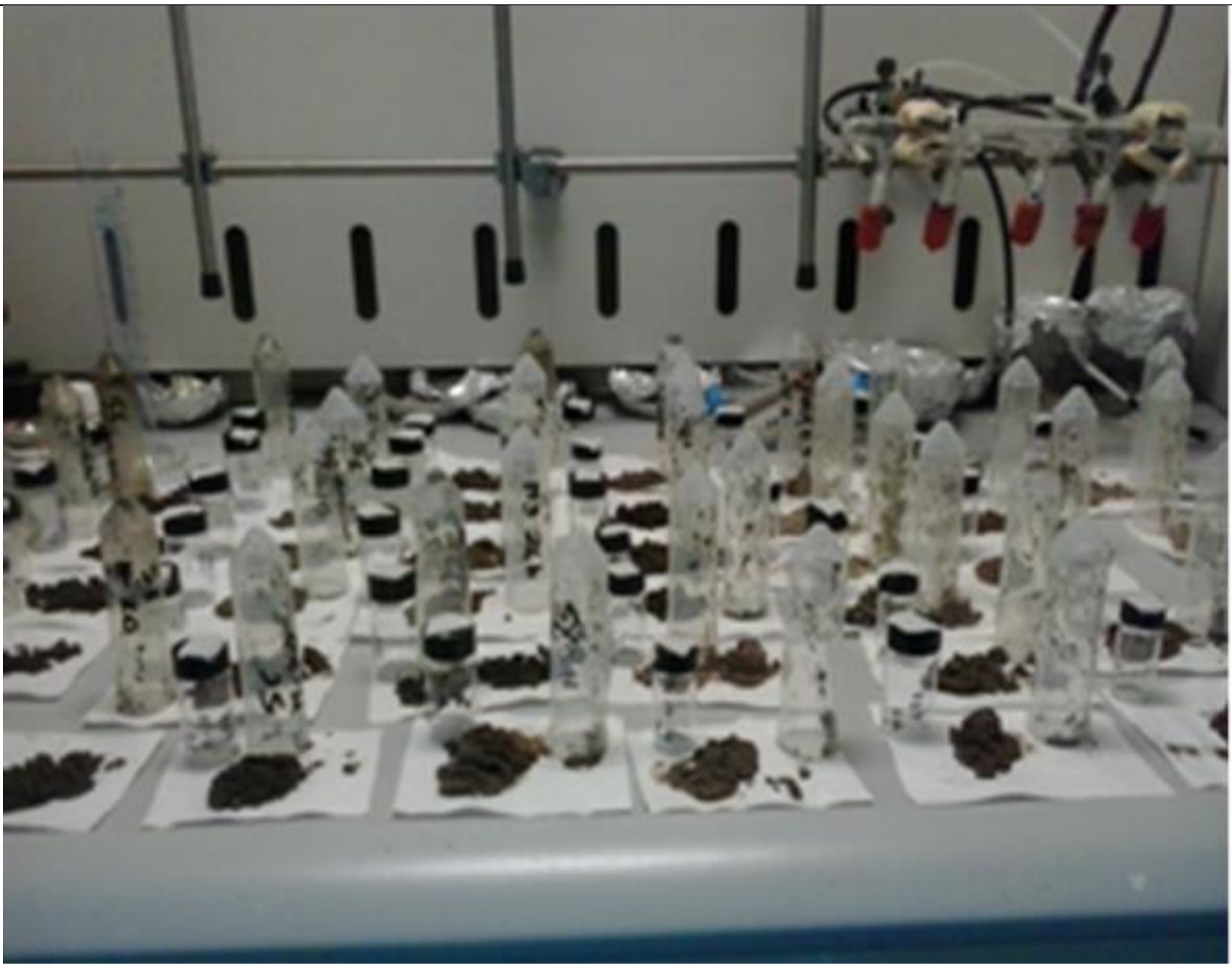
Fig. 1 Agents of plants and animal origin (Soy Lecithin – SL-1 e SL-2; β-cylodextrin – HPB-CD e RAMEB) and microbial surfactants (Rhamnolipids – RL; Sophorolipids - SR) compared to Triton X100

- **Preliminary screening of the agents in the washing of oil-contaminated beach sands**

In the first phase of the study, washing tests were performed on 50 g of contaminated beach sand with 350 mL of a water solution (sand:water ratio equal to 1:7) of each agent, in 1 L shaken reactors for 48h at room temperature under mixing at 150 rpm. All agents were used at 1% (w/v) concentration in the water phase, except for RL and SR that were employed at 0.1 % (w/v), due to their very low critical micelle concentration (0.1-0.2 g/L). The washing process was monitored after 4, 8, 24 and 48 hours. the most promising agents selected in the first phase, was SL-1, HPB-CD and SR in terms of hydrocarbons removal %, HC.

- **Sampling, extraction and analytical methods**

At each sampling during the washing procedure, an aliquot of homogeneous sand suspension was withdrawn from the reactor and sand allowed to settle. After removal of the water phase, sand was air dried overnight and hydrocarbons batch extracted overnight from 5 g of sand with 5 mL of the solvent mixture hexane:acetone (1:1). Batch extraction was assisted with ultrasonication for 5 min before and after overnight mixing. Qualitative and quantitative analysis of IFO180 fuel hydrocarbons (total hydrocarbons and n-alkanes) in the organic extracts was performed with an Agilent Technologies gas-chromatograph 6890N equipped with a HP-5 capillary column and a flame ionization detector (Hewlett-Packard Co., Palo Alto, CA, USA) under the analytical conditions described in Zanaroli et al. [8]. Total hydrocarbons were quantified, previus 12 points IFO180 calibration curve in concentration range 0.1-20 g/l (R2≥0.99). N-alkanes were quantified, previus 7 points standard mixture of n-C10 to n-C40 alkanes calibration curve in concentration range 0.01-50 ppm (R2≥0.99).



[8] Zanaroli G, Di Toro S, Todaro D, Varese GC, Bertolotto A, Fava F (2010). Characterization of two diesel fuel degrading microbial consortia enriched from a non acclimated, complex source of microorganisms. MICROBIAL CELL FACTORIES, vol. 9, pp. 10.

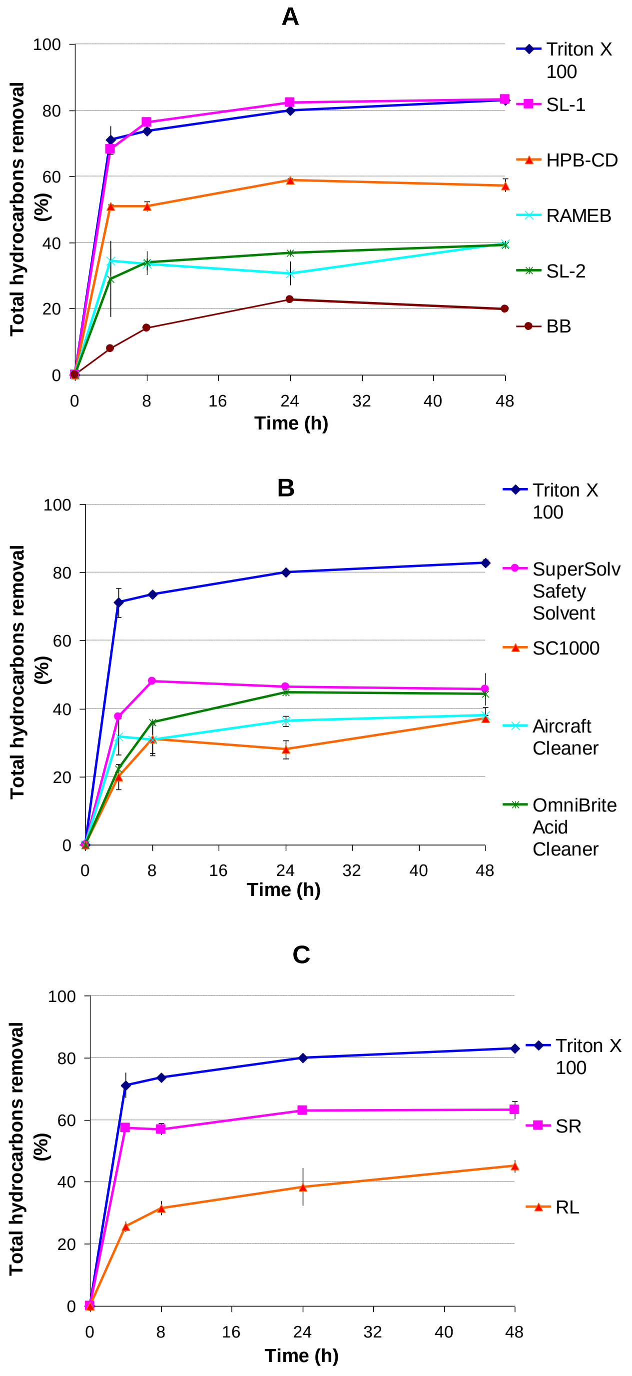
3.2 Feasibility study

- **Preliminary screening of the agents and selection of the most promising ones**

Total hydrocarbons removals of 71.2±4.3% and 82.9±0.7% and n-alkane removals of 57.4±4.3% and 76.0±0.5% were attained with the synthetic surfactant Triton X-100 (Triton X) after 4h and 48h of treatment, respectively. Comparable removals of both total hydrocarbons (68.2±1.5% and 83.2±0.3% after 4 and 48 hours, respectively) and n-alkanes (56.0±1.7% and 79.1±0.5% after 4 and 48 hours, respectively) were obtained with the more hydrophilic soy lecithin product (SL-1), whereas remarkably lower removals of both total hydrocarbons and n-alkanes were attained with the more hydrophobic soy lecithin (SL-2) after the same treatment time. Similarly, remarkably higher removals of total hydrocarbons and n-alkanes were obtained with the more hydrophilic cyclodextrins mixture (HPB-CD) compared to the more hydrophobic one (RAMEB-CD). Removals obtained with the best performing cyclodextrin (HPB-CD) were approximately 70% of those obtained with TX and SL-1 for total hydrocarbons (50.9±0.5% and 57.2±2.9% after 4 and 48 hours, respectively) and 80-90% of those obtained with TX and SL-1 for n-alkanes (53.9±3.2% and 64.2±5% after 4 and 48 hours of washing, respectively). All other plant derived products and BB exhibited both total hydrocarbons and n-alkanes removal efficiencies remarkably lower than that of TX. Among the two microbial surfactants, SR allowed to obtain higher removals of both total hydrocarbons (57.3±1.0% and 63.2±1.3% after 4 and 48 hours, respectively) and n-alkanes (36.8±1.0% and 76.8±9.3% after 4 and 48 hours, respectively) than RL. Although both microbial surfactants were applied at concentrations apparently well above their CMC, the typically lower CMC of SR (approximately one half of that of RL, i.e., approximately 0.1 g/L vs 0.2 g/L), might explain its higher hydrocarbons removal efficiency[9].

Overall, under the washing conditions used in these preliminary tests, only SL-2 exhibited hydrocarbons removals comparable to that of TX, and HPB-CD and SR hydrocarbons removals slightly lower (70% or more) than that of TX. These agents were therefore selected for the second phase of the study aiming at optimizing the washing conditions.

[9] Arelli A., Zanaroli G., Fava F (2014). Washing of oil-contaminated beach sands aided with biogenic, non toxic and biodegradable pollutant-mobilizing agents and microbial surfactants, in: Ecomondo 2014 - Green Economy: ricerca, innovazioni e azioni nel mediterraneo, RECLAIM EXPO, Maggioli Editore, pp. 528-533.



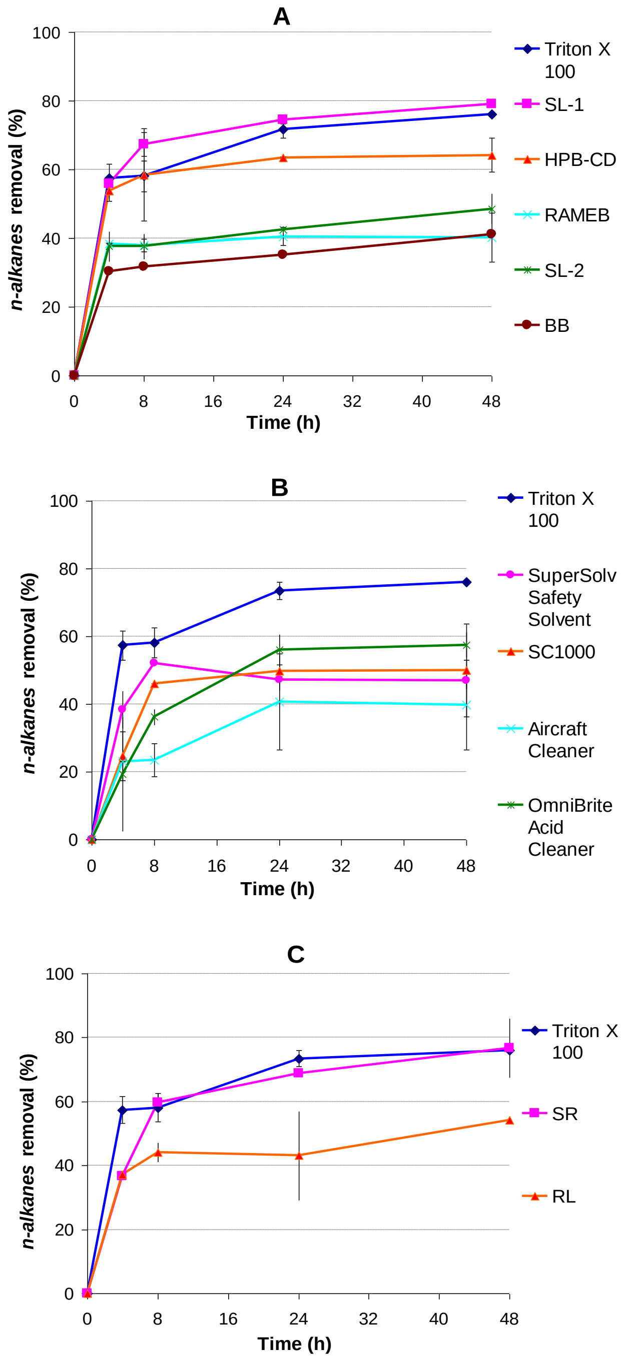


Fig. 2 *Total hydrocarbons removal (C/C_0) obtained with agents of plant and animal origin (A), cleaning products (B) and microbial surfactants (C) compared to Triton X-100*

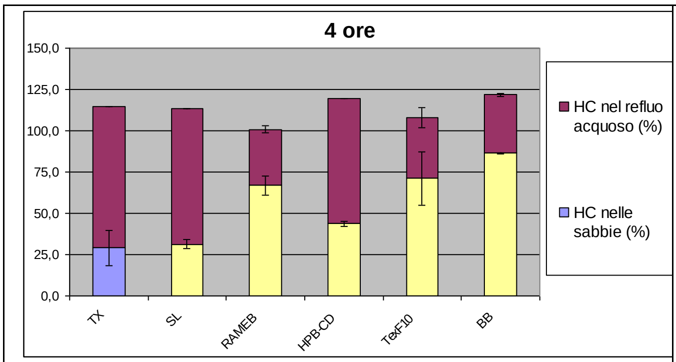
Fig. 3 *n-alkanes removal (C/C_0) obtained with agents of plant and animal origin (A), cleaning products (B) and microbial surfactants (C) compared to Triton X-100.*

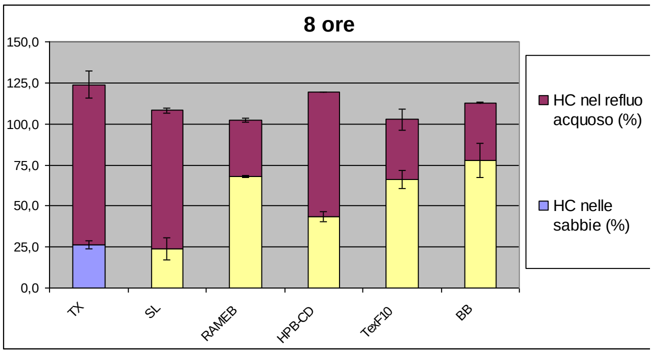
3.3 Water Treatment

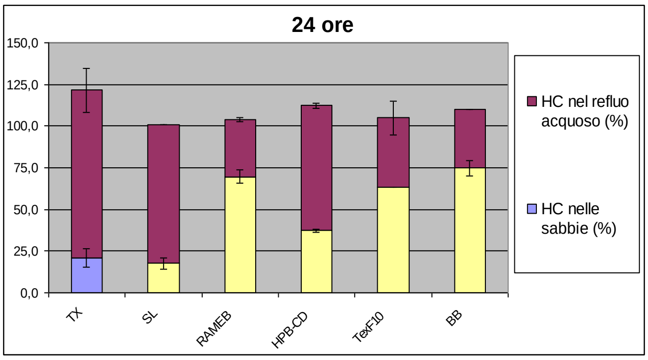
- **Mass balance (HC).**

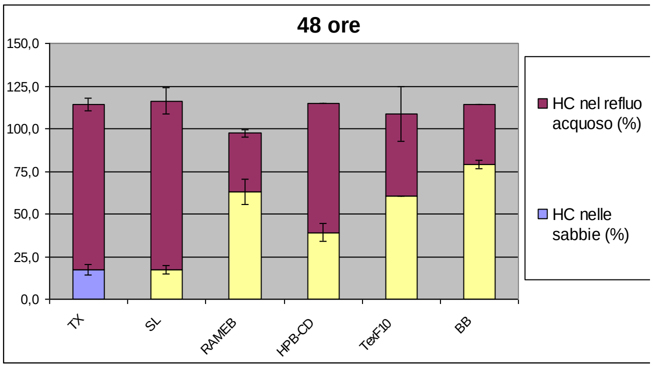
About water phase, was only verified the mass balance, to support the results obtained in the first experimental phase, relating to the removal percentages in terms of total hydrocarbons. For each tested surfactant, the aqueous wastewater was sampled during the washing treatment, in a quantity proportional to the sands extracted. Below are reported the results of the percentage mass balance observed between HC present in the sands and in the aqueous wastewater, in the samples taken after 4, 8, 24, 48 hours of washing for the agents of animal and vegetable origin compared with TX.

The results appear satisfactory; the mass balances mostly fall within the range of 100 - 120%.









3.4 Control Parameters

- **Control parameters and their optimization by ANOVA approach**

In the second phase of the study, the parameters mainly affecting the washing efficiency and the optimal washing conditions were investigated for the most promising agents selected in the first phase, namely SL-1, HPB-CD and SR, and for TX and the agent-free control. The following operating parameters were considered: surfactant concentration (% w/v), water/sand ratio (v/w), mixing rate (rpm), IFO180 concentration (g/kg). The statistical design of experiment (DoE) based on the Central Composite Design (CCD) was used for the above 4 parameters (except surfactant concentration in the case of the surfactant-free control) using 3 levels and 1 response (hydrocarbons removal %, HC). For the experimental design, ANOVA and identification of optimal washing parameters, the Design Expert software was used [10].

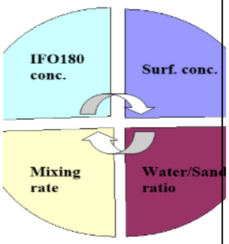
DoE (CCD) – 4 parameters (A, B, C, D) 3 levels (-1; 0; +1)

A – Sur. conc. (g/100 ml)

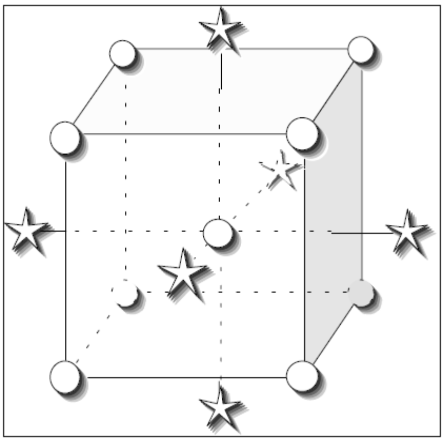
B – water/sand ratio (ml/g)

C – mixing rate (rpm)

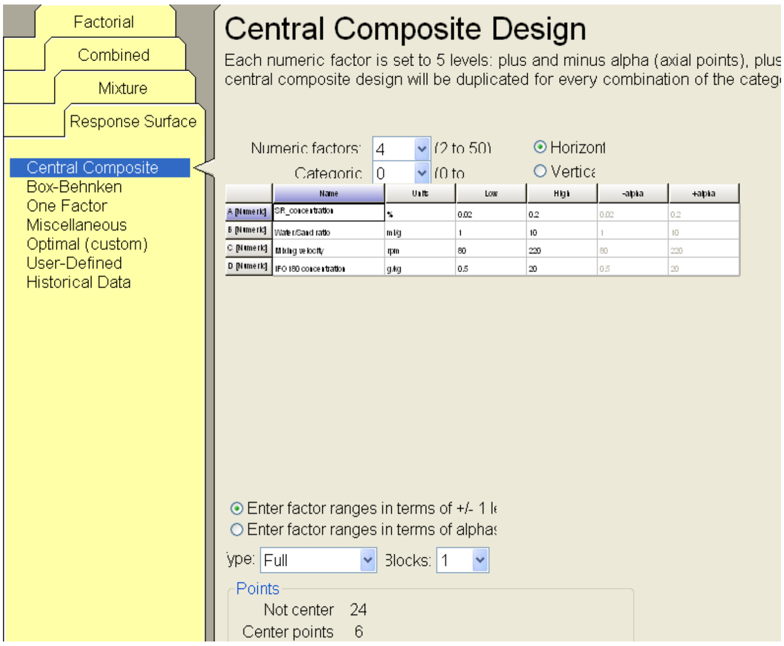
D – IFO180 conc. (g/kg)



i)



ii)



Central Composite Design

Each numeric factor is set to 5 levels: plus and minus alpha (axial points), plus central composite design will be duplicated for every combination of the categ

Numeric factors: 4 (2 to 50) ● Horizont

Categoric 0 (0 to ○ Vertica

	Name	Units	Low	High	-alpha	+alpha
A [Numeric]	SR_concentration	%	0.02	0.2	0.02	0.2
B [Numeric]	Water/Sand ratio	ml/g	1	10	1	10
C [Numeric]	Mixing velocity	rpm	80	220	80	220
D [Numeric]	IFO 180 concentration	g/kg	0.5	20	0.5	20

● Enter factor ranges in terms of +/- 1 l

○ Enter factor ranges in terms of alphas

ype: Full Blocks: 1

Points

Not center 24

Center points 6

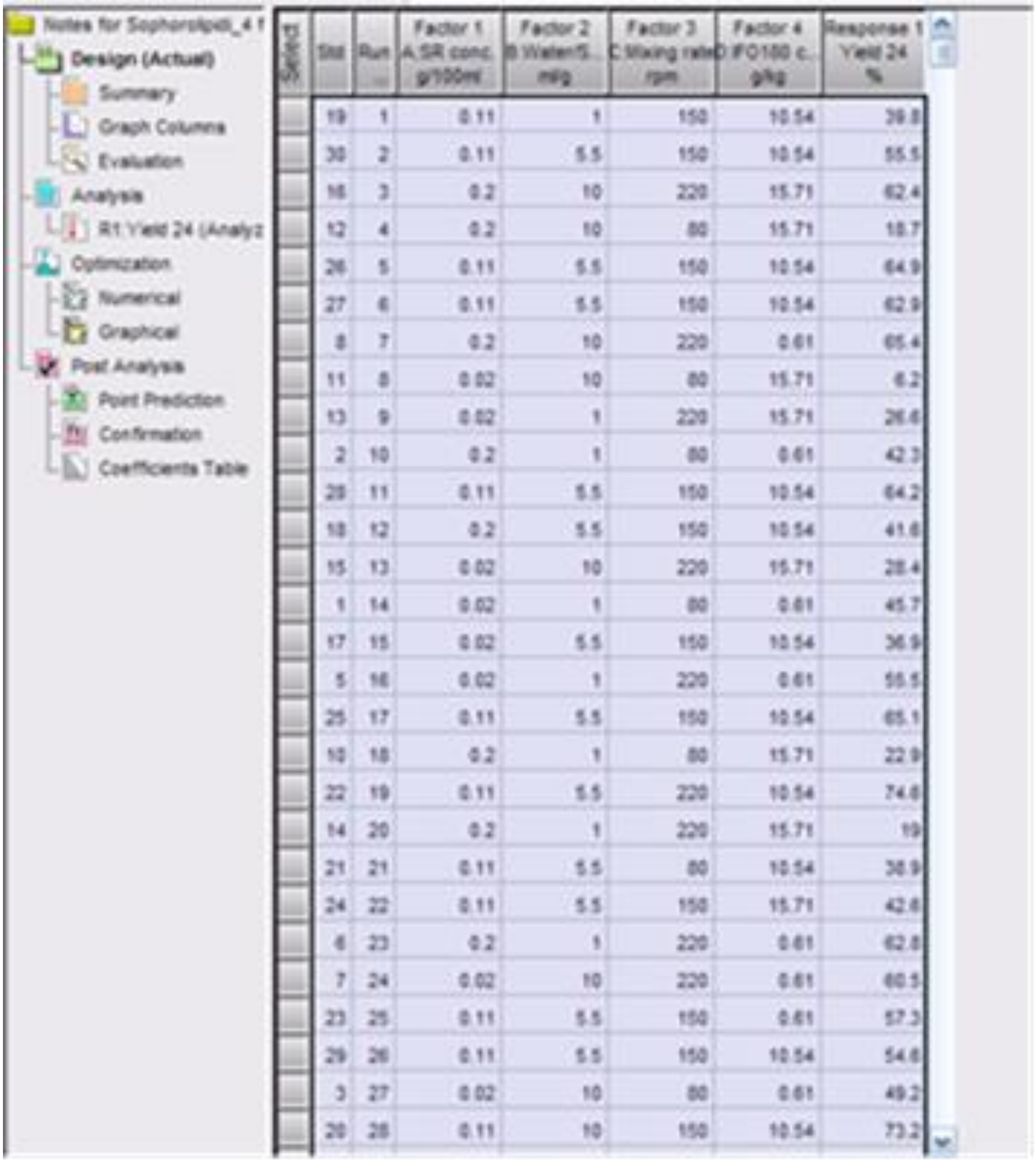
Design of experiment for TX, SL-1, HPB-CD, SR. A: surfactant concentration (% w/v), B: water: sand ratio (v/w), C: mixing rate (rpm), D: IFO180 concentration (g/kg). i) SL-1, HPB-CD, TX; ii) SR.

Design of experiment for surfactant-free water (blank). A: water: sand ratio (v/w), B: mixing rate (rpm), C: IFO180 concentration (g/kg).

Level	A	B	C	D
-1	$0.1^{i)}$ – $0.01^{ii)}$	1	80	0.5
0	$2.55^{a)}$ – $0.11^{b)}$	5.5	150	10.25
+1	$5^{a)}$ – $0.2^{b)}$	10	220	20

An example pf run’s list whith four factor (A, B, C, D) and Yeld respons (HC removal after 24 hour of washing):

Level	A	B	C
-1	1	80	0.5
0	5.5	150	10.25
+1	10	220	20



Select	Std	Run	Factor 1 A:SR conc. g/100ml	Factor 2 B:Water/S... ml/g	Factor 3 C:Mixing rate rpm	Factor 4 D:IFO180 c... g/kg	Response 1 Yield 24 %
	19	1	0.11	1	150	10.54	39.8
	30	2	0.11	5.5	150	10.54	55.5
	16	3	0.2	10	220	15.71	62.4
	12	4	0.2	10	80	15.71	18.7
	26	5	0.11	5.5	150	10.54	64.9
	27	6	0.11	5.5	150	10.54	62.9
	8	7	0.2	10	220	0.61	65.4
	11	8	0.02	10	80	15.71	6.2
	13	9	0.02	1	220	15.71	26.6
	2	10	0.2	1	80	0.61	42.3
	28	11	0.11	5.5	150	10.54	64.2
	18	12	0.2	5.5	150	10.54	41.6
	15	13	0.02	10	220	15.71	28.4
	1	14	0.02	1	80	0.61	45.7
	17	15	0.02	5.5	150	10.54	36.9
	5	16	0.02	1	220	0.61	55.5
	25	17	0.11	5.5	150	10.54	65.1
	10	18	0.2	1	80	15.71	22.9
	22	19	0.11	5.5	220	10.54	74.6
	14	20	0.2	1	220	15.71	19
	21	21	0.11	5.5	80	10.54	38.9
	24	22	0.11	5.5	150	15.71	42.6
	6	23	0.2	1	220	0.61	62.8
	7	24	0.02	10	220	0.61	60.5
	23	25	0.11	5.5	150	0.61	57.3
	29	26	0.11	5.5	150	10.54	54.6
	3	27	0.02	10	80	0.61	49.2
	20	28	0.11	10	150	10.54	73.2

30 washing tests were performed with each agent (20 tests for the surfactant-free control) under conditions combining the different levels for all investigated parameters. In this phase, each washing experiment was monitored after 24 hours. ANOVA was then applied to obtain the best fitting model describing the effect of the investigated parameters on hydrocarbons removal by each agent. Models were validated by performing additional washing tests using different conditions (i.e., combinations of surfactant concentration, water:sand ratio, mixing rate and IFO180 concentration) and comparing the observed removal efficiencies with those predicted by the model. Finally, optimal parameters for the washing of beach sand contaminated at different IFO180 concentrations were identified for each surfactant/mobilizing agent. In particular, two

optimization criteria were used:

- maximum hydrocarbons removal when all parameters are allowed to fall within the defined range (-1 to +1 level)
- maximum hydrocarbons removal when surfactant concentration and mixing range are allowed to fall within the defined range while minimizing the water:sand ratio.

[10] Design of Experiments (DOE) Made Easy
https://www.statease.com/software/design-expert/

https://www.youtube.com/watch?v=y0QovZHeubM

- **RESULTS: ANOVA 24h, model validation. Optimization criteria: Maximum and Optimum HC removal**

The ANOVA (Analysis of Variance) was applied to solve the following equation:

$Y = Cost + aA + bB + cC + dD + abAB + acAC + \ldots a^2A^2 +..$

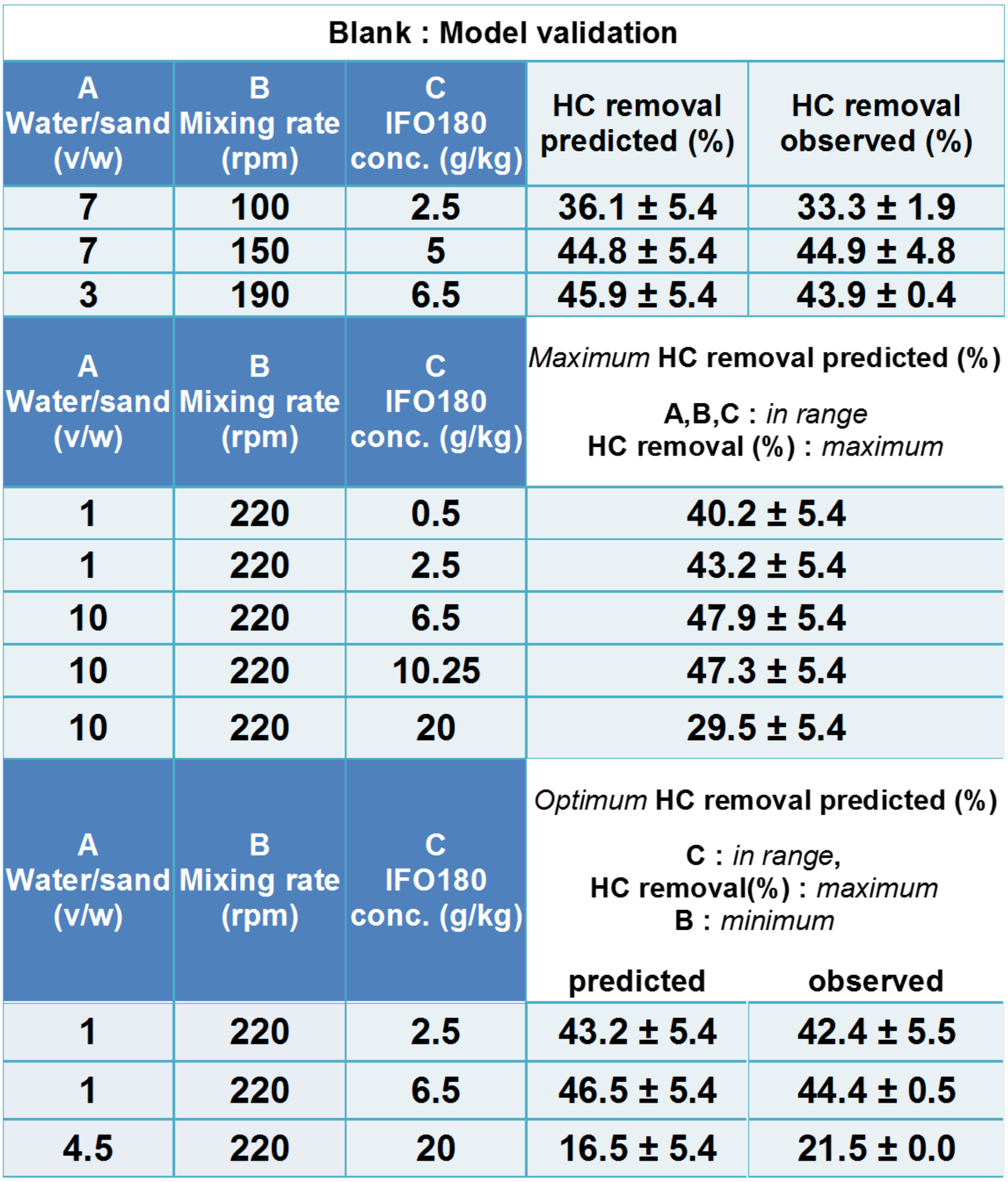
The simple model describes the effect of the investigated parameters (A, B, C, D) on hydrocarbons removal (Y) after 24h of tratment and can be rappresented by a response surface. Then, it is possible, to interrogate the model to find out the conditions of maximum removal, placing particular constraints, for example criteria i) and ii).

Model validation (experimental value versus the predicted value); maximum HC removal prediction (%); optimum HC removal prediction (%) (minimizing the water:sand ratio), are shown for surfactant-free water, TX, SL-1, HPB-CD and SR.

it is pointed out that:

- Every surfactant has error associated to predicted removals at level confidence of 95%; and errors associated to observed removals are experimental errors.
- Blank – surfactant free water. The sand washing under optimal conditions allows to obtain HC removals in the range 30-48% depending on HC concentration;
- TX. Under optimal washing conditions, TX allows to obtain HC removals from 50% to 86% at increasing IFO180 concentrations;
- Both under optimal washing conditions and by minimizing the water amount used, HPB-CD and SR perform better than TX only at low hydrocarbons concentrations, but at lower surfactant concentration;

- Both under optimal washing conditions and by minimizing the water amount used, SL performs better than TX at all hydrocarbons concentrations and at lower surfactant concentration.

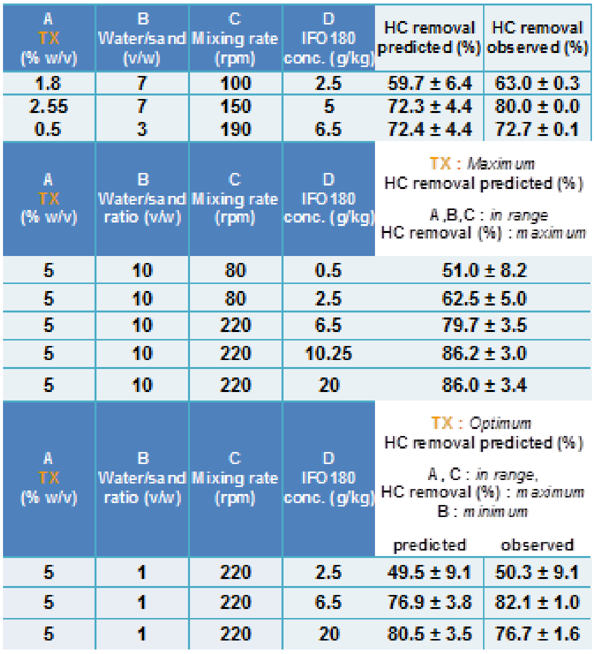


Blank : Model validation

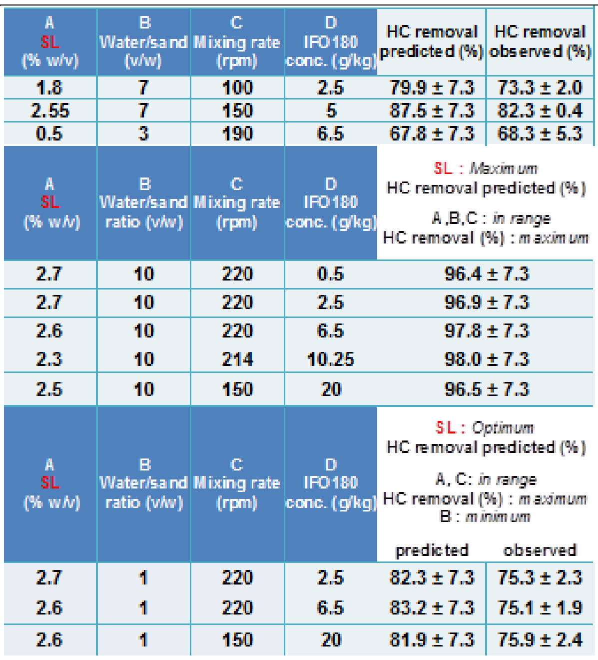
A Water/sand (v/w)	B Mixing rate (rpm)	C IFO180 conc. (g/kg)	HC removal predicted (%)	HC removal observed (%)
7	100	2.5	36.1 ± 5.4	33.3 ± 1.9
7	150	5	44.8 ± 5.4	44.9 ± 4.8
3	190	6.5	45.9 ± 5.4	43.9 ± 0.4

A Water/sand (v/w)	B Mixing rate (rpm)	C IFO180 conc. (g/kg)	*Maximum* **HC removal predicted (%)** **A,B,C :** *in range* **HC removal (%) :** *maximum*
1	220	0.5	40.2 ± 5.4
1	220	2.5	43.2 ± 5.4
10	220	6.5	47.9 ± 5.4
10	220	10.25	47.3 ± 5.4
10	220	20	29.5 ± 5.4

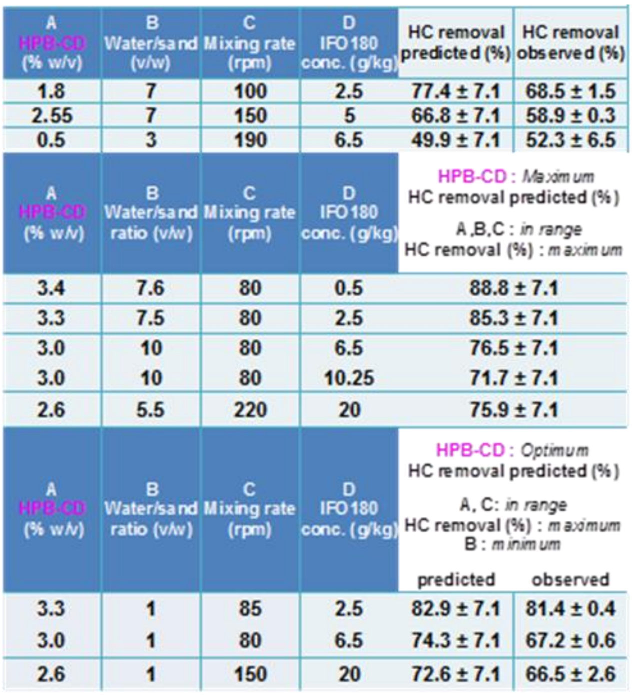
A Water/sand (v/w)	B Mixing rate (rpm)	C IFO180 conc. (g/kg)	*Optimum* **HC removal predicted (%)** **C :** *in range*, **HC removal(%) :** *maximum* **B :** *minimum*	
			predicted	observed
1	220	2.5	43.2 ± 5.4	42.4 ± 5.5
1	220	6.5	46.5 ± 5.4	44.4 ± 0.5
4.5	220	20	16.5 ± 5.4	21.5 ± 0.0



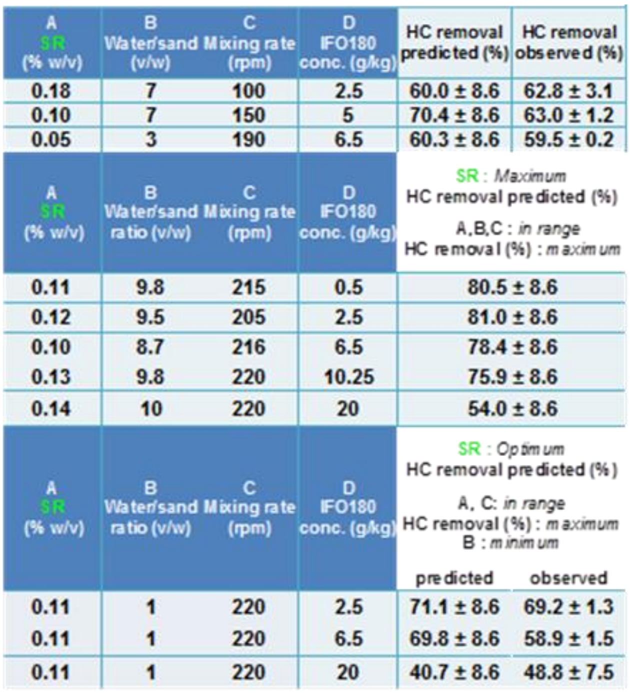
A TX (% w/v)	B Water/sand (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	HC removal predicted (%)	HC removal observed (%)
1.8	7	100	2.5	59.7 ± 6.4	63.0 ± 0.3
2.55	7	150	5	72.3 ± 4.4	80.0 ± 0.0
0.5	3	190	6.5	72.4 ± 4.4	72.7 ± 0.1
A TX (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	TX : *Maximum* HC removal predicted (%) A ,B,C : *in range* HC removal (%) : *maximum*	
5	10	80	0.5	51.0 ± 8.2	
5	10	80	2.5	62.5 ± 5.0	
5	10	220	6.5	79.7 ± 3.5	
5	10	220	10.25	86.2 ± 3.0	
5	10	220	20	86.0 ± 3.4	
A TX (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	TX : *Optimum* HC removal predicted (%) A , C : *in range*, HC removal (%) : *maximum* B : *minimum*	
				predicted	observed
5	1	220	2.5	49.5 ± 9.1	50.3 ± 9.1
5	1	220	6.5	76.9 ± 3.8	82.1 ± 1.0
5	1	220	20	80.5 ± 3.5	76.7 ± 1.6



A SL (% w/v)	B Water/sand (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	HC removal predicted (%)	HC removal observed (%)
1.8	7	100	2.5	79.9 ± 7.3	73.3 ± 2.0
2.55	7	150	5	87.5 ± 7.3	82.3 ± 0.4
0.5	3	190	6.5	67.8 ± 7.3	68.3 ± 5.3
A SL (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	SL : *Maximum* HC removal predicted (%) A ,B,C : *in range* HC removal (%) : *maximum*	
2.7	10	220	0.5	96.4 ± 7.3	
2.7	10	220	2.5	96.9 ± 7.3	
2.6	10	220	6.5	97.8 ± 7.3	
2.3	10	214	10.25	98.0 ± 7.3	
2.5	10	150	20	96.5 ± 7.3	
A SL (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	SL : *Optimum* HC removal predicted (%) A, C: *in range* HC removal (%) : *maximum* B : *minimum*	
				predicted	observed
2.7	1	220	2.5	82.3 ± 7.3	75.3 ± 2.3
2.6	1	220	6.5	83.2 ± 7.3	75.1 ± 1.9
2.6	1	150	20	81.9 ± 7.3	75.9 ± 2.4



A HPB-CD (% w/v)	B Water/sand (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	HC removal predicted (%)	HC removal observed (%)
1.8	7	100	2.5	77.4 ± 7.1	68.5 ± 1.5
2.55	7	150	5	66.8 ± 7.1	58.9 ± 0.3
0.5	3	190	6.5	49.9 ± 7.1	52.3 ± 6.5
A HPB-CD (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	HPB-CD : *Maximum* HC removal predicted (%) A ,B,C : *in range* HC removal (%) : *maximum*	
3.4	7.6	80	0.5	88.8 ± 7.1	
3.3	7.5	80	2.5	85.3 ± 7.1	
3.0	10	80	6.5	76.5 ± 7.1	
3.0	10	80	10.25	71.7 ± 7.1	
2.6	5.5	220	20	75.9 ± 7.1	
A HPB-CD (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO 180 conc. (g/kg)	HPB-CD : *Optimum* HC removal predicted (%) A, C: *in range* HC removal (%) : *maximum* B : *minimum*	
				predicted	observed
3.3	1	85	2.5	82.9 ± 7.1	81.4 ± 0.4
3.0	1	80	6.5	74.3 ± 7.1	67.2 ± 0.6
2.6	1	150	20	72.6 ± 7.1	66.5 ± 2.6

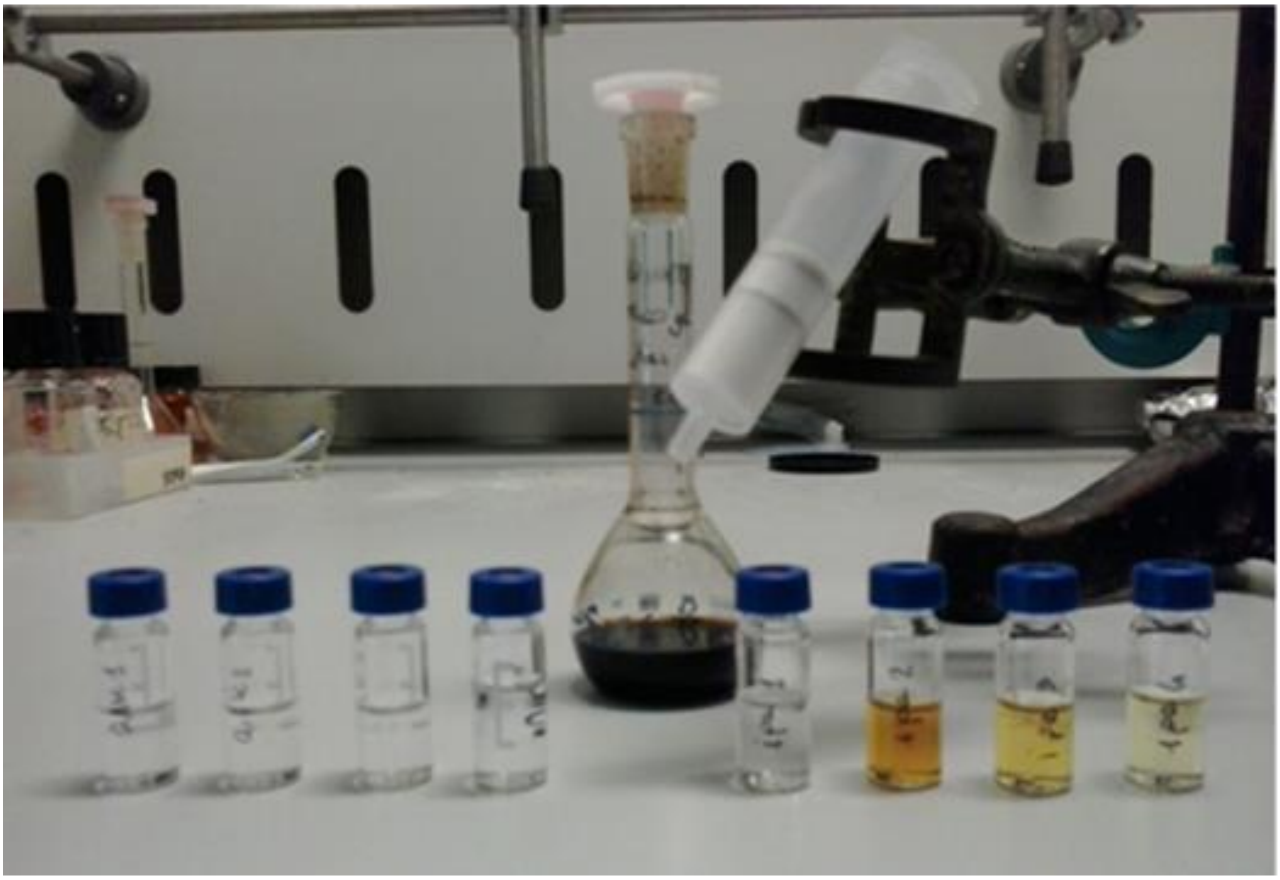


A SR (% w/v)	B Water/sand (v/w)	C Mixing rate (rpm)	D IFO180 conc. (g/kg)	HC removal predicted (%)	HC removal observed (%)
0.18	7	100	2.5	60.0 ± 8.6	62.8 ± 3.1
0.10	7	150	5	70.4 ± 8.6	63.0 ± 1.2
0.05	3	190	6.5	60.3 ± 8.6	59.5 ± 0.2
A SR (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO180 conc. (g/kg)	SR : *Maximum* HC removal predicted (%) A,B,C : *in range* HC removal (%) : *maximum*	
0.11	9.8	215	0.5	80.5 ± 8.6	
0.12	9.5	205	2.5	81.0 ± 8.6	
0.10	8.7	216	6.5	78.4 ± 8.6	
0.13	9.8	220	10.25	75.9 ± 8.6	
0.14	10	220	20	54.0 ± 8.6	
A SR (% w/v)	B Water/sand ratio (v/w)	C Mixing rate (rpm)	D IFO180 conc. (g/kg)	SR : *Optimum* HC removal predicted (%) A, C: *in range* HC removal (%) : *maximum* B : *minimum*	
				predicted	observed
0.11	1	220	2.5	71.1 ± 8.6	69.2 ± 1.3
0.11	1	220	6.5	69.8 ± 8.6	58.9 ± 1.5
0.11	1	220	20	40.7 ± 8.6	48.8 ± 7.5

- **PAH removal (%)**

In correspondence of the optimized conditions, samples were further analyzed in order to obtain the removing of PAH (%) from oil-contaminated sands compared to that of total hydrocarbons. was developed a protocol for n-alkane / PAH fraction separation using Upti - Clean SI/CN column. PAH compounds are environmentally critical because of their known toxicity, carcinogenicity and mutagenicity and presence in the environment.

Efficiency and removal mechanism of cyclodextrins in soil decontamination from PAH was studied by several authors [11,12,13,14,15,16], also was observed as microbial surfactants increase the apparent solubility of PAHs than 5 times compared to commercial products [17,18]. In IFO180 were identified a number of bi and tricycles compound: that represent 0.0042% (w/w) of IFO180.



Washing with no surfactant (blank) in optimal washing conditions for sands contaminated at different IFO180 concentrations: HC removal (%), n-alkanes removal (%), PAH removal (%)

Washing with TX in optimal washing conditions for sands contaminated at different IFO180 concentrations: HC removal (%), n-alkanes removal (%), PAH removal (%)

A – TX % (w/v)	B-Water/sand ratio (v/w)	C – Mixing rate (rpm)	D – IFO180 conc. (g/kg)	*HC* removal (%)	*n-alkanes* removal (%)	*PAH* removal (%)
1.8	7	100	2.5	63.0 ± 0.3	66.6 ± 1.2	83.2 ± 5.6
0.5	3	190	6.5	72.7 ± 0.1	72.0 ± 4.0	86.2 ± 1.8
5	1	220	2.5	68.9 ± 5.3	69.7 ± 7.9	87.8 ± 0.8
5	1	220	6.5	82.1 ± 1.0	81.9 ± 2.7	86.1 ± 6.8
5	1	220	20	76.7 ± 1.6	78.5 ± 1.3	81.3 ± 1.7

B-Water/Sand (ml/g)	C – Mixing rate (rpm)	D – IFO180 conc. (g/kg)	*HC* removal (%)	*n-alkanes* removal (%)	*PAH* removal (%)
7	100	2.5	33.3 ± 1.9	19.0 ± 0.2	49.6 ± 3.0
3	190	6.5	43.9 ± 0.4	23.0 ± 5.2	67.5 ± 1.2
1	220	2.5	42.4 ± 5.5	22.6 ± 8.2	43.1 ± 2.0
1	220	6.5	44.4 ± 0.5	29.0 ± 2.3	60.8 ± 7.8
4.5	220	20	21.5 ± 0.0	23.2 ± 0.7	42.5 ± 3.9

Washing with SL-1 in optimal washing conditions for sands contaminated at different IFO180 concentrations: HC removal (%), n-alkanes removal (%), PAH removal (%)

A –SL % (w/v)	B- Water/sand ratio (v/w)	C – Mixing rate (rpm)	D – IFO180 conc. (g/kg)	*HC* removal (%)	*n-alkanes* removal (%)	*PAH* removal (%)
1.8	7	100	2.5	73.3 ± 2.0	67.1 ± 2.4	79.4 ±1.2
0.5	3	190	6.5	68.3 ± 5.3	63.7 ± 0.4	77.5 ±4.1
2.7	1	220	2.5	75.3 ± 2.3	67.3 ± 1.3	77.3 ±9.6
2.6	1	220	6.5	75.1 ± 1.9	60.0 ± 1.4	74.8 ±1.6
2.6	1	150	20	75.9 ± 2.4	76.1 ± 2.5	82.5 ±1.4

Washing with HPB-CD in optimal washing conditions for sands contaminated at different IFO180 concentrations: HC removal (%), n-alkanes removal (%), PAH removal (%)

A – HPB-CD % (w/v)	B-Water/Sand (ml/g)	C – Mixing rate (rpm)	D – IFO180 conc. (g/kg)	*HC* removal (%)	*n-alkanes* removal (%)	*PAH* removal (%)
1.8	7	100	2.5	68.5 ± 1.5	61.6 ± 1.3	82.1 ± 2.3
0.5	3	190	6.5	52.3 ± 3.5	43.3 ± 3.4	67.0 ± 0.8
3.3	1	85	2.5	81.4 ± 0.4	67.8 ± 3.6	82.1 ± 3.3
3.0	1	80	6.5	67.2 ± 0.6	62.1 ± 0.2	67.1 ± 1.0
2.6	1	150	20	66.5 ± 2.6	62.3 ± 1.3	73.0 ± 4.0

Washing with SR in optimal washing conditions for sands contaminated at different IFO180 concentrations: HC removal (%), n-alkanes removal (%), PAH removal (%)

A – SR % (w/v)	B- Water/sand ratio (v/w)	C – Mixing rate (rpm)	D – IFO180 conc. (g/kg)	*HC* removal (%)	*n-alkanes* removal (%)	*PAH* removal (%)
0.18	7	100	2.5	62.8 ± 3.1	51.3 ± 4.6	67.4 ± 5.9
0.05	3	190	6.5	59.5 ± 0.2	49.2 ± 5.4	60.6 ± 4.3
0.11	1	220	2.5	69.2 ± 1.3	56.6 ± 6.1	83.5 ± 2.8
0.11	1	220	6.5	58.9 ± 1.5	38.0 ± 4.4	91.9 ± 0.1
0.11	1	220	20	48.8 ± 7.5	34.4 ± 2.2	62.9 ± 7.3

Glossary of Terms

Term (alphabetical order)	**Definition**
SL-1	*Soy lecithin commercial products: SOLEC™ F*
SL-2	*Soy lecithin commercial products: TEXTROL™ F*
HPB-CD	*Hydroxypropyl-β-cylodextrin*
RAMEB	*Randomly methylated β-cylodextrin*
BB	*Bovine bile acids*
SR	*Sophorolipids*
RL	*Rhamnolipids*
SF	*Surfactin*
TX	*Triton X-100*
PAH	*Polycyclic Aromatic Hydrocarbon*
DoE	*Design of experiment*
CCD	*Central Composite Design*
SD	*Standard Deviation*

[11] Wang JM., Marlowe EM., Miller-Maier RM., Brusseau ML (1998) Cyclodextrin enhanced biodegradation of phenanthrene. Environ. Sci. Technol. 32, 1907–1912

[12] Ye M, Sun M, Kengara FO, Wang J, Ni N, Wang L, Song Y, Yang X, Li H, Hu F, Jiang X (2014) Evaluation of soil washing process with carboxymethyl-β-cyclodextrin and carboxymethyl chitosan for recovery of PAHs/heavy metals/fluorine from metallurgic plant site. J Environ Sci (China) 26(8):1661-72

[13] Petitgirard A, Djehiche M, Persello J, Fievet P, Fatin-Rouge N (2009) PAH contaminated soil remediation by reusing an aqueous solution of cyclodextrins. Chemosphere 75:714-718

[14] Von Lau E, Gan S, Ng HK, Poh PE (2014) Extraction agents for the removal of polycyclic aromatic hydrocarbons (PAHs) from soil in soil washing technologies. Environmental Pollution 181:640-649

[15] Peng S, Wu W, Chen J (2011) Removal of PAHs with surfactant-enhanced soil washing: Influencing factors and removal effectiveness. Chemosphere 82:1173-1177

[16] Sánchez-Trujillo MA, Morillo E, Villaverde J,Lacorte S (2013) Comparative effects of several cyclodextrins on the extraction of PAHs from an aged contaminated soil. Environmental Pollution 178:52-58

[17] Heyd M, Kohnert A, Tan TH, Nusser M, KirschhÃfer F, Brenner-Weiss G, et al. (2008) Development and trends of biosurfactant analysis and purification using rhamnolipids as an example. Analytical and Bioanalytical Chemistry 391(5): 1579-90

[18] Nitschke M, Araújo L, Costa S, Pires R, Zeraik A, Fernandes A, et al. (2009) Surfactin reduces the adhesion of food borne pathogenic bacteria to solid surfaces. Letters in applied microbiology 49(2): 241-7

1. Your contact details - CASE STUDY: SW n.6

1.1. Name and Surname*	Prof. Dr. Domen Lestan
1.2. Country/Jurisdiction	Slovenia
1.3. Organisation	Envit Ltd.
1.4. Position	Assistant assistant manager & CTO of Envit Ltd.
1.5. Duties	Full professor at Biotechnical Faculty, University of Ljubljana
1.6. Email address	info@envit.si domen.lestan@bf.uni-lj.si
1.7. Phone number	+386 59 924 819

2. Site background

2.1 History of the site

In 1992 the Pb/Zn smelter (***Figure 1***) at Arnoldstein (Austria) closed and emissions ceased. Several hundred years of emissions (Pb, Zn, Cd, and to a lesser extent Cu, As) were dispersed over the surrounding area, which was used for housing (play- grounds), horticulture, forestry, and agriculture. The smelting activities at Arnoldstein date back to 1495, beginning with the smelting of lead, followed, in the 1950's, by the production of zinc, cadmium, and germanium. Besides the roasting and smelting of metal ores, different substances such as fertilisers (superphosphate), sulfuric acid, and dye- stuffs were also produced. Official emission figures were provided for 1989 by the Carinthian State government for SO_2 (1377 $t\ a^{-1}$), and metals (total dust up to 41.9 $t\ a^{-1}$, of which 13.5 $t\ a^{-1}$ was Pb-dust). By 1992 these emissions were reduced for SO2 to 570 $t\ a^{-1}$ and for metals (total dust) to 25.5 $t\ a^{-1}$, of which 8.9 $t\ a^{-1}$ was Pb-dust (Kasperowski, 1993). In the 1960s emission controls were improved but focused only on SO2 because of concerns relating to forest decline. The persistent heavy metals were not considered a priority at that time. The emissions consisted mainly of oxides and sulfides (Zn, Cd), sulfates (Zn, Pb, and Cd), chloride (Pb), and carbonate (Cd) (Halbwachs et al., 1982).

Figure 1: Lead smelter in Arnoldstein.

2.2 Geological setting

Arnoldstein (46°3YN, 13°42'E) is located in southern Carinthia, Austria, near the borders of Italy and Slovenia. The topography of the area is uniform at 560 m above sea level, except for some low hills originating from a landslide of the Villacher Alpe in 1348. Surrounding mountain ranges result in a typical, persistent inversion weather situation in autumn and winter. The heterogeneous soils were formed on prehistoric, limey material and replenished by glacial and alluvial sediments (Rabitsch, 1994).

The surroundings of the Pb/Zn-smelter show different geological and pedological properties. Glacial sediments (***Figure 2***) covered the western part where mostly Dystric Cambisols (WRB) have developed.

Figure 2: Grassland in Arnoldstein used as experimental site.

2.3 Contaminants of concern

Toxic metals and its concentrations:

- Lead - 795 mg/kg,
- Cadmium - 4.5 mg/kg,
- Zinc - 484 mg/kg.

2.4 Regulatory framework

In Austrian legislation there is ÖNORM S 2088-2:2014 standard which deals with Contaminated sites - Part 2: Use-specific assessment of soil contamination from old sites and old landfills. In this standard guide values for pollutant levels in the soil (0-20cm) for plant production in the use class agriculture and horticulture. Lead level should not exceded 100mg/kg, cadmium 0.5 mg/kg and cink 300 mg/kg. Reference values for assessing the mobilizable element content in the NH_4NO_4 extract of soil samples with regard to soil-plant transfer are also included. For lead 100 µg/kg and Cadium 40 µg/kg value represent a risk of impairment of the quality of the food plants or fodder plants based on *ÖNORM S 2088-2:2014.*

3. Pilot-scale application in field

3.1 Soil washing system

Washing solution is made by 60 mM EDTA (65% of calcium form, 20% of acid form, 15 % of sodium form). Soil/water ratio is 1:1. Soil are after filtration in filter press 3 times rinsed with recylcled solution from previous batch and at the end with fresh water Fresh water was added to the system to compensate for the losses of process water: due to the moisture difference between the soil entering and leaving the process, water lost with the wet solid wastes, and the hydration of the quicklime (***Figure 3***).

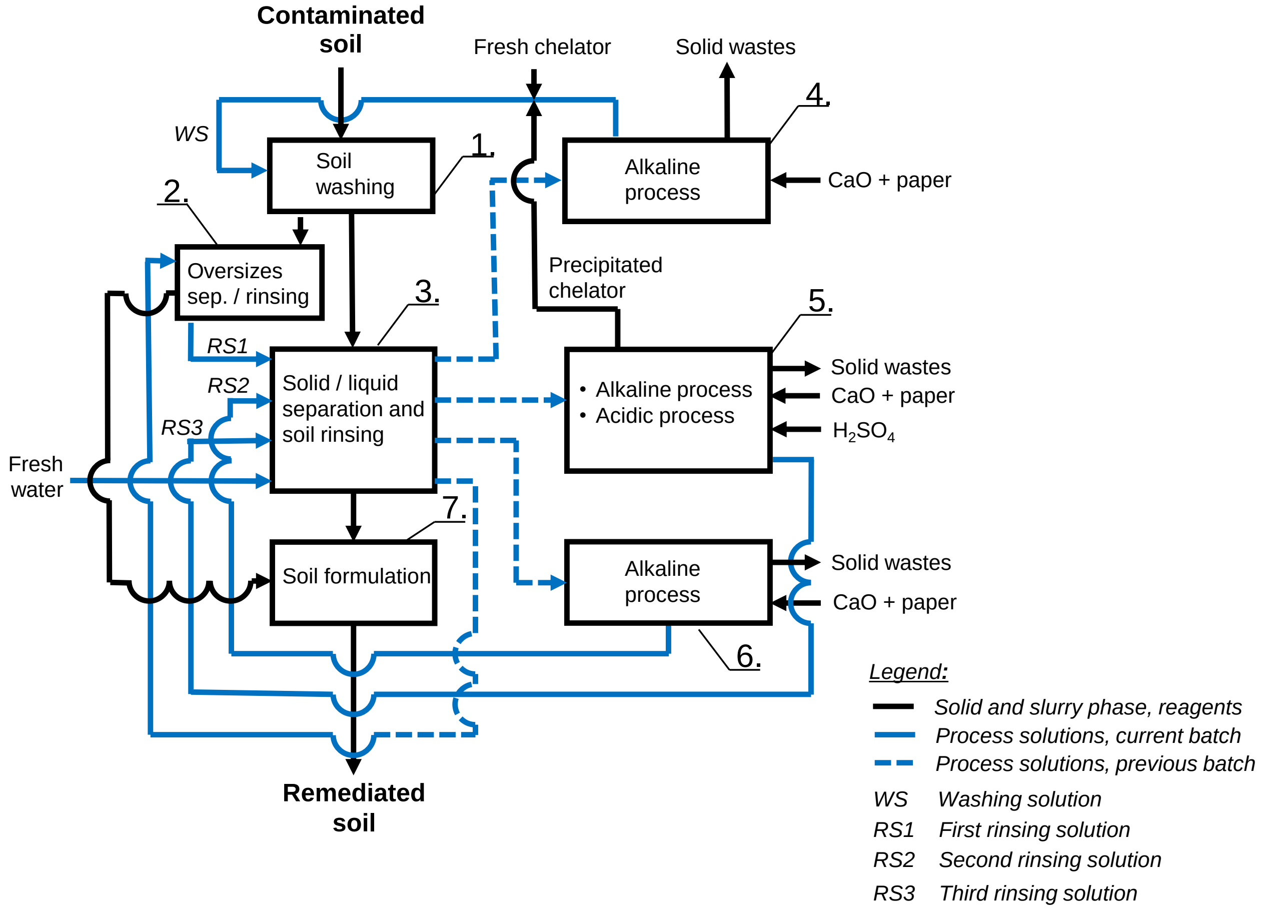


Figure 3: The flowchart of ReSoil® soil remediation process with material mass flows per batch.

The used RS1 (uRS1) from the previous batch is not treated; it issued directly as RS1 in the current batch. The used WS (uWS), used RS2 (uRS2), and used RS3 (uRS3) are treated by alkalinization with quicklime (CaO, pH > 12, 30 min) to remove toxic metals and recycle the chelator in the form of Ca salt (steps 6, 7, 8). The uWS, uRS3 and uRS2 are treated with waste paper for alkaline adsorption of toxic metals. The waste paper is applied into the uRS2 in step 6 and separated from the solution (RS2) by a filter press after 10 min of adsorption reaction. The paper from step 6 is reused in the same way, first in step 7 and then in step 8. Solid waste: hydrated lime from step 6, 7, 8 and the final paper enriched with toxic metals from step 8 is removed from the process solutions by filtration and disposed of safely. The uRS3 is acidified to pH 2 in step 7 by adding 96% H_2SO_4 to precipitate and recover (120 min reaction time) the remaining chelator in acidic form by filter press. The recycled WS is then prepared by adding acidic and fresh chelator to compensate for the loss of chelator in the process: the chelator is removed with the waste and bound to ZVI in the soil solid phase.

ReSoil® is designed as a close loop process (circular economy), everything is designed to have no negative impact on the environment, everything is emission free (no leakage, no gaseous emissions, only solid waste).

3.2 Feasibility study

The important parameter is difference between stability of EDTA-toxic metals complex and stability of chemicals form of toxic metals present in soil. The toxic metals which could not be removed by ReSoil® process are biological and chemical unattainable. Most of toxic metals after remediation is present in soil as soil minerals, which are inert and non-toxic.

Important parameter is also soil functionality and purpose to use soil as plant substrat after remediation:

Common biological indicators of soil quality (***Figure 4***) were used to assess soil functioning.

	Original	*Remediated*
pH (water)	*5.86*	*7.14*
SOC (%)	*2.86*	*2.93*
C/N	*9.5*	*10.1*
P_2O_5 (mg kg^{-1})	*116*	*63*
K_2O (mg kg^{-1})	*91*	*132*
Sand (%)	*38.2*	*32.8*
Silt (%)	*47.2*	*49.9*
Clay (%)	*14.6*	*17.3*
CEC_{eff} (cmol$_c$ kg^{-1})	*13.4*	*11.3*

Figure 4: Standard pedological analysis of soil.

3.3 Water Treatment

ReSoil® soil washing process does not produce waste water. All solution which are used are recyled in a closed process loop.

3.4 Control parameters

Field monitoring and sampling program that will adequately monitor the effectiveness of the treatment in three dimensions.

- Leaching of EDTA and metal complex from remediated soil.
- Checking soil rinsing efficiency in large filter press.

4. Full-scale application

4.1 Soil washing system

In ReSoil® (***Figure 5)*** the soil is excavated and grid sieved to remove oversize material. Soil is washed in mixer to remove Pb and other toxic metals (Zn, Cd). Washing solution contain ethylenediamine tetraacetate (EDTA), as washing agent. The mechanisms of contaminants removal are explained bellow (***Figure 6***). In a downstream process, the washed soil will be rinsed in a filter press with three consecutive rinsing solutions recycled from the previous batch and with fresh water to compensate for water losses.

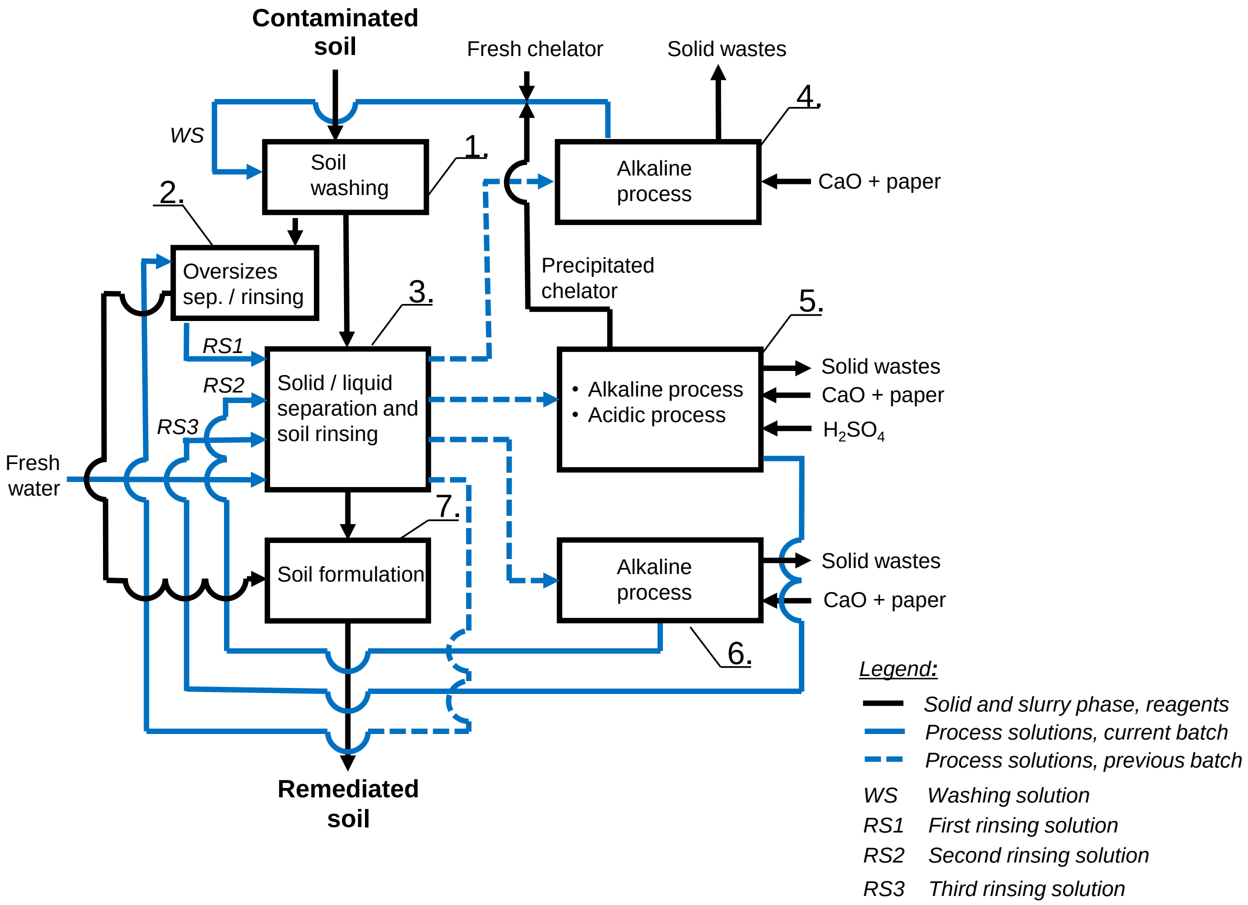
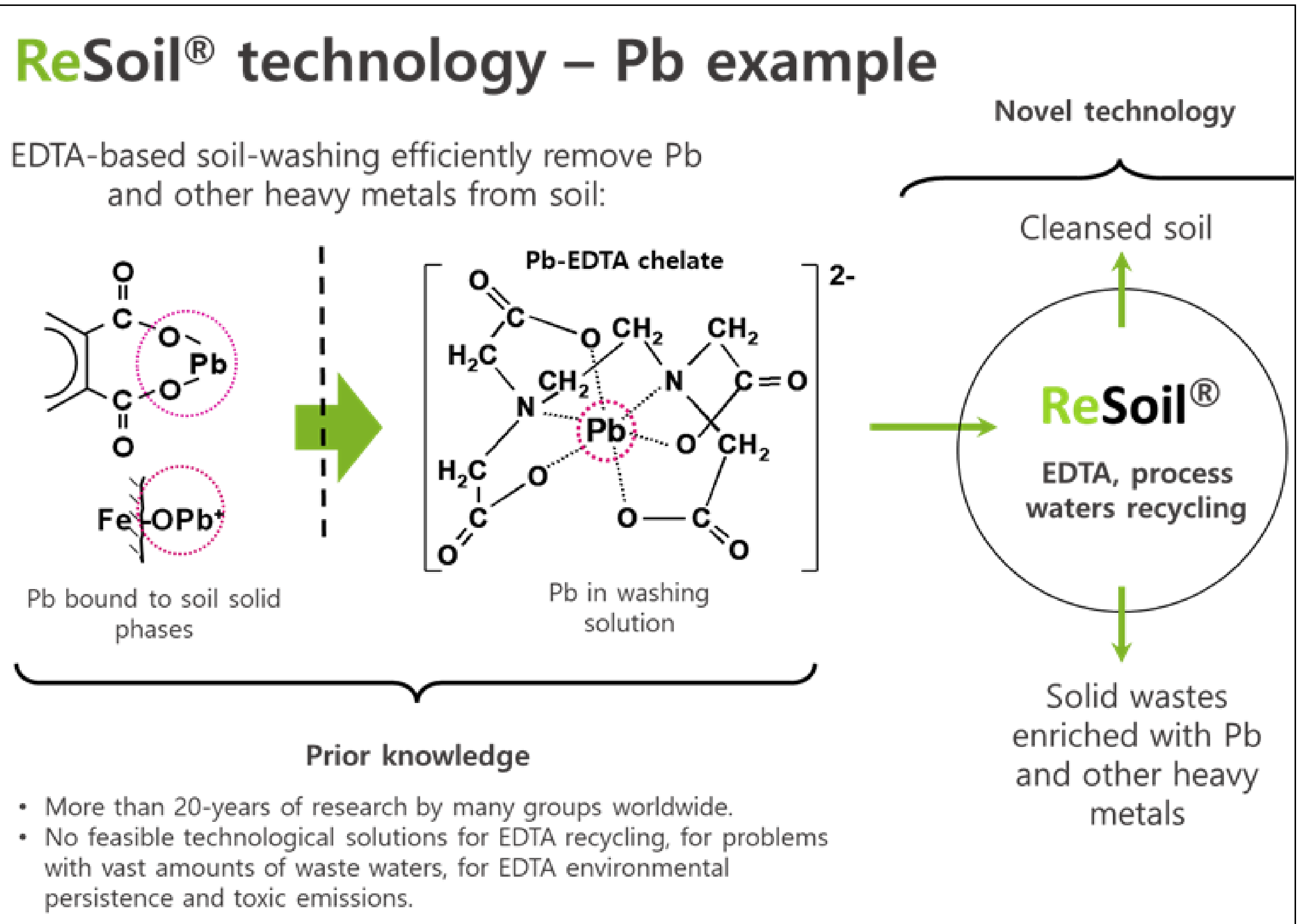


Figure 5: The flowchart of ReSoil® soil remediation process with material mass flows per batch.



ReSoil® technology – Pb example

EDTA-based soil-washing efficiently remove Pb and other heavy metals from soil:

Pb bound to soil solid phases

Pb in washing solution

Prior knowledge

- More than 20-years of research by many groups worldwide.
- No feasible technological solutions for EDTA recycling, for problems with vast amounts of waste waters, for EDTA environmental persistence and toxic emissions.

Novel technology

Cleansed soil

ReSoil®

EDTA, process waters recycling

Solid wastes enriched with Pb and other heavy metals

Figure 6: Example of successful Pb removal with ReSoil® technology.

Washing solution is made by EDTA (65% of calcium form, 20% of acid form, 15 % of sodium form). Soil/water ratio is 1:1. Soil are after filtration in filter press 3 times rinsed with recylcled solution from previous batch and at the end with fresh water Fresh water was added to the system to compensate for the losses of process water (***Figure 7)***: due to the moisture difference between the soil entering and leaving the process, water lost with the wet solid wastes, and the hydration of the quicklime.

Figure 7: Stationary ReSoil® facility with capacity of 6 t/day constructed under LIFE+ programme.

The used RS1 (uRS1) from the previous batch is not treated; it issued directly as RS1 in the current batch. The used WS (uWS), used RS2 (uRS2), and used RS3 (uRS3) are treated by alkalinization with quicklime (CaO, pH > 12, 30 min) to remove toxic metals and recycle the chelator in the form of Ca salt (steps 6, 7, 8). The uWS, uRS3 and uRS2 is treated with waste paper for alkaline adsorption of toxic metals. The waste paper is applied into the uRS2 in step 6 and separated from the solution (RS2) by a filter press after 10 min of adsorption reaction. The paper from step 6 is reused in the same way, first in step 7 and then in step 8. Solid waste: hydrated lime from step 6, 7, 8 and the final paper enriched with toxic metals from step 8 is removed from the process solutions by filtration and disposed of safely. The uRS3 is acidified to pH 2 in step 7 by adding 96% H_2SO_4 to precipitate and recover (120 min reaction time) the remaining chelator in acidic form by filter press. The recycled WS is then prepared by adding acidic and fresh chelator to compensate for the loss of chelator in the process: the chelator is removed with the waste and bound to ZVI in the soil solid phase.
Process is made in closed cycle loop (described above). In demonstrational plant (***Figure 7***) we are able remediated 1 ton of soil per day, with possibility to work 6 ton per day.

4.2 Feasibility study

The feasibility of ReSoil® novel soil remediation technology can be made in small scale. Only 1kg of soil is needed to make pre-treatment experiement to check efficiency of EDTA (concentration selection of EDTA).

4.3 Water Treatment

ReSoil® soil washing process does not produce waste water. All solution which are used are recyled in a closed process loop.

4.4 Control parameters

Field monitoring and sampling program that will adequately monitor the effectiveness of the treatment in three dimensions.

To assess the removal efficiency, the contaminants of concern are measured at the output of any washing cycle. Remediated soil water extraction test is used for assessing soil leaching suitability, by mesuring toxic metals and EDTA concentration in extracts.

5. Results

5.1 Removal rate

The average concentrations of toxic metals were 759 mg/kg Pb, 484 mg/kg Zn and 4.5 mg/kg Cd in the original soil and 189 mg/kg Pb, 409 mg/kg Zn and 2.4 mg/kg Cd in the remediated soil. On average, remediation reduced the concentration of Pb, Zn and Cd by 76, 15 and, 47%, respectively. Zn removal was characterized by lower extractability, likely due to the predominant Zn association with non-labile soil fractions.

The mobilizable element content in the NH_4NO_4 extract of soil samples with regard to soil-plant transfer was reduce for lead by 61.3 %, cadmium 63,3% and cink 97,7%.

Overall, the sequential extraction results suggest that most of the toxic metals remaining in the soil after ReSoil® were allocated in no labile soil fractions, making them less accessible and hazardous.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

We conducted raised (demonstrational) bed experiments (***Figure 8***). Demonstrational beds filled with homogenised remediated soil are constructed as lysimeters with drainage system for collection / sampling of soil leachates. The purpose of lysimeter beds was to demonstrate through monitoring that ReSoil® process does not produce toxic emissions / leachates e.g. prevents emissions into environment. Fast growing, all season plant species e.g. buckwheat were used. Lysimeters are installed in beds for easy to sample leachate collection: toxic metals and EDTA in leachates were measured.
We monitored different parameters like:

a. leaching of toxic metals and EDTA
b. soil physical properties
c. soil bilogical properties (microbial activity)
d. plant growth and toxic metal accomulation

Figure 8: Vegetable garden with remediated soil as a concept of post treatment as a/or longterm monitoring. The growth of chiness cabbage and beans is depicted.

Remediation enables growth of healthy and safe vegetables on Arnoldstein soil. Toxic metal uptake in Spinach, Radish, Chinese Cabbage and Bush Beans was reduced by over 80%. Biomass production on the remediated soil was systematically increased for all vegetables.

7. Additional information

7.1 Lesson learnt

1) methodology and procedures

Procedure was very effective, there was no problems with recylcling solutions. Equipment even on larger scale did here job as it should. There is some room for improvement of reduction dangereous waste after solutions recycling.

2) technical aspects

Tranfering contaminated soil trough border. After excavation soil is managed as hazarouds waste and a lot fo papers is needed to tranfer soil for on country to another.

3) organizational aspects

From organizational aspect we can say that it is very inportant to use right dissemination of the procedures. If local people are scared of your process is hard to work in that environment.

7.2 Additional information

Toxic metal fractionation, more mobile fraction better success of remediation.

7.4 Additional remarks

Remediated soil as an active ecosystem

Analysis of soil total C and N, DOC, NH_4, NO_3, microbial community (total microbial biomass, PLFA) and soil respiration indicated higher ecosystem activity and C/N turnover in remediated soil. Key soil micro- and mesofauna was preserved.

Glossary of Terms

Term (alphabetical order)	**Definition**
ZVI (Fe^0)	Zero valent iron
EDTA	ethylenediamine tetraacetate
H_2SO_4	Sulfuric acid
CaO	Quick lime