

WP T1. D3.5 Benchmark report on soil improvement & eco-catalyst production potential on Past Metallurgical Sites and Deposits

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[¹IXSANE, ²JUNIA]
Final version

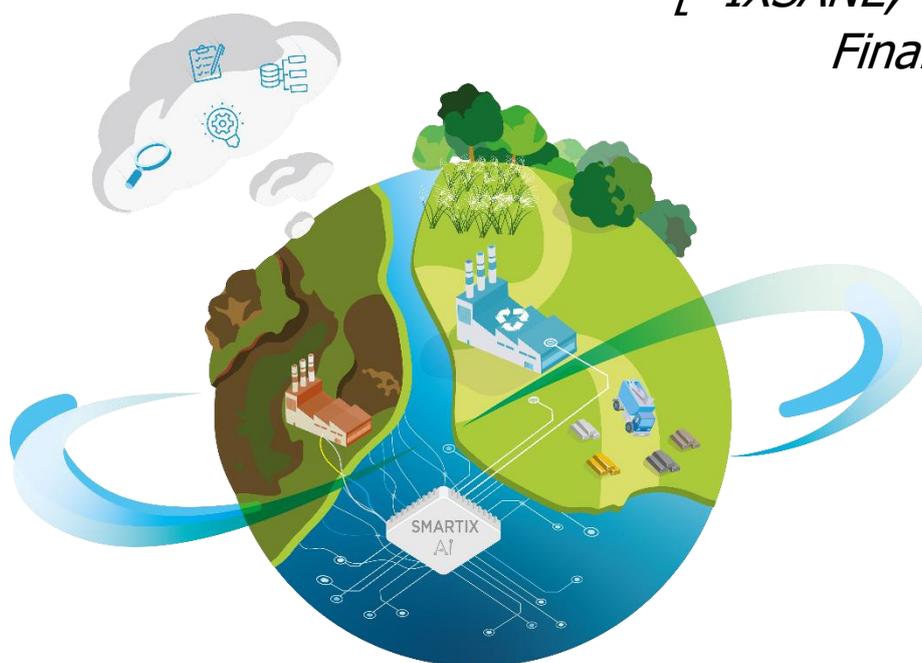


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EXECUTIVE SUMMARY

In 2006, the European Environment Agency (EEA) listed, in 39 countries, approximately 3 million of sites where polluting activities occurred. The main causes of contamination include mechanical, electronic and electrical processing industries as well as surface treatment industries, iron/steel metallurgy and coking and waste and sewage collection. The most often encountered contaminants are metals and metalloids, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Among the different brownfield types, Past Metallurgical Sites and Deposits (PMSD) are of great interest due to the presence of high quantities of reusable metallic wastes.

In addition to raw material recovery, revegetation of PMSD for their renaturation is also important. Before revegetation, an important step consists in evaluating the physical and chemical soil characteristics in order to determine if these soils can support soil vegetation, and, if not, which techniques can improve soil characteristics. However, plants cultivated on PMSD can potentially accumulate contaminants present in the soil, especially metals, and so when plants are harvested, they become a new waste that may need to be treated. Several options exist to reuse the biomass and among them, the concept of ecocatalysis, which is a new scientific approach that combines ecology and chemistry, is a promising and emerging concept.

This report focuses on soil improvement techniques and ecocatalyst production. It presents the main characteristics of brownfield sites and what are the main soil characteristics to be assessed in order to determine which improvement processes are necessary to allow plant establishment. Moreover, the report also presents different techniques to modify soil fertility and contaminant availability in soils. Finally, it describes the concept of ecocatalysis, a novel approach for remediating contaminated sites.

1 INTRODUCTION

The scale of the challenge posed by contaminated land is enormous; there are over 2.5 million contaminated sites reported across the EEA-39 that affect 231 million people and incur an annualised management cost of \$6 billion (EEA, 2014).

The main causes of contamination include mechanical, electronic and electrical processing industries as well as surface treatment industries (19.6%), iron/steel metallurgy and coking (18%) and waste and sewage collection (14.9%). The most often encountered contaminants are metals and metalloids (37.3%), hydrocarbons (33.7%) and polycyclic aromatic hydrocarbons (PAHs) (13.3%).

Thus, the requirement to make contaminated land fit for use places a large economic burden on stakeholders and so there is a pressing need for knowledge, products and technologies that can remediate such land rapidly and in a cost-effective and sustainable manner. Meanwhile land which is left derelict and unused puts a greater pressure on the development of 'greenfield' sites. The European Union is taken a leading international role in developing innovative solutions for the clean-up and regeneration of contaminated lands. It is also increasingly taking a leading role in the research and development of new technologies that tackle difficult-to-treat contaminants, improve sustainability and deliver costs savings for more traditional treatment solutions of contaminated land.

Among the various contaminated sites, Past Metallurgical Sites and Deposits (PMSD) are of great interest as high quantities of metallic wastes are expected to be found on these sites. However, these sites are often seen as an environmental, financial and societal burdens than as an opportunity for resource recovery and regeneration due to the costs involved in cleaning them up. This situation

might appear bleak, but it does present us with an exciting opportunity for a combined resource-recovery and remediation strategy, which will drastically reduce future remediation costs, reclaim valuable land, while at the same time unlocking billions of tonnes of valuable resources contained within these waste streams, improving the local environments and welfare and therefore contribute to progress on several sustainable development goals for EU and elsewhere.

In addition to raw material recovery including heavy metals, metalloids and rare earth elements from PMSD, biomass and revegetation can offer added value and benefit to these sites by i) improving soil physicochemical parameters (*i.e.* decrease soil erosion, stabilize the soil...), ii) enhancing aesthetic and landscaping aspects, and iii) augmenting ecological characteristics (Henry *et al.* 2011). Before revegetation, an important step consists in evaluating the physical and chemical soil characteristics in order to determine if these soils can support soil vegetation, and, if not, which techniques can improve soil characteristics.

However, plants cultivated on PMSD can potentially accumulate contaminants present in the soil, especially metals, and so when plants are harvested, they become a new waste that may need to be treated. Several outlets exist to reused these plants. Among them, the concept of ecocatalysis which combines phytotechnologies with innovative green chemistry to enhance ecological rehabilitation and restoration of contaminated sites (Grison *et al.* 2016). In ecocatalysis, the harvested plants, rich in pollutants, are considered as a bio-ore.

2 PAST METALLURGICAL SITES AND DEPOSITS DESCRIPTION

PMDS are often considered as degraded sites which present specific characteristics in terms of topographic, physical, chemical, and biological parameters as described above.

Degraded sites generally present severe topographic constraints such as a total absence of relief or, on the contrary, steep slope, often unstable and sensitive to erosion. They are also characterized by extreme values of apparent density (< 0.5 to $> 2 \text{ t m}^{-3}$) and the presence of sealing zone (concrete, compacted materials) on the surface or at depth. Moreover, high vertical and horizontal heterogeneity, linked to the presence of coarse elements, is often observed. Concerning soil texture, low clay and high sand contents are measured compared to natural soils. In extreme cases, no soil is observed (Morel *et al.* 2015; Séré 2007).

Chemical parameters are dependent of the past site uses. For industrial soils, a deficit in nutrients (nitrogen, phosphorus, and potassium) is often observed, exacerbated by low clay and organic matter contents. Moreover, an alkaline soil pH is commonly measured for urban soils compared to mining sites which are characterized by acidic pH values (Morel *et al.* 2005; Séré 2007). In addition, the presence of contaminants is often reported on past industrial sites. Indeed, the presence of technogenic wastes can greatly influence the soil contamination. Generally, the metal containing wastes and by-products of the metallurgical industries are in the form of slag, sludges, dust, tailings and by-products generated either in the end or as intermediate product (Lee & Pandey 2012). For example, fly ash from coal-fired electricity generating stations can contain several metallic elements like Cd, Cr, Cu, Ni, Pb, and Zn (Adriano, 2001).

To finish, all these characteristics generally lead to specific biological parameters such as more or less vegetation and particularities in the biological compartment in terms of nature and population density (Vetterlein & Hüttl 1999; Nahmani & Rossi 2003; Séré 2007).

3 PAST METALLURGICAL SITES AND DEPOSITS REHABILITATION

Before undertaking remediation techniques and revegetation, two questions should be addressed:

- What are the physicochemical characteristics of the soil?
- What processes can be used to improve soil fertility if the soil fertility does not allow plant establishment?

3.1 SOIL CHARACTERISATION

Soil characterisation is an essential step to obtain information in relation with the first question. It can be classified in three categories: soil texture, chemical characteristics (linked to soil fertility), and soil contamination.

3.1.1 Soil texture

Soil constituents are classified according to their size. Granulometric analyses distinguish two types of constituents. The fine soil corresponds to constituents with diameter lower than 2 mm, whereas the size of coarse elements is greater than 2 mm. Texture determination only takes into account the mineral fraction of soil. Three main soil fractions are considered to determine soil texture: clay with a size lower than 2 μm , silt with a size ranged between 2 and 50 μm , and sand between 50 μm and 2 mm (Gis Sol 2011).

Soil texture is determined according to the content of clay, silt and sand by using textural triangles. There are numerous different triangular diagrams of soil texture and the choice of the diagram depends on the user. In France, two different diagrams are often used: the Aisne diagram and the GEPPA diagram. The Aisne diagram determined 15 soil textures whereas the GEPPA diagram classified 17 textures. In Belgium, one specific textural triangle (16 classes) for Belgian soils is used. Internationally, the US Department of Agriculture (USDA) textural triangle is usually used and present 12 classes (**Figures 1 and 2**) (Richer-de-Forges *et al.* 2008).

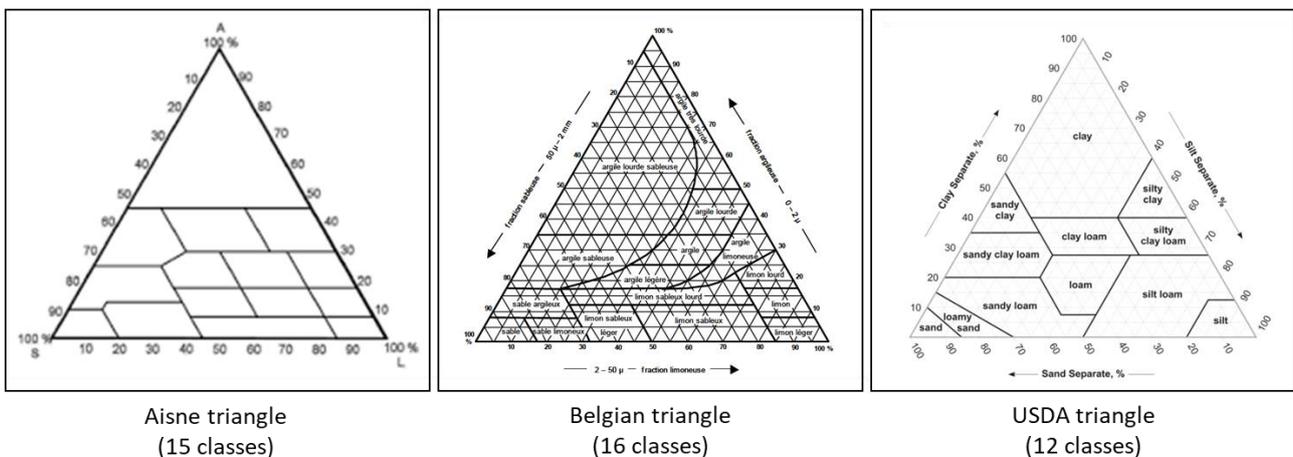


Figure 1 Different textural triangles

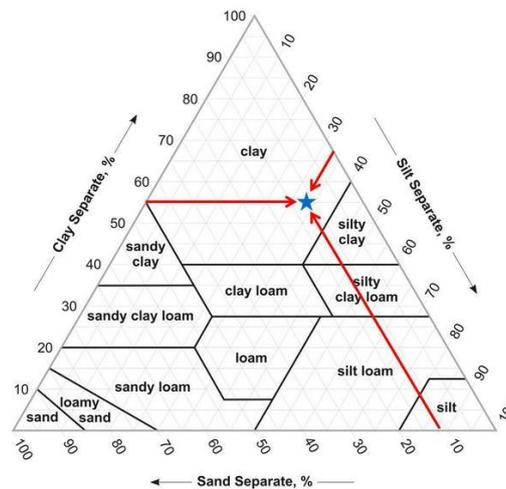


Figure 2 Example of texture determination (Crouse, 2018)

Texture is a key factor of soil fertility. Indeed, several physical and chemical properties are linked to soil texture. It acts on soil structure, and so, on its capacity to form aggregates and pores, which favour water, air, nutrient and organic element flows. Soil structure determines soil aeration and allows root, fauna and flora respiration as well as retention of usable water by the roots. Moreover, soil texture also determines other physical parameters such as the ease of tillage and soil temperature.

According to the texture, soil characteristics will differ:

- Sandy texture: aerated soil, easy to work, poor in water and nutrients;
- Silty texture: the low content of clay and the high content of silt can lead to the formation of a soil with low physical properties;
- Clay texture: good chemical properties but low physical properties (impermeable and poorly aerated soil limiting root penetration; difficult tillage...).

Thus, the ideal texture combines the quality of the three textures but without their defaults. For example, a soil texture favourable for culture development contains 40-50% of sand, 30-35% of silt and 20-25% of clay.

3.1.2 Chemical characteristics

In addition to soil texture, four main chemical parameters have to be measured to effectively characterise the soil, namely pH, cation exchange capacity (CEC), carbonates (CaCO_3), and organic carbon (Voltz *et al.* 2018). In addition to them, the amount of total nitrogen in soil, the content of phosphorus in soil available for plants and the electrical conductivity have to be taken into account because they can greatly influence soil fertility, and so, plant establishment and development.

Other parameters can be added including hydraulic conductivity, water reserve, density, structural stability, total nitrogen, phosphorus, iron and aluminium, and clay mineralogy.

3.1.2.1 pH

Soil pH corresponds to the measure of hydrogen concentration in soil solution. pH scale varies between 0 and 14; a pH lower than 7 is considered as acidic and higher than 7 as alkaline. Soil pH has a great influence on several soil parameters such as availability on soil nutrients and metallic

contaminants, soil structure, and biological activities. Plant tolerance to soil pH will greatly differ according to species. For example, ryegrass can establish on soil with pH ranged between 5.1 and 8.4 (Hannaway *et al.* 1999). **Table 1** classifies the soil pH according to its value and defines its impact on fertility.

Table 1 Soil pH classification and its impact on soil fertility

pH	Acidity	Description
< 4,5	Extremely acidic	Risk area
4,5-5	Very highly acidic	
5,1-5,5	Highly acidic	
5,6-6	Moderately acidic	Low
6,1-6,5	Slightly acidic	Optimal
6,6-7,3	Neutral	
7,4-7,8	Slightly alkaline	Risk area
7,9-8,4	Moderately alkaline	
8,5-9	Highly alkaline	
> 9	Very highly alkaline	

3.1.2.2 Cation exchange capacity

The cation exchange capacity (CEC) is defined as the potential of the soil to retain some cations which can be exchanged between the soil solution and the clay-humic complex: Ca^{2+} , Mg^{2+} , K^+ , Na^+ . Consequently, clays and organic matters mostly impact soil CEC. Permanent exchanges take place between the stock of cations presents in solid phases and those of the soil solution. A soil with high CEC will be more fertile than a soil with low CEC. Indeed, in this case, the availability of cations for plants will be the lowest and the risk of in-depth transport of cations will be the greatest. The distribution of CEC is very well correlated with the texture distribution (Gis Sol 2011). **Table 2** presents soil fertility according to the soil CEC measured with the Metson method.

Table 2 Soil fertility according to the soil CEC (Metson method; $\text{cmol}^+ \text{kg}^{-1} \text{DW}$)

CEC ($\text{cmol}^+ \text{kg}^{-1} \text{DW}^a$)	Description	Soil fertility
< 6	Very low	Low fertility
6-12	Low	Low fertility
12-25	Moderate	Medium fertility
25-40	High	High fertility
> 40	Very high	High fertility

^a $\text{cmol}^+ \text{kg}^{-1} \text{DW}$ is centimole of charge per kilogram of dry weight soil

3.1.2.3 Carbonates

Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are the most common carbonates in a wide variety of soils. According to chemical analyses, total and active lime can be distinguished. The latter represents the portion of finely fragmented carbonates that can quickly solubilize into bicarbonate. The importance of carbonates lies in the regulation of pH, in the supply of calcium for living organisms and in the structuring role of soil aggregation. Indeed, calcium has a flocculating impact on clays and stabilizes organic compounds. These mechanisms contribute to the organisation and stability of soil structure. **Table 3** presents soil description according to the CaCO_3 content.

Table 3 Soil description according to the CaCO₃ content (g kg⁻¹ DW)

CaCO ₃ (g kg ⁻¹ DW)	Description
< 50	Non calcareous
50-125	Slightly calcareous
126-250	Moderately calcareous
251-500	Highly calcareous
> 500	Extremely calcareous

3.1.2.4 Electrical conductivity

Soil electrical conductivity (EC) measures indirectly the concentration and salinity of soil solution. It gives an indication of the soluble salt content in soil solution and can often be related to soil pollution. EC has a great influence on the transport of nutrients from soil to plants. **Table 4** provides information about soil salinity.

Table 4 Soil salinity according to the electrical conductivity (mS cm⁻¹)

Electrical conductivity (mS cm ⁻¹)	Level	Soil quality
< 0,5	Low	Unsalted
0,5-1	Medium	Slightly salted
1-2	High	Salted
> 2	Very high	Highly salted

3.1.2.5 C_{org}/N_{total} ratio

The C_{org}/N_{total} ratio is calculated according to the concentration of organic carbon and total nitrogen in soil. It is an indicator of the degree of decomposition or maturation of soil organic matter. The ratio is also an indicator of the nitrogen richness of humus, and therefore of the soil nitrogen supply potential. **Table 5** presents soil description according to the C_{org}/N_{total} ratio.

Table 5 Soil description according to the C_{org}/N_{total} ratio

C _{org} / N _{total}	Description
< 6	very low
< 8	low
8-11	normal
11-12	slightly high
12-14	high
> 14	very high

3.1.2.6 Available phosphorus

Phosphorus is one of the main mineral elements used by plants for their growth and development. Thus, the availability of this element in soil is a major criterion for soil fertility. Phosphorus is present in soils in both mineral (about 2/3 of total P) and organic forms. The natural mineral phosphorus in soils is mainly retained in the form of calcium phosphates in carbonated soils and in iron- and aluminium-bound forms in other soils. Organic phosphorus is one of the constituents of soil organic matter, which is derived from the decomposition of plant and animal residues in the soil (Voltz *et al.* 2018). **Table 6** presents soil description according to the available phosphorus content.

Table 6 Soil description according to the available phosphorus concentration ($g\ kg^{-1}\ DW$)

Available P ($g\ kg^{-1}\ DW$)		Description
Olsen method	Joret-Hebert method	
< 0.05	< 0.08	Low concentration
0.05 – 0.08	0.08-0.15	Good concentration
> 0.08	> 0.15	High concentration

3.1.3 Contaminants

Contaminants the most identified on contaminated sites are metals and metalloids (37.3%), hydrocarbons (33.7%), and polycyclic aromatic hydrocarbons (PAHs) (13.3%) (CGDD 2013). In the REGENERATIS project, attention will be paid on metallic trace elements.

Soil is considered as a major sink of metallic trace elements (MTEs) originating from anthropogenic activities, and subsequently become a long-term contamination source. From a biological point of view, two types of MTEs can be distinguished: essential metals (copper, zinc...) and non-essential metals (cadmium, lead...). Nine MTEs have been listed as posing a risk to human health based on their concentrations. They are arsenic (As), cadmium (Cd), chrome (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), and zinc (Zn).

The risk of MTEs has given rise to specific laws of national or regional scope, which provide tools for monitoring soil quality. The Netherlands was the first country to create a national program for the assessment of soil contamination, establishing intervention levels, and being followed by countries like China, Austria, Poland, Germany, England, and Italy (Alfaro *et al.* 2015). However, it can be difficult to compare a measured value to threshold values of other countries. In order to determine if the soil is contaminated, it can be more pertinent to compare the measured values to background levels. According to countries, background levels can differ (**Table 7**).

Table 7 Background levels of metals ($mg\ kg^{-1}\ DW$) in several countries of North-West Europe

Metals	Background levels ($mg\ kg^{-1}\ DW$)			
	France	Holland	England	Belgium
As	1 - 25	29	32	12
Cd	0.05 - 0.45	0.8	1	0.2
Cr	10 - 90	100	/	34
Cu	2 - 20	36	62	14
Hg	0.02 - 0.1	0.3	0.5	0.05
Ni	2 - 60	35	42	24
Pb	9 - 50	85	180	25
Zn	10 - 100	140	/	67
Sb	0.05 - 1.5	3	/	/
Se	0.1 - 0.7	/	/	/

3.1.4 Influence of soil processes and properties

Soils are very diverse in composition and behaviour. The solid phase consists of mineral particles of various sizes and shapes and organic matter in various stages of degradation. Plant roots and the living soil population complete the system (Yaron *et al.* 1996). In nature, soils are heterogeneous

assemblies of materials, forming porous media. The open boundaries between the solid, liquid and gaseous phases lead to a pattern of continuously changing processes of chemical and biological origin, leading to transient soil properties. In soils, the solid particles tend to be moulded into aggregates or peds, either by a shrink-swell phenomenon under wetting and drying-freezing conditions, or by biologically induced moulding, due to soil animals, plant roots, and fungi.

Dynamic processes in soils occur both in solid and liquid phase. Soil organic matter is a heterogeneous mixture of products resulting from microbial and chemical transformation of organic residues. It is of major importance in defining the physical, chemical, and surface properties of the soil material (Yaron *et al.* 1996). The soil liquid phase, called soil solution, is a water solution with a composition and reactivity defined by the properties of the incoming water and affected by fluxes of matter and energy originated from the vicinal soil solid phase, biological system and atmosphere (Yaron *et al.* 1996). Finally, soil organisms are an integral part of the soil medium and promote a continuous interaction between the living and non-living soil populations. Both physical and chemical properties of the soil solid phase are affected by organism activity. The soil population also affects the properties of the soil liquid phase.

Soils undergo intensive changes in their physical, chemical and biological properties during natural soil development but also as a result of anthropogenic processes (e.g. sealing, erosion, amelioration, excavation) (Horn & Baumgartl 2002). Anthropogenic processes can alter ecosystem dynamic, namely ecological processes (e.g. pollination) and ecological functions (e.g. nutrient transformation). Unusual circumstances in degraded sites lead to an alteration of biogeochemical cycles and malfunctioning of ecosystems, especially for nitrogen, carbon, water, and nutrient cycles.

Yaalon (1971) categorized soil properties into three categories according to their changing speed:

- Properties that change rapidly (1 to 10^2 years) are those that respond to changes in external driving forces such as organic matter content and redistribution of salts and clays;
- Properties that change slowly (10^2 to 10^3 years) are horizons of clay, iron-humus, or carbonate accumulation;
- Properties that do not change for long periods of time (10^4 to 10^6 years) are characterized by large accumulations of secondary phases such as carbonates or profound depletions of soluble minerals leaving a nearly inert residue composed largely of iron oxides and kaolinite.

Thus, the evolution towards equilibrium is progressive and results in successive provisional equilibriums (Séré 2007).

3.2 TECHNIQUES TO IMPROVE SOIL CHARACTERISTICS

Different rehabilitation techniques exist to rehabilitate degraded ecosystems. The traditional method consists to cover the degraded soil with natural materials such as topsoil. Generally, these materials are applied in thin layers (10 – 30 cm) to allow herbaceous stratum establishment. However, this technic is very expensive and has a strong impact on the environment linked to the non-renewable resource consumption to which is also added the transport of materials over long distances. Thus, to overcome these disadvantages, others techniques consisting in introducing amendments in soils have been developed.

3.2.1 Amendments to improve soil texture

Soil texture reflects the size of the soil particles. Sandy soils have large soil particles and feel gritty. Clay soils have small soil particles and feel sticky. Thus, the choice of the amendment will depend on the initial soil texture.

When amending sandy soils, the goal is to increase the soil ability to hold moisture and store nutrients. To achieve this, the use of clay or organic amendments that are well decomposed, like compost, peat or aged manures is better. On the contrary, with clay soils, the objective is to improve soil aggregation, increase porosity, permeability, aeration, and drainage. Fibrous amendments like peat, wood chips, tree bark or straw are most effective (**Table 8** and **9**) (Davis & Whiting 2013).

Table 8 Water retention of various soil types (Davis & Whiting 2013)

Soil texture	Water retention
Sand	Low
Silt	High
Clay	High

Table 9 Water retention of various soil amendments (Davis & Whiting 2013)

Amendments	Water retention
Fibrous	
Peat	Very high
Wood chips	Low – medium
Hardwood bark	Low – medium
Humus	
Compost	Medium – high
Aged manure	Medium
Inorganic	
Vermiculite	High
Perlite	Low

3.2.2 Amendments to improve soil fertility

In June 2019, the European parliament and the council laid down rules on the making available on the market of EU fertilising products (EC2019/1009). A fertilising product is considered as a substance, mixture, microorganism or any other material, applied or intended to be applied on plants or their rhizosphere or on mushrooms or their mycosphere, or intended to constitute the rhizosphere or mycosphere, either on its own or mixed with another material, for the purpose of providing the plants or mushrooms with nutrient or improving their nutrition efficiency.

This regulation defined 7 product function categories: i) fertiliser, ii) liming material, iii) soil improver, iv) growing medium, v) inhibitor, vi) plant biostimulant, and vii) fertilising product blend.

3.2.2.1 Fertiliser

A fertilizer shall be an EU fertilising product the function of which is to provide nutrients to plants or mushrooms. Fertilisers are classified in three groups: organic, organo-mineral and inorganic fertilisers.

a) Organic fertilisers

An organic fertiliser shall contain organic carbon (Corg) and nutrients of solely biological origin. Threshold values for metal concentrations are the following (**Table 10**):

Table 10: Threshold values for metal concentrations in organic fertilisers

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	1.5	2	300	1	50	120	800

Moreover, pathogens must not exceed the following limits:

- *Salmonella* ssp.: absence in 25 g or 25 mL
- *Escherichia coli* or *Enterococcaceae* : 1000 in 1 g or 1 mL

Organic fertilisers can be in solid or liquid forms.

Solid organic fertilisers shall contain at least one of the following declared primary nutrients: nitrogen (N), phosphorus (P₂O₅) or potassium oxide (K₂O). When a solid organic fertiliser contains only one declared primary nutrient, that nutrient content shall be at least the following:

- 2.5% by mass of total N;
- 2% by mass of total P₂O₅;
- 2% by mass of total K₂O.

When a solid organic fertiliser contains more than one declared primary nutrient, fertilisers should have 1% by mass of total N, P₂O₅ or K₂O. Moreover, the sum of those nutrient contents shall be at least 4% by mass and organic carbon content shall be at least 15% by mass.

As for solid organic fertilisers, liquid organic fertilisers shall contain N (2%), P₂O₅ (1%) or K₂O (2%). When the fertiliser contains more than one nutrient, the nutrient contents shall be at least 1% by mass for N, P₂O₅ or K₂O. Moreover, the sum of nutrients contents shall be at least 3% by mass and the content of organic carbon shall be at least 5% by mass.

b) Organo-mineral fertiliser

An organo-mineral fertiliser shall be a co-formulation of one or more inorganic fertilisers and one or more materials containing organic carbon and nutrients of solely biological origin. When one or more of the inorganic fertilisers is a straight or compound solid inorganic macronutrient ammonium nitrate fertiliser of high nitrogen content, an organo-mineral fertiliser shall not contain 16% or more by mass of nitrogen as a result of ammonium nitrate (NH₄NO₃). Threshold values for metal concentrations are the following (**Table 11**):

Table 11: Threshold values for metal concentrations in organo-mineral fertilisers

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	3	2	600	1	50	120	1500

Threshold values for pathogens are similar than those for organic fertilisers.

Organo-mineral fertilisers can be in solid or liquid forms.

Solid organo-mineral fertilisers shall contain at least one of the following declared primary nutrients: N, P₂O₅ or K₂O. When a solid organic fertiliser contains only one declared primary nutrient, that nutrient content shall be at least the following:

- 2.5% by mass of total N, out of which 1% by mass shall be organic nitrogen (N_{org});
- 2% by mass of total P₂O₅;
- 2% by mass of total K₂O.

When a solid organo-mineral fertiliser contains more than one declared primary nutrient, fertilisers should have 1% by mass of total N, P₂O₅ or K₂O. Moreover, the sum of those nutrient contents shall be at least 4% by mass and organic carbon content shall be at least 15% by mass.

As for solid organo-mineral fertilisers, liquid organo-mineral fertilisers shall contain N (2%), N_{org} (0.5%), P₂O₅ (2%) or K₂O (2%). When the fertiliser contains more than one nutrient, the nutrient contents shall be at least 2% by mass for N, P₂O₅ or K₂O and 0.5% by mass for N_{org}. Moreover, the sum of nutrients contents shall be at least 6% by mass and the content of organic carbon shall be at least 3% by mass.

c) Inorganic fertilisers

An inorganic fertiliser shall be a fertiliser containing or releasing nutrients in a mineral form, other than an organic or organo-mineral fertiliser. Inorganic fertilisers are divided in two classes: inorganic macronutrient fertilisers and inorganic micronutrient fertilisers.

Inorganic macronutrient fertiliser shall be aimed at providing plants or mushrooms with one or more of the following macronutrients: i) primary macronutrients (N, P, K) and ii) secondary macronutrients (Ca, Mg, Na, S). Threshold values for metal concentrations are the following (**Table 12**):

Table 12: Threshold values for metal concentrations in inorganic macronutrient fertilisers

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	3	2	600	1	100	120	1500

Inorganic micronutrient fertiliser shall be an inorganic fertiliser other than an inorganic macronutrient fertiliser aimed at providing plants or mushrooms with one or more of the following micronutrients: B, Co, Cu, Fe, Mn, Mo or Zn. Threshold values for metal concentrations are the following (**Table 13**):

Table 13: Threshold values for metal concentrations in inorganic micronutrient fertilisers

Metal	As	Cd	Hg	Ni	Pb
Threshold (mg kg ⁻¹ of total micronutrients content ^a)	1000	200	100	2000	600

^a Micronutrients: B, Co, Cu, Fe, Mn, Mo, and Zn

3.2.2.2 Liming material

A liming material is a fertilising product the function of which is to correct soil acidity. It shall contain oxides, hydroxides, carbonates or silicates of the nutrients calcium or magnesium. Contaminants in a liming material must not exceed the following threshold values (**Table 14**):

Table 14: Threshold values for metal concentrations in liming materials

Metal	As	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	2	2	300	1	90	120	800

The following parameters must also be respected:

- Minimum neutralising value: 15 (equivalent CaO) or 9 (equivalent HO⁻);
- Minimum reactivity: 10% (hydrochloric acid test) or 50% after 6 months;
- Minimum grain size: at least 70% < 1mm, except for burnt limes, granulated liming material and chalk.

3.2.2.3 Soil improver

A soil improver shall be a product the function of which is to maintain, improve or protect the physical or chemical properties, the structure or the biological activity of the soil. They are classified as organic or inorganic soil improver.

An organic soil improver shall consist of material 95% which is solely biological origin. Threshold values for metal concentrations are the following (**Table 15**):

Table 15: Threshold values for metal concentrations in organic soil improver

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	2	2	300	1	50	120	800

The threshold values for pathogens are similar to those defined for fertilisers. An organic soil improver shall contain 20% or more dry matter and 7.5% or more of organic carbon.

For inorganic soil improvers, the threshold values for contaminants are similar to those defined for organic soil improvers, except for Cd (1.5 mg kg⁻¹ DW) and Ni (100 mg kg⁻¹ DW).

3.2.2.4 Growing medium

A growing medium shall be a product other than soil *in situ*, the function of which is for plants or mushrooms to grown in. Threshold values for metal concentrations are the following (**Table 16**):

Table 16: Threshold values for metal concentrations in growing medium

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	1.5	2	200	1	50	120	500

The threshold values for pathogens are similar to those defined for fertilisers and soil improvers.

3.2.2.5 Inhibitor

An inhibitor shall be a product the function of which is to improve the nutrient release patterns of a product providing plants with nutrients by delaying or stopping the activity of specific groups of microorganisms or enzymes. Nitrification, denitrification and urease inhibitors can be used.

3.2.2.6 Plant biostimulant

A plant biostimulant shall be a product the function of which is to stimulate plant nutrition processes independently of the product's nutrient content with the aim of improving one or more of the following characteristics of the plant or the plant rhizosphere:

- Nutrient use efficiency;
- Tolerance to abiotic stress;
- Quality traits;
- Availability of confined nutrients in the soil or rhizosphere.

Contaminants in a plant biostimulant must not exceed the following limit values (**Table 17**):

Table 17: Threshold values for metal concentrations in plant biostimulant

Metal	As (inorganic)	Cd	Cr (VI)	Cu	Hg	Ni	Pb	Zn
Threshold (mg kg ⁻¹ DW)	40	1.5	2	600	1	50	120	1500

Plant biostimulant can be considered as microbial or non-microbial. A microbial plant biostimulant consist of a microorganism or a consortium of microorganisms. Pathogens must not exceed the following limits:

- *Salmonella* ssp: absence in 25g or 25mL
- *Escherichia coli*: absence in 1g or 1mL
- *Listeria monocytogenes*: absence in 25g or 25mL
- *Vibrio* ssp: absence in 25g or 25mL
- *Shigella* ssp: absence in 25g or 25mL
- *Staphylococcus aureus*: absence in 25g or 25mL

- *Enterococcaceae*: 10 CFU g⁻¹
- Anaerobic plate count unless the microbial plant biostimulant is an aerobic bacterium: 10⁵ CFU g⁻¹ or mL⁻¹
- Yeast and mould count unless the microbial plant biostimulant is a fungus: 1000 CFU g⁻¹ or mL⁻¹

For non-microbial plant biostimulants, none *Salmonella* spp must be found and for *Escherichia coli* or *Enterococcaceae*, the number must not exceed 1000 in 1 g or mL.

3.2.2.7 Fertilising product blend

A fertilising product blend as a fertilising product composed of two or more fertilising product previously described.

3.2.3 Amendments to modify metal availability

The use of amendments to improve soil structure and fertility modifies soil physicochemical characteristics. However, several chemical soil characteristics greatly impact metal availability such as pH, CEC, organic matter content or clay content.

In general, the metal retention capacity in soils increases with increasing pH till slight alkaline conditions (pH=8). Exceptions are As, Mo, Se, V, and Cr, which are commonly more mobile under alkaline conditions. The pH can be viewed as the most important factor affecting metal availability because soil pH will impact several soil parameters also influencing metal availability. Indeed, soil pH can affect the surface charge of layer silicate clays, organic matter, and oxides of Fe and Al. pH will also influences the precipitation-dissolution reactions, redox reactions, mobility and leaching, dispersion of colloids, and the bioavailability of the metal ions. As for pH, the higher the CEC of a soil, the greater the amount of metals a soil can retain without potential hazards. The soil CEC is largely dependent on the amount and type of clay, organic matter, and the oxides of Fe, Al, and Mn. For example, the higher the clay content, the higher the CEC (Adriano, 2001). The effects of soil characteristics on the mobility and bioavailability of metals are summarized in **Table 18**.

Table 18 Effects of soil factors on trace metal mobility/bioavailability (Adriano, 2001)

Soil factor	Causal process	Effect on mobility/bioavailability
Low pH	Decreasing sorption of cations onto oxides of Fe and Mn	Increase
	Increasing sorption of anions onto oxides of Fe and Mn	Decrease
High pH	Increasing precipitations of cations as carbonates and hydroxides	Decrease
	Increasing sorption of cations onto oxides of Fe and Mn	Decrease
	Increasing complexation of certain cations by dissolved ligands	Increase
	Increasing sorption of cations onto (solid) humus material	Decrease

High clay content	Increasing ion exchange for trace cations (at all pH)	Decrease
High OM (solid)	Increasing sorption of cations onto humus material	Decrease
High (soluble) humus content	Increasing complexation for most trace cations	Decrease/increase?
Competing ions	Increasing competition for sorption sites	Increase
Dissolved inorganic ligands	Increasing trace metal solubility	Increase
Dissolved organic ligands	Increasing trace metal solubility	Increase
Fe and Mn oxides	Increasing sorption of trace cations with increasing pH	Decrease
	Increasing sorption of trace anions with decreasing pH	Decrease
Low redox potential	Decreasing solubility at low redox potential as metal sulphides	Decrease
	Decreasing solution complexation with lower redox potential	Decrease

Thus, amendment inputs to modify soil fertility will directly impact metal availability.

In addition, metallic elements will also interact with amendments and some fixation processes on amendments can occur such as cation exchange, adsorption, surface complexation and precipitation, decreasing metal availability. For many years, organic and inorganic amendments are studied for their ability to decrease metal availability (**Figure 3**).

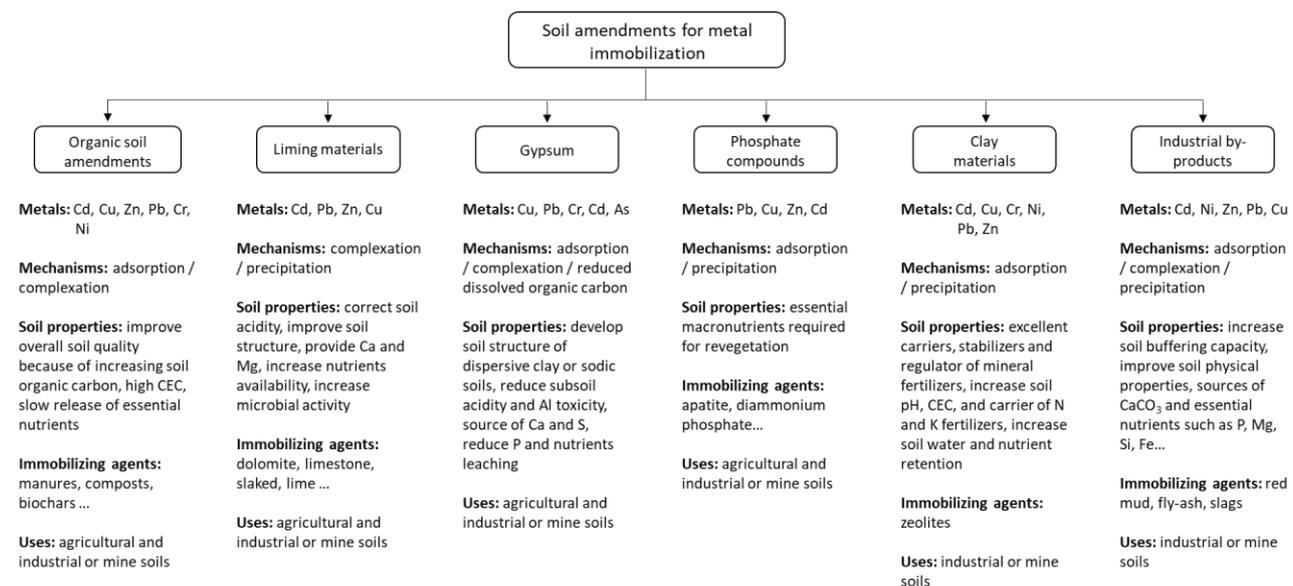


Figure 3 Common classes of metal immobilizing agents and their associated mechanisms and effects on soil quality (Lwin et al. 2018)

However, amendments also exist to increase metal availability. There are three main categories of amendments: i) inorganic amendments, ii) organic acids and amino acids, and iii) complexing agents, in particular aminopolycarboxylic acids (APCAs) (Meers *et al.* 2008).

Among the inorganic amendments, chloride is widely studied. It forms soluble chlorocomplexes that contributes to increase the availability of metals (Cd, Hg, Zn, Pb). Elemental sulphur is also studied for its ability to increase metal availability by decreasing soil pH when it is oxidised by soil microorganisms. Hydrogen peroxides has also been tested. They destroy organic compounds in soils, allowing for increased metal availability (Cu, Zn).

Organic acids and amino acids occur naturally in the soil. A wide variety of organic acid molecules, such as oxalic acid and citric acid, are excreted by plant roots. They function as chelating agents capable of solubilising metals.

APCAs are synthetic chelating agents that have the ability to form stable, soluble complexes with di- and trivalent cations. EDTA is most widely used and has been tested extensively for application in phytoextraction.

3.3 SOIL CONSTRUCTION

The soil reconstitution is an environmental technology which aims to ensure the rehabilitation of degraded soil by restoring its agronomic properties to allow revegetation and recolonization of soil fauna. The most basic approach consists in introducing vegetable soil brought from elsewhere and used as a covering (Bradshaw 2000). This allows immediate restoration but this technic is very expensive and can only be carried out when the soil is available. Moreover, the use of a non-renewable material poses a challenge from an environmental aspect.

A novel approach consists in using industrial by-products and processed land, instead of vegetable soils, to build a low-cost fertile soil. This technic is called "soil construction". It is based on the creation of a new soil ensuring high functionality (e.g. vegetation support, nutrient and water cycles). This process is based on the use of organic and mineral by-products (e.g. compost, urban and industrial sludges, ashes, decontaminated soils, demolition wastes). The aim is to mix products in order to construct functional soils. Materials are combined in different soil layers depending on the objectives of rehabilitation:

- Ecological restoration of the site;
- Landscape integration which may include in a most important redevelopment project;
- Non-food biomass production to improve the local land economic value;
- Water containment to prevent the pollutant transfer initially present on the sites.

The effects of by-products on soil properties are similar to those observed with classic amendments but they are also available at low costs (Séré 2007, Deeb 2020). **Figure 4** synthesises the process of soil construction.

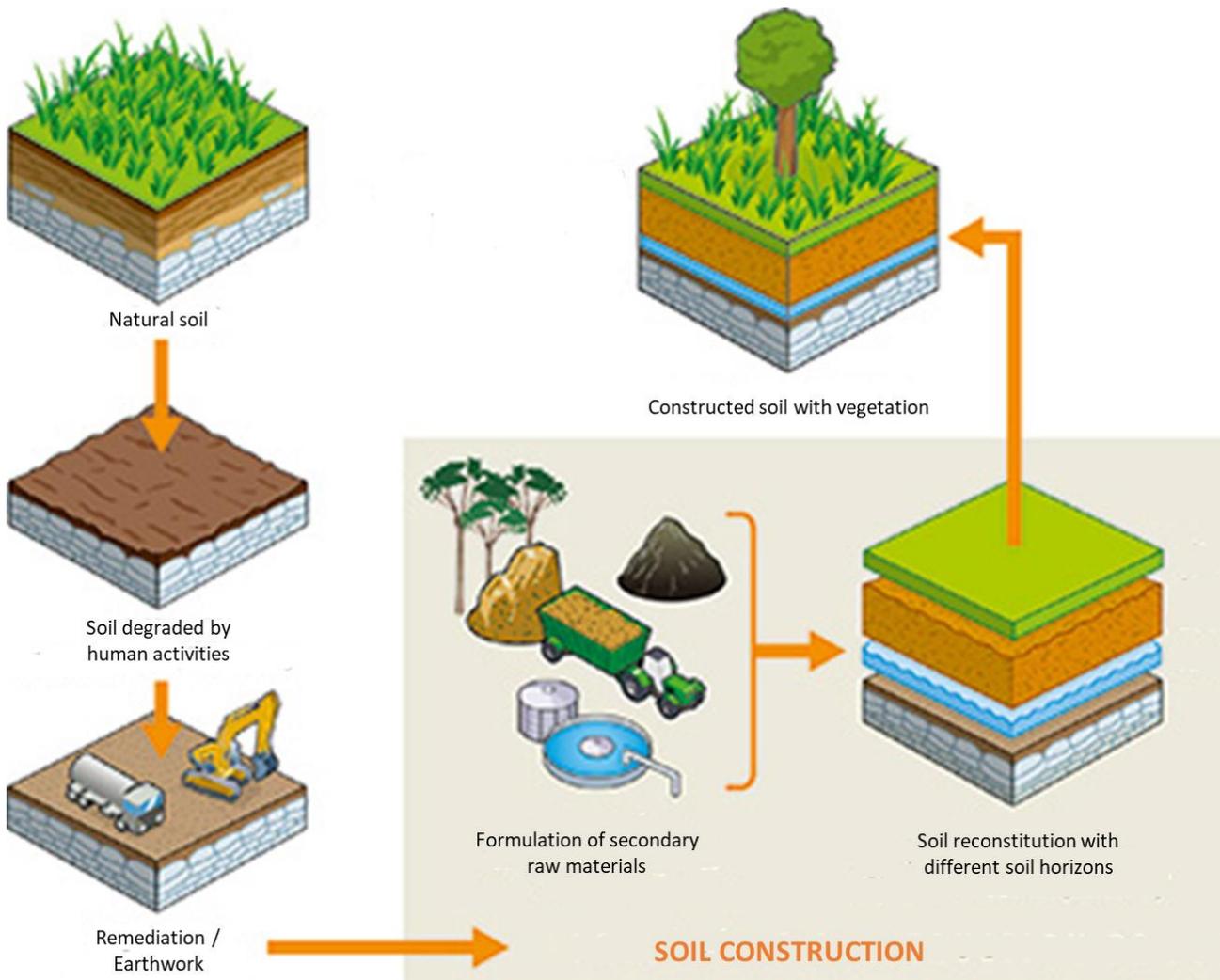


Figure 4 Soil construction process (adapted from BRGM 2017)

For several years, a high number of projects have been developed to evaluate the efficiency of soil rehabilitation by using wastes and by-products. Two examples are listed below:

- the LORVER project aimed at developing biomass production for industrial purposes by reusing degraded sites (e.g. brownfield soils) and abandoned materials (e.g. urban or industrial by-products). The project consisted of i) construct Technosols from by-products to reach the agronomic properties required for cultivation, ii) implement cultivations, iii) develop processes to produce energy, biochar, fibres, and metal-based compounds, and iv) assess the environmental and economic impacts of the chain. In this project, several wastes and by-products have been tested such as, excavated soil from decontamination or construction projects, dredging sediments, paper mill sludge or green wastes (Simonnot *et al.* 2016).
- the SITERRE project was dedicated to the construction of soils with urban wastes for city greening. The objectives were to: i) express the expected properties of soils that could fulfil optimally the main green area land-uses in terms of fertility, bearing capacity and environmental impacts, ii) define relevant indicators of the soil fertility and the expected quality for constructed soils, iii) propose constructed soil design profiles linked with land-uses, iv) identify and report the wastes that may be suitable for soil construction, v) evaluate soil agronomic properties evolution under *in situ* conditions, and vi) check the safety of the mixtures for the environment and the health of the inhabitants. For the project, 11 wastes

were selected: ballasts, bricks, demolition concrete, excavated soils (acidic and alkaline), demolition wastes, sludge compost, green waste, paper mill sludge, sewage sludge, and street-cleaning residues.

4 ECOCATALYST PRODUCTION

4.1 PHYTOTECHNOLOGY

The use of plants on contaminated soils is studied for several years and is called “phytotechnology”. Phytotechnologies are described as cost-effective, energetically inexpensive, environmentally sound, and is generally very well received by public opinion.

The goals of this technic are to decrease the concentration of bioavailable contaminants (e.g. phytoextraction), eliminate or degrade contaminants (e.g. rhizo/phytodegradation), protect water resources (e.g. rhizofiltration), stabilize or immobilize contaminants (e.g. phytostabilization) (Vangrosveld *et al.* 2009; Mench *et al.* 2010; Cundy *et al.* 2015; Kidd *et al.* 2015). The phytoremediation strategy employed depends on the type of contaminant present in the soil (**Figure 5**).

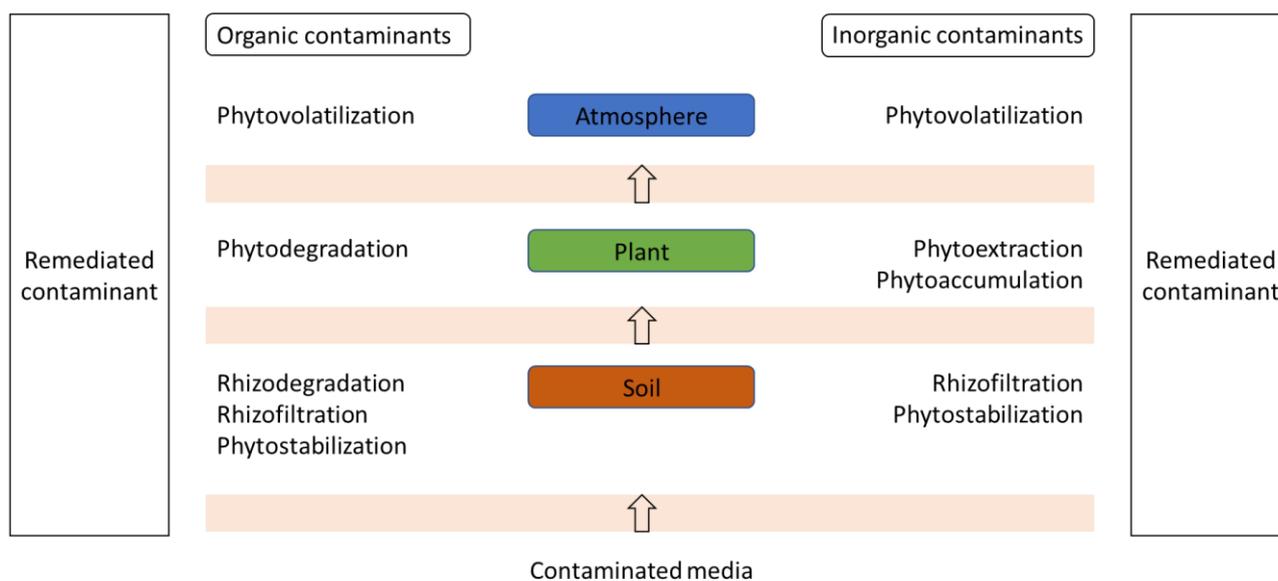


Figure 5 Uptake mechanisms of phytoremediation technology (Mahar *et al.* 2016)

Phytostabilization and phytoextraction are two forms of phytoremediation techniques used in the restoration of soils contaminated by inorganic contaminants. Phytostabilization aims to establish vegetation cover to limit and/or avoid the dispersion of pollutants through wind erosion. Moreover, phytostabilization decreases the leaching of pollutants through the soil and increases the content of organic matter in the soil which enhances aggregation of soil particles and binding inorganic pollutants. On the contrary, phytoextraction involves the uptake of metals from the soil and their translocation to harvestable plant parts. These plants are able to growth on contaminated soils and have the capacity to extract some pollutants from the soil. Plants used for phytoextraction requires some characteristics: i) high growth rate, ii) widely distribution, iii) enhance the accumulation of the pollutant, iv) tolerate the toxic effect of the pollutant, and v) easily cultivated and harvested. However, when plants have been harvested, they become a new waste that need to be treated.

Several outlets exist to reuse these plants such as: methanization, gasification, pyrolysis or composting for example (Bert 2012). Moreover, the concept of agromining also emerged. Agromining involves cultivation of selected hyperaccumulator plant species on low-grade ore bodies or mineralized soils, or anthropogenic metal-rich materials (e.g. contaminated soils, mine spoils, industrial sludge), prior to harvesting and incineration of the biomass to recover target metals or salts (van der Ent *et al.* 2015). Based on this technic, the potential of accumulator plants for ecocatalysis has been studied.

4.2 ECOCATALYSTS

A catalyst is considered as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. Lewis acids are the most famous catalysts used in organic synthesis. The first list of Lewis acids stable in water, established in 1998, was mainly composed of chlorate and triflate metal salts: Sc^{3+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Y^{3+} , Cd^{2+} , Ln^{3+} , Pb^{2+} , La^{3+} , Ce^{3+} , Pr^{3+} , Cd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Yb^{3+} , and Lu^{3+} (Kobayashi *et al.* 1998).

In ecocatalysis, the harvested accumulator plants, rich in pollutants, are considered as a bio-ore. To summarize, metallic elements in plants are recovered and transformed into eco-friendly plant-based catalysts called ecocatalysts. The process of ecocatalysis has been developed by Grison *et al.* which developed a series of novel approaches for the recycling and reuse of vital minerals for industrial chemistry, linked with the remediation, rehabilitation, or fully-fledged ecological restoration of contaminated soils on mining sites (Grison 2015; Losfeld *et al.* 2015a, b, c). The first results obtained by Grison *et al.* showed that ecocatalysts are more efficient and selective than traditional homogeneous and heterogeneous catalysts (Deyris & Grison 2018). Ecocatalysis process has two advantages: soil remediation by using hyperaccumulating plants and the reuse of metals extracted by the plants. Numerous accumulating plants have already been studied for their use in ecocatalysis (**Table 19**).

After being harvested, aerial parts of plants are dried and calcinated at high temperature (between 500 and 600°C) to convert biomass into ashes. Ashes are then treated with concentrated HCl under heating, depending on the hyperaccumulating plants. Then, the solution is concentrated and filtered. The solid residue obtained is an ecocatalyst (**Figure 6**). The conception of ecocatalysts is considered as interesting when the concentrations of metals that can be transformed into Lewis acids (LA), such as Zn, Cu, Fe, Mn, and Al, in plants are higher than 1000 mg kg⁻¹ DW (Oustrière *et al.* 2017; Hechelski *et al.* 2019). Moreover, the ratio between Lewis acids and carcinogenic, mutagenic, and reprotoxic (CMR) metals (such as Cd and Pb) is also important in order to produce ecocatalysts with respect to the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation (Hechelski *et al.* 2019).

Table 19: Reactions associated with metallophyte species and the metals involved (Hechelski et al. 2018)

Reactions	Plants	Metals
Diels-Alder reaction	<i>Noccaea caerulescens</i> , <i>Anthyllis vulneraria</i>	Zn
Friedel-Crafts alkylation and acylation	<i>N. caerulescens</i> , <i>A. vulneraria</i> , <i>Psychotria douarrei</i> , <i>Gessois pruinosa</i>	Zn, Ni
Halogenation of aromatics	<i>N. caerulescens</i> , <i>A. vulneraria carpatica</i>	Zn
Chlorination of alcohols	<i>Thlaspi caerulescens</i>	Zn
Selective protection/deprotection procedures	<i>N. caerulescens</i> , <i>Iberis intermedia</i> , <i>Grevillea exul</i> ssp. <i>exul</i> , <i>Psychotria major</i>	Zn, Tl, Mn, Ca
Ullmann reaction	<i>Anisopappus chinensis</i> , <i>Bacopa monnieri</i> , <i>Lolium multiflorum</i> , <i>Eichhornia crassipes</i>	Cu
Suzuki-Miyaura and Heck-Mizoroki reactions	<i>Brassica juncea</i> , <i>L. multiflorum</i>	Pd
2H-chromenes synthesis	<i>N. caerulescens</i> , <i>G. exul</i> ssp. <i>rubiginosa</i>	Zn
Green oxidations	<i>G. exul</i> ssp. <i>exul</i> , <i>G. exul</i> ssp. <i>rubiginosa</i>	Mn
Hydroacyloxy addition reaction	<i>N. caerulescens</i> , <i>A. vulneraria</i>	Zn, Ni
Biginelli reaction	<i>G. exul</i> , <i>P. douarrei</i> , <i>G. pruinosa</i>	Mn
Click reaction	<i>E. crassipes</i>	Cu
Garcia Gonzalez reaction	<i>N. caerulescens</i> , <i>A. vulneraria</i>	Zn, Fe, Al
Epoxidation	<i>G. exul</i> ssp. <i>rubiginosa</i>	Mn
Reductive amination of ketones	<i>G. exul</i> ssp. <i>rubiginosa</i>	Mn
Synthesis of complex biomolecules, such as 5'-capped DNA and RNA	<i>N. caerulescens</i> , <i>A. vulneraria</i>	Zn, Ni

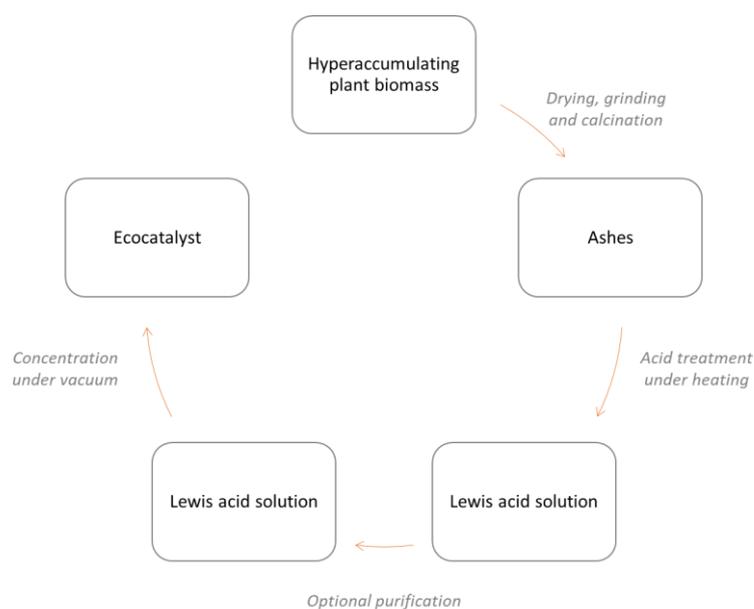


Figure 6 Schematic outline of the process for the preparation of ecocatalysts (Hechelski et al. 2018)

5 CONCLUSIONS

The objective of the benchmark report was to summarize the different techniques to improve soil characteristics of PMSD and how to valorise these sites through ecocatalyst production.

Firstly, this report highlighted the particular characteristics of PMSD. Indeed, it has been demonstrated that PMSD are often considered as degraded sites with some constraints concerning the topography, the chemical parameters but also the biological parameters. Moreover, PMSD are also often contaminated, especially by metals. Before rehabilitating these sites, it is therefore necessary to characterize the soil in terms of soil texture, chemical parameters and contaminants. The bibliography revealed that six chemical parameters are fundamental to estimate the soil fertility which are: i) pH, ii) cation exchange capacity, iii) carbonates, iv) electrical conductivity, v) C_{org}/N_{total} ratio, and vi) available phosphorus.

Different techniques exist to rehabilitate degraded soils. Among them, the use of amendments in soils to modify soil characteristics can be used. Amendments can improve soil texture and soil fertility but can also modify metal availability. Moreover, a novel approach consists in using industrial by-products and processed land to build a low-cost fertile soil; this technic is called "soil construction". The aim is to mix products in order to construct functional soils. All these modifications allow soil revegetation which will improve soil characteristics, enhance aesthetic and landscaping aspects, and augment ecological characteristics.

However, plants cultivated on PMSD can potentially accumulate contaminants, and then, become a new waste that need to be treated when they are harvested. On this basis, the concept of ecocatalysis emerged. In ecocatalysis, harvested plants are not considered as a waste but as a bio-ore. Indeed, the metallic elements present in plants are recovered and transformed into eco-friendly plant-based catalysts called ecocatalysts. Thus, this technic allows giving an economic function back to degraded sites.

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