# Restoration of polluted soils by plants (phytoremediation)

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*Human activities are largely responsible for soil and water pollution and more generally for global environmental damage. Each one of us has already been confronted with situations of very strong pollution or aggressions of nature, such as the impacts of biocides (herbicides, insecticides, fungicides...), hydrocarbons or metals and toxic inorganic elements (Cu, Ni, Cd, Pb, Cr, Hg, Sn, As, Tl...). Fortunately, in the long term, nature is capable of a certain resilience by adapting to* *certain types of pollution, in particular thanks to the activity of microorganisms and plants. This capacity of nature has long inspired mankind, especially for the treatment of their drinking water (> 3000 years). Today, nature is inspiring new approaches to integrated remediation of these polluted environments, particularly bio-inspired approaches. These approaches are part of a global ecology, which mobilizes different fields of scientific ecology (plant, microbial, molecular, evolutionary, functional, chemical...), biology, toxicology, physicochemistry and chemistry of the living. Among them, phytoremediation (a set of technologies using plants to extract, degrade or immobilize polluting compounds or elements) is one of the most promising approaches, even if it is rather intended for the resolution of environmental problems generated by trace metals, or TMEs.*

# 1. Why do we need to remediate soils?

Countless human activities are now affecting **biological dynamics and biogeochemical balances** (see The biosphere, a major geological player). Strong indicators, such as climate change, biodiversity erosion, soil, river and groundwater pollution, testify to the need to develop new strategies for preserving and even rehabilitating the biosphere and associated ecosystem services. Human activities and the waste generated, whether domestic, industrial or agricultural, contribute greatly to the extent of pollution and environmental damage.

## 1.1. Major soil pollutants

For example, **biocides** [1] are chemical compounds with toxicological properties, intended to control the spread of harmful insects or rodents, algae, invasive plants or phytopathogenic fungi. Their toxicity and ecotoxicity are of concern. Residues of phytosanitary products, pharmaceutical principles, solvents, plastic residues, cosmetics... and their degradation products constitute **problematic emerging pollutants**. Their misuse leads to their dispersion in the air, their absorption by plants or their penetration into soils where they are then carried to aquatic environments by rainwater, contaminating rivers, groundwater and coastal areas (Read Why and how to treat urban wastewater? & Pesticides: what the past teaches us).

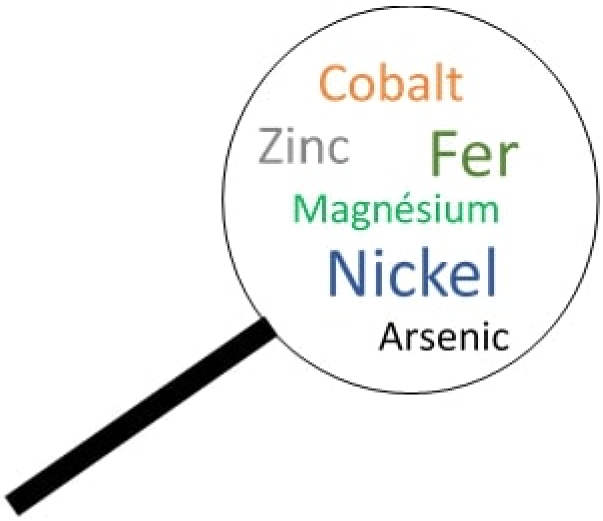


*Figure 1. Trace metals: compounds with various structures and functions. [Source: © C. Grison]*

In addition to organic pollutants, certain **intensive mining and metallurgical industrial activities** are the source of equally formidable pollution of soils and aquatic systems, that due to **trace metals**. This is a very serious problem, as soil performs essential functions that largely determine food production and water quality. Moreover, trace metals are among the **most problematic** pollutants: they are **not biodegradable** and therefore persist in contaminated organisms and ecosystems. Although most of these metallic elements are very useful to the organism (Zn, Fe, Mg, Cu, Ni, Co, Mo, Mn and B, Figure 1) as cofactors of enzymes, biocatalysts or constituents of molecules essential to life (Mg-chlorophyll, Fe-hemoglobin...), they become toxic from a certain level of concentration. Others are not essential elements for plants but are toxic even in very small quantities (Cd, Pb, Hg, Sn, As, Tl), although some organisms have developed resistance over time.

## 1.2. Significant toxicity and indirect effects

From a general point of view, their toxicity is due to their **structural similarity** with the essential elements, allowing them to substitute them in a **competitive** way, in particular in biological macromolecules such as enzymes contained in cells. Thus, for example:

**Lead** is able to displace calcium in bone tissue. It is then stored in an insidious and discrete way, then released massively during a fracture, a trauma or a stress.

In the case of **copper salts**, pollution is caused by frequent use (distribution pipes, electrical cables, algicides, antifungals, ...) and persistence of metal species. Harmful for mammals, they are also very toxic for marine organisms [2].

Metallic pollution therefore presents **real health risks**: damage to the nervous, renal, pulmonary systems or bone tissue is clearly established (Read Mercury, fish and gold miners). High levels of trace metals **reduce the biodiversity**, density and activity of flora and fauna, even on the smallest scale. **Soil fertility** is altered; animals are contaminated by contact, inhalation of metallic dust, ingestion of water and food... Metallic pollutants spread through the food chain.

*Figure 2: Montevecchio mine (Sardinia) Pollution of terrestrial and aquatic ecosystems by trace metal elements in the vicinity of mines or mining stockpiles. [Source: © C. Grison]*

The consequences are numerous:

Metal pollution leads to **phytotoxicity of** soil systems and, subsequently, to their increased erosion.

**Soil erosion** leads to migration of trace metals into soil-water systems and contamination of rivers (Figure 2);

These phenomena **reduce** soil **fertility** and lead to **contamination** of agricultural and food products.

## 1.3. Worrying consequences

The cumulative effects of climate change (droughts, intense but short rains, global warming) and the various forms of pollution mentioned above, combined with the over-consumption of water and food products, lead to fears of a **shortage of vital resources**. The deterioration of the quality of soils and arable land is a major concern (Figure 3). It is a major issue for world **food security**, which is subject to increasing constraints [2]:

A **demographic challenge**: the world population is expected to reach 9 billion inhabitants in 2050 with an increased urbanization of this population (2/3 of the world population in 2050 against half today);

**Climate change/global warming**: with consequences on extreme events and pressure on agricultural yields;

**Globalization of the world market** for agricultural and food products**,** coupled with a negative evolution of eating habits;

**Increased pressure on resources**, both in quantity and quality: decrease in the availability of drinking water accentuated by unequal distribution, depletion of mineral resources, decrease in the availability of arable land, changes in ecosystem services, conversion of land use, depletion of certain marine resources.

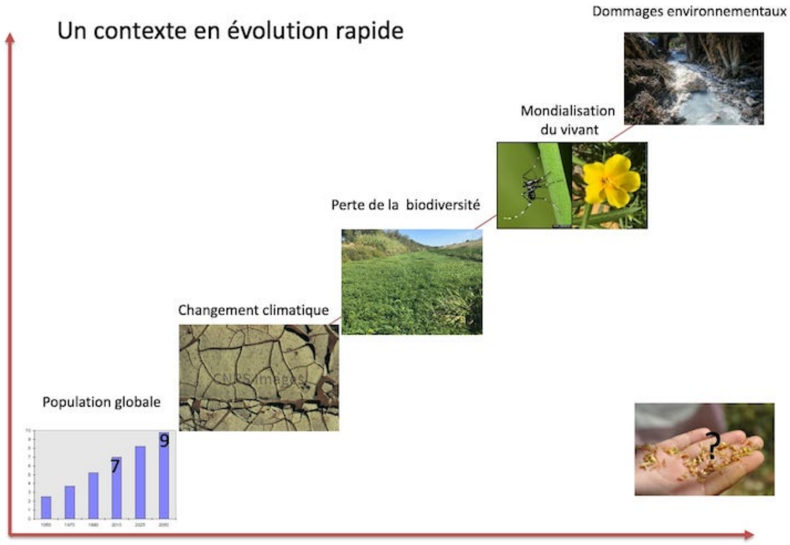


*Figure 3. Parameters contributing to current global changes. [Source: © C. Grison]*

Food and nutritional security has clearly become a European challenge. **Preserving soil quality has thus become a priority**. There is therefore a real need to develop inventive and efficient technologies for the restoration of polluted sites, areas and ecosystems.

# 2. Phytoremediation: a natural and sustainable solution

In 2002, Isenmann conceived **industrial ecology** as a discipline that took nature as a model [3]. Today, this concept has been transformed into concrete courses of action that do not involve a return to an initial situation. The lack of data on the detailed characterization of the biotic and abiotic interactions of a particular ecosystem prior to industrial pollution and the physico-chemical disturbances introduced by anthropic activities, exclude the return of a natural habitat to a pre-industrial situation. It is therefore not ecological restoration in the strict sense of its definition [4]. On the other hand, **the presence and the study of organisms adapted to an industrial pollution situation allow to define new integrated and bio-inspired remediation approaches**. They are part of a global ecology, which mobilizes different disciplinary fields of scientific ecology (plant, microbial, molecular, evolutionary, functional, chemical...), biology, toxicology, physicochemistry and chemistry of life.

Two scenarios are possible for degraded sites: **stabilization or active remediation**. These remediation techniques can be broadly divided into two main sectors: bioremediation and phytoremediation.

**Bioremediation** is based on **the already well known use of specific bacterial species adapted** to the decontamination of contaminated areas [5], in particular by organic or metallic pollutants or even recently radionuclides [6], [7].

**Phytoremediation** is rather intended for the **resolution of environmental problems generated** by metallic trace elements. Due to their phytotoxicity, metal-bearing soils exert a strong selection pressure and generate particular habitats for plant species and associated micro-organisms. This results in **a unique biological resource, the metallophytes** [8]. These metallophytes are defined as being able to tolerate TME concentrations, and thus survive and reproduce on such sites [9].

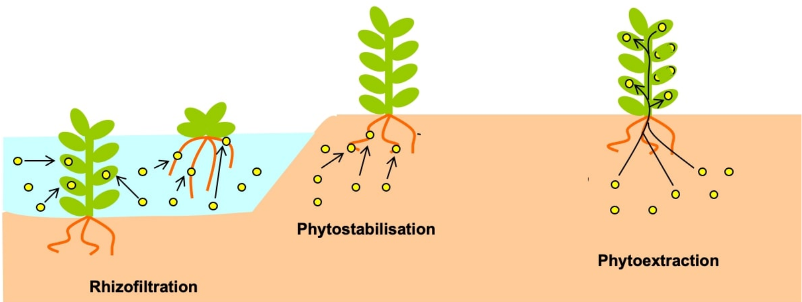


*Figure 4. Comparison of the main phytoremediation technologies [Source: © C. Grison]*

The most well-known phytoremediation processes are (Figure 4):

the ***phytoextraction*** ecocatalysis : pollutants are extracted by plants and stored in their tissues (leaves or roots);

the ***phytostabilisation*** pollution remediation : it consists in covering the soil with plant species capable of immobilizing the pollution;

the ***rhizofiltration*** phytoextraction: the process of phytoextraction is carried out in an aquatic environment at the level of the rhizosphere (part of the soil close to the plant roots). Phytoremediation is one of the few interesting solutions for the sustainable rehabilitation of soils degraded or contaminated by TMEs.

The most studied phytotechnologies are phytostabilization and phytoextraction [10], [11], [12], [13].

Various previous experiments have shown that **phytostabilization** can immobilize contaminants and contribute to the growth of vegetation in hostile areas. On the other hand, it favors the spontaneous appearance of plants that sometimes become capable of accumulating TMEs, with a risk for animals. Thus, the evolution over time of revegetated plots poses **the delicate problem of controlling risks over time**.

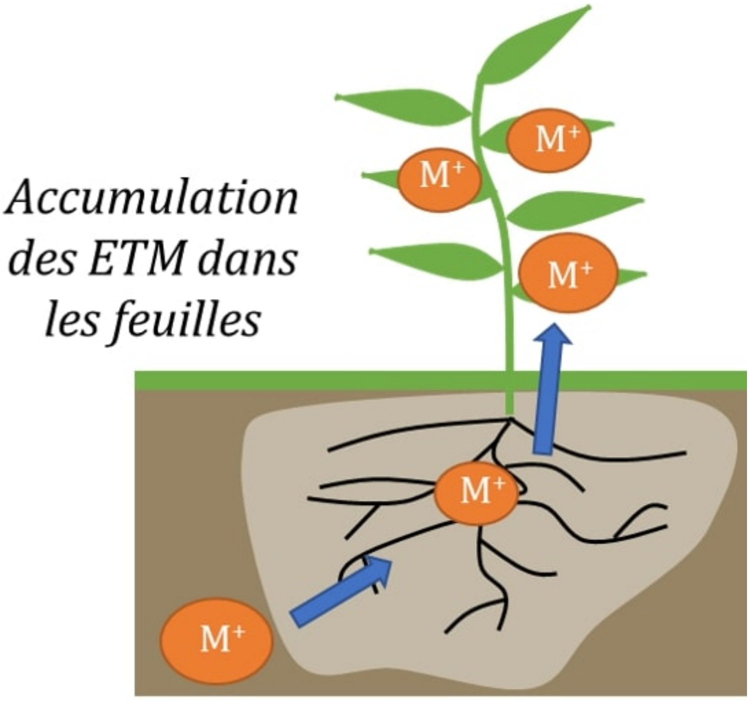


*Figure 5: Schematic representation of the principle of phytoextraction with the transfer of metals to the aerial parts of the plant. [Source: © C. Grison]*

**Phytoextraction** (Figure 5) is an eco-technology for partial soil and sediment remediation by accumulation of TMEs in the aerial parts of hyperaccumulative plants (e.g. *Alyssum murale, Grevillea exul rubiginosa or Geissois pruinosa*). Recent studies evaluating the adaptive performance of these plants have highlighted the presence of hyperaccumulative species, such as legumes, reinforcing the interest of phytoextraction in mine reclamation programs [14].

# 3. Some feedback from mine reclamation

In a **context of rapid depletion of the world'**s primary and strategic mineral **resources**, some of which have become critical, recycling techniques remain underdeveloped and the continued high demand for metallic elements suggests that current resources of critical metals will be depleted in the short term. These needs are leading mining operators to **extend their operations** and to use **new extraction techniques**, at the cost of **significant environmental impacts**: degradation of natural environments, loss of biodiversity, pollution of ecosystems, etc. [15],[16].

In order to restore (and therefore remediate) natural environments degraded or polluted by mining activities, the first research in mining reclamation consisted in developing **innovative phytoremediation programs on sites** and on a large scale in the main metal mining countries, and in particular in France (metropolitan France and overseas territories such as New Caledonia). The field work was most often carried out in **close collaboration with the mining operators** of the different countries.

**Table 1**. Advantages and disadvantages of phytoremediation approaches.

| Avantages | Limites |
|---|---|
| • Faibles coûts de traitement (10 à 100 fois inférieurs aux technologies classiques) | • Efficacité variable selon la nature du sol (comme la capacité de rétention en eau) et les conditions météorologiques |
| • Adaptation aux grandes superficies contaminées (dizaines d'hectares) | • Restriction aux surfaces colonisables par les racines et à la fraction « disponible » des sols |
| • Récupération des polluants | • Nécessité de grandes superficies et d'une pollution peu profonde (de 50 cm à 3 m ) |
| • Conversion possible de la biomasse en énergie | • Efficacité limitée par les attaques d'insectes ou des micro-organismes... |
| • Technologie visuellement attractive | • Nécessité de contaminations modérées pour la survie des plantes |
| • Faible perturbation du milieu contaminé | • Temps de traitement généralement très long (jusqu'à une cinquantaine d'années) |
| • Technologie verte ayant une bonne image auprès du public | • Performances liées aux objectifs de valorisation (économique ou écologique) |

## 3.1. Phytoextraction

Phytoextraction has often been favored as **one of the most promising phytotechnologies** capable of bringing a social and economic dimension to rehabilitation efforts. Phytoextraction is based on the use of plants capable of extracting metallic elements from soils and concentrating them in their aerial parts. We speak of hyperaccumulative species if they are capable of containing levels of 100 mg Kg-1 of Cd or As, 1000 mg kg-1 of Co, Cu, Cr, Pb or Ni, 10,000 mg kg-1 of Mn or Zn in dry matter.

This natural technology thus contributes to the slow and progressive decrease of TME content in contaminated soils. Above all, it allows the introduction of a **protective vegetation cover on the most polluted** or degraded **sites**, which is able to limit wind and/or water erosion of rehabilitated sites.

The two illustrative examples presented below were carried out in contexts where the environmental and economic expectations of the populations concerned are very different, but where the natural adaptation phenomena of certain plants and associated micro-organisms are common.

## 3.2. The case of the Avinières mine in the Gard, France

In the Gard French department, the Avinières mine site is a **high contamination site** (500 to 800 times more Zn, Cd and Pb than the European standards). Microbial and plant ecology efforts have established a first proof of concept for large-scale remediation using phytoextraction with the strong Zn hyperaccumulators present at the site, *Noccaea caerulescens and Anthyllis vulneraria* (Figure 6) [17], [18].

*Anthyllis vulneraria* is an amazing plant species. It is one of the few **legumes** able to grow on highly polluted land. *A. vulneraria has* been identified on the mining site of Avinières (Gard).

The phenotypic, genotypic and metabolic characterization of the new bacterial species*(Rhizobium metallidurans*) associated with the Zn-hyperaccumulating legume, *Anthyllis vulneraria*, has made it possible to understand the adaptation strategies of this unusual bacterium at the genetic level, but also at the physiological and molecular levels [19], [20], [21].

The degree of local pollution is theoretically incompatible with any form of life. However, *A. vulneraria* is **able to survive** in this toxic environment. More surprisingly, it **accumulates zinc to impressive and unprecedented concentrations**. It is one of the strongest zinc hyperaccumulators identified to date.

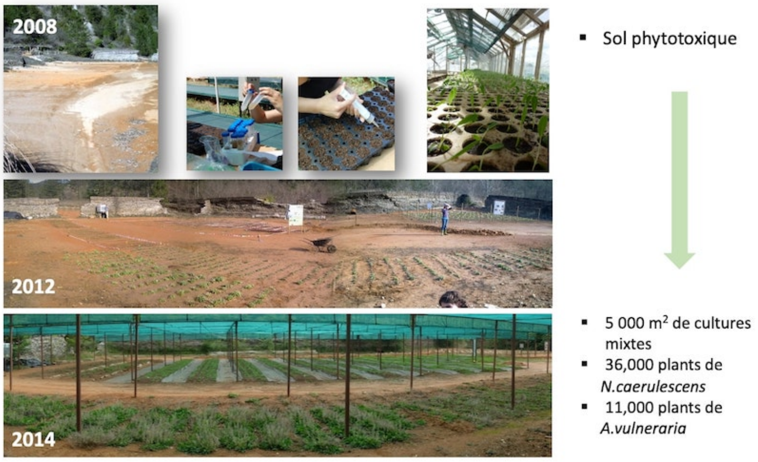


*Figure 6. First experiment in mine reclamation on a highly contaminated site: the Avinières site (Gard, France) [Source: © C. Grison]*

Thus, introducing legumes while stimulating the growth of associated bacteria on nutrient-poor land allows the soil to be enriched with natural fertilizers and promotes the establishment of a vegetation cover.

*Vulneraria* has become an opportunity for Zn extraction, thanks to its strong capacity to accumulate it, but also for its agronomic aptitudes, its abundant biomass, and its important root system capable of **increasing the nitrogenous organic matter of the** contaminated **soil** and thus its **fertility**, like any legume. It has allowed the development of a second zinc hyperaccumulator *(N. caerulescens)* on the mine site, which had been totally devitalized. Today, nature is slowly reclaiming its rights and other more common plant species have settled in, although it is estimated that it will take a few more decades to return to an initial ecological state.

## 3.3. The case of the New Caledonian open-pit mines

The success of this program has led to continued efforts to rehabilitate mining *in natura* in New Caledonia (Figure 3).

- New Caledonia, a **global biodiversity hotspot**, is home to 3,260 plant species with an endemism rate of approximately 74%. The floristic diversity of New Caledonia is closely linked to its geological history. This has led to very particular edaphic conditions (soil): a large part of the territory's soil is rich in phytotoxic elements: Ni, Co, Cr, Mn, Fe. These very particular geochemical conditions have generated the emergence of an original flora composed of plants that have adapted to **ultramafic*** soils (**glossary**: an ultramafic rock or ultrabasic rock is a magmatic and meta-magmatic rock rich in metals (iron, magnesium, etc.) and very poor in silica (less than 45% by mass), hence their basic character).

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*Figure 7. Pycnandra accuminata, one of the largest Ni hyperaccumulators. [Source: © C. Grison]*

Subjected to strong selection pressures, some species have become able to develop on soils rich in toxic metallic elements, but often poor in mineral elements essential for plant growth. Among them, we can find many endemic **metallophytes** that are (hyper) accumulators of Ni and Mn. After Cuba, New Caledonia is one of the richest regions in the world in nickel and manganese hyperaccumulating species. Hyper-nickelophores with impressive nickel contents can be found there. Thus, *Pycnandra accuminata,* the "nickel tree" (Figure 7), can contain up to 20% nickel in its latex.

This context is exceptional, and represents an example of remarkable adaptation of the plant world.

However, these **geochemical conditions** are also at the origin of **intense mining**, which threatens this same biodiversity. To date, more than 23,000 ha have been impacted by mining activities, leading to severe soil erosion, which pollutes the lagoon and threatens the coral reef. Since 2009, regulations have made **rehabilitation mandatory** (Figure 8), but only 371 ha have been revegetated because much scientific knowledge remains to be acquired, proof of the difficulty of implementing these new but complex approaches.

In this context, a **new approach** to mine reclamation has been developed [13].

*Figure 8. Six hectares of mine reclamation by phytoextraction in New Caledonia. Work carried out by the Laboratory of Bio-inspired Chemistry and Ecological Innovations (ChimEco) in collaboration with Société Le Nickel (SLN), Koniambo Nickel (KNS) and the Institut Agronomique Calédonien (IAC). They have led to the joint development of a revegetation program for barren slopes, using Ni and Mn hyperaccumulative plants. [Source: © C. Grison]*

The approach is based on the richness of New Caledonian biodiversity [22] and the existence of Ni and Mn (hyper) accumulator plants, capable of adapting to the multiple local constraints: open environment, tropical climate, edaphic and hydric constraints, high altitude, good germination capacity, degraded soils depleted in nutrients and micro-organisms, but rich in toxic elements.

The success of this work combines **large-scale field experiments** (>6 ha) and **fundamental research** [11], [23]. Indeed, it is still necessary to progress in the knowledge of the adaptive capacities of metallophytic plants on degraded mining sites. The objectives of remediation of degraded sites and/or sites contaminated by mining activities must clearly be deployed in the long term. The state of the sites, the reasoned and sustainable planning of the operations, the growth of the plants on bruised soils, the respect of the local biodiversity, the follow-up of the transplants, the speed of accumulation testify to this. In such a context, it is obvious that an **economic valuation of the remediation is essential** to support such efforts in the long term. This is "a guarantee of sustainability " and therefore of success. A database exists, listing the metal-hyperaccumulative species associations known to date [24], some examples of which are given in the following Table 2.

**Table 2.** Some examples of pollutant associations with hyperaccumulative plants (as of September 2017) for phytoextraction with global records of the highest concentrations reported to date.

| Elément | Seuil ($\mu g.g^{-1}$) | Familles | Genres | Espèces | Principales plantes identifiées |
|---|---|---|---|---|---|
| Arsenic, As | > 1 000 | 1 | 2 | 5 | *Pteris vittata* (2,3%) |
| Cadmium, Cd | > 100 | 6 | 7 | 7 | *Arabidopsis halleri* (0,36%) |
| Cuivre, Cu | > 300 | 20 | 43 | 53 | *Aeolanthus biformifolius* (1,4%) |
| Cobalt, Co | > 300 | 18 | 34 | 42 | *Haumaniastrum robertii* (1%) |
| Manganèse, Mn | > 10 000 | 16 | 24 | 42 | *Virotia neurophylla* (5,5%) |
| Nickel, Ni | > 1 000 | 52 | 130 | 532 | *Berkheya coddii* (7,6%) |
| Plomb, Pb | > 1 000 | 6 | 8 | 8 | *Noccaea rotondifolia cepaeifolia* (0,8%) |
| Terres rares (Lanthane, La ; Cérium, Ce) | > 1 000 | 2 | 2 | 2 | *Dicranopteris linearis* (0,7%) |
| Sélénium, Se | > 100 | 7 | 15 | 41 | *Astragalus bisulcatus* (1,5%) |
| Thallium, Tl | > 100 | 1 | 2 | 2 | *Biscutella laevigata* (1,9%) |
| Zinc, Zn | > 3 000 | 9 | 12 | 20 | *Noccaea caerulescens* (5,4%) |

# 4. A necessary valorization of phytoextraction

The development of phytoextraction remains **limited mainly by the absence of valorization of the contaminated biomass**. Without a credible outlet, the aerial parts of hyperaccumulative plants are considered as contaminated waste. Moreover, the phenomenon of extraction of metallic trace elements by the root system increases the fraction of soluble elements. **The development of phytoextraction is entirely linked to the valorization of the generated biomass.**

The two most significant strategies for **recycling plants that are hyper-accumulators of** trace metals are based on two classical and independent channels:

the sector inspired by the **treatment of biomass**: Bioenergy, and more particularly the wood-energy sector [25], [26];

the process inspired by **ore processing**: hydrometallurgy adapted to metals of plant origin or phytoextraction (phytomining [27], [28], [29], [30], [31]).

In the case of the wood-energy sector, two immediate problems still unresolved concern the fate of combustion residues (and their possible toxicity), as well as the volatility of metallic species during combustion [16],[17]. Many questions therefore remain unanswered.


*Figure 9. Representation of the valorization of phytotechnologies for depollution with, from left to right, phytoextraction and rhizofiltration which generate a biomass loaded with metallic trace elements. [Source: © C. Grison]*

A **novel recovery of phytoextraction**, rhizofiltration and other pollution control technologies has been developed over the last 10 years, and is called **ecocatalysis** [10],[11]. The plant waste generated is recovered through an innovative concept of ecological recycling. Taking advantage of the remarkable adaptive capacity of some plants to bioconcentrate metals, ecocatalysis is based on the novel use of metallic species of plant origin as reagents and catalysts of fine organic chemical reactions (see Focus on New ecocatalysts). It allows the preparation of biomolecules using an eco-responsible and bio-inspired approach (Figure 9).

Ecocatalysis has created a paradigm shift: transition **metal-rich biomass** is no longer a contaminated waste product, but a **natural remediation system** with **high added value**. This biomass is therefore a natural reservoir of valuable transition metals in organic synthesis. In other words, waste has become a useful, innovative and valuable chemical object.

# 5. Messages to remember

It is possible to develop **phytoextraction** as a technique for **mining rehabilitation** of degraded/contaminated soils by relying on local plant species adapted to the context of **high contamination** and degradation of the areas to be rehabilitated.

Phytoextraction of contaminants is a new and promising approach; it allows to combine the introduction of **pioneer and sustainable species** compatible with the objectives of reclamation.

The restoration of mining sites impacted by metallic pollution and the chemical valorisation of phytotechnologies developed by ecocatalysis make it possible to **reconcile ecology, technology and economy**.

Economic activities are not translated into environmental costs, but into **benefits**, allowing to support the remediation efforts of polluted sites.

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## Notes and references

**Cover image.** New Caledonia, a major mining area, is a pioneer in phytoremediation [Source : © C. Grison]

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