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THE UPTAKE OF HEAVY METALS IN PLANT SPECIES INDIGENOUS TO A POLLUTED STREAM NEAR AN INDUSTRIALIZED REGION OF PORTUGAL

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PHYTOREMEDIATION

is an emergent technology that uses plants (and rhizosphere microorganisms) to remove, degrade or immobilize chemical contaminants from polluted soils, sediments and water.

Phytoremediation – Pros and Cons

Advantages

- ☑ Performed *in situ*
- ☑ Use of solar energy
- ☑ Cost reduction
- ☑ Non destructive
- ☑ Acceptance from the public and regulatory agencies
- ☑ No disturbance to the landscape

SUSTAINABLE TECHNOLOGY

Disadvantages

- ☒ High concentrations of the contaminant may become toxic to the plants
- ☒ Not applicable to contamination at deep levels
- ☒ Contamination risk of the food chain through animal consumption
- ☒ Takes a long period of time
- ☒ Final destination of the plant material (?)

Factors to take in account
- Plant -

- Rapid growth
- High biomass rate
- Capacity to tolerate and accumulate the contaminant
- Adequate root length
- Adequate to the contaminated matrix
- Adequate to the nature of the contamination

Factors to take in account - Contamination -

– Bioavailability of the contaminant (can be enhanced using chelating and amendment agents, with natural leachability concerns)

– Existence of multiple contamination

– Three-dimensional distribution of the contaminant

Why are heavy metals a special environmental problem ?

- Metals occur naturally in the environment: plants and animals depend on some metals as micronutrients.
- Certain forms of some metals can be toxic, at levels that are only moderately above background levels
- Toxic metals contamination is long term persistent in the environmental compartments
- Metals can not be destroyed, so they have to be removed and recycled, which becomes very costly and can only affect the upper layers of the soil.

Environmental and human health risk

PHYTOREMEDIATION TECHNIQUES APPLICABLE TO HEAVY METALS

PHYTOSTABILIZATION

- Uses plants to IMOBILIZE contaminants
- The metals are absorbed by roots and accumulated or precipitated within the rhizosphere in stable forms (less mobile)
- Applicable for water, soil and mine spoils
- Reduces risk of including metals in the food chain

PHYTOEXTRACTION

- Uses plants to REMEDIATE contaminated sites
- Applicable for soil and mine spoils
- The metals are captured by the roots and translocated to the aboveground parts of the plants

RHYZOFILTRATION

- Uses plants to REMEDIATE contaminated sites
- The metals are captured by the roots
- Applicable for superficial and groundwater treatment
- The process may be aided by the rhizosphere microorganisms

Metals Phytoremediation
- Costs analysis -

Soil contamination	Phytoremediation	Other technologies
Metals	\$ 88/m^3	\$ 275/m^3
Pb (5 ha)	\$ 500 000	\$ 12 000 000
1 ha, 15 cm prof. with several contaminants	\$ 2 500 - \$ 15 000	--

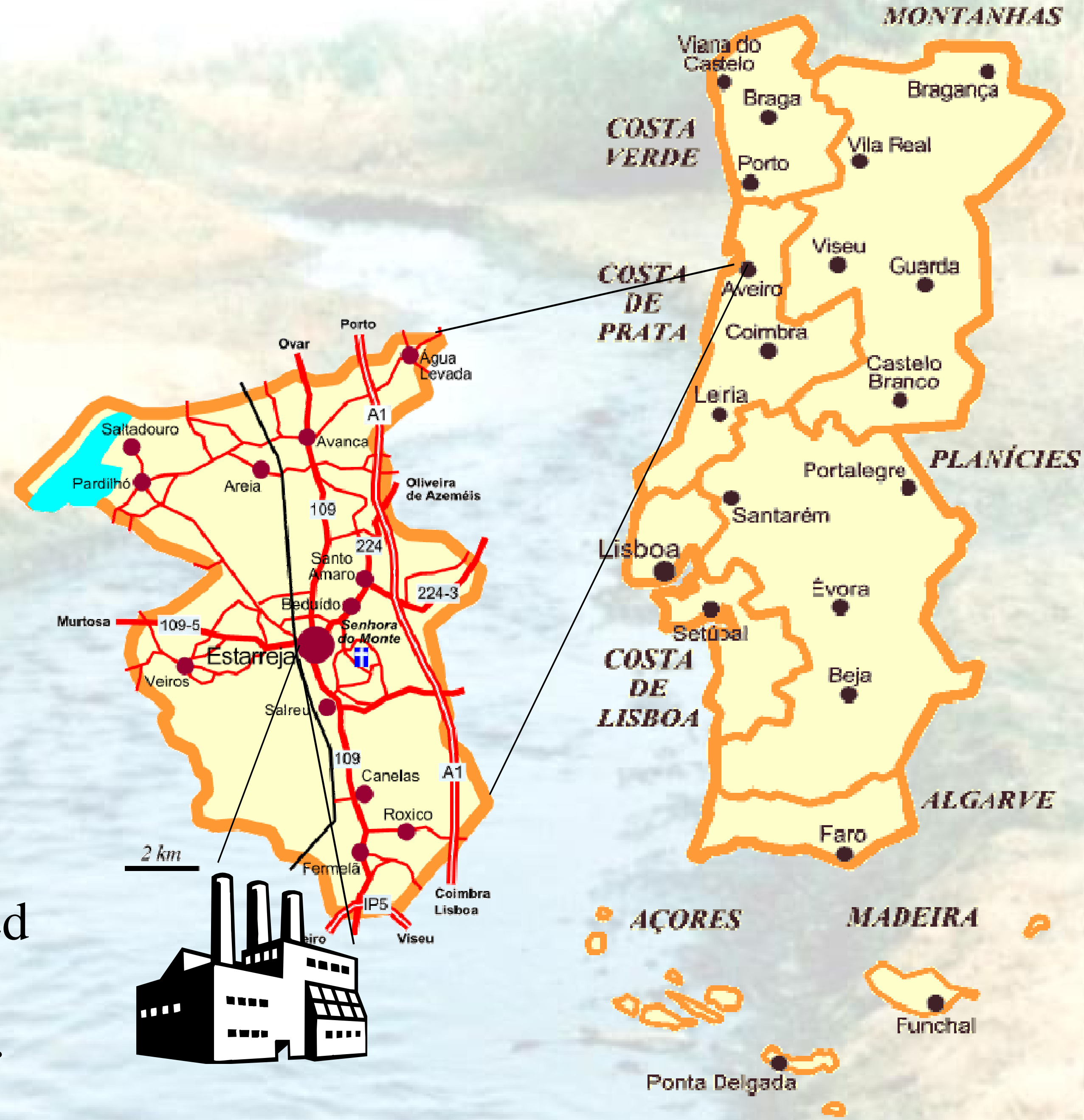
Source: US EPA, 1998

Problematic polluted sites in Portugal:

The Case Study of Estarreja

Estarreja

- Located in NE Portugal
- Traversed by a large stream ("Esteiro de Estarreja")- with several smaller connections
- Existence of a strong industrial complex, composed essentially by chemical facilities.



“Esteiro de Estarreja”: Past Situation analysis

- Discharge of solid residues in the surrounding area, with consequent contamination of the aquiferous;
- Conducting of the wastewaters of the factories into the stream nearby (“Esteiro de Estarreja”).
- Discharge of domestic sewer
- High permeability of the soils

Levels of heavy metals such as **Pb**, **Zn**, **As** and **Hg**, in the sediments of the stream to a depth of 50 cm, remain above the limits established by EC Directive 86/278/EC in the present

Estarreja: Past Main Contaminants

Wastewaters	Aniline, ammonia, **arsenic**, benzene, **mercury**, suspended solids, sulphuric acid, fats, hydrocarbons, chloride, sodium
Atmospheric emissions	Suspended particles, sulphur dioxide, nitrogen oxide, particles, **mercury**, hydrochloric acid
Soil residues	**Arsenic**, **lead**, **zinc**, vanadium, calcium hydroxide

Source: Environmental Impact Studies in the area (1994)

General view of the stream

General view of the stream and its vegetation

“Esteiro de Estarreja”: Site characterization

	Total metal (mg/ Kg soil)
Zn	898.9 (125-3620)
Pb	835.4 (16- 3740)
Hg	66.6 (0.3- 275)
As	1495 (45-5620)
Cr	26.0
Ni	37.3
Cu	0
Fe	16.8

Source: Environmental Impact Studies in the area (1994)

Zinc (Zn)

- Naturally present in the surface horizons of soils
- High affinity with organic soils
- Readily soluble
- Anthropogenic sources:
  - Application of pesticides or fertilizers
  - Mining activities
  - Sewage sludge and composted materials application

⇒ ESSENTIAL METAL for plants, humans and animals

☠ When present in high levels, causes disturbances in the muscular coordination

Mercury (Hg)

- Naturally present in rocks, volcanic areas and superficial layers of the soil
- Volatile
- Solubility depends on the form (inorganic species have relatively low mobility, contrary to organic species)
- Anthropogenic sources:
    - Chlorine production
    - Mining activities
    - Caustic soda production
    - Metal refining
    - Fertilizers application

Easily absorbed (specially in the metil Hg form) :

NON ESSENTIAL METAL

☠ It is bioamplified through the food chain, causing problems related with reproduction, physiology and morphology

Arsenic (As)

- Naturally present in hearth crust associated with sulphide minerals and volcanic areas
- Anthropogenic sources:
  - Metal processing
  - Mining activities
  - Burning of coal
  - Fertilizers and herbicides application

Easily bioavailable in acidified areas

NON ESSENTIAL METAL

☠ It is a carcinogenic agent

Lead (Pb)

- Naturally present at low levels in rocks (e.g. granite) and clay
- High affinity with organic soils
- Low mobility and solubility
- Anthropogenic sources:
  - Vehicle exhaust emissions
  - Mining activities
  - Sewage sludge application
  - Plastic and Paint Factories

→ Not bioavailable to a great extent: NON ESSENTIAL METAL

☠ It´s stored in the tissues, particularly in the brain and bones

☠ Causes disturbances of the nervous system and of the kidneys (specially of children)

Aims of the study

- Identification of plant species endemic to the site
- Determination of their ability to uptake heavy metals (particularly Zn, Pb, Hg and As)

Use phytoremediation as a method of cleaning heavy metal contaminated sites

Studied endemic plants

- Four plants, present in larger amount in the banks of the stream, were chosen:

  . Rubus sp (Drewberry)
  . Solanum nigrum (Blacknighshade)
  . Phragmites australis (Common reed)
  . Convolvulus sp. (creeper)

Sample of *Rubus* sp. collected in the area of the stream

Sample of *Convolvulus* sp. collected in the area of the stream

General view of *Phragmites australis* present in the area of the stream

General view of *Solanum nigrum* present in the area of the stream

Material and Methods

Harvesting of the complete plant samples

Washing

Drying in oven

Grounding of the complete plant samples

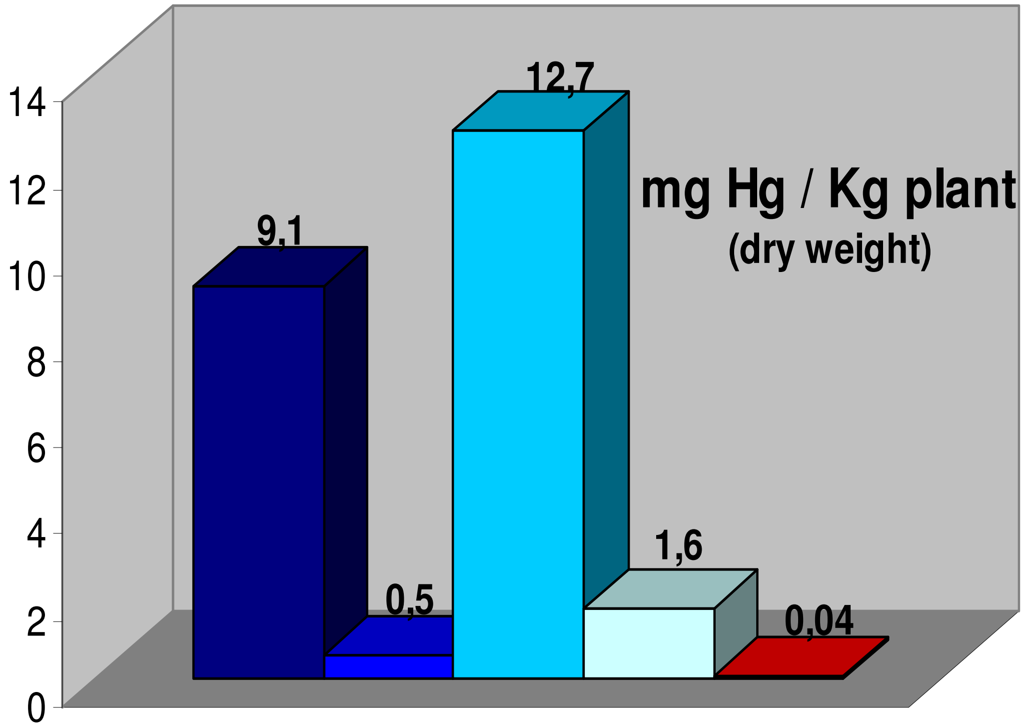
Addition of a sub sample to an appropriate acid mixture

Cold pre-digestion

Digestion with the adequate temperature

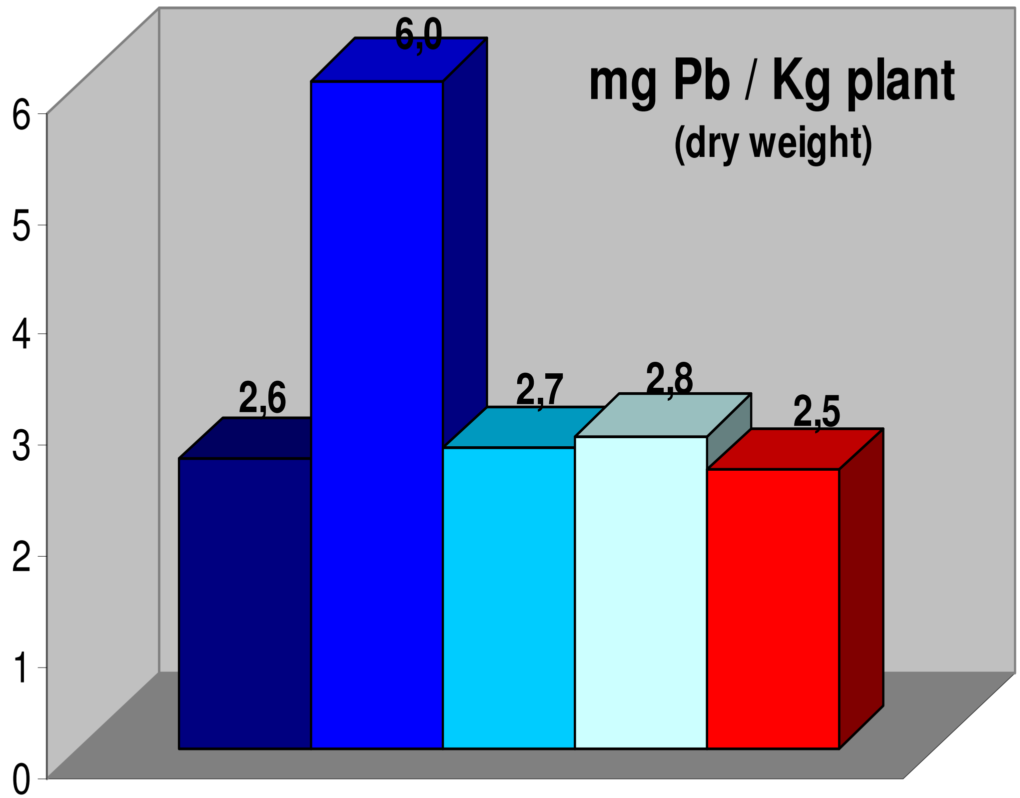
AAS analysis of the digests

Outcome and Conclusions - Hg -



	Hg
Solanum nigrum	9.1
Rubus sp.	0.5
Phragmites australis	12.7
Convolvulus sp.	1.6
Average maximum levels in plants not submited to contamination	0.04

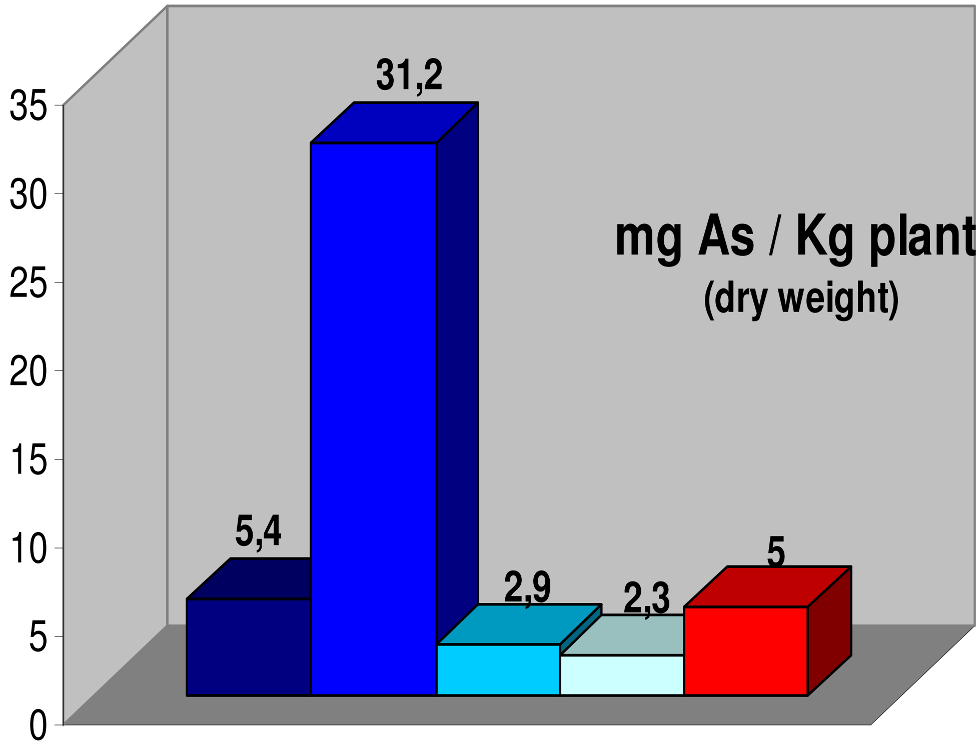
- ➢**Hg** levels are very fickle
- ➢The highest value corresponds to *Phragmites australis*



Outcome and Conclusions - Pb -

	Pb
Solanum nigrum	2.6
Rubus sp.	6.0
Phragmites australis	2.7
Convolvulus sp.	2.8
Average maximum levels in plants not submited to contamination	2.5

- **Pb** does not seem to be significantly accumulated in any of the plants

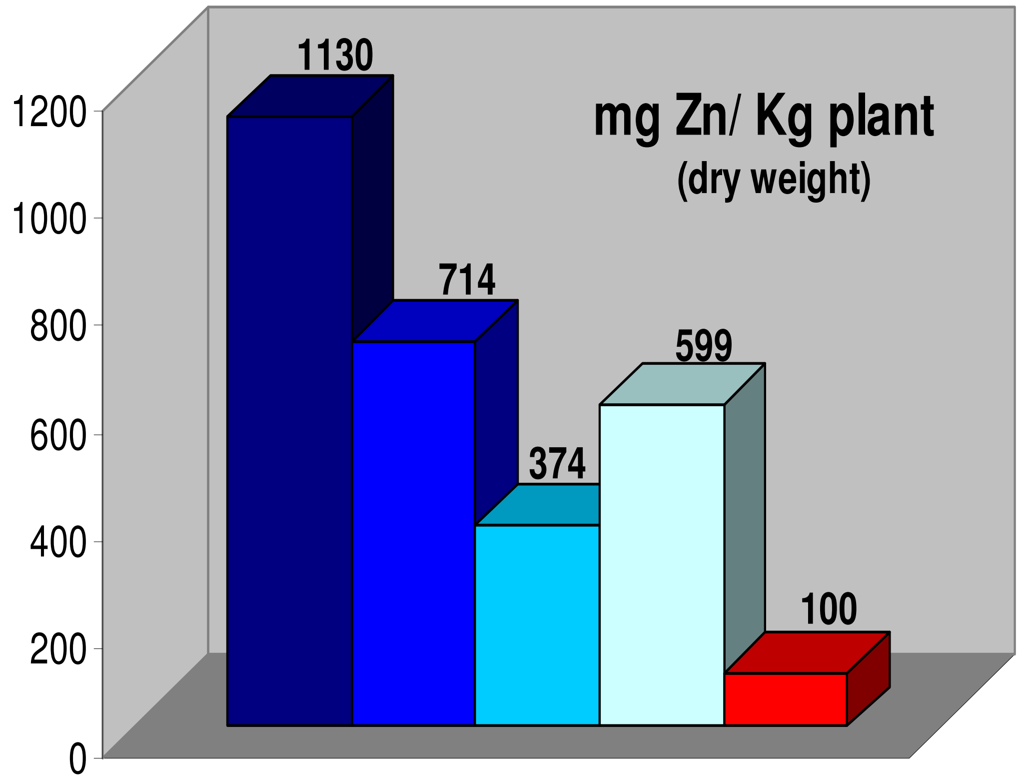


Outcome and Conclusions - As -

	As
Solanum nigrum	5.4
Rubus sp.	31.2
Phragmites australis	2.9
Convolvulus sp.	2.3
Average maximum levels in plants not submited to contamination	5

- The levels for **As** are moderate when comparing with the ones registered for polluted sites

- The highest value was registered for Rubus sp.



	Zn
Solanum nigrum	1130
Rubus sp.	714
Phragmites australis	374
Convolvulus sp.	599
Average maximum levels in plants not submited to contamination	100

Outcome and Conclusions - Zn -

- High levels of **Zn** were detected in all the plants, especially on *Solanum nigrum,*

Future work

- ✓ Coverage of a larger extent along the stream in a new plant sampling
- ✓ Determination of the metals level in different parts of the selected plants: root, shoot and leaves
- ✓ Comparison of total / bioavailable metal levels in the soils adjacent to the plant samples
- ✓ Determination of the effect of mychorrizae fungi on metal uptake

Relation of the metal levels in the soils with the concentrations in the plants

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