Phytoremediation of polluted soils:

a technology for after-war cleaning of contaminated soils in Ukraine

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On-line seminar within the project: *Education for sustainable development: transferring V4 countries' experience for Ukraine's recovery*, co-financed from the International Visegrad Fund, December 7, 2023

Outline of seminar

Introduction

Need for remediation of polluted soils

Main sources of soil pollution

Methods of remediation of polluted soils

Biological methods for soil remediation

Phytoremediation of polluted soils: modes of phytoremediation, selected results,

examples of application: pilot cases

Summary

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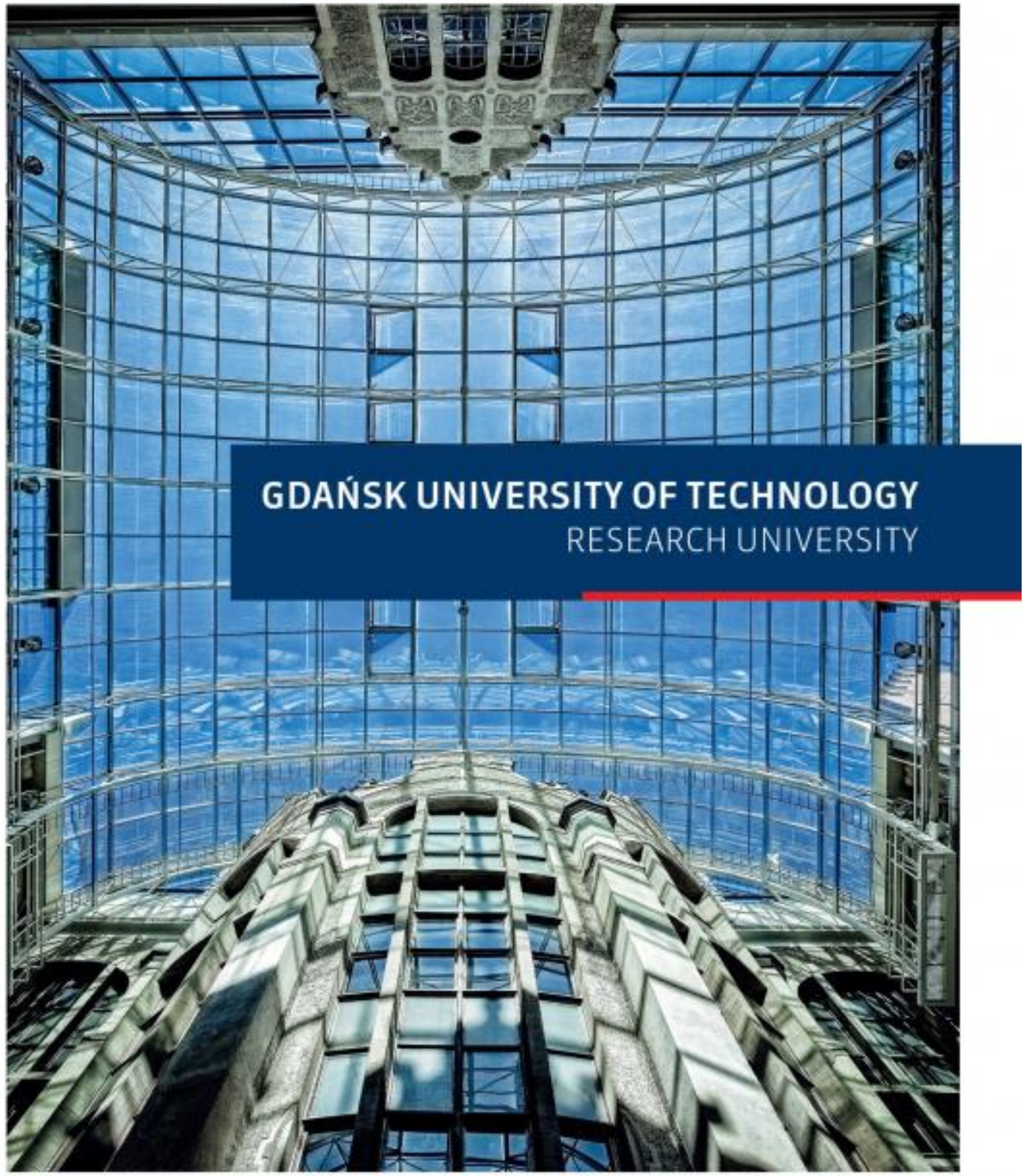
EXCELLENCE INITIATIVE



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Piotr Rybarczyk

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Environmental Protection and Management (BSc, MSc)
Chemical Technology (PhD)

Areas of interest: chemical systems for environment protection, ion flotation, air biofiltration, biomass processing towards energy, phytoremediation

FACULTY OF CHEMISTRY

DEPARTMENT OF PROCESS ENGINEERING AND CHEMICAL TECHNOLOGY

Development of new sythetic fuels
Hydrogen production and storage
Energetic valorization of biomass
Waste treatment towards value added products
Monitoring systems for air quality assessment
Chemical and biological systems for waste air treatment

NATIONAL SCIENCE CENTRE POLAND

NCBR Narodowe Centrum Badań i Rozwoju

BAPR Baltic Phytoremediation · Interreg South Baltic · European Union · European Regional Development Fund

BSAM Baltic Smart Asset Management · Interreg South Baltic · European Union · European Regional Development Fund

CAR-I Creating Automotive Renewal · Interreg South Baltic · European Union

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Restoration of polluted soils

Governed by national/international regulations (e.g. in Poland: Environmental Protection Law, Water Law, Act on the Protection of Agricultural and Forest Lands)

Remediation vs. recultivation

Degraded land, devastated land, post-industrial areas

Self-cleaning of environment – possible? Is it fast or slow?

Restoration of polluted soils

Remediation: restoring the degraded environment to its previous state, i.e. before its violation, or to its proper state in accordance with the law

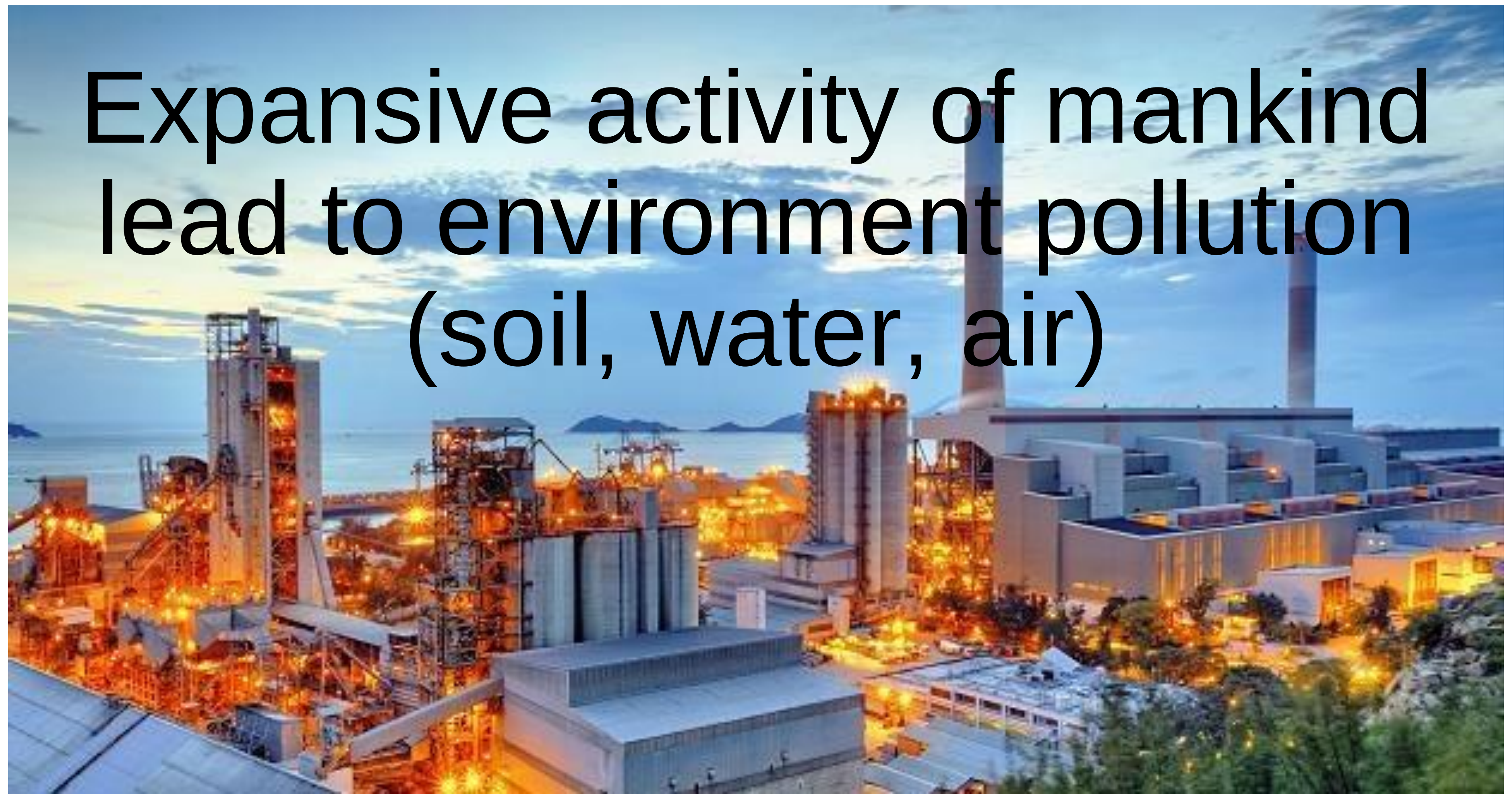
Degraded land: areas with decreased agricultural and forestry utility due to environment pollution or industrial/agricultural activities; crops yield and quality are decreased

Recultivation: giving or restoring utility or natural values to degraded land by appropriate landscaping, improving physical and chemical properties, regulating water relations, restoring soil, strengthening slopes and rebuilding or building necessary roads

Devastated land: a complete loss of utility value of land, usually it is impossible to manage and restore the land (mine areas, roads, highly-industrial areas)

Post-industrial areas: degraded areas, with no utylity or fully occupied with non-operating facililties

Pollution and self-cleaning of environment



Remediation of environement is an obligatory duty for the polluter land-owner or responsible national organization

Environmental pollution

Air	Water	Soil
SELF-CLEANING ↓	SELF-CLEANING ↓	↓
Air	Water	Soil
Days	Years	Hundreds of years

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Polluted lands treatment & remediation

POLLUTION

METALS & HEAVY METALS (energy sector, metallurgy, urbanization):
Cd, Hg, Pg, Cu, Zn, Mo, Mn, Ti

CYANIDES (chemical industry, synthetic fertilizers, plant protection agents, plants

ORGANIC POLLUTANTS (petrochemical industry, comunal activities, transport, heating, incidental spills of oils):
petrol and diesel hydrocarbons
aromatic hydrocarbons, polycyclic aromatic hydrocarbons
chlorinated hydrocarbons
pesticides
volatile organic compounds

REMEDIATION

Remediation plan

Environmental impact assessment

Remediation depends on: type of area, type of pollution, future use of the land, cost of treatment, available technology, law regulations

USE AFTER REMEDIATION

Agriculture or forestry: green areas, cultivation of industrial plants (oily plants, energetic plants), forest areas (mine areas)

Recreational use (high cost; e.g. transition of a landfill into a ski slope in Warsaw)

Natural (spontaneous restoration of nautral habitats)

Residential areas (post-industrial areas)

No utilization

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Soil remediation strategies

- Limitation of migration of pollutants and their bioaviability: immobilization
- Increase of pollutants’ mobility and extraction of organic and mineral compounds
- Biodegradation of organic pollutants (e.g. persistent organic pollutants are converted to simple and non-toxic organic and mineral end-products)
- Physical and physicochemical barriers (profile and horizontal control of pollutants migration)
- Self-cleaning approach

Method	In situ chemical binding	Transfer of polluted soil	Extraction and cleaning of soil	Phytoextraction
Cost of cleaning 1m^3 of soil, USD	90 – 100	100 – 400	250 – 500	15 – 40
Treatment time, months	6 – 9	6 – 9	8 – 12	18 – 60
Problems / waste generated	leachate	leachate	solid waste	soild waste

Methods of soil remediation

TYPE: PHYSICAL, CHEMICAL / MIXED OR BIOLOGICAL METHODS

IN SITU OR *EX-SITU* INTERACTIONS BETWEEN METHODS

TREATMENT AND DETOXICATION STABILIZATION

ENGINEERING METHODS: removal and storage of contaminated soil; izolation barriers

PROCESS METHODS: physical, biological, chemical, thermal, mixed

NOVEL TECHNOLOGIES: adsorption, photodegradation, photolysis, plasma processes, nitrification-assisted processes, electroosmosis, solidification, vitrification, nanotechnologies

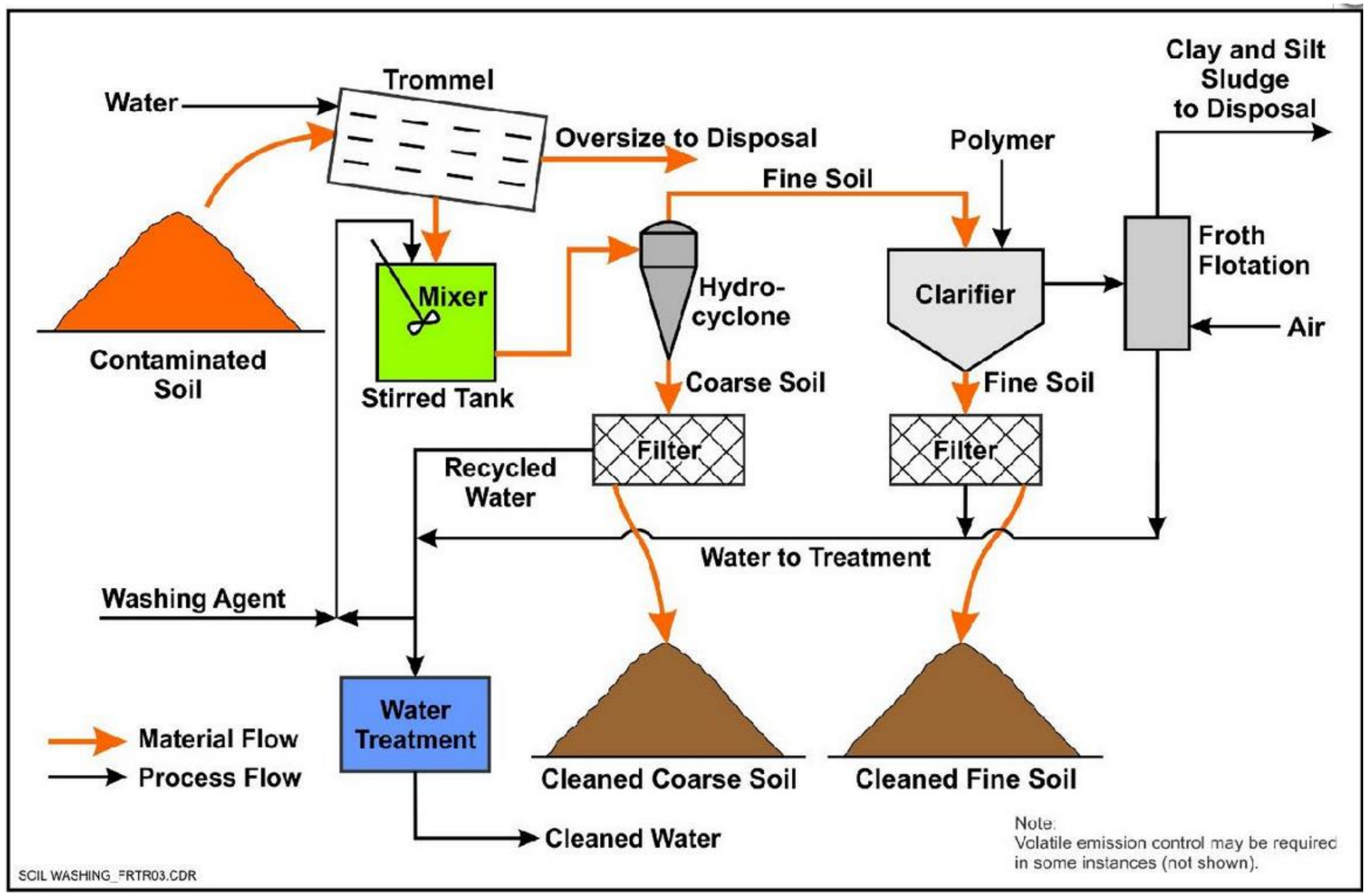
SELECTION OF REMEDIATION METHOD:

- characteristics of pollutants (volatility, solubility in water, concentration, biodegradibility etc.)
- characterisits of land and soil (pH, composition, concentration of pollutants, size of area)
- applicability and availability of method (suitability, cost, effectiveness, time, social acceptance)

Soil remediation methods

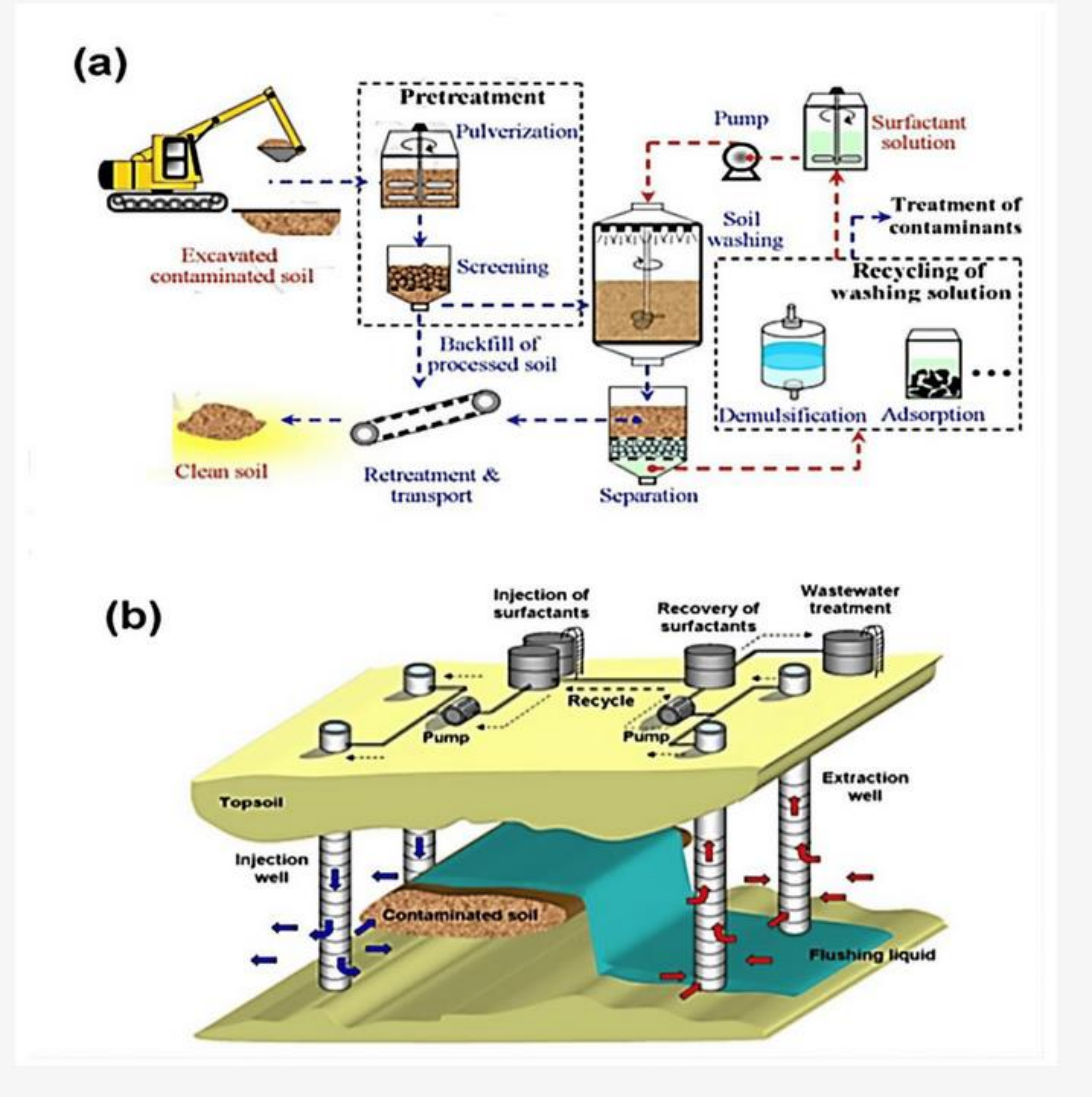
Ex-situ	*In-situ*
PHYSICAL METHODS	
Excavation and storage Incineration Thermal desorption Steam extraction Segregation of radioactive soil	Steam extration via aerification Barrier systems Electrocleaning
CHEMICAL METHODS	
Soil washing-out Solidification / stabilization / sorption / chemical immobilization Dehalogenation Solvent extraction Chemical and photochemical oxidation / reduction	Soil flushing Solidification / stabilization / sorption / chemical immobilization
BIOLOGICAL METHODS	
Composting Bioreactors / microbial filters	Bioremediation Phytoremediation

Examples of physico-chemical methods



Soil washing

https://doi.org/10.1016/j.chemosphere.2020.127606



Ex-situ soil washing (a) and *in-situ* flushing (b)

https://www.mdpi.com/2071-1050/15/17/13161

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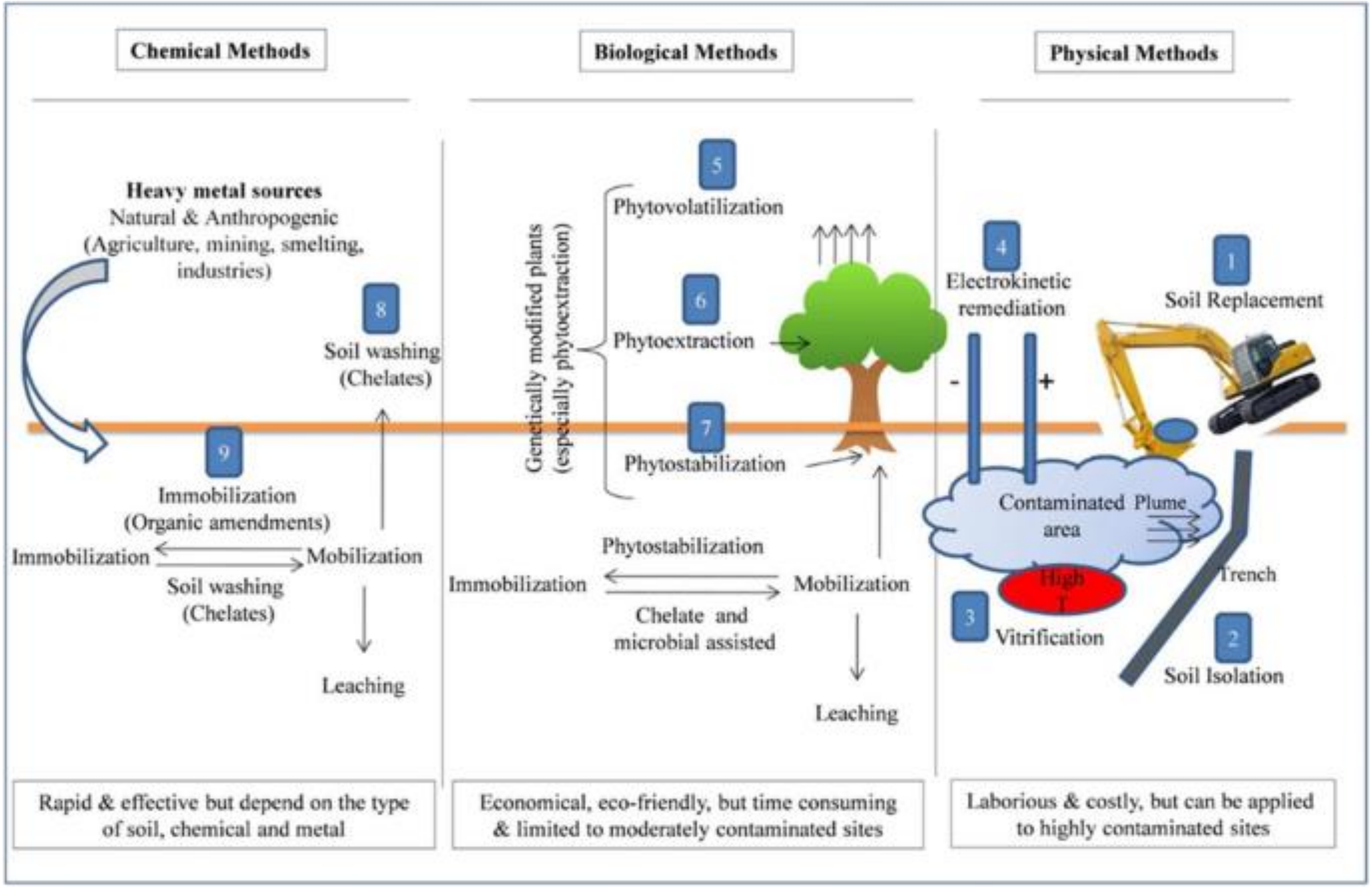
Comparison of soil remediation methods



https://doi.org/10.1007/s11270-023-06394-6

Maybe nautral-based solutions?

One drawback of phytoremediation: **time**

Many advantages:

- ✓ Environmentally friendly & sustainable
- ✓ Natural processes
- ✓ No destruction of soil structure
- ✓ Pleasant environment
- ✓ Social effects (e.g. park formation)
- ✓ Cheap
- ✓ Value-added effects (aesthetics, energy)

https://helendungert.com/tag/orrefors-park/

Orrefors park in Sweden in the Kingdom of Glass with soil historically polluted with heavy metals

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Biological methods for soil remediation

- Biological methods
  - Phytoremediation
  - Bioremediation
  - Bioleaching

BIOREMEDIATION
Use of microbes to remove pollutant or to transform tchem to less harmful forms: soil, water, air

BIOLEACHING
Removal of metals (from ores, flotation tailings etc.) by microbes through oxidation, dissolution, wathering into soluble metal sulfates

+ Broad application spectrum

+ Low cost comparing to other methods

+ Public acceptance

+ O_2 production, CO_2 consumption

- Biomass can be dangerous waste

- Cost of biomass utilization

- Climate / weather-dependance

- Concentration-dependent treatment time

Phytoremediation

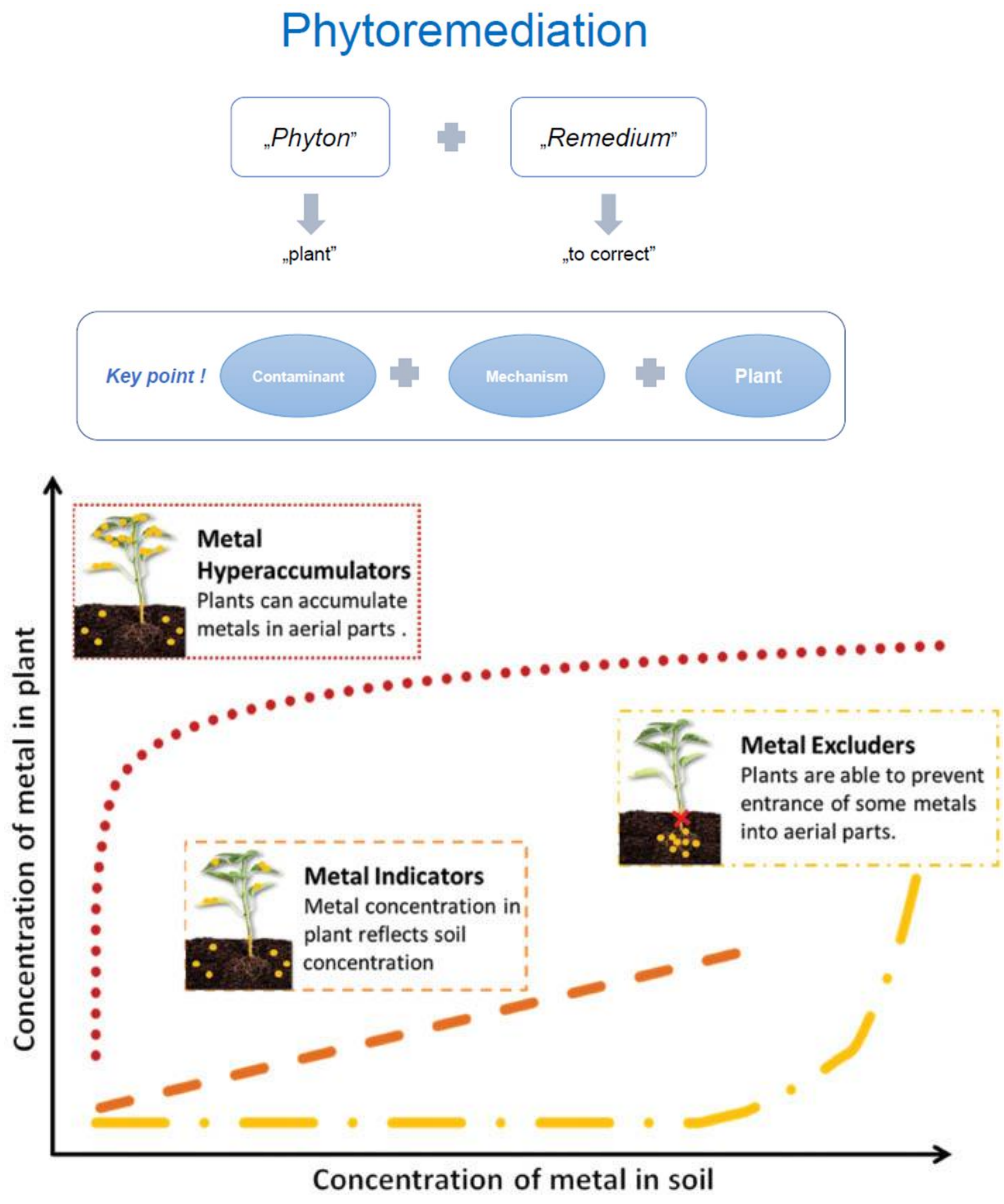
Phytoremediation: remediation and decontamination of polluted soil, underground and surface water as well as air by using plants

Applicable to removal of broad scope of pollutants (mineral oils, solvents, pesticides, heavy metals)

1st description in 18th century

Still under development, limited full scale applications

Special application to soil treatment as the richiest compartment of environment



https://www.degruyter.com/document/doi/10.1515/gps-2013-0103/html

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Pollutants and phytoremediation

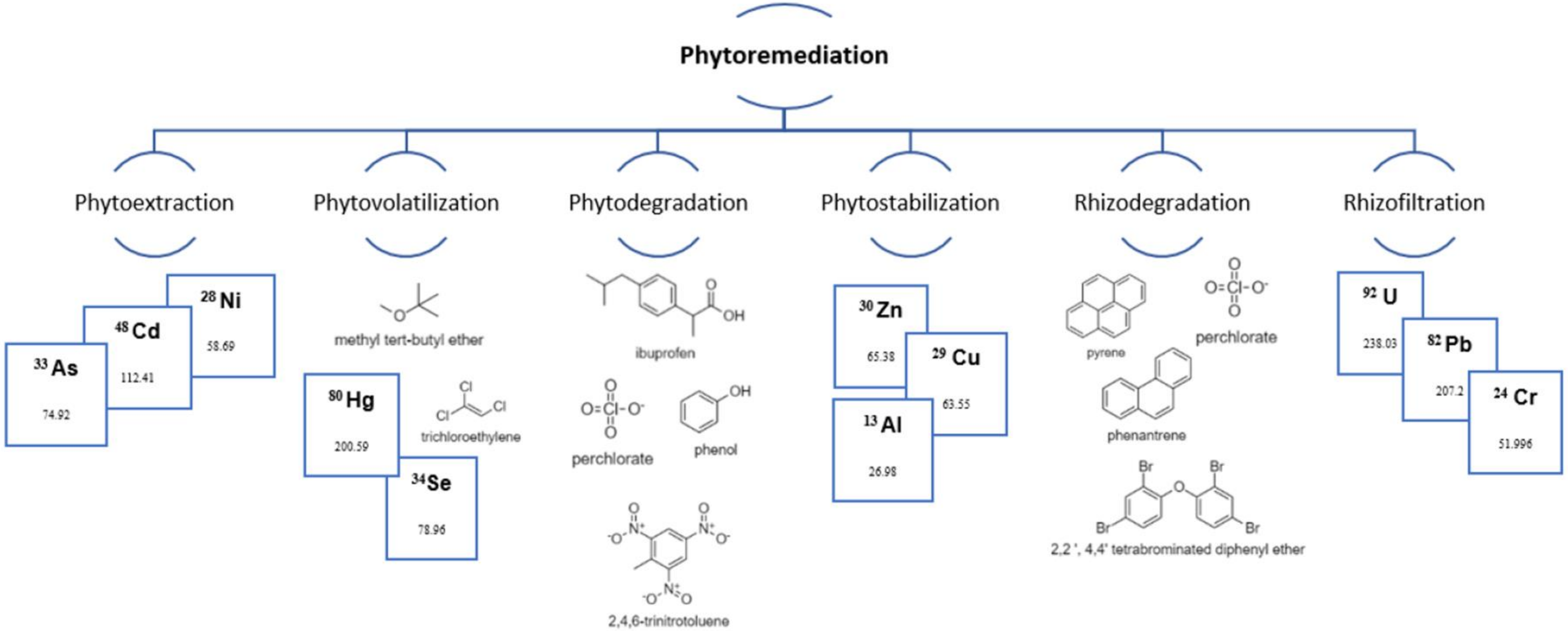
INORGANIC
Metals cannot disappear or be biodegraded: plants take up metals and then metals are removed by harvesting or stabilized in soil

ORGANIC
PAH, PCB, Dioxins: these can be degraded and metabolised by plants, but especially by microbes

VOLATILE COMPOUNDS
VOCs, VICs: these can be taken up from air via stomata

Advantages	Disadvantages
1. Environmentally friendly, cost-effective, and aesthetically pleasing	1. Relies on natural cycle of plants and therefore takes time;
2. Metals absorbed by the plants may be extracted from harvested plant biomass and then sustainably recycled;	2. Phytoremediation works best when the contamination is within reach of the plant roots, typically 1–2 m underground for herbaceous plants and 3–5 m for trees;
3. Phytoremediation can be used to clean up a large variety of contaminants;	3. Some plants absorb a lot of poisonous metals, making them a potential risk to the food chain if animals feed upon them.
4. May reduce the entry of contaminants into the environment by preventing their leakage into the groundwater systems.	

Mechanisms of phytoremediation

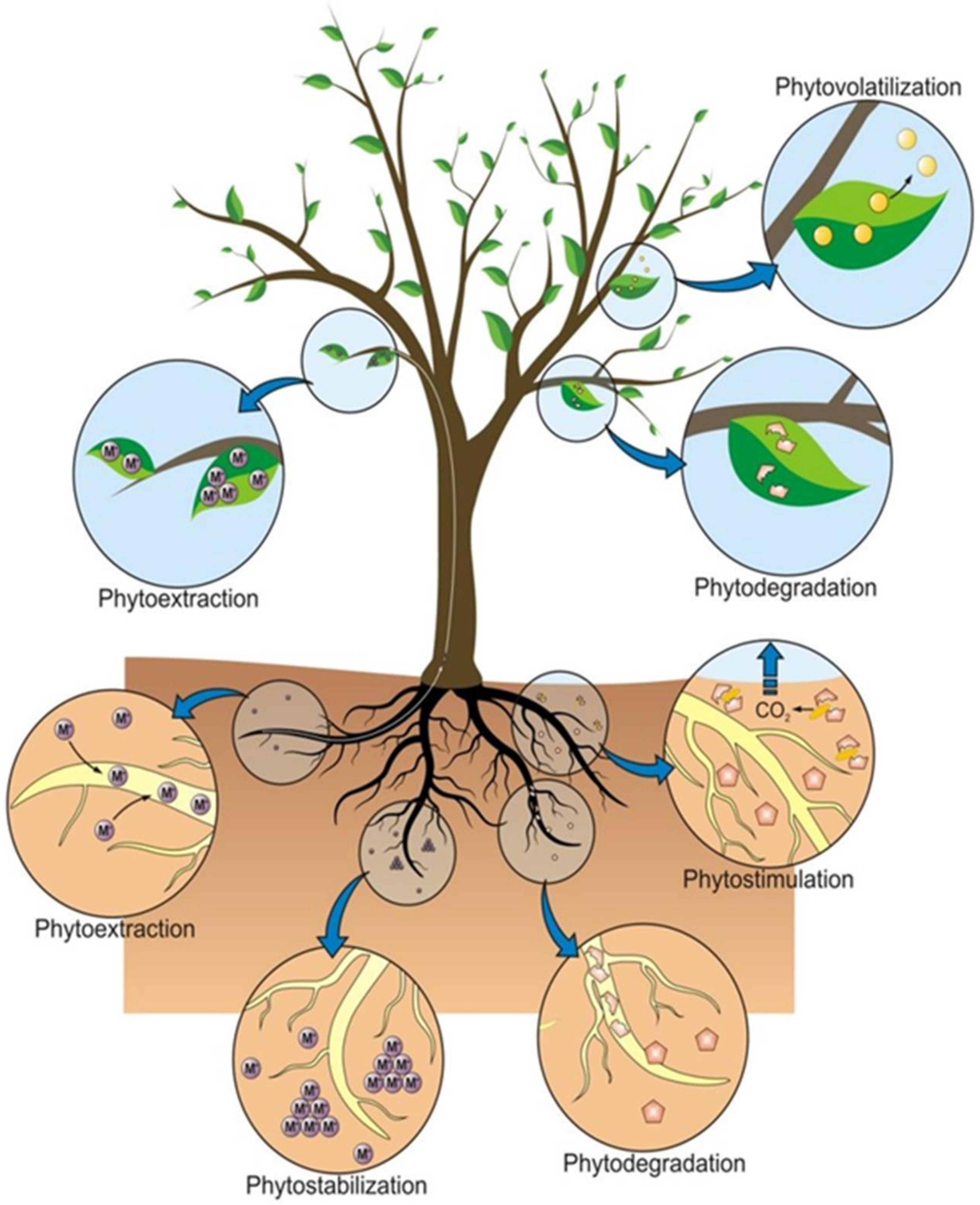


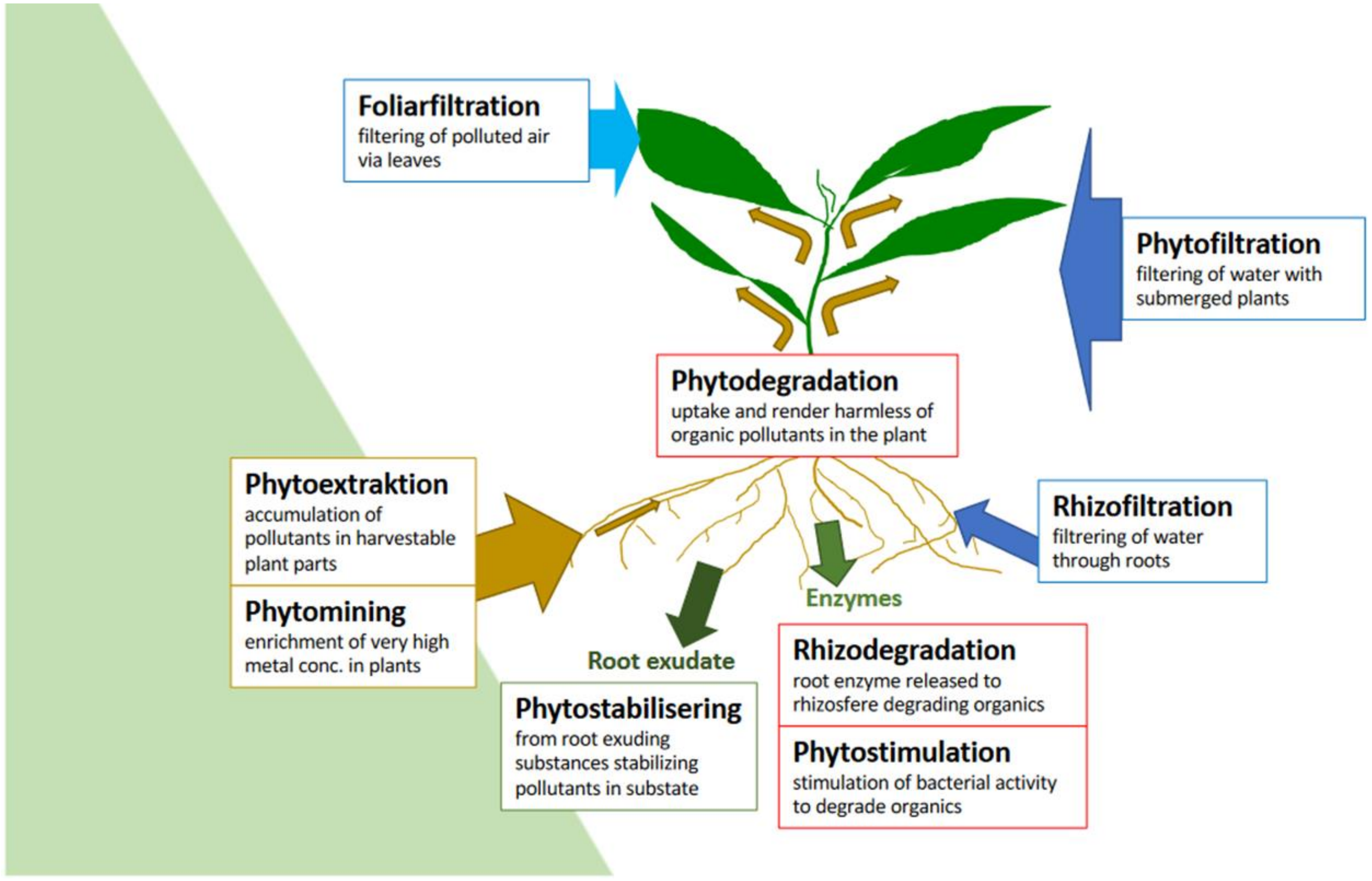
Removal of pollutants from environment:
Phytoextraction
Phytomining
Phytofiltation
Rhizofiltration
Foliarfiltration

Stabilization of pollutants:
Phytostabilization

Degradation of pollutants:
Rhizodegradation
Phydodegradation
Phytostimulation

Mechanisms of phytoremediation





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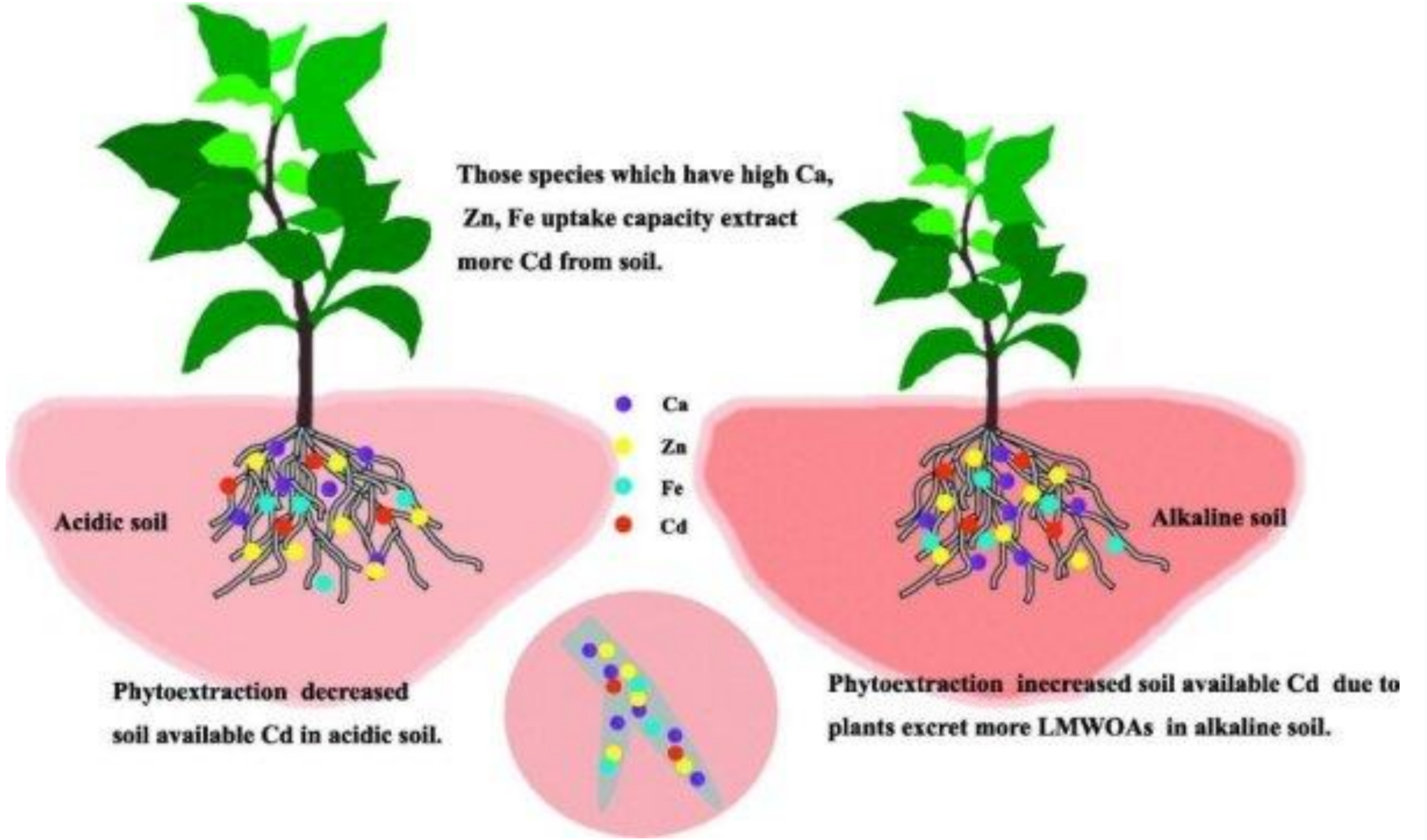
Phytoextraction

Pollutants are taken up by root system and are transferred to above-ground parts

Cumulation of microelements in higher than required levels (phytorecovery)

Mechanism involves secretion of exudates by roots which dissolve pollutants and make the accessible to plants



https://doi.org/10.1016/j.scitotenv.2020.137581

LMWOAs – low molecular weight organic acids

Phytoextraction

Plant	Medium	Experiment	Contaminant	Results
Helianthus annuus	wetland soil	greenhouse pot experiment	Cd (0.1 and 30 mg/kg soil	- Higher bioaccumulation of Cd in roots than in shoots - - Cd concentration *in T. latifolia* tissues was 77.0 and 410.7 mg/kg
Typha latifolifa	loamy topsoil from an agricultural field	greenhouse pot experiment addition of chelator: 10 mM EDDS	Cu (360 mg/kg) Zn (50 mg/kg)	-EDDS increased metal solubility in soil -EDDS significantly enhanced shoots Cu uptake
Brassica juncea	soil from farming area	greenhouse pot experiment addition of chelator: 5 mmol/kg NTA or citric acid	Cd (40 mg/kg soil) Cd (186 mg/kg soil) Cu (313 mg/kg soil) Pb (1331 mg/kg soil) Zn (3326 mg/kg soil)	- NTA treatment increased shoots metal concentrations by a factor of 2–3, whereas citric acid did not induce any diversity compared to the control

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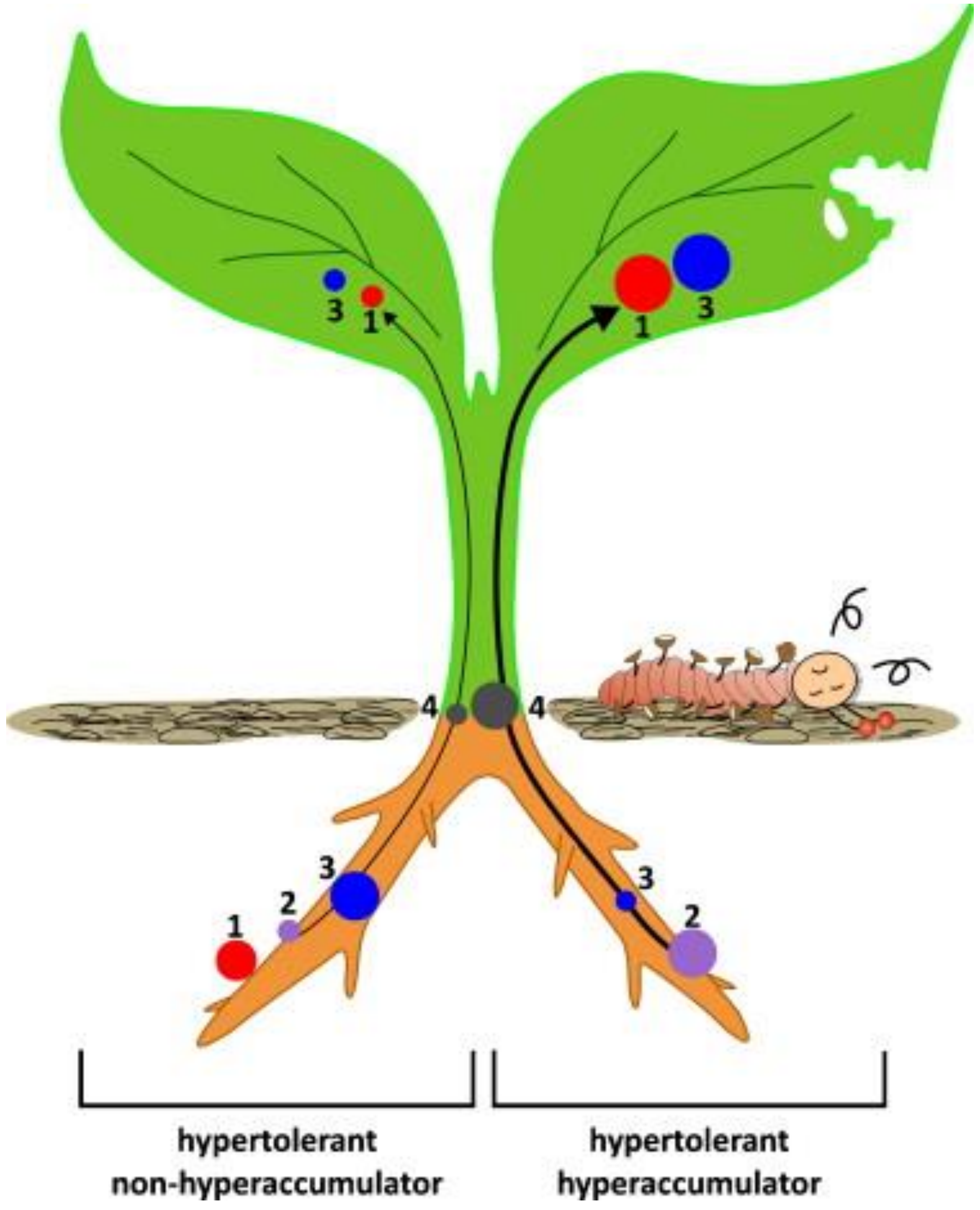
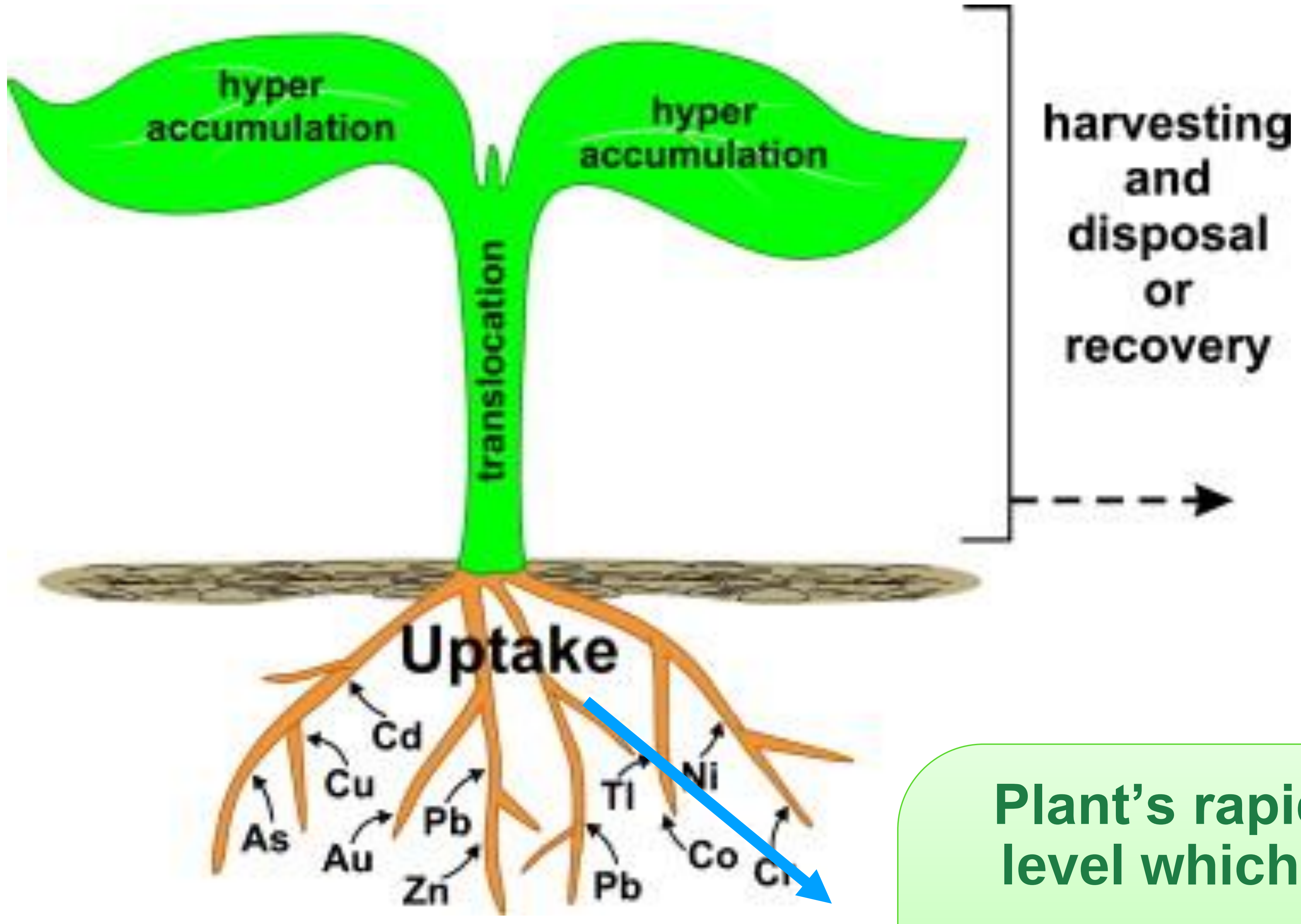
Hyperaccumulators and bioaccumulation of heavy metals



Plant must be able to hypertolerate high levels of the trace element in root and shoot cells



Plant must have the ability to translocate an element from root to shoot at high rates

Example: Normally root Zn, Cg or Ni concentrations are 10x higher than shoot concentration, but in hyperaccumulators, shoot metal concentration can exceed root levels.

Plant's rapid uptake of element at level which occur in soil solution

Example: ***Thlaspi caerulescens*** *requires much higer solutions Zn^{2+} and leaf Zn concentration 100-300 mg kg^{-1} vs.10-12 mg kg^{-1} in normal plants*

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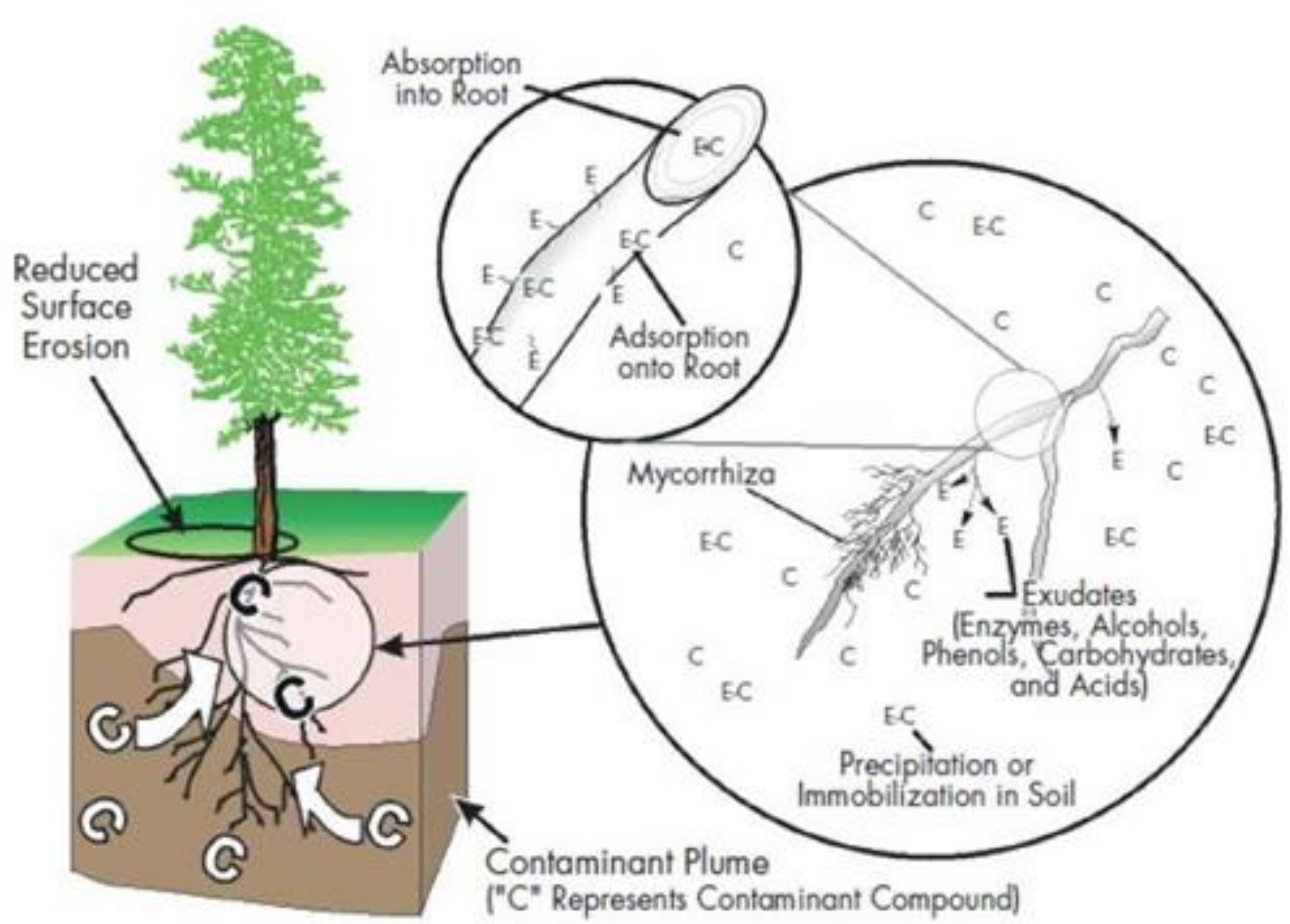
Phytostabilization

Chemical compounds secreted by plants immobilize (stabilize) pollutants in soil

There is no degradation of pollutants, but stabilization due to absorption and accumulation in roots, precipitation of pollutants in the rhizosphere, secretion of root exudates (phenols, sugars, organic acids, and miccorhiza



https://knowhowtogmo.wordpress.com/2011/01/31/phytostabilization/

Phytostabilization

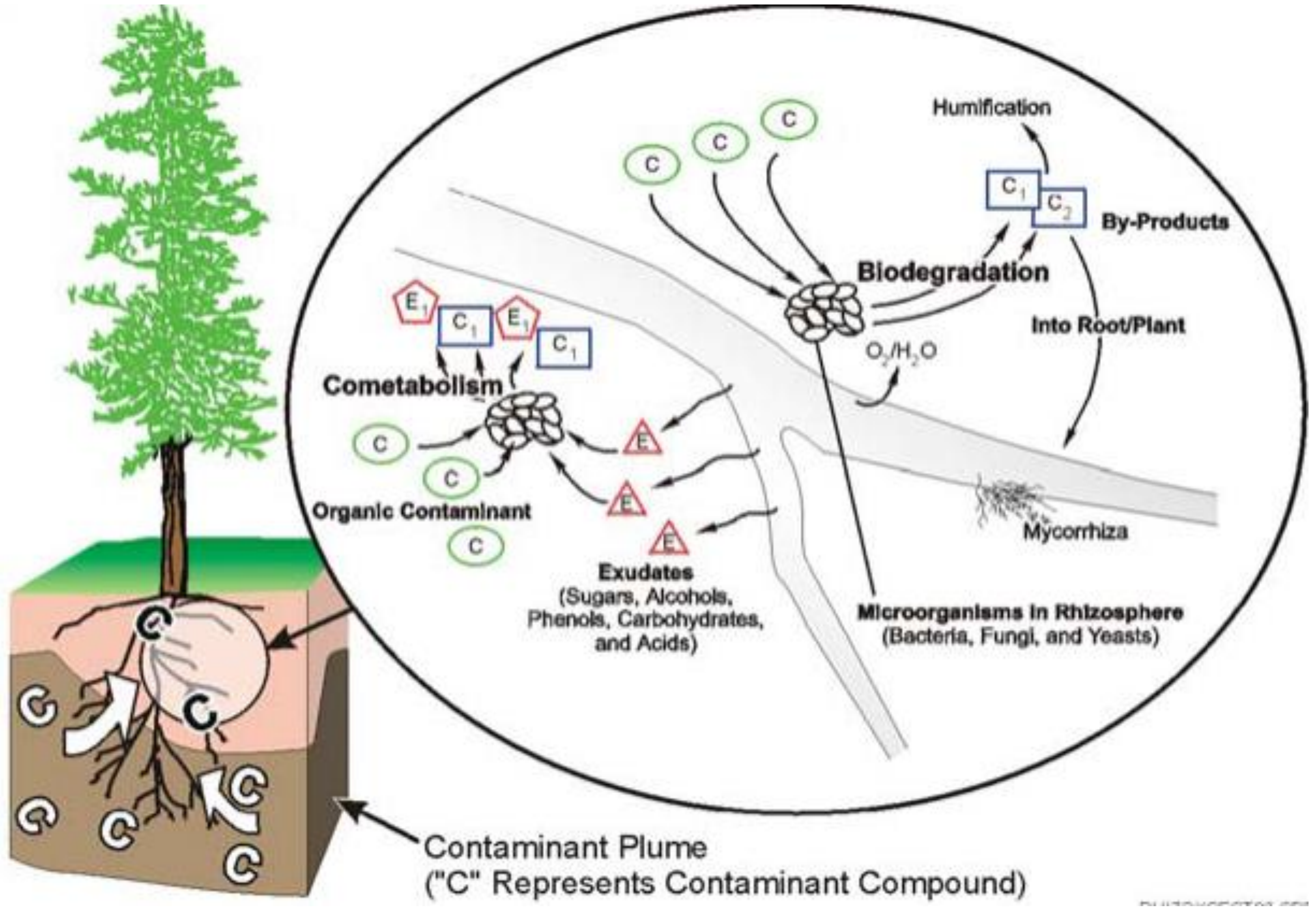
Plant	Medium	Experiment	Contaminant	Results
Lupinus albus	Soil affected by acid pyrite sludge	Greenhouse pot experiment Field experiment	As (60 mmol/kg soil) Cd (10 mmol/kg soil)	- The accumulation of heavy metals occurred mostly in root nodules
Vicia farba	Vineyard soil	Greenhouse pot experiment Bacteria inoculation	Cu (63.5 mg/kg soil)	- Bacteria inoculation caused increase the number and the weight of root nodules of 50%. -Significant reduction of accumulated copper in roots attending 35%.
Vetiveria zizanoides	Mine tailings	Greenhouse pot experiment Field experiment	Pb (>1000 mg/kg soil)	- Low translocation factor (<1) values and bioconcentration coefficients for root (>1) were observed.

Phytodegradation

Uptake, accumulation and degradation of organic pollutants undergo inside plant tissues due to secretion of endogenic enzymes (e.g. phosphatase, lactase)

Edible (potato) and energetic plants (populus) are utilized

Rhizodegradation: secretion by roots of substances facilitating microbial development and activity in the soil; microbes degrade the pollutants in soil



Phytodegradation/Rhizodegradation

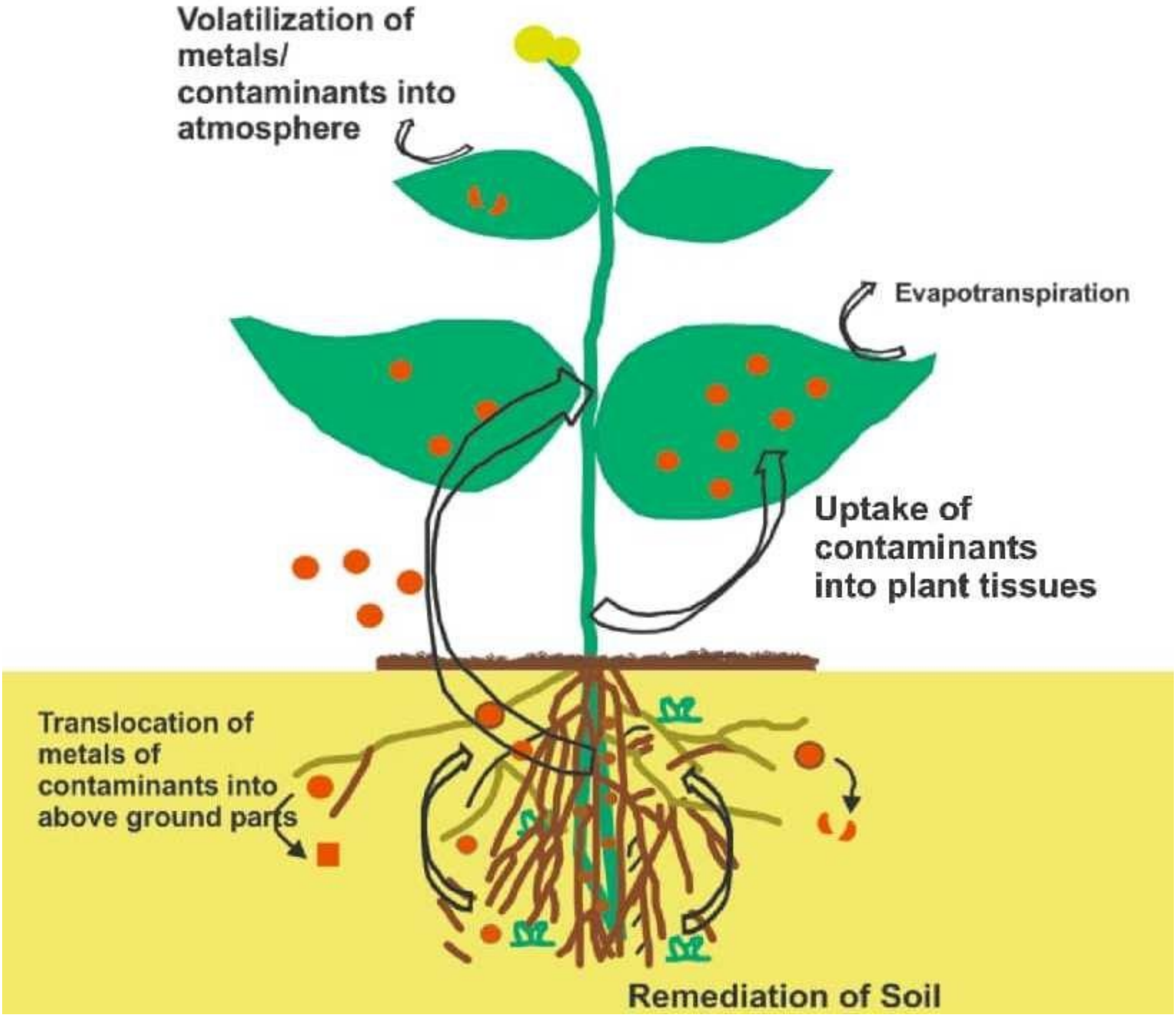
Plant	Medium	Experiment	Contaminant	Results
Brassica juncea	Aqueous solution	Greenhouse hydroponic experiment	Insecticide – phorate (5 mg/L)	- Over 5 days, Brassica juncea removed 54% of the highly toxic insecticide phorate from the medium with the formation of phorate sulfoxide -After 5 days, B. juncea tissue contained only 6.4% (0.32 mg/L)
Eichhornia Crassipes	Aqueous solution	Greenhouse hydroponic experiment	Phosphorus pesticide – ethion (0.01, 0.1, and 1 mg/L)	- Uptake and phytodegradation of ethion contributed 69%
Kandelia candel	Sediment of mangrove wetland	Greenhouse rhizobox experiment	Phenantrene Pyrene (10 mg/kg soil)	- After 60 days of plant growth, presence of the plant significantly enhanced the dissipation of Ph (47.7%) and Py (37.6%) from contaminated sediment

https://www.researchgate.net/publication/265191596_THE_FEASIBILITY_OF_POPLARS_FOR_PHYTOREMEDIATION_OF_TCE_CONTAMINATED_GROUNDWATER_A_Cost-Effective_And_Natural_Alternative_Means_Of_Groundwater_Treatment?enrichId=rgreq-059be685f91e3d03795d87537e0cdf4b-XXX&enrichSource=Y292ZXJQYWdlOzI2NTE5MTU5NjtBUzo0NTkxNzgxNTEwMjY2OTJAMTQ4NjQ4ODAxMDYxMA%3D%3D&el=1_x_3&_esc=publicationCoverPdf

Phytovolatilization

Uptake of pollutants (with water) from soil and transpiration through stomata to the atmosphere

Useful for removal of selected solvents from soil: plants uptake TCE and release it in ungaged form to the atmosphere: transfer of pollutants from one to another compartment



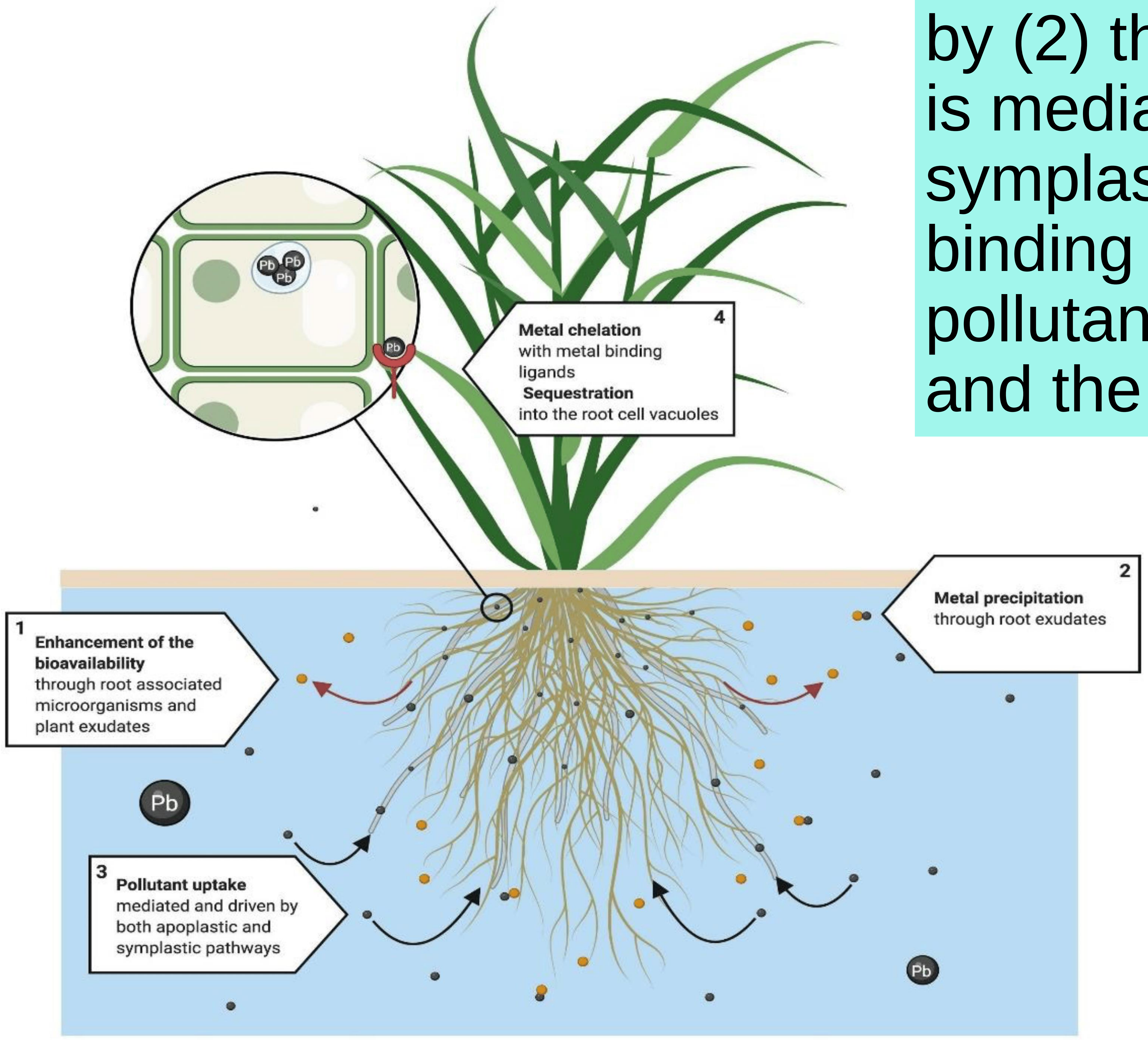
http://dx.doi.org/10.5281/zenodo.3244176

Phytovolatilization

Plant	Medium	Experiment	Contaminant	Results
Brassica juncea	upland and wetland soil	greenhouse pot experiment	Selenium compounds (20 and 200 μM)	-Brassica juncea treated with 20 μm SeCN removed 30% (w/v) of the supplied Se in 5 d. -Se volatilization by B.juncea accounted for only 0.7% (w/v) of the total SeCN removed.
Arabidopsis thaliana	aqueous solution	hydroponic experiment Plants engineered with a modified bacterial mercuric reductase gene	Hg (II) (1 and 5 mg/L)	- The transgenic plants volatilized 3 to 4-times more Hg(0) per mg of plant tissue than wild-type.
Salix babylonica	aqueous solution	hydroponic experiment in a climate control chamber	Methyl tert-butyl ether (10, 25, 50, 100, 200, and 400 mg/L)	- The amount of MTBE from 2,38 mg (10 mg/L) – 94.77 mg (400 mg/L) was removed by transpiration

Rhizofiltration

Rhizofiltration system: root exudates and microorganisms (1) enhance bioavailability, followed by (2) the precipitation of metals; (3) pollutant uptake is mediated and driven by both apoplastic and symplastic pathways. (4) Metals are chelated by metal binding ligands, phytochelatins and metalloteines, and pollutants are either sequestered into the cell vacuoles and the apoplast or bound to the cell wall



https://www.mdpi.com/1660-4601/18/10/5215

Rhizofiltration

Plant	Medium	Experiment	Contaminant	Results
Helianthus annuus	groundwater	Greenhouse hydroponic experiment	U (30-646 μg/L)	- More than 80% of the initial uranium in solution and genuine groundwater was removed within 24 h by using Helianthus annuus
Carex pendula	synthetic wastewater	Greenhouse hydroponic experiment	Pb (1, 5, 10 mg/L)	- For 10 mg/L roots were able to accumulate 1600 μg/g DW, with low TF = 0.1
Brassica juncea	aqueous solution	Greenhouse hydroponic experiment	U (25-5000 μM)	- B. juncea could take up 20–23% of uranium from the solution containing up to 5000 μM.

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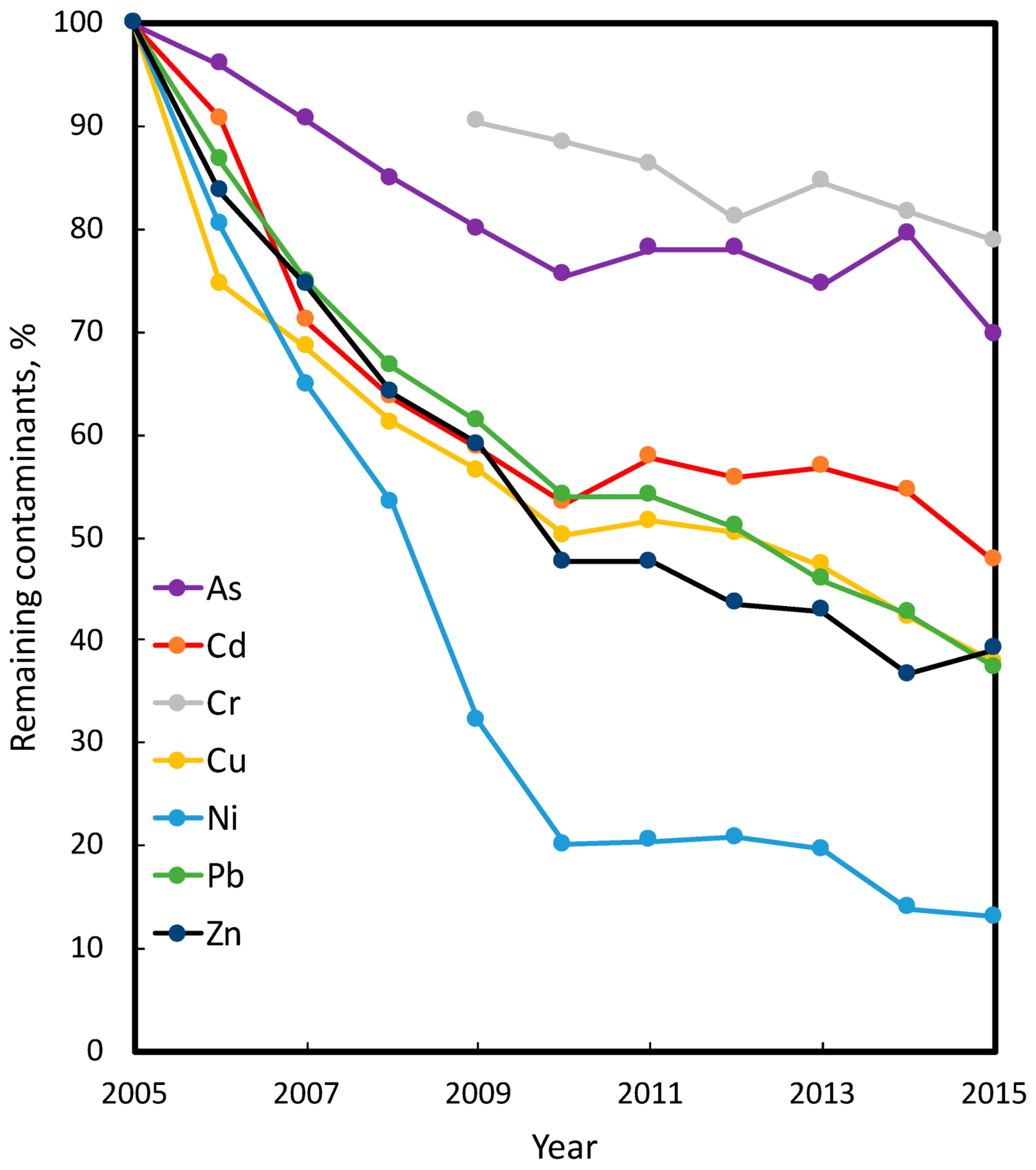
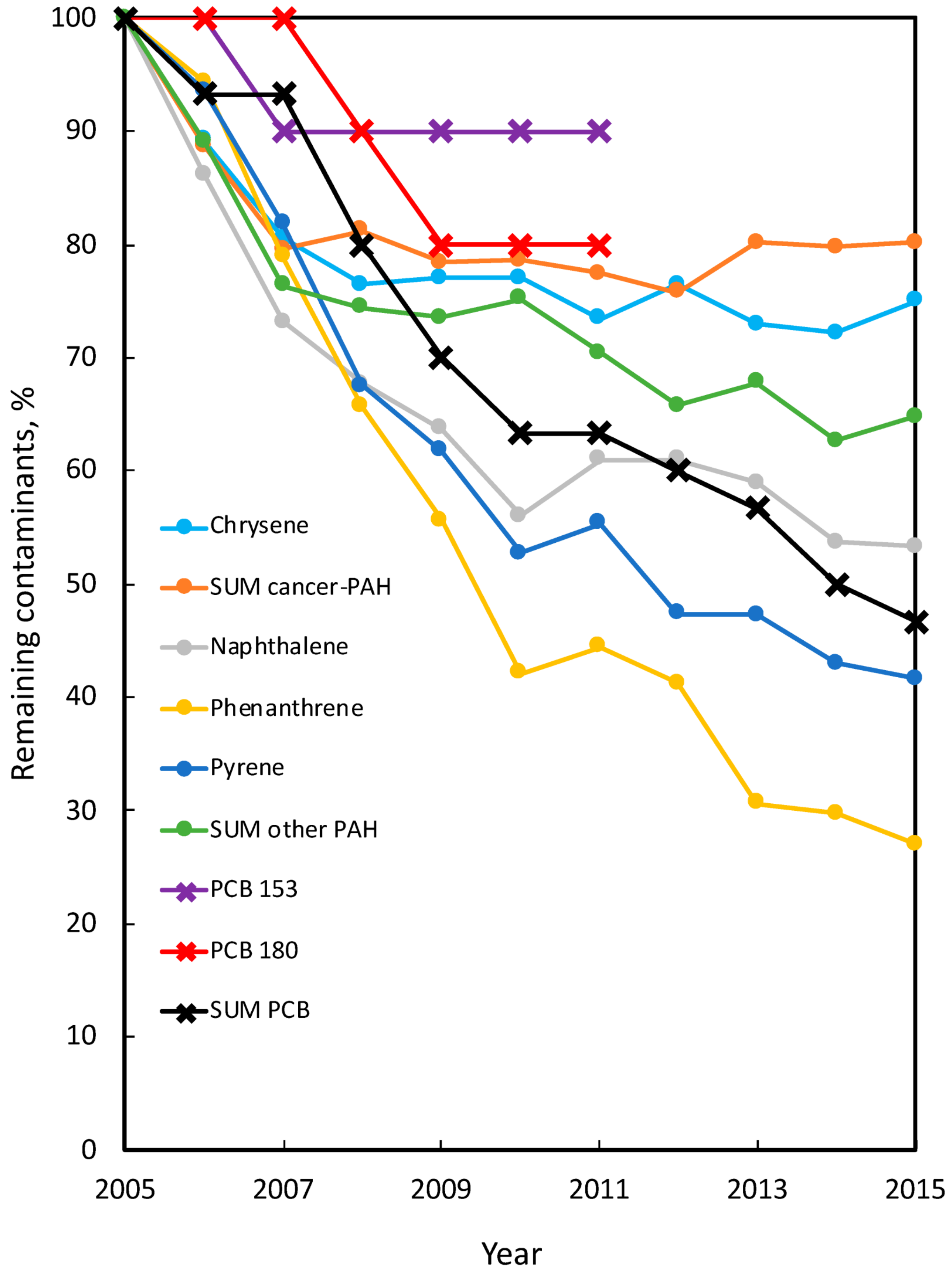
Examples:



Remaining percentage of heavy metals and arsenic each year in the soil at the contaminated location, with *S. viminalis* cultivation.



Remaining percentages of PAHs and PCBs each year in soil at the contaminated location, with *S. viminalis* cultivation.

https://www.mdpi.com/2071-1050/14/14/8449

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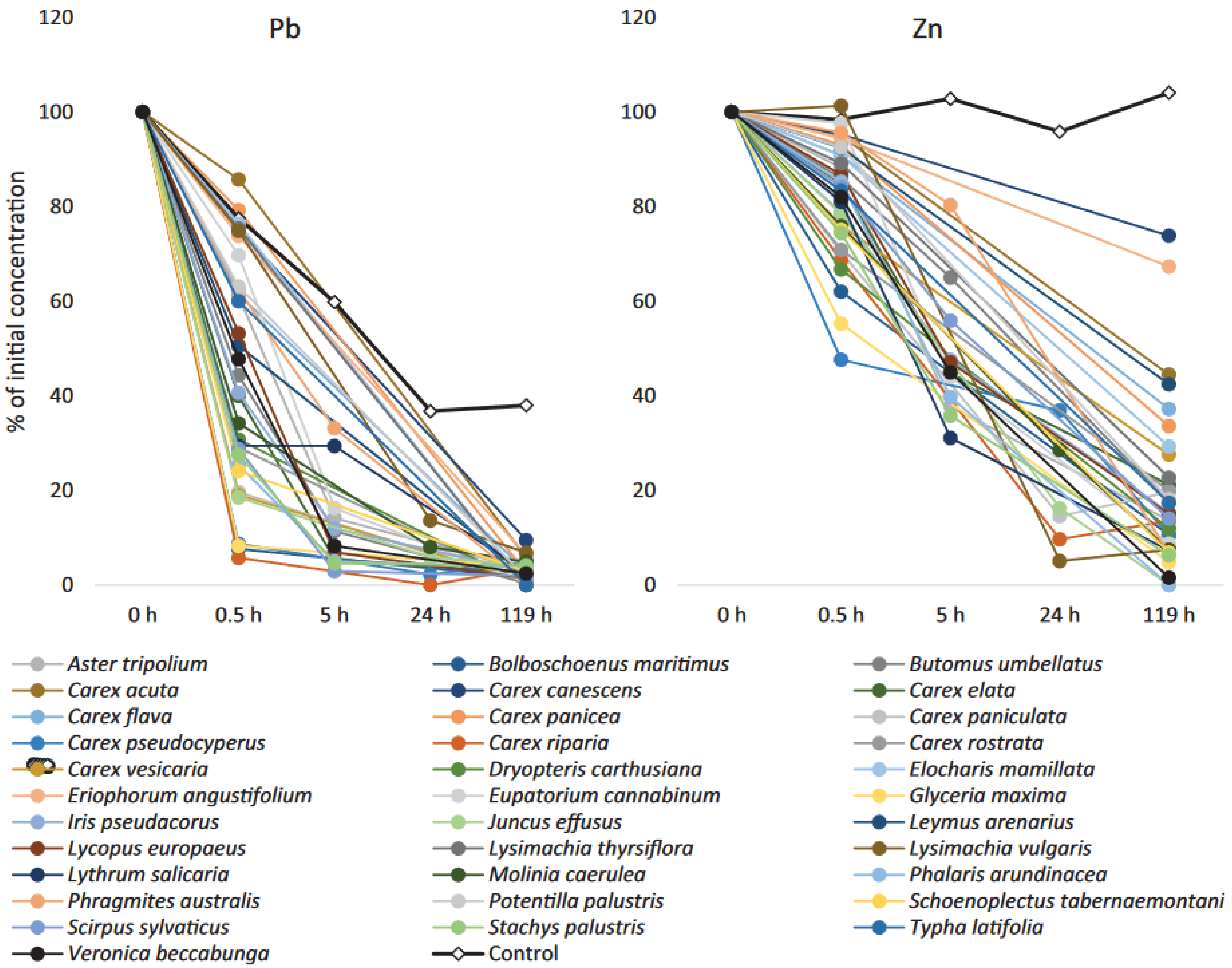
Examples:



https://doi.org/10.1080/15226514.2019.1669529

Plant-caused decreases in heavy metal concentrations in water during 119 h of exposure.

Rhizofiltration: floating wetlands on stormwater

Real-life examples of phytoremediation application:

Chernobyl (fire in nuclear reactor, Ukraine, 1986):

- in-situ phytoremediation of soil and water using flood plots for the removal of Cs and St
- sunflowers were applied, 90% reduction of contamination within 10 days

Detroit, USA (Daimler-Chrysler, 1991/1995): phytoremediation project to fight with Pb contamination

Poland:

- phytoextraction of heavy metals from sewage sludge (Virginia mallow)
- landfill sites restoration (sunflowers)
- post-mine territories

Plant selection for phytoremediation

Ease of planting and cultivation

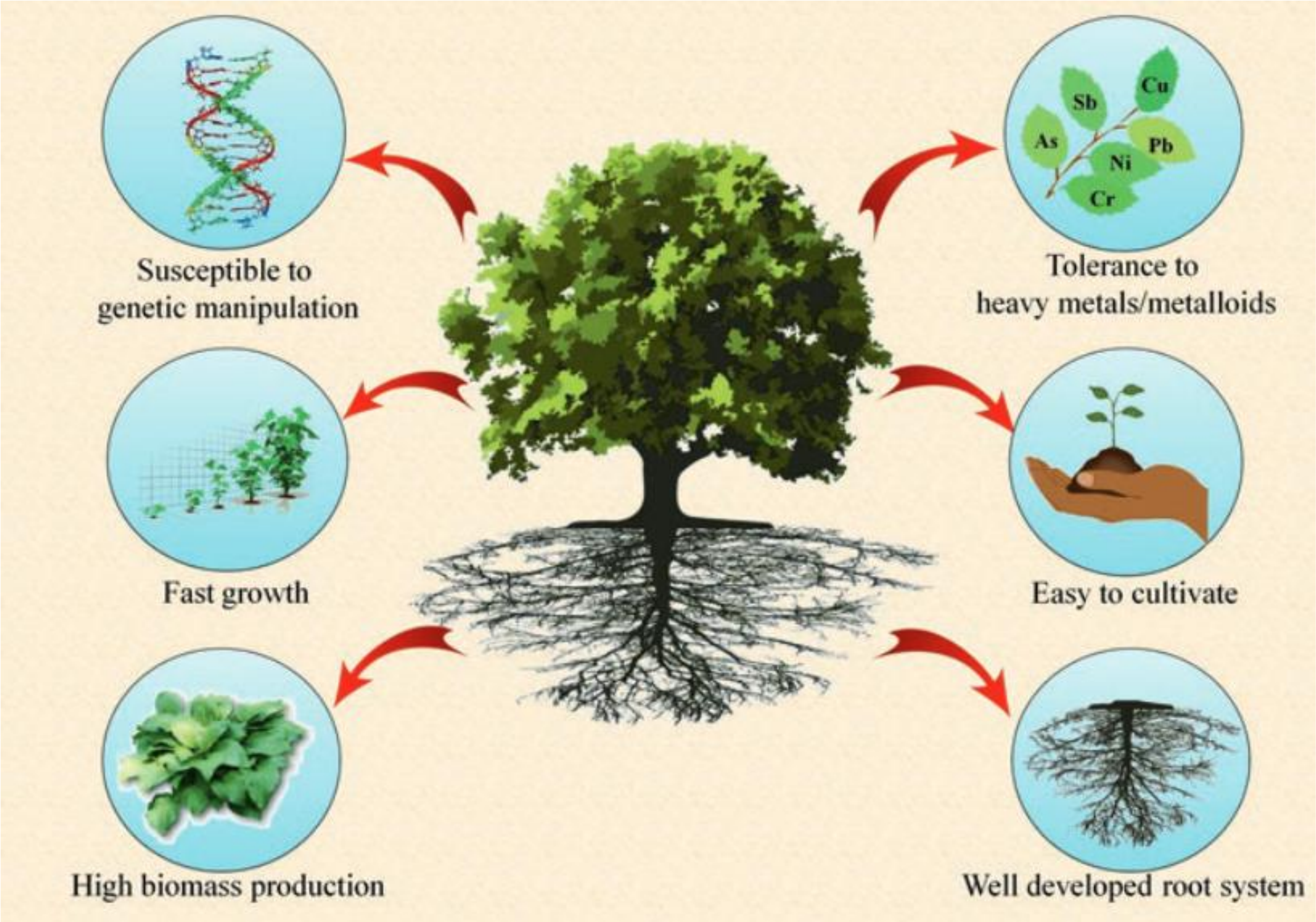
Good adaptability

Fast growth

High biomass yield

High tolerance for contaminants

Advantegous: energy plants



https://link.springer.com/chapter/10.1007/978-3-319-40148-5_17

Define the aim of treatment,
check conditions & concentrations

Select plant

Baltic Phytoremediation Project


Linnæus University

BAPR

Baltic Phytoremediation

Project objective

BAPR goal is to raise cross-border awareness of available green phytoremediation technologies to clean soil from pollutants such as oil, industry related contaminants, heavy metals, nutrients and microplastics through new arenas of cooperation that focus on a circular economy approach

Main outputs

Three pilot cases focusing on innovative plant-based phytoremediation technologies and methods for cleaning polluted soil and then process of energy production from grown crops.

Networking

Working together to promote the project results for further implementation of pilot projects and cross-border knowledge exchange.

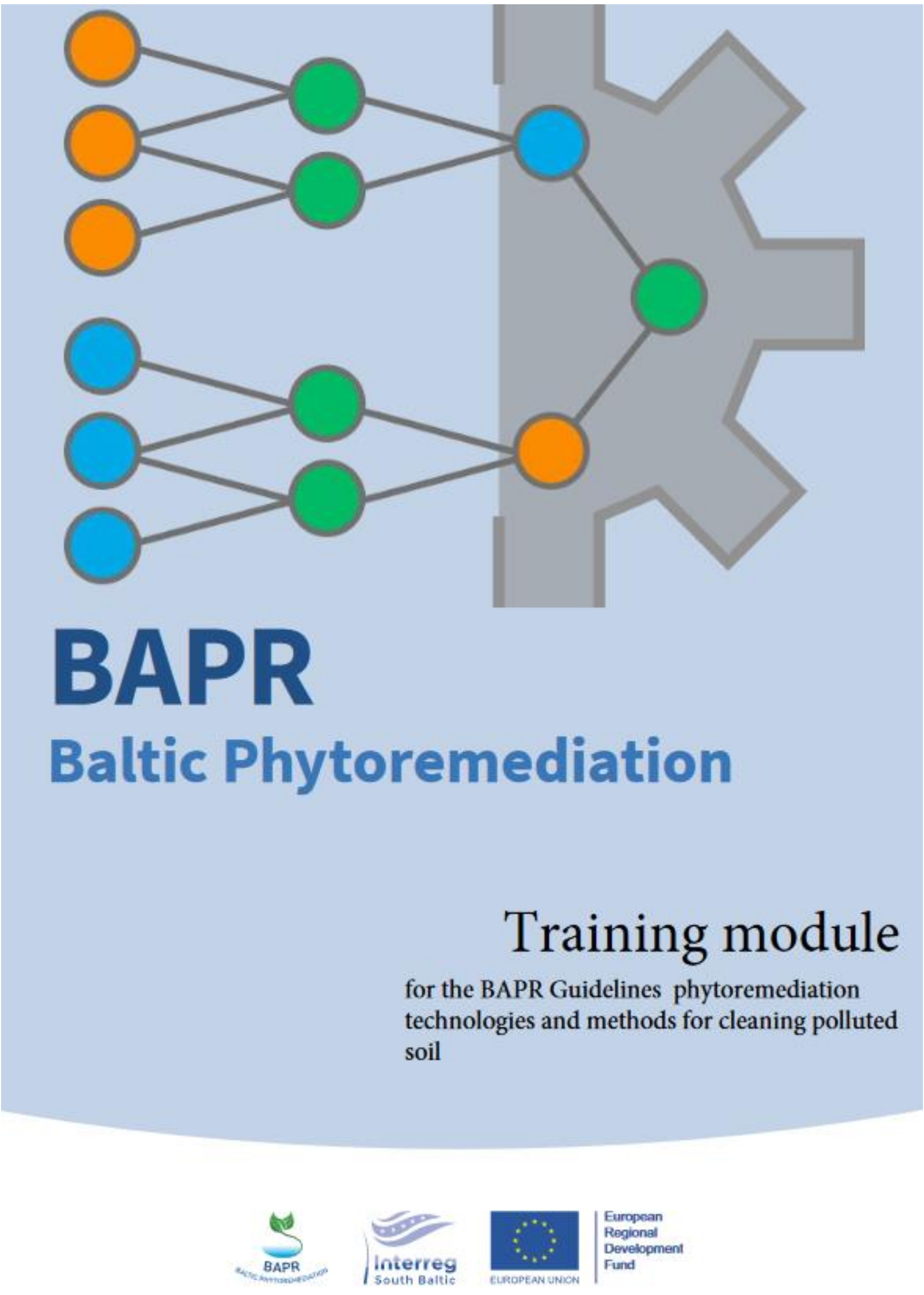
There are 11 partners and associated partners from Europe in the BAPR.

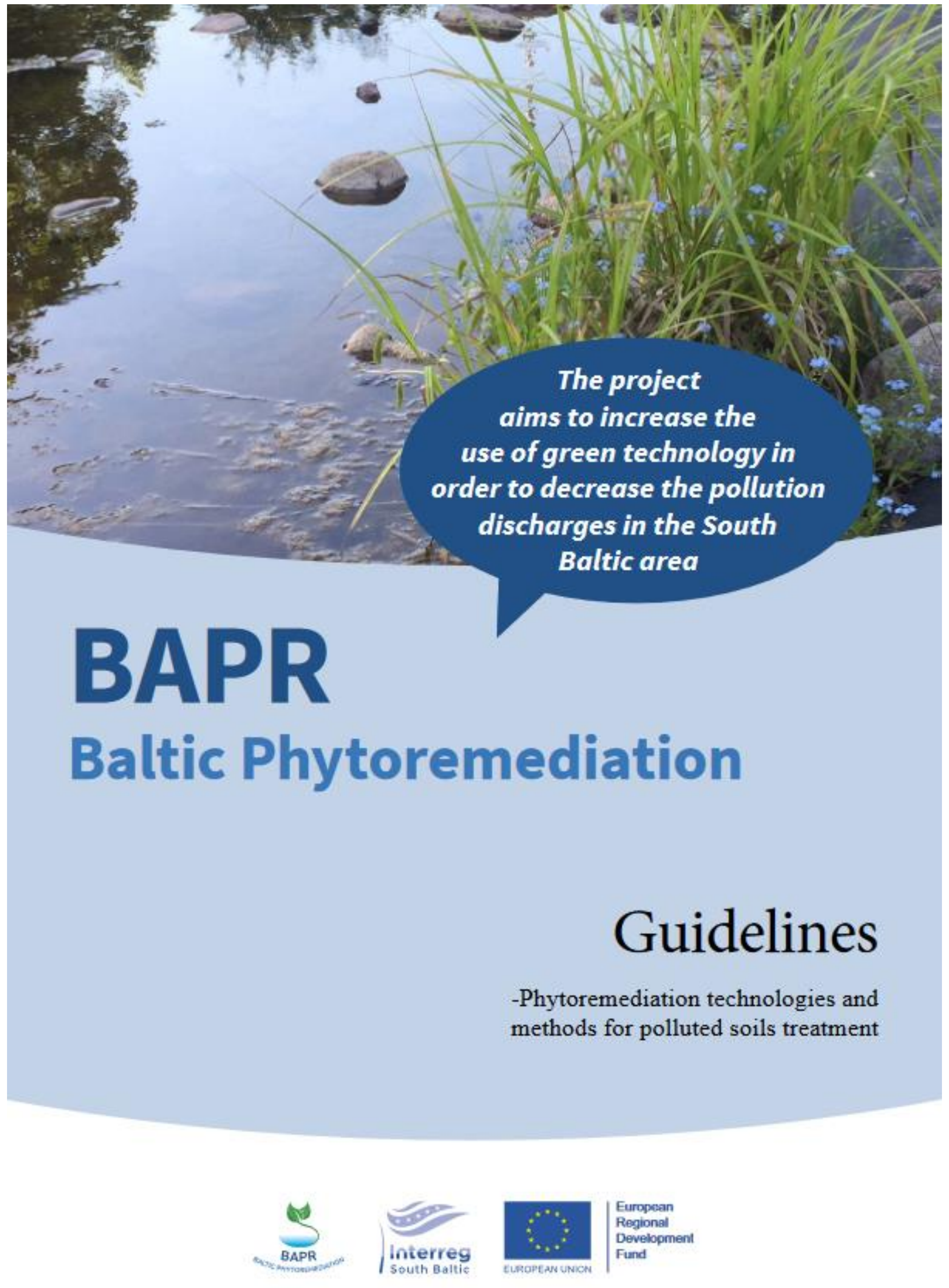
- **Linnaeus University,** Sweden **(lead partner)**
- **NSR AB,** Sweden
- **Gdańsk University of Technology,** Poland
- **Klaipėda University,** Lithuania
- **Gdańsk Municipal Waste Management,** Poland
- **Lithuanian Research Centre for Agriculture and Forestry,** Lithuania
- **Water, waste management and district heating company in Hässleholm,** Sweden
- **The Swedish Embassy in Warsaw,** Poland
- **Roskilde University,** Denmark
- **Latvia University of Life Sciences and Technologies,** Latvia
- **IUC Syd,** Sweden

About the project
BAPR
Baltic Phytoremediation
Lnu.se/en/bapr

Financier
Interreg South Baltic Programme 2014–2020
Total budget EUR 1 357 300

Duration time
1 June 2019–31 May 2022





Information and documents available at:
https://lnu.se/en/research/research-projects/project-baltic-phytoremediation-bapr/

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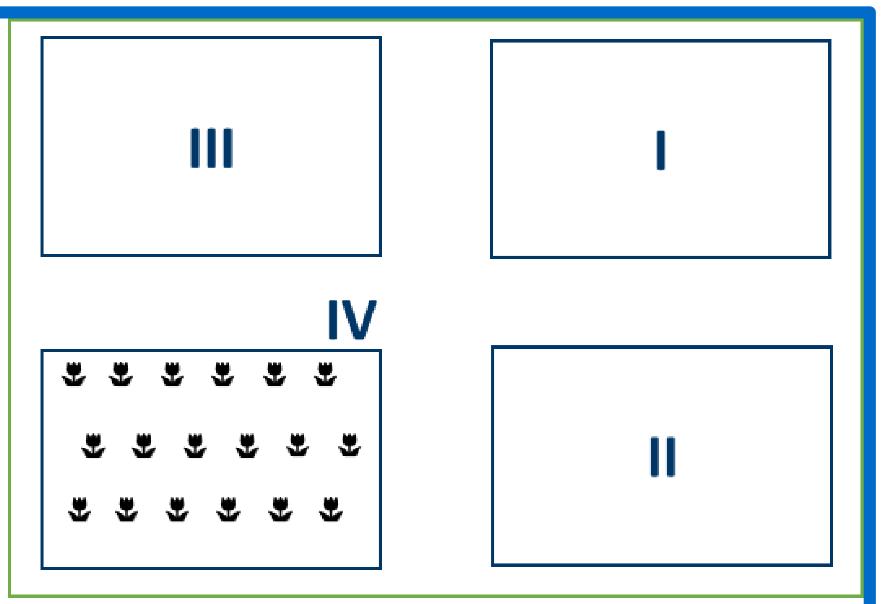
BAPR Pilot Case in Gdańsk

MODULE FOR BIOMASS PRE-TREATMENT AND PROCESSING

- H_2O deionizer
- pH meter
- Dryer
- Furnace for biomass incineration
- Biological assays (phytotoxicity)
- Determination of elements (AAS)
- Basic laboratory equipment

GREENHOUSE A | **GREENHOUSE B**

- *Miscanthus giganteus*
- Reygrass (*Lolium porenne*)
- Pot experiments
- Watering with deionized H_2O
- Additional LED light for growth enhancement
- Automatic regulation of humidity and temperature during vegetation



I – control field – native soil
II – native soil with soil quality improver
III – native soil with soil improver
IV – heavily polluted soil from landfill territory

Object No.	Material/Combination	Dose (Mg·ha^{-1})
1	Control	0
2	Single dose of soil improver	200
3	Double dose of soil improver	400
4	Anthropogenically transferred post-industrial soil	100

Miscanthus x giganteus in remediation of post-industrial soils

A field experiment performed on a Municipal Waste Rendering Plant

Enhancing phytoremediation effects by using a soil improver

10 metals investigated (Al, Fe, Zn, Cd, Cr, Co, Cu, Pb, Mn, Ni), ecotoxicity tests, biomass to energy evaluation

Greenhouse experiments using landfill leachate to test its toxicity and possible positive effects of giant miscanthus

BAPR Pilot Case in Gdańsk

OUTUMN 2020

2020/2021

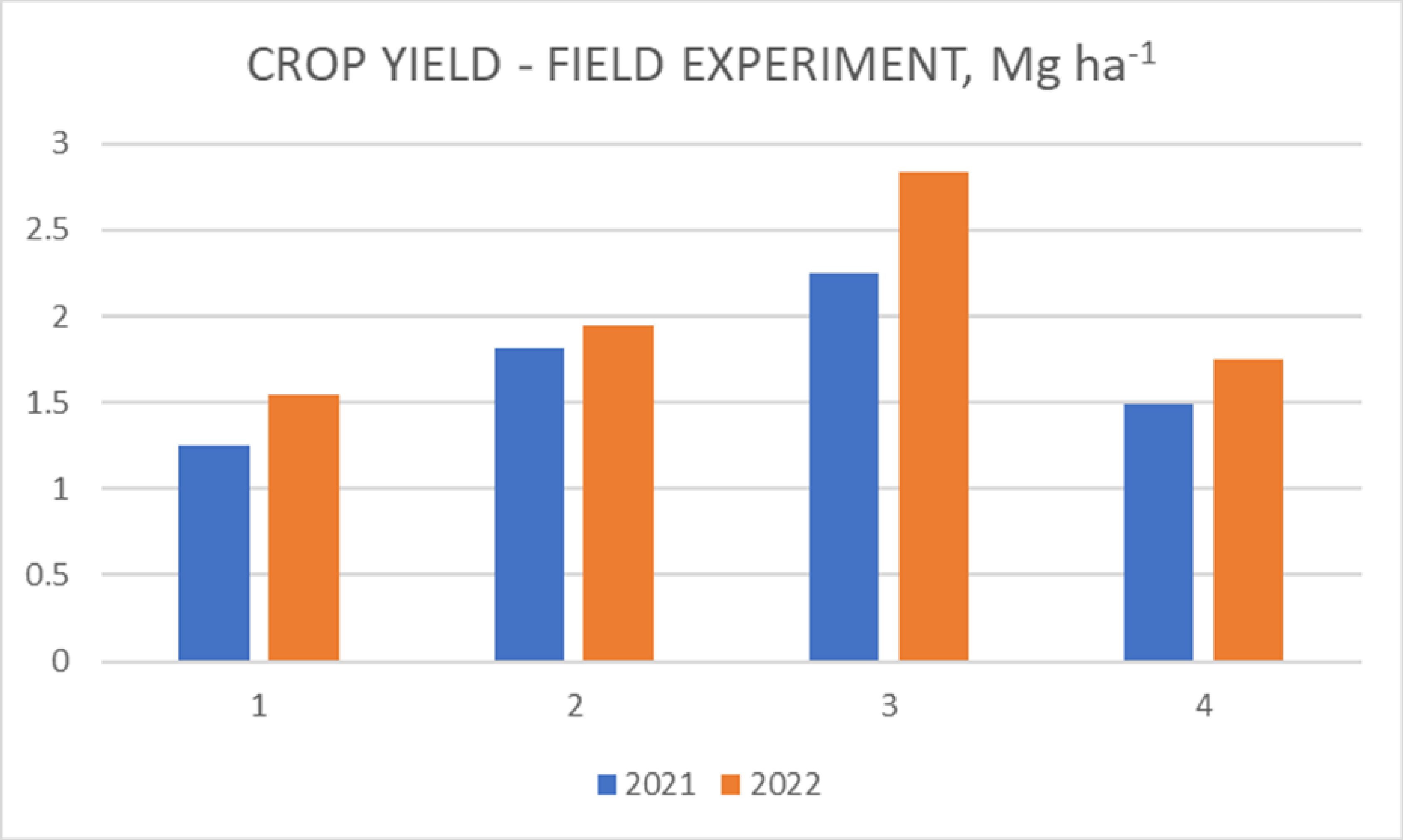
OUTUMN 2022

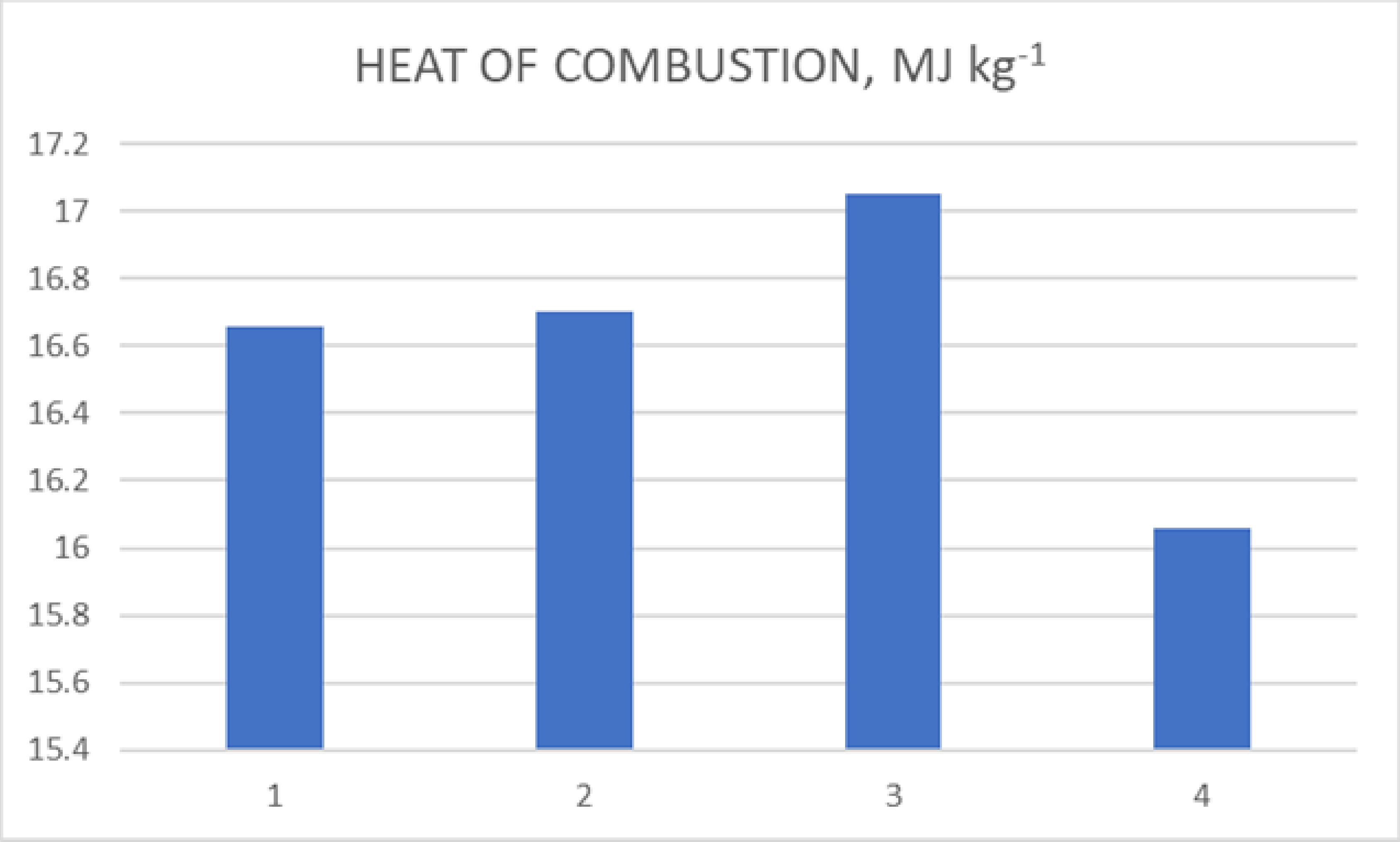
BAPR Pilot Case in Gdańsk

Plant uptake of contaminants, g ha^{-1}

Object	Al	Fe	Mn	Co	Cu
1	92.5 ±1.8	280.5 ±11.7	31.1 ±0.8	0.75 ±0.05	128.8 ±0.5
2	596.3 ±30.5	1036.3 ±83.0	40.3 ±2.3	1.16 ±0.10	17.1 ±0.8
3	273.1 ±1.5	482.6 ±24.1	24.5 ±2.3	1.48 ±0.04	21.7 ±0.7
4	161.8 ±1.5	333.0 ±16.8	33.4 ±2.1	0.93 ±0.08	8.9 ±1.0
Mean value	280.9	533.1	32.3	1.08	44.1
Object	Zn	Cd	Cr	Pb	Ni
1	162.5 ±1.3	0.15 ±0.02	15.5 ±0.6	3.6 ±0.3	8.7 ±0.4
2	92.6 ±5.2	0.30 ±0.04	10.3 ±0.8	11.7 ±1.2	21.4 ±1.7
3	121.1 ±9.0	0.28 ±0.03	7.4 ±0.4	15.5 ±0.9	6.1 ±0.4
4	88.3 ±1.0	0.25 ±0.06	9.9 ±0.9	5.8 ±0.1	10.3 ±1.0
Mean value	116.1	0.25	10.8	9.2	11.6

Uptake of elements (U): product of the dry matter yield (Y) and the content of the component (X), i.e. $U = Y \cdot X$





BAPR Pilot Cases in Lithuania and Sweden

Lithuania: Effects of using sewadge sludge on the accumulation of heavy metals and phytoremediation enhancement

Sweden: Reduction of nutrient levels in the landfil topsoil to reduce pollution of the leachate

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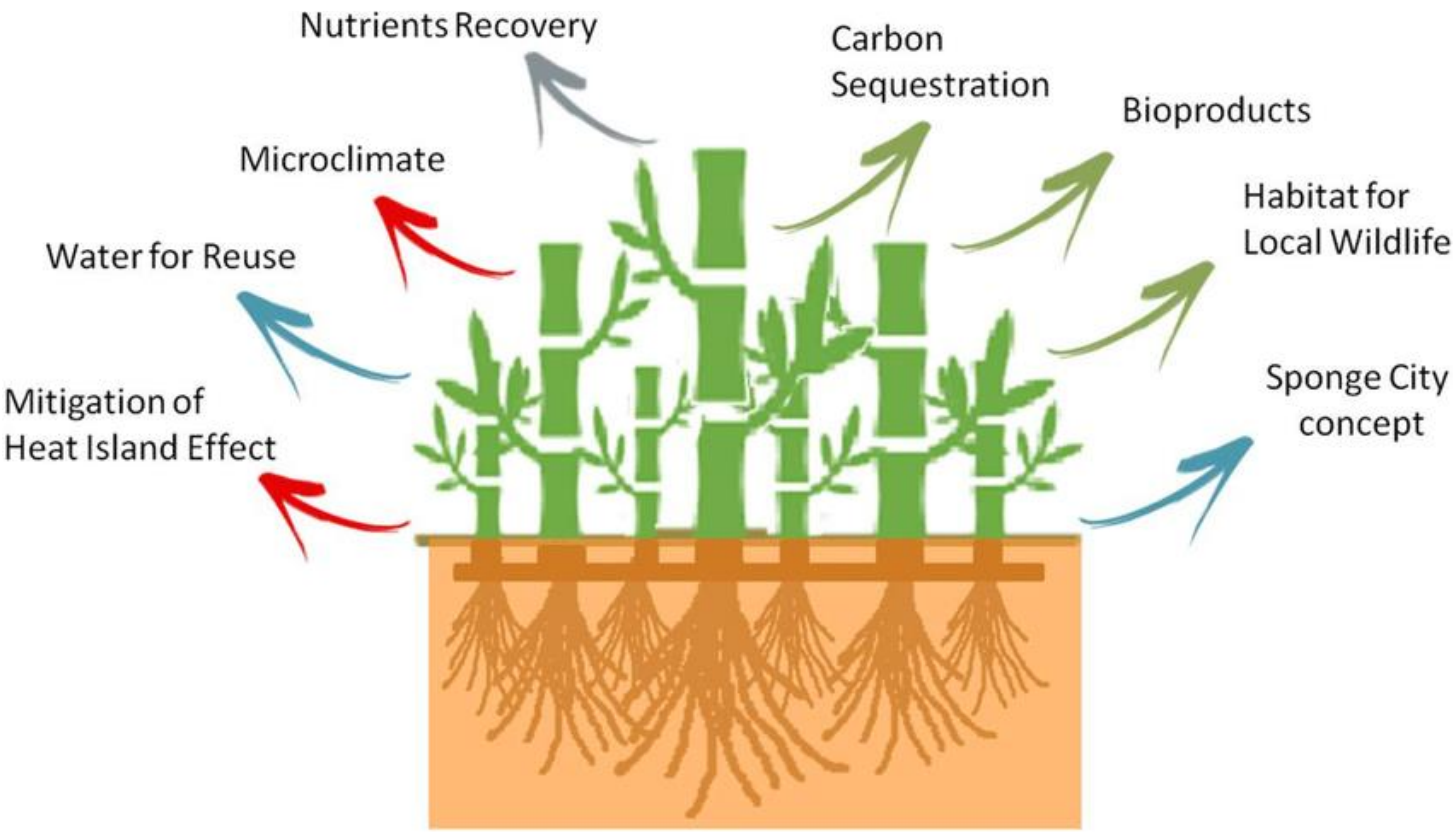

https://link.springer.com/article/10.1007/s11356-022-22304-5

And now: Your opinions / experiences in Your countries?

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