Environ Geochem Health (2021) 43:1319–1325
https://doi.org/10.1007/s10653-021-00852-y

EDITORIAL

Special Issue on "Metallophytes for soil remediation" - Preface

Jaume Bech

Published online: 8 March 2021

1. Background

This collection of papers submitted to this Special Issue is mainly an outgrowth from the Symposium C3.5.2. 21WCSS "Native metallophytes from mine spoils as a potential source for phytoremediation" held in Rio, August 2018.

The ensemble of papers of this Special Issue aims to offer the most recent findings, and state-of-the-art development in phytoremediation technologies using native metallophytes species. It implies a thorough identification of metallophytes colonizing contaminated sites and research in situ and laboratory experiments on the physiological behaviour of these species to cope with high concentrations of metals (loids) in mining, industrial and urban soils. The knowledge of plant physiology, anatomy, biochemistry, ecology, proteomics and genomics will also be essential for understanding the fundaments of plant tolerance.

This special issue contains 26 papers written by authors from 16 countries: Australia, Botswana, Brazil, Chile, China, France, India, Iran, Italy, Nigeria, Portugal, Republic of Armenia, Russian Federation, Spain, Turkey and USA.

This collection of papers is mainly focused on nine topics:

J. Bech (✉)
University of Barcelona, Barcelona, Spain
e-mail: jaumebechborras@gmail.com

1. Soil pollution in vicinity of mines, smelters and power stations.
2. Biochar, charcoal, waste compost.
3. Biochemical indicators and organic pollutants.
4. Treatment of effluents.
5. Chelating activity.
6. Phylogenetic analysis of hyperaccumulators.
7. Nanoparticles.
8. Microbial Activity.
9. Mangrove species.

Research topics

Soil pollution in vicinity of mines, smelters and power stations

There are eight papers in this Special Issue dealing with the topic, soil pollution in the vicinity of mines, smelters and power stations:

Ghazaryan et al. (2020) researched the Cu and Mo accumulation capability, the phytoextraction potential of *Melilotus officinalis* and *Amaranthus retroflexus* and the influence of ammonium nitrate and EDTA on phytoextraction effectiveness. The contaminated soil samples for this investigation under ex situ conditions were collected from the surroundings of the Zangezur Copper and Molybdenum Combine, Armenia. It was found out that *M. officinalis* and *A. retroflexus* are capable of growing in Cu-Mo polluted soils, but a decrease in their growth intensity and chlorophyll content index values was observed. This problem was solved using ammonium nitrate with EDTA. During the growing of the two citated plant species for phytoextraction of soils polluted by Mo are inefficient the use of EDTA, while for Cu the use of chelates is effective and necessary.

Ultra and Manywa (2021) investigated the influence of mycorrhiza and fly ash on the survival, growth and heavy metal accumulation in *Acacia albida*, *Acacia luederitzil* and *Acacia tortilis* grown in Cu-Ni mine soil from Botswana. A two-factor (arbuscular mycorrhiza (AM) inoculation x fly ash) in completely randomized designs was done on each of the three *Acacia* species consist of four treatments: (1) Control, (2) with mycorrhizal, but no fly ash, (3) no mycorrhizal but with fly ash and (4) with mycorrhizal and with fly ash. After 24 weeks results showed that combined mycorrhizal inoculation and fly ash amendment enhanced the establishment of A. luederitzii in heavy metal-contaminated soils by reducing heavy metal availability and metal uptake, thus increasing the survival and dry matter yield of plants.

Conesa and Párraga-Aguado (2021) evaluated the effect of an urban compost amendment on metal allocation in *Pinus halepensis* and *Tetraclinis articulata* growing in a metal enriched soil from an abandoned mine tailings at the La Union Mining, S. Spain. The investigation was made with a pot experimental set-up. A metal speciation was carried out. The amendment increased plant biomass for both trees. However, *T. articulate* is better suited for phytomanagement of metal enriched soils due its higher biomass and lower metal translocation into aerial tree compartments in relation to *P. halepensis*.

Garrido et al. (2020) investigated the accumulation of Sb in leaves of *Dittrichia viscosa* growing in soils of the abandoned Sb mine "San Antonio", Alburquerque, Badajoz, Spain and the effect on the oxidant/antioxidant systems and the photosynthetic efficiency. The authors found the high Sb accumulation capacity in the leaves and an increase in the carotenoids/chlorophyll ratio without affectation of the photosynthetic efficiency. Also they observed increases in total phenolics and in content of the ascorbate and glutathione pools, besides an imbalance between GSH and GSSG. Therefore, it is possible that the increased AsA and GSH content is a key factor in detoxification due to their capacity to chelate Sb. Since *D. viscosa* could be used for phytoremediation.

Hernández-Pérez et al. (2021) proposed the use of wetlands for phytoremediation of potentially toxic elements (PTEs) of areas of mining and maritime influence in Portman Bay (SE Spain). The authors used PTEs tolerant and salinity-resistant macrophytes (*Phragmites australis, Juncus effusus* and *Iris pseudacorus*) in an experiment carried out through an aerobic artificial wetland with representative sediments affected by mining activities in the study area. After six months, rhizosphere, root and aerial parts were collected and evaluated the content of As, Pb, Zn and Cu. From this data the TF and BCF were calculated for each plant in 15 different substrates. Results indicate that these plant species were tolerant to Zn, Pb and As and doubtful for Cu. Therefore the studied species can be considered as phytostabilizing plants and suitable for phytoremediation of polluted coastal mining areas.

Tripti et al. (2021) offered a comparative field study of Ni and Cu accumulation strategies in *Odontarrena obovata* growing on Karabash Cu-rich smelter influence (CSI) and non-Cu influenced (NCi) sites. The total and Na_2EDTA acid extractable metal concentration in soils and plant tissues (roots, stem, leaves and flowers) were determined for CSI and NCI sites. The results show that in the CSI the majority of Cu accumulation was restricted to *O. odorata* roots showing its excluder response. The translocation and bioconcentration factors of Ni > 1 and the foliar Ni concentration $> 1000\ \mu g^{-1}$ indicate that *O. obovata* has Ni-hyperaccumulation potential for both the sites. The species from CSI site showed higher viability due to formation of antioxidants. The high concentration of Cu in the soil has no detrimental effect on Ni-hyperaccumulation ability.

Maiti and Pandey (2021) evaluated the remediation potential of visibly dominant, naturally growing plants from an early colonised fly ash dump near a coal based thermal power station. The vegetation consisted of: grasses like *Saccharum spontaneum* L., *Cynodon dactylon* L., herbs such as *Chromolaena odorata* L., *Thephorosia purpurea* and *Sida rhombifolia* and trees like *Butea monosperma* Lam. Average metal concentrations in the ash samples were in order Mn $>$ Zn $>$ Ni $>$ Cu $>$ Cr $>$ Pb $>$ Cd and in plants Cr $>$ Zn $>$ Mn $>$ Cu $>$ Ni $>$ Pb $>$ Cd respectively. The plants showed fly ash dump phytostabilization potential and accumulated Cr (80,19-178,11 $mgKg^{-1}$) above maximum concentration for plant tissues. The growth of vegetation improved the N and P content of the ash. *S. spontaneum* showed highest biomass is the most efficient plant for restoration of ash dumps.

Chaplygin et al. (2021) estimated the sustainability of cultivated and wild plants of the Poaceae Family to aerotechnogenic pollution in the soil. The content of Pb, Zn, Ni and Cd in couch grass, meadow bluegrass and soft wheat plants grown in the impact zone of Novocherkassk Power Station (NPS) has been analyzed. The content of Pb, Ni and Cd in the grain of soft wheat has exceeded the maximum permissible concentration for food raw materials. Taking into account the translocation factor (TF) and the distribution factor (DC), bluegrass has been found to be the most resistant to anthropogenic pollution. Cultivated herbaceous of Poaceae family are more sensitive to man-made pollution than wild-growing ones.

Biochar, charcoal, waste compost

Five papers in this Special Issue refer to the second topic, biochar, charcoal, waste compost:

Meier et al. (2021) evaluated the effects of three biochars (BCs): chicken manure biochar (CMB), oat hull biochar (OHB) and pine bark biochar (PBB) on Cu immobilization and soil micro communities in a Cu-contaminated soil using *Oenothera picensis*, *Solanum lycopersicum* and *Lolium perenne*. The results showed that the BCs evaluated increased soil pH, reduced the exchangeable Cu and increased Cu bound to organic matter and residual fractions and promoting the plant grown and the soil microbial activity and community diversity. BCs also increased basal respiration and deshydrogenase activity. Authors add that BCs represent an effective tool to remediate Cu-contaminated sandy soils.

Nandillon et al. (2021) evaluate through a mesocosm experiment the effects of applying biochar, compost and iron sulphate alone or combined, to a former mine soil on the soil properties and *Agrostis capillaris* endemic metallicolus and non-metallicolus. Results showed that biochar, compost and iron sulphate amendments improved soil conditions such as soil acidity, reduction of lead bioavailability. The authors concluded that *A. capillaris* metallicolous ecotype, associated with a biochar-compost-iron sulphate amendment, could be a good option for the remediation of the studied former mine site in an assisted phytostabilization.

Rajput et al. (2021) studied the influence of application of biochar and metal tolerance bacteria in polluted soil on morpho-physiological and anatomical of *Hordeum vulgare* L. The model experiment with *H. vulgare* grown in polluted soil evidence an accumulation of heavy metals (HMs) in roots and above-ground parts, a decrease in photosynthesis and transpiration rate, degradation of cell organelles ultrastructure and at tissue level damage. The results of the combined application of biochar and metal-resistant bacteria reduced these adverse effects of soil pollution: reduction of metal bioavailability to *H. vulgare*, improvement of the transpiration rate and anatomical and ultrastructural level. Therefore the use of biochar in combination with metal-tolerant bacteria is an efficient tool for remediation of soils contaminated with HMs.

Lebrun et al. (2021) examined the effect of biochar, ochre and manure amendments (single or combined) associated to a metallicolous ecotype of *Agrostis capillaris* on As and Pb stabilization of a former mine technosol. The authors set up a phytoremediation mesocosm experiment using a technosol from Ag-Pb extraction mine site located in Pontgibaud (Auverne-Rhône-Alpes, France) mainly contaminated by Pb and As. They amended this technosol with biochar, ochre and manure, applied alone or combined. *A. capillaris* plants were grown from seeds collected at the polluted site to test its metal(loid) accumulation ability. The results showed the best improvement in the soil fertility and plant growth using the combined amendments. *A. capillaris* grown in these conditions showing higher root metal(loid) concentration and a lower translocation toward aerial parts.

Kiran and Prasad (2021) researched the phytostabilization of Pb-spiked soils amended with low-cost absorbents as *Prosopis juliflora* charcoal (PJC) and banana waste compost (BWC) and vegetated with *Ricinus communis* L. and increase of soil fertility and enhance plant growth rate. PJC and BWC increased plant growth (number and diameter of leaves, node, plant height) and reduced oxidative stress (lesser production of proline, H_2O_2 and malondialdehyde). FE-SEM coupled with EDS showed high macro and micropores on the surface of PJC while BWC showed significant rise in nutrient context. TG and FTIR analysis of BWC showed increase in carbohydrate and

N. Therefore PJC and BWC decrease Pb phytotoxicity and increase crop production.

Biochemical indicators and organic pollutants

There are three papers in this Special Issue referring to the third topic, biochemical indicators and organic pollutants:

Rossini-Oliva et al. (2021) studied the effect of exposure to high Mn concentration in a metallophyte species, Erica andevalensis using hydroponic cultures with a range of Mn concentrations. At harvest, biomass production, element uptake, and biochemical indicators of metal stress were determined in leaves and roots. Increasing Mn concentrations, decreasing biomass accumulation, increasing malate and oxalate contents in roots, while in leaves increasing citrate and malate contents. Mn was mostly accumulated in the roots and the Species was essential an Mn excluder. But due to the high leaf Mn concentration without toxicity symptoms E. andevalensis might be rated as a Mn tolerant species.

Adejumo et al. (2021) investigated the anatomical changes in roots and leaves of various plant species growing on Pb contaminated sites as well as osmolytes (Proline, PR, Glicine betaine, GB and Phenolics, PH) production and distribution in different parts of them. Authors collected Sporolobus piramidalis, Cynodon dactylon, Imperata cylindrical, Eleusine indica, Gomphrena celosioides, Rhincospora corymbosa and Echinochloa colona. Among these plant species S. pyramidalis had the highest value of PR and GB in the leaf and stem respectively, followed by C. dactylon. On the Pb accumulation in plant G. celosioides accumulated the highest, followed by E. indica. The lowest values were recorded for E. colona. In rhizospheric soils G. celosioides had the highest Pb content. In conclusion, the presence of G. celosioides, S. pyramidalis, I. cylindrical and C. datylon is indicative of Pb polluted soil.

Fedorenko et al. (2021) studied the effects of benzo (a) pyrene (BaP) toxicity on morphology and ultrastructure of Hordeum sativum through an experiment on his cultivation on artificially polluted BaP soil at different concentrations. The BAP content in H. sativum was determined by saponification. The increase concentration of BaP in the soil inhibit the plant growth. The results showed that 4–13% of BaP applied has been absorbed by H. sativum and caused ultrastructural damage. More significant alteration was found in the roots of the plants, and changes in the leaves were observed only at cytological level.

Treatment of effluents

There are two papers in this Special Issue referring to the fourth topic, treatment of effluents:

Minkina et al. (2021) studied the morphological, anatomical and ultrastructural features of macrophyte cattail (*Typha australis* Schum and Thonn) under heavy metals (HMs) contamination in the delta of the Don river and the coast of the Taganrog Bay of the Sea of Azov. The authors observed HMs pollution, mainly of Zn, Cd, Pb in Fluvisols and the Zn, Cr, Cd accumulated in the cattail tissues, that led to reduction of the diameter of the root and the area of its air cavities. Ultrastructural changes in the cell membranes and organelles of the root and leaves, especially in the leaf chlorenchyma have been identified. The degree of adaptative changes to the effects of contamination in the roots is higher than in the leaves. Therefore cattails can be used as biological indicators of Fluvisols pollution.

Santana et al. (2021) investigated the adsorption of Cu and Pb from effluents as an inexpensive efficient technique for removal them. The authors used fava d'anta fodder in its crude and alkalinized form to remove Cu^{2+} and Pb^{2+}. Equilibrium studies were carried out using adsorption isotherms in batch systems with mono and multi-elementary systems containing the two ions. Better results were obtained with the mono-elementary systems. The values of removal efficiency observed for Pb^{2+} were greater than those obtained for Cu^{2+}. This study shows that fava d'anta, especially in its crude form, is an efficient adsorbent for the treatment of synthetic effluents containing Cu^{2+} and Pb^{2+}.

Chelating activity

Two papers in this Special Issue refer to the fifth topic, chelating activity:

Peng et al. (2021) offered a review about a comparative understanding of metal hyper-accumulation in plants. The authors proposed a common mechanism by which elevated expression of key genes involved in chelation of metal contributes to hyper-accumulation and hyper tolerance mainly from studies examining two Brassicacea hyperaccumulators, namely *Arabidopsis halleri* and *Nocea caerulescens* (formerly *Thlaspi caerulescens*). Additionally the authors discussed the role of the cell wall in metal hyperaccumulation, which indicates a slight difference between the Crassulacea and Brassicacea families. Moreover the authors add which enhancements of physiological processes in the plant itself, interactions with rhizospheric and endophytic microorganisms, might also contribute to metal hyperaccumulation in plants.

Da Silva et al. (2021) evaluated the chelating and cytoprotective activity of vanillin against the toxic action of mercury chloride as an alternative for phytoremediation. The authors assessed the vanilling chelating activity and capacity for cytoprotection in prokaryotic, eukaryotic organism and mercury contaminated lettuce seeds, as well as to evaluate its antioxidant and chelating potential. Chelating activity was determined from vanillin's ability to reduce Fe^{3+}. The evaluation of cytoprotection of vanillin in lettuce seeds against mercury chloride was made by test in Petri dishes. The cytoprotection was evaluated with *Escherichia coli*, *Candida albicans* and lettuce seeds. For the microorganisms the evaluation assays against chloride were performed by microdilution. The results show that the vanillin not confer cytoprotection to the prokaryotic and fungal model but it did provide a protection for *L. sativa* seeds allowing a greater and better development of its stem and root.

Phylogenetic analysis of hyperaccumulators for HMs and PAHs

Two papers in this Special issue refer to the sixth topic, phylogenetic analysis of hyperaccumulators for HMs and PAHs:

Drozdova et al. (2021) investigated the accumulation of potentially toxic elements by plants of North Caucasian metallicolous and non-metallicolous Alysum populations and their molecular phylogenetic analysis. Results showed a high heterogeneity of Ni, Co and Zn concentrations between soils and plants. The highest concentration of Ni, Co and Zn had plants from ultramafic and mafic rocks derived soils, as metallicolous population of A. murale and A.gehamense respectively. The concentrations of these metals in plants of non-metallicolous populations from calcareous rocks derived soils, as A. dagestanicum, was lowest. A comparative molecular genetic analysis of the North Caucasian populations of A. murale indicated population differences that correlated with differences of the Ni accumulation in the plants from contrasting soil types. Therefore the selection of metal hyper-accumulator species enhanced phytoremediation efficiency should be considered at the population level.

Rajput et al. (2021) offered a review of phylogenetic analysis of hyperaccumulator plant species for heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs). The present review covers the potential of pollutant accumulation in various plant species; phylogenetic relationships, sources of HMs and PAHs in the soils; mechanisms of tolerance to these pollutants in hyperaccumulators; biotransformation and accumulation potential of hyperaccumulators for the priority HMs and PAHs; hyperaccumulators and their potentials as bioindicators and bioremediators; hyperaccumulators of HMs and of PAHs. The authors performed an evolutionary analysis for hyperaccumulators and found pairs of pollutants that tend to be accumulated by the same or different species and measure the phylogenetic signal for hyperaccumulators of different compounds.

Nanoparticles

Two papers cover the seventh topic of this Special Issue, nanoparticles:

Burachevskaya et al. (2021) investigate the transformation of CuO and CuO nanoparticles (CuO NPs) in Haplic Chernozem and their accumulation by *Hordeum sativum*. The authors used chemical method of analysis and synchrotron radiation X-ray power diffraction, XANES and EXAFS. Results shown that CuNPs underwent a stronger transformation due to the high reactivity of smaller particles due to the formation of complex forms of Cu with organic matter. The application of CuNPs had a greater toxic effect than the macrosized CuO on the plants. The XANES and EXAFS data revealed that CuONPs accumulated in the soil and plants, roots and the aerial parts of H. sativus. This indicates a higher environmental risk when soil is contaminated with CuNPs compared with CuO.

Fedorenko et al. (2021) studied the toxic effect of CuO of different dispersion degree on the structure and ultrastructure of spring barley (*Hordeum sativum* *distichum*) cells. The results shown that a greater toxic effect has been exerted of CuO nanoparticles as compared to the macro-dispersed form. A comparative analysis of the toxic effects of Cu oxides and Cu-nano-oxides on plants has shown changes in the tissue and intracellular levels in the barley roots, although qualitative changes in plant leaves have not been observed. The authors taking account cytomorphometric, ultrastructural data and data on the Cu content in plants, conclude that CuO nanodispersed entering from the soil into the plants and can accumulate in it.

Microbial activity

One paper in this Special issue refers to the eighth topic, microbial activity:

Shtangeeva (2021) has investigated couch grass and wheat for phytoextraction of large amounts of Br, Eu, Sc, Th and U by means of greenhouse ad field experiments. The author compared bioaccumulation abilities of the plants with those of some other plant species grown under the same conditions. Also tested effects of inoculation of seeds with *Cellulomonas* bacteria on phytoextraction of the trace elements from contaminated soils. The results showed that couch grass and wheat were capable of accumulating trace elements without side effects. Infection of seeds with bacteria stimulated an uptake of Eu, Th and U from contaminated soils and their translocation to upper plant parts. Therefore couch grass and/or wheat either alone or with microorganisms may be successfully used for phytoextraction of trace elements from contaminated soils.

Mangrove species

One paper in this Special issue refers to the ninth and last topic, mangrove species:

Wang et al. (2021) analyzed absorption, concentration and distribution of Cr, Cu, Zn, As, Cd and Pb in the mangrove species *Aegiceras corniculatum*, *Kandelia candel* and *Ceriops tagal* and their rhizosediment from Hainan Island, South China. The results found that the content of Zn and Cr was the highest, while that of Cd the lowest. The organ ranking of the bioconcentration factor BCF in the different mangrove species is: BCF root > BCF stem > BCF leaf. The transfer factors in leaves and stems of mangroves (TF) values of Cu and Zn were high, while Cd had the lowest TF value. Roots of mangroves had strong absorption capacity to availability of Cu and Zn.

Conclusions

The subject of this Special Issue "Metallophytes for soil remediation" is of great importance and the 26 papers cover significant aspects of fundamental theoretical and applied research in Metallophytes for soil remediation, providing advances to the existing knowledge.

Acknowledgments I would firstly to thank the Co-Guest Editor Prof. Dr. Maria Manuela Abreu (Universidade de Lisbon, Instituto Superior de Agronomia, Linking Landscape, Environment, Agriculture and Food Research Centre, LEAF, Portugal) and Co-Guest Editor Prof. Dr. Xunwen Chen for their valuable collaboration. Moreover, I would like to thank the authors for their contributions and for their patience with the reviewing process as well as the reviewers for their observations. Their efforts have improved the quality of this Special Issue. I am extremely grateful to Prof. Dr. Ming Hung Wong Editor –in-Chief of EGAH; Dr. Sherestha Saini, Senior Editor; Karthick Govindaraju, Production Editor; Dr. Suganya Manoharan, Production Editor; Ms. Sherine Joseph, Handling Editor; Crystal Lin Siyi, Assistant to Prof. Wong and Ms. Suganya Gunasekar JEO Assistant. Help with English from James Dove and IT assistance from Oriol Bech is also greatly appreciated. Without whose knowledge and experience this Special Issue could never have been published.

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