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Phytoremediation of potentially toxic elements and rare earth elements by perennial plants in floating wetlands

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Doctoral dissertation

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ABSTRACT

The impact of urbanization, industrialization, agriculture, mining, and stormwater runoff on ecosystems has resulted in significant water pollution concerns worldwide. Significant attention has been paid to the removal of potentially toxic elements (PTE) and metalloids (e.g., arsenic (As), selenium (Se) and lead (Pb)) by various plant species. However, little research has been published on the simultaneous accumulation of cadmium (Cd), chromium (Cr), and nutrient removal, by floating treatment wetlands (FTW), from stormwater runoff, and the accumulation and recovery of rare earth elements (REE) through energy biomass cultivation. This research bridges knowledge gaps in the remediation of REE using short-rotation willow (*Salix* spp.) and simulated stormwater remediation of Cd and Cr with *Phragmites australis* and *Iris pseudacorus*. In this context, three different microcosm experiments were conducted with perennial plants (*P. australis* and *I. pseudacorus*) in FTW. Stem growth, dry biomass, root length, chlorophyll content index (CCI), anatomical plant tissue changes, Cd accumulation and N and P removal from simulated stormwater were investigated over a 50-days period under different Cd doses (0, 1, 2 and 4 mg L^{-1}). In addition, the effects of Cr dose (0, 500, 1000 and 2000 µg L^{-1}) on the growth and anatomy of *P. australis* and *I. pseudacorus*, as well as on the accumulation of Cr in plant biomass and N and P removal were studied in FTW over a 50-day period. In addition, the effects of REE doses on stem growth, dry biomass, root length and their accumulation in biomass were investigated in two *Salix* species (*S. myrsinifolia* and *S. schwerinii*) and two cultivars (Klara and Karin) in FTW over a 28-day period. The REE treatments contained a single-dose of lanthanum (La: 50 mg L^{-1}), multi-solute of six-REE (La: 11.50 mg L^{-1} + yttrium (Y: 11 mg L^{-1}) + neodymium (Nd: 10.50 mg L^{-1}) + dysprosium (Dy: 10) + cerium (Ce: 12 mg L^{-1}) + terbium (Tb: 11.50 mg L^{-1})) and control (without REE). Moreover, REE recovery from biomass ash after combustion was investigated. In this study, *P. australis* and *I. pseudacorus* growth parameters were not hampered by Cd stress, their roots accumulated more Cd than the shoots and were capable of lowering N and P concentrations. The impact of Cr was more evident on plant growth under the low- and medium doses (500 and 1000 µg Cr L^{-1}). However, anatomical changes were observed under the high dose (2000 µg Cr L^{-1}, respectively). Both species were able to remove a substantial (98–99%) concentration of N and P within a 10-day period of increased Cr loading. The greatest amount of Cr was retained in *P. australis* and *I. pseudacorus* roots. *Salix* species and cultivars did not show REE toxicity symptoms and displayed a strong growth response compared to the control. All *Salix* accumulated REE in their biomass, although the greatest amounts of accumulated REE were found in the roots of the Klara and Karin cultivars. The substantial deposition of Cd and Cr in the roots of *P. australis* and *I. pseudacorus*, and REE in the *Salix* roots show their phytostabilization potential. Approximately 80% of the REE was retained in the *Salix* ash following combustion of the biomass at 1000 °C. The findings in this research reveal that these perennial plants could be suitable candidates to control the runoff from Cd, Cr and REE affected waterbodies into freshwater resources through immobilization aligned with efficient biomass production.

Keywords: phytostabilization; macrophytes; eutrophication; stormwater; biomass; *Salix*; *Phragmites australis*; *Iris pseudacorus*

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LIST OF ORIGINAL ARTICLES

Reprints of articles **I** and **III** are provided with permission from the respective journals.

I. Mohsin, M., Nawrot, N., Wojciechowska, E., Kuittinen, S., Szczepańska, K., Dembska, G., Pappinen, A (2023) Cadmium accumulation by *Phragmites australis* and *Iris pseudacorus* from stormwater in floating treatment wetlands microcosms: Insights into plant tolerance and utility for phytoremediation. Journal of Environmental Management, 331, p. 117339.

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Author's contribution

Muhammad Mohsin contributed to the experimental set-up, data collection and writing of the original draft of articles **I−III**. Ari Pappinen supervised and planned the experimental design of article **III**. Ewa Wojciechowska supervised and planned the experimental design of articles **I** and **II**. Nicole Nawrot contributed to the experimental set-up, data collection and writing of articles **I** and **II**.

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ABBREVIATIONS

Phragmites australis	*P. australis*
Iris pseudacorus	*I. pseudacorus*
Salix schwerinii	*S. schwerinii*
Salix myrsinifolia	*S. myrsinifolia*
Salix viminalis	*S. viminalis*
Salix dasyclados	*S. dasyclados*
Salix burjatica	*S. burjatica*
Heavy metals	HM
Copper	Cu
Nickle	Ni
Zinc	Zn
Cadmium	Cd
Lead	Pb
Chromium	Cr
Arsenic	As
Mercury	Hg
Manganese	Mn
Iron	Fe
Nitrogen	N
Total Nitrogen	TN
Phosphorus	P
Total Phosphorus	TP
Rare earth elements	REE
Lanthanum	La
Neodymium	Nd
Yttrium	Y
Cerium	Ce
Potentially toxic elements	PTE
Ethylenediaminetetraacetic acid	EDTA
Nitrilotriacetic acid	NTA
Ethylene diamine disuccinic acid	EDDS
Low-molecular weight organic acids	LMWOA
Floating treatment wetlands	FTW
Dry biomass tolerance index	DBTI
Stem length tolerance index	SLTI
Root length tolerance index	RLTI
Translocation factor	TF
Bioconcentration factor	BF

1 INTRODUCTION

Cadmium (Cd), chromium (Cr), lead (Pb) copper (Cu), nickel (Ni), zinc (Zn) and manganese (Mn) are all potentially toxic elements (PTE) that enter the environment through natural and human sources (Briffa et al. 2020). Of these, Cu, Ni, Zn and Mn are considered beneficial elements that are required in small concentrations by plants, but at high levels can become toxic for plants (Arif et al. 2016). In contrast, Cd, Cr and Pb are typically toxic to plants, even at low concentrations (Finnegan and Chen, 2012). Globally, PTE are discharged into soils and waters from the extraction and smelting of mineral resources, as well as from the use of chemical fertilizers and pesticides, thereby resulting in serious environmental pollution (Xu et al. 2019). According to Nkoh et al. (2022), around 9 million people die prematurely in the world each year due to environmental pollution. According to one estimate, 80% of global wastewater is released into the environment without adequate management (UN Water, 2018). Industrial wastewater usually contains multiple contaminants, including PTE such as arsenic (As), mercury (Hg), Pb, Cu, Cr, Cd, and nutrients, such as ammonium ($NH4^{+}$), nitrate (NO_3^{-}), phosphate ($PO4^{3-}$)), and organic pollutants (e.g., pharmaceuticals contained in personal care products and dyes). Once these pollutants are in the wider environment, they adversely affect animal and human health through the food chain (Nkoh et al. 2022). Rare earth elements (REE) are widely used in high-tech industries, and substantial amounts are released into soil and water ecosystems, which leads to the generation of environmental complications (Lu et al. 2022). According to Gwenzi et al. (2018), urban wastewater treatment systems and mining activities, which receive diverse run-offs or leachates from industrial and hospital wastewater, and solid waste disposal sites, are the predominant sources of REE discharge into aquatic ecosystems. Phosphate rock is mostly used for the manufacturing of phosphate (PO_4^{3-}) fertilizers, animal feed and detergents, while applications of phosphate fertilizers in agriculture have enhanced the PTE and REE concentrations in soils (Lima and Ottosen, 2021). In particular, roadside soils have been recognized as enriched in REE, for example Nd and Ce, as compared to adjoining areas (Mleczek et al. 2018), while rivers and estuarine environments are also subject to REE contamination (Barbera et al. 2021). A study conducted by Lima et al. (2022) identified stormwater retention ponds in the urban environment as sinks of leachable REE, and that substantial amounts of leachable REE were also been observed in coal fly ashes.

Urban stormwater runoff originates when rain or snow melts over the ground and is one of the main problems in the management of water pollution in the modern era. Moreover, it is a significant factor in the global degradation of water bodies. Stormwater holds a diverse range of contaminants, from large debris to microscopic particles, as well as soluble and insoluble chemical constituents (Malaviya and Singh, 2012). The main causes of stormwater pollution are discharges from human activities, such as fertilizers and pesticides, leaching and corrosion of pollutants from exposed materials, the washing of cars, the dumping of paint and oil into storm sewers, and traffic-related discharges, such as exhaust from moving vehicles, tire and brake dust, and road debris, the use of deicing agents, and paint marking on roads (Eriksson et al. 2007). Surface dust in the urban environment contains a large amount of organic pollutants and PTE, which originated from traffic and industrial activities (Wang et al., 2020; Yu et al. 2023), and is considered a major source of urban environmental pollution due to its interaction with the soil, surface water, and the atmosphere. In the urban environment, PTE are primarily introduced into stormwater through the wash-off of atmospherically transported material, such as vehicle emissions, and the breakdown of common building materials, such as concrete, galvanized materials, bricks and tiles (Davis et al. 2001), and surface dust (Yu et al. 2023). Therefore, environmentally sustainable measures are needed to protect society and the environment.

According to Leito et al. (2018), there are over 2.5 million potentially polluted sites in Europe, 14% of which require immediate attention. By 2025, the total number of polluted sites that will require remediation could increase by 50% (Rampanelli et al. 2021). In Finland, mining practices, shooting ranges, landfill leachates and impregnation plants have all contributed to a decline in ground water quality, through the release of PTE into aquatic ecosystems (Mohsin et al. 2019). Eutrophication is the main environmental problem in the Baltic Sea, which is driven by excessive inputs of nitrogen (N) and phosphorus (P) from rivers and the atmosphere and has led to increased sedimentation of organic material and oxygen depletion in the bottom layer and the internal loading of P (Petrov and Yakusheva, 2021). The presence of N and P in the aquatic environment is essential for the growth and function of diverse organisms, but elevated quantities can be detrimental (Tang et al. 2017). The leaching of N and P in Finnish watercourses has been reported as 47% and 38%, respectively, and agricultural activities have been recognized as the leading source of nutrient release (Lyytimäki et al. 2007; Mohsin et al. 2021). Moreover, N and P release to surface water bodies primarily originates from agricultural and industrial wastewater runoff, sewage, fossil fuels, stormwater runoff and domestic wastewater (Tang et al. 2017; Mustafa and Hayder, 2021). A study by Shen et al. (2021) reported that the concentration of total nitrogen (TN) and total phosphorus (TP) in most natural water bodies was within 0.95–8.56 mg $L^{-1}$and 0.04–0.73 mg L^{-1}, respectively. Moreover, about 301,565 tonnes of N and 14,845 tonnes of P have been discharged from Polish territory into the Baltic Sea, which is equivalent to 30% and 39% of total inputs into the Baltic Sea and makes Poland the fifth highest polluter among the Baltic region (Wojciechowska et al. 2019).

1.1 Heavy metals (HM) and rare earth elements (REE)

The terms "heavy metal" or PTE" denote the group of metals and metalloids with an atomic density > 4–5 g/cm^{-3}, an atomic number > 20 and atomic weights in the range of 63.5–200.6 g mol^{-1} (Garbarino et al. 1995). Various HM such as Pb, Cr, Zn, Cd, iron (Fe), Cu, Mn and Ni are released from different industrial manufacturing processes through water and solid waste discharges (Ghaly et al. 2014). The toxicity of PTE or HM is considered the main pollutant in European soils and groundwater (Bartucca et al. 2022). Approximately 23 metals have been classified as HM to date, with Pb, Cd, cobalt (Co), Cr, and Hg the most common, and have potentially toxic significances at both low and high concentrations (Al-Rubaie and Al-Kubaisa, 2015; Wani et al. 2023). Pourret and Hursthouse (2019) classify these elements as PTE rather than HM due to their toxic nature. The natural environment suffers from the pollution caused by the continuous accumulation of PTE and metalloids that are produced from various industrial practices, such as ore mining and from the improper disposal of metal-containing waste. Additional sources of pollution include chemical residues from gasoline and paint, excessive use of chemical fertilizers in agriculture, the application of sewage sludge, insecticides and pesticides, as well as the utilization of wastewater for agricultural purposes. Furthermore, residues from coal combustion, organic hydrocarbon spills and atmospheric deposition contribute to the pollution burden (Zhang and Wang, 2020). The extensive mining of ores exacerbates the issue, as the residues that contain elevated levels of metals find their way into the soil system, thus contaminating both the surface and groundwater (Verma and Dwivedi, 2013). From the soil and water, PTE then accumulate in animal manure through the intake of metal-contaminated food and water by livestock (Chen et al. 2020). Excessive amounts of PTE in the soil can cause disruption of plant function and metabolism, alter biochemical pathways, and impede nutrient uptake, leading to low productivity and growth retardation in plants. Potentially toxic elements can also affect the uptake of micro/macronutrients and inhibit the plant metabolic system (Finnegan and Chen, 2012).

Cadmium obstructs plant growth and elevated concentrations in cereals and fruits has been shown to induce a significant impact on human health through food chain bioaccumulation (Dou et al. 2022). Cadmium concentrations > 5 µg g^{-1} have been reported as toxic to many plants (White and Brown, 2010). Each year, approximately 30,000 tonnes of Cd are emitted into the atmosphere, of which 4000–13,000 tonnes are the result of human activities (Rios and Méndez-Armenta, 2019). The permissible concentration of Cd in the soil and water are reported as 0.01–1.1 mg kg^{-1} and 0.01 mg L^{-1}, respectively, and its exposure to plants inhibits various physiological processes, such as photosynthesis, respiration, cell division, mineral nutrition, protein degradation and gene expression, which consequently results in poor biomass production (Mathur et al. 2022).

Chromium is also another PTE that induces toxicity symptoms in plants, such as the inhibition of plant growth, germination, root development, chlorosis and necrosis, and alterations in physiological biochemical parameters (Di Luca et al. 2023). According to Sultana et al. (2014), Cr toxicity in aquatic environments is dependent on two oxidation forms: Trivalent Cr (III) and hexavalent Cr (VI), with the latter more harmful to plants and animals. Elevated Cr concentrations also have human health complications, leading to gastric, kidney and liver damage. According to the Environmental Protection Agency and the European Union, the highest permissible Cr discharge into surface and potable waters is set at < 0.05 mg L^{-1} (Baral and Engelken, 2002), while the World Health Organization has set the admissible Cr discharge limit in wastewater at 0.05 mg L^{-1} (Younas et al. 2023).

Rare earth elements were discovered in 1794 by the Finnish scholar John Gadolin (Tao et al. 2022) and are considered as a critical component in modern-day technology (Ramprasad et al. 2022). They contribute to advanced electronics, electrical motors, and diagnostic and scanning equipment in medical fields as they are highly conductive, magnetic, luminescent, phosphorescent, electrochemical and display catalytic properties (Rangabhashiyam and Vijayaraghavan 2019). However, REE use is not limited to the electronics industry, medicine, and production, as agriculture and renewable sources of energy have also significantly utilized REE (Lu et al. 2022). The International Union of Pure and Applied Chemistry (IUPAC) defines REE as 15 lanthanides with atomic numbers that range from 57–71, and two transition elements with atomic numbers 21 and 39. These include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc) and yttrium (Y). These elements exhibit similar chemical properties, as the configurations of their outermost and sub-outer electron layer are similar (Gwenzi et al. 2018; Tao et al. 2022).

Globally, there are approximately 110 million tonnes of REE reserves. In 2019, REE production was approximated 210,000 metric tonnes, which is likely to increase to almost 400,000 tonnes by 2035 (Hanana et al. 2022). There are two distinct types of REE namley light earth elements (LREE), which include La, Ce, Nd, Pr, Pm, Sm and Eu, and heavy earth elements (HREE), which include Gd, Tb, Dy, Y, Ho, Er, Tm, Yb and Lu (Zhou et al. 2017). Of these, Ce, La and Nd are the most abundant REE on the planet (Wall 2014). Moreoevr, REE are categorized as critical resource materials of modern industry, and so are extremely important constituents for high technology industrial applications (Arienzo et al. 2022). However, REE toxicity with regard to commercial plant species in terms of growth reduction, chlorosis, photosynthesis disruption, and eventually plant death, has been reported (Zhang et al. 2023). On the other hand, REE have contributed to agriculture as fertilizers to improve crop production (Pang et al. 2002), as substitutes for feed-growth antibiotics in the EU, and have the potential to enhance milk, meat and eggs production (Chen et al. 2022). To date, REE studies in plants have only been conducted in a few countries, and a better understanding of the effects of bioaccumulation in plants is needed (Ramos et al. 2016). Although significant REE contamination REE has been detected at mining sites, and REE has been recognized as a crucial resource in various fields, concerns with regard to REE pollution are still in their nascent stage. In this context, it is important to recover REE from natural deposits that include industrial wastes or mining areas, through the implementation of environmentally friendly green technologies that will also improve the circular economy.

1.2 Sustainable Solutions for Pollution Control — Phytoremediation and Floating Treatment Wetlands

The scientific community has shown interest in the restoration of PTE polluted soils and water by developing suitable economic technologies (Oladoye et al. 2022). In this context, the environmentally sustainable and cost-friendly "phytoremediation" approach is considered as a realistic substitute for more technologically advanced methods (Rezania et al. 2016). This approach is in line with those defined in the UN Sustainable Development Goals 13 (climate action) and 15 (life on land). Phytoremediation of polluted soil and water using plants is not only efficient, cost–effective and eco-friendly, but may also produce biomass, promote valuable metal recovery for the development of the bioeconomy, and fulfil environmental protection requirements (Nawrot et al. 2021). Thus, an integrated approach that combines land remediation with post-process energy and high-value element recovery from biomass could significantly increase the financial viability and reduce the environmental impact of biomass disposal (Jiang et al. 2015).

Plants provide a root surface area for microbial colonization and emit exudates that include nutrients, oxygen, enzymes and amino acids into the root zone/rhizosphere, which stimulate the microbial population and eventually enhance compound bioavailability and speed up the metal degradation process (Martin et al. 2014). To better understand how PTE respond within plants systems, phytoremediation technology has been categorized into a number of diverse strategies, such as phytoextraction, phytostabilization, phytovolatilization and rhizofiltration. Phytoextraction is a process that involves the absorption, accumulation and translocation of PTE from water or soil into the shoots of plants. The success of phytoextraction depends on factors such as the shoot biomass and root structure of the plant. Phytostabilization, on the other hand, involves the use of plants with productive root systems and high tolerance to PTE to sequester the elements in their roots or adsorb them in the root cell wall, thus preventing their migration into the surrounding environment. In phytovolatilization, plants absorb PTE from the water or soil and transform their toxic form into a less or non-toxic form through complex metabolic pathways, such as assimilation, or release it to the atmosphere in a gaseous form via evapotranspiration (Oladoye et al. 2022). Rhizofiltration is a promising biological method that uses plant roots to fix, extract, immobilize and adsorb PTE from contaminated water, and integrates both phytoextraction and phytostabilization (Glick, 2010; Bousbih et al. 2023). A concise representation of phytoremediation technologies is depicted in Figure 1.

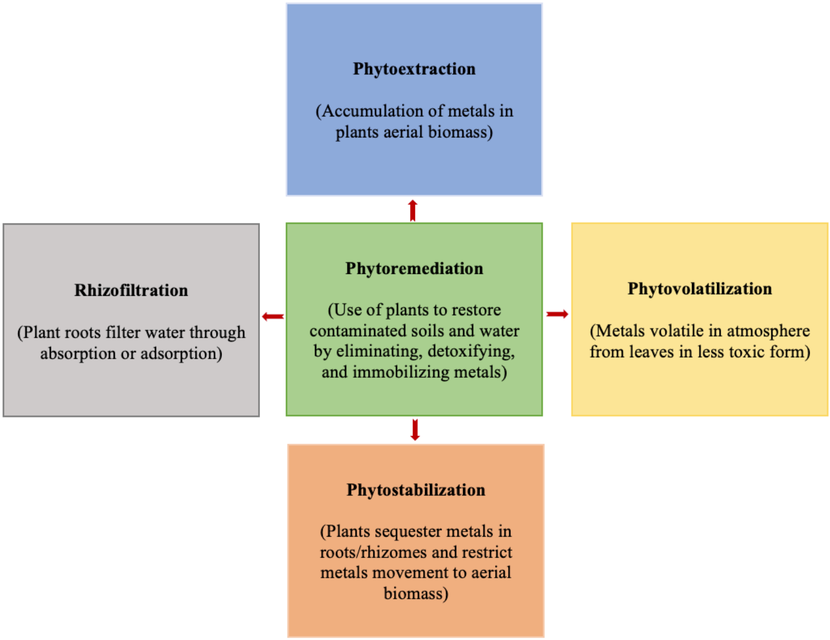


Figure 1. Plant-metal interactions during phytoremediation (Mohsin, 2016; Oladoye et al. 2022).

Floating treatment wetlands (FTW), also known as artificial islands or hydroponic root mats, are an engineering concept that has shown considerable promise in utilizing the phytoremediation process whereby plants grow in such a way that the aboveground parts of the plants are above the water and the roots are completely submerged within a water column, which is used to remediate different sources of wastewater (municipal and industrial). As such, FTW is considered a sustainable, economical and eco-friendly technology (Shahid et al. 2018; Wei et al. 2020). The mechanisms by which FTW remove PTE from stormwater runoff or polluted water are illustrated in Figure 2. The removal process involves the concerted action of biofilms, roots, shoots and leaves. Normally, PTE exist in water in two forms, particulate and dissolved. The particulate form is entrapped in the rhizosphere and biofilms, where it undergoes transformation into a non-toxic type. Conversely, plants absorb the dissolved metals via two mechanisms, namely, mass flow (e.g., nutrient and PTE are transported in plants along with water into the roots and transported to the leaves via xylem tissue under pressure generated by transpiration) and in the root adsorption process, where nutrients and PTE are actively taken up by the plant roots using specialized transport proteins (Sharma et al. 2021). Biofilms play a crucial role in facilitating the various biochemical processes involved in the transformation of PTE, the exchange of metabolites, the microbial degradation of organic matter, and the improved breakdown of PTE, which eventually facilitates its removal (DeSorbo et al. 2008). The root system of floating plants actively and passively extracts PTE from the surrounding wastewater through processes called rhizofiltration and phytostabilization. The extracted metals are subsequently translocated to the aboveground parts (shoots) of the plant (Sharma et al. 2021).

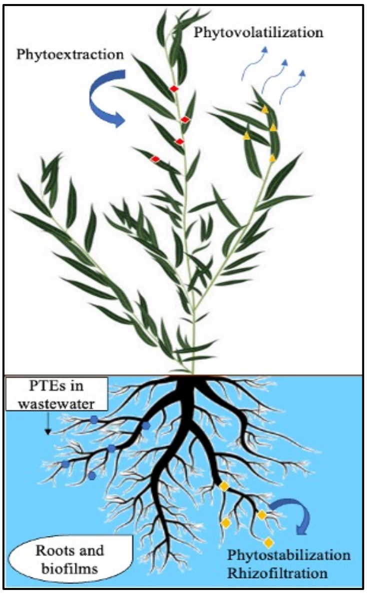


Figure 2. Processes involved in the removal of potentially toxic elements (PTE) in floating treatment wetlands (FTW).

Rainwater in the urban landscape is directed into the municipal drainage system, which is problematic during heavy rains and leads, for example, to river inundation, flooding and a reduction in water availability/quality (Deletic and Maksumovic, 1998). Stormwater runoff can be a significant source of water pollution, leading to pressure on water resources, and a decline in fishery and swimming areas. To reduce stormwater runoff in urban areas, an environmentally sustainable approach, such as FTW has been proposed as a substitute to traditional approaches (Zanin et al. 2018). It can minimize land area requirements and does not require infrastructure to by-pass the flow during *in situ* nutrient or PTE removal from watercourses (Fan et al. 2021). They can also be an attractive and alternative means of bioenergy production in cases where a lack of available land is a major obstacle facing the development of bioenergy feedstock production (Zhao et al. 2012). To date, this technology has only been installed in a limited number of applications, such as agricultural wastewater treatment, sewage effluent remediation and stormwater quality improvement to reduce nutrient and metal loading from wastewater. In addition, FTW could offer other benefits, such as ease of construction, low-cost, and provision of habitat for birds and fish (Xu et al. 2017).

1.3 Potentiality of willow (*Salix* spp.), *P. australis* and *I. pseudacorus* for phytoremediation

Willow (*Salix* spp.) are used as short rotation coppicing plants for small agroforestry, as hedging plants and shelter belts, as tree fodder, are utilized for basket and hurdle making, for biomass and medicinal uses (Kuzovkina and Quigley, 2005). Since the 1990s, they have been investigated as possible phytoremediation crop (Wani et al. 2020; Landberg and Greger, 2022). *Salix* species have the potential to accumulate significant concentrations of Cu, Ni and Zn in their biomass (Brieger, 1992; Cao et al. 2018; Mohsin et al. 2019), produce substantial biomass, have rapid growth and a deep-rooted system (Leiden, 1996; Salam et al. 2016; Mohsin et al. 2021), exhibit a wide adaptation to environmental stress, and can mitigate the negative effects of environmental change (Cao et al. 2022). Woody plants, such as *Salix* have been shown to actively taken up REE, which includes La and Tb (Kabata-Pendias 2011). Short-rotation *Salix* can be utilized as a vegetation filter to significantly improve plantation yield and improve the quality of processed wastewater before it is released into waterbodies (Jerbi et al. 2023). Common reed (*Phragmites australis* (Cav.) Trin. ex Steud.) has a wide geographical distribution and can accumulate pollutants and produce substantial biomass for bioenergy generation. It also has a strong tolerance for PTE and has a well-developed root and rhizome system that makes it suitable for the remediation of PTE in a flooded environment (Álvarez-Robles et al. 2022a). Yellow flag (*Iris pseudacorus*) is a wild ornamental wetland plant (herbaceous perennial) native to Europe, northwest Africa, and western Asia. It has a robust root system that grows well in water saturated environments and can remove PTE effectively (Yousefi et al. 2010; Yadav et al. 2021). Research has shown that *I. pseudacorus* was able to remove about 70% of TN and 80% of TP in wetlands sites in China and was able to remove PTE from contaminated areas in Spain (Huang et al. 2018).

Aquatic plant roots have been reported to secrete exudates and release oxygen, both of which control the type of microbial population in the root matrix and mitigate the impacts of algal blooms (Urakawa et al. 2017; Bi et al. 2019). Importantly, perennial herbaceous energy plants have been used as a feedstock as they do not need to be reseeded annually once established, and plant biomass can be transformed into energy through thermochemical processes, such as pyrolysis, combustion, gasification, or the fermentation of carbohydrates, to produce ethanol and methane (Zhao et al. 2012).

1.4 Existing gaps in phytoremediation research

Extensive research has been conducted worldwide on the phytoremediation capabilities of *P. australis* and *I. pseudacorus* in FTW with regard to various PTE. However, there is a noticeable gap in understanding as to their remediation potential, specifically for Cd and Cr in the presence of N and P applications, especially with regard to the accumulation and translocation of these metals within FTW. Furthermore, additional investigation is required to assess the effects of PTE concentrations on plant tissue development. To date, there is insufficient information on PTE accumulation and distribution in *I. pseudacorus* and the effects of other metals on the parameters that drive biomass production, such as plant growth, chlorophyll synthesis, photosynthetic performance, and plant nutritional status (Caldelas et al. 2012). Earlier studies on FTW have primarily focused on examining their efficacy in removing nutrients, chemical oxygen demand, biological oxygen demand, and suspended solids. However, these studies have been conducted in warm climates and with plant species not suited for cold climates. Consequently, further investigation is necessary to determine the effectiveness of FTW in the removal of PTE from stormwater in cold climates (Boynukisa et al. 2023). Currently, there is a paucity of information on the ability of terrestrial plants, such as *P. australis* and *I. pseudacorus*, to remove nutrients in a Cd or Cr polluted environment or how these PTE accumulate in plant biomass in FTW. In articles **I** and **II**, we describe the use of *P. australis* and *I. pseudacorus* to remediate PTE from stormwater in terms of removal of nutrients and the accumulation of PTE (here Cd and Cr) in biomass using FTW technology.

Such investigations could provide valuable insights into the economic benefits of this eco-technology, as well as its potential to enhance the aesthetic appeal of the landscape and encourage community engagement (Sandoval-Herazo et al. 2018; García-Ávila et al. 2023).

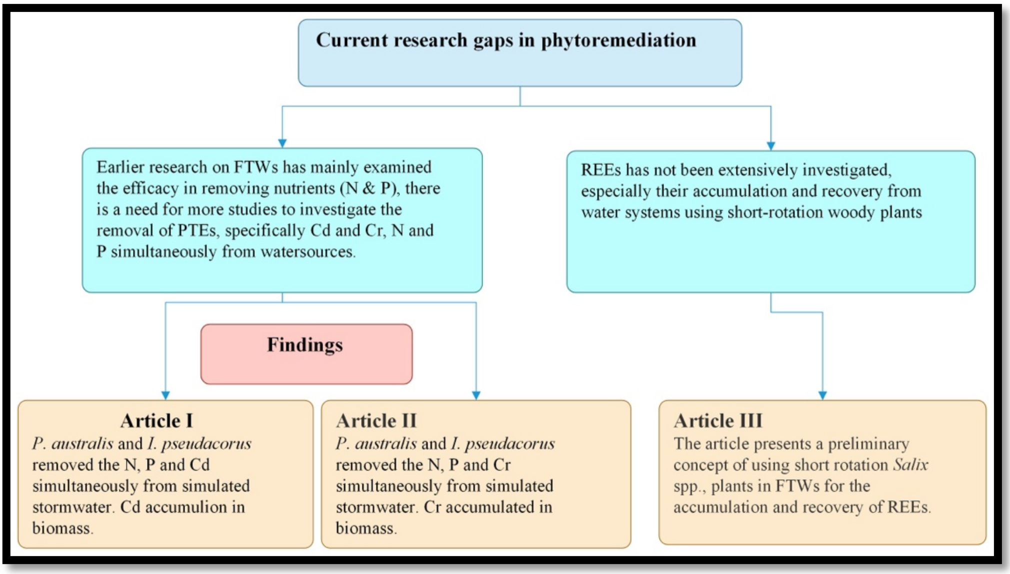


Figure 3. Graphical representation of current research gaps and findings. This presentation is based on an analysis of the scientific articles in the phytoremediation field.

Studies on the pollution caused by PTE have received significant attention from researchers worldwide. However, the pollution caused by REE has not been extensively investigated, particularly in terms of their accumulation and recovery from hydroponic systems using short-rotation woody plants, such as *Salix*. In a literature search in Scopus that covered the period 2000 to 2022 (as of January 16, 2023) using keywords, such as "phytoremediation of rare earth elements by *Salix*" and "recovery of rare earth elements by willow", only one article was found (Mohsin et al. 2022). In light of this limited research, article **III** presents a preliminary idea on the potential of bioenergy short rotation *Salix* plants in FTW for the accumulation and recovery of REE. This concept could prove useful in conducting in situ experiments aimed at controlling runoff. A graphical representation is depicted in Figure 3.

2 OBJECTIVES OF THE RESEARCH

This research is based on two peer-reviewed original scientific publications (**I** and **III**) and one unpublished manuscript (**II**). Three FTW trials were conducted (two trials at the Department of Sanitary Engineering, Gdansk University of Technology (GUT) and one trial at the School of Forest Sciences, University of Eastern Finland (UEF) where we studied the growth and phytoremediation potential of *P. australis* and *I. pseudacorus* under simulated stormwater that contain N, P, Cd, and Cr (at GUT), and where we assessed the growth and phytoremediation potential of short-rotation *Salix* under REE-treated wastewater (at UEF). The overall focus of the studies, their scope and contribution to the thesis are summarized in Figure 4.

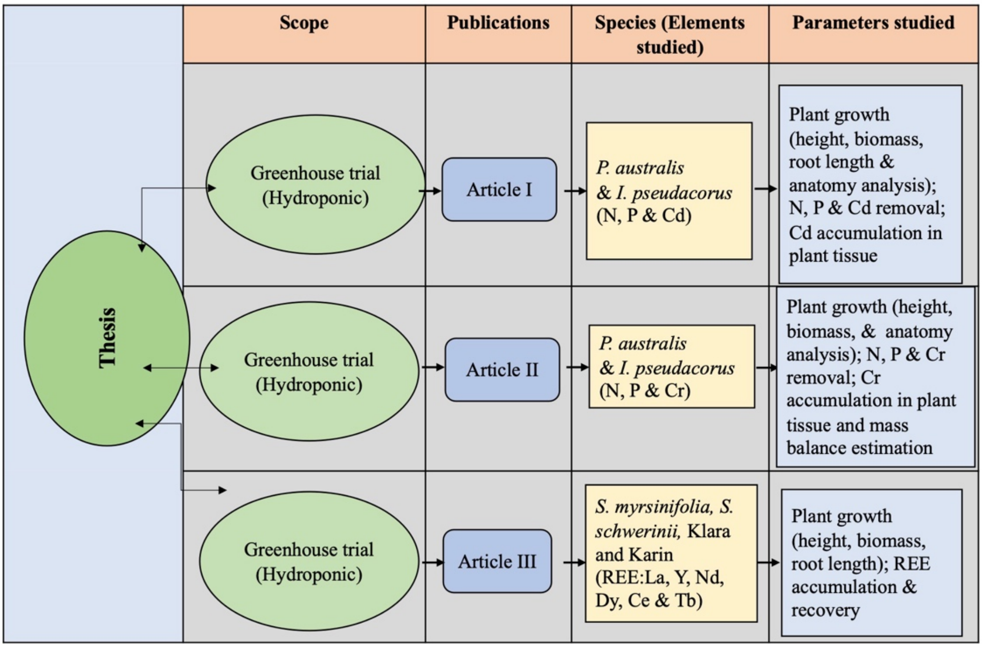


Figure 4. The schematic outline of the thesis is based on three articles.

The main objective of this research was to solve the knowledge gaps in the remediation of contaminated environments (water) by using a short-rotation woody crop (*Salix spp.*), grass (*P. australis*) and an ornamental flowering plant (*I. pseudacorus*). In short, my findings contribute to the field of phytoremediation by demonstrating the effectiveness of FTW in decreasing PTE and REE levels in wastewater and allowing them to be immobilize via phytostabilization using a wide range of plant species.

The specific aims of the three studies were as follows:

- To elucidate a) effects of Cd on *P. australis* and *I. pseudacorus* height growth, root length, biomass production, and chlorophyll content index, b) nutrients (N and P) and Cd removal under FTW, c) Cd accumulation in *P. australis* and *I. pseudacorus*, and d) Cd influence on *P. australis* and *I. pseudacorus* tissues development (**I**).
- To assess (a) the potential of wetland plants (*P. australis* and *I. pseudacorus*) for the removal Cr, N and P, (b) to evaluate Cr accumulation and translocation in the plant, and (c) to examine the anatomical response of the plants at the tissue-level under Cr loading (**II**).
- To investigate the effects of REE concentrations on the growth traits of two *Salix* species (*S. myrsinifolia* and *S. schwerinii*) and two *Salix* cultivars (Klara and Karin), as well as identify the potential of suitable *Salix* species for the accumulation of REE in FTW. Furthermore, the concentrations and compositions of the ash fraction (following biomass combustion) were assessed to explore how REE might be recovered for industrial use in a biomass boiler plant (**III**).

3 MATERIALS AND METHODS

3.1 Planting materials and experimental design

P. australis and *I. pseudacorus* were grown in FTW in a greenhouse at GUT for 50 days from June−July 2021 (**I**). A total of 8 traditional plastic buckets (TPB: capacity: 15L, diameter: 0.35 m and height: 0.4 m) were used and filled with 10 L of tap water. Three *P. australis* and *I. pseudacorus* seedlings were added to all TPB and exposed to three different doses of Cd (0, 1, 2 and 4 mg L^{-1} water), while tap water (without Cd) was used as the control. Initial doses of N (7.5 mg L^{-1}) and P (1.8 mg PO4-P L^{-1}) were added to all TPB (Table 1). Floating islands were created by rafts and buoyancy was provided by a PVC frame (surface area: 0.05 m^2). The plants grew in the water column with the aboveground plant parts above the water level and the roots below the water surface. During the trial period, the greenhouse temperature ranged between 19 and 22°C.

A second microcosm experiment (**II**) was set up at the same time in a greenhouse at GUT under semi-controlled conditions. *P. australis* and *I. pseudacorus* were collected from a plant nursery in Gdansk and passed through an acclimation period (for two months) before they were subjected to doses of Cr (0, 500, 1000 and 2000 µg L^{-1}), N (7.5 mg L^{-1}) and P (1.8 mg PO4-P L^{-1}) in FTW over a 50-day period. Three plants from each species were grown in 8 TPB that were filled with 10L of tap water. Tap water (without Cr) was again assigned as the control.

Two *Salix* species (*S. myrsinifolia* and *S. schwerinii*) and two *Salix* cultivars Klara (*S. viminalis* × *S. schwerinii* × *S. dasyclados*) and Karin (*S. schwerinii* × *S. viminalis*) × *S. viminalis*) × *S. burjatica*) were grown hydroponically in 5 L of tap water in a greenhouse at UEF in September 2018 for a 4−week period (**III**). The hydroponic solution was prepared using different doses of six−REE (La, Y, Nd, Dy, Ce and Tb) along with a Finnish NPK-based fertilizer (Kekkilä-kesälannoite). The fertilizer contained 17 g N, 4 g P, and 25 g K, which was applied at a rate of 200 mg L^{-1} water in all treatments to maintain the nutritional stability of the growing *Salix*. The water treatments were control (without REE), La (tap water + 50 mg La L^{-1} water) and a mixture of six−REE that include 11.50 mg La L^{-1} water + 11 mg Y L^{-1} water + 10.50 mg Nd L^{-1} water + 10 mg Dy L^{-1} water + 12 mg Ce L^{-1} water and 11.50 mg Tb L^{-1} water (Table 1).

3.2 Plants growth parameters estimation and chemical analysis

Parameters, such as stem height, dry biomass weight, and metal concentrations in the below and above ground plant biomass (**I−III),** root length and anatomical-morphological responses (**I**), plant stem diameter and root length (**III**) were scrutinized. A ruler was used to measure plant stem height and root length, an electric digital scale was used to determine the dry biomass weight, and a vernier caliper was used to calculate plant diameter.

Before chemical analysis, fresh *P. australis* and *I. pseudacorus* biomass were dried at 40°C, weighed and then ground in a mill (Mill Mix 20, Domel, Slovenia). The ground plant samples were passed through an acid digestion procedure in a microwave (Anton Paar) using a HCL, HNO_3, and H_2O_2 solution. In addition, Cd and Cr concentrations in *P. australis* and *I. pseudacorus* shoots and roots/rhizome were determined using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) spectrometer (Agilent 5800 VDV, Agilent Technologies, Australia).

Table 1. Scheme of experiments in articles **I-III**.

Article	Code: Treatment	Species/Cultivars
I	Cd_0: Control (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) Cd_1: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cd (1 mg L^{-1}) Cd_2: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cd (2 mg L^{-1}) Cd_4: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cd (4 mg L^{-1})	*P. australis* and *I. pseudacorus*
II	Control: Control (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) Cr500: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cr 500 mg L^{-1}) Cr1000: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cr 1000 mg L^{-1}) Cr2000: (tap water + N (7.5 mg L^{-1}) + P (1.8 mg L^{-1}) + Cr 2000 mg L^{-1})	*P. australis* and *I. pseudacorus*
III	T1: Control (tap water without REE) T2: La (tap water + single-La dose) T3: REE (tap water + mixture of La + Y + Nd + Dy + Ce + Tb)	*S. myrsinifolia, S. schwerinii,* Klara *(S. viminalis × S. schwerinii × S. dasyclados)* and Karin *(S. schwerinii × S. viminalis) × S. viminalis) × S. burjatica)*

Nitrogen and P concentrations in the water treatments were analyzed at specific intervals (at 0, 10, 20, 35 and 50 days) using a DR3900 (Hach Lange) spectrophotometer followed by cuvette tests. Cadmium and Cr concentrations in the water treatments were also analyzed at specific intervals (at 0, 10, 20, 35 and 50 days) with the ICP-OES method using a spectrometer. A detailed description of chemical analysis is presented in sections 2.2 (**I**) and 2.1 (**II**). Conductivity, pH, temperature, redox, and dissolved oxygen were measured in the water treatments rooted with *P. australis* and *I. pseudacorus* using a multi-parameter meter (HQ4300, Hach Lange, Germany) at days 0, 10, 20, 35 and 50. These measurements are presented in Supplementary Materials 1 (**I**).

For the combustion of *Salix* biomass, a mixture of hydroponically grown *Salix* roots, stems and leaves were dried in an oven for 24 hours at 105°C prior to being ground into a homogenized powder using a centrifugal knife mill with a 0.5 mm screen. The homogenized sample (550–850 mg) was then burned in a fixed-bed, batch tube reactor at two temperatures (800°C and 1000°C) to determine the concentrations of REE and other ash-forming elements (**III,** Table 2). At each temperature, duplicate and triplicate tests were run. An insertion probe was used in the reactor setup to rapidly transfer samples between the hot and cool zones. The samples were initially heated in a mixture of 2% O_2 and 98% N_2 for 15 minutes to prevent temperature overshoot before switching to air. The samples were heated at two temperatures 800°C and 1000°C, respectively, for 45 and 30 minutes to ensure complete burnout of the organic components. The standard ash content was determined using a muffle furnace (combusted at 250°C for 1 h and at 550°C for 2 h) and the ISO 18122 standard method. The combustion ashes from the reactor were removed at the end of each experiment, weighed to the nearest 0.01 mg, and then La, Nd, Y, Ce, Dy, Tb and other inorganic element concentrations were measured. After the combustion process, REE retention from the bottom ash was calculated using the mass balance equation (1):

$$R_i(\%) = \left(\frac{W_a}{W_b}\right)\left(\frac{C_{a,i}}{C_{b,i}}\right) \times 100 \qquad (1)$$

where R_i is the retention of REE i as a percentage of overall weight, W_a and W_b are the weights (mg) of the ash and *Salix* biomass, respectively, and $C_{a,i}$ and $C_{b,i}$ are the concentrations (mg kg^{-1}, dry basis) of REE i in the ash and *Salix* biomass, respectively.

3.3 Statistics analysis and calculations

SPSS software was used for statistical data analysis (**I**–**IIII**) to determine the effects of treatments on different growth parameters and metal accumulation using the analysis of variance (ANOVA) followed by the Tukey HSD test with significance level at $p < 0.05$. The accumulation of REE in the *Salix* biomass, and Cd and Cr in the *P. australis* and *I. pseudacorus* biomass was calculated as the metal concentration in each plant tissue multiplied by the dry weight of the respective tissue (Xu et al. 2019). Tolerance indices, namely dry biomass tolerance index (DBTI), stem length tolerance index (SLTI) and root length tolerance index (RLTI) were calculated for *P. australis* and *I. pseudacorus* (**I** and **II**) to assess their tolerance to Cd and Cr stress using the following formulas (1–3), as described by Feng et al. (2018):

$$DBTI = \frac{Plant\ dry\ biomass\ in\ contaminated\ water}{Plant\ dry\ biomass\ in\ tap\ water} \qquad (2)$$

$$SLTI = \frac{Plant\ stem\ length\ in\ contaminated\ water}{Plant\ stem\ length\ in\ tap\ water} \qquad (3)$$

$$RLTI = \frac{Plant\ root\ length\ in\ contaminated\ water}{Plant\ root\ length\ in\ tap\ water} \qquad (4)$$

A translocation factor (TF) and bioconcentration factor (BF) values were estimated (**I–III**) using the following expression (4 and 5), as documented by Li et al. (2023) and Haghnazar et al. (2023):

$$TF = \frac{Metal\ concentrations\ in\ plant\ stems}{Metal\ concentrations\ in\ plant\ roots} \qquad (5)$$

$$BF = \frac{Metal\ concentration\ in\ plant\ roots}{Metal\ concentrations\ in\ soil\ or\ water} \qquad (6)$$

4 RESULTS

4.1 Plants biometric parameters and anatomy changes assessment

P. australis produced greater mean stem growth (57 cm), root length (9.70 cm) and chlorophyll content index (CCI) value (2.30) in treatment Cd_2 than the control, Cd_1 and Cd_4 treatments. In the case of *I. pseudacorus*, the greatest mean stem growth (56.40 cm), root length (14.06 cm) and CCI value (3.72) were observed in treatments Cd_1 and Cd_4, respectively, compared to the control and treatment Cd_2 (Table 1 in article **I**). The greatest total mean dry biomass in *P. australis* (6.80 g) and *I. pseudacorus* (6.13 g) were observed in treatments Cd_2 and Cd_1, respectively (Figure 3AB). With regard to the tolerance indices, DBTI, SLTI and RLTI, *P. australis* showed the greatest tolerance under the different Cd doses: Cd_2 (143%), Cd_1 (106%) and Cd_2 (103%), respectively. Comparatively, the greatest Cd tolerance for *I. pseudacorus* was seen with DBTI (155%) and SLTI (152%) in Cd_1, and with RLTI (151%) in the Cd_4 treatment (Table 2 in article **I**).

With regard to the anatomy of plants roots under the control, Cd_1 and Cd_4 treatments, light microscopy showed different parts of a transverse section of *P. australis* roots forming the epidermis, the endodermis, the central cylinder, the cortex and the aerenchym. The findings showed that the arrangement of vessel elements, such as the stele in *P. australis* exhibited regularity. The epidermis and endodermis cells in *P. australis* showed no disruption and were densely packed across all treatments and the aerenchyma was nearly half the size in the Cd_4 treatment compared to the control. However, the results showed that the plant was healthy and that there were no differences between the control and Cd treatments (Figure 8a in article **I**). For *I. pseudacorus*, the cortex found between the epidermis and endodermis in the Cd_4 treatment exhibited an increase in cell size (25 layers compared to 11 layers in the control). In addition, the width of the cortex in the Cd_2 treatment was found to be twice as large compared to both the control and Cd_4 treatments. However, an increase in cell size and width implied certain changes in the plants, for example root hair, and lateral root development was seen in *I. pseudacorus* roots in the Cd_4 treatment (Figure 8b in article **I**). Moreover, root biomass in *P. australis* was greater than stem biomass across all treatments. When compared with the control, a decrease in root and shoot biomass was observed, by 6% and 34%, and by 26% and 44% under the Cd_1 and Cd_4 treatments, respectively, although an increment was noted for root (69%) and shoot (17%) biomass under the Cd_2 treatment (Figure 5A). In comparison to the control, the root biomass of *I. pseudacorus* increased by 30%, 62% and 113% in the Cd_1, Cd_2 and Cd_4 treatments, and shoot biomass decreased by 12% and 40% in Cd_2 and Cd_4 treatments but increased by 77% in the Cd_1 treatment (Figure 5B). However, *P. australis* root and shoot biomass reductions were more distinct in the high-dose Cd_4 treatment, while with *I. pseudacorus*, the reduction was only noted with shoot biomass in the high-dose Cr_4 treatment.

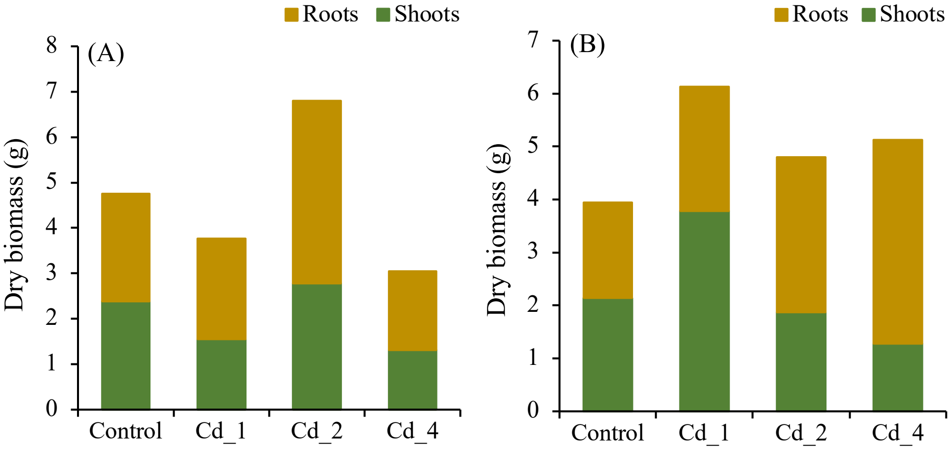


Figure 5. Shoot and root/rhizome dry biomass (g) produced by (A) *Phragmites australis* and (B) *Iris pseudacorus* under cadmium (Cd) loading over a 50-day period.

In the case of Cr pollution (Table 1 in article **II**), *P. australis* showed the greatest increase in stem height: 37%/29% and 18%/38% at the low-dose Cr treatment (Cr500) and the high-dose Cr treatment (Cr2000), respectively, as compared to the control. At the medium-dose Cr treatment (Cr1000), the initial stem height of *P. australis* increased by 6% and the final stem height decreased by 16% as compared to the initial/final stem height in the control. In addition, *I. pseudacorus* stem growth declined with increased Cr dose. *P. australis* exhibited an equivalent initial root length growth under the Cr500 and Cr2000 treatments with respect to the control, excluding the Cr1000 treatment where the initial and final root length growth declined by 28% and 7%, respectively. In contrast, an increment was noted for the final root length growth in the Cr500 (100%) and Cr2000 (46%) treatments as compared to the control. With regard to the tolerance indices, DBTI, SLTI and RLTI, the *P. australis* showed the greatest tolerance under the different Cr doses: Cr500 (76%), Cr2000 (138%) and Cr500 (200%), respectively. The growth of *P. australis* and *I. pseudacorus* under Cr loading is depicted in Figure 6.

Figure 6. Plants development after the 50-day trial period under chromium (Cr) loading (adapted from article **II**). *Phragmites australis* shown on the left, and *Iris pseudacorus* shown on the right.

When the initial/final stem height in the control was compared across the Cr treatments, the growth of *I. pseudacorus* increased by about 34%/18% (Cr500), 28%/22% (Cr1000) and 20%/4% (Cr2000). The initial root length growth of *I. pseudacorus* was someway reduced, compared to the control, in the Cr500 (14%) and Cr1000 (28%) treatments and increased by about 42% in the Cr2000 treatment. However, the final root length growth increased by 8%, 25% and 16%, respectively, in the Cr500, Cr1000 and Cr2000 treatments compared to the control. The greatest tolerance index values in *I. pseudacorus* were observed with the Cr500 (DBTI: 59%), Cr1000 (SLTI: 123%) and Cr1000 (RLTI: 125%) treatments.

P. australis produced a larger root biomass than stem biomass in all treatments. Compared to the control, we observed a decrease of 21% and 28%, 76% and 64%, 30% and 29% in the root and shoot biomass under the Cr500, Cr1000 and Cr 2000 treatments, respectively (Figure 7A). The lowest biomass value was also observed with *I. pseudacorus*. Compared to the control, the root and shoot biomass of *I. pseudacorus* was lower by 41% and 40%, 74% and 81%, 52% and 66% respectively under the Cr500, Cr1000 and Cr2000 treatments (Figure 7B). However, both the *P. australis* and *I. pseudacorus* biomass (roots and shoots) reduction was more evident in the medium-dose Cr1000 treatment (Figure 7AB).

The studied *Salix* species (*S. myrsinifolia* and *S. schwerinii*) and cultivars (Klara and Karin) showed the best results in terms of absolute mean stem height, total mean dry biomass, stem diameter and root length across all treatments. Klara was the best among all studied *Salix* species as it produced the greatest absolute mean stem height (110 cm), total mean dry biomass (7.78 g), stem diameter (7 mm) and root length (24.43 cm) when exposed to treatment T2 as compared to treatment T3 and the control (Table 1; Figure 1 in article **III**). The leaves, stem and root dry biomass varied among species, cultivars and treatments. For example, *S. schwerinii* produced nearly an equivalent amount of stem biomass as root biomass across all treatments, with the largest amount of *S. myrsinifolia* root biomass noted in the six-REE treatment and leaves and stem biomass in the control and single-La treatment. The root biomass produced by Klara was less than the leaves and stem biomass in all treatments, and the Karin stem biomass was greater than the leaves and root biomass (Figure 8A–D).

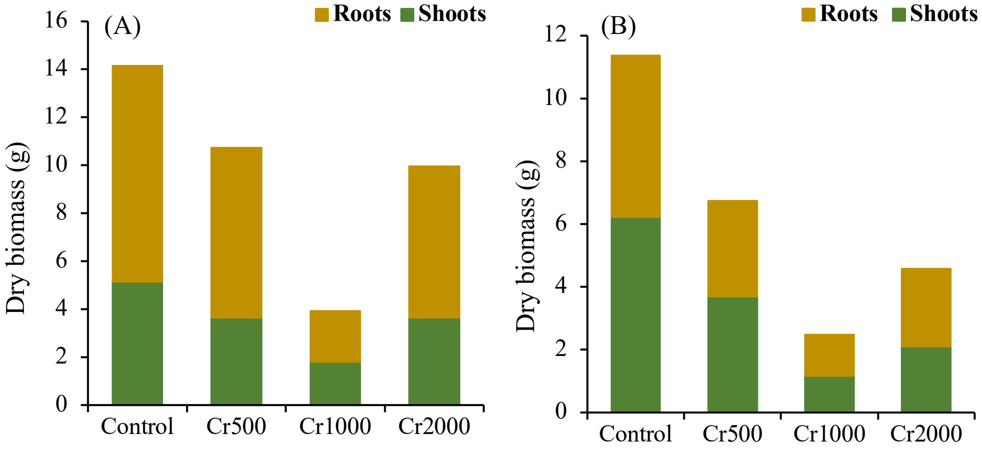
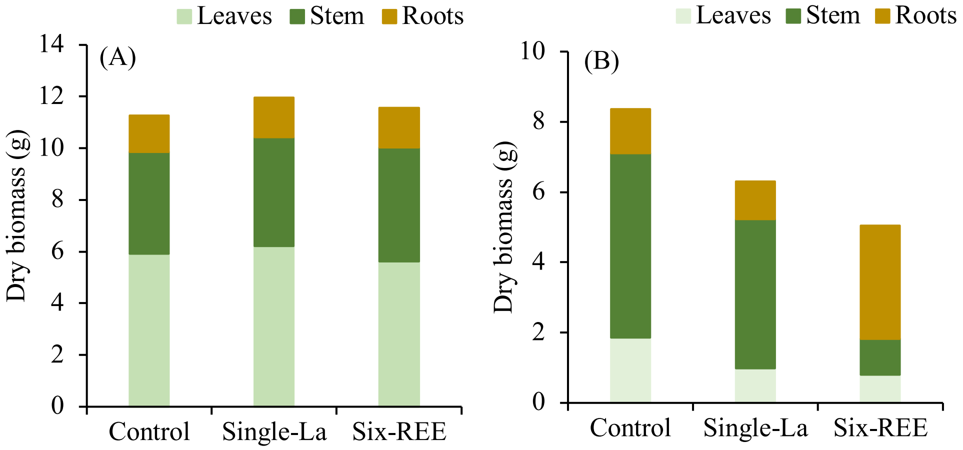


Figure 7. Shoot and root/rhizome dry biomass produced by (A) *Phragmites australis* and (B) *Iris pseudacorus* under chromium (Cr) loading over a 50-day period.



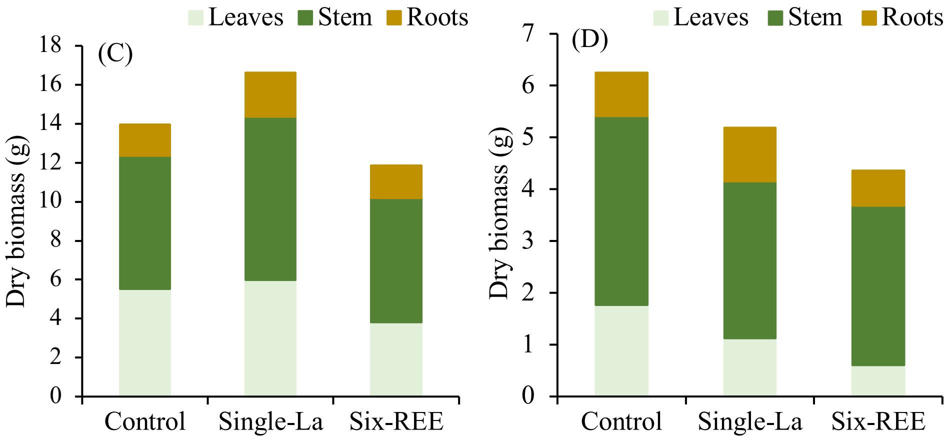


Figure 8. Leaves, stem and root dry biomass produced by (A) *Salix myrsinifolia*, (B) *Salix schwerinii*, (C) Klara and (D) Karin under different rare earth elements (REE) treatments over a 28-day period.

4.2 Phytoremediation efficiency of *Salix* spp., *P. australis* and *I. pseudacorus*

P. australis had greater Cd accumulation (1821.59 µg · (0.05 m^2)$^{-1}$) in the roots than in the shoots at the high-dose Cd_4 treatment. A similar trend was seen with *I. pseudacorus*, which had greater Cd accumulation (4900 µg · (0.05 m^2)$^{-1}$) in the roots compared to the shoots in treatment Cd_4 (Figure 6 in article **I**). Both species showed the potential to deposit maximal amounts Cd in the roots based on their TF values (Figure 7 in article **I**), which were 0.07–0.18 for *P. australis* and 0.24–0.12 for *I. pseudacorus* when exposed to treatments Cd_1 and Cd_4, respectively (TF < 1 indicates that both species could be a suitable choice for phytostabilization of Cd polluted wastewater).

Under Cr pollution (Table 3 in article **II**), *P. australis* and *I. pseudacorus* accumulated a greater amount of Cr in their roots than shoots. When *P. australis* was exposed to the high-dose Cr treatment (Cr2000) and the low-dose Cr treatment (Cr500), Cr accumulation in the shoots increased by 322% and decreased by 15%, respectively, compared to the control. While the greatest amount (2297 µg) of Cr accumulated in *P. australis* roots under the Cr2000 treatment. Cr accumulation in the *I. pseudacorus* shoots under the Cr500 and Cr2000 treatments increased by 643% and 1258%, respectively, compared to the control. The *I. pseudacorus* roots also accumulated the greatest amount of Cr (1321 µg) under the Cr2000 treatment. However, the TF (0.01 and 0.01) and BF values (1.53–1.53 and 1.70–0.66) for *P. australis* and *I. pseudacorus* demonstrated poor Cr translocation to the shoots, although efficient transportation from the water solution to the roots would suggest that these species could be utilized as a phytostabilizer for Cr-enriched wastewater sites.

With regard to the REE concentration in *Salix* (**III**), La concentration was greatest in *S. schwerinii* leaves in the single-La treatment T2 (2.55 µg g DW) and in the six-REE treatment T3 (12.40 µg g DW). Besides La, the Y (3.30 µg g DW), Ce (2.50 µg g DW), Nd (2.23 µg g DW), Tb (2.48 µg g DW) and Dy (2.79 µg g DW) concentrations were also greatest in *S. schwerinii* leaves in treatment T3 (Table 3A in article **III**). *S. schwerinii* was observed to have the greatest La concentrations (3.52 µg g DW) in the stem in the single-La treatment T2, while in the six-REE treatment (T3), the greatest concentrations of La (0.85 µg g DW), Y (0.35 µg g DW), Ce (0.33 µg g DW), Nd (0.27 µg g DW), Tb (0.37 µg g DW) were noted in the cultivar Karin and Dy (0.27 µg g DW) in *S. myrsinifolia* (Table 3B in article **III**). Furthermore, Karin contained a substantial amount of La (8404 µg g DW) in the roots in the single-La treatment T2, although the greatest concentrations of REE in the six-REE treatment T3 were found in the Klara roots: La (2082 µg g DW), Y (1058 µg g DW), Ce (2013 µg g DW), Nd (1956 µg g DW), Tb (2514 µg g DW) and Dy (1159 µg g DW) (Table 3C in article **III**). Noticeably, the *Salix* species and cultivars contained a significant concentration of REE in the roots, greater than in the stem and leaves. Their concentration-based TF value (Table 5 in article **III**) was < 1 in the REE-treated treatments (T2 and T3) and the control: TF values were as follows T2 (0–0.01), T3 (La: 0–0.08; Y: 0–0.02; Ce: 0–0.01; Nd: 0–0.01; Tb: 0–0.01; Dy: 0–0.02) and T1 (La: 0.08–0.41; Y: 0.12–0.22; Ce: 0.10–0.21; Nd: 0.10–0.26; Tb: 0.10–0.20; Dy: 0.10–0.23). However, the results indicated that *Salix* species and cultivars might be suitable for phytostabilization.

With regard to REE recovery from the *Salix* biomass, the leaves, stems and roots of four *Salix* spp. from the six-REE treatment were combusted at two temperatures: 800°C and 1000°C. The preliminary assessment of the ashes of the *Salix* biomass showed that overall, more than 80% of REE were retained in the bottom ashes after combustion at 1000°C, which would indicate that little REE was volatized during the combustion process. The REE concentrations in the ash (dry basis) were also greatest following combustion at 1000°C. However, there was no significant difference between these two temperatures with regard to REE retention and concentrations (Figure 9AB).

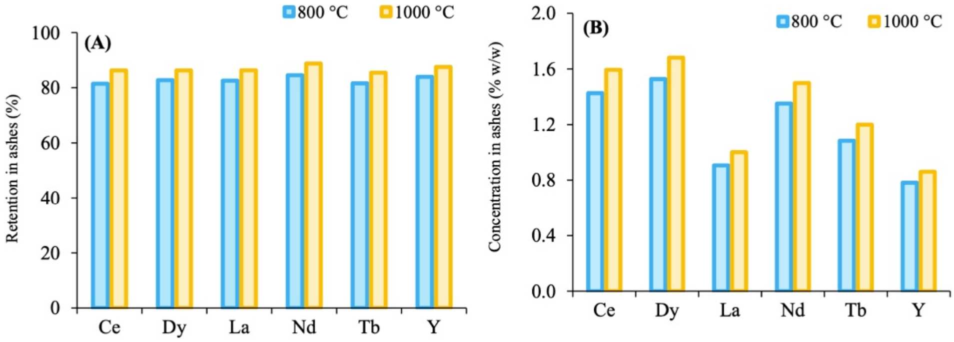


Figure 9. (A) Retention and (B) concentrations of six-rare earth elements (REE) in the *Salix* ashes after combustion at 800°C and 1000°C (Adapted from article **III**).

In addition to REE recovery, we also analyzed the non-REE components present in the ash. The results indicated that the *Salix* ashes mostly contained potassium (K: 20–23% dry basis), P (10–11%), and calcium (Ca: 5.4–6.2%). We also observed lower concentrations of sodium (Na), magnesium (Mg), aluminum (Al), iron (Fe), Zn, and Mn (Figure 2 in article III).

5 DISCUSSION

This work explores the use of *Salix spp*., *P. australis* and *I. pseudacorus* in FTW to remove PTE and REE from stormwater or wastewater. The findings suggest that *P. australis* and *I. pseudacorus* could remove Cd, N, and P from stormwater runoff in temperate climates, while *Salix* species could remove and recover REE from wastewater in boreal climates. The contaminated biomass produced by these plants could be further deployed in biorefineries to produce bio-based products and support the bioeconomy.

5.1 Cadmium impacts on *P. australis* and *I. pseudacorus* growth and its accumulation in biomass

Cadmium has a deleterious impact on plant growth and hampers the physiological and biochemical processes that take place in plants (Wu et al. 2018). However, *P. australis* and *I. pseudacorus* growth was not affected by Cd stress (Table 1 and Figure 2 in article **I**). The response of *P. australis* growth parameters (increase: ↑, decrease: ↓) to the different Cd treatments was observed as mean height (Cd_1: ↓12%, Cd_2: ↑1% and Cd_4: ↓1%), root length (Cd_1: ↓22%, Cd_2: ↑3% and Cd_4: ↓26%), CCI (Cd_1: ↑180%, Cd_2: ↑360% and Cd_4: ↑560%) and total mean dry biomass (Cd_1: ↓21%, Cd_2: ↑43% and Cd_4: ↓36%) when compared to the control. For *I. pseudacorus*, growth was noticeably increased when compared to the control: mean height (Cd_1: 52%, Cd_2: 39% and Cd_4: 50%), root length (Cd_1: 50%, Cd_2: 25% and Cd_4: 51%), CCI (Cd_1: 104%, Cd_2: 201% and Cd_4: 300%) and total mean dry biomass (Cd_1: 55%, Cd_2: 22% and Cd_4: 30%). When exposed to an elevated level of Cd (25 mg L^{-1}), *I. pseudacorus* plants eventually showed a decrease in growth and chlorophyll content (Zhou et al. 2010). The current findings show that productive growth response of *P. australis* and *I. pseudacorus* under simulated stormwater could be attributed to the high nutrient uptake required for optimal growth (Bullard et al. 2002; Mohsin et al. 2021). In this study, the superior root growth of *P. australis* and *I. pseudacorus* is indicative of their potential to endure in a polluted environment and their ability to accumulate PTE and remove nutrients in FTW due to their dense root system. A similar growth response was documented by Weragoda et al. (2012) for another macrophyte *Typha angustifolia* grown in FTW. However, the improvement in the studied parameters, such as plant height, dry biomass and root length reflects the tolerance of these species to PTE (Cd and Cr) and nutrients (N and P) enrichment, which corresponds to significant nutrient removal from the water and sufficient nutrient uptake needed to sustain optimum growth. With regard to the anatomical changes in both species under Cd stress, our results indicated that there were no substantial alternations in the stem and roots. This finding is in agreement with Ederli et al. (2004) who did not observe any structural changes in *P. australis* roots when subjected to 100 μM of Cd for 21 days, which again highlights the Cd detoxification potential of these perennial plants.

With regard to Cd accumulation (Cd concentration × dry biomass) in *P. australis* and *I. pseudacorus*, our findings show that both species limit the translocation of Cd into aboveground tissues and accumulated in roots. Our findings are consistent with Rocha et al. (2014) who reported that the greatest accumulation of Cd occurred in the *P. australis* roots and observed low translocation to the aerial parts under Cd exposure (0, 1, 10 mg L^{-1}), which indicates their potential for the phytostabilization of Cd. Ouyang et al. (2019) observed greatest Cd accumulation in *Phragmites* roots (0.86 mg kg^{-1}) than in the shoots (0.36 mg kg^{-1}), which supports our current findings, although the shoots of *Typha*, another wetland plant, have been shown to have greater Cd accumulation than the roots when exposed to 4 mg L^{-1} Cd. Ait-Ali et al. (2004) also noted greater accumulation of Cd in *P. australis* roots in hydroponic systems and proposed that this species could be suitable for the rhizofiltration of wastewater.

5.2 Cadmium, N and P removal by *P. australis* and *I. pseudacorus*

Removal of Cd, N and P from the simulated stormwater was observed at days 10, 20, 35 and 50 with regard to the initial doses applied at day 0. Cadmium removal (86%) by *P. australis* was remarkably high on day 50 under the low-dose Cd treatment (Cd_1 mg L^{-1}) compared to day 0. For *I. pseudacorus*, the greatest reduction in Cd levels (69%) was also noted at day 50 but under the high-dose Cd treatment (Cd_4 mg L^{-1}) as compared to the day 0 (Figure 5AB in article **I**). The greatest N reduction (81%) by *P. australis* was noted in the control (without Cd) at day 35, although a decline in N concentrations was also noted in the Cd treatments (Figure 3A in article **I**). Nitrogen concentration declined the most (80%) at day 50 in the low-dose Cd treatment (Cd_1 mg L^{-1}) planted with *I. pseudacorus*. Fluctuations in N concentrations were also evident in the other treatments (planted with *I. pseudacorus*) over the 50-day period (Figure 3B in article **I**). In the case of P, the greatest reductions were observed in the control treatment, for both *P. australis* (54%) and *I. pseudacorus* (60%), at day 50 with respect to the initial P concentrations at day 0 (Figure 4AB in article **I**). Our results support the opinion of Álvarez-Robles et al. (2022b) who documented the substantial removal of PTE by macrophytes due to factors, such as strong biomass production, efficient root and rhizome systems and high tolerance to PTE, which made them suitable to remediate stormwater. Noticeably, the removal concentrations values of N and P were sometimes slightly increased compared to their initial concentrations during the trial period. These fluctuations could be associated with plant senescence processes, where the decomposition processes may allow the retained nutrients in the plant to be released back into the water (Zhao et al., 2012; Rigotti et al. 2021).

5.3 Chromium, N and P removal by *P. australis* and *I. pseudacorus*

About 98−99% of Cr was removed by *P. australis and I. pseudacorus*, mostly over a 10-day period under the 500, 1000 and 2000 Cr µg L^{-1} treatments (Table 2 in article **II**). Our findings are generally consistent with Nwe et al. (2018) who reported 86% Cr and 83% Cd removal by *Eichhornia crassipes* over a 10-day period when exposed to Cr and Cd concentrations of 5 ppm, although their results are at odds with the Cd removal values achieved in our experiment (Figure 5 in article **I**): 18–40% for *P. australis* and 6–36% for *I. pseudacorus*. With regard to N and P removal over the 50-day period (Figure 3 in article **II**), *P. australis* removed 78% of TN and 58% of TP, while *I. pseudacorus* removed 80% of TN and 60% of TP. The efficient removal of N and P by *P. australis* and *I. pseudacorus* can be attributed to their ability to absorb and utilize nutrients for growth. Their root systems, microbial interactions, and nutrient storage mechanisms collectively contribute to the successful removal of N and P under Cr stress (Yousefi and Mohseni-Bandpei, 2010).

Keizer-Vlek et al. (2014) noted the efficient removal of N (98%) and P (92%) in FTW by *I. pseudacorus* exposed to about 4 mg N L^{-1} and 0.25 mg P L^{-1} over a 90-day period. Kyambadde et al. (2004) showed that removal and storage by macrophyte species, such as *Cyperus papyrus*, could be a reason for the removal of about 69% N and 88% P in FTW. In their study, *I. pseudacorus* was subjected to enhanced levels of TN, NH4-N, and TP in constructed wetlands, and removals after an overall hydraulic residence time of four months, were 39.47%, 84.65%, and 26.28%, respectively (Wu et al. 2011). These results support the performance of our studied macrophytes, in terms of N and P removal in FTW. Metal removal by plants, and accumulation in plant tissues, contributes to stormwater treatment (Ladislas et al., 2015). Numerous factors that include raft size, pollutant load, placement and season (McAndrew & Ahn, 2017), affect pollutant uptake in plants although the removal capability is reliant on the specific species (Boynukisa et al. 2017). Furthermore, TN removal primarily depends on the microbial processes that involve nitrification and denitrification, under aerobic and anaerobic conditions, respectively, while P removal is due to physical activities, such as fixation, sorption, and precipitation complexation (Zhang et al. 2016). In recent decades, nutrient accumulation has taken place, due to high doses of fertilizers. Although the impact of fertilizer input into the soil has a positive impact on crop production, their impact on the environment (e.g., eutrophication) has become a problem in Europe (Tóth et al. 2014) and elsewhere. Our findings indicate a substantial reduction in Cd, Cr, N and P concentrations by *P. australis* and *I. pseudacorus*, which indicates their potential to impede nutrient and PTE runoff from retention tanks, rain gardens or floating islands to clean waterbodies.

5.4 Rare earth elements impact on *Salix* growth and accumulation in biomass

Since 2021, global REE extraction has increased and has reached 280,000 tonnes yr^{-1} due to the extensive demand from high-tech industries (electronics, medicines, military). At the same time, REE have also been identified as "metals of emerging concern" (Duchna and Cieślik, 2022). China is the main producer of REE, and developed countries import these elements from China, therefore, REE mining is still under way globally to enhance REE supplies at the domestic level (Hanana et al. 2023). Aside from its significant usage in advanced technologies, anthropogenic activities, such as wastewater discharge (from mining and industrial processes) to lakes, rivers, coastal seas, municipal tap water and ground water have also contributed to REE pollution, which leads to a negative impact on ecosystems (Gwenzi et al. 2018). From this perspective, the results presented in article **III** indicate a strong potential for woody perennial plants, such as *Salix*, to alleviate the environmental issues (locally, nationally and globally) associated with REE, through accumulation in their biomass and REE recovery from the biomass ash.

Based on a visual assessment, the *Salix* species and cultivars in this research did not exhibit toxicity symptoms, such as necrosis, chlorosis and wilting throughout their growing period. All *Salix* plants produced a strong response to REE-treated water in terms of growth, biomass production, stem diameter and root length. This would indicate that the *Salix* plants were resilient to the applied doses of REE. Nevertheless, REE have been used commercially as fertilizer in different countries, including Korea, Japan, Philippines, Switzerland, and Australia (Redling 2006). In China, an increase in agricultural crop growth and quality has been reported after supplementation with REE (Tang and Tong 1988), which is consistent with our findings.

With regard to REE accumulation in *Salix* biomass (Table 4A–C in article **III**), our results show that all the *Salix* accumulated low to high amounts of REE, but that the accumulation was greatest in the roots, and also varied considerably between *Salix* species and cultivars. For example, the accumulation of La in the leaves was greatest in *S. myrsinifolia* (8.11 µg plant^{-1}) under the single-dose La treatment (T2), whilst Karin showed the greatest accumulations of La (45.07), Y (14.43), Ce (2.32), Nd (2.31), Tb (4.88) and Dy (11.44) in the leaves under the six-REE treatment (T3). For stems, La accumulation was greatest in Klara (20.21 µg plant^{-1}) in treatment T2, while *S. myrsinifolia* showed the greatest accumulations in treatment T3 (La: 20.21; Y: 1.42; Ce: 1.66; Nd: 1.50; Tb: 1.46; Dy: 1.60 µg plant^{-1}). However, Klara exhibited the greatest REE accumulations in the roots in treatments T2 (La: 10548 µg plant^{-1}) and T3 (La: 2468; Y: 1273; Ce: 235; Nd: 2307; Tb: 2880; Dy: 1416 µg plant^{-1}).

Sites in Finland, such as Sokli, Korsnäs, Otanmäki, Lamujärvi, Livaara, Juuka and Kovela, contain some natural deposits of REE (British Geological Survey, 2023). These deposits have the potential to provide at least 10% of the REE needed each year in Europe for the manufacture of permanent magnets, which are needed in wind turbines, consumer electronics, defence industry, electric vehicles, solar panels (Helsinki Times 2023). In Sokli, metal recovery relies particularly on ex-situ methods, such as excavation, and on chemical extraction using solvents (Royen and Fortkamp, 2016). In terms of REEs removal and recovery, these methods are neither cost-effective nor sustainable as they contribute to secondary pollution (Lebrun et al. 2016). The results described in article **III** suggest that growing *Salix* near REE-exposed sites in Finland could be a viable option to limit the translocation of REE to surrounding freshwater bodies and also permit their recovery. With regard to REE accumulation in *Salix*, our findings show that all the studied *Salix* accumulated the majority of REE in their roots followed by stem and leaves, which indicates metal immobilization potential. In particular, the cultivar Klara was able to accumulate substantial amounts of REE in its roots across all treatments (Table 4C in article **III**).

5.5 Metals translocation efficacy of *Salix spp., P. australis* and *I. pseudacorus*

Salix has shown the capability to accumulate different PTE simultaneously (Cd, Zn, Cu, Pb, and Mn) from multi-metal solutions (Yang et al. 2019). Similar results were described in article **III** where *Salix* accumulated more than one metal contemporarily from the REE solution, which indicates that phytoremediation success is dependent on the choice of plant and metal available forms (Yang et al. 2019). Barbera et al. (2021) reported that REE enrichment did not lead to greater accumulation in the above-ground tissues of *Vitis vinifera* (common grape wine) compared to below-ground tissues, which supports our findings. This limited transport of REE might be due to a potential detoxification mechanism created by plants, such as *Salix*, to deal with exposure to toxic non-essential trace elements (Pourrut et al. 2011). Furthermore, PTE uptake is mostly contingent on their nutrient concentration, the type of wastewater, vegetation species, rate of biomass development, nutrient storage potential, root structure, and storage location (roots or shoots) (Chance et al. 2011). For example, TF and BF patterns (TF <1 and BF <1; TF >1 and BF <1; TF <1 and BF >1) illustrate the strong phytostabilization potential of a plant (Gajić et al. 2018). Wetland plants accumulate metals based on a multiplicity of factors that include the metal concentration in the medium, the physical and chemical properties of the soil/water, the contact time, the conditions of plant growth, absorption mechanisms and the time of sampling (Ramachandra et al. 2018).

Furthermore, plants play a crucial role in protecting groundwater and reducing PTE pollution by facilitating their sorption or precipitation within the shoot system. Through the production and secretion of organic compounds into the rhizosphere, plants can influence soil pH, the oxidation/reduction potential, and convert PTE ions into forms that are less available. This process, known as phytostabilization, involves the immobilization of PTE in the soil, thereby preventing their movement deeper into the soil profile and ultimately into water bodies and the broader food chain (Radioman et al., 2023). In phytostabilization, plants act as a protective barrier, thereby preventing erosion of the contaminated soil by water and wind, and also reduce the production of leachate following rainfall events. However, for effective phytostabilization to occur, a dense plant cover must be established, and deep and highly-branched root systems must be developed (Radioman et al., 2022).

The perennial plants in this research, *P. australis* and *I. pseudacorus* (**I** and **II**), *S. schwerinii* (**III**), accumulated the most Cd, Cr and REE in the roots. This might be due to the roots of these plants to change the physical characteristics of their rhizospheres, which results in enhanced Cd, Cr and REE absorption by their roots and constrained translocation to the above-ground parts of the plant (Radziemska et al. 2017). This process activates enzymes involved in chelation, vacuolar sequestration and compartmentalization, the synthesis of phytochelatins and osmolytes, and other plant defense mechanisms, which results in increased accumulation of many metals in the root and restricted root-to-shoot translocation (Lux et al. 2011). The findings from Soda et al. (2012) support our results, in contrast, *Iris lactea* var. chinensis, in Cd polluted soils, has been shown to hold the greatest Cd concentrations in aboveground parts rather than in roots, which would suggest that metal accumulation might be influenced by the type and nature of the pollutant, as well as by the experimental conditions (Hou et al. 2020). Macrophytes are favored for the remediation of wastewater due to their large biomass and tolerance to PTE (Yadav et al. 2021). However, in FTW, plant biomass harvesting before senescence could help to remove nutrients and inhibit the nutrient discharge back into the water. In particular, nutrient removal could be expanded through the harvest of below-water biomass (roots/rhizomes), which holds a large amount of nutrients (Fan et al. 2021).

5.6 Factors that affect phytoremediation potential, and strategies for improvement

According to Lea et al. (2014), the presence of anthocyanins, thiols and antioxidants can lead to an increase in metal tolerance in plants, which is due to the elevated P levels in the roots (Longo and Ma, 2005). The absorption of dissolved metals by the roots is a critical part of plant metal uptake. The transportation of these metals to the root surface occurs via several mechanisms, which include mass flow, cation exchange, osmosis, capillary action, or ion diffusion (Sharma et al. 2021). The phytoremediation potential of plants might be restricted by the bioavailability and mobility of targeted PTE due to certain factors, such as nutrient availability and biomass production, which are influenced by soil properties (organic matter content, pH, density, and microbial composition) and the characteristics of the plants used for the phytoremediation purpose. These drawbacks could be overcome by the selection of suitable plant and soil amendments/chelators to improve the growth and phytoremediation efficiency (Okoroafor et al. 2022). In this context, different chelators, for example, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), ethylene diamine disuccinic acid (EDDS) and low-molecular-weight organic acids (LMWOA) have been widely exploited in phytoremediation research to enhance the bioavailability of PTE in the soil, as well as to foster PTE accumulation in plants (Guo et al. 2018; Duo et al. 2022). In general, chelators refer to a ligand that can form a cyclic structure complex with metal ions, and can, for example, chelate with PTE in the soil to configure water-soluble and exchangeable metal-chelating agent complexes, which subsequently increase metal mobility and bioavailability, and eventually enhance metal uptake by the plants (You et al. 2022).

Plants are considered ideal candidates for phytoremediation if they show a strong capacity to accumulate PTE in their roots (phytostabilization) or translocate PTE in their shoots (phytoextraction), display rapid growth and produce substantial biomass (Egendorf et al. 2020). Plant biomass contributes 13−15% of worldwide energy consumption, and around 50% of the global population depends on biomass as a crucial energy source (Zhao et al. 2012). Numerous factors, such as the type of floating mat, plant type, the development period and wastewater properties, nutrient amount and redox potential might have a negative impact on plant growth and biomass production (Mfarrej et al. 2023). However, the perennial plants used in research summarized in this thesis (**I−III**) did not show conflicting responses in terms of growth and biomass production, although certain anatomical anomalies were observed in the roots for instance, disruption in the vessel elements of the stele, and the cortex exhibited deformation under the high-dose Cr (Cr2000) treatment. In this context, hydroponic trials (employing FTW) could offer a means to develop biomass at an industrial scale (e.g., biorefinery for biofuel production). Nevertheless, energy production from FTW that employ a combination of different plant species with strong biomass production, could increase nutrient, PTE and REE removal, as well as alleviate global warming, while balancing nutrient-removal efficiency and reducing the energy crisis (Fan et al. 2021). Our findings prove that Cd, Cr and REE phytostabilization using *P. australis*, *I. pseudacorus* and *Salix* plants might be cost-effective and environmentally friendly, and avoid the need for disposal. However, the effectiveness of this technique may vary depending on site-specific conditions. Further research and field trials are needed to decide its suitability for different wastewater types and environments.

6 CONCLUSIONS

In this research, *P. australis* and *I. pseudacorus* did not show any visible signs of metal toxicity, such as necrosis, chlorosis, or withering, when exposed to an enhanced Cd and Cr environment. The results indicated that both plant species exhibited positive responses across a range of growth parameters (stem/root growth, biomass production, root length) and tolerance indices (DBTI, SLTI, RLTI, and CCI), under different Cd doses. Additional Cr doses (500 and 1000 µg/L) inhibited biomass development and growth in both species, although there was no negative effect of Cr on nutrient reduction in the system. *Salix* plants did not exhibit any REE toxicity symptoms. Among the studied *Salix*, the cultivar Klara produced the greatest absolute mean stem height and dry biomass values.

The findings show that *P. australis* and *I. pseudacorus* can respectively produce considerable amounts of biomass (6.80 g and 6.13 g) and efficiently accumulate Cd in roots (1821.59 µg $\cdot$ $(0.05\ m^2)^{-1}$ and 4900 µg $\cdot$ $(0.05\ m^2)^{-1}$) in a short exposure duration of 50 days. *P. australis* was able to overall remove 24−78% N and 10−54% P and 54−61% Cd in 50 days. On the other hand, *I. pseudacorus* removed overall 59−80% N and 0−60% P and 56−70% Cd. The highest accumulation of Cd was observed in the roots rather than the shoots of both P. australis and I. pseudacorus under high-dose (Cd: 4 mg/L) treatment. Moreover, the majority of Cr (97–100 %) was removed within 10 days. Like Cd, the highest Cr was also accumulated in the *P. australis* and *I. pseudacorus* roots than shoots system. Willows accumulated the highest amount of REE in roots as compared to stem and leaves. Concerning REE recovery, in the bottom ash formed at 1000 °C, the concentrations of individual REE metals varied between 1 and 1.68% and the total REE content was 8%, similarly, at 800 °C the concentrations varied between 0.90 and 1.52% and the total REE content was 7%.The preliminary assessment of REE recovery from willow biomass ashes shows overall more than 80% retention in the bottom ashes at 1000 °C indicating least volatilization of REE during combustion process.

Anatomical observations revealed that Cd toxicity significantly reduced the size of air cavities in the roots of *P. australis*, while increasing the size of cells in the cortical parenchyma (C) between the Ep and En layers in *I. pseudacorus* under Cd_4 treatments. Nonetheless, both species exhibited the development of resistance mechanisms, indicating the interconnectedness of different plant parts and organs within the overall plant system. These findings suggest that *P. australis* and *I. pseudacorus* could be used for the remediation of Cd-contaminated water bodies. In the case of Cr, microscopic analysis reveals no histological changes in the roots in the control, Cr 500 and 1000 µg/L treatments, whereas Cr 2000 µg/L dose caused disruptions in the arrangement of vessel elements in the stele and deformation of cortex.

However, the studied plant species prove their potential to restrict Cd, Cr, and REE translocations to shoot system along with high biomass production suggesting their potential as phytostabilizers for immobilizing metals in the root system. Nevertheless, further investigation is required to better understand the complex processes of Cd, Cr and REE removal, as well as their accumulation in the roots and its translocation to the shoots over a longer duration.

Future recommendation

The current findings were based on microcosm experiments. Future research should focus on the recovery of REE using diverse combinations of plant species in real-world wastewater environments over an extended period that considers seasonal variations and changing environmental conditions. In addition, it is recommended to conduct microbiome development analysis in FTW to gain a better understanding of the role of microorganisms in wastewater treatment and the phytostabilization processes. Prior to practical application, a combination of different grass, shrub and tree species should be evaluated for phytostabilization under field conditions, thereby aiming at the development of a more sustainable ecosystem. Given the significance of P removal described in this research, future studies should explore and develop innovative methods for P recovery from stormwater. This research would contribute to resource conservation and promote the reuse of P as a valuable fertilizer. Moreover, an exploration of the potential of FTW as a source of biomass is essential. Future studies should investigate the energy characterization of plant biomass and assess its suitability for bioenergy production. Lastly, the potential benefits of compounding FTW with other water treatment technologies, for example, electrochemical or biofilters processes should be explored to identify synergies and complementary effects that can enhance pollutant removal, system resilience and resource recovery.

REFERENCES

Arienzo M, Ferrara L, Trifuoggi M, Toscanesi M (2022) Advances in the Fate of Rare Earth Elements, REE, in Transitional Environments: Coasts and Estuaries. Water 14: 401. https://doi.org/10.3390/w14030401.

Álvarez-Robles MJ, Bernal MP, De Brasi-Velasco S, Sevilla F, Clemente R (2022a) Response of *Phragmites australis* to increasing As (V) concentrations: Accumulation and speciation of As, and plant oxidative stress. Chemosphere 302: 134937. https://doi.org/10.1016/j.chemosphere.2022.134937.

Álvarez-Robles MJ, Bernal MP, Clemente R (2022b) Differential response of *Oryza sativa* L. and *Phragmites australis* L. plants in trace elements contaminated soils under flooded and unflooded conditions. Environ Geochem Health 44: 99–115. https://doi.org/10.1016/j.chemosphere.2022.134937.

Al-Rubaie ASA, Al-Kubaisa ARA (2015) Removal of Lead from water using aquatic plants (*Ceratophyllum demersum* and *Eichhorina crassipes*). Int J Curr Microbiol Appl Sci 4: 45–5.

Ait Ali, N., Bernal, M.P., Ater, M., 2004. Tolerance and bioaccumulation of cadmium by *Phragmites australis* grown in the presence of elevated concentrations of cadmium, copper, and zinc. Aquatic Botany 80:163-176. https://doi.org/10.1016/j.aquabot.2004.08.008.

Arif N, Yadav V, Singh S, Singh S, Ahmad P, Mishra RK, Sharma S, Tripathi DK, Dubey NK, Chauhan DK (2016) Influence of high and low levels of plant-beneficial heavy metal ions on plant growth and development. Front Environ Sci 4:69. https://doi.org/10.3389/fenvs.2016.00069.

Baral A, Engelken RD (2002) Chromium-based regulations and greening in metal finishing industries in the USA. Environ Sci Policy 5:121–133. https://doi.org/10.1016/S1462-9011(02)00028-X.

Bartucca ML, Cerri M, Del Buono D, Forni C (2022) Use of Biostimulants as a New Approach for the Improvement of Phytoremediation Performance—A Review. Plants 11: 1946. https://doi.org/10.3390/plants11151946.

Barbera M, Zuddas P, Palazzolo E, Saiano F (2021) The distribution of Rare Earth Elements discriminates the growth substrate of *Vitis vinifera* L. Chemosphere 266: 128993. https://doi.org/10.1016/j.chemosphere.2020.128993.

Bousbih M, Lamhamedi MS, Abassi M, Khasa DP, Béjaoui Z (2023) Potential Use of Two Forest Species (*Salix alba* and *Casuarina glauca*) in the Rhizofiltration of Heavy-Metal-Contaminated Industrial Wastewater. Forests 14: 654. https://doi.org/10.3390/f14030654.

Bi R, Zhou C, Jia Y, Wang S, Li P, Reichwaldt ES, Liu W (2019) Giving waterbodies the treatment they need: a critical review of the application of constructed floating wetlands. J Environ Manage 238: 484–498. https://doi.org/10.1016/j.jenvman.2019.02.064.

Brieger G, Wells JR, Hunter RD (1992) Content in fly ash ecosystem. Water Air Soil Pollut 63: 87–103. https://doi.org/10.1007/BF00475624.

Briffa J, Sinagra E, Blundell R (2020) Heavy metal pollution in the environment and their toxicological effects on humans. Heliyon 6: e04691. https://doi.org/10.1016/j.heliyon.2020.e04691.

British Geological Survey (2023) Rare earth mineralization in Finland. https://www.eurare.org/countries/finland.html. Accessed 20 April 2023

Bullard MJ, Mustill, SJ, McMillan SD, Nixon PMI, Carver P, Britt CP, (2002) Yield Improvements through Modification of Planting Density and Harvest Frequency in Short Rotation Coppice *Salix* spp.—1. Yield Response in Two Morphologically Diverse Varieties. Biomass Bioenergy 22: 15–25. https://doi.org/10.1016/S0961-9534(01)00054-X.

Boynukisa E, Schück M, Greger M (2023) Differences in Metal Accumulation from Stormwater by Three Plant Species Growing in Floating Treatment Wetlands in a Cold Climate. Water Air Soil Pollut 234: 235. https://doi.org/10.1007/s11270-023-06199-7.

Caldelas C, Araus JL, Febrero A, Bort J (2012) Accumulation and toxic effects of chromium and zinc in *Iris pseudacorus* L. Acta Physiol Plant 34: 1217–1228. https://doi.org/10.1007/s11738-012-0956-4.

Cao Y, Tan Q, Zhang F, Ma C, Xiao J, Chen G (2022) Phytoremediation potential evaluation of multiple Salix clones for heavy metals (Cd, Zn and Pb) in flooded soils. Sci Total Environ 813: 152482. https://doi.org/10.1016/j.scitotenv.2021.152482.

Cao Y, Zhang Y, Ma C, Li H, Zhang J, Chen G (2018) Growth, physiological responses, and copper accumulation in seven willow species exposed to Cu—a hydroponic experiment. Environ Sci Pollut Res 25: 19875–19886. https://doi.org/10.1007/s11356-018-2106-z.

Clemens S, Aarts MG, Thomine S, Verbruggen N (2013) Plant science: the key to preventing slow cadmium poisoning. Trends Plant Sci 18: 92–99.

https://doi.org/10.1016/j.tplants.2012.08.003.

Chen X, Zhao Y, Zhang C, Zhang D, Yao C, Meng Q, Zhao R, Wei Z (2020) Speciation, toxicity mechanism and remediation ways of heavy metals during composting: A novel theoretical microbial remediation method is proposed. J Environ Manage 272:111109. https://doi.org/10.1016/j.jenvman.2020.111109.

Chen H, Chen H, Chen Z (2022) A review of in situ phytoextraction of rare earth elements from contaminated soils. Int J Phytoremed 24: 557–566. https://doi.org/10.1080/15226514.2021.1957770.

Chance LMG, Van Brunt SC, Majsztrik JC, White SA (2019) Short-and long-term dynamics of nutrient removal in floating treatment wetlands. Water Res 159: 153–163. https://doi.org/10.1016/j.watres.2019.05.012.

Davis AP, Shokouhian M, Ni S (2001) Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere 44: 997–1009. https://doi.org/10.1016/S0045-6535(00)00561-0.

Deletic A, Maksumovic CT (1998) Evaluation of water quality factors in storm runoff from paved areas. J Environ Eng 124: 869–879. https://doi.org/10.1061/(ASCE)0733-9372(1998)124:9(869).

DeSorbo CR, Fair J, Taylor K, Hanson W, Evers DC, Vogel HS, Cooley, JH (2008) Guidelines for constructing and deploying Common Loon nesting rafts. Northeastern Naturalist 15:75–86. https://doi.org/10.1656/1092-6194(2008)15[75:GFCADC]2.0.CO;2.

Di Luca GA, Mufarrege MDLM, Hadad HR, Maine MA, Nocetti E, Montañez F, Campagnoli MA (2023) Cr (III) and Cr (VI) removal in floating treatment wetlands (FTWs) using Typha domingensis. Int J Phytoremed: 1–11. https://doi.org/10.1080/15226514.2023.2199877.

Dou X, Dai H, Skuza L, Wei S (2022) Cadmium removal potential of hyperaccumulator Solanum nigrum L. under two planting modes in three years continuous phytoremediation. Environ Pollut 307: 119394. https://doi.org/10.1016/j.envpol.2022.119493.

Duchna M, Cieślik I (2022) Rare Earth Elements in New Advanced Engineering Applications. Rare Earth Elements - Emerging Advances, Technology Utilization, and Resource Procurement Dec 26; http://dx.doi.org/10.5772/intechopen.109248.

Ederli L, Reale L, Ferranti F, Pasqualini S (2004) Responses induced by high concentration of cadmium in Phragmites australis roots. Physiologia Plantarum 121:, 66–74. https://doi.org/10.1111/j.0031-9317.2004.00295.x

Egendorf SP, Groffman P, Moore G, Cheng Z (2020) The limits of lead (Pb) phytoextraction and possibilities of phytostabilization in contaminated soil: a critical review. Int J Phytoremed 22: 916–930. https://doi.org/10.1080/15226514.2020.1774501.

Eriksson E, Baun A, Mikkelsen PS, Ledin A (2007) Risk assessment of xenobiotics in stormwater discharged to Harrestrup Å, Denmark. Desalination 215:187–197.

https://doi.org/10.1016/j.desal.2006.12.008.

Fan X, Du Y, Luo B, Han W, Niu S, Gu W, Liu D, Chang J, Chang SX, Ge Y (2021) Increasing plant diversity to mitigate net greenhouse effect of wastewater treatment in floating constructed wetlands. J Cleaner Production10: 314:127955. https://doi.org/10.1016/j.jclepro.2021.127955.

Feng J, Lin Y, Yang Y, Shen Q, Huang J, Wang S, Zhu X, Li Z (2018) Tolerance and bioaccumulation of Cd and Cu in *Sesuvium portulacastrum*. Ecotoxicol Environ Safe 147: 306–312. https://doi.org/10.1016/j.ecoenv.2017.08.056.

Finnegan PM, Chen W (2012) Arsenic toxicity: the effects on plant metabolism. Front Physiol 3: 182. https://doi.org/10.3389/fphys.2012.00182.

García-Ávila F, Avilés-Añazco A, Cabello-Torres R, Guanuchi-Quito A, Cadme-Galabay M, Gutiérrez-Ortega H, Alvarez-Ochoa R, Zhindón-Arévalo C (2023) Application of ornamental plants in constructed wetlands for wastewater treatment: A scientometric analysis. CSCEE 7:100307. https://doi.org/10.1016/j.cscee.2023.100307.

Glick, B. Using soil bacteria to facilitate phytoremediation. Biotechnol. Adv. 2010, 28, 367–374. https://doi.org/10.1016/j.biotechadv.2010.02.001.

Gwenzi W, Mangori L, Danha C, Chaukura N, Dunjana N, Sanganyado E (2018) Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants[J]. Sci Total Environ 636: 299–313. https://doi.org/10.1016/j.scitotenv.2018.04.235.

Garbarino, J.R., Hayes, H., Roth, D., Antweider, R., Brinton, T.I. and Taylor, H., 1995. Contaminants in the Mississippi River US Geological survey circular 1133. Virginia USA.

Ghaly AE, Ananthashankar R, Alhattab MVVR, Ramakrishnan VV (2014) Production, characterization and treatment of textile effluents: a critical review. J Chem Eng Process Technol 5:1–19. http://dx.doi.org/10.4172/2157-7048.1000182.

Gaji´c G, Djurdjevi´c L, Kosti´c O, Jari´c S, Mitrovi´c M, Pavlovi´c P (2018) Ecological potential of plants forphytoremediation and ecorestoration of fly ash deposits and mine wastes. Front Environ Sci 20:124. https://doi.org/10.3389/fenvs.2018.00124.

Guo D, Ali A, Ren C, Du J, Li R, Lahori AH, Xiao R, Zhang Z, Zhang Z (2019) EDTA and organic acids assisted phytoextraction of Cd and Zn from a smelter contaminated soil by potherb mustard (*Brassica juncea*, Coss) and evaluation of its bioindicators. Ecotoxicol Environ Safe 167:396–403. https://doi.org/10.1016/j.ecoenv.2018.10.038.

Hanana H, Gagné F, Trottier S, Bouchard P, Farley G, Auclair J, Gagnon C (2022) Assessment of the toxicity of a mixture of five rare earth elements found in aquatic ecosystems in Hydra vulgaris. Ecotoxicol Environ Safe 241:113793. https://doi.org/10.1016/j.ecoenv.2022.113793.

Hanana H, Auclair J, Turcotte P, Gagnon C, Gagne F, (2023) Toxicity of Two Heavy Rare Earth Elements to Freshwater Mussels Dreissena Polymorpha.

Available at SSRN: https://dx.doi.org/10.2139/ssrn.4408153.

Haghnazar H, Sabbagh K, Johannesson KH, Pourakbar M, Aghayani E (2023) Phytoremediation capability of *Typha latifolia* L. to uptake sediment toxic elements in the largest coastal wetland of the Persian Gulf. Mar Pollut Bull 188: 114699. https://doi.org/10.1016/j.marpolbul.2023.114699.

Helsinki Times (2023) Significant deposits of rare earth metals discovered in Finnish Lapland. https://www.helsinkitimes.fi/finland/finland-news/domestic/22982-significant-deposit-of-rare-earth-metals-discovered-in-finnish-lapland.html#:~:text=Finnish%20Minerals%20Group%2C%20the%20state,permanent%20magnet%20production%20in%20Europe. Accessed 10 June 2023

Hou X, Teng W, Hu Y, Yang Z, Li C, Scullion J, Guo Q, Zheng R (2020) Potential phytoremediation of soil cadmium and zinc by diverse ornamental and energy grasses. BioResour 15:616–640.

Huang, J., Yan, C.N., Cao, C., Peng, C., Liu, J.L. and Guan, W.Z., 2018. Performance evaluation of Iris pseudacorus constructed wetland for advanced wastewater treatment under long-term exposure to nanosilver. Ecol Engineering 116: 188–195. https://doi.org/10.1016/j.ecoleng.2018.03.003.

Jerbi A, Laur J, Lajoie K, Gallant PP, Barnabé S, Pitre FE, Labrecque M (2023) Irrigation with primary wastewater alters wood anatomy and composition in willow *Salix miyabeana* SX67. Front Plant Sci 14: 662. https://doi.org/10.3389/fpls.2023.1087035.

Kabata-Pendias A (2011) Trace elements in soils and plants (4th ed.). Boca Raton: CRS Press Inc. https://doi.org/10.1201/b10158.

Keizer-Vlek HE, Verdonschot PF, Verdonschot RC, Dekkers D (2014) The contribution of plant uptake to nutrient removal by floating treatment wetlands. Ecol Eng 73: 684–690. https://doi.org/10.1016/j.ecoleng.2014.09.081.

Kyambadde J, Kansiime F, Gumaelius L, Dalhammar G (2004) A comparative study of Cyperus papyrus and Miscanthidium violaceum-based constructed wetlands for wastewater treatment in a tropical climate. Water Res 38:475–485. https://doi.org/10.1016/j.watres.2003.10.008.

Kuzovkina YA, Quigley MF (2005) Willows Beyond Wetlands: Uses of *Salix* L. Species for Environmental Projects. Water Air Soil Pollut 162: 183–204. https://doi.org/10.1007/s11270-005-6272-5

Ladislas S, Gérente C, Chazarenc F, Brisson J, Andrès Y (2015) Floating treatment wetlands for heavy metal removal in highway stormwater ponds. Ecol Eng 80: 85–91. https://doi.org/10.1016/j.ecoleng.2014.09.115.

Landberg T, Greger M (2022) Phytoremediation Using Willow in Industrial Contaminated Soil. Sustainability 14: 8449. https://doi.org/10.3390/su14148449.

Ledin S (1996) Willow wood properties, production and economy. Biomass Bioenergy11: 75–83. https://doi.org/10.1016/0961-9534(96)00022-0.

Leão GA, de Oliveira JA, Felipe RTA, Farnese FS, Gusman GS (2014) Anthocyanins, thiols, and antioxidant scavenging enzymes are involved in *Lemna gibba* tolerance to arsenic. J Plant Interact 9: 143–151. https://doi.org/10.1080/17429145.2013.784815.

Leguizamo MAO, Gómez WDF, Sarmiento MCG (2017) Native herbaceous plant species with potential use in phytoremediation of heavy metals, spotlight on wetlands—a review. Chemosphere 168: 1230–1247. https://doi.org/10.1016/j.chemosphere.2016.10.075.

Lebrun M, Macri C, Miard F, Hattab-Hambli N, Motelica-Heino M, Morabito D, Bourgerie S (2016) Effect of biochar amendments on As and Pb mobility and phy- toavailability in contaminated mine technosols phytoremediated by Salix. J Geochem Explor 182: 149–156. https://doi.org/10.1016/j.gexplo.2016.11.016.

Li J, Leng Z, Jia H, Wei L, Yuguda TK, Du D (2023) Effect of Seawall Embankment Reclamation on the Distribution of Cr, Cu, Pb and Zn Pollution in Invasive Spartina alterniflora and Native *Phragmites australis* Coastal Saltmarshes of East China. Biology12: 253. https://doi.org/10.3390/biology12020253.

Lyytimäki JM (2007) Temporalities and environmental reporting: press news on eutrophication in Finland. Environ Sci 4: 41–51.
https://doi.org/10.1080/15693430701295866.

Luongo T, Ma LQ (2005) Characteristics of arsenic accumulation by Pteris and non-Pteris ferns. Plant Soil 277: 117–126. https://doi.org/10.1007/s11104-005-6335-9.

Lu XX, Gu YG, Wang ZH, Liang RZ, Han YJ, Li HS (2022) Risk on assessment of 15 REEs and mixtures by DGT in Songhua River system sediments of China's largest old industrial base. Environ Res 212: 113368. https://doi.org/10.1016/j.envres.2022.113368.

Lima AT, Ottosen L (2021) Recovering rare earth elements from contaminated soils: Critical overview of current remediation technologies. Chemosphere 265:129163.
https://doi.org/10.1016/j.chemosphere.2020.129163.

Lima AT, Kirkelund GM, Ntuli F, Ottosen LM (2022) Screening dilute sources of rare earth elements for their circular recovery. J Geochem Explor 238:107000.
https://doi.org/10.1016/j.gexplo.2022.107000.

Leitão TE, Cameira MR, Costa HD, Pacheco JM, Henriques MJ, Martins LL, Mourato MP (2018) Environmental quality in urban allotment gardens: Atmospheric deposition, soil, water and vegetable assessment at LISBON City. Water Air Soil Pollut 229: 1–22. https://doi.org/10.1007/s11270-017-3681-1.

Lux A, Martinká M, Vaculík M, White PJ. Root responsesto cadmium in the rhizosphere: a review. J Exp Bot.2011;62(1):21-37. https://doi.org/10.1093/jxb/erq281.

Mathur J, Chauhan P, Srivastava S (2022) Comparative evaluation of cadmium phytoremediation potential of five varieties of Helianthus annuus L. Int J Phytoremed: 1–12. https://doi.org/10.1080/15226514.2022.2110036.

Malaviya P, Singh A (2012) Constructed wetlands for management of urban stormwater runoff. Critical Reviews in Environmental Science and Technology 42: 2153–2214. https://doi.org/10.1080/10643389.2011.574107.

Mleczek P, Borowiak K, Budka A, Niedzielski P (2018) Relationship between concentration of rare earth elements in soil and their distribution in plants growing near a frequented road. Environ Sci Pollut Res 25: 23695–23711. https://doi.org/10.1007/s11356-018-2428-x.

McAndrew B, Ahn C (2017) Developing an ecosystem model of a floating wetland for water quality improvement on a stormwater pond. J Environ Manage 202: 198–207. https://doi.org/10.1016/j.jenvman.2017.07.035.

Mohsin M, Kaipiainen E, Salam MMA, Evstishenkov N, Nawrot N, Villa A, Wojciechowska E, Kuittinen S, Pappinen A (2021) Biomass Production and Removal of Nitrogen and Phosphorus from Processed Municipal Wastewater by *Salix schwerinii*: A Field Trial. Water 3: 2298. https://doi.org/10.3390/w13162298.

Mfarrej MFB, Wang X, Fahid M, Saleem MH, Alatawi A, Ali S, Shabir G, Zafar R, Afzal M, Fahad S (2023) Floating treatment wetlands (FTWs) is an innovative approach for the remediation of petroleum hydrocarbons-contaminated water. J Plant Growth Regul 42:1402-1420. https://doi.org/10.1007/s00344-022-10674-6.

Martin BC, George SJ, Price CA, Ryan MH, Tibbett M (2014) The role of root exuded low molecular weight organic anions in facilitating petroleum hydrocarbon degradation: current knowledge and future directions. Sci Total Environ 472: 642–653. https://doi.org/10.1016/j.scitotenv.2013.11.050.

Mohsin M, Kaipiainen E, Salam MMA, Evstishenkov N, Nawrot N, Villa A, Wojciechowska E, Kuittinen S, Pappinen A (2021) Biomass Production and Removal of Nitrogen and Phosphorus from Processed Municipal Wastewater by Salix schwerinii: A Field Trial. Water 13: 2298. https://doi.org/10.3390/w13162298.

Mohsin M, Kuittinen S, Salam MMA, Peräniemi S, Laine S, Pulkkinen P, Kaipiainen E, Vepsäläinen J, Pappinen A (2019) Chelate-assisted phytoextraction: Growth and ecophysiological responses by Salix schwerinii EL Wolf grown in artificially polluted soils. J Geochem Explor 205: 106335. https://doi.org/10.1016/j.gexplo.2019.106335.

Mustafa, H.M. and Hayder, G., 2021. Recent studies on applications of aquatic weed plants in phytoremediation of wastewater: A review article. Ain Shams Engineering Journal, 12(1), pp.355-365. https://doi.org/10.1016/j.asej.2020.05.009.

Nkoh JN, Ajibade FO, Atakpa EO, Abdulaha-Al Baquy M, Mia S, Odii EC, Xu R (2022) Reduction of heavy metal uptake from polluted soils and associated health risks through biochar amendment: A critical synthesis. J Hazard Mater Adv: 6100086. https://doi.org/10.1016/j.hazadv.2022.100086.

Nwe ML, Oo TK, Linn NN (2018) Phytoremediator: Removal of Heavy Metals from Synthetic Aqueous Solution by Water Hyacinth (Eichhornia Crassipes). 3rd Myanmar Korea Conf Res J 3: p 1659–1666.

Okoroafor PU, Kunisch N, Epede MN, Ogunkunle CO, Heilmeier H, Wiche O (2022) Phytoextraction of rare earth elements, germanium and other trace elements as affected by fertilization and liming. Environ Technol Innov 28: 102607. https://doi.org/10.1016/j.eti.2022.102607.

Oladoye PO, Olowe OM, Asemoloye MD (2022) Phytoremediation technology and food security impacts of heavy metal contaminated soils: A review of literature. Chemosphere 288: 132555. https://doi.org/10.1016/j.chemosphere.2021.132555.

Ouyang Z, Yang Z, Feng G, Zhao Y (2019) Analysis on enrichment of aquatic plants response to434different heavy metal ions in polluted water taking duckweed as an example. Appl Ecol Environ Res 43517: 3469–3482. https://doi.org/10.15666/aeer/1702_34693482.

Pang X, Li D, Peng A (2002) Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. Environ Sci Pollut Res 9: 143–148. https://doi.org/10.1007/BF02987462.

Petrov DS, Yakusheva AM (2021) Assessment of the input of phosphorus and nitrogen compounds into the Gulf of Finland through tributaries of the Neva River within the borders of St. Petersburg. J Agri Environ 4: 20. https://doi.org/10.23649/jae.2021.4.20.4.

Pourret O, Hursthouse A (2019) It's time to replace the term "heavy metals" with "potentially toxic elements" when reporting environmental research. Int J Environ Res Public Health 16: 4446. https://doi.org/10.3390/ijerph16224446.

Pourrut B, Shahid M, Dumat C, Winterton P, Pinelli E (2011) Lead uptake, toxicity, and detoxification in plants. Reviews of environmental contamination and toxicology volume 213. pp 113–136.

Ramachandra TV, Sudarshan PB, Mahesh MK, Vinay S (2018) Spatial patterns of heavy metal accumulation in sediments and macrophytes of Bellandur wetland, Bangalore. J Environ Manage 206: 1204–1210. https://doi.org/10.1016/j.jenvman.2017.10.014.

Rangabhashiyam S, Vijayaraghavan K (2019) Biosorption of Tm (III) by free and polysulfone-immobilized Turbinaria conoides biomass. J Ind Eng Chem 80: 318–324. https://doi.org/10.1016/j.jiec.2019.08.010.

Rampanelli GB, Braun AB, Visentin C, Trentin AWDS, da Cruz R, Thomé A (2021) The Process of Selecting a Method for Identifying Potentially Contaminated Sites—a Case Study in a Municipality in Southern Brazil. Water Air Soil Pollut 232: 1–20. https://doi.org/10.1007/s11270-020-04970-8.

Ramprasad C, Gwenzi W, Chaukura N, Azelee NIW, Rajapaksha AU, Naushad M, Rangabhashiyam S (2022) Strategies and options for the sustainable recovery of rare earth elements from electrical and electronic waste. Chem Eng J 442: 135992. https://doi.org/10.1016/j.cej.2022.135992.

Radziemska M, Vaverková MD, Baryła A (2017) Phytostabiliza-tion-Management Strategy for Stabilizing Trace Elements in Contaminated Soils. Int J Environ Res Public Health 14:958. https://doi.org/10.3390/ijerph14090958.

Radziemska M, Gusiatin MZ, Mazur Z, Radzevicˇius A, Be ̨s ́ A, Šadzevicˇius R, Holatko J, Dapkiene M, Adamonyte ̇I, Brtnicky M (2023) Composite Biochar with Municipal Sewage Sludge Compost—A New Approach to Phytostabilization of PTE Industrially Contaminated Soils. Energies 16: 1778. https://doi.org/10.3390/en16041778.

Radziemska M, Gusiatin ZM, Mazur Z, Hammerschmiedt T, Bęś A, Kintl A, Galiova MV, Holatko J, Blazejczyk A, Kumar V, Brtnicky M (2022) Biochar-Assisted Phytostabilization for Potentially Toxic Element Immobilization. Sustainability 14: 445. https://doi.org/10.3390/su14010445.

Ramos SJ, Dinali GS, Oliveira C, Martins GC, Moreira CG, Siqueira JO, Guilherme LR, (2016) Rare earth elements in the soil environment. Curr Pollut Rep 2: 28–50. https://doi.org/10.1007/s40726-016-0026-4.

Redling K (2006) Rare Earth Elements in Agriculture with Emphasis on Animal Husbandry. PhD dissertation. Ludwig-Maximilians-Universität München.
Rocha ACS, Almeida CMR, Basto MCP, Vasconcelos MTS (2014) Antioxidant response of *Phragmites australis* to Cu and Cd contamination. Ecotoxicol Environ Safe 109:152–160. https://doi.org/10.1016/j.ecoenv.2014.06.027.

Rios C, M´endez-Armenta M (2019) Cadmium neurotoxicity. In: Nriagu, J. (Ed.), Encyclopedia of Environmental Health, second ed. Elsevier, pp. 485–491. https://doi.org/10.1016/B978-0-12-409548-9.11571-4.

Rigotti JA, Paqualini JP, Rodrigues LR (2021) Root growth and nutrient removal of *Typha domingensis* and *Schoenoplectus californicus* over the period of plant establishment in a constructed floating wetland. Environ Sci Pollut Res 28:8927–8935. https://doi.org/10.1007/s11356-020-11681-4.

Royen H, Fortkamp U (2016) Rare Earth Elements-Purification, Separation and Recycling. Report C211. IVL Swedish Environmental Research Institute, Stockholm Sweden, p. 34.

Sandoval-Herazo LC, Alvarado-Lassman A, Marín-Muñiz JL, Méndez-Contreras JM, Zamora-Castro SA (2018) Effects of the use of ornamental plants and different substrates in the removal of wastewater pollutants through microcosms of constructed wetlands. Sustainability 10:1594. https://doi.org/10.3390/su10051594.

Salam MMA, Kaipiainen E, Mohsin M, Villa A, Kuittinen S, Pulkkinen P, Pelkonen P, Mehtätalo L, Pappinen A (2016) Effects of contaminated soil on the growth performance of young *Salix* (*Salix schwerinii* EL Wolf) and the potential for phytoremediation of heavy metals. J Environ Manage 183: 467–477. https://doi.org/10.1016/j.jenvman.2016.08.082.

Sharma R, Vymazal J, Malaviya P (2021) Application of floating treatment wetlands for stormwater runoff: A critical review of the recent developments with emphasis on heavy metals and nutrient removal. Sci Total Environ 777: 146044.

https://doi.org/10.1016/j.scitotenv.2021.146044.

Shen S, Li X, Lu X (2021) Recent developments and applications of floating treatment wetlands for treating different source waters: a review. Environ Sci Pollut Res 28:62061–62084. https://doi.org/10.1007/s11356-021-16663-8.

Soda S, Hamada T, Yamaoka Y, Ike M, Nakazato H, Saeki Y, Kasamatsu T, Sakurai Y (2012) Constructed wetlands for advanced treatment of wastewater with a complex matrix from a metal-processing plant: bioconcentration and translocation factors of various metals in *Acorus gramineus* and *Cyperus alternifolius*. Ecol Eng 39:63–70. https://doi.org/10.1016/j.ecoleng.2011.11.014.

Sultana MY, Akratos CS, Pavlou S, Vayenas DV (2014) Chromium removal in constructed wetlands: a review. Int Biodeterior Biodegrad 96:181–190. https://doi.org/10.1016/j.ibiod.2014.08.009.

Tao Y, Shen L, Feng C, Qu J, Ju H, Yang R, Zhang Y (2022) Distribution of rare earth elements (REEs) and their roles in plants growth: A review. Environ Pollut 298:118540. https://doi.org/10.1016/j.envpol.2021.118540.

Tang X, Tong Z (1988) Effects of rare earth elements on the growth and activity of Chinese cabbage and cucumber roots[J]. Acta Hortic Sin 3:185–188.

Tang Y, Harpenslager SF, van Kempen MM, Verbaarschot EJ, Loeffen LM, Roelofs JG, Smolders AJ, Lamers LP (2017) Aquatic macrophytes can be used for wastewater polishing but not for purification in constructed wetlands. Biogeosciences 14:755–766. https://doi.org/10.5194/bg-14-755-2017.

Tóth G, Guicharnaud RA, Tóth B, Hermann T (2014) Phosphorus levels in croplands of the European Union with implications for P fertilizer use. Eur J Agron 55: 42–52.

UN Water (2018). Water quality and wastewater. https://www.unwater.org/sites/default/files/app/uploads/2018/10/WaterFacts_water_and_watewater_sep2018.pdf. Accessed 10 December 2022

Urakawa H, Dettmar DL, Thomas S (2017) The uniqueness and biogeochemical cycling of plant root microbial communities in a floating treatment wetland. Ecol Eng 108: 573–580. https://doi.org/10.1016/j.ecoleng.2017.06.066.

Verma R, Dwivedi P (2013) Heavy metal water pollution-A case study. Recent Research in Science and Technology, 5(5).

Wani KA, Sofi ZM, Malik JA, Wani JA Phytoremediation of heavy metals using *Salix* (willows). In Bioremediation and Biotechnology; Bhat R, Hakeem K, Dervash M (2020) Eds.; Springer: Cham, Swizerland, 2020; Volume 2, pp. 257–268.

Wani ZA, Ahmad Z, Asgher M, Bhat JA, Sharma M, Kumar A, Sharma V, Kumar A, Pant S, Lukatkin AS, Anjum NA (2023) Phytoremediation of Potentially Toxic Elements: Role, Status and Concerns. Plants 12: 429. https://doi.org/10.3390/plants12030429.

Wall F (2014) Rare earth elements. Critical metals handbook, 1st edn.Wiley, New York, pp 312–339.

Wei, F., Shahid, M.J., Alnusairi, G.S., Afzal, M., Khan, A., El-Esawi, M.A., Abbas, Z., Wei, K., Zaheer, I.E., Rizwan, M. and Ali, S., 2020. Implementation of floating treatment wetlands for textile wastewater management: a review. Sustainability, 12(14), p.5801. https://doi.org/10.3390/su12145801.

White PJ, Brown P (2010) Plant nutrition for sustainable development and global health. Ann Bot 105, 105: 073–1080. https://doi.org/10.1093/aob/mcq085.

Wang X, Liu E, Lin Q, Liu L, Yuan H, Li Z (2020) Occurrence, sources and health risks of toxic metal (loid) s in road dust from a mega city (Nanjing) in China. Environ Pollut 263:114518. https://doi.org/10.1016/j.envpol.2020.114518.

Weragoda SK, Jinadasa KBSN, Zhang DQ, Gersberg RM, Tan SK, Tanaka N, Jern NW (2012) Tropical application of floating treatment wetlands. Wetlands 32:955–961. https://doi.org/10.1007/s13157-012-0333-5.

Wojciechowska E, Pietrzak S, Matej-Łukowicz K, Nawrot N, Zima P, Kalinowska D, Wielgat P, Obarska-Pempkowiak H, Gajewska M, Dembska G, Jasin´ski P, Pazikowska-Sapota G, Galer-Tatarowicz K, Dzierzbicka-Głowacka L (2019) Nutrient loss from three small-size watersheds in the southern Baltic Sea in relation to agricultural practices and policy. J Environ Manage 252: 109637. https://doi.org/10.1016/j.jenvman.2019.109637.

Wu H, Zhang J, Li P, Zhang J, Xie H, Zhang B (2011) Nutrient removal in constructed microcosm wetlands for treating polluted river water in northern China Ecol Eng 37: 560–568. https://doi.org/10.1016/j.ecoleng.2010.11.020.
Wu M, Luo Q, Liu S, Zhao Y, Long Y, Pan Y (2018) Screening ornamental plants to identify potential Cd hyperaccumulators for bioremediation. Ecotoxicol Environ Safe 162: 35–41. https://doi.org/10.1016/j.ecoenv.2018.06.049.

Xu B, Wang X, Liu J, Wu J, Zhao Y, Cao W (2017) Improving urban stormwater runoff quality by nutrient removal through floating treatment wetlands and vegetation harvest. Sci Rep 7:1–11. https://doi.org/10.1038/s41598-017-07439-7.

Xu X, Yang B, Qin G, Wang H, Zhu Y, Zhang K, Yang H (2019) Growth, accumulation, and antioxidative responses of two *Salix* genotypes exposed to cadmium and lead in hydroponic culture. Environ Sci Pollut Res 26: 19770–19784. https://doi.org/10.1007/s11356-019-05331-7.

Yang, W., Zhao, F., Ding, Z., Shohag, M.J.I., Wang, Y., Zhang, X., Zhu, Z. and Yang, X., 2018. Screening of 19 Salix clones in effective phytofiltration potentials of manganese, zinc and copper in pilot-scale wetlands. International journal of phytoremediation, 20(13), pp.1275-1283. https://doi.org/10.1080/15226514.2014.898020.

Yadav, N., Govindwar, S.P., Rane, N., Ahn, H.J., Xiong, J.Q., Jang, M., Kim, S.H. and Jeon, B.H., 2021. Insights on the role of periphytic biofilm in synergism with Iris pseudacorus for removing mixture of pharmaceutical contaminants from wastewater. J Hazard Mater 418: 126349. https://doi.org/10.1016/j.jhazmat.2021.126349.

You Y, Dou J, Xue Y, Jin N, Yang K (2022) Chelating Agents in Assisting Phytoremediation of Uranium-Contaminated Soils: A Review. Sustainability 14: 6379. https://doi.org/10.3390/su14106379.

Yousefi, Z., Mohseni-Bandpei, A., 2010. Nitrogen and phosphorus removal from wastewater by subsurface wetlands planted with *Iris pseudacorus*. Ecol Eng 36: 777–782. https://doi.org/10.1016/j.ecoleng.2010.02.002.

Younas F, Bibi I, Afzal M, Al-Misned F, Niazi NK, Hussain K, Shahid M, Shakil Q, Ali F, Wang H (2023) Unveiling Distribution, Hydrogeochemical Behavior and Environmental Risk of Chromium in Tannery Wastewater. Water 15:391. https://doi.org/10.3390/w15030391.

Yu B, Lu X, Wang L, Liang T, Fan X, Yang Y, Lei K, Zuo L, Fan P, Bolan N, Rinklebe J (2023) Potentially toxic elements in surface fine dust of residence communities in valley industrial cities. Environ Pollut 327:121523. https://doi.org/10.1016/j.envpol.2023.121523.

Zanin G, Bortolini L, Borin M (2018) Assessing stormwater nutrient and heavy metal plant uptake in an experimental bioretention pond. Land 7:150. https://doi.org/10.3390/land7040150.

Zhang C, Geng N, Dai Y, Ahmad Z, Li Y, Han S, Zhang H, Chen J, Yang J (2023) Accumulation and distribution characteristics of rare earth elements (REEs) in the naturally grown marigold (*Tagetes erecta* L.) from the soil. Environ Sci Pollut Res: 1–13. https://doi.org/10.1007/s11356-023-25508-5.

Zhang, Q., Wang, C. Natural and Human Factors Affect the Distribution of Soil Heavy Metal Pollution: a Review. Water Air Soil Pollut 231, 350 (2020). https://doi.org/10.1007/s11270-020-04728-2.

Zhao F, Yang W, Zeng Z, Li H, Yang X, He Z, Gu B, Rafiq MT, Peng H (2012) Nutrient removal efficiency and biomass production of different bioenergy plants in hypereutrophic water. Biomass Bioenergy 42: 212–218. https://doi.org/10.1016/j.biombioe.2012.04.003.

Zhang L, Zhao J, Cui N, Dai Y, Kong L, Wu J, Cheng S. 2016. Enhancing the water purification efficiency of a floating treatment wetland using a biofilm carrier. Environ Sci Pollut Res. 23(8):7437–7443. https://doi-org.ezproxy.uef.fi:2443/10.1007/s11356-015-5873-9

Zhou B, Li Z, Chen C (2017) Global potential of rare earth resources and rare earth demand from clean technologies. Minerals 7:203. https://doi.org/10.3390/min7110203.

Zhou YQ, Huang SZ, Yu SL, Gu JG, Zhao JZ, Han YL, Fu JJ (2010) The physiological response and sub-cellular localization of lead and cadmium in *Iris pseudacorus* L. Ecotoxicol 19:69–76. https://doi/10.1007/s11356-015-5873-9.