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Phytoremediation of Heavy Metal Contamination From Terrestrial Enhanced Weathering: Can Plants Save the Day?

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Enhanced weathering is a promising approach to remove carbon dioxide from the atmosphere. However, it may also pose environmental risks through the release of heavy metals, in particular nickel and chromium. In this perspective article I explore the potential role of plants in modulating these heavy metal fluxes. Agricultural basaltic soils may be valuable study sites in this context. However, the effect of biomass harvesting on the accumulation of heavy metals is currently not well studied. Mostly caused by different parent rock concentrations, there is a large variability of heavy metal concentrations in basaltic and ultramafic soils. Hence, to minimize environmental risks of enhanced weathering, basalts with low heavy metal concentrations should be favored. Existing phytoremediation strategies may be used to “phytoremediate” the accumulation of nickel and chromium released from enhanced weathering in soils. As a result, elevated nickel and chromium concentrations in rocks must not preclude enhanced weathering in all settings. In particular, hyperaccumulating plants could be used as part of a crop rotation to periodically remove heavy metals from soils. Enhanced weathering could also be employed on fields or forests of (non-hyper) accumulating plants that have a high primary production of biomass. Both approaches may have additional synergies with phytomining or bioenergy carbon capture and storage, increasing the total amount of carbon dioxide drawdown and at the same time preventing heavy metal accumulation in soils.

Keywords: enhanced weathering, heavy metals, chromium, nickel, phytoremediation, hyperaccumulating plants, basalt

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INTRODUCTION

Limiting global warming to below 1.5 °C will require the development and implementation of carbon dioxide removal (CDR) technologies to offset residual and potential overshoot emissions (Fuss et al., 2018; IPCC, 2018). Among other CDR approaches (Fuss et al., 2018), terrestrial enhanced weathering (TEW) of silicate rocks has the potential to limit the accumulation of CO₂ in the atmosphere through the acceleration of natural weathering processes. Although TEW removes only ~0.3–1.1 tCO₂ per ton of rock (Köhler et al., 2010; Moosdorf et al., 2014; Strefler et al., 2018), when scaled up to large application rates (e.g. 40 t ha⁻¹; Beerling et al., 2020) it can remove between 0.5 and 4 GtCO₂ yr⁻¹ (Fuss et al., 2018; Beerling et al., 2020; Goll et al., 2021) or even up to 95 GtCO₂ yr⁻¹ (Strefler et al., 2018). Co-benefits of EW include (i) increasing the alkalinity of natural

waters which ameliorates ocean acidification and decreasing aragonite saturation (Taylor et al., 2016), (ii) stabilizing the soil pH which benefits plants and reduces emissions of other greenhouse gases (Kantola et al., 2017), (iii) improving soil hydrology (de Oliveira Garcia et al., 2020), and (iv) the release of nutrients which stimulates further biological carbon sequestration (Goll et al., 2021). Carbon dioxide removal through TEW does not require underground storage in geological reservoirs but still stores CO₂ in stable non-biological reservoirs such as the marine alkalinity pool or marine/pedogenic carbonates. Furthermore, selling carbon credits from TEW may also support livelihoods in the Global South and help progress toward multiple sustainable development goals (Smith et al., 2019).

Although models suggest that TEW could be a suitable CDR strategy (Strefler et al., 2018; Beerling et al., 2020; Goll et al., 2021), and pot and sediment core experiments detect increasing cation fluxes or bioavailable concentrations (Anda et al., 2009, 2013, 2015; ten Berge et al., 2012; Renforth et al., 2015; Amann et al., 2020), first field trials of TEW in agricultural settings do not detect an enhanced weathering signal in drainage waters (Andrews and Taylor, 2019). This is problematic because drainage waters integrate weathering signals over their catchment and would therefore be ideal to quantify TEW processes. Possible reasons include the retardation of weathering signals by the soil exchangeable cation pool (Pogge von Strandmann et al., 2021), precipitation of solutes in pedogenic carbonate (Haque et al., 2019, 2020b,c) and other secondary minerals, as well as the incorporation of released cations into biomass (Andrews and Taylor, 2019). Support for the latter mechanism can be drawn from (i) the fertilization potential of TEW implying cation uptake by plants (Hartmann et al., 2013; Amann and Hartmann, 2018; Goll et al., 2021), (ii) detectable cation flux responses in TEW experiments in forests (Peters et al., 2004; Shao et al., 2016; Taylor et al., 2021), and (iii) the observation that biomass constitutes a missing sink in weathering flux mass balances (von Blanckenburg et al., 2021).

Suitable rocks for enhanced weathering include basalt and dunite, an ultramafic rock mostly comprised of olivine. Both rocks, particularly dunite, often have elevated concentrations of Ni and Cr (Alloway, 2012). Alternatives with lower HM concentrations exist, for example wollastonite (Peters et al., 2004; Shao et al., 2016; Haque et al., 2019, 2020b,c; Taylor et al., 2021). However, they can be limited by availability (~0.1Gt global wollastonite reserves; USGS, 2021) or price. Upon release through weathering, Ni and Cr have the tendency to be incorporated into secondary phases or adsorb onto surfaces (Alloway, 2012). Hence, TEW may result in accumulation of these heavy metals in soils and biomass which can be toxic to living organisms at high concentrations (Miranda et al., 2009; Alloway, 2012; Hartmann et al., 2013; Beerling et al., 2018; Amann et al., 2020). For example, in an experiment using an agricultural soil core, ~99% of Ni and Cr released from olivine weathering are retained in the soil, limiting addition of olivine to soils to 95 t ha⁻¹ before permissible Ni concentrations are exceeded (Renforth et al., 2015). However, plants also take up trace elements like Ni and Cr (Pulford and Watson, 2003; Etim,

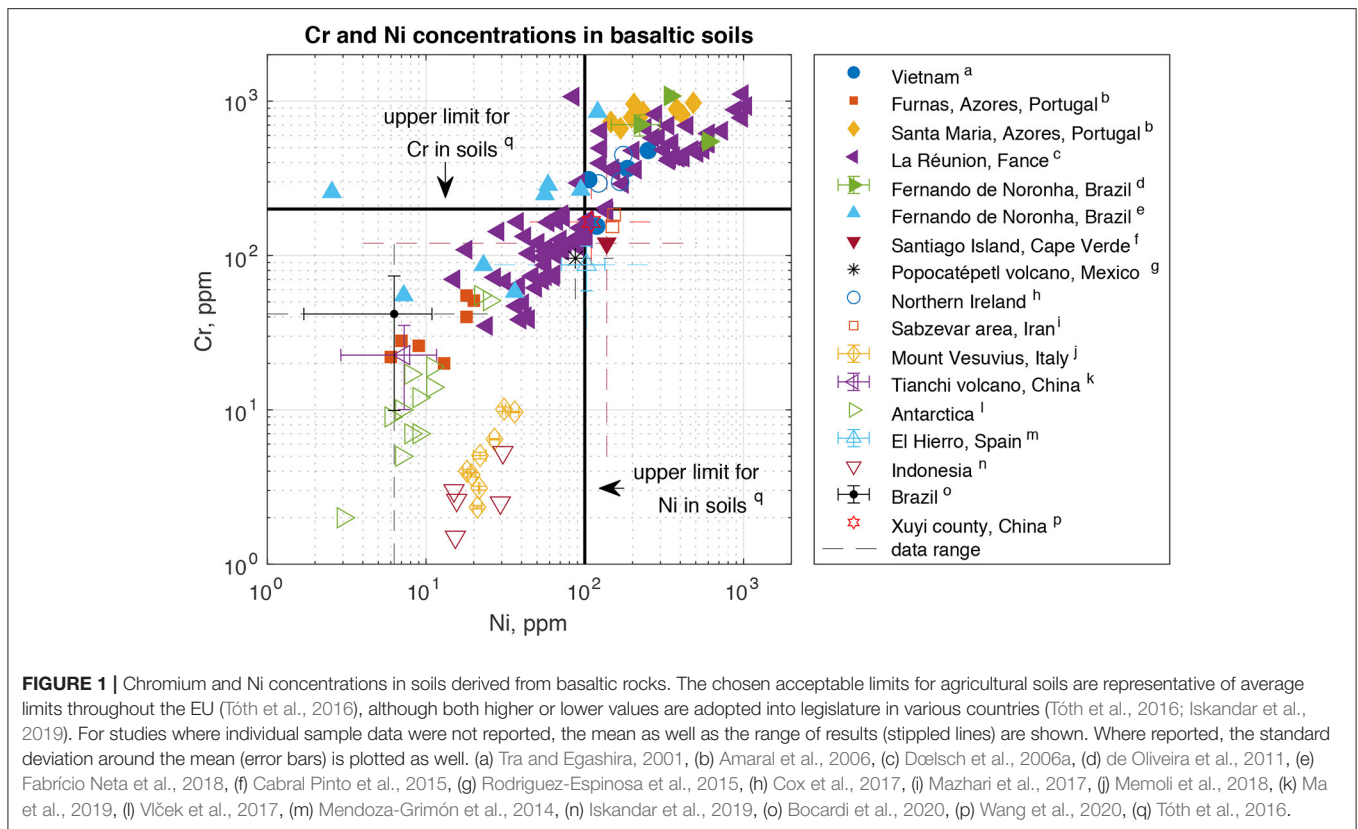
2012), which might result in accumulation of these elements in periodically harvested and removed biomass. As a result, grass grown on basaltic soils may have Ni and Cr concentrations of 2.2 and 0.3 ppm (Néel et al., 2007), and 11–39 and 0.4–7.1 ppm when grown on ultramafic soils (Miranda et al., 2009). While this may have implications for food safety, it could also mean that concentrations could remain at safe levels in both soil and biomass.

Clearly, both the quantification of TEW fluxes as well as TEW related heavy metal (HM) cycling require a deeper understanding of how plants interact with the solutes released through TEW. Focusing on the latter aspect, in this perspective article I explore the lessons from existing literature on HM in basaltic soils as well as using phytoremediation strategies to “phytoprevent” accumulation of HM in soils. Phytoremediation might prove useful since understanding and mitigating detrimental environmental consequences of TEW is an important prerequisite for its large-scale implementation. It is also important from a global climate justice perspective, as TEW might be employed in countries of the Global South (Strefler et al., 2018; Beerling et al., 2020; Goll et al., 2021) that have not substantially contributed to the climate crisis.

HEAVY METALS IN BASALTIC SOILS

Soils formed from ultramafic and basaltic parent materials exist in various locations where these rocks occur naturally. Many of these soils are well studied, giving the opportunity to derive implications for TEW. Although basalt weathers (and removes CO₂ from the atmosphere) much slower than ultramafic lithologies (Strefler et al., 2018), I focus on basalt due to the high abundance of basalt outcrops (Hartmann and Moosdorf, 2012), its phosphorous fertilization potential (Gillman et al., 2002; Hartmann et al., 2013), and lower HM concentrations of ~130 ppm Ni and ~250 ppm Cr compared to ~2000 ppm Ni and ~2300 ppm Cr in ultramafic rocks like dunite (Alloway, 2012). As an upper limit for acceptable concentrations of Ni and Cr in soils I use 100 ppm and 200 ppm respectively, which are broadly representative of average limits throughout the EU (Tóth et al., 2016).

Globally, Ni and Cr concentrations in basaltic soils vary over two (Ni) to three (Cr) orders of magnitude (**Figure 1**). Some soils fall below, and some above, these thresholds. The main factor controlling soil concentrations is the composition of the parent material (Tra and Egashira, 2001; Doelsch et al., 2006a,b; de Oliveira et al., 2011; Mendoza-Grimón et al., 2014; Cabral Pinto et al., 2015; Cox et al., 2017; Mazhari et al., 2017; Vlček et al., 2017; Fabrício Neta et al., 2018; Memoli et al., 2018; Iskandar et al., 2019; Bocardi et al., 2020; Wang et al., 2020). This is expected given the tendency of Ni and Cr to be retained in soils (Alloway, 2012). Similarly, reflecting elevated parent materials concentrations, soils formed from ultramafic rocks have much higher concentrations of Ni and Cr – on average ~2000 ppm Ni and ~2750 ppm Cr (Kierczak et al., 2021). Only few studies assess the impact of biology on HM concentrations in basaltic soils. On La Réunion, Ni and Cr concentrations are similar in



cultivated and uncultivated soils (Doelsch et al., 2006b), though it is not clear whether this is due to vegetation having no effect, or a canceling out of HM removal in biomass and inputs from fertilizer which can contain HM like Ni (McMurtry et al., 1995). At Mount Vesuvius, plant cover determines the HM fraction that is reducible or oxidizable mostly through its control on soil organic matter quality and associated impacts on pH, oxidation state and element mobility (Memoli et al., 2018). Although few studies report the composition of the parent material, some find HM concentrations in soils that are lower than in the parent material (McMurtry et al., 1995; Wang et al., 2020), indicating the presence of a HM sink.

This analysis shows that, first, there is large variability of Ni and Cr concentrations in soils formed from basalt (Figure 1), which is also valid for soils formed from ultramafic rocks (Kierczak et al., 2021). Second, much of this variability seems to depend on the composition of the parent material. This highlights that if HM exposure is to be minimized based exclusively on parent rock composition, the variability within the respective rock classes should be taken into account, favoring rocks with low concentrations in both rock types (i.e. also differentiating between high and low HM concentrations in basalts). Thus, choosing basalt or ultramafic rocks becomes a decision based on other factors like the required rate of CO₂ uptake or nutrient requirements, rather than environmental risk alone. Third, the extent to which biology effects buildup of HM in basaltic soils is currently poorly understood. Given this

limited state of knowledge and the fact that additional sinks of Ni and Cr exist at least in some settings (McMurtry et al., 1995; Wang et al., 2020), further studies assessing the effect of different types of vegetation cover and agricultural practices on HM concentrations in basaltic (and ultramafic) soils would be valuable in the TEW context.

PHYTOREMEDIATION

Although high concentrations of HM in ultramafic soils make them toxic for many plants, they are also a niche habitat for plant species that are adapted to coping with these conditions by either excluding HM from, or (hyper-)accumulating HM in, their plant tissues (Kierczak et al., 2021). While hyperaccumulation has probably evolved as a defense mechanism of plants against herbivores (Rascio and Navari-Izzo, 2011), excluders use one or several separate strategies to either break down contaminants or make them less bioavailable (e.g. phytodegradation, rhizodegradation, and phytostabilization; Etim, 2012; Yadav et al., 2021).

In phytoremediation, appropriate plants are used to decontaminate soils or water bodies polluted from anthropogenic impacts either by extracting HM or making them less bioavailable. To remove metals from soils, phytoextracting plants that accumulate metals of interest, ideally in the above ground biomass, are particularly useful (Pulford and Watson,

2003; Vara Prasad and de Oliveira Freitas, 2003; Etim, 2012; Yadav et al., 2021). These plants are usually separated into hyperaccumulators having a metal concentration of >1000 ppm of some HM (including Ni and Cr) in their dried biomass (Baker and Brooks, 1989) and non-hyperaccumulators that have lower HM concentrations but may still accumulate HM from soils (called accumulators here). Hyperaccumulating plants usually have a lower biomass production (Pulford and Watson, 2003). As a result, accumulating plants of lower HM concentration but high biomass production can be just as effective at removing HM from soils.

“PHYTOPREVENTION” OF HEAVY METAL CONTAMINATION FROM TEW

In phytoremediation, plants are used to treat soils *after* they have been contaminated. The existence of these approaches suggests that they could be used preemptively to prevent accumulation and contamination of soils with HM released from TEW (Haque et al., 2020a) – termed “phytoprevention” here. In combination with TEW, this seems a promising approach given that plant species have been identified that (hyper-)accumulate Ni and Cr from soils and waters. While several hundred Ni hyperaccumulating taxa have been identified (Lone et al., 2008), Cr hyperaccumulation is generally scarce (Han et al., 2004; Singh et al., 2013; Teuchies et al., 2013; van der Ent et al., 2013) due to the low bioavailability of Cr(III) (dominating over Cr(IV) in most soils; Kotaś and Stasicka, 2000; Alloway, 2012). In the context of phytoprevention, I outline two synergistic approaches between phytoprevention and TEW below, as well a third approach to remove HM from effluent waters. A comprehensive review of potentially suitable species is beyond the scope of this perspective article, but a selection of promising species for each approach can be found in **Table 1**.

In approach one, TEW is employed on agricultural fields (including for food production) and hyperaccumulating plants periodically remove Ni and Cr from the soils as part of a crop rotation. Many hyperaccumulators can reach metal concentrations of 1–3% of Ni. Given that their ashes may contain 12% to >20% of Ni, this approach might also enable the commercial retrieval of the metals initially contained in the basalt or ultramafic rocks, i.e. phytomining (Chaney et al., 2007; Alloway, 2012) in addition to limiting HM buildup in soil and biomass. Although some examples like southern cutgrass (*Leersia hexandra*) or Chinese brake (*Pteris vittata*; in hydroponic experiments) of Cr hyperaccumulation exist (Zhang et al., 2007; Kalve et al., 2011), it is not clear whether this strategy could work for Cr due to its limited bioavailability.

In approach two, managed fields or forests of accumulating plants, ideally grown for non-food applications, are used for TEW. While the concentrations of HM in these plants are lower, their larger biomass production may still make them suitable for phytoprevention. This approach has potential synergies with bioenergy carbon capture and storage (BECCS) discussed in the next section. Low translocation from roots to above ground

biomass may limit HM extraction efficiency for some of these plants or require laborious root harvesting (Pulford et al., 2001; Pulford and Watson, 2003; Were et al., 2017; Ranieri et al., 2020). An additional benefit of this approach is that many involved plant species, like bamboo and willow, stabilize soils and prevent erosion, decreasing the risk of spreading potential contamination to adjacent areas (Riddell-Black, 1994; Were et al., 2017). Intercropping accumulating plants with hyperaccumulating plants may increase overall crop metal accumulation, protect the accumulating plants, and increase overall biomass production (Kidd et al., 2015; Bian et al., 2020).

In the third approach, hyperaccumulating aquatic freshwater plants are used to remove HM from surface runoff and/or groundwater springs or wells to prevent contamination of rivers and freshwater resources. Many terrestrial hyperaccumulators like Indian mustard (*Brassica juncea*) or Chinese brake (*Pteris vittata*) presented in approach one can also extract HM from hydroponic solutions (Diwan et al., 2008; Kalve et al., 2011; Ansari et al., 2015) enlarging the pool of suitable species.

POTENTIAL SYNERGIES WITH BECCS

Using accumulating plants of high biomass production for phytoprevention of HM pollution from TEW, i.e. approach two above, has the benefit that this biomass might be used for other CDR approaches like BECCS. For example, bamboo has a high net primary productivity of 12–26 t ha⁻¹ yr⁻¹ (Nath et al., 2015). Willows can be frequently harvested and yield as much as 10–15 t ha⁻¹ dry biomass (Pulford and Watson, 2003). Both plants have been suggested as energy feedstocks in BECCS (Fajardy and Mac Dowell, 2017; Quader and Ahmed, 2017; Albanito et al., 2019). Removal of nutrients from soils through harvested biomass results in soils that are often nutrient deficient in terms of P and K in bamboo forests (Guan et al., 2017) and forests in general (Thiffault et al., 2011), limiting biomass production. As a result, combining TEW and phytoprevention with BECCS may produce a synergistic system where TEW supplies additional nutrients, increases growth rates, and CO₂ fixation of the BECCS feedstock. At the same time, regular harvesting of HM bearing biomass could phytoprevent the accumulation of HM in soils. While increased HM concentrations in biomass may pose challenges to bioenergy power plants from a pollution point of view, it may be possible to extract these metals through phytomining (Edgar et al., 2021).

FURTHER PHYTOPREVENTION OPPORTUNITIES

For all three approaches, plants should be chosen that are adjusted to the local climate conditions, favoring native plant varieties (Arreghini et al., 2017; Wei et al., 2021). Further research and a large database of plants that can potentially ameliorate HM contamination would therefore greatly benefit the management of environmental consequences of TEW.

Phytoremediation draws on a few other strategies, which may also be relevant in the context of phytoprevention. Examples

TABLE 1 | Selected plants that have been used to remove Cr and/or Ni from soils or water and might be useful in one of the three phytoremediation scenarios outlined in the main text.

Plant	Enriched metal	Concentration in dry biomass, ppm	Comment	Reference
Hyperaccumulating plants with potential for crop rotation (approach one)				
Mustard family plants (<i>Brassicaceae</i>), e.g. <i>Alyssum markgrafii</i> , <i>Brassica juncea</i> , and <i>Thlaspi apterum</i>	Ni, Cr, HM	19100 (Ni, <i>A. markgrafii</i>) and 21500 (Ni, <i>T. apterum</i>), 890 (Cr, <i>Brassica juncea</i>)	Mustard family plants can thrive in polymetallic contaminated soils. Indian Mustard (<i>Brassica juncea</i>): Ni concentration in roots is 208 times higher than in medium, Cr 179 times; ~1.2 t ha ⁻¹ biomass production. Can also extract HM from hydroponic solutions.	Dushenkov et al., 1995; Kidd and Monterroso, 2005; Diwan et al., 2008; Bani et al., 2010; Ansari et al., 2015; Rathore et al., 2019
Fern species Chinese brake (<i>Pteris vittate</i>)	Cr	20675 (in the stem) at 150 mg L ⁻¹	Grown in hydroponic solution for 20 days (concentration might be lower when grown in soils due to lower bioavailability of Cr). Cr concentration in biomass increased until 150 mg L ⁻¹ and decreased at higher concentrations.	Kalve et al., 2011
<i>Pycnantha</i> (formerly <i>Sebertia acuminata</i>) (Sapotaceae)	Ni	257400 (latex), 24500 (trunk bark), 1700 (wood)	One of many hyperaccumulating species discovered in New Caledonia, others include <i>Psychotria gabriellae</i> , <i>Hybanthus austrocaledonicus</i> , <i>H. caledonicus</i> (Violaceae), <i>Geissois pruinosa</i> (Cunoniaceae), and <i>Homalium guillainii</i> (Salicaceae).	Brooks et al., 1974; Jaffr and Schmid, 1974; Jaffré et al., 1976, 2013
Accumulating plants with high biomass production (approach two)				
Bamboo (e.g. <i>Bambusa bambos</i>)	Cr	547 in plant shoots	Bamboo has been successfully used to extract Cr from a contaminated tannery site, Ni requires further studies. Chromium concentration is higher in roots than shoots.	Were et al., 2017; Bian et al., 2020; Ranieri et al., 2020
Black poplar (<i>Populus nigra</i>) and princess tree (<i>Paulownia tomentosa</i>)	Ni		In a study of soils contaminated with hydrocarbons and heavy metals, these trees removed on average ~40% of Ni within three years.	Macci et al., 2013
Combination of five different woody species (<i>Terminalia arjuna</i> , <i>Prosopis juliflora</i> , <i>Populus alba</i> , <i>Eucalyptus tereticornis</i> and <i>Dendrocalamus strictus</i>)	Cr, Ni	~250–250 (Cr), ~12–17 (Ni)	Concentrations in tannery sludge (628 ppm Cr, 76 ppm Ni) were reduced by 70% (Cr) and 59% (Ni) after 1 year.	Shukla et al., 2011
Willow (<i>Salix</i> spp.)	HM		Willow has shown potential to remove metals from soils. The translocation from root to plant is possibly low and requires further studies.	Pulford et al., 2001; Pulford and Watson, 2003
Aquatic hyperaccumulators removing HM from TEW runoff (approach three)				
Water hyacinth (<i>Eichhornia crassipes</i>)	Cr, Ni	2000 (Cr) and 1000 (Ni) in culturing experiments at 10 mg L ⁻¹	Water hyacinths have been widely used to remove both Cr and Ni from natural and industrial waste waters, removing up to 95% of Ni and 99% of Cr.	Zaranyika and Ndapwadza, 1995; Zhu et al., 1999; Ingole and Bhole, 2003; Mishra and Tripathi, 2009; Fazal et al., 2015; Pandharipande and Gadpayle, 2016; Saha et al., 2017; Panneerselvam and Priya, 2021
Floating ferns (<i>Salvinia natans</i> , <i>Salvinia minima</i>)	Cr, Ni	~12000 (Cr) of which ~9000 after 48 h in 50 mg L ⁻¹ (<i>Salvinia natans</i>), 2210 (Cr) in submerged leaves in 10 mg L ⁻¹ (<i>Salvinia minima</i>), 16300 (Ni at 160 mg L ⁻¹ ; <i>Salvinia minima</i>)	Uptake increases at higher aqueous concentrations. Uptake is quick in early stages (6–12h for Ni, 24 h for Cr), followed by slower uptake.	Dhir et al., 2009; Prado et al., 2010; Fuentes et al., 2014
Eel grass (<i>Vallisneria spiralis</i>)	Cr, Ni	2870 (Cr) and 2100 (Ni) at 30 mg L ⁻¹ in a polymetallic solution	Uptake increases at higher aqueous concentrations.	Verma et al., 2008
Lesser bulrush (<i>Typha angustifolia</i>), marshpennywort (<i>Hydrocotyle umbellata</i>)	Cr	130 (<i>T. angustifolia</i>) and ~1850 (<i>H. umbellata</i>), both grown at 50 mg L ⁻¹	<i>T. angustifolia</i> removed 99.78% of Cr from the water within 9 days, <i>H. umbellata</i> 99.67%.	Taufikurrahman et al., 2019

are the use of rhizobacteria (Yadav et al., 2021) or mycorrhiza (Coninx et al., 2017) that may encourage plant growth, and increase the bioavailability and uptake efficiency of metals. The latter effect could also be achieved by adding chelating agents like EDTA to soils (Lim et al., 2004; Wu et al., 2004), although this should be viewed with caution and tested meticulously as the increased bioavailability and element mobility might promote runoff of HM into surface and groundwaters (Cooper et al., 1999; Pulford and Watson, 2003; Wu et al., 2004). Another interesting potential phytorevention strategy common in phytoremediation is using phytostabilizing plants, which may have a similar effect as biochar in that they reduce HM bioavailability and runoff (Amann and Hartmann, 2018).

Upper limits of environmentally safe addition of olivine or basalt to soils may easily be calculated based on the cumulative amount of rocks added and their HM concentrations (Renforth et al., 2015). However, this may overestimate the environmental impact in the presence of additional HM sinks. In principle, a limit to TEW application at which HM do not accumulate in soils may be calculated from the heavy metal fluxes in biomass and rock:

$$\begin{aligned} & \text{max. TEW rock flux} \\ &= \frac{(\text{biomass flux}) (\text{max. HM concentration in biomass}) u}{(\text{HM concentration in TEW rock}) d} \end{aligned}$$

Where u is the uptake efficiency of HM in biomass, and d the fraction of source rock dissolved in the given period. For example, in a simplified case where u and d are 1 (biomass HM concentration as high as it is at high soil concentrations, source rock dissolved completely), bamboo could extract the Cr equivalent of up to $\sim 55 \text{ t basalt ha}^{-1} \text{ yr}^{-1}$, and mustard family plants the Ni equivalent of $\sim 180 \text{ t basalt ha}^{-1} \text{ yr}^{-1}$. In practice, this would require a more realistic parametrization of weathering (d) and plant HM uptake (u) processes at the given soil and source rock conditions, including of concentrations of

HM in biomass at lower concentrations in soils. Potentially, elevated HM concentrations in rocks must not preclude TEW in all settings: If HM are continuously removed from soils through phytorevention, even prolonged TEW might not exceed acceptable HM thresholds in either soil, drainage water, or harvested biomass. Overall, the approach of phytorevention highlights the need for TEW studies to assess the fate of HM, as well as weathering fluxes in general, in terms of all input and output fluxes including biomass.

DATA AVAILABILITY STATEMENT

Publicly available datasets were analyzed in this study. The data sources are referenced in the article.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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