Occurrence and cycling of trace elements in ultramafic soils and their impacts on human health: A critical review

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ABSTRACT

The transformation of trace metals (TMs) in natural environmental systems has created significant concerns in recent decades. Ultramafic environments lead to potential risks to the agricultural products and, subsequently, to human health. This unique review presents geochemistry of ultramafic soils, TM fractionation (i.e. sequential and single extraction techniques), TM uptake and accumulation mechanisms of ultramafic flora, and ultramafic-associated health risks to human and agricultural crops. Ultramafic soils contain high levels of TMs (i.e. Cr, Ni, Mn, and Co) and have a low Ca:Mg ratio together with deficiencies in essential macronutrients required for the growth of crops. Even though a higher portion of TMs bind with the residual fraction of ultramafic soils, environmental changes (i.e. natural or anthropogenic) may increase the levels of TMs in the bioavailable or extractable fractions of ultramafic soils. Extremophile plants that have evolved to thrive in ultramafic soils present clear examples of evolutionary adaptations to TM resistance. The release of TMs into water sources and accumulation in food crops in and around ultramafic localities increases health risks for humans. Therefore, more focused investigations need to be implemented to understand the mechanisms related to the mobility and bioavailability of TMs in different ultramafic environments. Research gaps and directions for future studies are also discussed in this review. Lastly, we consider the importance of characterizing terrestrial ultramafic soil and its effect on crop plants in the context of multi-decadal plans by NASA and other space agencies to establish human colonies on Mars.

1. Introduction

A thorough understanding of the importance of the abiotic environment and its interaction with living organisms is a challenge in soil and environmental research. Trace metals (TMs) are common environmental contaminants whose toxicity is an increasing concern from

an ecological and nutritional viewpoint (Kazakou et al., 2008; Sungur et al., 2015). The term "TM" has been adopted to describe any metallic element with a relatively high density that can be toxic to living organisms at low concentrations (Nagajyoti et al., 2010). However, it is not the density but the chemical characteristics of TMs that are most influential in determining their toxicity. Nieboer and Richardson (1980) classified heavy metals as class B metals, which are non-essential and highly toxic elements such as Hg, Ag, and Pb. TMs can be bioaccumulative by not being degraded in an ecosystem or easily metabolized. For this reason, uptake of TMs by plants may lead to the accumulation at different levels in the food chain (Antoniadis et al., 2017).

Both anthropogenic activities and natural processes lead to the release of TMs into the environment. Industrial inputs of TMs to the biosphere are of great environmental concern (Wijesekara et al., 2016; Young et al., 2005). The process of weathering rocks and minerals can also serve as inputs for TMs into the environment (Cooper, 2002; Robles-Camacho and Armienta, 2000). The deleterious effects on the environment of TMs of natural origins cannot simply be neglected, as these effects can be extreme. An example of an environment which is extremely affected from TMs is ultramafic soils, which contain elevated concentrations of TMs such as chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), lead (Pb), zinc (Zn), copper (Cu), and vanadium (V) coupled the with low availability of calcium (Ca) (Lee et al., 2001; Ndjigui et al., 2008). The exceedingly high concentrations of TMs in ultramafic soils may cause challenges to agricultural crops, due to the potential risk of bioaccumulation (Bandara et al., 2017a; Bandara et al., 2017b; Herath et al., 2015). For instance, Kanellopoulos et al. (2015) found that agricultural soils near an ultramafic source contained high levels of Cr, Ni, and Co. Acidic conditions in the ultramafic soil matrix may promote the release of TMs (i.e., Ni and Mn) from ultramafic soils into surrounding environments (Kumarathilaka et al., 2016b; Rajapaksha et al., 2012; Vithanage et al., 2014).

A limited number of extremophile plants (extremophytes) have evolved to grow in hostile ultramafic environments. Ultramafic rocks have dramatic effects on the vegetation that grows on them. Most plants cannot grow on ultramafic soils, leaving distinctive suites of extremophytes to occupy ultramafic habitats. The floristic diversity associated with serpentine soils formed above ultramafic rocks is surprising, considering that these soils are toxic to most plants. The species richness observed in ultramafic environments in some instances has been reported as a result of divergent selection leading to speciation where ultramafic adapted species are sister taxa of species growing in non-ultramafic soils (Anacker and Strauss, 2014; Baldwin, 2005). Ultramafic barrens of California often look like moonscapes, however, different plant species of low biomass, rarely found in other parts of the world, are present there (Richard, 2009). Ultramafic flora exhibits unique adaptations to its extreme micro-environment (Brooks, 1987; Roberts and Proctor, 2012; Teptina et al., 2018; Van der Ent et al., 2015). The rocky, granular textured soils, lack of organic material, low soil water-holding capacity, low Ca/Mg ratio, low nutrient content, and TM toxicity in ultramafic soils create an unfavorable environment for plant growth and development (Brady et al., 2005; Rajakaruna et al., 2003; Seneviratne et al., 2015). Adaptations to ultramafic soils have independently evolved multiple times in terrestrial plants and within finer geographic scales (Brady et al., 2005; Kay et al., 2018; Krämer, 2018). These endemic plants have developed molecular to macro-level adaptations to withstand the unfavorable conditions created by the ultramafic edaphic factors (Reeves et al., 2015). Phytoremediation approaches seek to use the capacity of such plant species to be sequestrate heavy metal(loid)s (Seneviratne et al., 2016; Wójcik et al., 2017). A comprehensive understanding of cellular and biochemical processes is essential to this work. However, a few studies have focused on comprehensive reviews of plant life on ultramafic soils (Richard, 2009).

Understanding TM behavior provides useful information on the mobility, bioavailability and potential toxicity of TMs in the ultramafic

environment. A handful of studies have been reported related to the geochemistry (Dissanayake, 1982; Dublet et al., 2017; Dublet et al., 2012; Fan and Gerson, 2011; Noël et al., 2017; Noël et al., 2015; Rajakaruna et al., 2002; Rajapaksha et al., 2012) and plant ecology of ultramafic environments (Hidalgo-Triana et al., 2018; Kay et al., 2018; Teptina et al., 2018; Weerasinghe and Iqbal, 2011). Fewer studies have been conducted to explore important issues such as the mobility, bioavailability, and release rates of TMs; the mechanisms of cellular uptake and conduction of TMs within plants; and the influence of TMs released from ultramafic environments on the health of the ecosystem (Tashakor et al., 2017; Tashakor et al., 2018). Reviews in the context of physicochemical properties of ultramafic soils, TM fractionation in ultramafic soils (i.e. sequential and single extraction techniques) are limited and TM uptake and accumulation mechanisms of ultramafic flora, and ultramafic-associated risks to human and agricultural crops are non-existent (Vithanage et al., 2014). Hence, given that ultramafic substrata constitute a stressful environment for plant growth, the objectives of this review are i) to assess recent findings concerning TM distribution, speciation, and plant availability in ultramafic soil profiles, and ii) to highlight TM uptake, translocation, and accumulation mechanisms in plant species. We also briefly discuss recent insights into the ecosystem health impacts of TMs in ultramafic soils and the importance of characterizing terrestrial ultramafic soil sites as references for martian regolith that future human colonists may need to use as a growth substrate for crop plants. Hence, this becomes a unique review for ultramafic soils, which gathers a variety of data on geological origin, trace metal release and fractionations, environmental risk and uptake, and risk to human health.

2. Geological setting of serpentine bodies

The term ultramafic refers to igneous or metamorphic rocks containing < 45 wt% silica (SiO_2) (Susaya et al., 2010). Serpentinite is a metamorphic rock formed as a result of low temperature (300–600 °C) hydrothermal alteration of ultramafic rocks (Page et al., 1999). The general formula for all members of the serpentine group is $(Mg,Mn,Fe,Co,Ni)_{3-x}SiO_2O_5(OH)_4$ (Bayliss, 1981). Serpentinites contain one or more serpentine group minerals such as lizardite ($Mg_3Si_2O_5(OH)_4$), chrysotile ($Mg_3Si_2O_5(OH)_4$) and antigorite ($(Mg,Fe^{2+})_3Si_2O_5(OH)_4$). More precisely, those serpentine group minerals are formed through the metamorphic transformation of ultramafic rocks such as peridotite and pyroxenite, which consist of iron (Fe) and Mg-rich silicate minerals such as olivine ($(Mg,Fe^{2+})_2[SiO_4]$) and pyroxene ($XY(Si,Al)_2O_6$) from the Earth's mantle. Magnetite ($Fe^{2+}Fe_2^{3+}O_4$), Cr-rich magnetite ($Fe^{2+}(Fe^{3+},Cr)_2O_4$) and chromite ($FeCr_2O_4$) can largely be associated with serpentinites. Similarly, mixed-composition minerals including talc ($Mg_3Si_4O_{10}(OH)_2$), chlorite ($(Mg,Fe)_5Al[(OH)_8AlSi_3O_{10}]$), tremolite ($[Ca_2][Mg_5][(OH)_2Si_8O_{22}]$), and brucite ($Mg(OH)_2$) are associated with serpentinites (Morrison et al., 2009; Oze et al., 2004b). Recent synchrotron-based Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy revealed that Ni resided in layered-phyllosilicate and chain-inosilicate minerals and was associated with Fe oxides and primary serpentine minerals such as lizardite (Siebecker et al., 2017).

Soils derived from peridotite and serpentinite are also referred to as serpentine soils due to the fact that similar plant species exist on peridotite soils as on serpentine soils (Oze et al., 2004b). Peridotite and serpentinite possess similar chemical compositions. For example, they both contain a high level of magnesia (> 35 wt% of MgO) and low amount of silica (< 45 wt% of SiO_2). However, serpentinite has relatively higher water content (up to 13%) than peridotite (Coleman, 1971). In addition, the two rock types are characterized by different mineral compositions. Thus, soils derived from these two rock types possess different properties as well as different morphologies (Alexander, 2004). For instance, soils formed on peridotites are typically redder than soils derived from serpentines. Additionally,

Table 1
Total metal concentration with respect to depth in different ultramafic environments in the world.

Location	Depth (cm)	Concentration (mg kg^{-1})									Reference
		Ni	Cr	Mn	Co	Cd	Cu	Pb	Zn	V	
World average in soils	–	2–750	5–1500	1–4000	1–40	0.01–2.0	2–250	2–300	1–900	90–150	(Alfaro et al., 2015; Cappuyns and Slabbinck, 2012; Grygo-Szymanko et al., 2016; Nagajyoti et al., 2010)
Rudnik mountain, Serbia	0–20	550	–	–	–	–	–	–	–	–	(Antić-Mladenović et al., 2011)
Galicia, NW Spain	20	76–373	1499–4309	–	1472–7132	–	–	–	–	21–140	(Arenas-Lago et al., 2016)
Marivan, Iran		1600	–	–	–	–	–	–	–	–	(Ghasemi and Ghaderian, 2009)
Ranau Valley, Malaysia	0–20	6322	4873	43,063	1005	–	239	–	597	–	(Aziz et al., 2015)
Borneo, Sabah, Malaysia	5–20	1080–5450	420–10,980	1427–7330	170–690	–	–	–	–	–	(van der Ent et al., 2017)
Central Greece	0–25	334	234	823	31	–	36	13	66	57	(Kanellopoulos et al., 2015)
Serra de Nogueira, Portugal	10–30	102–2342	200–6822	1007–1853	56–175	–	31–225	19–41	63–242	–	(Freitas et al., 2004)
Niquelandia, Brazil	0–20	4577	5533	6667	–	–	–	–	–	–	(Garnier et al., 2006)
	20–60	3660	7015	1045	–	–	–	–	–	–	
Szklary Massif, SW Poland	4–25	1329	2671	–	119	–	25	40	108	–	(Kierczak et al., 2008)
Tras-os-Montes, NE Portugal	0–15	1574	4384	2451	180	–	150	21	88	–	(Díez Lázaro et al., 2006)
Mt. Prinzera, Italy	0–20	2466	2231	–	106	–	17	10	56	62	(Lombini et al., 1998)
Melide, NW Spain	0–15	6–940	10–1162	–	–	–	2–80	–	–	–	(Miranda et al., 2009)
Barazón, Spain	0–20	937	–	1297	73	–	–	–	–	–	(Álvarez-López et al., 2016)
Nove Dvory, Czech Republic	Bed rock	3054	2682	–	103	–	–	–	–	–	(Quantin et al., 2008)
Mohelno, Czech Republic	Bed rock	2198	3206	–	97	–	–	–	–	–	
Holubov, Czech Republic	Bed rock	2824	1802	–	112	–	–	–	–	–	
Bitincka, Albania	15	1737	513	–	184	4	6	80	52	–	(Shallari et al., 1998)
Gjegjan, Albania	15	1104	574	–	289	4	27	87	49	–	
Guri I Kuq, Albania	15	819	365	–	130	2	44	85	51	–	
Pogradec, Albania	15	2442	635	–	259	5	8	98	63	–	
Prrenjas, Albania	15	3579	3865	–	476	14	36	172	93	–	
Redlschlag, Eastern Australia	–	2580	1910	–	172	4	52	16	61	–	(Wenzel et al., 2003)
Haut Limousin, France	60–80	4142	7466	5886	724	–	–	–	–	–	(Caillaud et al., 2009)
	80–100	5320	6756	4569	750	–	–	–	–	–	
	100–120	4625	8675	1936	248	–	–	–	–	–	
	120–140	4018	5812	465	117	–	–	–	–	–	
	Rock (> 140)	1587	2262	620	86	–	–	–	–	–	
Ussangoda, Sri Lanka	15	6776	10,707	1117	157	–	30	–	173	–	(Vithanage et al., 2014)
Yudhaganawa, Sri Lanka	15	6567	14,880	2609	555	–	14	–	307	–	
Ginigalpelessa, Sri Lanka	15	5945	9948	2543	219	–	15	–	182	–	
Indikolapelessa, Sri Lanka	15	4705	6737	1349	241	–	24	–	108	–	
Niquelandia, Brazil	0–15	3606	5185	–	980	–	–	–	–	–	(Garnier et al., 2009)
	15–30	25,767	8066	–	115	–	–	–	–	–	
	30–70	73,786	5960	–	295	–	–	–	–	–	
	70 +	32,216	9400	–	189	–	–	–	–	–	
Shih-Tao, Taiwan	0–15	3222	3192	–	–	–	–	–	–	–	(Cheng et al., 2011)
	15–50	2352	2548	–	–	–	–	–	–	–	
	50–80	3458	3146	–	–	–	–	–	–	–	
	80–110	3991	3214	–	–	–	–	–	–	–	
Wan-Ron Hill, Taiwan	0–10	950	650	735	–	–	–	–	–	–	(Ho et al., 2013a)
Soroako, Indonesia	0–15	7051	17,216	1076	57	–	–	–	–	–	(van der Ent et al., 2013a)
Klamath mountains, USA	0–12	2718	1247	1750	173	–	24	–	72	–	(Alexander, 2014)
Morais Massif, Portugal	0–15	2800	2800	2400	–	–	29	–	73	–	(Alves et al., 2011b)
Samar island, Philippines	0–20	1840	–	–	–	–	–	–	–	–	(Susaya et al., 2010)
California, USA	10–20	4060	11,670	–	–	–	–	–	–	–	(Morrison et al., 2009)
Trazy-Guerioum, Koniambo massif, Kone, New Caledonia	NA	3300	–	–	–	–	–	–	–	–	(Jourand et al., 2010)
Pindjen Water Fall Road, Kone, New Caledonia	NA	3500	–	–	–	–	–	–	–	–	
Mont-Dore, Plum Road, New Caledonia	NA	2800	–	–	–	–	–	–	–	–	
Euboea, Greece	20	1200-8900	540–3800	600–2200	60–460	0.1–1	15–44	3–370	16–900	25–70	(Megremi, 2010)
Hudenisht, Albania	0–20	3180	677	1760	182	–	15.7	–	3,18	–	(Bani et al., 2014)
Velika (Great) Morava River valley, Serbia	0–20	138	–	–	–	–	–	–	–	–	(Rinklebe et al., 2016)

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Table 1 (*continued*)

Location	Depth (cm)	Concentration (mg kg^{-1})									Reference
		Ni	Cr	Mn	Co	Cd	Cu	Pb	Zn	V	
Western Anatolia and the Eastern Thrace, Turkey	0–15	25.7–2680	631	1570	166	–	15.9	47.7	164	29	(Ünver et al., 2013)
Malbog, Philippines	0–20	1840	–	–	–	–	–	–	–	–	(Susaya et al., 2010)
Beni Bouchra, Morocco	0–10	1821	311	–	88	–	–	–	–	–	(Ater et al., 2000)
Andaman Islands	10–15	4316	4437	–	533	–	–	–	–	–	(Pal et al., 2005)

magnetite, which is resistant to weathering, is the main source of Fe in serpentines, whereas, olivine is easily weathered and is the major source of Fe in peridotites (Alexander, 2004). Thus, peridotites produce more (oxy)hydroxides than serpentines, leading to the red color of the peridotite-derived soils. Due to serpentinization, related deformation, and diapiric migration, serpentinites are more fractured than peridotites. As a result, steeper slopes tend to develop on peridotites while serpentinites yield shallower slopes (Alexander and DuShey, 2011).

3. Global distribution of ultramafic soils

Ultramafic rocks, which cover approximately 1% of the surface of the Earth, are commonly found in ophiolite belts along tectonic plate margins (Garnier et al., 2009; Lee et al., 2001). The weathering processes of ultramafic rock and the resulting soils differ between locations due to climate, the nature of the parent material, and other environmental factors such as topography, biota, and time (Garnier et al., 2009). Ultramafic outcrops are well documented on every continent except Antarctica (Table 1) (Morrison et al., 2009; Mun, 1988; Ndjigui et al., 2008; Oze et al., 2004b; Rajapaksha et al., 2012; Wenzel et al., 2003; Westerbergh and Saura, 1992). Fig. 1 shows a typical ultramafic environment found in tropical countries. Ultramafic soils were reported on islands (such as Shetland) over 40 years ago, but have not been recently investigated (Shewry and Peterson, 1975). Ultramafic environments are also present in cold environments such as in Greenland (Pons et al., 2011). The uniqueness of flora inhabiting on ultramafic environments has long been explored (Brooks, 1987; Roberts and Proctor, 2012; Van der Ent et al., 2015). The most extensively studied ultramafic flora is those of tropical and Mediterranean climatic regions. The plant communities in tropical and Mediterranean regions are found to decreased floristic diversity and lower productivity in comparison to those on non-ultramafic environments. Ultramafic environments in tropical and Mediterranean regions are home to unique flora, significantly rich in endemic species and ecotypes (Galey et al., 2017). The number of endemics in Northern Hemisphere is remarkably lower than that of the tropical and Mediterranean regions (Teptina et al., 2018).

Ultramafic outcrops occur in highly populated areas. For instance, a wide distribution of ultramafics has been identified in populous areas within the Circum-Pacific margin and the Mediterranean (Oze et al., 2004b). An ultramafic body in Shih-Tao Mountain in the coastal range of eastern Taiwan, which is 2 km away from Taitung city, contains peridotite, pyroxenites, and serpentinite (Cheng et al., 2011). The ultramafic soil in the Eastern part of the Rudnik Mountain, near Salasi Village, Serbia, is extensively used for crop cultivation (Antić-

Fig. 1. An ultramafic environment at Indikolapelessa, Sri Lanka.

Mladenović et al., 2011). Extensive ultramafic coverage is found in Atalanti, central Greece, where ultramafics cover 64 km² (Kanellopoulos et al., 2015). A few ultramafic localities are also found in the villages of Malbog, Napataan and Palanas in Eastern Samar, Philippines (Susaya et al., 2010). Ultramafic outcrops located in and around populated areas may increase the risks of TM accumulation in agricultural soils and vegetation and the groundwater contamination (discussed in detail in Section 5.7).

4. Physicochemical characteristics of serpentine soils

Serpentine soils are red, green, blue, or black, depending on their chemical compositions (Kazakou et al., 2008; Kierczak et al., 2016). The variations in the mineralogy of serpentine outcrops have been investigated in detail (Caillaud et al., 2009; Kelepertzis et al., 2013; Kierczak et al., 2007). The characteristic chemical properties of serpentine soils are as follows:

(1) Low Ca: magnesium (Mg) ratio

Plant growth is significantly affected by the proportions of exchangeable cations in soil. The high abundance of Mg released from ultramafic weathering makes it the dominant cation present on soil exchange sites, resulting in the characteristic low exchangeable Ca: Mg ratios of serpentine soils (Burt et al., 2003). Serpentine soils are not necessarily Ca-limited where the low Ca:Mg ratios are commonly the result of an overabundance of Mg (Oze et al., 2008). Serpentine soils, thus, impose strong limitations on the fertility of plants. In temperate climates, Mg is only partially leached during soil formation due to incomplete hydrolysis. In comparison, in tropical climates, complete hydrolysis occurs and, consequently, almost all available Mg is leached (Kierczak et al., 2007).

(2) Deficiencies in essential plant nutrients

Low levels of plant-available macronutrients are a prevailing issue in serpentine soils. Low organic matter in the soils inevitably leads to low macronutrient concentrations. Additionally, the lack of P and K in the parent materials results in low concentrations of P and K in serpentine soils (Burt et al., 2001). For this reason, only a few plant species can survive in serpentine substrata. However, the identity of the limiting nutrient varies from one serpentine soil location to another. For example, serpentine soils in California, USA, have low N concentrations, whereas European serpentine soils contain low levels of P (Chiarucci et al., 1999).

(3) High levels of toxic TMs

Serpentinite parent materials and the resulting soils contain high levels of toxic metals such as Cr, Ni, Co, Mn, Zn, and V. Therefore, serpentinites act as a non-anthropogenic source of toxic elements by releasing them into the environment during natural weathering processes. The toxicity of serpentine soils is termed "serpentine syndrome" and leads to endemism and low primary productivity (Oze et al., 2008).

4.1. Total TM content

Ultramafic environments display a high geochemical background of TMs due to the weathering of minerals (Amir and Pineau, 2003; Quantin et al., 2002). The distribution of TMs along with the soil profile primarily depends on the weathering susceptibility of their initial host minerals, although climatic conditions (i.e., humidity, rainfall, snowfall, and temperature) influence the soil forming processes (Caillaud et al., 2009). Geochemical studies have shown that TM concentrations in ultramafic soils are remarkably higher than that of non-ultramafic soils, summarized in Table 1.

Studies related to TMs distribution at the mineral scale demonstrate how TMs may be released into the environment. Ultramafic soil profiles in the Czech Republic have been studied using a combination of geochemical and mineralogical techniques and results show that Cr is

mainly mobilized from pyroxenes, amphiboles, and Cr-spinels in bedrock, whereas, Ni is released from olivines and small Fe-Ni sulfide inclusions (Quantin et al., 2008). The distribution of TMs along the ultramafic soil profile in South Limoges in France has shown that silicates (i.e. serpentine and clinochlore) retain Cr, Ni, and Mn while oxides retain Co and Cr (Caillaud et al., 2009). During the initial weathering stage, Ni and Cr can be concentrated in secondary clays such as Fe-montmorillonite and trioctahedral vermiculite whereas Mn and Co are mainly retained in secondary oxides. At the top of the ultramafic profile, Ni, Mn, and Co have been found to retain in secondary oxy-hydroxides, possibly due to the Fe segregation. An assessment of the ultramafic massif in south west Poland has revealed that Ni content in Cr-magnetite, forsterite, iddingsite and serpentine are up to 0.96, 0.55, 0.99 and 0.55 wt% of NiO, respectively. Additionally, the levels of Cr in Cr-magnetites and clinochlores were up to 21.77 and 1.68 wt% of Cr_2O_3, respectively (Kierczak et al., 2007).

Chemical and mineralogical investigations have further demonstrated that Cr and Ni in Shih-Tao Mountain in Taiwan are dominantly concentrated in chromites and silicates, respectively (Cheng et al., 2011). Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analysis has revealed that chemical modification of the chromites was more common near the soil surface and the available Cr concentration from the shoulder to the footslope also increased (Cheng et al., 2011). Kelepertzis et al. (2013) investigated two weathering profiles of Thiva Valley in central Greece and found that Ni is primarily associated with serpentine (0.5 wt% of NiO) and secondary weathering products such as smectites and goethite (0.5 and 1.1 wt% of NiO, respectively). In contrast, Cr was predominantly bound to chromite (54.7 wt% of Cr_2O_3) and a lesser extent to Cr-magnetite and enstatite (12.2 and 0.8 wt% of Cr_2O_3) (Kelepertzis et al., 2013). Geochemical and mineralogical analyses were also performed in the agricultural region of Mouriki-Thiva in central Greece (Antibachi et al., 2012). The geology of that area is characterized by ultrabasic rocks and the total concentrations of Ni and Cr ranged from 621 to 2639 and 134 to 856 mg kg^{-1}, respectively. In addition, Cr was mainly incorporated into chromite, whereas Ni was mainly associate with in olivine and serpentine (Antibachi et al., 2012).

Regional scale geochemical studies demonstrate that geochemistry and mineralogy of ultramafics are strongly influenced by the transport of weathered parent materials. Weathering processes lead to the concentration of TMs in the secondary phases (Caillaud et al., 2009). However, their distribution does not show a consistent pattern at most of the investigated ultramafic weathering profiles (Shallari et al., 1998). This could be attributed to variations in weathering rates of different TM-bearing minerals as well as variations in the TM mobility in the soil profile (Table 1).

Total TM concentrations are useful as references for assessing contamination levels and the associated environmental risks (Kierczak et al., 2008). Nickel concentrations have been found to range from 1510 to 5970 mg kg^{-1} in ultramafic soils in Oregon and Maryland, whereas, Cr, Mn, and Co concentrations were 580–2910, 1380–3360 and 87–311 mg kg^{-1}, respectively (Siebecker et al., 2017). However, total TM concentrations do not provide sufficient information regarding the mobility and availability of TMs. Assessing the chemical fractionation of TMs in ultramafic soils is therefore important to determine the mobility and bioavailability of TMs (Díez Lázaro et al., 2006; Garnier et al., 2006).

4.2. TM fractionation

The distribution of TMs within their various geochemical binding forms, which is referred as TM fractionations, is an important factor to determine the mobility and bioavailability of TMs in the environment (Kierczak et al., 2008). Sequential extraction is a commonly used method to evaluate the speciation of TMs in ultramafic environments (Amir et al., 2005; Dère et al., 2007). The extraction efficiency of TMs

bound to different fractions is found to depend on the strength of the extractant, a number of steps involved, and the geochemical properties of the ultramafic soil.

Tessier et al. (1979) defined five metal bound fractions (i.e. (I) exchangeable, (II) carbonate, (III) Fe and Mn oxides, (IV) organic and (V) residual) in his sequential extraction method. Using the method described by Tessier et al. (1979), Antić-Mladenović et al. (2011) determined that Ni in Rudnik Mountain ultramafic soils was mainly remained in the residual fraction (91.3%). The remaining Ni was retained in different fractions in the following order: Fe and Mn oxides bound > organic matter bound > carbonate bound > exchangeable (Antić-Mladenović et al., 2011). Similarly, metal bound fractions in four different locations in Sri Lanka (Ussangoda, Yudhaganawa, Indikolapelessa and Ginigalpelessa) were evaluated following the method described by Tessier et al. (1979) and the portion of Mn, Ni, and Cr retained in different fractions from greatest to least were as follows: (1) Mn: Fe and Mn oxides bound > residual > organic matter bound > exchangeable > carbonate-bound, (2) Ni: residual > Fe and Mn oxides bound > organic matter bound > exchangeable > carbonate-bound, and (3) Cr: residual > organic matter bound > Fe and Mn oxides bound > exchangeable > carbonate bound (Vithanage et al., 2014).

A seven-step sequential extraction method (i.e. (I) water soluble, (II) exchangeable, (III) bound to Mn oxides, (IV) bound to amorphous or poorly crystallized Fe oxides, (V) bound to well crystallized Fe oxides, (VI) oxidizable fraction and (VII) residual) has been used to evaluate the solid-phase fractionation of Cr in ultramafic soil localities in Niquelandia, Brazil (Garnier et al., 2006). The results showed that Cr was mainly bound to well crystallized Fe oxides (50 to 85 wt% of Cr). The same sequential extraction procedure was used to investigate Cr fractionation in paddy soils derived from serpentine in Wan-Ron Hill in Eastern Taiwan (Hseu and Iizuka, 2013). The results showed that Cr is primarily associated with recalcitrant minerals in the serpentine derived paddy soil matrix. Similarly, ultramafic soils in Galicia (NW Spain) contain high portions of Co, Cr, Ni, and V in the residual fraction (Arenas-Lago et al., 2016). Rinklebe et al. (2016) also found that Ni is mainly retained in the residual fraction in ultramafic soils in the Morava River Valley, Serbia.

A six-step sequential extraction method (i.e. (I) exchangeable, (II) acid-soluble, (III) easily reducible, (IV) moderately reducible, (V) sulfide/organic and (VI) residual) has been used to evaluate the TM fractionation in an ultramafic massif in Szklary, SW Poland. The Cr in ultramafic soils in Szklary is found to be mainly retained in the residual fraction (> 76%), and mineralogical analysis further confirmed that Cr is incorporated into highly resistant spinels (Cr-magnetite) (Kierczak et al., 2008). In addition, Co was largely retained in sulfide/organic and residual fractions. Díez Lázaro et al. (2006) also followed a six-step sequential extraction method (i.e. (I) exchangeable, (II) Mn oxide bound, (III) organic matter bound, (IV) amorphous Fe oxide bound, (V) crystalline Fe oxide bound, and (VI) residual and demonstrated that Cr in ultramafic soils is largely retained in the residual fraction, whereas, Ni, Co, and Cu are predominantly bound to Fe oxides, Mn oxides, and organic matter fractions, respectively. Moreover, a four-step sequential extraction method (i.e. (I) reducible, (II) oxidizable, (III) acid-extractable and (IV) residual) has been used by Hseu (2006) and the results have demonstrated that Cr and Ni are predominantly associated with the residual fraction.

In summary, direct comparisons of the results of various sequential extraction studies are hampered due to different extraction methods using various extractants and involving an assorted number of extraction steps. In addition, the limited selectivity of extractants and the redistribution of metals among newly formed phases may confounded sequential extraction results. For instance, an exchangeable fraction of a particular TM may is easily leached by a natural salt. The carbonate-bound fraction is sensitive to changes in pH of the environment, as it is soluble under acidic conditions (Tokalioglu et al., 2000). Metals bound

to the Fe-Mn oxides fraction can mobilized due to the changes of redox conditions in the environment (Hursthouse et al., 2003). Natural organic matter (i.e. humic and fulvic acids) has a high capacity to complex with metal ions (Tessier et al., 1979). The residual fraction can retain metals in recalcitrant crystalline structures. Strong oxidizing acids such as hydrofluoric, nitric and perchloric acids are required to decompose the residual fraction. Therefore, the metals associated with the residual fraction can only be mobilized due to the process of natural weathering, which is a slow and long-term process (Tessier et al., 1979). Climatic conditions also affect the weathering patterns of minerals (i.e., Fe/Mn oxides precipitate in humid tropical climates but are formed in cold and temperate climates) (Antić-Mladenović et al., 2011). To obtain a more precise and accurate data about TM fractionation in ultramafic soils, a combined method of sequential extraction and non-destructive analytical methods (i.e. XRD, SEM-EDX, and EMPA) is therefore suggested.

5. Risks to plants in ultramafic soils from TM mobilization

5.1. Bioavailability of metals

For a comprehensive ecotoxicological risk assessment, it is essential to determine the bioavailability of TMs in ultramafic soils (Díez Lázaro et al., 2006). As reported from the various definitions of bioavailability existing in the literature, the term "bioavailability" used in this manuscript refers to the availability of TMs in the soil-water systems for the uptake by plant species. Bioavailability of metals in soil systems is dependent on a multitude of factors such as climatic conditions (i.e. temperature and water regime), the origin of the metal, distribution among the soil constituents, edaphic properties (i.e. pH, redox potential, distribution coefficients of TMs (K_d), texture, cationic exchange capacity, carbonate, organic matter, amount of oxides (i.e. Mn and Fe oxides) (Antić-Mladenović et al., 2017; Kumarathilaka et al., 2018a; Shaheen et al., 2013), microbial activity of the rhizosphere microflora, and the chemical composition of root exudates (Alves et al. 2011c; Antoniadis et al., 2017; Echevarria et al., 2006; Kumarathilaka et al., 2018c; Oze et al., 2004a). At present, no single method can fully determine TM bioavailability in ultramafic soil systems, and thus a variety of chemical extraction techniques are used to assess TM bioavailability
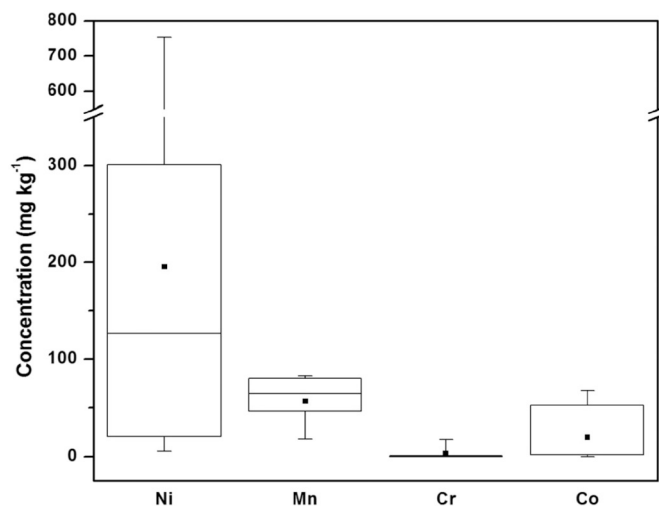

Fig. 2. Box and whisker plot for bioavailability of TMs in selected ultramafic locations. Data from Álvarez-López et al. (2016), Ater et al. (2000), Aziz et al. (2015), Díez Lázaro et al. (2006), Ho et al. (2013b), Jourand et al. (2010), Pal et al. (2005), Ünver et al. (2013), van der Ent et al. (2013a), van der Ent et al. (2017), Vithanage et al. (2014), and Wenzel et al. (2003). Different extractants have been used to obtain these levels of TMs. The black dots in the figure show the mean of the data set.

in ultramafic soil systems (Quantin et al., 2008).

Fig. 2 shows bioavailable concentrations of TMs in various ultramafic locations around the world. In comparison, the bioavailability of Ni is high (6–754 mg kg^{-1}) followed by Mn (18–83 mg kg^{-1}) and Co (1–68 mg kg^{-1}). Cr shows the least bioavailability (0.02–17.80 mg kg^{-1}). Different extractants have been used to evaluate the bioavailability of TMs in various ultramafic locations. In one study, diethylene triamine pentaacetic acid (DTPA) has extracted 13–90 mg kg^{-1} of Ni (Quantin et al., 2008). In contrast, Cr was not found to be bioavailable, suggesting that Cr is tightly bound to well-crystallized Fe-oxides and primary rock-derived phases. Similarly, DTPA and ammonium acetate (NH$_4$OAc)-extractable Cr concentrations have been examined in the ultramafic toposequence in eastern Taiwan, and extractable Cr concentrations were found to be below 5 mg kg^{-1} (Hseu, 2006). The bioavailability of Ni, Mn, and Cr in Sri Lankan ultramafic soils have also been assessed and neither calcium chloride (CaCl$_2$) nor DTPA extractants were found to release Cr, which was consistently < 0.5 mg kg^{-1}, suggesting that Cr in ultramafic soils may tightly bound to the mineral phases (Vithanage et al., 2014). High amounts of Ni and Mn can be released by CaCl$_2$ or DTPA extractants although the concentration of TMs (i.e. Ni, Mn) extractable by CaCl$_2$ was approximately 50% lower than that extractable by DTPA. Use of ethylene diamine tetraacetic acid (EDTA) as an extractant has shown the highest concentrations of bioavailable metals in the most acidic locations (Díez Lázaro et al., 2006). The majority of the Ni and Co has been released from a combination of the exchangeable and Mn oxide bound fractions. Six different single extraction procedures (i.e. distilled water, 0.11 M acetic acid, 1 M NH$_4$OAc; pH 7.0, 0.01 M CaCl$_2$, DTPA and 0.1 M hydrochloric acid (HCl)) for Co extractability of ultramafic soils in eastern Taiwan have shown that water extractable Co concentrations ranged between 0.15 and 0.93 mg kg^{-1}, whereas, HCl-extracted Co concentration is 22.1 mg kg^{-1} (Hsiao et al., 2009).

The mobility of Ni, Cr, and Co, using the EDTA extraction method has been investigated at six ultramafic sites in Poland (Kierczak et al., 2016). The results have shown that Ni possessed the highest EDTA extractable fraction, whereas Cr has the lowest mobility in all studied soils. The lowest concentrations of EDTA-extractable Ni and Co (up to 7 and 4% of total concentrations, respectively) have been found in serpentinites devoid of primary minerals (i.e. olivine and pyroxene) that had non-pseudomorphic textures. In contrast, the highest concentrations of EDTA-extractable Ni and Co (up to 18 and 16% of total concentration, respectively) have been observed in partially serpentinized peridotite (i.e. hornblende peridotite with a pseudomorphic texture), suggesting that the type and origin of the ultrabasic parent rock governs the mobility of Ni and Co (Kierczak et al., 2016). Amir and Pineau (2003) analyzed the relationship between the activity of microorganisms and extractable concentrations of TM in ultramafic soils in New Caledonia and found that extractable concentrations of Ni and Co in New Caledonian ultramafic soils are directly proportional to the microbial activity.

To date, most studies have focused on Cr and Ni mobility in ultramafic-related systems. Soil concentrations of Ni are generally reported to be between 2 and 750 mg kg^{-1}; however, they occasionally exceed 10,000 mg kg^{-1} (Alves et al. 2011c). Typically, Ni substitutes for Mg^{2+} in olivine and pyroxenes (Becquer et al., 2006). Consequently, during ultramafic soil development, Ni released by weathering of primary minerals is in a position to substitute for Mg in clay minerals (i.e. smectites and vermiculite) (Lee et al., 2004). Ni is adsorbed on Fe and Mn oxide surfaces at pH ≥ 5, although it is retained only weakly on clay and Fe and Mn oxide surfaces (Lee et al., 2004). Under near-surface conditions, Ni is also released from ultramafic silicates. As a result, Ni is readily adsorbed by exchangeable sites in soil systems as hydroxyl-oxide precipitates. Thus, Ni is more extractable than Cr in ultramafic soils (Lee et al., 2001; Oze et al., 2004b).

Average concentrations of Cr in soils from around the world are about 5–1500 mg kg^{-1} (Hseu and Iizuka, 2013). In ultramafic rocks,

oxides (i.e. chromite and magnetite) and to a lesser extent silicate phase (i.e. serpentine and pyroxene) are the main Cr-bearing minerals (Oze et al., 2004b; Quantin et al., 2008). During serpentinization, magnetite and serpentine minerals are incorporated different amounts of Cr into their structures (Oze et al., 2004b). Chromite undergoes incongruent dissolution during metamorphism, and, consequently, forms ferrichromite and magnetite rims (Garnier et al., 2008; Oze et al., 2004b). In general, the availability of Cr is found to be relatively low by various chemical extractions, since Cr-bearing minerals tend to be nearly insoluble as well as slowly weathered (Garnier et al., 2008). Garnier et al. (2008) demonstrated that the total amounts of potentially labile Cr increased from the shoulder to the footslope, suggesting that increased availability of Cr is due to the weathering of chromite (Garnier et al., 2008). Cr released from chromite remains in the soil system in both Cr (III) and Cr(VI) states (Cheng et al., 2011). High-valent Mn oxides may stimulate the oxidation of Cr(III) to Cr(VI) in serpentine soil solutions (Oze et al., 2004b).

From previous studies, it is clear that weathering of ultramafic minerals leads to the mobilization of TMs, particularly Cr into the surface and groundwater. Cr(VI) is of particular concern because of its high mobility and toxicity (Gil et al., 2006). The speciation of Cr in the environment is primarily controlled by redox potential (E$_H$) and pH. In general, Cr(VI) is the dominant form under oxidizing conditions, while Cr(III) predominates under more reducing conditions. Despite being highly resistant to weathering, it appears that chromite and more soluble Cr-containing silicates are possible sources of mobilized Cr in ultramafic soils, where Cr oxidation is induced by the presence of Fe, Mn, and dissolved organic carbon under specific environmental conditions (Rajapaksha et al., 2013). A study reported that rapid dissolution of chromite and subsequent oxidation of Cr(III) to Cr(VI) might occur in the presence of birnessite (Oze et al., 2007). The sources of Cr in groundwater in Leon Guanajuato Valley, Central Mexico were also examined by Robles-Camacho and Armienta (2000) who found that Cr is released into the groundwater from the Guanajuato ultramafic outcrops. Similarly, groundwater contamination with Cr(VI) has been assessed in La Spezia province, Italy by Fantoni et al. (2002). The Cr(VI) concentrations in groundwater samples in La Spezia province, Italy, ranged from 5 to 73 µg L^{-1}, exceeding the permissible level for drinking water (5 µg L^{-1}). The authors suggested that Cr-rich ultramafics are the major source of the Cr contamination in the groundwater.

TM oxidation and mobilization may be influenced by the presence of hydrogen peroxide (H$_2$O$_2$) produced by serpentinization, biological weathering, and photochemical processes in a wide variety of terrestrial environments (Cooper and Zika, 1983; Cooper et al., 1987; Willey et al., 1996; Oze et al., 2016). For example, Cr(III) from chromite (FeCr$_2$O$_4$) has been shown to be rapidly oxidized with low concentrations of H$_2$O$_2$, especially at neutral to basic conditions (Oze et al., 2016). As H$_2$O$_2$ can be presented to serpentine soils by a variety of means, even prior to pedogenesis, this is a relatively unknown factor related to TM fractionation and release into the soil solution.

The mobilization of TMs from ultramafics may increase the risk of TMs accumulation in animals and humans. However, an understanding of the fate and transport mechanisms of TMs in groundwater systems remains limited. It is clear that the availability of TMs in ultramafic soils is predominantly influenced by the identity of the TM bearing phases, which are in turn affected by the climatic conditions in the region as well as the weathering history of the soil. For instance, Ni availability is much higher when Ni is bound to phyllosilicates than when it is bound to well-crystallized Fe oxides (Massoura et al., 2006). Similarly, soils with large amounts of amorphous Fe oxides and small amounts of goethite possess a high Ni availability (Massoura et al., 2006). Accordingly, moderately weathered ultramafic soils have higher Ni availabilities than very intensively weathered goethite-rich soils. While these conditions are important, they are sometimes insufficient to explain the availability of TMs in ultramafic environments, since other factors also affect TM release.

5.2. Uptake of ultramafic TMs into plants

Many researchers have assessed TMs in plants growing in ultramafic environments with the goal of identifying hyperaccumulators. Nickel has been particularly studied in plants to assess the potential for phytomining via hyperaccumulation (Chaney, 1983; Reeves, 2003; Reeves et al., 2007; van der Ent et al., 2013a). In Brazil alone, hyperaccumulation ($> 1000\,mg\,kg^{-1}$ in dry plant matter) of Ni has been found in > 30 different species (Reeves et al., 2007). In the Mediterranean and California, a clear distinction between the accumulator and non-accumulator plants was observed; however, in Brazil, the distribution is more continuous, and median Ni concentrations are much higher (Reeves et al., 2007). Globally, around 400 Ni hyperaccumulators have been identified to date (van der Ent et al., 2013b) although hyperaccumulation is generally considered a relatively rare phenomenon, as only 0.5–1% of native ultramafic plant species exhibit Ni hyperaccumulation (van der Ent et al., 2013b). Nickel hyperaccumulators have been listed by country, where Cuba has 140, Southern Europe and Minor Asia have 80–90, Brazil has about 40, and New Caledonia has 65 Ni hyperaccumulators (Jaffré et al., 2013; Reeves et al., 2007; Reeves et al., 1996). However, due to a lack of research efforts, very few Ni hyperaccumulators have been recorded in Malaysia, Indonesia, and Sri Lanka, despite these countries being biodiversity hot spots. Additionally, ecological studies have revealed that the number of hyperaccumulator species in serpentinite environments is less in comparison with the non-ultramafic environments (Baker and Brooks, 1989; Roberts and Proctor, 2012; Teptina et al., 2018; Teptina and Paukov, 2015). However, recent research investigating ultramafic occurrences in South and South East Asia has documented many different plant species with unusually high concentrations of TMs in their foliage (Galey et al., 2017).

5.3. Translocation factor

Iron, Cu, Mn, Ni, and Zn are essential to plant health and growth. However, Cr and Co are non-essential elements and are toxic to plant species even at low concentrations. They can also be transported to humans via the food chain (Aziz et al., 2015). The translocation factor (TF) describes the translocation of metals from one part to another within a particular plant species. For instance,

$$TF = \frac{Concentration\,(shoot)}{Concentration\,(root)}$$

If TF > 1, translocation of metals from root to shoot in a particular plant species takes place in an efficient manner (Fayiga and Ma, 2006). Table 2 summarizes TM levels in roots, stem, and leaves of different plant species in and around ultramafic localities. Most of the plant species successfully stimulate translocation of TMs including Cr, Cu, Mn, Ni, Zn and Co, indicating that high levels of metals are found in plant shoots and leaves compared to the roots (Table 2). In contrast, certain plant species such as *Oryza sativa*, *Cerastium arvence*, and *Biscutella laevigata* lack the capability for translocation of TMs and consequently, less TMs are accumulated in the shoots and leaves of those plants compared to their roots (Table 2).

The accumulation of metals in the different plant tissues (i.e. leaf, stem, and root) are significantly affected by the identity of the metal and the plant species under consideration (Díez Lázaro et al., 2006). Plant species such as *Cytisus multiflorus*, *Daphne gnidium*, and *Genista hystrix* has been reported to contain the lower metal concentrations in their roots, stems and leaves, while species including *Cistus ladanifer*, *Lavandula stoechas*, *Phlox subulata*, and *Thymus mastichina* have shown high metal concentrations distributed throughout the plant (Díez Lázaro et al., 2006). There are several studies on the mechanisms of metal translocation and the role of different types of ligands in metal transportation in plants. The xylem sap of a Ni hyperaccumulator (*Alyssum serpyllifolium* ssp. *lusitanicum*) endemic to the ultramafic soil in northeast Portugal was studied to determine Ni translocation mechanisms (Alves et al., 2011a). The results demonstrated that 70% of Ni was transported as a free, hydrated cation in the xylem, whereas, 18% of Ni was transported by complexation of Ni with carboxylic acids, mainly citric acid. Altogether, oxalic acid, malic acid, malonic acid, and aspartic acid complexed $< 13\%$ of total Ni. Furthermore, $< 1\%$ of Ni complexes are transported via amino acids (i.e. glutamic acid and glutamine).

Interestingly, a recent study done by van der Ent et al. (2017) showed that Ni was concentrated in the phloem in roots and stems. A maximum of 16.9% Ni in the phloem sap of *Phyllanthus balgooyi* was reported; however, in some species (i.e. *Phyllanthus securinegioides* and *Rinorea bengalensis*), the maximum concentrations were reported in the epidermis and in the spongy mesophyll (van der Ent et al., 2017). The above-mentioned study showed that shoot translocation of TMs is a major feature of ultramafic vegetation. In hyperaccumulating plants in the *Euphorbiaceae* family, higher levels of Ni have been found to accumulate in the epidermis of leaves and the laticifer tubes of the stems (Berazaín et al., 2007). A study by Robinson et al. (2003) has confirmed that a Ni hyperaccumulating plant, *Berkheya coddii*, has significantly higher Ni levels in the upper epidermis in leaves than the rest of the leaf. Similarly, *Streptanthus polygaloides* retain high levels of Ni in the leaf epidermis (Sánchez-Mata et al., 2014). Despite these recent advances, further research is needed to understand the role of metal chelation in long-distance transport, the role transporters play in crossing the plasma membrane, and the involvement of organic acids in TM transport through the xylem.

5.4. The bioaccumulation factor

Metal uptake by plant species is dependent on the availability of metals, which in turn depends on the supply of metals from less plant-available forms in the soil system (Lu et al., 2016; Moon et al., 2016). Plant uptake mechanisms for TMs including As, Cd, and Ni at the molecular level have also been investigated in detail. The bioaccumulation factor (BAF) is a measure of the transfer of metals from one trophic level to another. For instance,

$$BAF = \frac{Concentration\,(shoot)}{Concentration\,(soil)}$$

Based on their BAF values, plant species are divided into hyperaccumulators (BAF $> 1\,mg\,kg^{-1}$) and excluders (BAF $< 1\,mg\,kg^{-1}$) (Baker, 1981). Metal hyperaccumulator plants can accumulate TMs in their shoots at levels (in $mg\,kg^{-1}$) of $> 10,000$ (Mn and Zn), > 1000 (Cu, Co, Cr, Ni and Pb) and > 50 (Cd) (Wenzel and Jockwer, 1999; Wenzel et al., 2003). For instance, the Ni concentration in plants growing in non-ultramafic soils ranges from 0.1 to $5\,mg\,kg^{-1}$ dry weight, while plants growing on ultramafic soils may contain up to $100\,mg\,kg^{-1}$ dry weight of Ni. In addition, Ni hyperaccumulator plant species can contain over $1000\,mg\,kg^{-1}$ in dry leaf tissue (Brooks et al., 1977; van der Ent et al., 2013b). The study conducted by Shallari et al. (1998) in eight ultramafic and industrial sites of Albania found $9\,mg\,kg^{-1}$ of maximum Cd concentration in stems and leaves of *Dittrichia graveolens* and BAF was approximately one. In comparison, BAF of the *Herniaria hirsute* reached $2\,mg\,kg^{-1}$ for Cd. Co concentrations in plant tissues ranged from 1 to $86\,mg\,kg^{-1}$, and Cr concentrations were between 3 and $275\,mg\,kg^{-1}$. A wide range of Ni concentration was detected in the investigated plant species (a minimum of $4\,mg\,kg^{-1}$ for *Epilobium dodonaei* and a maximum of $12,625\,mg\,kg^{-1}$ for *Alyssum markgrafii*). None of the plant samples investigated was found to be a metal hyperaccumulator, as the BAF of all the investigated samples was < 1 (0.02, 0.10, 0.01 and 0.03 for Mn, Zn, Co, and Cu, respectively) (Aziz et al., 2015). All plant species investigated in Salcedo watershed in eastern Samar Island, Philippines contained low Ni concentrations with the mean of $14.7\,mg\,kg^{-1}$ (Susaya et al., 2010). The authors, therefore, suggested that food plants (i.e. Gabi, watermelon,

Table 2

Metal concentrations in the different plant parts of the various study species.

Plant species	Plant part	Concentration (mg kg^{-1})						Reference
		Cr	Cu	Mn	Ni	Zn	Co	
Alyssum serpyllifolium	Root	3.3–19	2.5–9	10–80	90–2340	15–70	–	(Díez Lázaro et al., 2006)
	Stem	2.5–34	2.5–12	20–85	150–4500	13–140	–	
	Leaves	5–27	3–18	50–180	670–31,200	10–255	–	
Cistus ladanifer	Root	1.4–17	2.5–15	25–350	1.6–75	5.5–140	–	
	Stem	2.5–26	3–11	30–467	2–50	15.5–500	–	
	Leaves	1.8–128	2.5–15	20–2000	3–50	30–300	–	
Lavandula stoechas	Root	1.8–20	3.5–16	12.5–340	0.8–80	8–44.5	–	
	Stem	1.2–17	4.5–11.2	15.5–325	2.5–40	15–165	–	
	Leaves	1.6–51	3–27.5	40–2200	2.5–95	30–170	–	
Santolina semidentata	Root	3–26	6–15.5	20–70	25–85	10–20	–	
	Stem	4.5–5.5	8.5–10.5	15–30	14.5–20	15–25	–	
	Leaves	4–21	21.5–33	55–135	39.5–55	40–70	–	
Thymus mastichina	Root	2.5–30	5.5–25	14.5–235	2.5–100	4–240	–	
	Stem	2.5–19	4.5–10.5	14.5–145	2.5–35	8–65	–	
	Leaves	2.4–55.5	5.5–19	21.5–485	4–180	17.5–145	–	
Oryza sativa L.	Root	585	12	477	430	18	48	(Aziz et al., 2015)
	Shoot	15	0.75	602	8	37	3	
Silene armeria	Root	55	69	–	51	189	57	(Lombini et al., 1998)
	Shoot	14	9	–	21	66	11	
Cerastium arvence	Root	77	69	–	83	172	16	
	Shoot	29	9	–	45	40	5	
Minuartia laricifolia	Root	24	13	–	124	87	8	
	Shoot	32	9	–	54	68	11	
Dianthus gr. sylvestris	Root	130	8	–	144	65	12	
	Shoot	175	6	–	148	52	13	
Biscutella gr. laevigata	Root	65	8	–	91	102	11	
	Shoot	15	6	–	27	61	11	
Alyssum bertolonii	Root	26	4	–	91	49	11	
	Shoot	52	8	–	27	108	24	
Herniaria hirsuta	Whole plant	275	22	–	808	29	63	(Shallari et al., 1998)
Inula germanica	Whole plant	89	20	–	211	24	31	
Filago eriocephala	Whole plant	35	14	–	460	46	14	
Alyssum murale	Whole plant	13	7	–	5057	49	24	
Alyssum markgrafii	Whole plant	19	56	–	12,625	291	23	
Verbascum blattaria	Whole plant	23	23	–	60	26	8	
Consolida orientalis	Whole plant	12	13	–	49	54	3	
Lotus ornithopodioides	Whole plant	63	14	–	232	75	21	
Teucrium polium	Whole plant	50	9	–	167	12	19	
Colocasia esculenta	Leaves	–	–	–	14.2	–	–	(Susaya et al., 2010)
Phyllanthus amarus	Leaves	–	–	–	53.7	–	–	
Artocarpus heterophylla	Leaves	–	–	–	19.2	–	–	
Moringa oleifera	Leaves	–	–	–	10.5	–	–	
Lycopersicon esculentum	Leaves	–	–	–	11.1	–	–	
Solanum melongena	Leaves	–	–	–	6.22	–	–	
Alyssum chalcidicum	Leaves	–	–	–	2910	–	–	(Kanellopoulos et al., 2015)
Allium cepa	Bulb	0.7	6	22	2.9	39	2.3	(Economou-Eliopoulos et al., 2011)
Allium cepa	Shoot	1.8	6	60	2	24	3.8	
Allium sativum	Bulb	0.7	8	15	3.1	46	6.1	
Allium sativum	Shoot	1.4	4	34	1.8	28	2	
Allium porrum	Root	8	8	23	11	19	1.9	
Allium porrum	Shoot	0.7	5	16	1.6	17	2	
Beta vulgaris	Root	0.6	8	23	0.5	12	2.7	
Beta vulgaris	Shoot	0.8	7	115	1.3	11	2.4	
Triticum spp.	Root	100	14	140	150	12	20	
Triticum spp.	Shoot	1.7	2.5	25	1.2	12	16	
Triticum spp.	Seeds	1.3	4.6	30	3	26	6.5	
Solanum nigrum	Leaves	120	–	94	140	42	–	(Megremi, 2010)
Cichorium intybus	Leaves	48	–	89	88	78	–	
Sonchus oleraceus	Leaves	54	–	100	93	37	–	
Allium sativum	Leaves	6	–	32	17	15	–	
Sinapis arvensis	Leaves	79	–	82	72	92	–	
Daucus carota	Leaves	3.5	–	52	17	9	–	
Verbascum spp.	Leaves	82	–	73	210	86	–	
Alyssum murale	Leaves	–	–	30	20,100	310	90	(Bani et al., 2014)

Table 2 (*continued*)

Plant species	Plant part	Concentration (mg kg^{-1})						Reference
		Cr	Cu	Mn	Ni	Zn	Co	
Crotalaria micans	Root	13	–	33.2	19.5	–	–	(Ho et al., 2013a)
	Shoot	6.08		10.4	48.3			
Miscanthus floridulus	Root	28.2	–	53	45	–	–	
	Shoot	8.99		11.6	11.1			
Leucaena leucocephala	Root	20.4	–	28.9	15.7	–	–	
	Shoot	7.03		15.2	22.9			
Bidens pilosa	Root	36.9	–	69.4	32.7	–	–	
	Shoot	12.5		27.4	45.9			
Pueraria lobata	Root	18.7	–	46	30.1	–	–	
	Shoot	12.1		17.3	51.4			
Melilotus indicus	Root	15.8	–	30.2	22.4	–	–	
	Shoot	7.18		21.8	17.2			
Conyza canadensis	Root	13	–	44.6	24.7	–	–	
	Shoot	13.5		20.6	42.7			
Phyllanthus balgooyi	Root	–	–	120	4780	120	7	(van der Ent et al., 2017)
	Bark	–	–	37	310	8.8	4	
	Wood	–	–	20	560	11	5.8	
	Branches	–	–	89	5270	64	26	
	Leaves	–	–	240	4680	88	31	
Phyllanthus securinegioides	Root	–	–	26	1270	24	16	
	Bark	–	–	68	5860	78	8.8	
	Wood	–	–	11	860	10	5	
	Branches	–	–	94	7630	74	20	
	Leaves	–	–	190	16,530	92	30	
Rinorea bengalensis	Root	–	–	–	–	–	–	
	Bark	–	–	36	3970	240	5.1	
	Wood	–	–	13	880	35	4.8	
	Branches	–	–	57	5140	120	13	
	Leaves	–	–	370	5740	95	19	
Alyssum pintodasilvae (Barazón)	Shoot	–	–	–	5713	–	–	(Álvarez-López et al., 2016)
	Whole plant				148			
(Samil)	Shoot	–	–	–	6665	–	–	
	Whole plant				117			
Alyssum malacitanum (S. Bermeja)	Shoot	–	–	–	9527	–	–	
	Whole plant				279			
(S. Aguas)	Shoot	–	–	–	5178	–	–	
	Whole plant				152			
Alyssum bertolonii	Shoot	–	–	–	8727	–	–	
	Whole plant				299			
Noccaea goesingense	Shoot	–	–	–	6241	–	–	
	Whole plant				211			

jackfruit, horse-radish tree, guava, tomato, eggplant) grown in eastern Samar Island, Philippines, may not have adverse health effects on humans.

Crops and pasture grown on ultramafic soils are likely to accumulate high concentrations of TMs and thus may constitute a health hazard for animals such as cattle. For example, Miranda et al. (2009) demonstrated that Ni and Cu levels in the kidneys of cattle near the ultramafic locality in Galicia, NW Spain have been increased by 20% and 32%, respectively. In contrast, Cr levels in cattle tissue were within the normal range (Miranda et al., 2009). This study shows that ultramafic soils significantly influence Ni and Cu accumulation in animals, leading to the risk of toxicity. Additional direct threats to human consumption of crops grown in ultramafic soils have been reported for crops such as rice. For example, the Ni content from brown and polished rice grown in paddy fields inclusive of ultramafic soils in eastern Taiwan was shown to exceed the tolerable Ni intake for adults recommended by the World Health Organization (WHO) (Hseu and Lai, 2017). Hence, further studies are required to evaluate the risk that TMs pose through the soil-plant and animal cycle.

5.5. TM uptake mechanisms in plants

Ultramafic flora possesses a remarkable ability to tolerate TMs and develop under TM stress. They excel at both uptake and translocation of TMs throughout the plant body. The adapted plant species to ultramafic environments can be metal hyperaccumulators or excluders (Baker, 1981; Rascio and Navari-Izzo, 2011). The metal hyperaccumulator plant species can uptake and translocate metals 100 to 1000 times more efficiently than non-hyperaccumulating plant species (Krämer, 2010; van der Ent et al., 2013b). The translocation of metals from roots to aerial parts of the plant through the xylem transport is a characteristic feature of hyperaccumulator phenotypes (Brady et al., 2005; Clemens et al., 2002). The metal hyperaccumulator, *Arabidopsis halleri* has been used as a model plant to study TM uptake and translocation (Briskine et al., 2017; Chiang et al., 2006; Frérot et al., 2010; Hanikenne and Nouet, 2011). *A. halleri* can accumulate high Zn and Cd levels as high as 2.2% and 0.28% respectively in its leaf in dry biomass (Talke et al., 2006).

Transport of soil TMs across the plasma membrane is an important feature of hyperaccumulators. Membrane transport proteins and intracellular high-affinity binding sites play an essential role in metal transport across the plasma membrane. The six major transporter systems effectuating TM transport across the membrane are: the Zn-regulated transporter and Fe-regulated transporter protein (ZIP) family, the cation diffusion facilitator (CDF) family, the P$_{1B}$-type subfamily of P-type ATPases, the natural resistance-associated macrophage protein (NRAMP) family, the yellow-stripe 1-like (YSL) subfamily of the oligopeptide transporter (OPT) superfamily, and three subfamilies of ATP-binding cassette (ABC) transporters (Hall and Williams, 2003; Kumarathilaka et al., 2018b; McGrath and Zhao, 2003).

Interestingly, the genes coding the ZIP transporter family members were found to be expressed at very high levels in the roots and shoots of hyperaccumulators such as *Thlaspi caerulescens* (Assunção et al., 2001). The high constitutive expression of metal ion transporter genes in extremophytes even in the absence of high concentrations of the relevant ion in control soil treatments has been suggested as one of the hallmark genetic features of extremophytes adapted to extreme soils (Krämer, 2018; Oh et al., 2013). The extremophyte model, *Arabidopsis halleri* is naturally adapted to high Zn and Cd and this is thought to be partly a result of high gene copy number of the *HEAVY METAL ATPASE4* (*HMA4*) gene as well as its high constitutive expression leading to enhanced partitioning of Zn from roots into shoots (Briskine et al., 2017; Hanikenne et al., 2008; Talke et al., 2006). The genes highly expressed in *A. halleri*, compared to its close TM-sensitive Arabidopsis relatives, contribute to its hypertolerance to TMs include, Ca^{2+}/H^+ antiporter, *CAX1*, and *METAL TOLERANCE PROTEIN1* (*MTP1*) (Baliardini et al., 2015; Talke et al., 2006). Furthermore, increased Zn influx in roots of the hyperaccumulating *Thlaspi* species was detected with respect to high Ni and Zn concentration of the roots (Kazakou et al., 2010; Pence et al., 2000). Moreover, the ultramafic and the non-metallicolous populations of *Thlaspi caerulescens* showed low affinity for Cd and Zn over Ni. This may be due to the Ni hyperaccumulation of the ultramafic population in its natural environment. Moreover, this suggests that a Zn transport system might also lead to the entrance of Ni into roots (Assunção et al., 2008).

Non-hyperaccumulator plants retain most of the TMs they uptake in their root cells, detoxifying them by chelation in the cytoplasm or accumulating them in vacuoles. In contrast, hyperaccumulators characteristically translocate TM to the shoot through the xylem in an efficient manner (Haydon and Cobbett, 2007). Enhanced chelation of Ni (II) by nicotianamine in the xylem has also been suggested as a Ni tolerance mechanism in the hyperaccumulator *Thlaspi caerulescens*. Ni–nicotianamine (Ni-NA) complexes have been detected in the roots of Ni-treated Zn-hyperaccumulator *Thlaspi caerulescens* (Vacchina et al., 2003). In *Arabidopsis halleri*, *NA synthase* is highly expressed in roots facilitating high Zn accumulation (Weber et al., 2004). Vacchina et al. (2003) demonstrated that the introduction of nicotianamine synthase gene expressed in *Arabidopsis thaliana* into transgenic tobacco plants led to an increase in Ni tolerance. Furthermore, transgenic tobacco plants which produce nicotianamine by overexpressing *HvNAS1*, grew with minimal toxicity symptoms in a Ni-enriched ultramafic soil (Kim et al., 2005).

Free histidine also acts as a Ni-binding ligand that facilitates the xylem transport of Ni. In the hyperaccumulator, *Alyssum lesbiacum*, free histidine production was found to be activated in the presence of high Ni concentrations, but not in the non-accumulator, *Alyssum montanum* (Charnock and JAC, 1996). Similarly, enhanced release of Ni into the xylem is coincident with the release of histidine from the free histidine pool in the roots of both *Alyssum lesbiacum* and *Brassica juncea* (Kerkeb and Krämer, 2003). In addition to histidine, YSL family members also help in xylem loading and unloading Ni-NA chelates (Colangelo and Guerinot, 2006). The upregulation and the localization of the expression of these *TcYSL* genes together with the transport activity of Ni-NA chelates around the vascular system was shown to be required for the long-distance transport of metal ions in *T. caerulescens*. The entry of Ni–NA into the symplastic transport in the root and the unloading of the Ni–NA complexes from the xylem in the leaves both depended on the capacity of *TcYSL3* to catalyze the influx of Ni–NA. That catalysis was vital for direct detoxification and storage of Ni, which is another mechanism of TM tolerance in plants (Freeman et al., 2006). Both processes are prominent in hyperaccumulators (Bidwell et al., 2004). Interestingly, leaves are considered to be the major storage organs of TMs as well as the major detoxification sites, while avoiding damage to the photosynthetic machinery (Freeman et al., 2006). The accumulation of Ni in the vacuoles of epidermal cells in the leaves of *Hybanthus floribundus* (a hyperaccumulator of Ni) was found to be concentrated on the outside of cell walls, indicating that apoplastic compartmentation facilitating Ni tolerance (Bidwell et al., 2004). Metal cations bound to smaller ligands of organic acids can be highly accumulated inside vacuoles. For example, citrate is the main Ni-bounded ligand in the leaves of *Thlaspigoesingense* (Bernal et al., 1994). Bioaccumulation of TMs may cause allelopathic effects on neighboring plants (Seneviratne et al., 2016); however, our knowledge is not sufficient to confirm this with ultramafic soils. Studies on TMs such as Cu and Co-accumulation in plants are even more limited (Lange et al., 2017) mainly due to the scarcity of the sites and the absence of model plants equipped with genetic and physiological resources. More studies are required to assess those physiological and biochemical damages and their mechanisms in plants in ultramafic ecosystems.

5.6. Tolerance to low Ca:Mg ratio

The Ca:Mg ratio is an important factor for ultramafic flora (Álvarez-López et al., 2016). High concentrations of Mg in ultramafic soils are antagonistic to plant Ca uptake. Ca shows a unidirectional transport from the root elongation zone to the shoot due to immobilization of Ca in the shoot. High concentrations of Mg in the ultramafic soil induces a Ca deficiency in the growing root tips, which leads to necrosis of the root tip (O'Dell et al., 2006). The plants grown in ultramafic environments show the tolerance towards high Mg and comparatively lower Ca levels in ultramafic soils (Ghasemi et al., 2015; Palm and Van Volkenburgh, 2014). For instance, *Mimulus guttatus* grown in ultramafic environments has shown an increased tolerance to low Ca:Mg than that of non-ultramafic populations (Selby, 2014). A single, major QTL (quantitative trait locus) of LG13 was found to control both the ability of plants to survive on ultramafic soils and their tolerance to low Ca:Mg ratios. Furthermore, native ultramafic plant species have exhibited more Ca absorption and less Mg absorption than plants in non-ultramafic soils (Ghasemi et al., 2015). Ultramafic plants have the ability to maintain a sufficient internal concentration of Ca under the lower Ca:Mg (< 1) found in ultramafic soils (Ghasemi et al., 2015). *Alyssum inflatum*, a Ni hyperaccumulator which is endemic to ultramafic habitats was found to demonstrate a high tolerance to a low Ca:Mg ratio and increase in plant Ni accumulation with increasing Ca:Mg ratio (Ghasemi and Ghaderian, 2009). However, an increase in soil Ca content was found to lower the Ni uptake of *A. serpyllifolium* (a non-hyperaccumulator), leading to a decrease in shoot Ni concentration (Brooks et al., 1981). Substantial work has been done on Ca^{2+} and Mg^{2+} transport systems and the homeostatic balance between the two nutrients (reviewed in Tang and Luan (2017)). However, limited studies (reviewed in Brady et al., 2005) have looked into molecular, genetic, and physiological mechanisms unique to ultramafic flora adapted to high Mg^{2+} and low Ca^{2+} soils.

5.7. Ecosystem and human health-related medical geology

Ultramafic localities are being used as croplands and residence areas in many different regions globally. The fractionation, release, and availability of TMs depend on both environmental factors and pedogenic activities (Fig. 3). Hence, ultramafic soil localities pose risks to human and ecosystem health. The ultramafic body in Shih-Tao Mountain in Taiwan is part of an urban watershed, directly influencing 100,000 residents (Cheng et al., 2011). The release of TMs can influence water quality. Subsurface waters in ultramafic terrains in Peninsular Malaysia and the State of Subah in Malaysia contained elevated concentrations of Cr and Ni (23–172 and 95–936 $\mu g\,L^{-1}$, respectively). However, surface waters contained safe levels of TMs for human consumption (Tashakor et al., 2018). Some ultramafic soils are under cultivation, including viticulture and rice. Wheat (*Triticum aestivum*) has been cultivated on ultramafic soils in the eastern part of the Rudnik Mountain, near Salasi Village in Serbia (Antić-Mladenović et al., 2011). Rice grown on ultramafic environments in Hualien and Taitung in
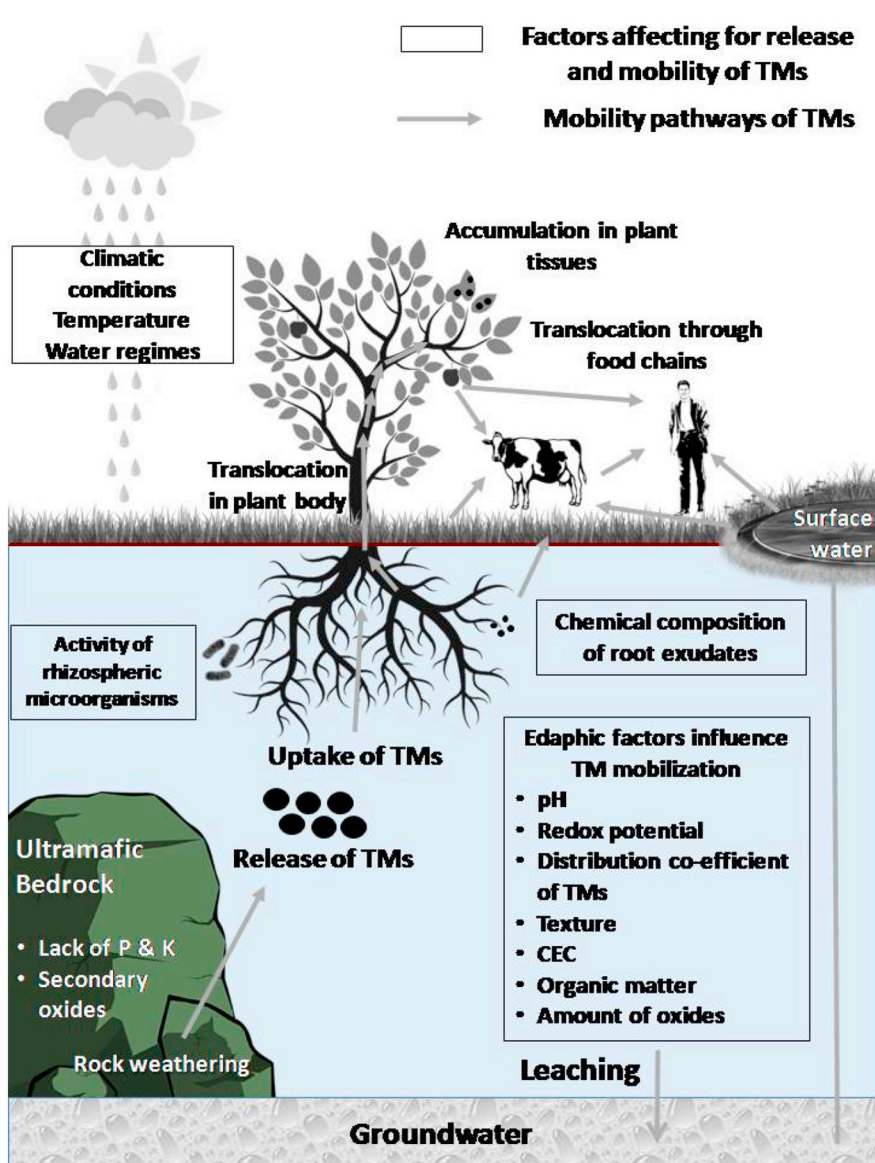
Fig. 3. Schematic diagram of the trace element release into the environment.

eastern Taiwan has been found to have high Ni levels (1.50–4.53 and 2.45–5.54 mg kg^{-1} in brown and polished rice, respectively) (Hseu and Lai, 2017). On the basis of the WHO's provisional tolerable Ni intake for adults, daily consumption of rice may lead to an excessive Ni intake by humans. Intensive agricultural activities and livestock farming are also taking place on ultramafic terrains (64 km^2) in Atalanti, central Greece (Kanellopoulos et al., 2015). The measured Ni level in the leaves of *Alyssum chalcidicum* in Atalanti was 2910 mg kg^{-1}. This characteristic example shows the relationship between soil geochemistry and metal uptake by plant species.

When food plants contain increased concentrations of TMs, this can create health problems. High Ni accumulations were noted in *Phyllanthus amarus* Schum. & Thonn (54 mg kg^{-1}) and *Stachytarpeta jamaicensis* (65 mg kg^{-1}), in the villages of Malbog, Napataan, and Palanas in Eastern Samar in the Philippines (Susaya et al., 2010). However, none of the investigated plants met the criterion for a hyperaccumulator plant (< 10,000 mg kg^{-1}), and non-food plants had higher maximum Ni concentrations than did food plants. The recommended daily intake of Ni is < 1 mg kg^{-1} (Susaya et al., 2010). The possible concentrations of Ni intake per food plant species at daily consumption levels of 1000, 250, and 125 g were calculated. For most food plant species consumed in great quantities (1000 g day^{-1}), the Ni

intake level would be higher than the recommended daily intake. Additionally, even the consumption of 125 g day^{-1} of *Psidium guajava* L., *Artocarpusheterophylla* Lam., *Moringa oleifera* Lam., *Solanum melongena* L., and *Lycopersicon esculentum* Mill. would exceed the daily recommended threshold (Susaya et al., 2010). Another study examined the effect of high soil concentrations of Ni and Cr on perennial grapevines growing in ultramafic soil in Serbia (Licina et al., 2010). The levels of Ni and Cr in the grapevines showed the pattern root > leaves > shoots > grapes. The Ni and Cr concentrations in roots were 40.7–68.8 and 23.3–41.3 mg kg^{-1}, respectively, whereas in grapes the concentrations were 0.4–0.9 and 0.1–0.6 mg kg^{-1} (Licina et al., 2010).

Around 100,000 ha of floodplain soils in the Velika Morava valley, central Serbia, were found to have high Ni level (Jakovljevic et al., 1997). Later studies confirmed that the Ni in the floodplain soils originated from the weathering of ultramafic rocks which outcrop in the Velika Morara River system. The Velika Morava River valley is an important agricultural region which is exposed to frequent flooding. Rinklebe et al. (2016) investigated the release dynamics of Ni at controlled redox potentials (E$_H$) in floodplain soils in this valley. The authors found that Ni can be mobilized at low E$_H$, while an elevation in E$_H$ from reducing to oxidizing conditions results in immobilization of Ni. The mobilization of Ni was attributed to the formation of Ni-dissolved

organic carbon complexes at low E_H, and the immobilization of Ni was suggested to result from the formation of Fe/Mn (hydro)oxides and subsequent co-precipitation of Ni during oxidation (Rinklebe et al., 2016). The influence of ultramafic rocks on the contamination of agricultural plants by Cr due to natural processes was studied in the Assopos basin in Greece (Economou-Eliopoulos et al., 2011). Mineralogical studies revealed that Cr in the soil is mainly associated with chlorite, chromite, Fe-chromite, Cr-bearing goethite, and silicates. The Cr content in plants ranged from 1.8 to 2.3 mg L^{-1} in shoots, 1.3 to 100 mg L^{-1} in roots, and 1.5 mg L^{-1} in a bulb plant. It is interesting to note that some plants which possess small, fine fibrous roots located near the surface of the soil (i.e. wheat (*Triticum* spp.), onion (*Allium cepa*) and leek (*Allium porrum*)), contained higher Cr concentrations than plants which possess a thick main root extending deeper into the soil, such as beets (*Beta vulgaris*) and verbascum (*Verbascum* spp.). It is thus important to obtain a better ecological risk assessment of floodplain sites under agricultural use.

Both geogenic and anthropogenic sources have contributed to high levels of Cr present in groundwater in many countries. Leaching of geogenic Cr(VI) in Greece has led to an elevated level of total Cr (28.5 μg L^{-1}) and Cr(VI) (25.3 μg L^{-1}) in the groundwater (Dermatas et al., 2012). However, a few wells contained up to 190 μg L^{-1} total Cr, most of which occurred as Cr(VI) (up to 160 μg L^{-1}). Additionally, it was suggested that the presence of Cr(VI) in that area was due to a combination of geogenic (i.e. ophiolites) and anthropogenic sources. Similarly, up to 212 μg L^{-1} of Cr(VI) was detected in irrigated groundwaters from the wider area of Thiva Basin in central Greece (Tziritis et al., 2012). In Thiva town, the Cr(VI) concentration ranged from 13 to 212 μg L^{-1}, whereas, in Mouriki village, Cr(VI) values ranged from < 9 to 14 μg L^{-1}. Ultramafic formations are a possible source of elevated Cr(VI) in groundwater. Therefore, investigation of the geo-chemical properties is required to ensure the quality of agricultural products of that region. Additionally, tap water from 600 groundwater-supplied sites in Greece was assessed for potential Cr(VI) contamination (Kaprara et al., 2015). Notably, 25% of the samples contained Cr(VI) levels above 10 μg L^{-1}. The higher Cr(VI) concentrations in aquifers may be related to the underlying geology which is rich in ultramafics. Kaprara et al. (2015) suggested that high Cr(VI) levels in drinking water may occur due to MnO_2-catalyzed oxidation of Cr(III) into Cr(VI). Groundwater contamination due to ultramafics has also been identified in Leon Guanajuato Valley, Central-Mexico (Robles-Camacho and Armienta, 2000) and Sacramento Valley, California, USA (Mills et al., 2011). High Cr(VI) concentrations were found in the exchangeable soil fraction in Wan-Ron Hill in eastern Taiwan, ranging from 34.8 to 183 μg kg^{-1} (Ho et al., 2013b). In a California Coast Range ultramafic deposit, water-extractable Cr(VI) in soil has been found to increase with depth, with a total soil reservoir of 7.8 to 12 kg/km^2 Cr(VI) and soil concentrations ranging from 25 to 172 μg L^{-1} (McClain et al., 2017).

Open cast mining of ultramafic ore deposits has also been found to threaten the surrounding environment. The overburden and ore dumps in mining sites are commonly stored on the ground surface. Leaching of TMs from mining wastes, particularly during the rainy seasons, and dispersion of fine particles via wind lead to the contamination of groundwater, surface water bodies, and nearby lands (Losfeld et al., 2015). For instance, mine seepage and leachate migration from a chromite ore deposits (i.e. Sukinda mine, Orissa, India) have caused high Cr(VI) concentrations in nearby groundwater sources (0.032–0.452 mg L^{-1}) (Dhakate et al., 2008). Pattnaik and Equeenuddin (2016) also demonstrated that soils in the area near the Sukinda mine, Orissa, India, have been contaminated by Cr(VI) (1.45–16.7 mg kg^{-1}) due to the weathering of ultramafic rocks. Mining of laterite ore deposits has also been found to increase the risks to environmental health (Losfeld et al., 2015; Lweya et al., 2015).

Lateritisation involves in situ neoformation of mineral phases which host TMs such as Cr, Ni, and Cu (Quesnel et al., 2017). Economou-Eliopoulos et al. (2016) demonstrated that Cr(VI) concentrations in leachates from laterite ore in Kastoria, Greece, reached levels as high as 1.3 mg L^{-1}. Groundwater sources near a laterite ore in central Evia, Greece, have also contained values ranging from < 2 to 360 μg L^{-1} (Economou-Eliopoulos et al., 2017). The groundwater samples near a laterite mine in North Western Zambia contained 0.12–0.15 mg L^{-1} of Cu, well below the WHO drinking water quality guideline of 2 mg L^{-1} (Lweya et al., 2015). At present, mining of Ni has shifted from high-grade Ni sulfides to low-grade ore Ni laterites, containing approximately half of the mined Ni ores. The spatial distribution of Cr in soils near Ni-laterite ores in C. Evia and Assopos-Thiva basins, Greece, has been investigated by Megremi et al. (2019) and the Cr levels in the respective locations ranged from 50 to 190 mg kg^{-1} and 130 to 310 mg kg^{-1}. Therefore, it is essential to restore or rehabilitate mining sites to minimize the potential for TM contamination of agricultural lands and water sources.

The release of TMs from ultramafic outcrops has garnered significant attention in recent years, with a particular focus on understanding the mechanisms (i.e. oxidation, reduction, adsorption, and desorption) which affect TM fates in water resources. More precisely, physicochemical properties (pH-Eh and natural organic matter) and adsorption-desorption reactions govern the mobility and bioavailability of TM in the environment (Kumarathilaka et al., 2016a; Kumarathilaka and Vithanage, 2017; Lilli et al., 2015). Mobility studies have demonstrated that TM (i.e. Cr) leaching phenomena from ultramafic soils are very fast; however, sorption capacities are also significant. For example, Cr complexation with ferric oxide surfaces limits Cr mobility and transport in the environment. Further, soils and sediments with calcareous components more efficiently adsorb Cr(VI) compared to siliceous clusters. The presence of Fe and Mn may increase Cr(VI) concentrations, as it can be released from the surface of Mn oxides, be oxidized, and subsequently re-adsorb onto Fe oxides (Ho et al., 2013b; Rajapaksha et al., 2013). Thus, it is necessary to investigate the leaching mechanisms of TMs in different lithologies to fully elucidate the processes which govern their fate and transport in the subsurface.

The far-reaching significance of ultramafic-rich soil and associated TM bioavailability is apparent from the role of such soils as an analog to regolith that humans may encounter on Mars. Pioneering work has highlighted that ultramafic-bearing soil may readily leach TM, especially in the presence of perchlorate (Kumarathilaka et al., 2016b) which has been detected at reactive abundance across several sites on Mars (Wilson et al., 2016). Combined with the expected higher abundance of serpentine-bearing regolith on Mars, any use Martian regolith materials to grow crop plants to support human habitats will need to address the health risks potentially associated with the higher bioavailability of TMs. Meanwhile, ongoing in situ and laboratory work on the martian halogen cycle (Karunatillake et al., 2013; Zhao et al., 2018) suggest that the regolith can serve as a source for reactive halogen phases on Mars via photochemical processes, which may, in turn, enhance the pervasiveness of salts like perchlorates and the associated TM bioavailability in serpentine-bearing soil. Collectively, such observations can be best understood only with additional work on soil analogs to complement current soil simulants (Cannon et al., 2019), particularly at poorly characterized settings on Earth, such as in Sri Lanka. Furthermore, given endemic extremophytes in and their genetic adaptations to serpentine soils (Oh et al., 2014; Turner et al., 2010), the serpentine-bearing soil along the suture zone in Sri Lanka likely harbors extremophyte species. Characterizing their physiological responses and underlying genetic adaptations will help identify ways to genetically modify crop plants for reduced TM hazards on extended human missions on Mars, wherein regolith will serve as a key growth substrate (Wamelink et al., 2014) as already anticipated in lunar settings (Liu et al., 2008).

6. Conclusions

Ultramafic outcrops have a higher concentration of TMs, particularly Ni, Cr, and Co, than non-ultramafic soils. For this reason, fauna and flora in and surrounding areas of ultramafic localities may be at potential risk of TM accumulation. Cr mainly binds with the residual fraction of ultramafic soils and is not readily bioavailable under natural environmental conditions. The mineralogy of ultramafic soil profiles is largely dependent on the location. Many extremophytes growing in ultramafic soils are effective at the translocation of TMs, but several species are not. Plant species grown in ultramafic substrata can accumulate high levels of TMs in their vegetative and reproductive tissues.

Limited information is currently available on TM fractionation, translocation, bioaccumulation, and their allelopathic effects on other plants in the ultramafic environment. Key knowledge gaps regarding the mobility and bioavailability of TMs in ultramafic environments remain. These include the following: (1) investigation of the relationship between physicochemical properties and the mobility and bioavailability of TMs in different ultramafic localities, (2) assessment of temporal and spatial variations of groundwater and surface water quality in and around ultramafic environments, (3) the long-term effect of natural and anthropogenic activities on the process of ultramafic weathering, and (4) risk assessment studies related to TM ingestion and bioaccessibility for humans in and around ultramafic localities. Such studies should seek to enhance current knowledge on TM release mechanisms in ultramafic soils and the metabolism of TMs in ultramafic flora at molecular levels. This knowledge could then be used to develop effective strategies to mitigate the mobilization of TMs in the ultramafic environment or develop methods to extract TMs through the process of phytoremediation -. Such work will also provide necessary insight on refining Mars soil simulants to advance crop-plant experiments for future human habitats.

Declaration of Competing Interest

Authors declare no conflict of interest.

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