

The extent and applications of metal accumulation and hyperaccumulation in Philippine plants

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1 The extent and applications of metal accumulation and

2 hyperaccumulation in Philippine plants

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10 Summary text for the Table of Contents

- 11 Soils of the Philippines often have high concentrations of heavy metals and low nutrient content,
- 12 which are conditions that are normally unfavourable for plant growth. Many plants in the area,
- 13 however, have adapted to these conditions and can grow well. Here we have compiled the data that
- 14 is currently available on Philippine plants that can accumulate metals in their tissue, and the
- 15 potential applications of these plants in restoration efforts.

16 Abstract

- 17 To examine the potential applications of hyperaccumulator plants in the Philippines we reviewed
- current data on the extent of metal hyperaccumulation in native species, and partitioning of metalswithin the plant tissue.
- 20 Twenty-eight species had reported tissue concentrations above the hyperaccumulator threshold,
- 21 eleven species were endemic to the Philippines. Nickel was present in higher concentrations in the
- 22 aboveground tissue than the belowground tissue, but the reverse was found for copper, aluminium,
- and chromium.
- 24 The fact that copper accumulates belowground rather than above, and most hyperaccumulators of
- 25 nickel identified were trees has implications for the potential of phytoextraction using native
- 26 Philippines flora.

27 Key words:

- 28 Metallophyte; hyperaccumulator; phytoremediation; phytomining; phytoextraction; Philippine flora;
- 29 metal tolerance; translocation factor; bioaccumulation factor

31 **1** Introduction

32 The Philippines is the fifth richest country in mineral resources worldwide, including nickel, copper, 33 chromite, and gold (Maddox et al., 2019) and mining activity is extensive in the region as a result. 34 The ultramafic areas in the Philippines account for about 5% of its estimated total land area of 35 298,170 km² (Baker et al., 1992). Ultramafic areas are often deficient in the essential macronutrients 36 (e.g. phosphorus, potassium and calcium) and have high concentrations of potentially phytotoxic 37 elements (e.g. magnesium, iron, nickel, cobalt, and chromium) --- conditions that are normally 38 adverse to plant growth (Galey et al., 2017). However, some plants called 'metallophytes' have an 39 ability to tolerate metal toxicity and survive and reproduce in these environments (Baker and 40 Whiting, 2008; Whiting et al., 2004). Plant species that evolved on ultramafic soils are generally 41 metal tolerant. Such native species could be an important source of metal tolerant and accumulator 42 plants that are most likely to be able to survive the edaphic and climatic conditions of locally 43 contaminated lands (Carvalho et al., 2013; Claveria et al., 2020, 2019b; de Castro et al., 2020). 44 Metallophytes are able to grow in soils with high heavy metal concentrations through two different 45 strategies: avoidance and tolerance (Baker, 1981). Avoidance is achieved when the plant invests in 46 external mechanisms to keep metals chelated outside of the plant tissue (Carvalho et al., 2013; 47 Claveria et al., 2010). Whereas tolerance is developed through physiological adaptations to 48 accumulate metals in high concentrations in the plant biomass. 49 Tolerance can be achieved through exclusion, or hyperaccumulation (Jaffré et al., 1976). Exclusion 50 means there is limited translocation from the roots of the plant to the shoots (Hunt et al., 2014; 51 Lange et al., 2017; Sanqui et al., 2020). Hyperaccumulators, have evolved the capability to 52 accumulate certain metal elements in their shoots, especially the leaves, that are at levels 100x 53 greater than those typically measured in shoots of the common non-accumulator plants (Brooks et 54 al., 1998, 1977; Jaffré et al., 1976). Reeves (1992) stated that concentrations must be recorded in the dry matter of any above-ground tissue in at least one specimen growing 'in its natural habitat' i.e. 55 56 not under artificial conditions, such as through metal-salt amendments to an experimental soil or

hydroponic nutrient solutions (van der Ent et al., 2013). More than 700 hyperaccumulating plants
have been reported worldwide, the majority of which (>70%) hyperaccumulate nickel (Reeves et al.,
2017).

As a result of their unusual tolerance for heavy metals and restricted distribution, metallophytes
have potential benefits for the restoration of vegetation in mined-out areas within their geographic
range (Erksine et al., 2012; Reeves, 2006; Whiting et al., 2004). Hyperaccumulators have been of

30

considerable interest in the mineral exploration (Jaffré et al., 1976) and are the optimal choice for
future 'green' phytoremediation technologies, such as phytoextraction and phytomining. However,
for plants to be applicable for phytomining or phytoextraction efforts they need to be examined in

66 terms of: (i) their ability to bioaccumulate metals so that the concentration in the plant tissue is

- 67 greater than the soil (Reeves, 2006); and (ii) translocate those metals to their aboveground biomass
- 68 (Figure 1).
- 69 The total number of native vascular plant species in the Philippines is currently estimated at 9,433
- 70 (Pelser et al., 2011) with ~50% endemic species. Of this, the exact number of metallophytes remains
- 71 unknown and many new species of metallophytes endemic to the Philippines continue to be
- discovered (Fernando et al., 2018; Fernando and Wilson, 2021; Fritsch et al., 2020; Robinson et al.,
- 73 2019; Tamayo et al., 2023). This paper aims to consolidate current data on the extent of metal
- 74 hyperaccumulation in the Philippines, the species of heavy metal accumulating plants, and
- partitioning of metals within the plant tissue. We also aimed to identify any knowledge gaps and
- 76 future research needs on metal hyperaccumulation in the Philippines. Our review considers solely

native plant species in the Philippine flora naturally growing in the wild (rather than controlled or

78 laboratory conditions).



79

Figure 1- Schematic of principles of phytomining in phytoremediation of a given metal. a) Soils with
large concentrations of a given metal present in the soil solution (1) are sown with plants. Plant
uptake through the roots take place (2) and are translocated into the aboveground biomass (3).
Metal accumulates in the aboveground tissue (4); b) Bioaccumulation in the plant tissue reduces the
concentration of the metal in the soil (5). Aboveground biomass is harvested and removed from the
site, this is phytoextraction (6) and ashed to generate a high metal concentrated material for
processing for their intrinsic value, this is phytomining (7). Drawn with biorender.com

87 2 Materials and methods

88 2.1 Literature searches and data extraction

Searches on Web of Science were carried out (24th February 2023) using the terms: (i) *4ccumulate*
metal* plant* AND Philippine*; (ii) metallophyte* plants AND Philippine*; and (iii) metal toleran*
plants AND Philippine*. The references list in each of the papers returned were also checked to find

additional papers. Observations on species that were not native to the Philippines, laboratory trials,
or duplicates were not included. If a paper reported concentrations of two metals for a single plant,
this was recorded as two observations, one for each metal.

95 Each paper reported results in a different manner. The majority reported a total plant tissue 96 concentration. A large proportion also partitioned into aboveground tissue concentration and 97 belowground concentration. For papers that separated plant biomass into roots, shoots/stems and 98 leaves: roots were classed as belowground biomass, shoots/stems and leaves were summed and 99 classed as aboveground biomass. There were insufficient studies that discriminated between stems 100 and leaves to analyse this data independently, hence these were summed to generate an 101 above ground concentration to provide parity with other studies. All data were converted to $\mu g/g$. A 102 total of 440 observations of metal concentrations in the tissue of species native to the Philippines, 103 from 59 plant families, were extracted from the literature (see supplementary information for full 104 list of references, Table S1). More than half of the observations focused on nickel and copper (35%

105 and 22% respectively).

106 Threshold aboveground concentrations for hyperaccumulation status have been established for

107 various elements (van der Ent et al., 2013): 100 μ g/g for Cd, Se and Tl; 300 μ g/g for Co, Cu and Cr;

108 1,000 μ g/g for Ni, Pb, Al and As; 3,000 μ g/g for Zn; and 10,000 μ g/g for Mn. If an observation had an

aboveground concentration above this threshold then the species was classified as a

110 hyperaccumulator.

111 2.2 Metal partitioning and translocation factor

112 Not all papers reported both the aboveground and belowground tissue concentrations, but those 113 that did were collated to examine the partitioning of the metals they were reporting between the 114 aboveground and belowground biomass. In addition, a translocation factor (TF) was also calculated 115 as follows:

$$TF = \frac{Above ground \ tissue \ concentration \ (\mu g \ kg^{-1})}{Below ground \ tissue \ concentration \ (\mu g \ kg^{-1})}$$

A TF >1 indicates that a plant species has the capability to extract metals, because the aboveground
biomass concentrations are higher than the belowground biomass (Aribal et al., 2016; Balafrej et al.,
2020; Claveria et al., 2019a; Novo et al., 2013).

120 2.3 <u>Bioaccumulation factor</u>

121 For papers that also reported the soil concentration from where the plant tissue was collected, a

122 bioaccumulation factor (BF) was also calculated as follows:

$$BF = \frac{Above ground \ tissue \ concentration \ (\mu g \ kg^{-1})}{Soil \ concentration \ (\mu g \ kg^{-1})}$$

A BF greater than one indicates that a species is a hyperaccumulator, and a BF less than one is
indicative of an excluder (Ancheta et al., 2020; Claveria et al., 2020; Novo et al., 2013; Usman et al.,
2019; Yashim et al., 2014).

127 3 <u>Results</u>

128 3.1 Species identified

129 Of the 115 plant species whose aboveground tissue concentrations were reported in the literature, 130 twenty-eight were above the hyperaccumulator threshold concentrations outlined by van der Ent et 131 al., (2013) in the introduction (Table 1). Nineteen species were found to contain more than 1,000 μ g/g Ni in samples taken; four species contained more than 1,000 μ g/g Al; three species had 132 133 observations above 300 μ g/g Cu; three species were above 300 μ g/g Cr; one species had observations above 3,000 µg/g Zn; and one species was above 10,000 µg/g Mn. Some species have 134 135 been observed to contain above-threshold concentrations for more than one metal. Mitragyna 136 speciosa, for example, was above threshold concentrations for Aluminium, Copper and Manganese 137 (Table 1). However, it is important to note that concentrations reported in the literature, were not 138 always above the threshold for every species. Nickel concentrations reported for Dichapetalum 139 gelonioides, for example, ranged from 39 – 25,820 µg/g Ni. Furthermore, despite, being over the 140 aboveground tissue concentration threshold, not all species had a translocation factor or 141 bioaccumulation factor greater than one (e.g. Elaeocarpus merrittii and Pneumatopteris laevis). Most 142 of the species identified as hyperaccumulators in Table 1 were trees, and eleven species were 143 endemic to the Philippines.

Table 1 – Metal hyperaccumulation in twenty-eight Philippine native plants. Aboveground tissue concentration, translocation factor (TF) and
 bioaccumulation factor (BF). Threshold aboveground concentrations for hyperaccumulation status (van der Ent et al., 2013); 300 μg/g for Cu and Cr; 1,000 μg/g for Ni and Al; 3,000 μg/g for Zn; and 10,000 μg/g for Mn.

					Aboveground						
Species	Family	Plant Type	Distribution	Metal	tissue concentration	TF	BF	Reference			
		71 -			(µg/g)						
Brackenridgea fascicularis	Ochnaceae	Tree	Philippines; endemic	Nickel	1027 – 4,489	-	-	(Fernando et al., 2020)			
Brackenridgea foxworthyi	Ochnaceae	Tree	Philippines; endemic	Nickel	3,770 – 7,600	-	-	(Baker et al., 1992)			
				Nickel	3,113 – 6,288	-	-	(Fernando et al., 2020)			
Brackenridgea mindanaensis	Ochnaceae	Tree	Philippines; endemic	Nickel	1,546 – 3,114	-	-	(Fernando et al., 2020)			
Breynia cernua	Phyllanthaceae	Tree	Philippines; also in Australia, Java, Lesser	Nickel	4,533	6.50	0.56	(Gotera et al., 2014)			
			Sunda Islands, Moluccas, New Guinea &	Nickel	4,270	1.20	-	(Gotera et al., 2020)			
			Sulawesi								
Breynia sp.	Phyllanthaceae	Tree		Nickel	4,195	-	0.54	(Fernando et al., 2013)			
Callicarpa sp.	Lamiaceae	Tree		Nickel	1,383	-	0.18	(Fernando et al., 2013)			
Cratoxylum sumatranum	Hypericaceae	Tree	Philippines; also in Borneo, Java &	Copper	200-421	2.56-	10.96-	(Castaňares and Lojka,			
			Thailand			7.19	57.49	2020)			
Decaspermum blancoi	Myrtaceae	Tree	Philippines; endemic	Nickel	3,841	-	0.50	(Fernando et al., 2013)			
Dichapetalum gelonioides	Dichapetalaceae	Shrub to	Philippines; also in Borneo & Malay	Nickel	9 – 20,300	-	-	(Baker et al., 1992)			
subsp. <i>Pilosum</i>		Tree	Peninsula	Zinc	390 – 26,360	-	-	(Baker et al., 1992)			
Dichapetalum gelonioides	Dichapetalaceae	Tree	Philippines; also in Borneo, Malay	Nickel	39 – 25,820	-	-	(Baker et al., 1992)			
subsp. Tuberculatum			Peninsula, Sumatra, Thailand & Vietnam								
Elaeocarpus merrittii	Elaeocarpaceae	Tree	Philippines; endemic	Chromium	835	0.57	0.41	(Aribal et al., 2016)			
Falcatifolium gruezoi	Podocarpaceae	Shrub to	Philippines; also in Moluccas; Sulawesi	Chromium	326	0.04	1.60	(Aribal et al., 2016)			
		tree									

Memecylon sp.	Melastomataceae			Aluminum	2,300	-	-	(Proctor et al., 2000)
Mitragyna speciosa	Rubiaceae	Tree	Philippines; also in Borneo, Malay	Aluminum	3,960	0.40	1.22	(Castaňares and Lojka,
			Peninsula, New Guinea, Sumatra &					2020)
			Thailand	Copper	358	3.83	21.24	(Castaňares and Lojka,
								2020)
				Manganese	39,554	3.66	2909	(Castaňares and Lojka,
								2020)
Phyllanthus balgooyi*	Phyllanthaceae	Tree	Philippines; also Borneo	Nickel	3,920 – 16,230	4.04	2.94	(Baker et al., 1992)
				Nickel	6,913	1.02	0.75	(Quimado et al., 2015)
Phyllanthus erythrotrichus**	Phyllanthaceae	Shrub	Philippines; endemic	Nickel	18,492	-	2.40	(Fernando et al., 2013)
				Nickel	12,287	9.28	2.63	(Quimado et al., 2015)
Phyllanthus	Phyllanthaceae	Tree	Philippines; endemic	Nickel	1050 - 34,750	-	-	(Baker et al., 1992)
securinegoides***				Nickel	13,481	2.91	1.81	(Quimado et al., 2015)
Planchonella obovata	Sapotaceae	Tree	Philippines; also in Andaman Islands,	Nickel	2,645	-	0.34	(Fernando et al., 2013)
			Australia, Bangladesh, China, India,					
			Indochina, Malay Peninsula, Myanmar,					
			Nicobar Islands, Pacific Ocean, Solomon					
			Islands & Thailand					
Pneumatopteris glabra	Thelypteridaceae	Fern	Philippines; endemic	Aluminum	3,263	0.38	0.89	(Castaňares and Lojka,
								2020)
Pneumatopteris laevis	Thelypteridaceae	Fern	Philippines; endemic	Aluminum	1,035	0.12	0.35	(Castaňares and Lojka,
								2020)
Polyosma integrifolia	Escalloniaceae	Tree	Philippines; also in Borneo, Java, Malay	Chromium	780	0.21	0.79	(Aribal et al., 2016)
			Peninsula					
Psychotria sp.	Rubiaceae	Tree		Nickel	2,197	-	0.29	(Fernando et al., 2013)
Pteris sp.	Pteridaceae	Fern		Copper	371	0.76	1.46	(Claveria et al., 2010)

Rinorea bengalensis	Violaceae	Tree	Philippines; also in Andaman Islands,	Nickel	1,000 - >10,000	-	-	(Brooks and Wither,
			Australia, Bangladesh, Borneo, Cambodia,					1977)
			China, India, Java, Laos, Lesser Sunda					
			Islands, Malay Peninsula, Moluccas,					
			Myanmar, New Guinea, Nicobar Islands,					
			Pacific Ocean, Solomon Islands, Sri Lanka,					
			Sulawesi, Sumatra, Thailand & Vietnam					
Rinorea niccolifera	Violaceae	Tree	Philippines; endemic	Nickel	15,215 – 22,241	7.27	8.07	(Fernando et al., 2014)
Syzygium sp.	Myrtaceae	Tree		Nickel	1,113	-	0.14	(Fernando et al., 2013)
Walsura monophylla	Meliaceae	Tree	Philippines; endemic	Nickel	2,360 – 7,090	-	-	(Baker et al., 1992)
Xylosma luzonense	Salicaceae	Tree	Philippines, also in Lesser Sunda Islands,	Nickel	1,936	-	0.25	(Fernando et al., 2013)
			Moluccas, Sulawesi					

*more recently known as Nymphanthus balgooyi (Bouman et al., 2021)

**more recently known as *Emblica erythrotricha* (Bouman et al., 2021)

*** more recently known as *Dendrophyllanthus securinegioides* (Bouman et al., 2021)

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149 3.2 Metal partitioning in hyperaccumulator species

150 Error! Reference source not found. Table 2 shows how metal concentrations were partitioned in the 151 aboveground and belowground tissue (when both were reported) in the species identified as hyperaccumulators in Table 1. Whether a metal accumulated in the aboveground or belowground 152 153 biomass is dependent on the metal in question. Nickel (Error! Reference source not found. Table 2) 154 was present in higher concentrations in the aboveground tissue than the belowground tissue. 155 Conversely, concentrations of copper), aluminium and chromium were higher in belowground tissue 156 than aboveground (Table 2). However, the errors for belowground concentrations of copper and 157 chromium were quite large. There was not sufficient data to examine the partitioning of Zinc or 158 Manganese in hyperaccumulators.

159Table 2 – Reported aboveground and belowground tissue concentrations of hyperaccumulators160identified in Table 1, and plants that were not identified as hyperaccumulators

Plant Type	Metal	n	Aboveground Tissue	Belowground Tissue		
			Concentration ($\mu g g^{-1}$)	Concentration ($\mu g g^{-1}$)		
Hyperaccumulator	Ni	8	12,912 ± 2,792	3,408 ± 836		
	Cu	5	273 ± 74	562 ± 391		
	Al	4	2,573 ± 882	9,145 ± 411		
	Cr	3	647 ± 161	4,592 ± 2,133		
Non-Hyperaccumulator	Ni	10	70 ± 24	76 ± 33		
	Cu	41	60 ± 10	612 ± 211		
	Al	4	471 ± 51	5,598 ± 1,816		
	Cr	14	54 ± 16	117 ± 46		

161

-It is also important to note that species that were not classed as hyperaccumulators, because their
 aboveground concentrations of metals was not above the threshold, still had high concentrations in
 their belowground biomass in the in the case of copper and aluminium (Table 2Error! Reference
 source not found.).

166 –

167 4 Discussion

168 4.1 Metal partitioning and phytoextraction/phytomining potential

Metals such as nickel and copper have been suggested as good candidates for phytoextraction efforts (Mahajan et al., 2016) with the Philippines being highlighted as a potential location for such efforts (Van Der Ent et al., 2015). Nickel had the greatest concentrations in the aboveground biomass compared to the belowground parts, which is that phytomining is more suitable for the recovery of nickel. However, it is important to note that many of the papers from which data was extracted were papers specifically looking for nickel hyperaccumulators which may have skewed the results.

176 The finding that copper accumulated at higher concentrations in the root than the shoot, is in

177 concordance with several studies (Ancheta et al., 2020; Chua et al., 2019; Claveria et al., 2010;

178 Dahilan and Dalagan, 2017). High root concentrations, or low translocation factors, could indicate

179 phytostabilisation as this process binds the substrate to the plant roots thus reducing mobility of the

180 metal in the soil (Claveria et al., 2010) or the sequestered metal remains solely in the roots, enabling

the plant to grow and mature without its health being impacted (Claveria et al., 2010). This suggests

182 that phytomining or extraction techniques may not be appropriate for copper, chromium or

aluminium in general.

In addition to performance, key aspects of social acceptance of phytoextraction or phytomining
techniques are the utilisation of by-products and economic viability (Aladesanmi et al., 2019). To be
economically viable it is important to have fast growing plants that have high accumulation
combined with high biomass (Chua et al., 2019; Marques et al., 2009; Paz-Alberto and Sigua, 2013).
The majority of species identified as hyperaccumulators are trees. While this suggests they may have
high biomass, it is also possible that these are slow growing which may affect their suitability.

190 Transfer and accumulation of metals from soil to plants is complex and often site-specific. Factors 191 influencing this include: the chemical forms of the heavy metal; the pH of the soil; the soil organic 192 matter content; soil nutrient contents; root exudation of organic acids and flavonoids; soil texture 193 (particularly clay content); mycorrhizal symbiosis, microbial activity and abundance; the plant 194 species; the plants stage of growth; climatic conditions and irrigation with polluted waters 195 (Aladesanmi et al., 2019; Claveria et al., 2019b; Dahilan and Dalagan, 2017; de la Torre et al., 2016; 196 De Oliveira et al., 2020; Domingo and David, 2014; Feigl et al., 2020; Mahajan et al., 2016; Navarrete 197 et al., 2017; Sanqui et al., 2020; Susaya et al., 2010; Tibbett et al., 2021; Yashim et al., 2014). 198 Furthermore, although our review focused on native species to the Philippines, it is important to 199 note that each island has developed a slightly different plant community, so not all native plants to

- the Philippines is found on every island of the archipelago (Romeroso et al., 2021). Therefore, it
 would be impossible to find a species that is appropriate in every scenario, in every community, so
 planning needs to be site specific (Koelmel et al., 2015).
- 203 4.2 Issues, knowledge gaps, and future research needs

204 4.2.1 Agreed definition of hyperaccumulators

205 Despite having supra-threshold aboveground concentrations, some of the plant species we have 206 identified did not have translocation and bioaccumulation factors greater than one. As discussed 207 below, the literature did not report the data required to calculate the bioaccumulation factor or the 208 translocation factor in all instances. If it is agreed that the bioaccumulation factor and translocation 209 factor are important determinants of hyperaccumulation then papers need to report these if an 210 accurate list of hyperaccumulators is to be compiled. Alternatively, if translocation and 211 bioaccumulation factors are deemed to not be of importance, and therefore not reported in several 212 cases this could put into question whether they should be included in the definition of

213 hyperaccumulators.

214 4.2.2 Consistency in reporting metal concentrations in plant tissue

Many papers do not distinguish between above-ground and belowground concentrations of metals.
Furthermore, papers that do separate above-ground tissue do not always distinguish between
different parts of the plant (stem, leaves, flowers, seeds etc.). van der Ent et al., (2013) state that

- 218 above-ground tissue should be regarded as plant leaves only for establishing hyperaccumulator
- 219 status. Therefore, papers that fail to distinguish between the different parts of the plant may lead to
- 220 potential hyperaccumulators have been missed. The failure to report the surrounding soil
- 221 concentration in several papers, combined with no distinction between above and belowground
- biomass also makes the calculation of the translocation and bioaccumulation factors impossible, asdiscussed above.

Larger errors were observed in belowground concentrations than aboveground. This could be due to the difficulty of cleaning roots of particulate soil and externally sorbed metal ions before analysis (Reeves, 2006; van der Ent et al., 2013). This will have implications for partition data and calculations of the translocation factor.

228 4.2.3 Large scale screening

There were no hyperaccumulators identified in the literature for rare earth elements, and only one
 each for manganese and zinc. Historically, discoveries of trace element hyperaccumulator plants
 relied on destructive and time-consuming chemical analysis, however recent advances in hand held

- Xray fluorescence spectroscopy (XRF) systems have enabled nondestructive analysis of herbarium
 samples in other regions (van der Ent et al., 2019; Isnard et al., 2020; Belloeil et al., 2021;). This will
 allow larger scale rapid assessment of Philippine flora and may lead to the discovery of more
 hyperaccumulator species, and species that accumulate more than one element, as XRF will allow
- for rapid analysis of multiple elements at the same time.

237 4.2.4 Botanical explorations

247

238 Hyperaccumulators are often rare species and are often endemic to small regions (Reeves, 2006), 239 eleven of the reported hyperaccumulators in our review are endemic to the Philippines. Therefore to 240 locate hyperaccumulators, extensive botanical surveys are needed. The reviewed papers only 241 reported botanical surveys in small portions of ultramafic areas in Palawan, Surigao, Zambales, Bicol, 242 Samar, and north central Mindanao. Considering the extent of ultramafic forest in the Philippines, 243 more botanical surveys are necessary to identify metal accumulators. In addition, there can be 244 significant variation among isolated populations of hyperaccumulators (Reeves, 2006). Therefore, 245 collection of plant samples of the same species from multiple locations will provide better 246 information on their potential to hyperaccumulate.

4.2.5 *Physiological characteristics and toxicity thresholds*

248 It is important to note that there are potential trade-offs in the use of hyperaccumulators. For 249 example, hyperaccumulator species may have essentially substituted one defence mechanism (e.g. 250 metal tolerance) for another (e.g. defence against pathogens) which may impact on the overall 251 health of the plant (Boyd, 2013; Fones et al., 2019). Although many papers report the metal 252 concentrations of the plant tissue, there was no comment on the health of the plants they 253 measured. It is important that hyperaccumulators accumulate metal without evidence of 254 physiological stress or impaired plant growth (Pasricha et al., 2021; Quimado et al., 2015). Therefore, 255 moving forward, surveys should assess the health of the plants as well as the tissue analysis. There is 256 also a need for research into the physiological processes that govern absorption, translocation and 257 accumulation of metals in plants to gain understanding of the phytoremediation capacity of plants 258 (Nescu et al., 2022). This will also give some indication of the nutrient requirements of 259 hyperaccumulators, and whether fertilization would be necessary in a large scale phytoremediation 260 effort. Phytoextraction/ phytomining, for example, could also lead to removal of soil nutrients

alongside the target metal (Van Der Ent et al., 2015).

262 *4.2.6 Potential impacts on higher trophic levels*

The concept of phytomining is that metals accumulate in the aboveground biomass, which is more easily harvested and removed. However, elevated concentrations in the aboveground biomass could

- lead to exposure of herbivores, and subsequently other species in the food chain (Koelmel et al.,
- 266 2015; Tibbett et al., 2021), including humans. It has been suggested that plants may develop the
- ability to hyperaccumulate metals, as a means of protecting themselves from herbivorous predators
- and pathogens that would experience serious toxic side effects from ingesting large concentrations
- of metals in the plants above-ground biomass (Fones et al., 2019; Paz-Alberto and Sigua, 2013;
- 270 Remigio et al., 2020). In addition, hyperaccumulators can also lead to an increased metal
- 271 concentration in the topsoil through high metal concentration litterfall (Tisserand et al., 2021), which
- 272 could have an impact on soil biology. Metal rich pollen could also have potential risks for pollinators,
- an important consideration when planning large-scale cultivation of high metal containing plants
- 274 (Schiavon and Pilon-Smits, 2017). Due to the potential risk to human health, edible agricultural crops
- should not be used for phytomining (Pasricha et al., 2021).

276 5 <u>Conclusions</u>

- 277 Metals such as nickel and copper have been suggested as good candidates for phytoextraction
- 278 efforts and the Philippines has been highlighted as a potential location for such activities. While
- 279 several species endemic to the Philippines have been highlighted as hyperaccumulators, the majority
- of these are woody plants. More research on the ecology and physiology of these species will be
- 281 necessary to explore their potential for large-scale planting and subsequent development of
- 282 phytomining or agromining in the Philippines.

283 Data availability statement

284 The data that support this study is available upon reasonable request to the corresponding author.

285 Conflicts of interest

286 The authors declare no conflicts of interest.

287 Declaration of funding

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291 **References**

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