

# 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,
- 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
- 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 metals
- 19 within 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
- aboveground tissue than the belowground tissue, but the reverse was found for copper, aluminium,
- 23 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.

#### Key words:

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

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2017).

#### 31 <u>Introduction</u> 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 57 hydroponic nutrient solutions (van der Ent et al., 2013). More than 700 hyperaccumulating plants 58 have been reported worldwide, the majority of which (>70%) hyperaccumulate nickel (Reeves et al.,

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

63 considerable interest in the mineral exploration (Jaffré et al., 1976) and are the optimal choice for 64 future 'green' phytoremediation technologies, such as phytoextraction and phytomining. However, 65 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 greater than the soil (Reeves, 2006); and (ii) translocate those metals to their aboveground biomass 67 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 72 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 75 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 77 native plant species in the Philippine flora naturally growing in the wild (rather than controlled or 78 laboratory conditions).

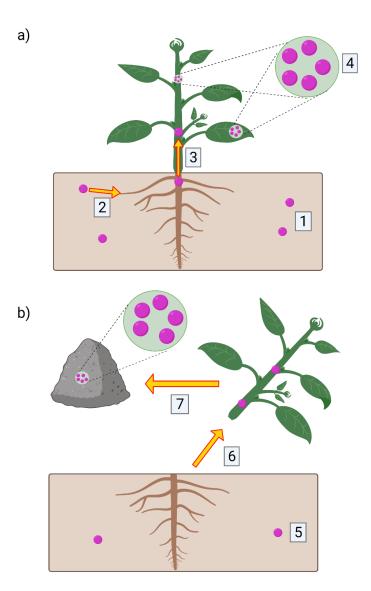


Figure 1- Schematic of principles of phytomining in phytoremediation of a given metal. a) Soils with large concentrations of a given metal present in the soil solution (1) are sown with plants. Plant uptake through the roots take place (2) and are translocated into the aboveground biomass (3). Metal 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

#### 2 Materials and methods

## 2.1 <u>Literature searches and data extraction</u>

Searches on Web of Science were carried out (24<sup>th</sup> 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.

Each paper reported results in a different manner. The majority reported a total plant tissue concentration. A large proportion also partitioned into aboveground tissue concentration and belowground concentration. For papers that separated plant biomass into roots, shoots/stems and leaves: roots were classed as belowground biomass, shoots/stems and leaves were summed and classed as aboveground biomass. There were insufficient studies that discriminated between stems and leaves to analyse this data independently, hence these were summed to generate an aboveground concentration to provide parity with other studies. All data were converted to  $\mu g/g$ . A total of 440 observations of metal concentrations in the tissue of species native to the Philippines, from 59 plant families, were extracted from the literature (see supplementary information for full list of references, Table S1). More than half of the observations focused on nickel and copper (35% and 22% respectively).

Threshold aboveground concentrations for hyperaccumulation status have been established for various elements (van der Ent et al., 2013): 100  $\mu$ g/g for Cd, Se and Tl; 300  $\mu$ g/g for Co, Cu and Cr; 1,000  $\mu$ g/g for Ni, Pb, Al and As; 3,000  $\mu$ g/g for Zn; and 10,000  $\mu$ g/g for Mn. If an observation had an aboveground concentration above this threshold then the species was classified as a hyperaccumulator.

#### 2.2 <u>Metal partitioning and translocation factor</u>

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

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

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).

#### 2.3 Bioaccumulation factor

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

#### 3 Results

### 3.1 Species identified

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

|                            |                 |          |  |          | Aboveground                    |       |        |                         |
|----------------------------|-----------------|----------|--|----------|--------------------------------|-------|--------|-------------------------|
| Species                    | Family          | Plant    | Distribution                                 | Metal    | tissue<br>tal<br>concentration | TF    | BF     | Reference               |
| Species                    | raililly        | Туре     | Distribution                                 | ivietai  |                                | IF    | БГ     |                         |
|                            |                 |          |  |          | (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. <i>Tuberculatum</i> |                 |          | 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, Ch    |                  | 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                         |        |                 |      |      |                         |

<sup>\*</sup>more recently known as Nymphanthus balgooyi (Bouman et al., 2021)

<sup>\*\*</sup>more recently known as Emblica erythrotricha (Bouman et al., 2021)

<sup>\*\*\*</sup>more recently known as *Dendrophyllanthus securinegioides* (Bouman et al., 2021)

#### 3.2 Metal partitioning in hyperaccumulator species

Error! Reference source not found. Table 2 shows how metal concentrations were partitioned in the 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 biomass is dependent on the metal in question. Nickel (Error! Reference source not found. Table 2) was present in higher concentrations in the aboveground tissue than the belowground tissue. Conversely, concentrations of copper ), aluminium and chromium were higher in belowground tissue than aboveground (Table 2). However, the errors for belowground concentrations of copper and chromium were quite large. There was not sufficient data to examine the partitioning of Zinc or Manganese in hyperaccumulators.

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

| Plant Type           | Metal | n  | Aboveground Tissue                  | Belowground Tissue                  |
|----------------------|-------|----|-------------------------------------|-------------------------------------|
|                      |       |    | Concentration (µg g <sup>-1</sup> ) | Concentration (µg g <sup>-1</sup> ) |
| 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                            |
|                      |       |    |                                     |                                     |

—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.).

#### 4 <u>Discussion</u>

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168 Metal partitioning and phytoextraction/phytomining potential 169 Metals such as nickel and copper have been suggested as good candidates for phytoextraction 170 efforts (Mahajan et al., 2016) with the Philippines being highlighted as a potential location for such 171 efforts (Van Der Ent et al., 2015). Nickel had the greatest concentrations in the aboveground 172 biomass compared to the belowground parts, which is that phytomining is more suitable for the 173 recovery of nickel. However, it is important to note that many of the papers from which data was 174 extracted were papers specifically looking for nickel hyperaccumulators which may have skewed the 175 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 181 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 183 aluminium in general. 184 In addition to performance, key aspects of social acceptance of phytoextraction or phytomining 185 techniques are the utilisation of by-products and economic viability (Aladesanmi et al., 2019). To be 186 economically viable it is important to have fast growing plants that have high accumulation 187 combined with high biomass (Chua et al., 2019; Marques et al., 2009; Paz-Alberto and Sigua, 2013). 188 The majority of species identified as hyperaccumulators are trees. While this suggests they may have 189 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

200 the Philippines is found on every island of the archipelago (Romeroso et al., 2021). Therefore, it 201 would be impossible to find a species that is appropriate in every scenario, in every community, so 202 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. 215 216 Furthermore, papers that do separate above-ground tissue do not always distinguish between 217 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 222 biomass also makes the calculation of the translocation and bioaccumulation factors impossible, as 223 discussed above. 224 Larger errors were observed in belowground concentrations than aboveground. This could be due to 225 the difficulty of cleaning roots of particulate soil and externally sorbed metal ions before analysis 226 (Reeves, 2006; van der Ent et al., 2013). This will have implications for partition data and calculations 227 of the translocation factor. 4.2.3 Large scale screening 228 229 There were no hyperaccumulators identified in the literature for rare earth elements, and only one 230 each for manganese and zinc. Historically, discoveries of trace element hyperaccumulator plants 231 relied on destructive and time-consuming chemical analysis, however recent advances in hand held

232 Xray fluorescence spectroscopy (XRF) systems have enabled nondestructive analysis of herbarium 233 samples in other regions (van der Ent et al., 2019; Isnard et al., 2020; Belloeil et al., 2021; ). This will 234 allow larger scale rapid assessment of Philippine flora and may lead to the discovery of more 235 hyperaccumulator species, and species that accumulate more than one element, as XRF will allow 236 for rapid analysis of multiple elements at the same time. 237 4.2.4 Botanical explorations 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 247 248 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 261 alongside the target metal (Van Der Ent et al., 2015). 262 4.2.6 Potential impacts on higher trophic levels 263 The concept of phytomining is that metals accumulate in the aboveground biomass, which is more 264 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., 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; Remigio et al., 2020). In addition, hyperaccumulators can also lead to an increased metal concentration in the topsoil through high metal concentration litterfall (Tisserand et al., 2021), which 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 (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).

#### **Conclusions**

Metals such as nickel and copper have been suggested as good candidates for phytoextraction efforts and the Philippines has been highlighted as a potential location for such activities. While 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 necessary to explore their potential for large-scale planting and subsequent development of phytomining or agromining in the Philippines.

## **Data availability statement**

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

#### **Conflicts of interest**

The authors declare no conflicts of interest.

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