Leaf-age and soil-plant relationships: key factors for reporting trace-elements hyperaccumulation by plants and design applications

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Abstract Relationships between the trace-elements (TE) content of plants and associated soil have been widely investigated especially to understand the ecology of TE hyperaccumulating species to develop applications using TE phytoextraction. Many studies have focused on the possibility of quantifying the soil TE fraction available to plants, and used bioconcentration (BC) as a measure of the plants ability to absorb TE. However, BC only offers a static view of the dynamic phenomenon of TE accumulation. Accumulation kinetics are required to fully account for TE distributions in plants. They are also crucial to design applications where maximum TE concentrations in plant leaves are needed. This paper provides a review of studies of BC (i.e. soil-plant relationships) and leaf-age in relation to TE hyperaccumulation. The paper focuses of Ni and Mn accumulators and hyperaccumulators from New Caledonia who were previously overlooked until recent Ecocatalysis applications emerged for such species. Updated data on Mn hyperaccumulators and accumulators from New Caledonia are also presented and advocate further investigation of the hyperaccumulation of this element. Results show that leaf-age should be considered in the design of sample collection and allowed the reclassification of *Grevillea meisneri* known previously as a Mn accumulator to a Mn hyperaccumulator

Keywords Hyperaccumulation · Phytoextraction · Bioconcentration · Leaf-age · Nickel · Manganese

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Introduction

The discovery of Ni concentrations ranging from 1.8 to 4.7 % in the dry leaves of *Psychotria gabriellae* (ex. *Psychotria douarrei*), a Rubiaceae endemic to New Caledonia (Jaffré and Schmid 1974), led to the emergence of the concept of Ni hyperaccumulation (Jaffre et al. 1976). Such concentrations are comparable to those in ores currently exploited for Ni production in New Caledonia: an average 2.5 % Ni in saprolites, and 1.7 % Ni in low-grade limonites (DIMENC 2008). Potentially economic applications were quickly considered as species accumulating other metals such as Au, Cu, or Zn were also discovered in other countries (Baker et al. 1988). Phytoextraction was developed industrially for phytomining (Brooks et al. 1998; Chaney et al. 2007) and phytoremediation to decontaminate soils containing high concentrations of trace-elements (TE) (Cunningham and Berti 1993; McGrath and Zhao 2003). Yet both probably failed to meet the expectations initially raised (Ernst 2000; Ernst 2005; van der Ent et al. 2013b).

Ecocatalysis has emerged as a new Green Chemistry approach (Escande et al. 2014a, b), with a high potential for the valuation of TE-rich biomass (Hunt et al. 2014). The TE-rich biomass obtained from these metallophytes can be directly used as reagents or catalysts in organic chemical reactions (Grison and Escande 2013a, b; Losfeld et al. 2012c). Ecocatalysis provides the first perspective of enhancing the unique TE-rich biomass from New Caledonia (and elsewhere) and promoting a new field in Green Chemistry (Escande et al. 2014a, b). The first results showed that polymetallic ecocatalysts could perform better and provide much higher selectivity than classical homogeneous and heterogeneous catalysts (Losfeld et al. 2012a, b). The development of this new concept is creating paradigm shifts in phytoextraction and Green Chemistry because leaves from Ni and Mn hyperaccumulators or accumulators have become new efficient and eco-friendly catalytic systems (Escande et al. 2013; Thillier et al. 2013).

The development of such applications spurred massive research efforts for understanding the hyperaccumulation of TE by plants. Cutting-edge techniques allow for in-vivo localisation of some elements, e.g. Cd (Hu et al. 2013) or Mn (Fernando et al. 2013), and a precise determination of TE speciation in plants, e.g. Ni (Callahan et al. 2012, 2008) or Mn (Fernando et al. 2010). Molecular and genetic mechanisms underlying TE accumulation are also thoroughly investigated (Verbruggen et al. 2009) for this purpose New Caledonia may well prove a place of major interest because of its flora (Jaffre et al. 2013; Merlot et al. 2014). Yet apparently more simple questions remain elusive: why do plants accumulate TE (Boyd 2013)? What are the biogeochemical processes at work in the rhizosphere (Alford et al. 2010)? The latter is particularly crucial to design applications, where yields (phytomining) or efficiency (phytoremediation by way of phytoextraction) are determined by soil-plant relationships. Bioconcentration (BC), the ratio of a TE concentration in plant to that in soil has often been used as a measure of the ability of plants to take up a TE (Morrison et al. 1980; Zhao et al. 2003).

This paper aims to discuss the relevance of this approach as TE hyperaccumulation is also a dynamic phenomenon with kinetic factors. Ni and Mn hyperaccumulators or accumulators endemic to the metallophyte hotspot (Whiting et al. 2004) of New Caledonia are the main focus of this paper, as few tropical evergreen species have been examined. The development of Ecocatalysis requires the assessment of the possibilities of these species. Considering leaf-age (a proxy for accumulation kinetics) in the design of sample collection allowed the reclassification of *Grevillea meisneri* (previously known as a Mn accumulator) as Mn hyperaccumulator. It also provides insights on leaves harvest design for maximum TE concentrations that are required for potential applications. Updated data on Mn hyperaccumulators and accumulators from New Caledonia are also presented and advocate further investigation on the hyperaccumulation of this element.

TE hyperaccumulation: what and why?

The term 'hyperaccumulator' was coined by Jaffre et al. (1976) in a report of the extraordinary ability of New Caledonian species *Pycnandra acuminata* (ex. *Sebertia acuminata*) to accumulate Ni in its tissues. The term hyperaccumulator was generally used to describe plant species containing Ni over 1,000 mg.kg^{-1} on a dry-weight basis in their aerial tissues. Thirteen Ni hyperaccumulators from New Caledonia, Italy and Australia were known in the 1970s (Jaffre et al. 1976). Reeves (1992) then clarified the definition of Ni hyperaccumulation: a species may be considered a Ni hyperaccumulator if a concentration of Ni above 1,000 mg.kg^{-1} has been reported in the dry leaves of at least one specimen growing in its natural habitat. Furthermore, active uptake only should be considered, from soil to leaves through roots and sap. Direct deposition of soil particle on leaves should be taken care of as a potential perturbation on measurements (Faucon et al. 2007). TE hyperaccumulation was recently reviewed (van der Ent et al. 2013a) and can be defined in a similar manner for various other elements, with specific thresholds for each 100 mg.kg^{-1} for Cd, Se and Tl; 300 mg.kg^{-1} for Co, Cu and Cr; 1,000 mg.kg^{-1} for Ni, Pb and As and 3,000 mg.kg^{-1} for Zn. In the case of Mn, this threshold is set at 10,000 mg.kg^{-1}.

By now, 450 Ni hyperaccumulators have been reported throughout the world (van der Ent et al. 2013a) and New Caledonia is definitely a metallophyte hotspot, with 65 Ni hyperaccumulating species (Jaffre et al. 2013). Only Cuba, where 135 Ni hyperaccumulators have been found, is more diverse than New Caledonia (Reeves 2003). Although dismissed by van der Ent et al. (2013a), studies of the flora of New Caledonia have led to the use of a dedicated terminology. For some species, e.g. *P. acuminata* (Jaffre et al. 1976) or *P. gabriellae* (Jaffré and Schmid 1974), Ni concentrations above 1 % in the dry leaves of some individuals were observed in their natural environment. This is one order of magnitude greater than the 'hyperaccumulation' threshold, and such species are referred to as 'hypernickelophore' (Jaffré and Schmid 1974). So far, 17 such species have been reported in New Caledonia (Table 1).

The "raison d'être" for TE hyperaccumulation remains largely elusive with various hypotheses brought out (Boyd and Martens 1992) and two major hypotheses investigated:

1. According to the defensive enhancement hypothesis (Boyd 2012), TE hyperaccumulation evolved as it provided hyperaccumulators with stronger defences against herbivores or pathogens. Accumulation of more than one TE and complex formation with organic compounds could also result in further improved defence, referred to as 'the joint effect' by Boyd (2012).
2. 'The interference hypothesis', or elemental allelopathy (Baker and Brooks 1989; Boyd 2004; Boyd and Martens 1998), suggests TE-enriched litter under hyperaccumulators, e.g. *P. acuminata* (Boyd and Jaffre 2001), would exert a selective pressure on soil micro-

Table 1 Hypernickelophore species from New Caledonia adapted from Jaffre et al. (2013)

Family	Genus	Species	Max Ni level (%)
Cunoniaceae	*Geissois*	*bradfordii*	1.3
		lanceolata	2.3
		pruinosa	1.5
Phyllantaceae	*Phyllanthus*	*baraouaensis*	1.5
		favieri	4.2
		lucilae	3.4
		memaoyaensis	3.0
		parangoyensis	2.7
		serpentinus	3.1
Rubiaceae	*Gynochthodes*	to be identified	1.5
	Psychotria	*gabriellae*	6.4
Salicaceae	*Homalium*	*francii*	1.5
		guillainii	1.2
		kanaliense	1.2
Sapotaceae	*Pycnandra*	*acuminata*	2.6
Violaceae	*Hybanthus*	*austrocaledonicus*	2.6
		caledonicus	1.8

organisms, and also prevent other non-adapted plant species from settling. However, TE hyperaccumulation does not always result in TE-enriched litters, as exemplified by *P. gabriellae* (Boyd et al. 1999). Limits to this hypothesis were recently reviewed, with many studies found to present unclear conclusions (Morris et al. 2009). An improved understanding of soil-plant relationships could possibly clarify the scope of this hypothesis.

Recent efforts to understand TE speciation (Callahan et al. 2012, 2008; Fernando et al. 2010; Grison et al. 2013), their location in plants (Fernando et al. 2013, 2008), as well as genetic and molecular factors involved in TE hyperaccumulation could shed new light on how TE hyperaccumulation evolved. However assessing costs and benefits of this trait remain difficult (Boyd 2013). At present, the question why TE hyperaccumulation evolved remains elusive.

Models for soil-plants relationships

Initial studies of bioconcentration

Figure 1a adapted from Baker (1981) frequently appears when dealing with the ecology of TE hyperaccumulators. It is based on using Ni-spiked soil to observe the respective responses of various *Alyssum* species to Ni exposure (Morrison et al. 1980). Figure 1a can also be represented in terms of bioconcentration (BC) (Fig. 1b). BC for an element X is defined as a measure of the ability of plants to take up a TE:

$$C(X) = \frac{\text{Concentration of } X \text{ in dry leaves}}{\text{Total concentration of } X \text{ in soil}}$$

The measure of total elemental concentrations in soil can be performed using acid digestions and gives reliable results regardless of the method (Sauve et al. 2000). Such methods were used in studies by Morrison et al. (1980).

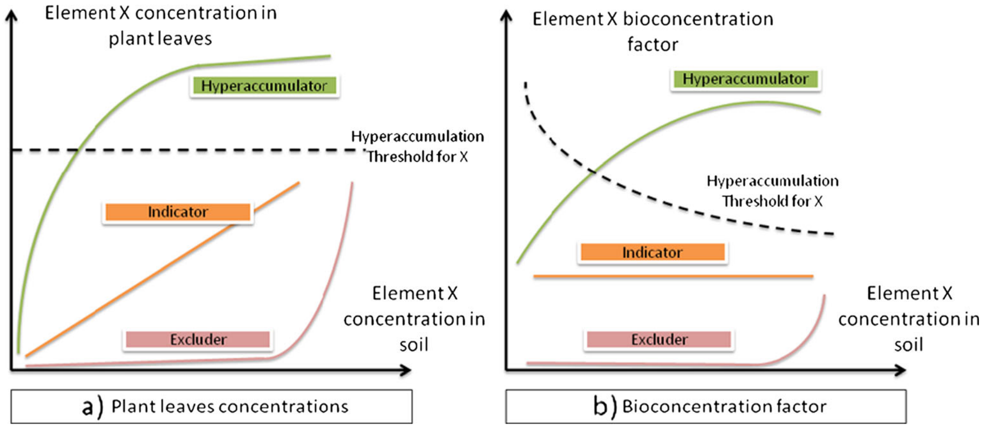
TE hyperaccumulators are usually expected to display high BC (Baker 1981; van der Ent et al. 2013a) because of their ability to accumulate TE at high concentrations in their leaves, regardless of respective concentrations in soil (Assuncao et al. 2003; Bert et al. 2002). However, in certain circumstances evident in Fig. 1b, BC is expected to decrease at high soil TE concentrations. This effect was described not only for Ni hyperaccumulating *Alyssum* species (Morrison et al. 1980), but also for Zn hyperaccumulator *Noccaea caerulescens*, which also belongs to the Brassicaceae family (Zhao et al. 2003). In the case of *N. caerulescens*, a detailed meta-analysis showed BC to vary by over 3 orders of magnitude as a function of soil total Zn concentration. Soil total Zn concentrations could explain 82 % of the observed variance in a power law relationship. Zn transporters saturation, or uptake regulation were mentioned as potential causes for the decrease in BC at high soil concentrations (Pence et al. 2000). However, BC cannot be considered a simple function of total elemental concentrations in soil because the actual availability of TE is also of interest, as it may vary regardless of total concentrations in soil (Diesing et al. 2008; Ross 1994).

Total versus available concentrations

Design applications for TE hyperaccumulating species were a major motive for developing measurements describing the soil TE fractions that are available to plants. They determine not only the possibility of phytoremediation by way of phytoextraction (Koopmans et al. 2008; Robinson 1997) but also potential yields of phytomining operations (Li et al. 2003; Robinson et al. 1999). Nevertheless, accurate quantification of the soil TE fractions available to plants is technically difficult (Young et al. 2005; Zhang and Young 2005) and was performed using various methods without a general agreement on the results (Feng et al. 2005; Robinson 1997; Sauve et al. 2000).

Available TE in soils from New Caledonia were generally studied using diethylene triamine pentaacetic acid (DTPA) extractions (Becquer et al. 1995; L'Huillier 1996), adapted from the methods developed by Lindsay and Norvell (1978). It proved useful for agricultural purposes mainly (L'Huillier and Edighoffer 1996; Lhuillier et al. 1996). Ion-exchange resins were introduced later (Becquer et al. 2002) providing

Fig. 1 Different plant responses to soil trace-elements adapted from Baker (1981) **a** in terms of leaves concentration and **b** in terms of bioconcentration factor



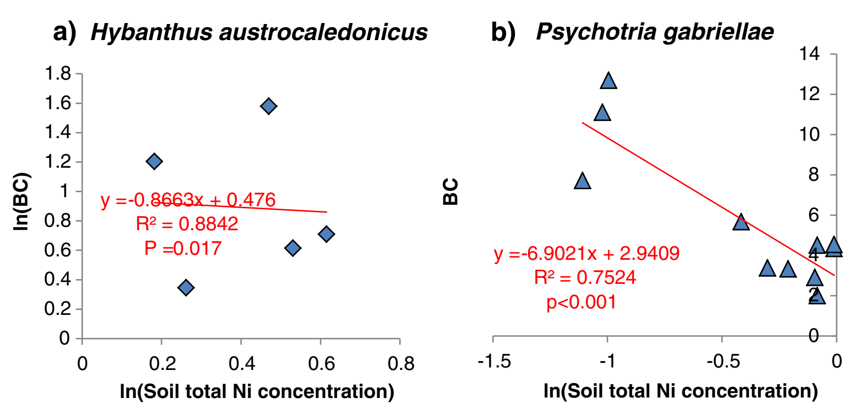
improved results for five species that were not Ni or Mn hyperaccumulators or accumulators. In-depth studies of soil may provide increased insights (Diesing et al. 2008), but are not readily applicable. Numerous physical parameters, such as bulk density, compactness, water holding capacity, as well as chemical parameters including elemental speciation, pH, Eh and oxygen availability are significant components of soil properties (Ernst 1996). Moreover, active processes are involved in the accumulation of TE by plants, as shown in studies of their rhizosphere (Alford et al. 2010).

Nickel hyperaccumulators from New Caledonia

There are few comprehensive studies of soil-plant relationships concerning nickel hyperaccumulators from New Caledonia. Initial studies of Ni hyperaccumulation by *P. gabriellae* and *Hybanthus austrocaledonicus* nonetheless provide meaningful soil-plant data (Jaffré and Schmid 1974). In this study, total Ni concentrations were used to characterise soil at each sampling station, whilst Ni concentrations in leaves were measured in an average individual for each station, i.e. leaves from several individuals in each station were analysed as a single sample. In spite of small sample sizes (n=5), results for *H. austrocaledonicus* (Fig. 2a) show significant relationships (P<0.05): soil total Ni concentrations may explain 88 % of the variance observed in BC in a power law relationship. Regression coefficients are of the same order of magnitudes as those found by Zhao et al. (2003) for *N. caerulescens*, and the questions of whether it originates from similar biological mechanisms could be of interest. This relationship was confirmed later by Lee et al. (1977). The case of *P. gabriellae* (Fig. 2b) is also meaningful as 75 % of the variance observed in BC can be explained by the logarithm of soil total Ni concentration (P<0.001). Thus, according to these initial studies (Jaffré and Schmid 1974; Lee et al. 1977), it would not be irrelevant to consider total soil concentration for a single element when studying its hyperaccumulation by plants. Yet using these data, it was not possible to highlight significant relationships between leaf Ni and soil total Ni concentrations.

First investigations of the relationships between soil Ni assessed by DTPA extraction and the Ni concentrations in the dry leaves of Ni hyperaccumulators focused on *Homalium kanaliense* and *H. austrocaledonicus*. Performed at the individual level, they showed significant relationships for both species (Lee et al. 1977). Subsequent studies focused on *P. gabriellae* using a similar approach, but were inconclusive

Fig. 2 Soil-plant relationships for Ni hyperaccumulating species **a** *Hybanthus austrocaledonicus* **b** *Psychotria gabriellae*



(Boyd et al. 1999). A major difference with the previous study by Jaffré and Schmid (1974) was that all analyses were performed at the individual level. The hypothesis tested was also different. Jaffré and Schmid (1974) investigated the response of plant to the soil on which they grow, whilst Boyd et al. (1999) were investigating the influence of Ni-rich leaves litter on soil. This may result in differences in soil sampling depth. Using the latter approach for *P. acuminata* led to conclusive results; a significantly higher Ni concentration (DTPA) was observed in soil under the canopy of *P. acuminata* compared to that under non-hyperaccumulating trees (Boyd and Jaffre 2001). However, correlation is not causal and whether *P. acuminata* preferentially established on Ni-rich soil or enriched soil in Ni was not resolved. More recently, Amir et al. (2007) worked at the species level and confirmed significant relationships between soil Ni measured by DTPA extraction and leaves Ni concentrations for *Geissois pruinosa*, *Geissois hirsuta*, *H. kanaliense*, *H. austrocaledonicus*, *Phyllanthus favieri*, *P. gabriellae* and *P. acuminata*. They also found significant correlations at the individual levels within species *G. pruinosa*, *P. favieri* and *P. gabriellae* but not *P. acuminata*. Large sample sizes in the study by Amir et al. (2007) ensured the statistical reliability of the tests performed.

Finally, the broader picture that can be drawn from the literature on Ni hyperaccumulators from New Caledonia clearly shows that current models using soil-plant relationships are not fully satisfactory, regardless of the method used to assess Ni concentrations in soil. A considerable limit also lies within the different volumes of soil roots actually explore which is larger for shrubs or trees such as Ni hyperaccumulators from New Caledonia than for *Alyssum* species or *N. caerulescens*.

Manganese hyperaccumulation

Species hyperaccumulating and accumulating manganese

New Caledonia has long been recognised as a metallophyte hotspot for its Ni hyperaccumulators: these were recently reviewed (Jaffre et al. 2013) and species such as *P. gabriellae* or *P. acuminata* remain emblematic for their extraordinary abilities to concentrate and tolerate Ni (Jaffre et al. 1976; Jaffré and Schmid 1974). Yet there are also detailed records of Mn hyperaccumulation: *Alyxia poyaensis* (ex. *Alyxia rubricaulis*) and *Denhamia* (ex. *Maytenus*) species were reported to accumulate Mn at concentrations above 1 % in their dry leaves (Jaffré 1977). Such species were termed 'hypermanganesophore' by Jaffré (1977) but this denomination has now been replaced by 'Mn hyperaccumulator', according to the definition by van der Ent et al. (2013a). In a similar way, numerous species from New Caledonia accumulate manganese at levels ranging from 3,000 to 10,000 $mg.kg^{-1}$ (Jaffré 1977, 1979, 1980). Although less remarkable than hyperaccumulators and dismissed by van der Ent et al. (2013a), they were classified as manganese accumulators (Jaffré 1980).

Acknowledged manganese hyperaccumulators

Table 2 presents an updated review of acknowledged Mn hyperaccumulators after Fernando et al. (2013). Species *Phytolacca americana* (Min et al. 2007; Pollard et al. 2009), *Polygonum hydropiper* (Wang et al. 2008; Yang et al. 2013) and *Schima superba* (Yang et al. 2008) were excluded from Table 2 as records of manganese concentrations above 10,000 $mg.kg^{-1}$ in natural conditions are not published. Similarly, an unidentified *Eugenia* species was reported as a Mn hyperaccumulator (Proctor et al. 1989) and could be included when further evidence is available. As regards Mn hyperaccumulators from New Caledonia, the following additions were made:

1. Latest taxonomic revisions are included:

    a. *A. poyaensis* is no longer a subspecies of *A. rubricaulis* but a new Mn hyperaccumulator. Latest data from Jaffré indicate Mn concentrations up to 1.4 % in the dry leaves of this species.
    b. Various *Maytenus* species were reported to be Mn hyperaccumulators (Jaffré 1977). They now belong to the *Denhamia* genus with a single species, *Denhamia fournieri* occurring as two subspecies, *drakeana* and *fournieri* (Fernando et al. 2008). The subspecies *drakeana* was shown to hyperaccumulate Mn by Fernando et al. (2008). Older results considering species other than *Maytenus drakeana* are relevant for assessing the Mn accumulation ability of *D. fournieri* ssp. *fournieri*. Thus, reports of Mn concentrations up to 3.3 % in the dry leaves of *D. fournieri* ssp. *fournieri* are still valid (Jaffré 1977)
    c. *Eugenia clusoides* now belongs to the *Gossia* genus and the Mn hyperaccumulator described by Jaffré (1980) is *Gossia clusoides* ssp. *ploumensis*.
    d. *Macadamia* species from New Caledonia now belong to the *Virotia* genus.

2. New data on Mn hyperaccumulation are presented:

    a. *Gossia diversifolia* is reported for the first time to hyperaccumulate Mn with concentrations in the dry leaves up to 1.8 %
    b. *Polyscias pancheri* reported as a Mn accumulator (Enright et al. 2001) is as a new Mn hyperaccumulator, which highlights the interest of the Araliaceae family with other reports of Mn

Table 2 Mn hyperaccumulators updated from Fernando et al. (2013)

Family	Genus	Species	Max Mn level (%)	Location	Reference
Apocynaceae	*Alyxia*	*poyaensis*	1.4	New Caledonia	This study
Araliaceae	*Chengiopanax*	*sciadophylloides*	2.4	Japan	Mizuno et al. 2008
	Polyscias	*pancheri*	1.4	New Caledonia	This study
Celastraceae	*Denhamia*	*cunninghamii*	2.5	Australia	Fernando et al. 2013
		fournieri ssp. *drakeana*	2.0*	New Caledonia	Fernando et al. 2008
		fournieri ssp. *fournieri*	3.3	New Caledonia	Jaffré 1977
Clusiaceae	*Garcinia*	*amplexicaulis*	1.2	New Caledonia	Jaffré 1980
Myrtaceae	*Gossia*	*bamagensis*	4.0	Australia	Fernando et al. 2013
		bidwillii	1.9	Australia	Bidwell et al. 2002
		clusioides var. *ploumensis*	1.0	New Caledonia	Jaffré 1980
		diversifolia	1.8	New Caledonia	this study
		fragrantissima	3.5	Australia	Fernando et al. 2013
		gonoclada	1.5	Australia	Fernando et al. 2013
		lucida	1.5	Australia	Fernando et al. 2013
		sankowskiorum	3.0	Australia	Fernando et al. 2013
		shepherdii	1.5	Australia	Fernando et al. 2013
Phytolaccaceae	*Phytolacca*	*acinosa*	1.9	China	Xue et al. 2004
Polygonacea	*Polygonum*	*pubescens*	1.6	China	Deng et al. 2010
Proteaceae	*Beaupreopsis*	*paniculata*	1.2	New Caledonia	Jaffré 1979
	Grevillea	*meisneri*	1.1	New Caledonia	This study
	Virotia	*angustifolia*	1.2	New Caledonia	Jaffré 1979
	(ex *Macadamia*)	*neurophylla*	5.5	New Caledonia	Jaffré 1979

*=average values

hyperaccumulation in *Chengiopanax sciadophylloides* from Japan.

c. *G. meisneri*, previously known to accumulate Mn at concentrations ranging from 450 to 4,500 mg.kg^{-1} was found to hyperaccumulate Mn.

Finally, there are currently 22 acknowledged Mn hyperaccumulators, 11 of them originating from New Caledonia and 8 from Australia.

Interest of manganese accumulators

Table 3 gathers the latest data available on Mn accumulators from New Caledonia. Such species are of interest because in spite of Mn concentrations under the hyperaccumulation threshold, they can provide an interesting starting material for Ecocatalysis that can be directly used as green oxidant reagents and catalysts in organic chemical reactions. The ecocatalysts derived from Mn accumulators, called Eco-Mn, allow the development of the first substitute reagents to oxidants forbidden in the European Union by the REACH regulation. They are also interesting because further sampling efforts could probably lead to the discovery (or reclassification) of new Mn hyperaccumulators as was the case for *G. meisneri*. Revising existing data concerning Mn accumulators raised the following comments:

1. According to unpublished data from Jaffré, *Apiopetalum glabratum* should be considered a Mn accumulator as it showed Mn concentrations up to 5,300 mg.kg^{-1} in its dry leaves. It is also the case for an unidentified *Styphelia* species.
2. Latest taxonomic revision of the *Alyxia* genus led to the description of 10 synonyms. However, existing data on their Mn accumulation ability (Brooks et al. 1981) are difficult to re-use. Thus, this genus would require a thorough revision. Existing data from the literature are nonetheless presented.
3. In a similar way, species of the *Polyscias* genus other than *P. pancheri* were identified to accumulate high levels of Mn which suggest *Polyscias dioca* and *Polyscias jaffrei* merit further investigation of interest.

Finally, there are currently 24 species from New Caledonia that were observed to accumulate Mn at concentrations above 3,000 mg.kg^{-1} (yet under 10,000 mg.kg^{-1}) in the dry leaves of at least one individual. In addition to be potentially Mn

Table 3 Mn accumulators from New Caledonia updated from Jaffré (1980)

Family	Genus	Species	Max Mn level (mg.kg-1)	Reference
Apiaceae	*Apiopetalum*	*glabratum*	5,300	This study
Apocynaceae	*Alyxia*	*baillonii*	6,630*	Jaffré 1980
		caletioides	9,400	Jaffré 1980
		coriaceae	4,500	Jaffré 1980
		leucogyne	5,250	Jaffré 1980
		sarasinii	5,000*	Jaffré 1980
		tisserantii	4,875	Jaffré 1980
Casuarinaceae	*Gymnostoma*	*intermedium*	4,180	Jaffré et al. 1994
Cunoniaceae	*Pancheria*	*confusa*	4,500	Jaffré 1980
		hirsuta	5,000	Jaffré 1980
		billardieri	6,500	Jaffré 1980
Eriacaceae	*Styphelia*		4,000	This study
Loganiaceae	*Geniostoma*	*densiflorum* ssp. *oleifolium*	7,250	Jaffré 1980
Picrodendraceae	*Austrobuxus*	*rubiginosus*	4,125	Jaffré 1980
Proteaceae	*Beauprea*	*gracilis*	3,000	Jaffré 1979
		montana	3,625*	Jaffré 1979
	Grevillea	*exul* ssp. *exul*	3,900	Jaffré 1979
		exul ssp. *rubiginosa*	6,200	Jaffré 1979
		gillivrayi	8,200	Jaffré 1979
	Virotia	*francii*	5,480	Jaffré 1979
	Stenocarpus	*milnei*	3,900	Jaffré 1979
Santalaceae	*Exocarpos*	*neocaledonicus*	4,750	Jaffré 1980
Sapindaceae	*Guioa*	*glauca*	4,500	Jaffré 1980
Violaceae	*Hybanthus*	*caledonicus*	7,750	Jaffré 1980

*=average values

hyperaccumulators, such species also showed interesting responses toward aluminium (Jaffré 1979, 1980). Proteoid or cluster roots found in the Proteaceae family are also subject to extensive investigation (Lamont 2003), and highlight the interest of considering active processes at work in the rhizosphere of TE hyperaccumulators (Alford et al. 2010).

Soil-plant relationships

Noccaea caerulescens is often considered a model species to study Zn hyperaccumulation (Peer et al. 2003). Yet in the case of Mn hyperaccumulators, there is no such species available and existing datasets are far less comprehensive. It must be noted that many hyperaccumulating species were discovered in the last decade (see Tables 2 and 3), whilst Zn and Ni hyperaccumulators have been studied for at least 35 years now (Jaffre et al. 1976; Reeves and Brooks 1983). The following observations gathered in Table 4 are nonetheless possible:

1. *Phytolacca acinosa* (Xue et al. 2004), *P. americana* (Min et al. 2007) and *Polygonum pubescens* (Deng et al. 2010) display low BC with mean values at 0.18, 0.06 and 0.12, respectively. For these species, foliar manganese concentrations increase with soil total manganese concentrations, whilst BC decreases. However no significant correlations could be highlighted from the available data, except in the case of *P. pubescens* where BC was significantly related to soil total Mn concentrations in a power law relationship. In this case, more than 90 % of the variance in BC can be explained by soil total Mn.
2. All Mn hyperaccumulators from New Caledonia except *Garcinia amplexicaulis* show average BC above 1.5 and it is also the case of Australian species *Gossia bidwillii*. Yet there are also larger variations in BC, especially in the case of *G. diversifolia*. In all cases except for *G. amplexicaulis*, BC decreases with increasing soil total Mn concentrations. Variations in BC can be significantly related to variations in total Mn concentration in soil for *A. poyaensis*, *G. meisneri* and *P. pancheri* but without a unified model applicable.
3. In most cases, leaf Mn concentrations can be explained by soil total Mn concentrations. Relationships are significant except for *G. meisneri* and *P. pancheri* (and Mn hyperaccumulators from China). However, there is no

Table 4 Meta-analysis of soil-plant relationships for 10 acknowledged Mn hyperaccumulators

Species		*Alyxia poyaensis*	*Denhamia fournieri ssp. fournieri*	*Garcinia amplexicaulis*	*Gossia diversifolia*	*Grevillea meisneri*	*Polyscias pancheri*	*Gossia bidwillii*	*Phytolacca acinosa*	*Phytolacca americana*	*Polygonum pubescens*
Number of observations		5	13	30	8	9	12	8	6	6	5
Average BC		4.12	5.64	0.48	12.3	1.50	3.9	5.22	0.18	0.06	0.12
(±standard deviation)		2.25	3.87	0.46	17.7	1.02	2.4	2.24	0.04	0.01	0.06
Leaves Mn/soil total Mn correlation (best fit)	Type	Linear	Linear	Power law	linear	ns	ns	Power law	ns	ns	ns
	Variance explained (%)	98.9	64.5	25.10	71.0			56.1			
	p value	0.001	0.001	0.005	0.008			0.03			
BC/soil total Mn correlation (best fit)	Type	Linear-ln	Power law	ns	ns	Ln-linear	Linear	ns	ns	ns	Power law
	Variance explained (%)	99.96	68.71			83.00	34				91.54
	p value	0.0005	0.0005			0.0005	0.05				0.0107
Data from		Jaffré 1977	Jaffré 1977	This study	This study	This study	This study	Fernando et al. 2007	Xue et al. 2004	Min et al. 2007	Deng et al. 2010

ns not significant (at the 95 % level)

unique model that may account for the mechanism of Mn hyperaccumulation, possibly because of different responses at the species level, or because of differences in other soil parameters.

The major difference that can be highlighted from these data is a bimodal response of species to soil of natural origins, e.g. in New Caledonia or Australia, or soil disturbed by mining for Mn, e.g. in China. Taking into account currently available data, it appears difficult to find a single reliable model for soil-plant relationships in the case of Mn hyperaccumulators. Restrictions emphasised for Ni hyperaccumulators are also valid for Mn whose chemistry is more complex than Ni or Zn.

Leaf-age effects and their implications for designing applications

Leaf-age effects on the elemental composition of plant tissues

Another reason why the study of soil-plant relationships brings little advance in understanding TE hyperaccumulation in general is because TE accumulation is a dynamic phenomenon: early reports of Ni hyperaccumulation by *Alyssum* species highlighted a quick phenomenon, where maximum concentrations in plant leaves were reached within 5 days after exposure to Ni-spiked soil (Morrison et al. 1980). The first report of a significant effect of plant aging was made much later studying Ni hyperaccumulation in *Streptanthus* species (Kruckeberg and Reeves 1995). Similar observations concerning Ni hyperaccumulators were made for *Alyssum pintodasilvae* from Portugal (deVarennes et al. 1996), for *Berkheya* species from South Africa (Boyd et al. 2004; Robinson et al. 2003b), and for *P. gabriellae* (Boyd et al. 1999; Davis et al. 2001), *H. kanaliense* and *G. pruinosa* (Boyd and Jaffre 2009) in New Caledonia. Interestingly, other Ni hyperaccumulators such as *Agatea longipedcillata*, *Caesaria silvana*, *Homalium guillainii*, *H. austrocaledonicus* and *P. acuminata* did not show significant leaf-age effects (Boyd and Jaffre 2009). As regards hyperaccumulators of other elements, significant leaf-age effects were observed for the Japanese Mn hyperaccumulator *C. sciadophylloides* (Mizuno et al. 2008), the Chinese As hyperaccumulator *Pteris vtitata* (Gonzaga et al. 2007) as well as various Zn hyperaccumulators (Macnair and Smirnoff 1999; Robinson et al. 1998).

Recent data were obtained by collecting *G. meisneri* (Fig. 3) leaves in the 'Creek à Paul' valley near the Tiébaghi massive, New Caledonia (20° 29′ 35.03″ S, 164° 12′ 22.76″ E). Leaf sampling was performed as follows. A qualitative assessment of leaf-age was performed according to the position of leaves on stems and visual assessment of their colours. The collected leaves

Fig. 3 *Grevillea meisneri*, Creek à Paul, New Caledonia and litter under *Grevillea meisneri* including young plants

were separated in two age-categories, i.e. 'young leaves' and 'mature leaves'. Approximately 500 g of fresh leaves per age-category was collected on each individual sampled, to ensure the reliability of the concentrations measured. Litter composed of dry fallen leaves was also collected under each tree as it was readily accessible. The results obtained are gathered in Fig. 4 and show a significant difference between young leaves (YL) and older leaves (OL). Litter composed of fallen *G. meisneri* leaves show intermediate Mn concentrations, but they are not statistically different from young leaves or old leaves. Concentrations up to 1.1 % of Mn were found in old *G. meisneri* leaves, which make this species a new Mn hyperaccumulator. Similar trends were also observed for *Grevillea exul* (Fig. 5) growing at the 'Camp des Sapins' mine, Thio, New Caledonia. Lower Mn concentrations in *G. exul* are also possibly related to plant age (3.5 years in this case). This shows the necessity of considering leaf-age when assessing the ability to accumulate TE of a plant species and also advocates further investigation of Mn accumulating species from New Caledonia.

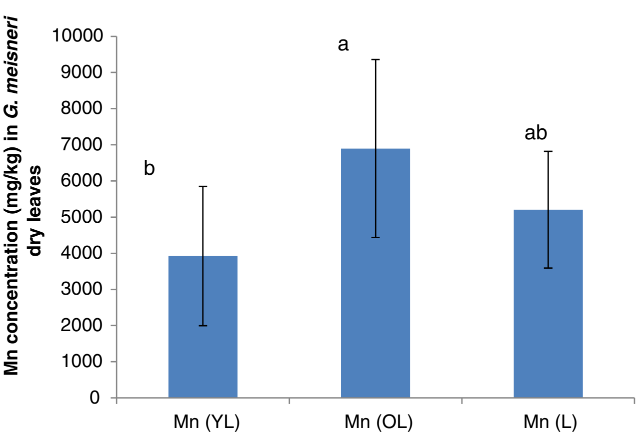


Fig. 4 Incidence of leaf-age on the Mn concentrations (mg/kg) in *Grevillea meisneri* leaves

Implications for designing applications

Usual applications

Potential applications are generally referred to as TE phytoextraction, which is the extraction of TE from soil by plants (Robinson 1997). Two different approaches for phytoextraction can be distinguished, both termed by Cunningham and Berti (1993) but devised earlier (Baker et al. 1988):

1. Phytoremediation by way of TE phytoextraction addresses the issue of TE contaminated soil and aimed to provide a way to clean them.
2. Phytomining, initially termed 'biomining' (Cunningham and Berti 1993), refers to the use of plants, usually TE hyperaccumulators, to produce bio-ores subsequently used in metal production (Brooks et al. 1998).

Deemed unrealistic in a first instance (Baker et al. 1988), phytomining probably raised the greatest expectations. It was developed for nickel to an industrial level using *Alyssum* species. Usual pyrometallurgical processes (Chaney et al. 2007), or other chemical separation techniques (Barbaroux et al. 2012) can be used to recover nickel. Phytoremediation by way of phytoextraction on the other hand appeared more convincing (Baker et al. 1988): yet it raised more questions than it actually solved. Feasibility and cost-effectiveness are

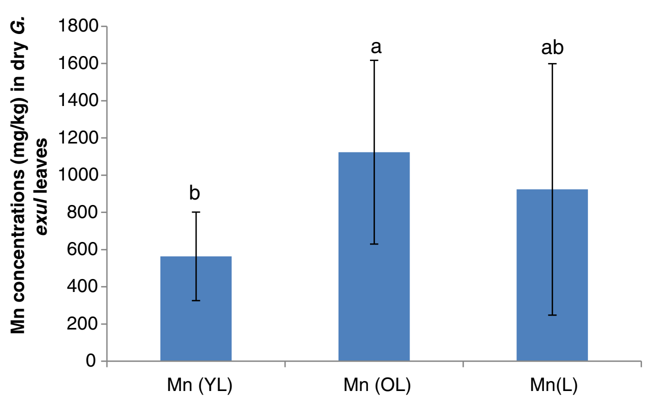


Fig. 5 Incidence of leaf-age on the Mn concentrations (mg/kg) in *Grevillea exul* leaves

still questioned (Conesa and Schulin 2010; Ernst 2005; Robinson et al. 2003a), as well as the issue of contaminated-biomass disposal (Ernst 2000; Sas-Nowosielska et al. 2004).

However, in both cases ecological principles should guide action and site-specific approaches using local species:

1. May avoid poor results, e.g. using *Alyssum* species in Indonesia (van der Ent et al. 2013b)
2. May avoid the emergence of invasive species, e.g. *Alyssum* species in the USA, as reported by the Oregon Department of Agriculture (2014)
3. Is a way to promote the conservation of metallophyte species (Whiting et al. 2004)

Ecocatalysis

The emerging concept of Ecocatalysis may also use TE-rich biomass from phytoremediation by way of phytoextraction (Losfeld et al. 2012a) as well as from phytomining (Escande et al. 2014a, b; Losfeld et al. 2012b; Thillier et al. 2013) and was covered by various patents (Grison and Escande 2013a, 2013b). It leads to original (unusual oxydation states, new associated chemical species) and effective catalysts and reagents. Ecocatalysis offers a unique opportunity of cooperative catalysis, where the synergetic action of diverse TE presents a huge potential. Activities, chemo-, stereo-selectivity and recyclability of ecocatalysts are higher than classical catalysts in various reactions. This is conceptually very different from phytomining and phytoremediation by way of phytoextraction and could overcome the limits of these technologies. Ecocatalysis specifically tackles TE-rich biomass regardless of the metal considered, and it is fully compliant with the end use of metals obtained, i.e. Green Chemistry, thus allowing greener and broader perspectives for present environmental and socio-economic challenges.

Developing applications

Considering Mn hyperaccumulators, e.g. *G. meisneri* or Mn accumulators, e.g. *G. exul* as potential sources of Mn for application in Ecocatalysis requires the design of leaf harvesting schemes. Taking into account their lower Mn concentration, lower biomass and potential plant stress, collecting young leaves would probably be unproductive. Older leaves show the highest Mn concentration and thus could be considered of utmost interest. However, their collection would also result in plant stress and species from New Caledonia are known to grow slowly. Moreover, the age parameter was assessed on a qualitative basis, and it would be quite difficult to implement a collection based on such a qualitative parameter. The most practical proposal is then to focus on litters: they have an intermediate Mn concentration and although litter biomass would need to be measured precisely to assess yield, it is certain that this option would ensure sustainable yields, compared to the two others.

Various metallophyte species (e.g. *Geissois* spp., *Grevillea* spp., *Phyllanthus* spp.) proved useful for the reclamation of mining areas in New Caledonia. The development of new outlets, e.g. Ecocatalysis could provide supplementary revenues for the restoration of such areas. Developing reclamation schemes for highly degraded quarries or spoils storage areas using metal hyperaccumulators along with Cyperaceae and other soil-improving species could provide an efficient way to control watershed erosion of degraded land. Generating alternative incomes through the promotion of metal-rich biomass used in organic chemistry could not only cover the cost of the revegetation operation but also generate post revegetation economic activities for New Caledonia as well as other mining countries.

Conclusion

From this review and from the new data presented, it clearly appears that usual soil-plant studies of TE hyperaccumulation based on measuring TE concentrations in soil to assess BC are limited. Although useful for the study of Zn or Ni hyperaccumulators from the Brassicaceae family, they are far from conclusive when applied to Ni or Mn hyperaccumulators from New Caledonia. Some trends may be highlighted but contradictory results are possible and no general model emerges from this study. This is partly due to issues in measuring soil TE concentrations:

1. Total concentrations are easily measured but do not reflect soil chemistry, and the amount of a TE that is actually available to a plant is different from that assessed by acid digestions. Soils from New Caledonia were studied using DTPA extractions as a way to assess TE availability, with a main focus on Ni and Mn. However, although useful for agricultural purposes, the method failed to account for Ni or Mn hyperaccumulators response to soil TE concentrations.
2. The volume of the rhizosphere of Ni or Mn hyperaccumulating shrubs or trees from New Caledonia is larger than that of Brassicaceae resulting in difficulty in assessing rhizosphere properties, including TE concentrations.

Investigating *G. meisneri* and *G. exul* with Ecocatalysis applications in mind allowed to highlight temporal patterns in Mn accumulation for these species: young leaves contained significantly less Mn than older leaves. This is useful to design applications, but also allowed to reclassify *G. meisneri* as a hyperaccumulator of Mn. Latest data on Mn hyperaccumulators are also presented, and New Caledonia is clearly a hotspot for Mn hyperaccumulation. Various Mn accumulators from the island could be investigated further taking into account leaf-age, which would probably lead to the discovery of new Mn hyperaccumulators and revision of their current accumulation status. The development of Ecocatalysis applications for Mn-rich biomass could spur massive research efforts for understanding Mn hyperaccumulation by plants. It should also encourage the development of integrative studies of Mn hyperaccumulation, as is the case for Ni or other TE.

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