Environmental Science & Technology

Feature

pubs.acs.org/est

Agromining: Farming for Metals in the Future?

Antony van der Ent,*[,†,○] Alan J. M. Baker,[†,‡,○] Roger D. Reeves,[‡] Rufus L. Chaney,[§] Christopher W. N. Anderson,[∥] John A. Meech,[⊥,@] Peter D. Erskine,[†] Marie-Odile Simonnot,[#] James Vaughan,[∇] Jean Louis Morel,[○] Guillaume Echevarria,[○] Bruno Fogliani,[◆] Qiu Rongliang,[¶] and David R. Mulligan[†]

[†]Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, Queensland 4072, Australia

[‡]School of BioSciences, The University of Melbourne, Parkville, Victoria 3010, Australia

[§]USDA-Agricultural Research Service, Crop Systems and Global Change Laboratory, Beltsville, Maryland 20705, United States

[∥]Institute of Agriculture & Environment, Massey University, Palmerston North 4474, New Zealand

[⊥]NBK Institute of Mining Engineering, University of British Columbia, Vancouver V6T 1Z4, Canada

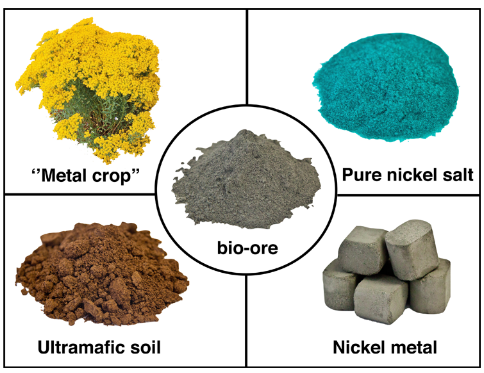
[#]Université de Lorraine − CNRS, Laboratoire Réactions et Génie des Procédés, UMR 7274, Nancy 54000, France

[∇]School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

[○]Université de Lorraine − INRA, Laboratoire Sols et Environnement, UMR 1120, Nancy 54000, France

[◆]Diversités biologique et fonctionnelle des écosystémes terrestres, Institut Agronomique néo-Calédonien (IAC), Nouméa 98851, New Caledonia

[¶]School of Environmental Science and Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou, China



Phytomining technology employs hyperaccumulator plants to take up metal in harvestable plant biomass. Harvesting, drying and incineration of the biomass generates a high-grade bio-ore. We propose that "agromining" (a variant of phytomining) could provide local communities with an alternative type of agriculture on degraded lands; farming not for food crops, but for metals such as nickel (Ni). However, two decades after its inception and numerous successful experiments, commercial phytomining has not yet become a reality. To build the case for the minerals industry, a large-scale demonstration is needed to identify operational risks and provide "real-life" evidence for profitability.

■ INTRODUCTION

In 2012 the International Council on Mining and Metals (ICMM) released statistics on global ore reserves showing that ore grades continue to decline, with a major shift from high-grade low-bulk to low-grade but high-bulk ores.[1] The consequence is an ever-increasing volume of waste generated by the mining industry, posing challenges for rehabilitation.[2] The type of ore exploited by the mining industry is also changing, and with respect to nickel (Ni), there is a move from high-grade Ni-sulfide to low-grade Ni-laterite (ultramafic) ores.[3] This has, in part, been driven by the global economy, as ultramafic ores are commonly found in tropical countries, especially in the Asia-Pacific region, where setup and operating costs are considerably lower than in industrialized countries. These trends have an impact on globally important centers of biodiversity where Ni-laterite deposits are often colocated. Coincidentally, this offers opportunities to make innovative use of biodiversity to deal with the challenges of rehabilitating mining wastes. Although the elemental profile of most plants generally reflects that of the environment,[4] some plants accumulate very high concentrations of certain metals. These are collectively known as hyperaccumulator plants.[5,6] Hyperaccumulator species are known with high concentrations of metals such as Ni, Mn, or Zn in their aboveground biomass.[7,8] Such plants may be utilized in prospecting (locating ore-bodies), phytoextraction (soil clean up), and phytomining (commercially producing metals, metal products, or catalysts) or its variant "agromining" (in which phytomining is conceived to be part of an integrated agricultural chain). Growing hyperaccumulator plants on subeconomic ore (e.g., ultramafic soils) or mineral wastes, with subsequent harvesting and biomass incineration, generates a product that may be termed "bio-ore".[9,10] The concentration of Ni, for example, in such bio-ore (10−25 wt %) is high compared to current lateritic ores (<1.5%) and free of Fe and Mg silicates present in the soil matrix which increases the cost of metal extraction.

■ NI HYPERACCUMULATOR PLANTS

The greatest number of hyperaccumulators are known for Ni (defined for this element as having >0.1% in the dried leaves). This partly reflects the fact that worldwide surface exposures of

Published: February 20, 2015

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

Figure 1. Phytomining/agromining operations with harvesting of biomass and processing of bio-ore. The top four panels show the parallel strategies of phytomining and agromining on degraded/mined land or on low productive agricultural land, respectively. The lower four panels show harvesting of biomass and production of Ni (intermediate) products. Photo credits: EcoRCE/IAC/G Losfeld, A Baker, Société le Nickel, R. Chaney, A. Bani, J. Vaughan.

naturally Ni-enriched ultramafic soils cover >3% of the Earth's surface.[11] Furthermore, Ni, unlike other common elements in ultramafic soils (Fe, Co, Cr), is usually relatively plant-available.[12] Since the early 1970s there has been a concerted effort to identify Ni hyperaccumulator plants, both through the analysis of specimens from herbaria and through field exploration. By 2015, approximately 400 such Ni hyperaccumulators had been documented including: 130 species in Cuba,[13] 65 species in New Caledonia[14] and 59 species in Turkey.[15] There are records of leaf Ni concentrations up to 6%[13] and latex Ni concentrations up to 25%.[5] Phytomining should focus on species showing the highest levels of hyperaccumulation, and in practice only those with >1% Ni in foliar dry matter will likely be of commercial relevance. Such plants have been termed "hypernickelophores".[16] They constitute a subset of known Ni hyperaccumulators but include a broad range of plant life forms including herbs, shrubs and trees. However, not all are suitable candidates for phytomining, as the utility of a plant species for phytomining is ultimately determined by the annual harvestable biomass.[17] Unfortunately, in some species the high-Ni tissue is a low proportion of total biomass, or the total annual biomass production is not sufficiently high.[18] High biomass yield and metal hyperaccumulation are both required to make phytomining a commercially viable proposition.

AGROMINING TECHNOLOGY

Agromining involves growing hyperaccumulator plants as a crop, then harvesting biomass, drying, ashing and processing it to recover target metals such as Ni. This type of operation is most efficient using perennial species that regenerate above-ground biomass rapidly after harvesting; ensuring that the substrate-stabilizing function of established vegetation is

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

maintained. Figure 1 shows the parallel strategies of phytomining and agromining operations on either mined/degraded land or low productive agricultural (ultramafic) land respectively, followed by harvesting of biomass and processing of the bio-ores. In summary, two main approaches may be considered for phytomining/agromining:

1. Phytomining on Degraded or Mined Land. This can be part of broader rehabilitation strategies for Ni laterite mines, smelter contaminated land, ore beneficiation tailings or otherwise degraded metal-rich land. Phytomining could also form a first stage in the development of tropical lateritic mining projects, and then progress as part of the rehabilitation strategy during mine operation. This presents an opportunity for generation of cash flow from laterite projects during the project development phase. It does not interfere with the mainstream project, as phytomining would initially use the overburden that would be cleared before extracting the underlying minerals.

2. Agromining on Low-Productivity Agricultural Soils. This would target large and relatively flat ultramafic areas, which have low productivity for food production. Agromining here would be superior to conventional agricultural production, generating better economic returns to farmers. A cocropping approach might also be possible: for example, in Greece, olive plantations could be intercropped with *Alyssum*; and in Malaysia, palm oil estates could be intercropped with *Phyllanthus*.

■ ECONOMICS OF AGROMINING

Agromining may in principle be undertaken to produce As, Se, Cd, Cu, Co, La, Mn, Ni, Pb, Tl, and Zn, as hyperaccumulator plants are known for all of these elements.[6] However, Cu, Co, La, and Pb hyperaccumulators have poor accumulation characteristics and are therefore not (currently) considered for agromining. Economic feasibility depends on the element market price, the annual yield per unit area (biomass produced and contained amount of target element), and the availability of surface areas enriched in this element. Current (2015) prices per metric ton are high for Ni (US$15,000), Se (US$52,000), and Tl (US$60,000), but low for As (US$1550), Mn (US $2350), Cd (US$1750), and Zn (US$2100). Therefore, agromining may be feasible for Ni, Se, and Tl, but of these elements, large surface areas with enrichment exist only for Ni and Se. Two exceptions can be made for instances where the actual metal/metalloid-rich biomass has a value in itself apart from the sole metal value: (i) Zn or Mn-based catalysts prepared from hyperaccumulator biomass;[19,20] and (ii) organic micronutrient fertilizers made from hyperaccumulator biomass rich in either Zn, Ni, Mn, or Se.[21,22]

Based on field trials with Ni hyperaccumulator species such as *Alyssum murale* or *A. corsicum*, we can expect to harvest 5−10 t of dry matter per ha containing 2% Ni, yielding 100−200 kg Ni ha^{-1}. In agricultural conditions in Albania, a yield of 105 kg Ni ha^{-1} was achieved with *A. murale*.[23] This yield substantiates earlier studies conducted over smaller areas, including those with *Streptanthus polygaloides* in California that yielded 100 kg Ni ha^{-1},[24] *A. bertolonii* in Italy, 72 kg Ni ha^{-1},[25] and *Berkheya coddii* in South Africa, 100 kg Ni ha^{-1}.[26] At 2015 prices of US$15 kg^{-1}, and a potential yield of ≥100 kg Ni ha^{-1}, agromining could become a part of a substantial and integrated income stream for "metal farmers" worth more than most food crops. By means of comparison, a premium rice crop on fertile "normal" soils makes approximately US$850 per ha^{-1} year in Indonesia, while Ni phytomining on local ultramafic soils has the potential to make US$1000 ha^{-1} year. It should be emphasized that due to inherent infertility ultramafic soils have low economic returns if used for producing food crops such as wheat or rice. Under these circumstances, agromining could be a viable alternative generating better economic returns to local communities. Therefore, unlike the competition between food crops and biofuels on fertile soils, agromining does not replace food crop production, but is a temporal activity that may improve soil quality sufficiently to allow food crop production after the metal resource has been extracted.

The raw bio-ore produced from experimental phytomining has been processed via an arc furnace to produce Ni metal.[17] Alternatively; the bio-ore is compatible as feedstock for major Ni hydrometallurgical plants. The high purity of the bio-ore also makes it uniquely suited to produce Ni catalysts for industrial synthetic organic chemistry,[27] or to be converted into high value Ni chemicals for use in the electroplating industry.[28] The choice for bio-ore processing options depends on local conditions, integrating or innovating supply chains and desired outcomes. We estimate that the raw bio-ore itself is worth approximately 85% of the contained Ni value, but if a higher value product is made, this could further increase the profitability of phytomining.

Factors to be considered in economic feasibility studies include (1) total development and optimization costs through trial stages to full operation; (2) predicted annual costs, which include labor and machinery costs of propagation, fertilization, irrigation (if needed), plant protection and harvesting; (3) land costs; (4) current and predicted price of the metal (or its compounds) on world markets, and (5) the value of alternative land uses. Ideally the venture would include a large tract of land under single or simple ownership. The agromining entity then either buys or leases the land and employs workers, or makes arrangements with farmers and landowners to manage all aspects of crop production, with payment being made according to the proven Ni content of the harvested crop. Environmental evaluation must be integrated into the process to minimize negative environmental outcomes. Specifically, the use of native plant species should be encouraged so as to avoid possible spreading of invasive species.

■ PRACTICAL IMPLEMENTATION OF NI AGROMINING

Extensive ultramafic laterite soils, naturally rich in Ni, are found in the Asia−Pacific region, especially in Indonesia, the Philippines and New Caledonia.[29] Although large-scale Ni strip-mining occurs there, the Ni concentrations of most of these ultramafic regoliths are <1%, below concentrations required for a traditional mining enterprise. Hyperaccumulator plants can achieve high Ni yields from soils with only 0.1% total Ni.[30] Because the hyperaccumulator crop will deplete soil Ca, P, N, and K[30] these elements will need to be applied to retain good growth, as ultramafic soils are inherently deficient in these elements. However, most hyperaccumulator plants are highly nutrient-efficient. For example, P-uptake in *Alyssum murale* and *A. corsicum* was so efficient that only small amounts of P-fertilizer optimized plant yield without reducing plant Ni levels.[30] Besides plant nutrients required for maximum biomass production of the metal crop, managing other soil properties might improve Ni yield. For example, in *Alyssum*-species, Ni accumulation increases as soil pH is increased, a response opposite to "normal" plants.[31]

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

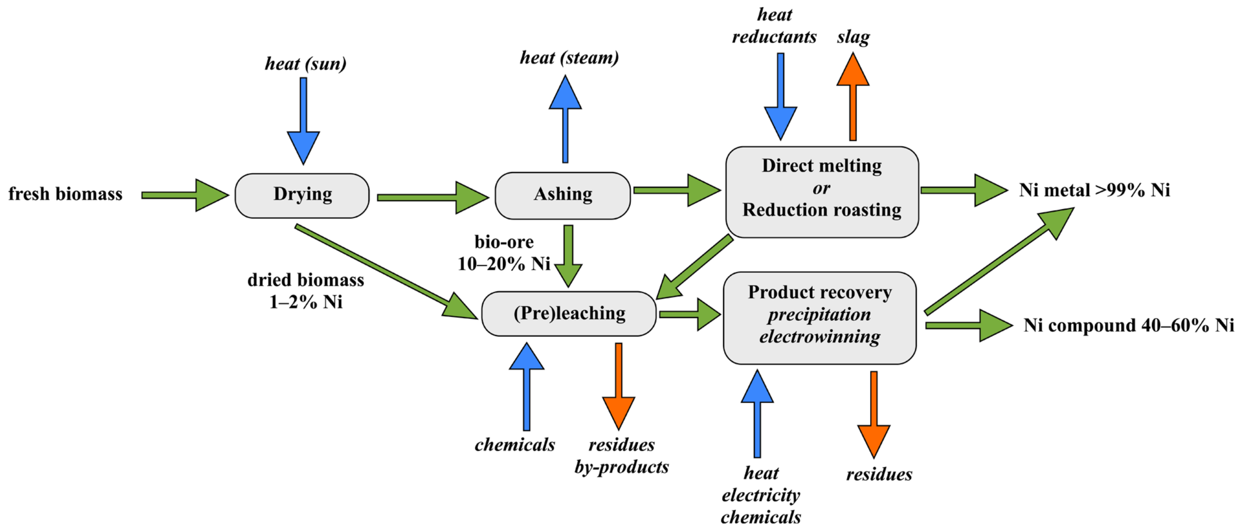


Figure 2. Flow sheet of bio-ore processing options as discussed in the text. Major inputs, intermediate products and wastes are indicated. Approximate Ni concentrations of the biomass, bio-ore and products are also indicated.

Current rehabilitation practices following strip-mining of laterite Ni include using local species and well-proven plant species to stabilize mined landscapes. Alternatively, phytomining could be employed to provide initial vegetative stabilization with the added advantage of a longer-term income stream. Phytomining thus adds to the progressive rehabilitation strategy. In New Caledonia, coplanting of native hyperaccumulator species with nitrogen-fixing plant species (Casuarinaceae, Fabaceae) has been conceived as a viable option for getting rehabilitation started on mine spoils.[32] We believe that there are two broad strategies to implement agromining related to geographical area:

1. **Mediterranean and Eurasian Regions**
   Countries: Turkey, Albania, Greece, and Iran
   Land strategy: Low productive ultramafic land under agricultural (food) use
   Phytomining crops (genera): Alyssum, Leptoplax, Bornmuellera
   Cropping system: Annuals or perennials, mowing/haymaking
   End points: Release more fertile land to more productive food cropping (the enhancement of soil fertility is effectively subsidized by agromining)
2. **Tropical Asia–Pacific Regions**
   Countries: Malaysia, Indonesia, Philippines, PNG, and New Caledonia
   Land strategy: Degraded Ni-rich land (burnt, logged-over, strip-mined)
   Phytomining crops (genera):Phyllanthus, Rinorea, Geissois
   Cropping system: Ligneous shrubs with coppicing or leaf harvesting
   End points: Agroforestry (timber, teak, rubber, palm oil), biodiversity

Agriculture on ultramafic soils often has a low productivity due to lack of Ca, K, and P and excess Mg and Ni.[33] Over time, agromining here can improve fertility and significantly decrease Ni availability; this can be regarded as a significant ecosystem service. Knowledge of suitable "metal crop" species is essential for selecting areas to establish agromining operations. In the Eurasian region, particularly in Albania and Turkey, suitable phytomining crops and soils have been identified. In Indonesia, Malaysia and the Philippines several potentially suitable species have also been identified alongside appropriate soils, but the technology remains untested in the tropical biome. However, field trials have recently started in New Caledonia to produce biomass from *Geissois pruinosa* (Ni) and *Grevillea exul* (Mn) for use in the production of catalysts.[34] Species native to the area are more likely to be suitable than introduced ones, for several reasons. They are already adapted to the local climate, pests and diseases, and will not have biosecurity risks that accompany introduction of species from elsewhere.[35] Not all Ni-rich ultramafic soils are suitable for phytomining as potential Ni yield depends on soil available Ni pools.[30] Recent studies have shown that tropical Ni hyperaccumulators (in Sabah, Malaysia) were distributed mainly on circum-neutral young serpentinitic and saprolite soils.[36] In weathered serpentinite-rich soils high-exchange clay minerals bear most Ni, which is highly plant-available.[12] The barren landscapes after conventional strip-mining, where the limonite laterite is scraped-off to expose the saprolite, might therefore be particularly promising for phytomining.

POTENTIAL LIFETIME OF AN AGROMINING OPERATION

The commercial returns from an agromining venture will be finite due to the diminishing concentrations of the target metal in the substrate. However, the time scale for economic agromining may be considerable. In many ultramafic areas the soil and subsoil may extend many meters in depth. For 1 ha with (theoretically) total Ni at an average of 2000 mg kg^{-1} over a depth of 1 m, the resource contains about 30 t of Ni. Crops with 5 t ha^{-1} dry weight of plant material at 2% Ni yield 100 kg Ni ha^{-1}, which is only 1/300 of the total resource. Conservatively assuming that 10–20% of the total amount of soil Ni is part of the plant available-pool that is replenished/buffered by mineral phases on the time scale of the extraction process, the agromining operation could be sustainable over at least 30–60 years.

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773–4780

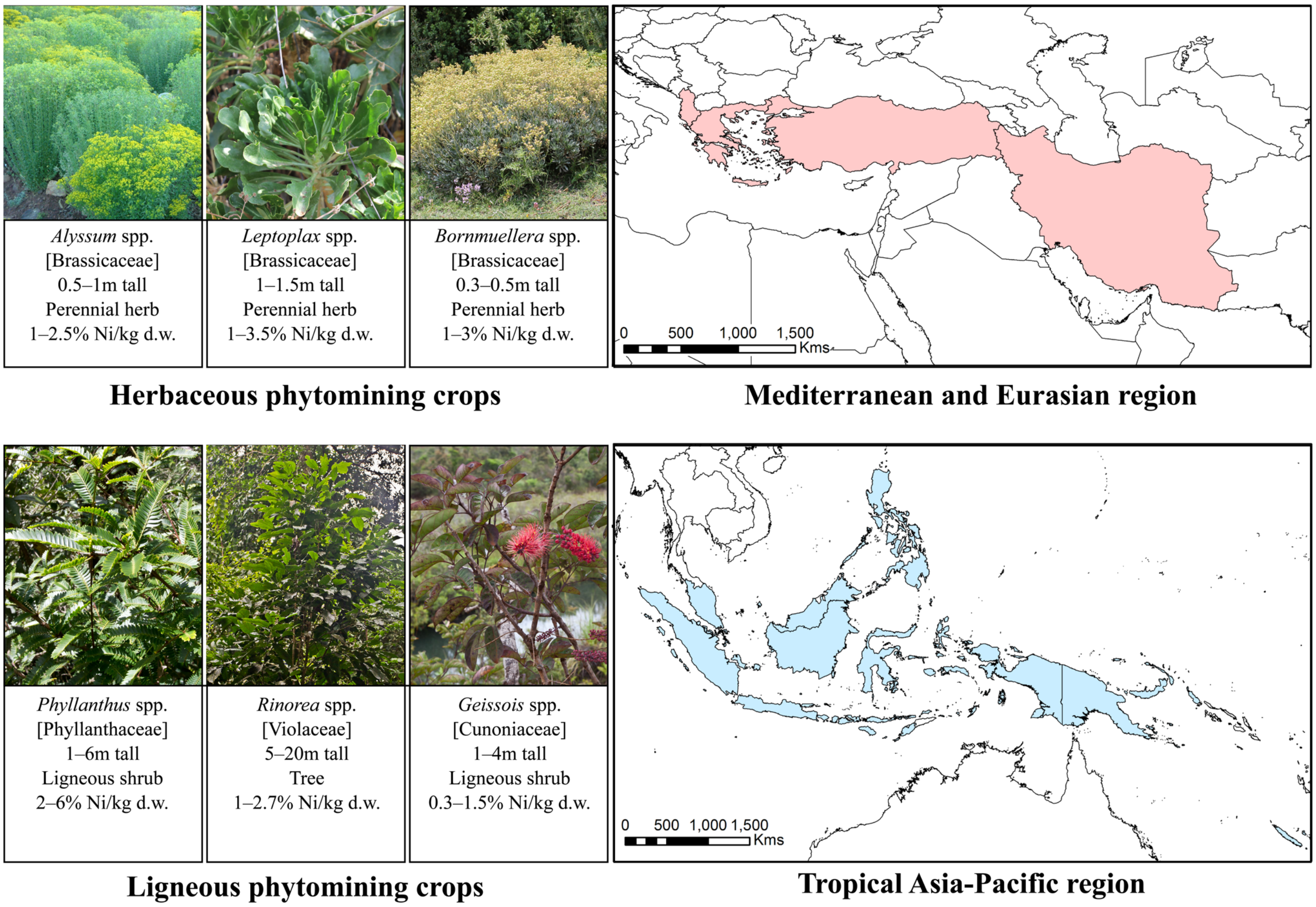


Figure 3. Global target regions for phytomining/agromining and main metal crop genera with key data on growth form and Ni yield. Note that the color-shaded areas indicate countries with significant surface expanses of ultramafic soils, but not potentially suitable areas for phytomining/agromining. Photo credits: A. Bani, G. Echevarria, A. van der Ent, P. Erskine.

■ PROCESSING OF NI BIOMASS AND BIO-ORES

The extraction of Ni from hyperaccumulator biomass is an important aspect of the development of the technology. Concerted efforts to obtain Ni metal by both pyro- and hydrometallurgical processing of *A. murale* ash have been made during the last 10−15 years.[30] A simplified process flow sheet of options for processing Ni bio-ore is illustrated in Figure 2. Options include a pyrometallurgical step (ashing) followed by smelting Ni in a high temperature reducing reactor, a hydrometallurgical option of leaching followed by product recovery and a pyro-hydro combination where the biomass is first ashed and then Ni is extracted by leaching. Known technical and economic considerations include (1) building and maintenance costs for the processing facility and associated infrastructure, (2) power, reagents, labor and other operational costs, (3) the magnitude and value of the product(s), (4) waste material disposal, (5) access to suitable skilled labor to ensure the process can be operated at design specifications, and (6) access to a reliable market to sell the product.

Ashing. In most processes, biomass is ashed yielding Ni content up to 20 wt % as NiO, among other phases.[18,28,30,37] Careful control of the reactor conditions is required in order to obtain the desired Ni phase and mineralize organic matter without volatilizing Ni.[18] As the combustion is exothermic, heat energy derived from this reaction could potentially be recovered. Co-incineration of hyperaccumulator plants along with municipal waste has been suggested[38] as has using hyperaccumulator biomass as fuel for pyrolysis with a further step of metal recovery from biochar.[39] With high-temperature ashing (>500 °C), the residue consists mainly of carbonates and oxides of the major metallic elements present in the plant: K, Ca, Mg, and Ni. There may be an advantage in lower-temperature ashing (<400 °C), where C is retained in a reduced form, which can be used as fuel or a reducing agent in subsequent pyrometallurgical processing stages. Prewashing can help increase the Ni content of the ash, as contained K_2CO_3 is highly water-soluble.[28]

Smelting. The thermo-chemical treatment of bio-ore to yield Ni metal requires heat input as well as a suitable chemical reductant and flux to control the slag properties. The production of ferro-nickel or nickel pig-iron from laterite ore is currently economically feasible for grades above about 1.5 wt % Ni.[40] Once dried, biomass or bio-ore could be integrated into the feed of existing Ni smelters, reducing the capital investment at initial stages of process development. An argument against doing this is that the hyperaccumulator plant has already effected an efficient separation of Ni from iron. The Ni:Fe mass ratio can be upgraded from 1:100 in the soil to 40:1 in the plant dry matter; the hyperaccumulator plant is thus responsible for a 4000-fold relative enrichment of Ni. This natural purification is wasted if the plant ash is then fed to a ferro-nickel operation and recombined with Fe.

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

Other Pyrometallurgical Processing Options. The dry high-Ni carbon-rich biomass can be used as a supplement to the existing processes following a cotreatment strategy and this can reduce the risk of capital investments at initial stages of development. The use of inherently present carbon taken from the Earth's atmosphere during plant growth can make Ni production not only CO_2-neutral, but even CO_2-negative when the heat generated during the pyrometallurgical treatment of the Ni-rich biomass is captured and utilized. Therefore, to take full advantage of the organic matter in the biomass as a fuel and chemical reductant, three pyrometallurgical options could be considered which would involve recycling low quality heat generated in the reactor to dry the biomass. The first option, analogous to the Caron process,[41] begins with a low temperature reductive roast (600−800 °C) to generate a Ni metal intermediate product followed by hydrometallurgical refining. The second option is a medium temperature (1250 °C) reductive roast in a rotary kiln where Ni is isolated by physical separations similar to Nippon Yakin Kogyo operations.[42] The third option is to convert dried biomass directly to liquid Ni metal in a high temperature reactor.[43]

Leaching. Another extraction method is to leach the metal into an aqueous solution.[44] Hydrometallurgical processing of Ni typically uses H_2SO_4,[45] NH_4OH-$(NH_4)_2CO_3$,[46] or NH_4OH-$(NH_4)_2SO_4$.[47] Existing hydrometallurgical operations could integrate bio-ore into their feed; for example, pressure acid leaching where concentrated H_2SO_4 is injected into an autoclave at 250 °C would likely solubilize the Ni. The disadvantage of this is again the Ni recombination with impurity elements such as Fe, which must then be separated. Conventional hydrometallurgical Fe removal processes result in 2−10% of the leached Ni being lost to the tailings stream.

Product Recovery. Hydrometallurgical processes tend to be more flexible in product and byproduct recovery options. Once present in aqueous solution at sufficient concentration and purity, a Ni product can be recovered in numerous forms such as in the metallic state by electrochemical reduction to plates, rondelles, powders, or as a compound by chemical or evaporative precipitation. A Ni compound product may be attractive due to either process operational simplicity or added market value. A simple option would be to chemically precipitate Ni as a hydroxide consisting of ≈40 wt % Ni (dry basis).[48,49] Value-added options include producing catalysts from Ni hyper-accumulator biomass for organic chemistry[27] or crystallizing pure Ni salts, such as $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (ANSH) which has been produced from ash of *A. murale*.[28,50] These processes are currently proceeding to pilot-scale demonstrations. The production of $K_2Ni(SO_4)_2 \cdot 6H_2O$ from H_2SO_4-treated hyperaccumulator plant ash has also been demonstrated[51] but not developed beyond the laboratory scale. Byproducts from hydrometallurgical processing of bio-ore (e.g., K_2CO_3) can be recycled to the phytomined area to sustain macronutrient fertility in soils.

WHERE COULD PHYTOMINING OR AGROMINING TAKE PLACE?

There is potential for Ni phytomining or agromining in countries that are leading producers of mined Ni. Currently these are, in order: Indonesia and the Philippines (each with more than 400 000 t of the total world production of 2.4 million t), Russia, Australia, Canada, Brazil, New Caledonia, China, Colombia, and Cuba. However, countries that are not major Ni producers but which may support a Ni agromining industry include Greece, Bosnia, Serbia, Portugal, Italy, France (Corsica), Russia (Urals), Puerto Rico, the Dominican Republic, and Zimbabwe. Immediate application is likely to be seen in Albania and Turkey (using established *Alyssum*-based technology) and Indonesia or the Philippines (using coppice management of local ligneous species). Figure 3 shows these global target regions and main metal crop genera with key data on their growth form and Ni yield. Key factors are the availability of (i) ultramafic soils with 0.1−0.8% Ni, allowing hyperaccumulator species to maximize uptake, (ii) a suitable native hyperaccumulator species, and (iii) for the soils to be capable of being easily cropped with local agricultural methods.

CONCLUSIONS AND OUTLOOK

Despite scientific validation of phytomining/agromining over the last two decades, the mining industry has yet to test the system on a large scale. The impending expiry of unexploited Ni phytomining patents[10] in 2015 should create an opportunity to reassess technology transfer. The lack of large-scale agromining may also result from a lack of awareness of hyperaccumulator plants and the scientific advances made in capturing Ni from plant biomass. This highlights the need to further encourage industry to apply these new technologies that have the potential to improve mine site rehabilitation while providing opportunities for sustainable postmining livelihoods, especially in tropical regions As part of improving degraded land to make it suitable for other uses, agromining could provide local communities with an income and training in modern agricultural practices. To build the case for the minerals industry, however, a large-scale demonstration is first needed to work through operational challenges and provide "real-life" evidence of profitability.

AUTHOR INFORMATION

Corresponding Author

*E-mail: a.vanderent@uq.edu.au.

Notes

The authors declare no competing financial interest.
[@]Deceased.

Biography

Antony van der Ent is a Postdoctoral Research Fellow at Université de Lorraine (France) and The University of Queensland (Australia). His work focuses on trace element chemistry in the soil/plant interface, specifically in hyperaccumulator plants. He is part of a team developing agromining/phytomining in the Asia-Pacific Region.

Alan Baker is an Honorary Professor of Botany at The University of Melbourne and also at the Centre for Mined Land Rehabilitation at The University of Queensland (Australia). His work focuses on the phytoremediation of contaminated lands, as well as carrying out fundamental research on heavy metal accumulation. He has been at the forefront of developing phytomining technology from its beginnings.

Roger Reeves was formerly Professor in Chemistry at Massey University (New Zealand). He also held a position as Honorary Professorial Associate in the School of Botany at The University of Melbourne (Australia). Together with colleagues he has discovered and reported the majority of nickel-hyperaccumulator plants known to date.

Rufus Chaney is a Senior Research Agronomist in the Crop Systems and Global Change Laboratory of the US Department of Agriculture where he conducts research on the fate, food-chain transfer, and

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

potential effects of soil microelements. He first spawned the idea for phytomining in 1983.

Christopher Anderson is an Associate Professor in Soil and Earth Sciences at the Institute of Agriculture and Environment of Massey University (New Zealand), and Adjunct Professor at the Institute of Geochemistry of the Chinese Academy of Sciences, and also at the NBK Institute of Mining Engineering, The University of British Columbia (Canada).

The late John Meech was a Professor of Mining Engineering and the Director of the Centre for Environmental Research in Minerals, Metals and Materials at The University of British Columbia (Canada).

Peter Erskine is a Senior Research Fellow at The University of Queensland (Australia) who focuses on restoration and mine rehabilitation and spatial ecology.

Marie-Odile Simonnot is Professor of Chemical Engineering and Head of the research group Processes for Environment, Safety and Resource Valorization in the Laboratory for Reactions and Chemical Engineering at Université de Lorraine - CNRS (France). She focuses on the synthesis of Ni products from biomass, from the bench to the pilot scale.

James Vaughan is Senior Lecturer in Hydrometallurgy and Director of the UQ RTA Bauxite & Alumina Technology Centre at The University of Queensland (Australia). He specializes in Ni hydrometallurgy and holds several patents on process improvements.

Jean-Louis Morel is Professor in Environmental Biology at the Université de Lorraine (France), where he teaches soil and environmental sciences. He created, and until 2012, led the Laboratory for Soil and Environment at the University of Lorraine and INRA. His group has been working on phytoremediation for 20 years and he has also developed research on urban soils (he is chairman of the International Working Group SUITMA)

Guillaume Echevarria is Professor in soil biogeochemistry at the Université de Lorraine (France) and Head of the Phytoremediation group at Laboratory for Soil and Environment (LSE), where his research focuses on soil and rhizosphere biogeochemistry of trace elements, metal hyperaccumulation and optimization of phytoextraction.

Bruno Fogliani is the Deputy Director of the New Caledonian Agronomic Institute, and was previously Assistant Professor at the University of New Caledonia. He coordinates conservation, revegetation and ecological restoration projects in New Caledonia.

Rongliang Qiu is Professor and Dean of the School of Environmental Science and Engineering at Sun Yat-sen (Zhongshan) University, Guangzhou (China), and Director of the Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation.

David Mulligan is Professor and Director of the Centre for Mined Land Rehabilitation at The University of Queensland (Australia). Over the past 20 years he has led scientific research to support decisions made to minimize the environmental risks by the mining and mineral processing industries both in Australia and overseas.

■ ACKNOWLEDGMENTS

We thank The University of Queensland (Australia) for hosting the "Phytomining Workshop: from discovery to full-scale application" on 21−22 July 2014 in Brisbane. We thank the workshop participants for constructive discussions that sharpened our views on future directions of phytomining/agromining, and acknowledge the insights provided by Evgueni Jak and Jeff Chen about the pyrometallurgical options for processing bio-ore.

■ REFERENCES

(1) *Trends in the Mining and Metals Industry*; International Council on Mining and Metals (ICMM): London, UK, 2012.

(2) Bian, Z.; Miao, X.; Lei, S.; Chen, S.-E.; Wang, W.; Struthers, S. The challenges of reusing mining and mineral-processing wastes. *Science* **2012**, *337* (6095), 702−703 DOI: 10.1126/science.1224757.

(3) Mudd, G. M. Historical trends in base metal mining: backcasting to understand the sustainability of mining. In *Proceedings of the 48th Annual Conference of Metallurgy*; Canadian Metallurgy Society: Sudbury, Ontario, Canada, 2009.

(4) Baxter, I.; Dilkes, B. P. Elemental profiles reflect plant adaptations to the environment. *Science* **2012**, *336* (6089), 1661−1663 DOI: 10.1126/science.1219992.

(5) Jaffré, T.; Brooks, R. R.; Lee, J.; Reeves, R. D. *Sebertia acuminata*: A hyperaccumulator of nickel from New Caledonia. *Science* **1976**, *193*, 579−580 DOI: 10.1126/science.193.4253.579.

(6) Van der Ent, A.; Baker, A. J. M.; Reeves, R. D.; Pollard, A. J.; Schat, H. Hyperaccumulators of metal and metalloid trace elements: Facts and fiction. *Plant Soil* **2012**, *362*, 319−334.

(7) Reeves, R. D.; Baker, A. J. M. Metal accumulating plants. In *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment*; Raskin, I.; Ensley, B. D. Eds.; Wiley & Sons: New York, 2000; 193−229.

(8) Reeves, R. D. Tropical hyperaccumulators of metals and their potential for phytoextraction. *Plant Soil* **2003**, *249*, 57−65.

(9) Chaney, R. L. Plant uptake of inorganic waste constituents. In *Land Treatment of Hazardous Wastes*; Parr, J. F., Marsh, P. B., Kla, J. M., Eds.; Noyes Data Corp.: Park Ridge, NJ, 1983, 50−76.

(10) Chaney, R. L.; Angle, J. S.; Baker, A. J. M.; Li, Y.-M. *Method for Phytomining of Nickel, Cobalt and Other Metals from soil*. US Patent 1998, 5, 711,784.

(11) Guillot, S.; Hattori, K. Serpentinites: Essential roles in geodynamics, arc volcanism, sustainable development, and the origin of life. *Elements* **2013**, *9*, 95−98 DOI: 10.2113/gselements.9.2.95.

(12) Echevarria, G.; Massoura, S.; Sterckeman, T.; Becquer, T.; Schwartz, C.; Morel, J. L. Assessment and control of the bioavailability of nickel in soils. *Environ. Toxicol. Chem.* **2006**, *25*, 643−651.

(13) Reeves, R. D.; Baker, A. J. M.; Borhidi, A.; Berazaín, R. Ni hyperaccumulation in the serpentine flora of Cuba. *Ann. Bot.* **1999**, *83*, 29−38.

(14) Jaffré, T.; Pillon, Y.; Thomine, S.; Merlot, S. The metal hyperaccumulators from New Caledonia can broaden our understanding of nickel accumulation in plants. *Front. Plant. Sci.* **2013**, *4*, 279 DOI: 10.3389/fpls.2013.00279/abstract.

(15) Reeves, R. D.; Adigüzel, N. The nickel hyperaccumulating plants of the serpentines of Turkey and adjacent areas: a review with new data. *Turk. J. Biol.* **2008**, *32*, 143−153.

(16) Jaffré, T.; Schmid, M. Accumulation du nickel par une Rubiacée de Nouvelle-Calédonie, *Psychotria douarrei* (G. Beauvisage) Däniker. *Compt. Rendus Acad. Sci., Paris* **1974**, *278*, 1727−1730.

(17) Chaney, R. L.; Angle, J. S.; Broadhurst, C. L.; Peters, C. A.; Tappero, R. V.; Sparks, D. L. Improved understanding of hyperaccumulation yields commercial phytoextraction and phytomining technologies. *J. Environ. Qual.* **2007**, *36*, 1429−1443.

(18) Zhang, X.; Houzelot, V.; Bani, A.; Morel, J. L.; Echevarria, G.; Simonnot, M.-O. Selection and combustion of nickel-hyperaccumulators for the phytomining process. *Int. J. Phytoremed.* **2014**, *16*, 1058−1072 DOI: 10.1080/15226514.2013.810585.

(19) Losfeld, G.; de La Blache, V.; Escande, V.; Grison, C. Zinc hyperaccumulating plants as renewable resources for the chlorination process of alcohols. *Green Chem. Lett. Rev.* **2012**, *5* (3), 451−456 DOI: 10.1080/17518253.2012.667157.

(20) Escande, V.; Renard, B.-L.; Grison, C. Lewis acid catalysis and Green oxidations: sequential tandem oxidation processes induced by Mn-hyperaccumulating plants. *Environ. Sci. Pollut. Res.* **2014**, *1−20*. DOI: 10.1007/s11356-014-3631-z.

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780

(21) Wood, B. W.; Chaney, R.; Crawford, M. Correcting micronutrient deficiency using metal hyperaccumulators: *Alyssum* biomass as a natural product for nickel deficiency correction. *HortScience.* **2006**, *41* (5), 1231−1234.
(22) Bañuelos, G. S.; Arroyo, I.; Pickering, I. J.; Yang, S. I.; Freeman, J. L. Selenium biofortification of broccoli and carrots grown in soil amended with Se-enriched hyperaccumulator *Stanleya pinnata*. *Food Chem.* **2015**, *166* (C), 603−608 DOI: 10.1016/j.foodchem.2014.06.071.
(23) Bani, A.; Echevarria, G.; Sulçe, S.; Morel, J. L. Improving the agronomy of *Alyssum murale* for extensive phytomining: A five-year field study. *Int. J. Phytoremed.* **2015**, *17*, 117−127.
(24) Nicks, L. J.; Chambers, M. F. A pioneering study of the potential of phytomining for Ni. In *Plants that Hyperaccumulate Heavy Metals*; Brooks, R. R., Ed.; CAB International: Wallingford, Oxon, UK, 1998, 313−325.
(25) Robinson, B.; Chiarucci, A.; Brooks, R.; Petit, D.; Kirkman, J.; Gregg, P.; De Dominicis, V. The nickel hyperaccumulator plant *Alyssum bertolonii* as a potential agent for phytoremediation and phytomining of Ni. *J. Geochem. Explor.* **1997**, *59*, 75−86.
(26) Robinson, B. H.; Brooks, R. R.; Howes, A. W.; Kirkman, J. H.; Gregg, P. E. H. The potential of the high-biomass nickel hyperaccumulator *Berkheya coddii* for phytoremediation and phytomining. *J. Geochem. Explor.* **1997**, *60*, 115−126.
(27) Losfeld, G.; Escande, V.; Jaffré, T.; L'Huillier, L.; Grison, C. The chemical exploitation of nickel phytoextraction: an environmental and economic opportunity for New Caledonia. *Chemosphere* **2012**, *89*, 907−910.
(28) Barbaroux, R.; Plasari, E.; Mercier, G.; Simonnot, M. O.; Morel, J. L.; Blais, J. F. A new process for nickel ammonium disulfate production from ash of the hyperaccumulating plant *Alyssum murale*. *Sci. Total Environ.* **2012**, *423*, 111−119.
(29) Van der Ent, A.; Baker, A. J. M.; van Balgooy, M. M. J.; Tjoa, A. Ultramafic Ni laterites in Indonesia (Sulawesi, Halmahera): Mining, nickel hyperaccumulators and opportunities for phytomining. *J. Geochem. Explor.* **2013**, *128*, 72−79 DOI: 10.1016/j.gexplo.2013.01.009.
(30) Li, Y.-M.; Chaney, R. L.; Brewer, E.; Roseberg, R. J.; Angle, J. S.; Baker, A. J. M.; Reeves, R. D.; Nelkin, J. Development of a technology for commercial phytoextraction of nickel: Economic and technical considerations. *Plant Soil* **2003**, *249*, 107−115.
(31) Li, Y.-M.; Chaney, R. L.; Brewer, E. P.; Angle, J. S.; Nelkin, J. P. Phytoextraction of nickel and cobalt by hyperaccumulator *Alyssum* species grown on Ni-contaminated soils. *Environ. Sci. Technol.* **2003**, *37*, 1463−1468.
(32) Losfeld G.; L'Huillier L.; Fogliani B.; McCoy S.; Grison C.; Jaffré T. Leaf-age and soil-plant relationships: key factors for reporting trace-elements hyperaccumulation by plants and design applications. *Environ. Sci. Pollut Res.*, **2014**. In press. DOI: 10.1007/s11356-014-3445-z.
(33) Bani, A.; Echevarria, G.; Montargès-Pelletier, E.; Gjoka, F.; Sulçe, S.; Morel, J. L. Pedogenesis and nickel biogeochemistry in a typical Albanian ultramafic toposequence. *Environ. Monitor. Assess.* **2014**, *186*, 4431−4442.
(34) Losfeld G.; Mathieu R.; L'Huillier L.; Fogliani B.; Jaffré T.; Grison C.; Phytoextraction from mine spoils: insights from New Caledonia. *Environ. Sci. Pollut Res.* **2014**, DOI: 10.1007/s11356-014-3866-8.
(35) Gall, J. E.; Rajakaruna, N. The physiology, functional genomics, and applied ecology of heavy metal-tolerant Brassicaceae In *Brassicaceae*; Lang, M., Ed.; Nova Science Publishers, Inc., 2013; ISBN: 978-1-62808-856-4.
(36) Van der Ent, A.; Erskine, P.; Sumail, S. Ecology of nickel hyperaccumulator plants from ultramafic soils in Sabah (Malaysia). *Chemoecology* **2015**, in press.
(37) Boominathan, R.; Saha-Chaudhury, N. M.; Sahajwalla, V.; Doran, P. M. Production of nickel bio-ore from hyperaccumulator plant biomass: Applications in Phytomining. *Biotechnol. Bioeng.* **2004**, *86*, 243−250.
(38) Keller, C.; Ludwig, C.; Davoli, F.; Wochele, J. Thermal treatment of metal-enriched biomass produced from heavy metal phytoextraction. *Environ. Sci. Technol.* **2005**, *39*, 3359−3367.
(39) Koppolu, L.; Agblevor, F. A.; Clements, L. D. Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator biomass. *Biomass Bioenergy* **2003**, *25*, 651−663.
(40) Oxley, A.; Barcza, N. Hydro−pyro integration in the processing of Ni laterites. *Min. Eng.* **2013**, *54*, 2−13.
(41) Caron M. Process for recovering values from nickel and nickel-cobalt ores. 1924, US Patent # 1,487,145.
(42) Watanabe, T.; Ono, S.; Arai, H.; Matsumori, T. Direct reduction of garnierite ore for production of ferro-nickel with rotary kiln at Nippon Yakin Kogyo Co. Ltd., Oheyama Works. *Int. J. Min. Process.* **1987**, *19*, 173−187.
(43) Bergman, R. A. Nickel production from low-iron laterite ores: process descriptions. *CIM Bull.* **2003**, *96* (1072), 127−138.
(44) Barbaroux, R.; Mercier, G.; Blais, J. F.; Morel, J. L.; Simonnot, M.-O. A new method for obtaining nickel metal from the hyperaccumulator plant *Alyssum murale*. *Sep. Purif. Technol.* **2011**, *83*, 57−65.
(45) Carlson, E. T.; Simons, C. S. Acid leaching Moa Bay's nickel. *J. Metals.* **1960**, *3*, 206−213.
(46) Caron, M. H. Fundamental and practical factors in ammonia leaching of nickel and cobalt ores. Transactions AIME. *J. Metals* **1950**, *188*, 67−90.
(47) Forward, F. A. Ammonia pressure leach process for recovering nickel, copper and cobalt from Sherritt Gordon nickel sulphide concentrates. *Trans. CIM 56* **1953**, 373.
(48) Harvey, R.; Hannah, R.; Vaughan, J. Selective precipitation of mixed nickel−cobalt hydroxide. *Hydrometallurgy* **2011**, *105* (3), 222−228.
(49) Vaughan, J.; Hawker, W.; Keating, T.; Cox, J. Engineering aspects of the selective acid leaching process for refining mixed nickel-cobalt hydroxide. In *4th Annual Nickel-Cobalt-Copper Event, ALTA Metallurgical Services*, 2013; pp 473−484.
(50) Mercier G.; Barbaroux R.; Plasari E.; Blais J. F. Simonnot M.-O.; Morel J. L. Procédé de production d'un sel de sulfate double de nickel et d'ammonium à partir de plantes hyperaccumulatrices. 2011. WO 2012/103651 A1.
(51) Kirk, A. H. P. *Recovery of nickel from hyperaccumulator plant ash.* M.Sc. Thesis, Massey University, Palmerston North, N.Z.,2000.

DOI: 10.1021/es506031u
Environ. Sci. Technol. 2015, 49, 4773−4780