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Towards financially viable phytoextraction and production of plant-based palladium catalysts

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Title: Towards financially viable phytoextraction and production of plant-based palladium catalysts

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ABSTRACT

Although a promising technique, phytoextraction has yet to see significant commercialization. Major limitations include metal uptake rates and subsequent processing costs. However, it has been shown that liquid-culture-grown Arabidopsis can take up and store palladium as nanoparticles. The processed plant biomass has catalytic activity comparable to that of commercially available catalysts, creating a product of higher value than extracted bulk metal. We demonstrate that the minimum level of palladium in Arabidopsis dried tissues for catalytic activity comparable to commercially available 3% palladium-on-carbon catalysts was achieved from dried plant biomass containing between 12 and 18 $g \cdot kg^{-1}$ Pd. To advance this technology, species suitable for in-the-field application: mustard, miscanthus and sixteen willow species and cultivars, were tested. These species were able to grow, and take up, palladium from both synthetic and mine-sourced tailings. Although levels of palladium accumulation in field-suitable species are below that required for commercially available 3% palladium-on-carbon catalysts, this study both sets the target, and is a step towards, the development of field-suitable species that concentrate catalytically-active levels of palladium. Life cycle assessment on the phytomining approaches described here indicates that the use of plants to accumulate palladium for industrial applications has the potential to decrease the overall environmental impacts associated with extracting palladium using present-day mining processes.

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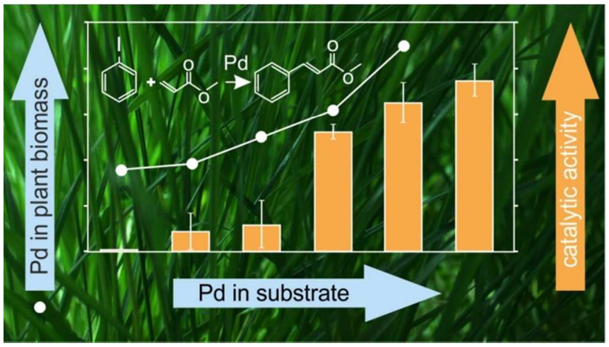

INTRODUCTION

A number of plant species have been found to take up gold and deposit it as gold nanoparticles (NPs) in their tissues[1], a phenomenon that has also been demonstrated for platinum group metals (PGMs) in Arabidopsis (*Arabidopsis thaliana*)[2]. Following a low-energy, pyrolysis treatment, the metal NP-containing plant biomass derived material can have catalytic activity comparable to that of commercially available catalysts and, critically, creates a product of higher value than the extracted bulk metal alone. These features present a potentially financially viable opportunity for the phytoextraction of these metals from PGM-rich sources and mine wastes[3].

Phytoextraction was initially described in 1995 as 'the use of metal-accumulating plants to remove toxic metals from soil'[4], and expanded in 2001 as 'the utilization of plants to transport and concentrate metals from the soil into the harvestable parts of roots and above-ground shoots'[5]. However, phytoextraction has now been around for several decades and, although a promising technique, it has yet to see significant commercialization [6]. A key factor for successful phytoextraction is that the value of the metal extracted needs to exceed the cost of the recovery method. In the case of PGMs, the bulk value is relatively high. However, the costs of phytoextraction and subsequent harvesting, processing and smelting can still be inhibitory. By exploiting the natural ability of plants to accumulate PGMs as NPs, phytoextraction may be financially viable[7].

The material potentially available for phytomining is the waste material (the ‘tailings’) that is separated from the valuable metals in mineral ores. Depending on the efficiencies of separation, tailings can contain variable amounts of a variety of metals, some valuable, and some toxic. Tailings, which typically consist of highly liquid slurries of silicates and other rock debris, are deposited in ponds during active ore processing and subsequently stabilized for long-term storage upon mine closure.

So far, the production of biomass which has catalytic activity has only been demonstrated in non-field conditions, using the non-crop species Arabidopsis[2]. There is a need to develop this technology in species suitable for field testing. While plants can grow in a diverse array of challenging environments, land for phytoextraction often contains deleterious traits, such as toxic levels of metals, sub-optimal pH, low organic matter content and low nutrient content. These properties result in suboptimal plant growth and low plant biomass. Even so, some species can be well-suited to the harsher conditions found in metal-rich land. Willows (*Salix* sp.), for example, are able to withstand concentrations of metals (copper, cadmium, nickel and zinc) considered toxic to many other plant species and can achieve high biomass in relatively poor soils[8-12]. Additionally, there is considerable genetic diversity within the willow genus that could be exploited to develop cultivars optimized for the environmental conditions present at a field site[13]. Other species with phytoextraction potential include miscanthus (*Miscanthus* x *giganteus*)[14] and switchgrass (*Panicum virgatum*)[15,16]. These species are currently grown as bioenergy crops, and the necessary agricultural infrastructure for growing and harvesting is already in place[17].

At the biological level, a major factor limiting the realization of phytoextraction is the low levels of PGMs taken up naturally by the plant. Significant progress towards the commercialization of nickel phytoextraction is being made with the use of hyperaccumulator species such as *Alyssum* sp.[18,19]; but, only a limited number of elements are known to be concentrated by hyperaccumulator species, and no suitable species have yet been found for PGMs.

At the physico-chemical level, poor metal uptake is linked to the chemical form of the metal. In the case of PGMs, these elements exist in field locations predominantly as chemically inert, zero-valent forms, or are bound to minerals. A highly effective recovery method for gold and PGMs is the use of cyanide for solubilization[1].

However, irresponsible use of cyanide as a lixiviant in the mining industry has resulted in examples of serious, large-scale environmental pollution where toxic cyanide-containing complexes such as ferri- and ferro-cyanide, have accumulated in soils[20, 21]. Cyanide use is now tightly regulated in many countries, but is still the principal method used by the mining industry to recover gold, and silver, with this use representing approximately 15% of cyanide consumption globally[22].

To achieve palladium NP formation in plants, and catalytic activity in the subsequently processed biomass, an as-yet-unknown threshold concentration of palladium in the tissues needs to be exceeded. In the present study, we have aimed to establish the minimum concentration of palladium needed in dry plant biomass to achieve catalytic activity comparable to that of commercially available 3% palladium-on-carbon catalysts. As an extension to previous studies in Arabidopsis[2,23], we have extrapolated the experiments to plant species suitable for in-field application, including miscanthus and willow. The levels of palladium uptake by these species have been compared with target levels determined using our model Arabidopsis system.

Life cycle assessment (LCA) is a methodology that accounts for the environmental impacts associated with products and processes along the lifecycle of a material. In the mining industry, LCA has been utilized extensively[24-28], and its application to understand the environmental implications of phytoaccumulation; and to highlight the related potential for opportunities of metal recovery from mine tailings, have been previously proposed[3]. Recently, LCA has been applied for nickel phytomining[19]. Here, we have used LCA to test if our phytomining approaches have the potential to decrease the overall environmental impacts associated with the current mining processes.

MATERIALS AND METHODS

Synthetic and mine-collected tailings for plant growth

Synthetic, palladium-rich tailings were created for the initial stages of this research, based on protocols for synthetic gold tailings, which have been extensively used for gold uptake experiments[29]. The elemental composition of the synthetic tailings, prior to dosing with palladium, is shown in Table S1. Use of synthetic tailings enabled the concentration of palladium to be controlled in a background material that did not contain phytotoxic levels of metals, such as nickel, that are often present in mine samples and wastes. The use of synthetic tailings also meant that variables underpinning the process of palladium-uptake by plants (*i.e.*, lixiviant and metal concentration in soil) could be explored at a relatively low cost prior to using genuine mine wastes, which are more difficult to acquire in significant quantities. Mine-collected tailings were obtained from North American Palladium. Table S2 shows the elemental profiles, and Table S3 the gold and PGM profiles, of this material. Mustard plants were also grown on equivalent (v/v) amounts of vermiculite in palladium-free control experiments.

Growing Arabidopsis, mustard, miscanthus, and willow

Arabidopsis plants, ecotype Col0, were grown in liquid culture as described elsewhere[2]. For mustard, plastic P2 trays containing 1 kg of synthetic, or mine-collected, tailings were sown with 4.2g of mustard (*Brassica alba* L., cultivar Rivona) seed. The trays were placed in a glasshouse and watered as required. To measure the effect of a palladium solubilizing treatment on the uptake of palladium by the mustard plants, a potassium cyanide treatment was applied as follows: After seven days in the glasshouse, 100 ml of potassium cyanide (1 mg ml^{-1} cyanide) was applied to selected P2 trays, the plants were then harvested 24 h later and dried overnight at 60 °C.

Miscanthus (*Miscanthus* x *giganteus*) rhizomes and willow rods (*Salix* sp.; Yorkshire Willow Ltd, UK) were rooted in sand for four weeks. Rooted, in-leaf plants were transferred to 1.5l pots containing either 1 kg (for miscanthus), or 1.5 kg (for willow), of synthetic tailings or mine-collected tailings. A general purpose fertilizer was added weekly according to the manufacturer's instructions and the plants grown for four weeks. To measure the effect of a palladium solubilizing treatment on the uptake of palladium by the plants, half of the plants were dosed with 100 ml (for miscanthus), or 150 ml (for willow) of potassium cyanide (1 mg ml^{-1} cyanide). One week later, all the plant roots and shoots were harvested and dried overnight at 60 °C.

ICP-MS analysis

Plant tissues were ground to a fine powder using ball bearings in an end-over-end mixer. To 0.5 g of tissue, 5 ml of aqua regia (3:1 hydrochloric acid (37%): nitric acid (70%)) was added. The samples were heated for 2 h at 70 °C then diluted to 50 ml with ultrapure water and filtered using a 0.45 μm filter. Metal content was determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700x and calibrated against multi-element and precious calibration standards (Agilent Ltd).

Testing catalytic activity

To produce the catalyst, dried plant material was pyrolysed using the Barnstead Thermolyte 6000 Furnace under N_2 (1 K m^{-1}) at 573 K (300 °C) as described[2]. For the reaction of iodobenzene with methyl acrylate, 5.00 mmol iodobenzene, 6.25 mmol methyl acrylate, and 6.25 mmol triethylamine in 1.75 mL of N-methyl-2-pyrrolidone, were added to a 25 ml round bottom flask. Once the flask had been heated to 393 K, 10 mg of palladium catalyst were added. For control experiments, no catalyst was added. Control reactions with 10 mg of pyrolysed, palladium-free plant material were also run. The reaction was allowed to proceed for 2 hours at 393 K and the levels of substrate and product measured using a Gas Chromatography-Flame Ionization Detector (GC-FID) using diethyl succinate as a standard.

Life cycle assessment comparisons

Details of the two LCA models developed are shown in Supplementary Material.

Two scenarios were developed to conduct a comparative LCA. The first scenario compared the environmental impacts associated with the production of Arabidopsis catalyst material relative to the commercial route for activated carbon-palladium catalysts. A second scenario modeled the phytoaccumulation of palladium from mine tailings and the processing of the biomass for the production of valuable products such as bio-gas, bio-oil, and bio-char containing palladium.

The models were carried out in accordance with the ISO 14040 guidelines, and developed using the SimaPro 8.0 software. To enable a comparative LCA study with real systems, the investigated processes were scaled up to a hypothetical facility based on extrapolation from laboratory scale studies and literature data. Modules of inventory data for raw material and chemical production, heat generation and grid electricity production mix, and transportation were derived from the ecoinvent 3.0 database. Direct and indirect mass and energy flows were accounted for according to the system boundaries set for the two systems investigated. A selection of standardized indicators was used for the assessment of environmental impacts to midpoint and endpoint categories, and is shown in Table S4. A detailed description of the two LCA scenarios is reported in the Supplementary Material.

RESULTS

In previous studies, catalytic activity was recorded for pyrolysed Arabidopsis biomass containing 5 g·kg^{-1} palladium. The biomass was derived from plants grown in liquid culture and dosed with 10 mM potassium tetrachloropalladate[2]. This experimental system was replicated in the current work as a model in which metal doses could be accurately controlled in a small-scale system. Using this model, the relationship between the *in planta* palladium concentration and catalytic activity of liquid-culture grown Arabidopsis plants dosed with a range of palladium concentrations (from 0.5 mM to 1 mM of potassium tetrachloropalladate) was investigated.

Testing catalytic activity in Arabidopsis

The concentration of palladium in the dried Arabidopsis material was found to increase from 0.18 to 18 g kg^{-1} palladium with increasing concentrations (0.5 mM to 1 mM respectively) of potassium tetrachloropalladate (Figure 1). For pyrolysis of the plant biomass, the temperature chosen was 300 °C. This was based on an earlier study which demonstrated that at this temperature the mean nanoparticle diameter and frequency distributions were unaltered, with the remaining biomass comprising predominantly carbon and oxygen[2]. Previous studies using thermal gravimetric-infrared (TGIR) analysis of the post-pyrolysis material showed a 45% mass loss between 100 - 300°C, attributed to the loss of water and carbon dioxide[2]. Catalytic activity was tested using the Heck reaction between iodobenzene and methyl acrylate to form *trans*-methyl cinnamate. Figure 1 shows that there was no catalytic activity from plants dosed with 0.5 mM potassium tetrachloropalladate. However, product was observed from plants dosed with concentrations of 0.6 mM and above, with product yields increasing with higher concentrations of potassium tetrachloropalladate. Palladium on carbon 3% (Pd/C), a commercially available palladium catalyst, was used to compare with the performance of the pyrolysed biomass. The yields obtained from plants dosed with 1 mM palladium were comparable to those obtained by Pd/C (64.9 % and 74.9 % respectively).

The results presented in Figure 1 indicate a palladium concentration of between 12 and 18 $g \cdot kg^{-1}$ in dried Arabidopsis biomass is the target level above which catalytic activity would be comparable to that of commercially available catalysts. In order to assess if this target could be reached in species more suited to in-field application, mustard, willow, and miscanthus were tested in studies using synthetic tailings. To increase uptake by solubilizing the palladium, potassium cyanide was used. While there is currently no data available for palladium, a review comparing gold uptake by a number of plant species treated with a range of cyanide-based compounds indicated that potassium and ammonium thiocyanate yield the highest levels of gold uptake[1]. For *Brassica juncea*, the highest levels of uptake were observed using potassium cyanide[1]. As mustard and Arabidopsis are also in the Brassicaceae, and willow has been shown to effectively remediate potassium cyanide[40], this compound was chosen as the lixiviant.

Growth and palladium uptake by mustard

The biomass of mustard plants grown on synthetic tailings containing up to 50 $mg \cdot kg^{-1}$ palladium was not significantly different to the biomass of plants grown on the no-Pd control material, but the biomass of plants grown on synthetic tailings containing 100 $mg \cdot kg^{-1}$ palladium was a third lower than in the absence of palladium ($p < 0.05$; Figure 2A). The addition of cyanide significantly ($p < 0.001$) increased the uptake of palladium by 26, 20, 30, and 23-fold in plants grown in synthetic tailings containing 5, 10, 50, and 100 $mg \cdot kg^{-1}$ palladium, respectively (Figure 2B and Table S5). The pie charts shown in Figure S1 and data in Table S5, illustrate both the effect of increasing levels of palladium on the uptake of other metals present in the synthetic tailings and the effect of the exogenous application of cyanide. The mustard plants grown on the synthetic tailings in the absence of cyanide or palladium contained predominantly zinc and copper. With increasing palladium concentration, and in the absence of cyanide, levels of palladium in the plant increased predominantly at the expense of copper, whereas in the presence of cyanide, levels of copper, which is also solubilized by cyanide, were less affected.

However, mine sourced materials often contain other elements at concentrations inhibitory to plant growth. To test growth and palladium uptake in this inhibitory background, PGM-rich mine-collected tailings from North American Palladium were used. The mine-collected tailings contained approximately 20 mg·kg^{-1} palladium; a concentration that the synthetic tailings study (Figure 2) indicated was below the phytotoxicity level. In agreement with this result, no toxicity symptoms were seen in the mustard plants grown on the mine material (Figure S2). The biomass of seven-day-old seedlings grown on the mine-collected tailings was higher than those grown on vermiculite alone. We speculate that this could be due to additional nutrients present in the mine-collected tailings that were lacking in the vermiculite. As seen with the palladium-dosed synthetic tailings experiment (Figure 2), the addition of cyanide significantly ($p < 0.001$) increased the uptake of palladium by 89, 333, and 8.4-fold in plants grown in mine-collected tailings containing 5, 10, and 20 mg·kg^{-1} palladium, respectively (Figure S2).

Growth and palladium uptake by miscanthus and willow

Given the dramatic increase in the ability of mustard to take up palladium conferred by the application of cyanide, the potential of the more field-suitable species miscanthus and willow was next investigated. For miscanthus, the application of cyanide had no effect on the biomass of root or shoot tissues (results not shown), whereas aerial tissues of the cyanide treated plants had almost 500-fold more palladium than those from untreated plants grown on synthetic tailings (undosed plants contained 0.0013 ± 0.0001 $g \cdot kg^{-1}$; cyanide-treated plants contained 0.505 ± 0.039 $g \cdot kg^{-1}$ palladium).

For the willow experiments, a fast-growing, bioenergy hybrid of *Salix viminalis*, 'Super Willow' was chosen. As seen with miscanthus, *S. viminalis* 'Super Willow' leaf biomass was unaltered by the cyanide treatment. At the lower concentrations of palladium-dosed synthetic tailings (5 and 10 $mg \cdot kg^{-1}$), leaf biomass was not significantly affected, however, at the higher concentrations of palladium (50 and 100 $mg \cdot kg^{-1}$) total leaf biomass significantly decreased ($p < 0.05$; Figure 3A). The application of cyanide dramatically, and significantly ($p < 0.001$), increased the uptake of palladium by 126, 127, 19 and 23-fold in plants grown at 5, 10, 50 and 100 $mg \cdot kg^{-1}$ palladium respectively (Figure 3B). In agreement with the data for mustard, (Figure 2B and Table S5), the cyanide treatment was observed to be less effective at promoting palladium uptake at palladium concentrations above 20 $mg \cdot kg^{-1}$.

Salix viminalis ‘Super Willow’ was grown on mine-collected tailings and growth and palladium uptake measured. Figure S3A demonstrates that the application of cyanide did not affect leaf or stem biomass, yet it dramatically, and significantly ($p < 0.001$), increased the levels of palladium in the leaf and stem by 65 and 49-fold, respectively (Figure S3B and C). The effect of the cyanide treatment moderately increased uptake of other metals present in the mine-collected tailings (cobalt, nickel, copper, cadmium and lead), with the greatest effect observed for copper: the treatment of *S. viminalis* ‘Super Willow’ with cyanide increased copper levels by 9.5 and 12.5-fold, respectively, in the leaves and stems (Figure S3 and Table S6).

There is a wealth of genetic variability for metal uptake within the willow genus[13]. To investigate the variation in palladium uptake, 16 different species and cultivars of willow were selected. Figure 4A shows the variation in leaf and stem dry weights. Across the 16 species and cultivars of willow, there was an 11.5 and 4.7-fold variation in leaf and stem biomass, respectively. *Salix alba*, *S. candida,* and *S. purpurea* (cv. Green Dicks) had consistently high leaf and stem biomass. In this experiment, the concentration of palladium in the leaves of *S. viminalis* was higher (Figure 4B, 0.313 $g \cdot kg^{-1}$) than in the previous experiment (Figure 3B, 0.094 $g \cdot kg^{-1}$), the discrepancy may have resulted from different environmental conditions in the glasshouse during the experiment for Figure 4: warmer, sunnier conditions would have increased transpiration rates and could lead to enhanced palladium uptake. Overall, across the 16 species and cultivars, there were 6.7 and 4.5-fold variations, respectively, in leaf and stem palladium content, with 6-fold more palladium present in the leaves than in the stems. Of the two species with consistently high palladium levels, *S. nigricians* and *S. purpurea* (cv. Green Dicks), the latter species also produced high leaf and stem biomass.

The palladium concentration in the non-Arabidopsis species tested in this work was below the 12 $g \cdot kg^{-1}$ threshold established for catalytic activity. However, preliminary testing of the mustard, miscanthus, and willow (cv. Green Dicks) containing respectively 0.5, 1.5, and 0.8 $g.kg^{-1}$ palladium post-pyrolysis resulted in catalytic yields of 5, 7, and 1.2 % respectively.

Life Cycle Assessments

To conduct the LCA, midpoint impact categories for the processes were defined (Table S4). This translated the total impact of a process into individual environmental themes. Figure 5A compares the commercial production route for Pd/C with that using liquid-culture grown

Arabidopsis for each selected midpoint impact category. The commercial production route for the Pd/C catalyst has higher impacts for climate change, metal depletion, fossil depletion, cumulative energy demand, and water scarcity single midpoints. The catalyst material obtained through the Arabidopsis process was found to have greater impacts for those categories associated with outputs to water and terrestrial compartments. Figure 5B shows aggregated scores for the two processes after weighting each (midpoint) impact category to damage impact categories (endpoint) for human health, ecosystems, and resources. Overall, the commercial Pd/C catalyst has a total environmental impact about three times higher than that produced through the Arabidopsis process.

The difference in environmental impacts between the two processes clearly favors the Arabidopsis process. However, phytoaccumulation efficiency is the most relevant parameter in influencing the LCA results. The Arabidopsis process was modeled by assuming that plants are dosed with the same amount of palladium required for the commercial production process. If the Arabidopsis process should require a greater input of palladium, or if part of the non-phytoaccumulated palladium is unrecovered, environmental impacts would increase significantly. Given that the environmental impacts favor the Arabidopsis process over the common production route for the Pd/C catalyst, the use of willow to make a Pd/C-equivalent catalyst is likely to be even more favorable. However, this would rely on the willow accumulating palladium to a level to be commercially viable as a catalyst.

Pyrolysis to 300 ^{o}C under N_2 is used for stabilization of the Arabidopsis Pd/C-equivalent catalyst. Whilst being very simple, this approach is not optimal to maximize value and process large volumes of biomass. Microwave assisted pyrolysis (MAP) is an alternative approach that is being developed as a green technology for use as part of a holistic biorefinery[30, 31].

Using this technique the biomass is stabilized via microwave heating at lower temperatures and shorter times than needed for conventional pyrolysis. In addition to the solid bio-char catalyst, bio-oil and bio-gas are collected during MAP and this not only prevents the release of greenhouse gasses but also brings extra value to the process.

In the second scenario the impacts of bio-gas, bio-oil, and palladium-containing bio-char production from willow biomass (Pd-willow) were compared to the impacts that would derive from the production of the same amount of gas, oil, and palladium from common extraction routes. Figure 6A shows that production of these three products from Pd-willow decreases the overall impact for all midpoint categories, with the exception of particulate matter formation and agricultural land occupation. In most cases, the environmental impacts were reduced by up to 100 %. The environmental benefits associated with the avoided production of natural gas, oil, and palladium concentrate lead to a distinct improvement in total environmental performance, with the avoided damage to resources being the endpoint category for which the best score was derived (Figure 6B). The results of the sensitivity analysis support the confidence of the model.

DISCUSSION

Arabidopsis plants were grown hydroponically and dosed with solutions of potassium tetrachloropalladate, factors chosen to favour palladium uptake, and establish whether palladium concentrations in the biomass would be sufficient to obtain catalytically active material comparable to commercially available 3% carbon on palladium. The studies presented indicate that to obtain catalytically active material comparable to commercially available 3% carbon on palladium, the dried plant biomass, prior to pyrolysis, needs to contain a minimum concentration of between 12 and 18 g·kg^{-1} palladium. At this concentration, we have shown previously that the Arabidopsis tissues contain palladium NPs which confer catalytic activity[2]. We infer that tissues from other species containing above 12 to 18 g·kg^{-1} palladium would also contain palladium nanoparticles, but this should be tested in future studies. In combination with the application of cyanide, the highest concentrations of palladium achieved from plants grown on synthetic tailings in this study were 0.53 g·kg^{-1} for mustard (with a KCN treatment 24 h pre-harvest), and 0.51 and 0.82 g·kg^{-1} palladium (with a KCN treatment 1 week pre-harvest) for miscanthus and willow (cv. Green Dicks), respectively. At these levels, catalytic activity, albeit low (5, 7, and 1.2 % yields, respectively), from subsequently pyrolysed material was observed. However, the levels of palladium accumulated in biomass from KCN-treated plants grown on mine-collected tailings were significantly lower: 0.0085 g·kg-1 for mustard and 0.0142 g·kg-1 for willow leaf. Although not tested, it was considered unlikely that pyrolysed material from the plants grown on mine-collected tailings would yield detectable catalytic activity. The technology developed in these studies is aimed at phytoextracting PGMs from wastes such as mine tailings which have levels of palladium typically between 0.7- 1 mg·kg^{-1}; significantly lower than for the mine-collected tailings used here. Thus, achieving plant biomass with between 12 and 18 g·kg^{-1} palladium is still a significant biotechnological challenge. However, our results demonstrate that in just one week, and following a single, non-optimized, cyanide treatment, the best performing willow cultivar had the biological capacity to take up approximately 10 % of the palladium required to reach the target concentration. Given the extensive genetic resources available in this genus, screening or selective breeding programs would likely identify willow lines with further enhanced palladium uptake ability. Furthermore, this study shows that willows and miscanthus are able to withstand the toxicities present in mine-sourced material; relative to ores and concentrates, tailings and other wastes will likely have correspondingly lower levels of phytotoxic metals. In field scenarios, species such as willow and miscanthus would be grown on significantly larger scale. Harvesting coppiced willow on a three to five year rotation in combination with repeated lixiviant treatments would be predicted to lead to further increases in palladium uptake.

On a global scale, implementing phytoaccumulation in field scenarios would maximize the extraction of valuable forms of palladium and other PGMs from natural deposits. Overall recovery rates of palladium from the processing of virgin ores are estimated at 80-90% [32-35], resulting in considerable losses during comminution and concentration steps: the amount of cumulative palladium lost in mine tailings is estimated to represent about 5% of global reserve and reserve base values[3]. Thus, should palladium phytoaccumulation efficiency increase at levels to be financially viable, the exploitation of mine tailings would have a strong potential for supplementing primary palladium supply. From a perspective of resource conservation and environmental protection, the resulting potential benefits associated with recoverable palladium tailings would be greater still if phytoaccumulation led to lower environmental impacts of mining activity.

Results from the preliminary LCA reported in this paper are limited by the estimates used to enable the scaling of lab-based results up to a hypothetical full-scale facility. However, our analysis suggests that the use of plants to accumulate palladium, either for catalysts, or bio-gas, bio-oil, and palladium-containing bio-char production, as outlined here for willow, has the potential to decrease the overall environmental impacts (*i.e.*, computed as environmental impacts associated with the process, less the environmental burdens resulting from the avoided production of equivalent products such as natural gas or oil) associated with palladium extraction by current mining processes.

Such a net-environmental performance improvement is of particular importance when considering the use of cyanide for palladium phytoaccumulation. In support of the use of cyanide in controlled phytoextraction conditions, it has been shown that plants can degrade cyanide, taking up both free cyanide and iron cyanides and metabolizing them to the amino acid asparagine[36-40]. These findings present the perhaps paradoxical situation whereby the application of cyanide might be the only mechanisms to enable the phytoextraction of PGMs to be financially viable.

However, in addition to environmental concerns, the use of cyanide treatments causes co-solubilization of significant levels of other metals such as gold, copper, and nickel. The presence of these metals in the pyrolysed biomass could affect subsequent catalytic activity[41]. Furthermore, the application of cyanide directly to the land results in the indiscriminate solubilization of the target metal throughout the material. This approach is inefficient for phytoextraction, because much of the solubilized metal is beyond the reach of the roots and is thus lost as leachate. Targeting solubilization to the rhizosphere, a microecological zone closely surrounding the roots, would enable more efficient metal uptake. This is an approach that could perhaps be combined with biomining, using precious metal accumulating bacteria such as *Cupriavidus metallidurans*[42] in the rhizosphere.

Whatever approaches to increase PGM accumulation are tested, there are large areas of land containing increasingly valuable PGM metals reserves that are currently un-vegetated and contain toxic levels of metals and wastes as by-products from the mining industry. The combination of the phytoextraction process, in tandem with phytoremediation to re-vegetate, stabilize and restore ecological diversity, could be a win-win situation for the environment and for catalysis technologies. The approach described here increases the viability of green technologies and aids in promoting the use of biomass to replace fossil fuels.

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FIGURE LEGENDS

Figure 1. Palladium uptake by Arabidopsis plants dosed with a range of concentrations of potassium tetrachloropalladate. Left axis (line), level of palladium in the dried plant biomass; right axis (column), catalytic activity of the pyrolysed plant biomass in the Heck reaction of iodobenzene and methyl acrylate to yield *trans*-methyl cinnamate (for Pd in dried plant material, n = 3 biological replicates ± s.e.m.; for % yield, n = 3 technical replicates ± r.s.d).

Figure 2. Growth and palladium uptake by mustard (*Brassica alba* L.) germinated and grown on synthetic tailings dosed with a range of palladium concentrations. After seven days, seedlings were dosed with 100 $mg\cdot kg^{-1}$ cyanide (in the form of KCN), then harvested 24 h later. A) Biomass of aerial tissues, and B) concentration of palladium in the aerial tissues (n = 6 biological replicates ± s.e.m.).

Figure 3. Growth and palladium uptake by *Salix viminalis*, 'Super Willow' grown on synthetic tailings dosed with a range of palladium concentrations. After four weeks, plants were dosed with 100 $mg\cdot kg^{-1}$ cyanide (in the form of KCN), then harvested after seven days. A) Leaf dry weight, and B) concentration of palladium in the leaf tissues (n = 5 biological replicates ± s.e.m.).

Figure 4. Growth and palladium uptake by a range of willow species (*Salix* sp.). Rooted cuttings were grown for four weeks on synthetic tailings containing 50 $mg\cdot kg^{-1}$ palladium, dosed with 100 $mg\cdot kg^{-1}$ cyanide (in the form of KCN), then harvested after one week. A) Leaf and stem dry weight, and B) concentration of palladium, in the leaf and stem tissues (n = 5 biological replicates ± s.e.m. except *Salix. alba*, *S. chermesina* and *S. alba vitelline* where n = 2).

Figure 5. (A) Characterization results for midpoint categories. (B) Characterization results for endpoint categories; the y-axis reports absolute single points for total damage on resources, ecosystems, and human health according to the Europe ReCiPe H/A method.

Figure 6. (A) Characterization results for midpoint categories. (B) Characterization results for endpoint categories; the y-axis reports absolute single points (1 mPoint = 10^{-3} Point) for total damage on resources, ecosystems, and human health according to the Europe ReCiPe H/A method. Negative values refer to avoided impacts.

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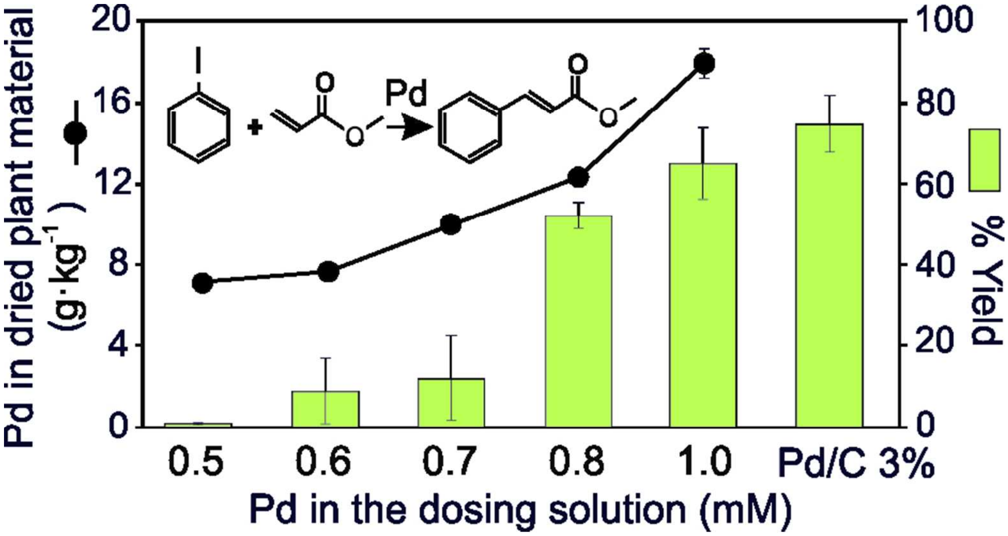

Figure 1. Palladium uptake by Arabidopsis plants dosed with a range of concentrations of potassium tetrachloropalladate. Left axis (line), level of palladium in the dried plant biomass; right axis (column), catalytic activity of the pyrolysed plant biomass in the Heck reaction of iodobenzene and methyl acrylate to yield trans-methyl cinnamate (for Pd in dried plant material, n = 3 biological replicates ± s.e.m.; for % yield, n = 3 technical replicates ± r.s.d).
Figure 1
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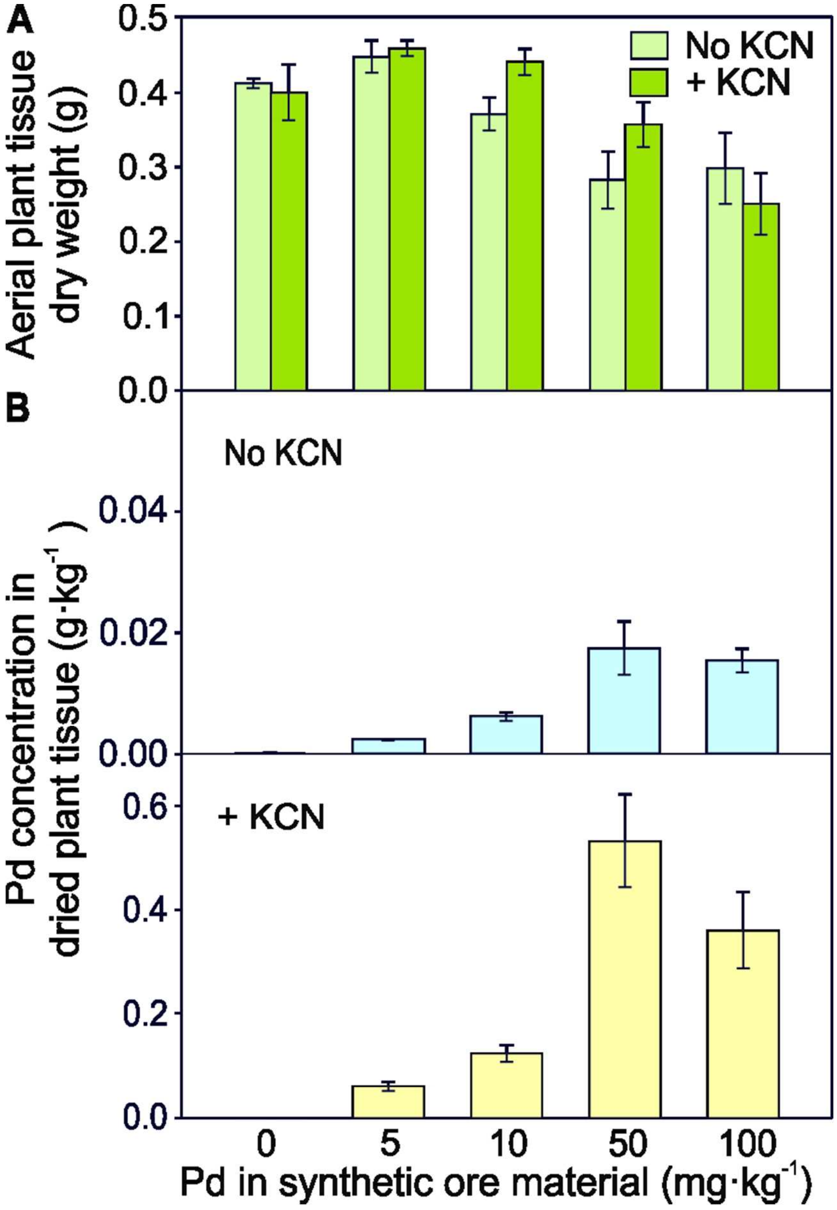

Figure 2. Growth and palladium uptake by mustard (Brassica alba L.) germinated and grown on synthetic tailings dosed with a range of palladium concentrations. After seven days, seedlings were dosed with 100 mg·kg-1 cyanide (in the form of KCN), then harvested 24 h later. A) Biomass of aerial tissues, and B) concentration of palladium in the aerial tissues (n = 6 biological replicates ± s.e.m.).
Figure 2
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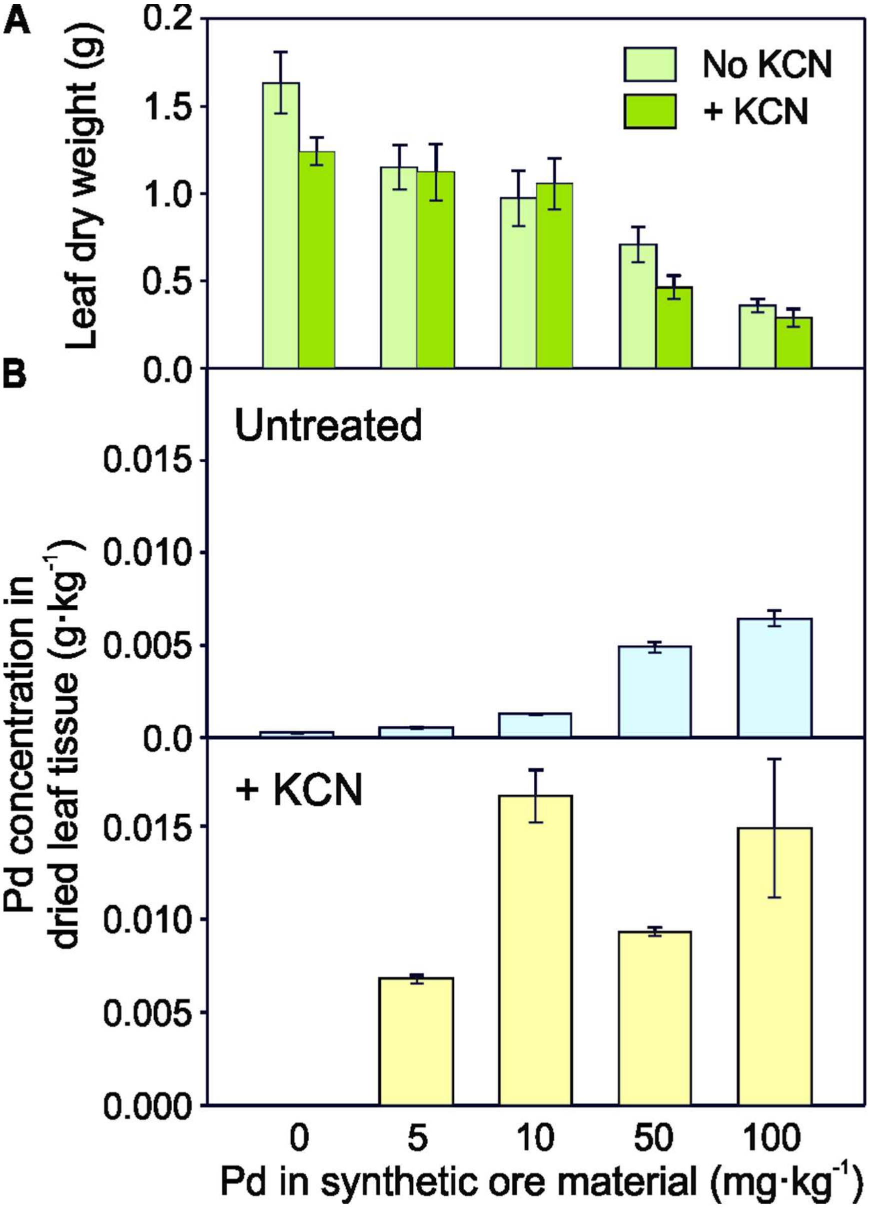

Figure 3. Growth and palladium uptake by Salix viminalis, 'Super Willow' grown on synthetic tailings dosed with a range of palladium concentrations. After four weeks, plants were dosed with 100 mg kg-1 cyanide (in the form of KCN), then harvested after seven days. A) Leaf dry weight, and B) concentration of palladium in the leaf tissues (n = 5 biological replicates ± s.e.m.).
Figure 3
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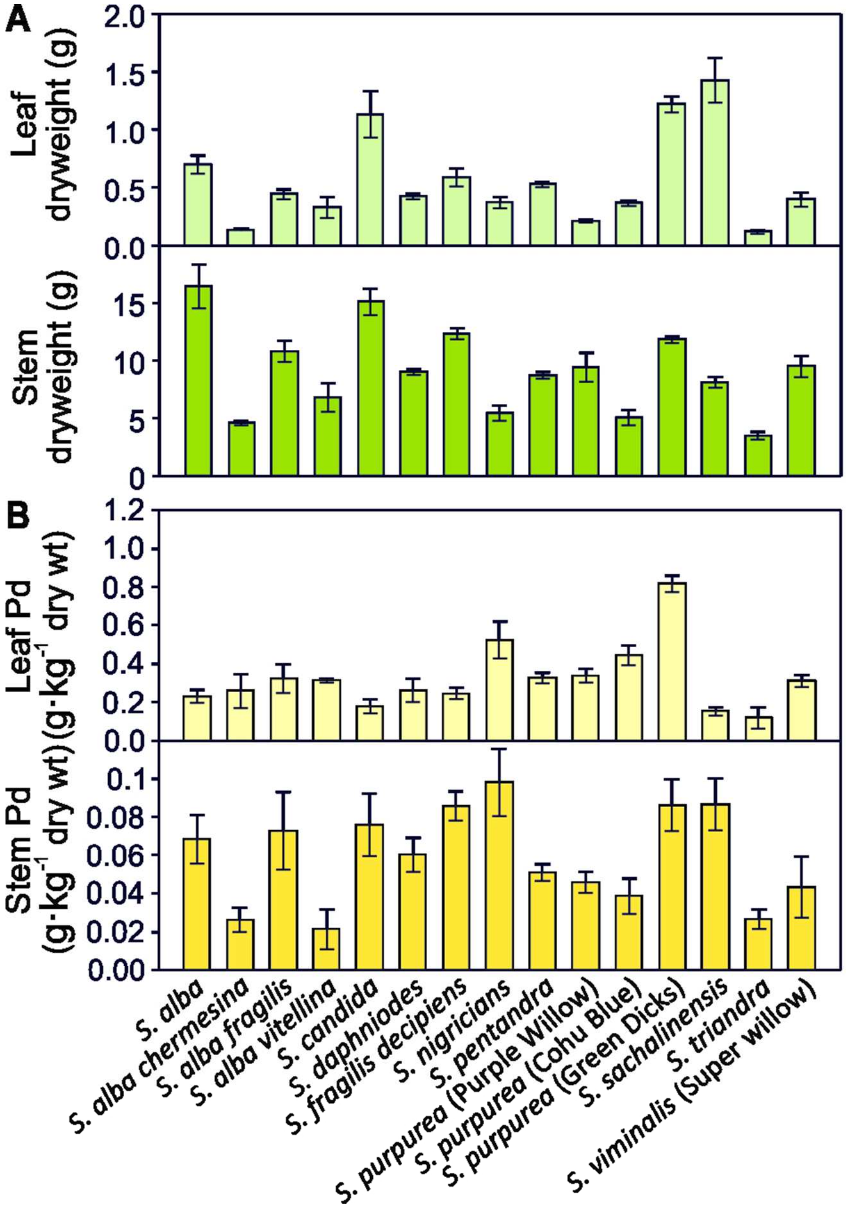

Figure 4. Growth and palladium uptake by a range of willow species (Salix sp.). Rooted cuttings were grown for four weeks on synthetic tailings containing 50 mg kg-1 palladium, dosed with 100 mg kg-1 cyanide (in the form of KCN), then harvested after one week. A) Leaf and stem dry weight, and B) concentration of palladium, in the leaf and stem tissues (n = 5 biological replicates ± s.e.m. except Salix. alba, S. chermesina and S. alba vitelline where n = 2).
Figure 4
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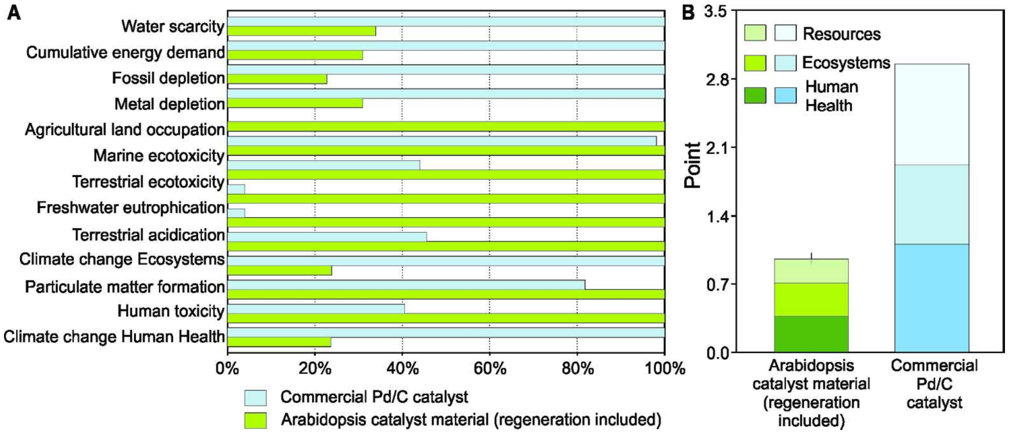

Figure 5. (A) Characterization results for midpoint categories. (B) Characterization results for endpoint categories; the y-axis reports absolute single points for total damage on resources, ecosystems, and human health according to the Europe ReCiPe H/A method.

Figure 5

173x73mm (300 x 300 DPI)

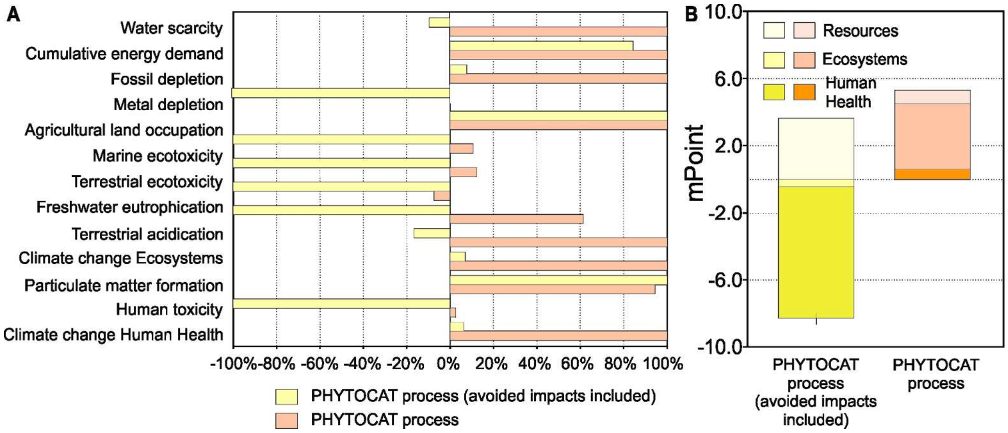

Figure 6. (A) Characterization results for midpoint categories. (B) Characterization results for endpoint categories; the y-axis reports absolute single points (1 mPoint = 10-3 Point) for total damage on resources, ecosystems, and human health according to the Europe ReCiPe H/A method. Negative values refer to avoided impacts.

Figure 6

174x74mm (300 x 300 DPI)