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**Phytoextraction of Palladium and Gold
from Broken Hill Gossan**

Phytoextraction of Palladium and Gold from Broken Hill Gossan

A thesis presented in partial fulfilment of the requirements for the degree of

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Abstract

The research in this thesis was conducted as part of the Phytocat Project; a collaborative effort between University of York (UK), Yale University (USA), University of British Columbia (Canada) and Massey. The aim of the Phytocat project was to yield a target concentration of $1,000 \mu\text{g g}^{-1}$ palladium in plants, so that the plants could be used as catalysts in chemical reactions. This thesis focussed on the phytoextraction of palladium from Broken Hill gossan, a platinum group element-rich rock collected from Australia. The gossan and surrounding soil has an elevated concentration of iron, copper, nickel and precious metals.

Samples of species native to the Broken Hill gossan and the associated rhizosphere soil were collected from the field and analysed to screen natural levels of metal accumulation in plants of the area. Five native plant species were identified: *Solanum centrale* (bush tomato), *Brassica* sp, *Ptilotus obovatus* (silver tail), *Sclerolaena lanicuspis* (copper burr) and *Tetragonia moorei* (annual spinach). The copper concentration in all plant tissues had a strong relationship with copper in soil. An individual *Solanum centrale* plant recorded a copper concentration of $277 \mu\text{g g}^{-1}$ from soil with concentration of $796 \mu\text{g g}^{-1}$ suggesting that this species is a copper tolerant plant from Broken Hill. No anomalous levels of nickel were recorded in plant tissues. The average palladium concentration measured in the rhizosphere soil was 28.8 ng g^{-1} . However, the five native plant species could not concentrate palladium in their biomass. Solubility of palladium was suggested to be poor in natural environment.

To study the potential of induced hyperaccumulation to increase the palladium uptake in plants, 60 kg of gossan from the field was collected, crushed and used as a plant growth medium for controlled plant trials at Massey University. Two types of gossan rock were collected, classified by the dominant form of iron oxide mineral in the rock structure: goethite dominated (soil A) and hematite dominated (soil B). The goethite material (A) has a higher total and soluble metals concentration than the hematite material.

Initial trials focused on *Brassica juncea*. However, despite germinating, this plant grew poorly on both types of gossan. Insufficient biomass was available to induce uptake of metals, and therefore only the natural levels of metal uptake in the poorly developed plants was quantified. Total harvested aerial biomass was 5.1 g from 39 pots each containing 800 g of gossan. The mean metal concentrations in plants grown in the two soils was not significantly different ($p < 0.05$). The concentration of palladium in the plant biomass ranged from 2,130 to 2,909 ng g^{-1} . This study proposed that $1,000 \text{ ng g}^{-1}$ is a suitable hyperaccumulation

threshold level and therefore *B. juncea* on the gossan was able to hyperaccumulate palladium. The average copper concentration in the biomass was $759 \mu\text{g g}^{-1}$ and it is likely that high copper solubility in the growth substrate affected plant growth performance.

A second trial used *Cannabis sativa* (Hemp) due to recorded metal tolerance of this species. Pots were re-seeded with *C. sativa*. Hemp germinated and grew well relative to *B. juncea*. Potassium cyanide solution ($50 \text{ mL of } 8 \text{ g L}^{-1}$) was applied to each pot at the point of maximum biomass to induce the solubility of precious metals and therefore to induce hyperaccumulation. Significant metal concentration values after KCN treatment were as follows: Copper ($6,726 \mu\text{g g}^{-1}$) > nickel ($184 \mu\text{g g}^{-1}$) > palladium ($62 \mu\text{g g}^{-1}$) > gold ($9 \mu\text{g g}^{-1}$). Following established criteria values, copper, palladium, and gold hyperaccumulation was observed. The mean metal concentrations of copper, nickel, and palladium from Hemp grown in soil B were greater compared to Hemp grown in soil A and control plants ($p < 0.05$). However, gold concentration between Hemp A and Hemp B was not different significantly ($p > 0.05$). These results were anomalous compared to the recorded total and soluble metal concentration of the two rocks.

This study concluded that total metal in soil is not an indication for metal concentration in plant tissues. Accumulated metal in plants is a function of the concentration of soluble metal in soil that can be readily absorbed by plants. Different characteristics of the substrate (in this case iron oxide) may influence metal uptake in plants. Iron oxide minerals were identified as plant competitors for soluble metals in soil solution. In this case, goethite adsorbs more soluble metal ions than hematite and therefore plants grown on the goethite substrate accumulated less metal relative to the hematite soil despite the goethite rocks having a greater total and soluble metal concentration. Metal tolerance was also highlighted as an important factor in the induced accumulation of palladium. Palladium is often associated with copper in soils and tolerance to copper is a key factor. In this work, *Brassica juncea* was proven less tolerant to copper than *C. sativa*. The target of $1000 \mu\text{g g}^{-1}$ palladium in plants has not yet been reached but the Broken Hill gossan is highlighted as a useful substrate for ongoing work. There is good potential to test the native copper tolerant species *Solanum centrale*, for induced metal uptake in the future.

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