Gold phytomining. Novel Developments in a Plant-based Mining System

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Abstract

Induced hyperaccumulation of gold by plants was first reported in 1998 by researchers from Massey University in New Zealand who proposed the idea of mining gold using plants (phytomining). Since that time research has been conducted to understand the conditions under which plants can be made to take up economic amounts of the metal. One key focus has been on the geochemistry of gold-rich soils, leading to a diagnostic test that can predict how suitable a particular soil might be to gold phytomining. Field trials have been conducted at several locations around the world in collaboration with industry partners. A Decision Support System has been developed to assist in the design and management of phytomining operations, and economic modeling has been carried out to set targets levels for phytomining technology. Novel studies are now examining the form of gold in plants. Research suggests that plants may store gold as discrete metallic nanoparticles in leaf and stem tissues, an observation that may lead to new ways to recover the metal from harvested biomass.

Hyperaccumulation, phytoremediation and phytomining

The link between plants and mineralisation has been recognised since medieval times, but it was not until the 20th century that it became possible to analyse plant tissues for their metal concentrations. The first quantitative record of a plant that could accumulate and store inordinately high concentrations of metal was made in the 1940's when two Italian scientists reported that a small herb named *Alyssum bertolonii* growing on ultramafic soils in Tuscany, Italy had a tissue nickel concentration of 0.79 per cent (7900 mg/kg dry weight) (1). This plant was growing on soil with a nickel concentration of 0.42 per cent, hence the plant showed an ability to accumulate metal to a concentration greater than that in the ground.

In the 1970's a New Zealand scientist formally named this ability of plants to accumulate high concentrations of metal. Robert Brooks and his colleagues coined the term *hyperaccumulation* to describe the natural process by which certain plant species could accumulate metals to a concentration greater than 1000 mg/kg dry weight (2). Brooks' definition was set with a focus on nickel accumulating plants, however today hyperaccumulators are known for the metals Cd, Cu, Co, Mn, Se, Tl and Zn. A more accepted criterion to define hyperaccumulation is plants that accumulate metal to a concentration that is 100 times greater than 'normal' plants growing in the same environment (Table 1).

TABLE 1. Element concentrations in a 'normal' plant (*Alphitonia neocaledonica*) and a nickel hyperaccumulator (*Hybanthus austrocaledonicus*). Plant and soil data from New Caledonia (3)

Element	'Normal' plant (mg/kg)	Hyperaccumulator plant (mg/kg)	Total soil conc. (mg/kg)
K	5600	7500	500
Ca	9600	9500	6800
Mg	1600	7100	57,500
Fe	240	220	258,000
Co	<2	25	610
Cr	4	20	180
Mn	330	226	6100
Ni	27	12,400	5900

During the 1980's phytoremediation became recognised as a potential technology application for hyperaccumulator plants. Phytoremediation is defined as the 'use of plants and their associated root-bound microbial communities to remove, contain, degrade or render harmless environmental contaminants' (4) and was first proposed by scientists in the USA (5) and Europe (6). Phytoremediation using hyperaccumulator species involves cropping plants on metaliferous or contaminated soil that accumulate one or more metals in their above-ground tissues during a growth cycle (phytoextraction). These plants are then harvested and incinerated to generate a metal-rich ash that can be safely disposed of. Where metals contained in the plants are relatively valuable it may be economic to recover the metal in a pure form. An operation where metals are mined using plants is known as phytomining. Phytoremediation is being used to clean-up metal contaminated land in some parts of the world. Phytomining of nickel is a patented technology (7), although the opinion of the authors of this paper is that the technology may not yet be commercially viable. Phytomining of gold is the subject of this paper.

Induced hyperaccumulation

The uptake of gold by plants has fascinated scientists for over 100 years, but no hyperaccumulator species for this metal has been reliably reported. This is due to gold's low solubility in a soil environment. Hyperaccumulator species presumably have a physiological mechanism that regulates the soil solution concentration of metals. Exudation of metal chelates from root systems, for example, will allow for increased flux of soluble metal complex through the root membrane. No plant thus far discovered has such a physiological mechanism to promote gold solubility at the soil-root interface.

Another metal for which no hyperaccumulator species are reliably recognised is lead. Lead is a common industrial contaminant that coats literally thousands of square kilometers of land around the world. An aim of many scientists has been to develop a phytoextraction system to remediate this heavy metal from lightly contaminated soil. The answer to making plants accumulate lead lay in medical treatments for humans with symptoms of lead poisoning. The chemical ethylenediaminetetraacetic acid (EDTA) will chelate with lead, leading to the excretion of the metal when administered intravenously. In 1996, two United States scientists published a paper in which they described how a non-accumulator plant (*Zea mays* - maize) was 'induced' to accumulate lead from soil after treatment with EDTA (8). The chemical increased the soil solution concentration of lead, thereby making the metal available for uptake. In this first demonstration of induced-hyperaccumulation technology, maize was induced to accumulate over 1% dry weight concentration lead, approximately 1000 times more than control plants that received no EDTA treatment.

New Zealand scientists were the first workers to report induced hyperaccumulation of gold using thiocyanate and thiosulphate (9). These authors realised that gold from auriferous substrates could be made soluble with dilute thio-solutions and applied this knowledge to plant uptake studies. The mining industry has experimented with or used such chemicals for the past 100 years, as lixiviants for gold in heap-leach operations (experimental use of thiocyanate, thiosulphate and thiourea as well as commercial use of cyanide). The translation to induced hyperaccumulation was a progression of this work. Hyperaccumulation of gold was defined in 1998 as accumulation

greater than 1 mg/kg, this limit being based upon a normal gold concentration in plants of only 0.01 mg/kg. Gold concentrations must be several orders of magnitude higher than this, however, for gold phytomining to become an economically viable system.

Gold phytomining

The sequence of events associated with a gold phytomining operation is as follows:

- **Stage one**: find an old gold mining site or auriferous area with 'soil' that contains gold.
- **Stage two**: plant a hardy species that is fast growing, has a large biomass, and is tolerant of the dry, acid and/or saline conditions that are often indicative of mineralisation.
- **Stage three**: as the plants near maturity and reach their maximum biomass, treat the soil with a chosen chemical. This introduces a pulse of metal into the 'soil' that the plants accumulate.
- **Stage four**: once the plants show signs of poor health, a function of the metal shock and any chemical toxicity, harvest them. At this point transpiration will have ceased with no further metal uptake.
- **Stage five**: recover the gold from the biomass.

It is important to note that for a phytomining operation the chemical solution used to dissolve gold is only applied once, when a crop reaches its maximum biomass and therefore has the greatest transpiration potential. For canola (*Brassica* sp. a plant commonly used in phytoextraction studies) this occurs just prior to the onset of flowering. The rate of chemical application is expressed as g of chemical applied per kg of soil, not as a solution concentration, as the volume of liquid irrigated onto a site is determined by climatic conditions and the water-use efficiency of the crop species being used. A Decision Support System has been created to assist in the design of a chemical irrigation strategy. A phytomining operation will only target the gold within the root zone of plants; at Massey University we limit this to the top 20 cm of the soil profile. The target resource is therefore gold in the top 20 cm of the area of land being phytomined. Chemical application rate calculations are limited to the root zone. The question of what to do after gold is depleted from this top 20 cm is often asked. As will be shown in the following sections, not all gold will be removed from the resource during one cropping cycle. Depending of the initial gold concentration in the soil, several years of cropping may be sustainable. Upon eventual resource depletion it may be possible to remove the exhausted soil, exposing fresh material for further cropping. Alternatively, should phytomining become a proven technology, it may be able to compete with conventional heap-leaching such that the ore is spread over a wider land area only to a depth of 20 cm. Upon exhaustion of gold in this soil layer, a new layer of ore can be placed on top.

Laboratory and greenhouse trials

One key focus of the gold phytomining research being conducted at Massey University is to gain an understanding of the geochemical conditions under which gold can be made soluble using dilute thioligand solutions. A diagnostic test has been developed that can screen gold-bearing substrates (tailings, waste rock and low-grade ore) to determine gold solubility. This test is based upon a 0.2% thiocyanate solution extraction at a ratio of 1 g of substrate to 10 mL of extractant solution (10). Solubility results are then expressed as ng of metal made soluble per g of substrate. Where greater than 50 ng/g gold is made soluble then the material becomes of interest for further plant-based studies, using thiocyanate as a chemical to induce gold uptake. This requirement is generally met for mildly acidic and oxidizing substrates, or for heavily oxidized laterite material (for example gold-bearing rock and soil from the Carajas region in Brazil). Gold-bearing material with an alkaline pH is more suited to thiosulphate-induced solubility for plant uptake. A diagnostic test has also been developed that uses thiosulphate as the extractant.

Thioligands are not the only chemicals that have been used to induce gold uptake. The mining industry uses cyanide as the primary lixiviant to dissolve gold, hence it seems logical to use cyanide in phytomining. Cyanide is highly toxic to animals that have a requirement for iron-based 'heme' compounds for oxygen transport. Cyanide preferentially binds to this iron, causing oxygen starvation in a poisoned animal. Cyanide is, however, non-toxic to plants that have no requirement for iron-based oxygen transport compounds. Toxicity at high concentrations can presumably be attributed to changes in osmotic potential and to cations associated with cyanide compounds (e.g. Na and K).

The concentration of gold that can be induced into a plant is dependant upon the gold concentration in the soil on which a plant is growing. Experience at Massey University shows that plants will accumulate approximately 20% of the total amount of gold available within a root zone based on any one treatment. The amount of gold that plants will accumulate is therefore a function of the gold concentration in the soil. Figure 1 describes the relationship between the gold concentration in the soil and that in the plant. Canola (*Brassica* sp.) was used for this greenhouse experiment. Potassium cyanide, applied at a rate of 0.2 g of CN per kg of soil was used to induce gold solubility.

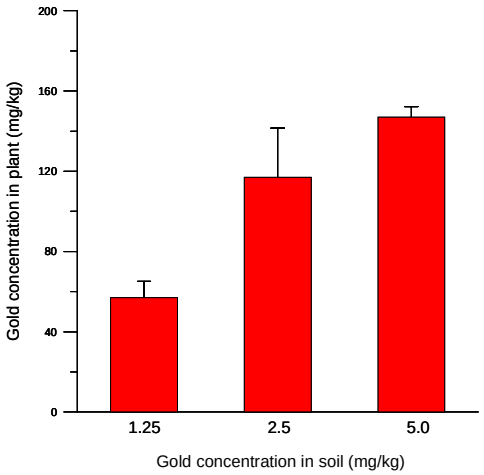

FIGURE 1. Gold concentration in greenhouse grown canola plants treated with 0.2g/kg KCN as a function of the gold concentration in the soil

The gold recovery rate in plants of 20% has been observed for many tested artificial (9) and 'real' substrates. The 20% recovery rule also appears to be true for most tested plant species. Extrapolation of the 20% rule therefore allows target limits to be placed on the total gold concentration in soil necessary to generate a certain concentration of gold in plants. The target plant-gold concentration for experiments at Massey University is 100 mg/kg. Using the 20% recovery rule, if we consider a soil profile of 20 cm depth, approximately 2 mg/kg gold is needed in the soil to achieve 100 mg/kg in the plant.

Field trials

Small-scale field trials have been run at several locations in New Zealand, Australia and South Africa during the years 2000-2003. Mixed results have resulted from this trial work. Work in Australia has suffered due to drought conditions since 2001. Experience gained from running these trials has been applied to a new phase of field work conducted over the period April to July 2003 in Brazil.

At the time of writing this paper (July 2003), a field demonstration trial had been completed by the authors at the Fazenda Brasileiro gold mine, north of Salvador, Brazil, in collaboration with the Brazilian mining company CVRD. A constructed pad of approximately 1.5 g/t ore was used for this trial with total dimension of 15m x 15m. Half of this area was made up with $Ca(OH)_2$ amended ore (pH 9.5), and half with non $Ca(OH)_2$ amended ore (pH 8.9). Seeds of canola (Brassica sp.) and corn (Zea mays) were sown in 50 cm rows across both ore types to give a vegetated area of 10 m x 10m. Plants were treated with solutions of cyanide and thiocyanate after six weeks of growth, and then harvested one week later (Figure 2).

FIGURE 2. Brazil phytomining field trial at time of treatment (left photo) and harvest one week later. The treatment is being administered by doctoral student Fabio Moreno with the assistance of CVRD mine staff

Gold uptake values for plants harvested from the trial plot are not yet available, but will be presented during the Gold 2003 conference. Results from the Brazil fieldwork will prove the current viability of gold phytomining in the field environment. The plot was managed and irrigated on a daily basis. Growth conditions were good, there was a relatively high concentration of gold in the substrate, and average daytime temperatures greater than 25^{o}C ensured significant plant transpiration.

Modeling gold uptake, a Phytoextraction Decision Support System (DSS)

Phytoextraction is driven by climatic conditions such as length of day and temperature (transpiration or evapo-transpiration). Plants "suck-up" very little water, for example, during winter months in mid-latitude climates when they are essentially dormant. The opposite is true during a hot dry summer, when plants transpire large amounts of water to facilitate photosynthesis. Plants will accumulate any soluble metals present in soil water during transpiration and this fact is exploited to induce hyperaccumulation of metals.

Evapotranspiration can be quantified, based upon parameters such as water-use efficiency, temperature and solar hours. When metal solubility is added to the equation, and an estimate is made about a plant's behavior towards this soluble metal, phytoextraction can be modeled. Research at the Horticultural and Food Research Institute of New Zealand in Palmerston North has generated a decision support system that can be used to examine scenarios for gold phytomining. Outputs of the model are generally complicated (see Figure 3) and an operator needs to be given appropriate training to generate meaningful results, however, the DSS allows important questions such as ‘How much solution should be irrigated to ensure maximum uptake and minimum leaching?’ and ‘when is the best time to apply treatment?’ to be answered.

Economic considerations of Gold Phytomining

An economic model has been created at Massey University that can predict the likely economic viability of gold phytomining based upon the modeled costs of an operation. Costs can be split into three categories:

1. the cost of growing the biomass,
2. the cost of the chemical used to induce uptake of gold, and
3. the cost of recovering the gold from the biomass.

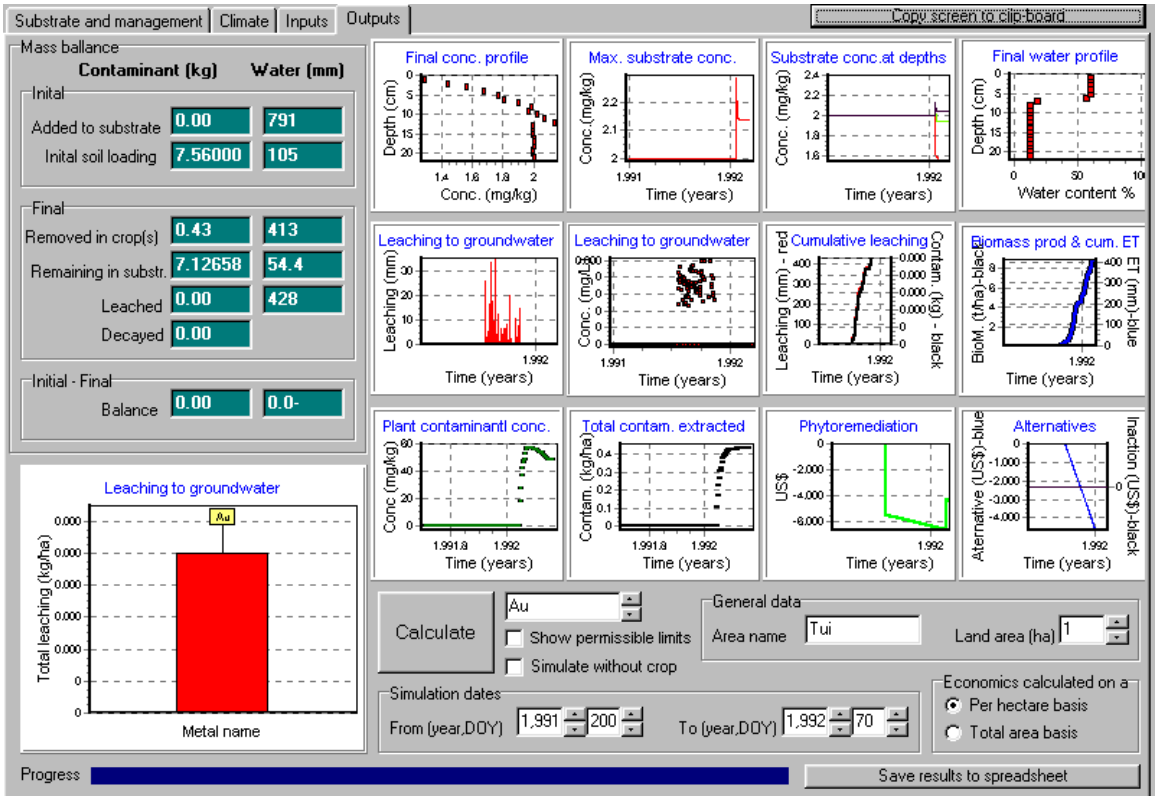

FIGURE 3. Example output screen of the Phytoextraction Decision Support System

Costs for growing the biomass have been calculated based on normal agricultural techniques. No allowance is made for irrigation, or crop maintenance for the scenario presented in this paper. Seeding is modeled as the most cost-effective means of vegetating a site. The total costs of growing, treating and harvesting the biomass are fixed according to the surface area being treated, and do not change significantly with fluctuations in the price of gold, the metal concentration of the biomass, or the mass of biomass harvested. Economic modeling allows for variable input of harvested biomass and accumulated gold concentration. The output shown in Table 2 assumes a harvested biomass of 10 t/ha and a gold concentration of 100 mg/kg. This will yield 1 kg of gold per hectare and is the gold recovery target that has been set for the Massey gold phytomining research project.

The highest modeled cost associated with phytomining is that of processing the biomass to recover gold. Table 2 assumes that conventional solvent extraction will be the most viable processing technology. Solvent extraction to recover gold from plant material was the subject of a recent graduate study at Massey University (11). Two processing routes are considered. The first assumes that the harvested 10 t/ha biomass is incinerated, with the resulting 1 t of ash subjected to solvent extraction. This route is described as ASH. The second route assumes that each of the 10 t of dry biomass is subjected to solvent extraction, and is described as DW.

Table 2 shows that if the target of 10 t/ha biomass with a gold concentration of 100 mg/kg is reached, a profit may be generated from a phytomining operation: US$24 per hectare for the DW route or US$6437 per hectare for the ASH route. This modeling exercise shows that the viability of gold phytomining is dependant upon technology costs and on the market price for gold. If processing costs can be lowered and a higher concentration of gold reached in the plants, phytomining may prove an economically attractive niche market technology to mine gold from certain auriferous areas.

TABLE 2. Economic model for a gold phytomining operation

Economic model for gold phytomining			current for 28/07/03	
			US$	
Cost of ploughing	(per hectare of land)		35	
Cost of cultivation			35	
Cost of drilling			20	
Cost of seed			65	
Cost of spraying prior to planting			12	
Price of chemical (ammonium thiocyanate or cyanide)				1.73/kg
Application rate @ 0.50 g/kg - kg chemical needed				975
Cost of chemical			1687	
Cost of chemical application			1000	
Cost of fertilizer and application			60	
Cost of spraying			30	
Cost of harvesting			70	
	Subtotal - cost of producing biomass / ha		3014	
Biomass per hectare (kg/annum dry)				10000
Au concentration in plant (mg/kg)				100
Total gold (g)				1000
Solvent extraction				
	Operating cost/tonne plant matter		643	
DW	Capital cost/tonne (straight line after 5 years)		214	
	Subtotal - cost of extraction / ha		8570	
	Incineration of DW @ $130/t		1300	
ASH	Conversion DW to ash @ 10%		1	
	Operating cost/tonne ash		643	
	Capital cost/tonne (straight line after 5 years)		214	
	Subtotal - cost of extraction / ha		2157	
Gold recovery			assume 100%	
Total gold recovered			1kg	
Total cost of obtaining gold / ha		DW	11584	
		ASH	5171	
Market price of gold $US/oz				$361
Market prize of gold $US/g				$11.61
Value of gold extracted US$			11608	
Energy value of biomass		no value at current time	0	
Total value of crop / ha			**11608**	
Gross profit / ha	(value-cost)	DW	**US$24**	
		ASH	**US$6437**	

The discovery of gold nanoparticles in plants

Research conducted at the University of Texas in El Paso, USA, has shown that gold accumulated by plants and stored in leaf and stem biomass can be present as discrete nanoparticles of pure metal (12). This discovery was made after alfalfa sprouts germinated on gold chloride-enriched agar (320 mg/kg Au) were analysed using X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM). Discrete nanoparticles of 2 to 20 nm in diameter, as well as coalesced particles of 20-40 nm scale were observed distributed through certain zones of plant tissues. A similar study by the same authors (13) showed that silver nanoparticles were formed in alfalfa plants grown on a silver-enriched medium. Atomic wires or clusters of silver were also reported in this work.

To apply the findings of the El Paso team to gold phytomining work being conducted in New Zealand, the growth medium used must be considered. Nanoparticles discovered by the El Paso team were made by growing plants on an artificial monometallic medium enriched with gold or silver at a much higher concentration than that expected in soil (320 mg/kg). No chemical was used to induce uptake. Equilibrium conditions and/or root exudates may have made a small fraction of metal soluble and available for uptake. Alternatively, plants may have taken up gold or silver in the metallic form (the authors of the El Paso work suggest this second mechanism based upon their detection of reduced gold in the agar). Real 'ores' or gold-rich soils are not, however, monometallic. Other precious and non-precious metals will exist in the mineral matrix. After treatment the solubility of these metals will also be increased to some level and made available for uptake. Table 3 presents select metal concentrations found in the aerial tissues of *Lupinus* sp. (blue lupin) grown on base-metal mine tailings in New Zealand after suitable treatment to induce uptake.

TABLE 3: Select metal concentrations in aerial plant tissues after chemical treatment of soil relative to expected 'normal' metal concentrations (from Anderson *et al.*, 14)

Metal	Induced plant concentration (mg/kg)	Natural plant concentration (mg/kg)
Pb	58	0.8
Ag	126	0.2
Cu	401	11
Au	6.3	0.1
Fe	154	59
Mg	2,800	nc
Na	4,294	nc
K	23,800	nc
Ca	17,340	nc

Note. No change (nc) in major element concentrations (Mg, Na, K, Ca) was observed in plant tissues after treatment.

The treatment in Table 3 caused an increase in gold uptake by a factor of 63, and an increase in silver uptake by a factor of 620. The plant also accumulated greater amounts of copper and lead as a result of chemical treatment. We do not currently know how a plant will respond to such high concentrations of a range of other metals, such as Au, Cu and Ag. Will a plant store each of these metals in separate location as discrete nanoparticles? Or will a plant synthesize nano-alloys within certain tissues?

Using the TEM facilities of Akzo Nobel Chemicals bv in Arnhem, The Netherlands, nano-scale gold particles have been observed in plant material generated through induced-accumulation pot experiments conducted by the authors of this paper in New Zealand (unpublished data). Study of these nanoparticles has only recently begun, hence no conclusive data on their form and location can be reported at this time. The plant material used was, however, grown on a poly-metallic gold ore. Nanoparticle studies will also be made on material generated through the Brazilian field trials described in this paper.

Consideration of nanoparticles in plants may lead to important new directions for gold phytomining. The form of metals stored may give rise to new methods for the processing of plant material. It has been suggested that gold nanoparticles could be amenable to centrifugation (15). Under the correct spin conditions an aqueous slurry of plant material may separate into bands based upon the specific gravities of pure metals or metal alloys. Such a recovery method could be significantly more cost effective than solvent extraction and improve the economics of a phytomining operation. The nanoparticles in a plant may have a value in themselves. Might plants be living factories for these important metallic structures? Further study of current biomass should answer this question.

The future direction for gold phytomining

Research conducted at Massey University over the past three years has constituted a pre-feasibility study into the economic viability of gold phytomining. Analysis of biomass generated from the Brazil field trial will show how realistic attainment of a plant gold concentration of 100 mg/kg dry weight will be under field conditions. Where pre-feasibility is proven, a one-hectare scale feasibility trial would be justified. Feasibility should involve the design and construction of a processing facility to recover gold and other metals from the harvested biomass. Successful outcome of the feasibility trial would see a viable technology that could be implemented at numerous sites around the world.

Ongoing research and development will refine gold phytomining technology. Some of the current technology limitations have been described in this paper. The target gold concentration of 100 mg/kg is an arbitrary level and any increase will change the economic model of Table 2. The highest gold concentration observed in plants during experiments at Massey University was in excess of 1000 mg/kg (unpublished data). There is also much room for development in processing technology. Solvent extraction is unlikely to be the most cost effective means to recover gold from biomass. Perhaps the most exciting area for future research lies in the characterization of metals stored in plant tissues. Studies on this subject have recently begun.

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