Recovering metals from sewage sludge, waste incineration residues and similar substances with hyperaccumulative plants

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ABSTRACT*:* Sewage sludges and ashes from waste incinerators are known sinks of many elements that are either important nutrients for biological organisms (phosphorus, potassium, magnesium, etc.) or valuable metals (nickel, chrome, zinc, etc.). On the other hand, Austria and many other industrial countries have to import up to 90% of the material inputs of metals from abroad. Purpose: This project explored the capacity to concentrate some valuable target metals in harvestable plant tissue in a process, which requires almost no energy input and little technical equipment. Methods: Five different accumulator plant species were grown under laboratory conditions on substrates containing 50% sewage sludge and 5% ashes from waste incineration plants. The results are promising. Results: Higher levels of waste incineration ashes and metal loads in the substrate are acceptable for plants, if some soluble salts (chlorides, sodium, etc.) are eluded first. Chromates may be the most limiting factor when it comes to plant toxicity. Accumulation rates of more than 10 occurred for some metals. Conclusion: The results of this project provide the groundwork for further research and development steps that may bring to practical implementation a technological option with potentially huge benefits.

Keywords: phytomining, bioaccumulation, bioleaching, waste incinerators, hyperaccumulators.

1. INTRODUCTION

Sewage sludges as well as ashes from waste incineration plants are known accumulation sinks of many elements that are either important nutrients for biological organisms (phosphorus, potassium, magnesium, etc.) or valuable metals when considered on their own in pure form (nickel, chrome, zinc, etc.); they can also be serious pollutants when they occur in wild mixtures at localized anthropogenic end- of-stream points. Recovering these metal and mineral resources requires high energy input and sophisticated equipment, making it an uneconomic process.

Austria and many other countries have to import up to 90% of the material inputs of metals from abroad [1,2]. These primary resources are becoming more expensive and their availability more uncertain as easily mineable reserves are becoming scarce. On the other hand agriculture uses large volumes of mineral fertilizers, which are often sourced from mines as well. These converted biological nutrients are taken up by crops and through the food chain and human consumption end up in sewage systems and in wastewater treatment plants in great quantities. The metabolized nutrients mostly do not return to agriculture, but due to contamination with heavy metals are diverted to be used as construction, aggregates or are thermally treated and end up rather uselessly in landfills [3].

Some plants are naturally adapted to grow on soils with high metal loads, with concentrations that would be toxic to most other plants. And some of these metal tolerant plants have the notable capacity to accumulate and store high quantities of some metals in their tissue, they are known as metal hyperaccumulators [4,5]. The project Bio-Ore aimed to explore new pathways to concentrate metals from diluted sources such as sewage sludge and wastewater by using highly efficient biological absorption and transport mechanisms. These enzymatic systems from plants work with very little energy input. The process is called bioaccumulation and can be most effectively observed in so-called hyperaccumulating metalophytes, which are studied for its suitability to be incorporated in metal recovery processes.

2. METHODS

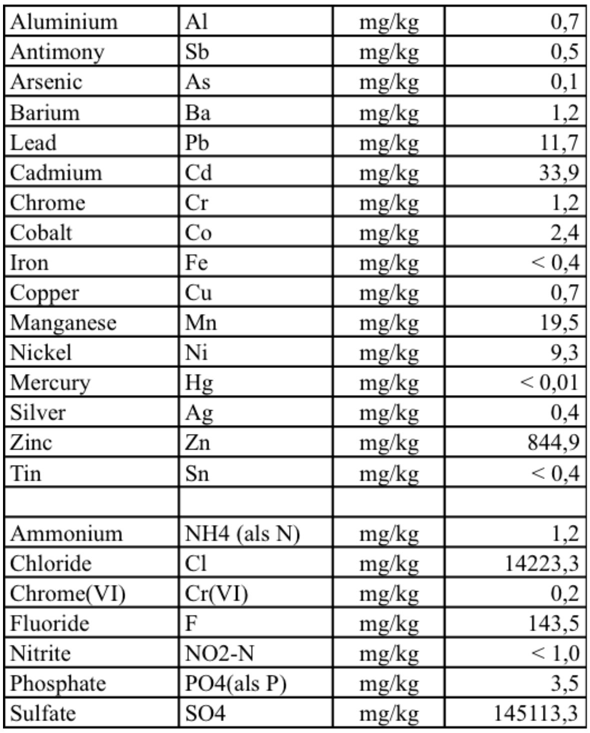
2.1 Substrate

A mixture of sewage sludge and waste incineration ashes (fluidized bed furnace) was to be used as a basis for the growth substrate for the metal accumulating plants. The selected plants are mentioned in various publications to be adapted to high metal concentrations in substrates and to accumulate certain metals of economic interest, they are members of the Brassicaceae, Asteraceae, Pontedericaceae, Pteridaceae and Gleicheniaceae families.

A series of preliminary tests were carried out to find out the best substrate mixture, in order to optimize the concentration of heavy metals without resulting in fatal acute toxicity for the selected plants. It was found that the high concentration of soluble salts (chloride, sulphate, sodium) in both sewage sludge and the waste incineration ashes where a limiting factor for plant growth. These salts can be washed out with water with only very minimal losses of heavy metals (see Table 1). Only about 2% or 3% or less of the metals are washed out this way.

In the end, a mixture of 50% (w/w) sewage sludge, 5% waste incineration ashes and the rest common sand, some compost and straw clippings was found to be an acceptable substrate for all the plants involved. In this mixture the presence of chromates probably plays a key role in setting

Table 1 - Amount of metals and salts washed out through elution from incineration ashes



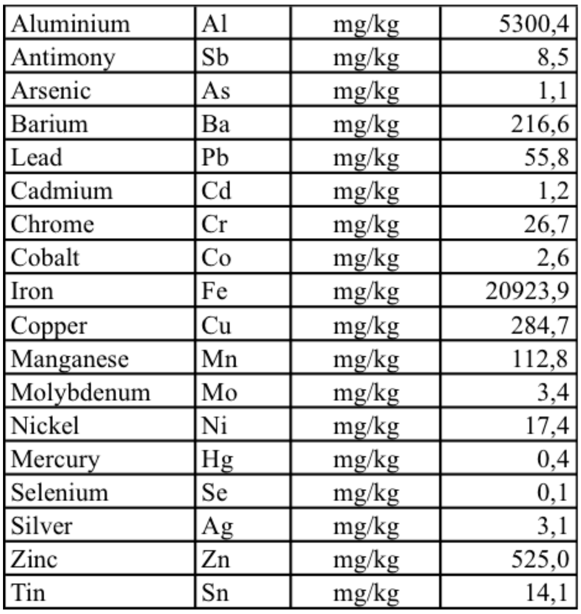
Aluminium	Al	mg/kg	0,7
Antimony	Sb	mg/kg	0,5
Arsenic	As	mg/kg	0,1
Barium	Ba	mg/kg	1,2
Lead	Pb	mg/kg	11,7
Cadmium	Cd	mg/kg	33,9
Chrome	Cr	mg/kg	1,2
Cobalt	Co	mg/kg	2,4
Iron	Fe	mg/kg	< 0,4
Copper	Cu	mg/kg	0,7
Manganese	Mn	mg/kg	19,5
Nickel	Ni	mg/kg	9,3
Mercury	Hg	mg/kg	< 0,01
Silver	Ag	mg/kg	0,4
Zinc	Zn	mg/kg	844,9
Tin	Sn	mg/kg	< 0,4
Ammonium	NH4 (als N)	mg/kg	1,2
Chloride	Cl	mg/kg	14223,3
Chrome(VI)	Cr(VI)	mg/kg	0,2
Fluoride	F	mg/kg	143,5
Nitrite	NO2-N	mg/kg	< 1,0
Phosphate	PO4(als P)	mg/kg	3,5
Sulfate	SO4	mg/kg	145113,3

a limit regarding toxicity for higher plants. Citric acid was used to lower the slight alkaline pH to a level between 5,5 and 6, and to aid in the mobilisation of metals. The exception was *Eichornia crassipes*, which was cultivated floating in 7 litres of water mixed with 1 kg of sewage sludge and 0.5 kg of waste incineration ashes.

2.2 Planting

It was found that planting seeds directly into the sewage sludge substrate led to very poor germination results. It turned out best to pre-germinate plants in normal seedling substrates and then transplant the young plants into the target substrates after they had some centimetres of height and a basic root-ball developed. Plants where potted into 13 litre planting-pots where each pot received 10 kg of substrate. All plant species are grown with three repetitions (three pots) and each 13 l pot holds at least three plants. The concentrations of metals in the final substrate mixture can be seen in Table 2.The planted pots where placed under artificial lighting by using LED-lights that are optimized for the photoactive light spectrum for plant photosynthesis (PAR), starting in May 2013 (see Figure 1). All plants receive between 3500 and 5000 Lux at the topmost set of leaves. Artificial light is kept on for 15 hours per day. Temperatures were kept above 15°C at all times. An automatic irrigation system is used, where a sensor based on soil electric resistance automatically initiates an irrigation process when a certain threshold is reached. Irrigation is delivered through low flow drippers. The water used is deionized in order to avoid having any metals added to the substrate through tap water, particularly calcium and magnesium cations, which can be antagonists for the uptake of some target metals.

Table 2 - Starting metal concentration in cultivation substrate



Aluminium	Al	mg/kg	5300,4
Antimony	Sb	mg/kg	8,5
Arsenic	As	mg/kg	1,1
Barium	Ba	mg/kg	216,6
Lead	Pb	mg/kg	55,8
Cadmium	Cd	mg/kg	1,2
Chrome	Cr	mg/kg	26,7
Cobalt	Co	mg/kg	2,6
Iron	Fe	mg/kg	20923,9
Copper	Cu	mg/kg	284,7
Manganese	Mn	mg/kg	112,8
Molybdenum	Mo	mg/kg	3,4
Nickel	Ni	mg/kg	17,4
Mercury	Hg	mg/kg	0,4
Selenium	Se	mg/kg	0,1
Silver	Ag	mg/kg	3,1
Zinc	Zn	mg/kg	525,0
Tin	Sn	mg/kg	14,1

Fig. 1. Bio-Ore trial set up under laboratory conditions. The LED lighting causes a red shift in the colours

3. RESULTS AND DISCUSSION

Sewage sludge tends to form a heavy substrate; one that forms dense, amorphous aggregates and it does not facilitate good exchange of water and air in the root system. When it dries up it tends to form pellets that can be described as brick-like in their consistency, though lightweight. The physical properties of sewage sludge in the substrate can be as much a limiting factor as the chemical properties. Therefore some soil additives are unavoidable when using raw sewage sludge for plant growth, so that important soil functions like oxygenation and water percolation and storage are performed properly.

When sewage sludge is mixed with soil forming and structure giving components like sand, straw clippings and compost and when water contents are brought to reasonable levels, live literally explodes on this rich substrate, despite the fact that the smell might be obnoxious for humans. The activity of fungi and microorganisms in the soil becomes immediately evident and soon a number of insects also populate the substrate. After surprisingly few days the repulsive smell recedes and after a few weeks the mixed substrate acquires an earthly smell which is no longer unpleasant at all.

Fig. 2. Sunflowers growing vigorously on the sewage sludge substrate in the laborator2y

The organic rich nature of sewage sludge substrates favours plants that are naturally quick growers and produce a lot of biomass. The sunflowers used in the trials evidence impressive growth (see Figure 2). Plants of small habitus had a bit more trouble establishing themselves on the substrate.

Eichornia crassipes growing on water with 12,5 % (w/w) sewage sludge and 6,25% incineration ashes did not fare very well. The mixture started to ferment, probably considerable amounts of methane and swamp gasses were produced and the plants were overwhelmed by fungi, bacteria and some algae. A second trial where *Eichornia* was grown on 7 litres of water above 1 kg of incineration slag, with very little organic content, shows a much more promising development and the plants were thriving very well.

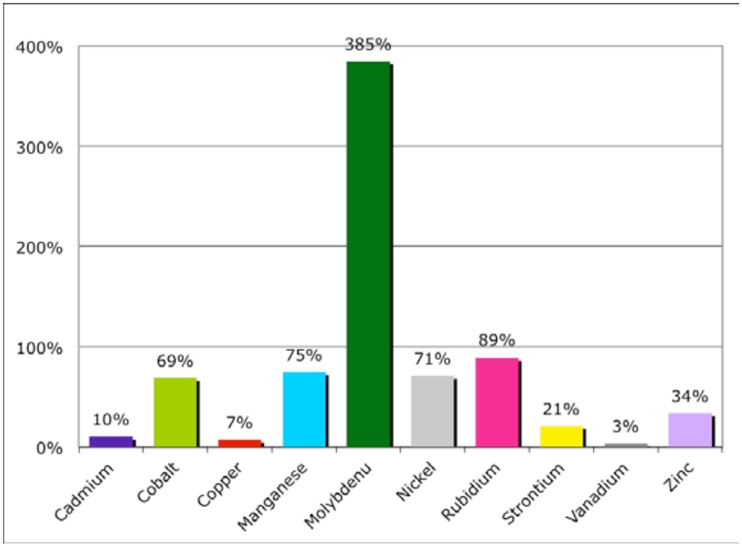
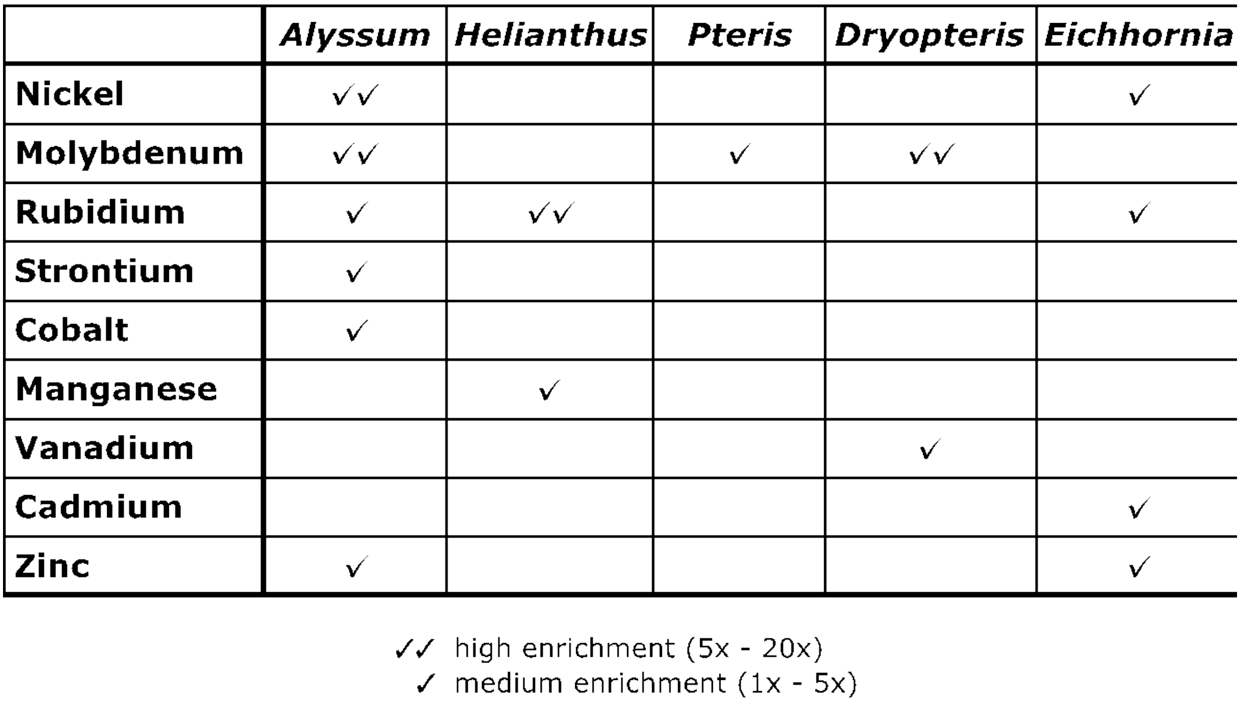


Fig. 3. Accumulation in leaves of *Alyssum* grown on sewage sludge substrate shown as enrichment rates in percen3t

The accumulation behaviour for antimony, chrome, cobalt, manganese, nickel, zinc and rare earth metals of the selected plants were assessed at the end of the growth cycle of each plant. The analysis was done separately for the leaves, stems and roots. At the end of the growth cycle the sewage sludge substrate was analysed again and the balance of metal contents from the soil and the biomass was performed. An accumulation rate of a factor of up to 20 occurred for certain metals, comparing metal concentration of the soil at the beginning of the growth cycle to the metal concentration of the plants. In Figure 3 an example of the plant *Alyssum* is shown, in this case grown on sewage sludge.



	Alyssum	***Helianthus***	***Pteris***	***Dryopteris***	***Eichhornia***
Nickel	✓✓				✓
Molybdenum	✓✓		✓	✓✓	
Rubidium	✓	✓✓			✓
Strontium	✓				
Cobalt	✓				
Manganese		✓			
Vanadium				✓	
Cadmium					✓
Zinc	✓				✓

✓✓ high enrichment (5x - 20x)
✓ medium enrichment (1x - 5x)

Table 3 – Accumulation overview of certain elements in the plants

Further on differences on nitrogen availability occurred, which seemed to change the accumulation behaviour. The same plant, as shown in Figure 3, *Alyssum* accumulated more nickel with nitrogen insufficiency.

In Table 3 an overview is shown of the accumulation properties of certain plants on the tested waste streams. More and/or other details will be highlighted in other publications to come.

4. CONCLUSIONS

Known hyperaccumulating metalophytes are growing and prospering on artificial substrates containing waste and sewage sludge. Sewage sludge substrates high in organic content seem to be suitable growth mediums for high biomass producing plants. Fast growing bulky plants that can tolerate and accumulate metals seem the way to go, if one aims to use plants to remove heavy metal contaminants from sewage sludge and use them for phyto-mining purposes.

For waste streams that are more mineral-like in nature, like incineration ashes or the leaching condensates from wastewaters, plants that naturally grow on more rocky substrates can be an interesting option for phytomining and for accumulating some valuable metals.

These hyperaccumulating plants can be used as raw material for metal recovery and therefore serve as “bio-ore”. They naturally have high carbon content, which may serve in some metallurgic processes as a reduction agent for the metals.

Interest from companies working in the management of end-of-live waste-streams has been high for this innovative bio-ore approach, as stakeholder consultations indicated. By this natural way of accumulation metal recovery with rather low energy input could be possible. A follow-up research project, that started in March 2014 takes advantage of the “Bio-Ore” results and deals with more practical situations in field trials and the recovery process as such.

The results of this project provide the groundwork for further research and development steps that may bring to practical implementation a technological option with potentially huge benefits:

- The recovery of valuable metal resources from sewage sludge, incineration ashes and metal rich wastewaters by environmentally friendly and low energy means.
- Simultaneous decontamination of the input substrates from heavy metals, opening the possibility for these nutrient streams to be redirected to biological regeneration processes (for example use as fertilizers in agriculture) without fear of polluting soils with heavy metal loads.
- Simultaneous generation of biomass on contaminated substrates, which may yield usable energy surplus through incineration during processing.

ACKNOWLEDGEMENTS

The project “Bio-Ore” was funded in large parts and made possible by the program “Intelligent Production” from the Austrian Federal Ministry for Transport, Innovation and Technology, whose program is managed by the Austrian Research Promotion Agency FFG. Furthermore thanks should go to the municipality of Vienna, which also supported the project with all kinds of insights and abundance of sampling material.

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