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

Johannes Kisser [a], Heinz José Gattringer [a], Monika Iordanopoulos-Kisser [b]

[a] *alchemia-nova, institute for innovative phytochemistry & closed loop processes, Baumgartenstrasse 93, 1140 Vienna, Austria, office@alchemia-nova.net*

[b] *Technical office M.J. Kisser, Hauptstrasse 118, 3001 Mauerbach, Austria, office@mjkisser.at*

Corresponding author:

Johannes Kisser

Email: jk@alchemia-nova.net

Address: Baumgartenstrasse 93, 1140 Vienna

Tel: 0043/650/8101000

Abstract: Sewage sludges and ashes from waste incineration plants 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.). Often these end-of-stream-resources end up in landfills. On the other hand, Austria and many other industrial countries have to import up to 90% of the material inputs of metals from abroad.

Some plants have a notable capacity to accumulate high concentrations of various metals in their tissues while growing on soils with high metal loads, hence called metal hyperaccumulators. This project examined the capacity to concentrate valuable target metals in harvestable plant tissue in a process, which requires almost no energy input and little technical equipment. The aim is to recover these metals for technical applications. Five different plant species were grown under laboratory conditions on substrates containing sewage sludge, ashes from waste incineration plants and industrial residues.

The evaluated results are promising: Plant species with natural fast growth and large biomass production are very suitable to the sewage-sludge substrate. Other metal accumulators with slower growth and smaller habitus have less affinity with this substrate rich in organic nutrients. Higher levels of waste incineration ashes and metal loads in the substrate are acceptable for plants, if soluble salts (chlorides, sulphates, etc.) are partly eluded first.

Keywords: hyperaccumulation; metalophytes; sewage sludge; waste incineration residues; metal recovery

1. Introduction

Sewage sludge can be found, wherever human interaction occurs and wastewater is collected in any sewage system. The same is true for municipal waste, which if properly collected needs to be treated for landfilling afterwards. In Central and Northern Europe treatment very often means incineration of these waste streams. This treatment reduces volume, usually produces energy and also increases the metal content of the leftover.

At the same time it is well known for many years that sewage sludge and ash 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.) (Kenahan, 1971; Muchova, Bakker, & Rem, 2008). These valuable heavy metals, including Critical Raw Materials (CRM) as defined by the European Commission (European Commission, 2010) can also be serious pollutants when they are leached into the environment (Mor, Ravindra, Dahiya, & Chandra, 2006; Van Gerven et al., 2005). Recovering these secondary resources in traditional mining approaches requires energy input and sophisticated equipment, as described in Shen and Forsberg (Shen & Forssberg, 2003) where drying, crushing, milling, sieving, magnetic and eddy-current separation as well as leaching led to a possible recovery of Fe, Al, Cu, Zn, Pb, Sn and Ag. With this established techniques the diffusely contained ‘high-tech’ metals like Hf, Rh, Ga, Ge, As, In, and Sb where recycling quota is beneath 1%, cannot yet be recovered, hence an enormous potential is inherent (Dodson, Hunt, Parker, Yang, & Clark, 2012).

Austria and many other countries have to import up to 90% of the material inputs of metals from abroad (Holnsteiner & Weber, 2011; Krutzler, Reisinger, & Schindler, 2012). Moreover, the supply of primary resources is finite which underpins the demand for exploration of alternative concepts improving metal accessibility. Such strategies are highly needed in terms of provision of metals for technological processes and crucial for economic viability. Furthermore, technologies for the recovery of metals in economic approaches from very diffuse sources are still poorly investigated and basically require large amounts of energy and chemicals with environmental risks (Morf et al., 2013). This actuality further supports the need for development of novel strategies and procedural methods. Additional considerations regard the challenges for the exploration of metal resources in densely populated areas (often refered to as urban mining), limited availability of metal sources due to occurrence in extreme environments or in great depth, as well as presence in too small amounts for large mining concepts. As a matter of fact the exploitation of new metal resources is cost intensive. In addition, basic economic and strategic reasoning demands an increase in recycling activities and waste minimization.

On the other hand, agriculture uses large volumes of mineral fertilizers, which are often sourced from mines as well (Kauwenbergh, 2010). 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 (Syers et al., 2011). The metabolized nutrients mostly do not return to agriculture especially if collected in urban areas due to contamination with heavy metals. In Austria and other countries where incineration is state-of-the-art, these waste streams are differentially utilized as construction aggregates or are thermally treated and end up in landfills (BAWP 2011). In this context, the presented concept of recovering metals from waste streams via hyperaccumulating plants provides the possibility for elaboration of novel and innovative decontamination concepts for substrates consisting of heavy metals opening the opportunity for these material streams to be redirected to biological regeneration processes such as fertilizers in agriculture.

Some plants are naturally adapted to grow on soils with high metal loads, with concentrations that would be toxic to most other plants. Some of these metal tolerant plants have the notable capacity to accumulate and store high quantities of some metals such as nickel, cadmium, arsenic and zinc in their tissue. These species are termed metal hyperaccumulators, although hyperaccumulation threshold are set at different levels, depending on the element (Ent et al. 2012; Hassan & Aarts, 2011; Verbruggen, Hermans, & Schat, 2009).

Table 1 here

Table 1: ***Known hyperaccumulators with their families and element thresholds" Source:*** **(Ent et al., 2012; Reeves, 2003; Sheoran, Sheoran, & Poonia, 2009)**

Element	Threshold for hyper-accumulation (mg/kg)	No. of hyper-accumulators	Families of hyperaccumulators
Arsenic	1000	5	Pteridaceae
Cadmium	100	6	Brassicaceae, Asteraceae, Crassulaceae, Chenopodiaceae, Solanaceae, Violaceae
Cobalt	300	30	Lamiaceae, Scrophulariaceae
Copper	300	34	Commelinaceae, Cyperaceae, Lamiaceae, Brassicaceae, Poacea, Scrophulariaceae
Chromium	300	2	Poaceae
Gold	1	-	Brassicaceae
Lead	1000	14	Compositae, Brassicaceae
Manganese	10000	11	Apocynaceae, Cunoniaceae, Myrtaceae, Phytolaccaceae, Proteaceae
Nickel	1000	320	Brassicaceae, Cunoniaceae, Flacortiaceae, Violaceae, Euphorbiaceae
Selenium	100	20	Fabaceae, Brassicaceae
Silver	1	-	Brassicaceae
Thallium	100	3	Brassicaceae, Caryophyllaceae
Uranium	1000	-	Brassicaceae
Zinc	3000	16	Brassicaceae, Crassulaceae, Leguminosae
LREE	100	2	Gleicheniaceae, Thelypteridaceae

LREE: light rare earth elements

Since the value for the hyperaccumulation threshold of the light rare earth elements (LREE) in Table 1 is not yet defined and according to the description made in Ent et al., 2012 the value of 100 mg/kg might be suitable.

Within this work described in this paper the metal contents of plants and the corresponding substrates were also explored. This work 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 (Verbruggen et al., 2009). The enzymatic systems from plants work with very little energy input, require little amounts of chemicals and can be characterised as low carbon energy technology. The presented resource efficient concept also aiming at waste minimization goes in one line with the topics of the Horizon 2020 research programme and associated promotional programs (e.g. H2020-WASTE-2014-2015 or H2020-SFS-2014-2015). The bioaccumulation process can be most effectively observed in so-called hyperaccumulating metalophytes, which are studied for its suitability within this work to be incorporated in metal recovery processes.

2. Material and methods

2.1 Substrate

A mixture of sewage sludge and waste incineration ash (fluidized bed furnace) was primarily used as a basis for the growth substrate for metal accumulating plants, besides a small set of additional exploration trials with bottom ash and industrial residues, see Table 2: Overview substrate mixtures.

Table 2: Overview substrate mixtures

substrate mixtures

Component	**sewage sludge trial**	**bottom ash trial**	**industrial substrate trial**	**floating plants on sewage sludge**	**floating plants on ind. residues**
sewage sludge	50,00%	-	-	91,00%	4,76%
bottom ash 0-6 mm	-	70,15 %	-	-	-
fluidized bed ash	5,00%	-	-	9,00%	-
industrial retentate	-	-	34,76%	-	47,62%
ind. leaching residue	-	-	47,62%	-	47,62%
planting soil	6,00%	22,35 %	14,29%	-	-
sand	38,00%	7,50%	3,33%	-	-
straw clippings	1,00%		-	-	-

The used fluidized bed ash derives from incineration of sewage sludge, the bottom ash from solid municipal waste incineration of a grate furnace in Lower Austria. For the industrial substrate mixtures two different residues from the same metal processing industrial enterprise was used. The retentate is the residue after the filtration step within their own water treatment unit, whereas the leaching residues refers to an industrial process where certain metals are leached out and an iron-aluminium-magnesium-manganese and titanium rich bluish residue is left. Both residues streams are usually landfilled in their own on-site landfill. For the experiments with the floating plants about 7 times deionized water was added. Generally only small amounts of the bottom ash and the industrial residues were available at that time, since they were sourced from older reference samples.

All slightly alkaline substrate mixtures were regulated with less than 1% citric acid to reach a pH of about 6.

2.2 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. In Table 3 used plants on different substrates are listed.

Table 3: Used plants on the different substrates

Plant	sewage sludge	bottom ash	industrial substrate	floating plants	industrial floating plants
Helianthus annus AE702xRE 819	X				
Helianthus annus Mutharoc	X	X	X		
Pteris cretica	X				
Alyssum murale	X	X	X		
Dryopteris filix-mas	X				
Phytolacca americana	X				
Eichhornia crassipes	X			X	X

Preliminary tests like the cress test (according to OENORM S 2021 – Growing media – Quality requirements and test methods) 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 high concentration of soluble salts (chloride up to 30.000 mg/kg, sulphate up to almost 200.000 mg/kg) in sewage sludge and especially waste incineration bottom ash where a limiting factor for plant growth. These salts can be washed out with water with only very minimal losses of heavy metals. Only about 2% to 3% or less of the metals are washed out this way, see Table 4: Salts washed out from bottom ash with elution.

Table 4: Salts washed out from bottom ash with elution

		Amount [mg/kg]
Aluminium	Al	0,7

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

2.3 Planting

The planting of 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. The former substrate was only partly shaken off not to harm the freshly developed roots. Plants where potted into 13 L planting-pots where each pot received 10 kg of substrate (except for the floating plants). For the sewage sludge trials all plant species were grown with two repetitions (three pots) and each 13 L pot held at least three plants. For the other exploration trials with little amounts of the substrate material in each case only one pot was used.

For the rhizofiltration trials with floating plants 7 L pots were used with 1 kg of substrate at the bottom.

The planted pots where placed under artificial lighting using LED-lights that are optimized for the photoactive light spectrum for plant photosynthesis (PAR), starting in May 2013 (see Figure 1).

Figure 1: Early stage of trial set-up in laboratory

All plants receive between 3500 and 5000 Lux at the topmost set of leaves. Artificial light was kept on for 15 hours per day. The temperature was stabilized above 15°C at all times. An automatic irrigation system was used, where a sensor based on electric resistance in the substrate automatically initiates an irrigation process when a certain threshold is reached. Irrigation is delivered through low flow drippers. Deionized water was used in order to avoid the addition of any metals to the substrate via tap water, particularly calcium and magnesium cations, which can be antagonists for the uptake of some target metals.

2.4 Sampling

As a starting point all the different components that were used for substrate optimization were sampled and analysed separately. For the main trial with sewage sludge the final mixture was also sampled and analysed. Separate samples were taken for petals, leaves, stems, roots (where applicable) and substrate after the growing period of all the pots and different plants for the sewage substrate trials. In case the plants died at early stages the leftovers from plant material was collected and if big enough added to the other final sample.

During this work the bottom ash and industrial substrate trials were an add-on to the original proposal, so the aboveground parts (leaves, stems and petals) were in some cases combined as one mixed sample for analysis.

2.5 Analysis

The analysis was done with ICP-MS by AGES, the Austrian Agency for Health and Food Safety, an accredited laboratory. All the samples were digested in triple repetition with hydrofluoric acid (HF) for total metal content and, additionally in double repetition with Aqua regia. For further calculations the mean HF values were used. Only for the soil-like samples the elements As, S, Ti, and Sc were additionally measured.

Since AGES is an accredited laboratory and the focus of this particular one-year's work was not the analysis itself but a brief exploration on what to focus in a more detailed work plans, these values were fully accepted. Neither the method validation nor the correlation or regression of the calibration were questioned.

For the repetitions of the pot trials a standard deviation was calculated, where applicable. If not all plants survived on these difficult substrates, the mean values or even single values were used instead.

3. Results

3.1 Analysis of samples

The list of all the analysed elements in used soil components is given in Table 5.

Place Table 5 here

Table 5: Metal concentrations in different soil components in [mg/kg]

	sewage sludge	straw clippings	planting soil	sand	bed furnace ash	ind. leaching residue	industrial retentate	bottom ash - 0-6 mm	bottom ash - 6-12 mm
Al	10418,78	155,03	7083,04	17736,44	36302,89	36883,52	763,29	46121,35	45655,43
Ba	254,87	43,95	92,48	658,92	1137,73	263,83	59,98	1735,76	2135,41
Be	0,31	0,00	0,27	0,31	0,74	3,08	< 0,5	1,17	1,35
Bi	1,96	< 0,02	0,05	< 0,02	10,62	< 0,5	< 0,5	5,63	2,32
Ca	29596,68	3610,81	20565,94	1457,19	146835,86	23617,96	16815,85	150539,56	140262,93
Cd	0,77	0,07	0,51	0,03	8,02	0,60	1,30	4,01	1,48
Cs	0,98	0,01	0,62	< 0,02	1,98	0,09	0,19	1,56	1,22
Cu	228,60	1,50	28,17	3,79	2801,52	18,85	< 1	4557,10	2823,06
Fe	35332,91	73,31	5098,28	1092,46	147186,97	229870,61	95,53	107127,83	125535,78
K	3224,86	11274,93	5953,57	18647,48	18040,64	349,50	250,69	7617,92	8637,60
Li	7,04	0,22	5,92	4,52	22,55	18,09	0,69	34,22	35,52
Mg	4701,05	1049,86	2947,80	497,82	15812,07	16497,19	1486,41	18232,32	19076,51
Na	825,94	17,59	801,07	2453,58	10644,35	56533,16	25089,65	17811,25	20562,69
P	22554,92	600,59	1200,53	59,76	83833,41	< 100	70,87	2687,62	2557,67
Pb	47,63	0,11	7,45	15,17	339,58	0,20	20,22	1049,25	807,65
Rb	12,89	1,13	16,82	18,88	30,46	-0,17	3,83	17,33	14,21
S	5297,62	876,21	1137,98	41,68	8817,22	2372,74	21531,90	6458,00	3514,30
Sn	11,87	1,63	1,45	0,16	55,10	0,22	0,79	78,61	31,00
Sr	141,48	6,61	54,12	77,32	725,48	176,89	599,92	490,17	331,11
Ti	870,38	6,26	260,28	138,42	4095,64	45227,06	17,70	6487,22	6610,34
Tl	0,42	0,01	0,13	0,09	0,58	0,08	1,06	0,54	0,11
As	3,23	0,62	2,36	0,68	11,05	37,54	< 0,5	21,69	21,94
Co	3,38	0,05	2,39	0,06	16,74	19,88	0,18	31,12	48,05
Cr	44,60	0,22	16,44	1,68	169,71	20764,27	275213,00	591,42	549,98
Mn	175,76	47,56	555,68	13,92	735,59	22388,97	262,26	1692,19	1615,05
Mo	3,69	0,33	0,99	0,17	24,05	0,40	644,95	74,06	40,49
Ni	33,09	0,74	5,02	0,28	140,30	53,95	2,83	257,27	144,24
Sb	0,41	0,15	< 0,2	< 0,2	43,85	3,50	39,26	39,63	21,02
V	20,19	< 0,2	12,17	2,47	72,49	12252,37	35188,95	58,24	51,07
Zn	1000,33	6,03	104,98	4,55	4174,61	88,70	4,33	3869,55	2366,25
Ce	7,15	0,14	6,28	7,67	18,94	28,29	2,63	50,99	39,54
Er	0,21	0,00	0,19	0,04	0,51	1,23	0,03	1,83	6,63
Eu	0,16	0,01	0,12	0,16	0,53	0,45	0,05	0,94	0,90

Gd	0,51	0,01	0,48	0,14	1,30	2,17	0,07	2,06	2,29
Ho	0,07	0,00	0,06	0,01	0,16	0,41	0,01	0,27	0,35
La	4,23	0,07	3,15	4,25	12,23	13,25	< 0,2	28,58	28,93
Lu	0,02	0,00	0,02	0,01	0,06	0,14	< 0,01	0,12	0,18
Nd	2,76	0,07	2,75	0,88	6,73	10,63	0,63	15,36	12,52
Pr	0,75	0,02	0,73	0,24	1,94	2,87	0,25	5,78	3,42
Sc	1,35	0,04	0,92	0,27	2,84	17,42	< 0,1	3,16	2,30
Sm	0,53	0,01	0,53	0,17	1,27	2,17	0,15	1,98	2,41
Tb	0,075	0,002	0,067	0,021	0,167	0,349	0,009	0,357	0,434
Y	1,964	0,043	1,853	0,395	7,024	11,472	0,530	15,475	14,883

Many elements can be found in higher concentrations in the root area, but since this work wants to develop new phytomining concepts only the translocated elements are the ones of interest. The concentrations of certain elements in plant leaves for the sewage sludge trials are shown in Table 6.

Place Table 6 here

Table 6: Metal concentration in plant leaves grown on sewage sludge in [mg/kg]

	H. annus AE702xRE819	*H. annus* Mutharoc	*Pteris cretica*	*Alyssum murale*	*Dryopteris filix-mas*	*Phytolacca americana*	*Eichhornia crassipes*[a]
	3	1	3	3	3	1	1
Al	44,17 ± 7,27	68,48	106,43 ± 25,29	246,65 ± 249,19	57,02 ± 2,97	81,32	7638,51
Ba	3,80 ± 1,13	13,56	4,56 ± 0,99	7,78 ± 8,86	3,91 ± 0,32	6,12	282,84
Be	< 0,02	< 0,02	< 0,02	0,04 ± 0,01	< 0,02	0,02	0,20
Bi	< 0,02	< 0,02	< 0,02	0,18 ± 0,11	< 0,02	< 0,02	2,31
Ca	35084,08 ± 943,48	31246,28	10249,84 ± 3192,32	30941,16 ± 1210,12	6612,63 ± 1182,41	22137,77	52099,87
Cd	0,20 ± 0,03	0,29	0,06 ± 0,00	0,12 ± 0,05	< 0,02	0,35	1,37
Cs	0,12 ± 0,03	0,07	0,04 ± 0,01	0,12 ± 0,05	0,02	< 0,02	0,55
Cu	18,57 ± 1,69	5,60	6,08 ± 1,66	18,94 ± 13,88	6,90 ± 0,85	8,35	438,54
Fe	142,73 ± 16,55	175,62	165,40 ± 36,88	1219,61 ± 1591,31	158,23 ± 18,31	128,20	36908,03
K	52625,51 ± 10692,24	65441,36	13891,37 ± 1094,37	37603,08 ± 3582,09	23787,96 ± 6167,17	59848,96	5619,66
Li	1,05 ± 0,10	1,54	2,75 ± 0,84	1,53 ± 0,64	1,69 ± 0,57	1,81	5,47
Mg	6930,00 ± 300,65	5586,20	4446,75 ± 1448,24	2029,86 ± 426,23	1918,44 ± 490,07	19552,77	6406,10
Na	88,16 ± 21,64	128,16	2690,36 ± 533,12	260,23 ± 270,27	680,66 ± 268,65	520,39	954,05
P	7658,54 ± 932,28	6050,27	1961,69 ± 102,74	6860,90 ± 2004,60	2441,26 ± 276,06	3868,77	22711,92
Pb	0,68 ± 0,07	1,62	0,89 ± 0,20	1,80 ± 2,19	0,46 ± 0,01	0,91	48,86
Rb	53,58 ± 4,33	65,04	15,84 ± 2,21	27,90 ± 3,70	11,72 ± 2,79	37,26	8,90
Sn	0,39 ± 0,11	1,04	0,37 ± 0,05	0,67 ± 0,75	0,16 ± 0,02	0,34	17,90
Sr	47,72 ± 1,74	58,12	23,29 ± 8,29	37,59 ± 6,32	15,37 ± 2,42	41,66	227,94
Tl	< 0,02	0,02	< 0,02	< 0,02	< 0,02	0,10	<0,2
Co	0,10 ± 0,01	0,11	0,08 ± 0,02	2,08 ± 0,46	0,03 ± 0,00	0,22	6,02

Cr	5,75 ± 1,86	12,72	6,15 ± 0,20	3,29 ± 1,61	7,92 ± 2,67	3,00	38,80
Mn	112,17 ± 16,37	361,41	61,93 ± 11,49	133,64 ± 35,67	10,85 ± 1,71	109,42	309,62
Mo	2,12 ± 0,48	1,72	1,74 ± 0,27	17,78 ± 3,22	0,65 ± 0,23	0,72	5,96
Ni	2,34 ± 0,88	0,79	18,05 ± 5,48	17,78 ± 1,76	4,19 ± 5,20	0,81	28,61
Sb	< 0,1	< 0,1	0,13 ± 0,09	0,27 ± 0,28	0,06 ± 0,01	0,08	20,64
V	1,01 ± 0,31	2,40	0,89 ± 0,03	0,68 ± 0,64	1,33 ± 0,47	0,22	17,40
Zn	112,44 ± 12,05	73,50	34,40 ± 4,61	265,63 ± 79,05	46,34 ± 6,78	121,22	804,91
Ce	0,07 ± 0,02	0,10	0,23 ± 0,03	0,35 ± 0,22	0,08 ± 0,02	0,43	3,96
Er	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	0,12
Eu	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	0,11
Gd	< 0,02	< 0,02	< 0,02	0,04 ± 0,01	< 0,02	0,03	0,30
Ho	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	0,04
La	0,04 ± 0,02	0,05	0,15 ± 0,03	0,19 ± 0,13	0,05 ± 0,02	0,21	2,24
Lu	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	0,02
Nd	0,03 ± 0,01	0,04	0,09 ± 0,01	0,17 ± 0,10	0,03 ± 0,01	0,16	1,54
Pr	< 0,02	< 0,02	0,03 ± 0,00	0,06 ± 0,01	< 0,02	0,05	0,41
Sm	< 0,02	< 0,02	< 0,02	0,05 ± 0,00	< 0,02 ± < 0,02	0,03	0,29
Tb	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	0,04
Y	0,03 ± 0,01	0,03	0,04 ± 0,00	0,08 ± 0,06	0,02 ± 0,00	0,11	1,20

Table 7 shows the results for the industrial substrate and the trial grown on bottom ash and the industrial residues.

Place Table 7 here

Table 7: Metal concentration in plant leaves grown on bottom ash and industrial residues in [mg/kg]

	H. annus on BA	*H. annus* on IS	*A. murale* on BA	*A. murale* on IS	*E. crassipes* on IS
n	1	1	1	1	1
Al	176,253	83,904	6517,798	36,607	207,862
Ba	10,490	5,983	222,698	5,686	119,621
Be	0,031	0,016	0,147	0,036	0,088
Bi	< 0,02	< 0,02	0,666	< 0,02	< 0,02
Ca	22815,675	13762,380	50369,721	36091,693	11057,594
Cd	0,099	0,068	0,922	0,269	2,879
Cs	0,087	0,073	0,309	0,031	0,028
Cu	16,005	8,466	**394,558**	9,503	13,189
Fe	855,851	137,250	6590,417	333,849	2273,151
K	49204,510	42516,571	23848,819	32371,291	6971,966
Li	1,720	0,840	7,487	2,401	1,729
Mg	5182,596	3915,223	6834,659	2247,081	3100,687
Na	535,645	10135,837	2115,860	16780,793	39540,008
P	1150,249	1583,417	2499,629	2064,322	3102,752
Pb	1,607	0,545	163,957	0,212	1,706

Rb	46,120	43,934	32,788	28,930	3,798
Sn	0,192	0,162	7,430	0,105	0,510
Sr	56,444	96,112	135,862	424,445	178,764
Tl	< 0,02	< 0,02	0,024	< 0,02	< 0,02
Co	0,196	0,234	5,148	11,580	1,945
Cr	145,838	34,220	217,543	192,579	**311,265**
Mn	122,888	86,375	631,718	597,552	3545,182
Mo	6,391	2,889	42,448	34,846	15,990
Ni	7,814	0,946	58,275	130,681	30,966
Sb	0,399	0,033	12,266	0,034	0,181
V	26,271	4,547	35,250	28,669	439,683
Zn	143,516	59,790	864,001	90,964	164,785
Ce	0,205	0,063	4,613	0,092	0,543
Er	< 0,02	< 0,02	0,131	< 0,02	< 0,02
Eu	< 0,02	< 0,02	0,106	< 0,02	0,029
Gd	0,017	< 0,02	0,274	< 0,02	0,032
Ho	< 0,02	< 0,02	0,035	< 0,02	< 0,02
La	0,106	0,035	2,766	0,048	0,870
Lu	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02
Nd	0,083	0,028	1,648	0,040	0,244
Pr	0,022	< 0,02	0,461	< 0,02	0,087
Sm	< 0,02	< 0,02	0,272	< 0,02	0,030
Tb	< 0,02	< 0,02	0,041	< 0,02	< 0,02
Y	0,079	0,023	1,162	0,043	0,198

All results are corrected for their water content. The yellow elements are the critical raw materials according to the definition of the Austrian critical element definition of 2012, when the project was submitted; the orange elements are rare earth elements. In the following years the Austrian definition of CRM went in accordance with the European one and although Ni, Mn, Mo and Zn are still of high economic importance in the year 2014 the supply risk is not that high and they are not any more considered CRM. For example phosphate rock on the other hand made it into this list.

4. Discussion

4.1 Observations

Sewage sludge tends to form a difficult substrate; one that forms dense, amorphous aggregates and it does not facilitate good exchange of water and air in the root system. When dry, pellet-like structures are formed 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 other structure giving components like sand, straw clippings and soil and when water contents are brought to reasonable levels, live explodes on this rich substrate. The only initial drawback of the planting set-up is the generated smell, which might be obnoxious for humans. The activity of fungi and microorganisms in the soil becomes evident immediately and soon a number of insects also populate the substrate. After about three days the repulsive smell recedes and after a few weeks the mixed substrate acquires an earth-like smell.

The nutrient rich nature of sewage sludge substrates favours plants, which naturally grow fast and produce a lot of biomass. The sunflowers used in the trials evidence impressive growth, see Figure 2.

Place Figure 2 here

Figure 2: Sunflowers growth

Plants of small habitus have a bit more trouble establishing themselves on the substrate.

Eichhornia crassipes growing on water with sewage sludge and fluidized bed furnace ashes showed an unsatisfying performance. The mixture started to ferment and presumably considerable amounts of methane and swamp gasses were produced. Moreover, the plants were overwhelmed with fungi, bacteria and some algae. A second trial where *Eichhornia c.* was grown above incineration slag, with very little organic content, showed better plant development.

The other trials with bottom ash and the industrial residues were quite difficult substrates to cope with, especially within amount, time and budget constraints. Nonetheless they are considered in this paper, since the concept to also use such residues for a theoretical metal recovery is a totally new approach.

4.2 Analysis

4.2.1 Validation

The analysis of the elements is the key part in this work. However, the analysis was completely outsourced to an accredited laboratory. Although the whole method validation or calibration for all these different substrates would be of interest, the outcome is in focus here. Generally the standard deviation for the triple measurements is usually well below 10%, except for very small absolut amounts at around 0,001 mg/kg the range might logically also be higher.

The standard deviation for the plants with n=3 seems to be in normal range except for one outlier leave sample within the *A. murale* set-up. There one of the three repetitions in many cases has two to four times the value of the other two pots. The other samples like the stems, the roots and the substrate of these set-up do behave regularly.

Unfortunately the detection limit for elements in all the plant samples is at 0,02 mg/kg, which is not really satisfying in comparison to the small amounts of some elements that were found in the substrate samples.

The additional non-sewage-sludge trials with n=1 might give interesting results, but should not be relied on, since no statistical confidence is given.

4.2.2 Economic approximation

The results of the first component analysis, especially the ones for the industrial residues and the bottom ash made us see the high inherent potential of these waste streams. A rough economic calculation with available bulk market prices of element oxides of CRM and Rb showed that one ton of sewage sludge is worth about 21 € and one ton of bottom ash about 47 €. Suggesting that around 67.500 tons of sewage sludge and 150.000 tons of bottom ash are produced only in Vienna, more than 1,4 Mill. € are dumped with sewage sludge and almost 7 Mill. € with bottom ash. These numbers made us realize the enormous potential of bottom ash. That’s why they were also included in the exploration trial and they are the basis of a three-year follow-up study that already started in April 2014. First results will be published soon.

4.2.3 Accumulation

Generally the results can be shown either in absolute numbers as presented in Table 6 and 7 or in accumulation rates (see Table 8), which is the ratio between the element concentration in the leaves or aboveground parts to the concentration in the substrate. For soil and phytoremediation purposes this proportional rate might give a better overview, for this study and low plant availability of the metals the accumulation factor (accumulation rate not in per cent) from the elements of interest (Cd, Co, Cr, Cu, Mn, Mo, Ni, Rb, Sr, V, Zn, and the REE) seldom exceeded 1 (meaning higher element concentration in the leaves than in the substrate).

Place Table 8 here

Table 8: Accumulation factors of selected elements

	sewage sludge							bottom ash		industrial substrate		
	H. annus AE702xRE819	*H. annus* Mutharoc	*P. cretica*	*A. murale*	*D. filix-mas*	*P. americana*	*E. crassipes*	*H. annus* Mutharoc	*A. murale*	*H. annus* Mutharoc	*A. murale*	*E. crassipes*
Cd	0,17	0,25	0,71	0,10	0,00	0,30	0,96	0,04	0,40	0,08	0,33	**2,66**
Co	0,03	0,04	0,42	0,69	0,01	0,07	**1,31**	0,01	0,20	0,02	**1,17**	0,15
Cr	0,15	0,33	0,14	0,09	0,21	0,08	0,69	0,25	0,37	0,00	0,00	0,00
Cu	0,07	0,02	0,12	0,07	0,03	0,03	0,95	0,00	0,09	0,63	0,71	0,52
Mn	0,63	**2,03**	0,39	0,75	0,06	0,61	**1,37**	0,11	0,54	0,01	0,06	0,28
Mo	0,46	0,37	**2,41**	**3,85**	0,14	0,15	**1,08**	0,13	0,87	0,01	0,16	0,05
Ni	0,09	0,03	0,28	0,71	0,17	0,03	0,67	0,05	0,41	0,03	**4,77**	**1,19**
Rb	**1,72**	**2,08**	0,12	0,89	0,38	**1,19**	0,61	**1,49**	**1,06**	**10,26**	**6,75**	**2,98**
Sr	0,27	0,33	0,31	0,21	0,09	0,23	**1,17**	0,18	0,43	0,32	1,40	0,48
V	0,05	0,12	0,12	0,03	0,07	0,01	0,70	0,44	0,60	0,00	0,00	0,02
Zn	0,14	0,09	0,11	0,34	0,06	0,15	0,63	0,06	0,36	**1,02**	**1,54**	**1,49**
Ce	0,01	0,01	0,21	0,05	0,01	0,06	0,48	0,00	0,11	0,00	0,01	0,03
La	0,01	0,01	0,19	0,04	0,01	0,05	0,45	0,00	0,12	0,01	0,01	0,09
Nd	0,01	0,01	0,23	0,05	0,01	0,05	0,49	0,01	0,11	0,00	0,01	0,03
Y	0,01	0,01	0,30	0,04	0,01	0,05	0,50	0,01	0,10	0,00	0,01	0,04

As expected, the well-known hyperaccumulators *Alyssum murale* and *Eichhornia crassipes* showed best accumulation results, *Phytolacca americana* (where two of three plants had difficulties to survive the transfer) with the tuberous root system has the possibility to sprout again after harvest and might also be an interesting option for future trials. *Helianthus annus* Mutharoc is slightly smaller in its growth habit and seems to extract higher quantities of interesting elements, other sunflower hybrids should even perform better. Since the absolute numbers still refer to one kg of biomass the high biomass plants like the sunflower can be in favour, depending on the elements of interest. *Pteris cretica* and *Dryopterix filix-mas* did not show promising results.

The absolute accumulation of interesting elements is mostly higher for the bottom ash and the industrial residues trials in comparison to the sewage sludge trials.

5. Conclusions

The investigated hyperaccumulating metalophytes are growing and prospering on artificial substrates containing waste and sewage sludge, see Figure 1 and 2. Sewage sludge high in organic nutrients is a suitable growth medium for plants, if amended with structure given components that air and water percolation is assured. Fast growing, high biomass producing plants, which are able to tolerate and accumulate metals proved to be most suitable plant species for the removal of heavy metal contaminants from sewage sludge and probably also utilization for phyto-mining purposes.

For waste streams consisting of higher amounts of minerals, like ashes or industrial residues, plants species, which naturally grow on more rocky substrates can be an interesting option for phytomining and might even be used for separating certain metals from these waste streams.

The examined plants can be used as raw material for metal recovery and therefore, if further processed serve as “bio-ore”.

Stakeholder consultations indicate that companies dealing with the management of end-of-live waste-streams are very interested for this innovative bio-ore gaining approach. The use of the plant inherent accumulation capabilities enables the recovery of metals with rather low energy input and low resource consumption. Follow-up research, taking advantage of the gathered results with higher statistical backup and under more practical situations in field trials with industrial partners has already started. This research will also deal with new recovery processes of the metals as such. So far the plant biomass is usually once more burned and the ashes need again conventional treatment to separate the elements. There might also be more efficient (and economically interesting) methods to gain higher metal enrichments without prior burning the biomass.

The results of this project provide the basis for further research and developments focussing on the practical implementation of the presented novel technology and provide huge benefits:

- Valuable metal resources can be recovered from sewage sludge, incineration ashes and metal rich wastewaters by environmental friendly and low energy means.
- Substrates can be decontaminated 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 or after processing.

Acknowledgements

The project “Bio-Ore”, with the project number 838960 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.

References

Dodson, J. R. R., Hunt, a. J. J., Parker, H. L. L., Yang, Y., & Clark, J. H. H. (2012). Elemental sustainability: Towards the total recovery of scarce metals. *Chemical Engineering and Processing: Process Intensification*, *51*(0), 69–78. doi:10.1016/j.cep.2011.09.008

Ent, A., Baker, A. J. M., Reeves, R. D., Pollard, a. J., & Schat, H. (2012). Hyperaccumulators of metal and metalloid trace elements: Facts and fiction. *Plant and Soil*, *362*(1-2), 319–334. doi:10.1007/s11104-012-1287-3

European Commission. (2010). *Critical Raw Material for the EU – Report of the Ad-hoc Working Group on Defining Critical Raw Materials*.

Hassan, Z., & Aarts, M. G. M. (2011). Opportunities and feasibilities for biotechnological improvement of Zn, Cd or Ni tolerance and accumulation in plants. *Environmental and Experimental Botany*, *72*(1), 53–63. doi:10.1016/j.envexpbot.2010.04.003

Holnsteiner, R., & Weber, L. (2011). *Ressourcennutzung in Österreich*.

Kauwenbergh, S. Van. (2010). *World phosphate rock reserves and resources*.

Kenahan, C. B. (1971). Solid waste. Resources out of place. *Environmental Science & Technology*, *5*(7), 594–600. doi:10.1021/es60054a009

Krutzler, T., Reisinger, H., & Schindler, I. (2012). *Ressourcenverbrauch der Industrie in Österreich*.

Mor, S., Ravindra, K., Dahiya, R. P., & Chandra, A. (2006). Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring and Assessment*, *118*(1-3), 435–56. doi:10.1007/s10661-006-1505-7

Morf, L. S., Gloor, R., Haag, O., Haupt, M., Skutan, S., Di Lorenzo, F., & Böni, D. (2013). Precious metals and rare earth elements in municipal solid waste--sources and fate in a Swiss incineration plant. *Waste Management (New York, N.Y.)*, *33*(3), 634–44. doi:10.1016/j.wasman.2012.09.010

Muchova, L., Bakker, E., & Rem, P. (2008). Precious Metals in Municipal Solid Waste Incineration Bottom Ash. *Water, Air, & Soil Pollution: Focus*, *9*(1-2), 107–116. doi:10.1007/s11267-008-9191-9

Reeves, R. D. (2003). Tropical hyperaccumulators of metals and their potential for phytoextraction. *Plant and Soil*, *249*(1), 57–65. doi:10.1023/A:1022572517197

Shen, H., & Forssberg, E. (2003). An overview of recovery of metals from slags. *Waste Management*, *23*(10), 933–949. doi:http://dx.doi.org/10.1016/S0956-053X(02)00164-2

Sheoran, V., Sheoran, A. S., & Poonia, P. (2009). Phytomining: A review. *Minerals Engineering*, *22*(12), 1007–1019. doi:10.1016/j.mineng.2009.04.001

Syers, K., Bekunda, M., Cordell, D., Corman, J., Johnston, J., Rosemarin, A., & Salcedo, I. (2011). Phosphorus & Food Production. In *UNEP Yearbook: Emerging Issues in Our Global Environment*. Nairobi.

Van Gerven, T., Geysen, D., Stoffels, L., Jaspers, M., Wauters, G., & Vandecasteele, C. (2005). Management of incinerator residues in Flanders (Belgium) and in neighbouring countries. A comparison. *Waste Management (New York, N.Y.)*, *25*(1), 75–87. doi:10.1016/j.wasman.2004.09.002

Verbruggen, N., Hermans, C., & Schat, H. (2009). Molecular mechanisms of metal hyperaccumulation in plants. *New Phytologist*, *181*(4), 759–776. doi:10.1111/j.1469-8137.2008.02748.x