Journal of the Serbian Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

ACCEPTED MANUSCRIPT

Please cite this article as G. Andrejić, M, Kovačević, Ž, Dželetović, U. Aleksić, I. Grdović and T. Rakić, *J. Serb. Chem. Soc.* (2023) https://doi.org/10.2298/JSC230113028A

Journal of the Serbian Chemical Society
version electronic
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. **00(0)**1-11 (2023)
JSCS–12228

Original scientific paper
Published DD MM, 2023

Potentially toxic element accumulation in two *Equisetum* species spontaneously grown in the flotation tailings

GORDANA ANDREJIĆ[1]* MILIJANA KOVAČEVIĆ[2], ŽELJKO DŽELETOVIĆ[1], UROŠ ALEKSIĆ[1], ISIDOR GRDOVIĆ[2] AND TAMARA RAKIĆ[2]

[1]*University of Belgrade, Institute for the Application of Nuclear Energy, Banatska 31b, 11080 Belgrade, Serbia and* [2]*University of Belgrade, Faculty of Biology, Studentski trg 16, 11000 Belgrade, Serbia*

(Received 13 January; Revised 21 June; Accepted 1 July 2023)

Abstract: Decades of mining activity have resulted in the accumulation of significant amounts of tailings that are deposited over the natural vegetation, forming deposits tens of meters thick. The tailings are poor in organic matter and macronutrients and contain a high concentration of potentially toxic elements (PTE). Their surface remains unvegetated for long periods of time and is susceptible to fluvial and wind erosion. *Equisetum arvense* and *E. telmateia* appear to be the first colonizers in the tailings of the Pb-Cu-Zn mine in Serbia. Each plant was sampled along with its associated substrate. Pseudototal and available metals in the substrate, as well as total As, Cd, Cu, Fe, Mn, Ni, Pb and Zn concentrations in the plant parts were determined by atomic absorption spectrophotometry. The findings show that both species have high bioaccumulation capacity and tolerance to otherwise toxic concentrations due to efficient accumulation, immobilization, and detoxification of these elements in their underground parts. It is expected that the long-term presence of metal-tolerant horsetail species would increase the organic matter content of flotation residues, thus gradually improving their physical, chemical, and biological properties. This, in turn, would promote the natural succession of other metal-tolerant plant species and soil microorganisms.

Keywords: potentially toxic elements, pollution, phytoremediation.

INTRODUCTION

As a result of the substantial global demand for mineral raw materials and their extensive use in various industries, mining and ore processing remain prominent sectors within the primary industry of certain countries, yielding significant financial profits. Despite advancements in mining technology and waste reduction strategies, mining activities continue to pose a significant threat to

---

*Corresponding author. E-mail: gordanaa@inep.ac.rs

https://doi.org/10.2298/JSC230113028A

the environment due to the generation of spoils and effluents containing exceedingly high concentrations of potentially toxic elements (PTEs). It is worth noting that only a small fraction of the total processed material is extracted as a concentrated metal product, while a substantial proportion, up to even 97-99% of the mined ore, becomes flotation tailings. Flotation tailings share a similar composition to the original ore, and containing significant amounts of unrecovered minerals, contribute to the environmental pollution.[1-3] Flotation tailings consists of fine particles (ø=<75 μm) that remain after the technological processing and extraction of desired elements from the polymetallic ore, and are discarded with water into the tailing pond. Further release of PTEs from these particles occurs through various processes of chemical and physical particle disintegration. Eventually, PTE enter the food web, often leading to adverse effects on the health and biodiversity of surrounding ecosystems, as well as posing risks to human health.[4] This issue is particularly prominent in countries where regulatory framework to mitigate environmental pollution risks is not effectively enforced. Furthermore, the flotation tailings are also abundant in process chemicals, including organic solvents like xanthate, which are utilized for the effective separation of metals during mineral flotation processes. It is noteworthy that a significant portion, nearly half, of the xanthates employed in the mineral flotation process is ultimately discharged into the flotation tailings.[5] The presence of these process chemicals within the tailings, further emphasizes the complex composition and potential environmental impact of these waste materials. Additionally, flotation tailings surface layers are prone to fluvial erosion and the dispersion of fine particles through wind, further exacerbating their environmental impact.[4,6-7] Therefore, PTE contamination can extend several kilometres beyond the mining site, significantly affecting local and regional land use and posing health risks to nearby human communities.

Restoring large areas covered by flotation tailings presents significant challenges due to unfavourable physical and chemical properties of these technosols, which strongly hinder plant growth and result in consequent long-term lack of vegetation cover.[8-10] Vascular plants that establish themselves as the initial colonizers of flotation tailings are uncommon and exhibit remarkable adaptability to the challenging environmental conditions found in such areas. Among these rare plant species that pioneer the colonization of polymetallic flotation tailings, several belong to the genus *Equisetum*. *Equisetum* is an ancient genus of vascular plants with a long evolutionary history dating back to the Upper Devonian period.[11] All species within the *Equisetum* genus are perennial plants, possessing erect herbaceous stems that emerge from an extensive rhizome system bearing adventitious roots.[11-12] Horsetails have demonstrated a remarkable ability to tolerate unfavourable physical and chemical properties of substrates, even allowing for the accumulation of metals at higher concentrations.[13-14] This resilience in the face of challenging soil conditions is thought to be linked to their archaic adaptation to geothermal environments characterized by high levels of potentially toxic metals and metalloids harmful to most plant species, such as arsenic (As) or mercury (Hg).[15] In the specific context of this study, the two horsetail species, *Equisetum arvense* and *E. telmateia*, were observed as the initial colonizers in the flotation tailings of a lead-copper-zinc mine in Serbia. The objectives of this research were twofold: (i) to analyse the concentrations of potentially toxic elements (PTEs) in the flotation tailings as well as in the underground and aerial parts of the two *Equisetum* species, and (ii) to evaluate their capacity for bioaccumulation and their potential for utilization in the initial stages of bioremediation efforts.

EXPERIMENTAL

Site description

Plants and their belonging substrates were collected from two different parcels of the flotation tailings of the active Pb-Cu-Zn mine on Mt. Rudnik (44,11 N; 20,495 E; 500 m asl), located in central Serbia (Fig. 1A). *Equisetum arvense* and *E. telmateia* populations are distributed across two distinct sections within the peripheral area of the flotation tailings, adjacent to the surrounding natural vegetation. These sections benefit from a sufficient water supply as a result of the presence of a nearby stream (Fig. 1B). It is worth noting that no deposition of waste material has occurred in either of these tailing parcels for the past four years preceding the sampling. The climate in this region and at this altitude is temperate.

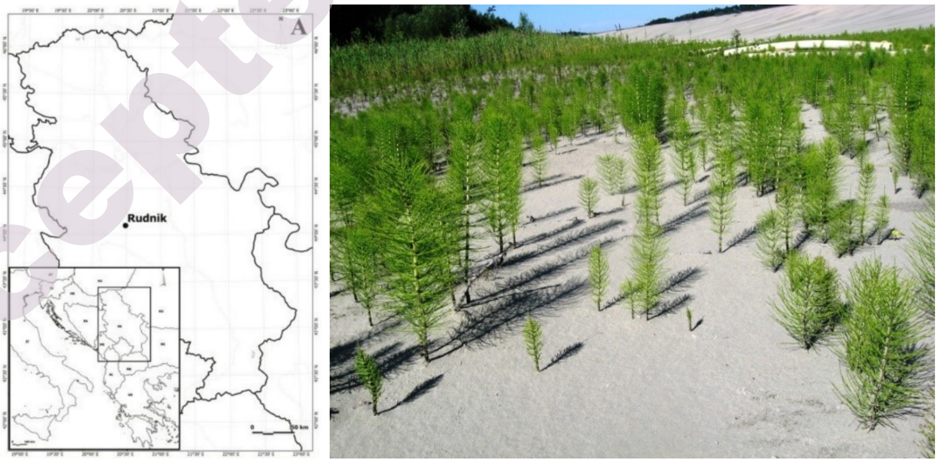

Fig. 1 Location of the mine (A) and strands of *Equisetum arvense* and *E. telmateia* in the flotation tailings dump (B).

Substrate and plant sampling

Each plant was sampled together with the substrate surrounding the rhizome and its adventitious roots, from the depth 0-20 cm, in August 2017. Each composite substrate sample

(F_{EA}, *E. arvense* flotation tailings substrate; F_{ET}, *E. telmateia* flotation tailings substrate) was composed of well mixed substrate samples collected from the rhizosphere of 15 individuals.

Substrate analysis

The substrate samples were cleaned from stones and biotic material. After air drying, the samples were ground and sieved (pore diameter 200 μm). Ten grams of a homogenized substrate was mixed with 25 ml of distilled water or with 25 ml of 1M KCl to determine active (pH_{H2O}) and exchangeable (pH_{KCl}) substrate acidity, respectively.[16] The samples were stirred for 30 min and the pH was measured directly in the suspension (Iskra MA 5730).

For determination of the pseudo-total PTE concentration (As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) in the substrate, samples were dried to constant weight at 100°C, and digested in 65% HNO_3 at 150°C in Kjeldaltherm® digestion block (Gerhardt, Germany), according to the US EPA method 3051.[17] Solutions for determining available PTE concentrations were made by extraction for 2 h in 1 M ammonium acetate and 0.01 M EDTA mixture (pH 7).[18] The concentrations of PTE were determined by atomic absorption spectrophotometer (Shimadzu AA-7000, Japan) comparing sample absorption values with those of known standards. The precision of the procedure for PTE was evaluated by analyzing the certified soil material (Soil 90-0115-0106, BIPEA-Bureau Interprofessionnel d ´Etudes Analytiques).

Plant analysis

To avoid contamination by residual substrate particles, the collected plant samples were carefully washed in tap water and then thoroughly rinsed with deionized water. The plant material was divided into (vegetative) shoots and underground parts, air-dried, powdered, oven-dried at 100°C for 24h, and completely digested in 65% HNO_3 at 150°C in Kjeldaltherm® digestion block, according to the US EPA method 3051.[17] Concentrations of PTE (As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) in plant samples were determined by atomic absorption spectrophotometer (Shimadzu AA – 7000, Japan), comparing the sample absorption values with those of known standards. Analytical procedure accuracy was assessed by analysis of the standard reference plant material NIST 1515 (apple leaves).

Phytoremediation potential

The phytoremediation potential of two horsetail species was determined on the basis of bioconcentration factor (BCF) and translocation factor (TF).[19] BCF provides information on the accumulation of PTE in the underground plant parts and their efficiency of PTE removal from the substrate. Translocation factor (TF) is the ratio of the PTE concentration in the aboveground part of the plant and its concentration in the undergound parts, and provides information on the plant’s efficiency in tranlocating a certain PTE from underground to its aboveground parts. BCF and TF values were calculated using the following formulas:

$$BCF = c_{\text{underground plant parts}} / c_{\text{substrate}} \tag{1}$$

$$TF = c_{\text{shoot}} / c_{\text{underground plant parts}} \tag{2}$$

where $c_{\text{underground plant parts}}$ and c_{shoot} represent PTE concentrations in plant underground parts and shoots, respectively, whereas $c_{\text{substrate}}$ is the available PTE concentration in the belonging substrate.

Statistical analysis

Data are expressed by the mean ± standard deviation of eight replicates. All data were initially tested by the Shapiro-Wilk test for normality. Statistically significant differences between two independent groups were calculated using the non-parametric Mann-Whitney U test because of the non-normality of the data. Statistical analyses were performed in R (v3.5.1; R Core Team 2018).

RESULTS AND DISCUSSION

Flotation tailings chemical properties

As indicated in Table I, both the active (pH_{H2O}) and exchangeable soil acidity (pH_{KCl}) were within the neutral range. The pH_{H2O} was statistically significantly lower in *E. arvense* substrate compared to that of *E. telmateia*, whereas pH_{KCl} was lower again in the *E. arvense* substrate, but without statistical significance (Table I). At a soil pH around neutral, it is assumed that all the studied elements are well dissolved in the soil water solution, although their availability would increase with decreasing pH, except for As.

Both substrates exhibited elevated pseudo-total concentrations of several elements (As, Cd, Cu, Pb, Zn) that surpassed the maximum allowable concentrations (MAC) specified in international soil guidelines (Table I). These concentrations were several-fold higher (Ni, Pb, Zn, Cd, Cu) and approximately 25-fold higher (As) than the MAC values. Since the substrates studied were solid waste materials from extractive metallurgical processes, it was expected that such high concentrations of potentially toxic elements (PTEs) would be observed. Although detected pseudo-total PTE concentrations were very similar between the substrate samples, there were statistically significant differences regarding all elements, with exception of As. This heterogeneity is a common characteristic of the flotation tailings resulting from the deposition of waste material originating from different mined ores, which can vary in their metal content.[20]

The portion of EDTA-available elements in the pseudo-total content in F_{ET} and F_{EA} substrate is listed in descending order, respectively, and was as follows: Pb (45%, 44%) > Cd (36%, 37%) > Mn (16%, 20%) > Ni (13%, 8%) > Zn (8%, 10%) > Cu (7%, 10%) > Fe (0.2%). The presence of elevated metal availability in flotation tailings has been previously established in the literature for various metals. For instance, Kasowska *et al.*[21] highlighted the considerable presence of readily available copper (Cu) in copper ore flotation tailings, which constituted approximately 41% of its pseudo-total concentration. Additionally, Karczewska and Milko[22] reported that EDTA exhibited the highest effectiveness as a chelating agent, enabling the release of up to 16% of EDTA-available lead from the pseudo-total metal content. The prominent metal availability in the investigated flotation tailings may be attributed to the presence of residual metal xanthates and their degradation products in the tailings. The highest Pb and Cd EDTA-availability can be attributed to very high EDTA efficiency for desorption of listed metals from xanthates.[23-24] While it is commonly known that metal availability is moderate at neutral and tends to be higher under acidic conditions, it is important to consider that in substrates already colonized by plants the metal bioavailability can be further increased in plant rhizosphere. This enhanced bioavailability of metals can be attributed to some microbiome and plant roots exudates, such as organic acids and hydrogen ions (H^+), that acidify the root microenvironment and desorb metals at the negatively charged reactive sites of soil particles making them more available for uptake by roots.[25]

Table I. pH values and PTE concentrations (mg kg^{-1}) in the flotation tailings

	F_{ET}	**F_{EA}**	MAC (mg/kg)*
pH_{H2O}	7.6 ± 0.05^b	7.5 ± 0.03^a	
pH_{KCl}	7.4 ± 0.1^a	7.0 ± 1.3^a	
Pseudo-total			
As	484 ± 243^a	533 ± 36^a	15-20
Cd	9.6 ± 0.2^b	8 ± 0.1^a	1-5
Cu	349 ± 12^b	300 ± 4^a	60-150
Fe	25848 ± 95^b	25399 ± 145^a	
Mn	2003 ± 25^b	1759 ± 61^a	1500-3000
Ni	68 ± 1.3^a	75 ± 1^b	20-60
Pb	448 ± 43^a	558 ± 6^b	20-300
Zn	1823 ± 24^b	1445 ± 30^a	100-300
EDTA available			
Cd	3.5 ± 1.6^a	3.0 ± 0.2^a	
Cu	25 ± 18^a	33 ± 0.8^a	
Fe	49 ± 4.6^a	62 ± 7^b	
Mn	328 ± 24^a	348 ± 11^a	
Ni	8.5 ± 7^a	6 ± 4^a	
Pb	200 ± 7^a	247 ± 21^a	
Zn	153 ± 37^a	149 ± 40^a	

*MAC - maximum allowable concentration.[26] Values with no letter in common are significantly different (Mann-Whitney U, $p<0.05$)

Potentially toxic element accumulation by horsetails

The analysis of concentrations of potentially toxic elements in the investigated species, *E. arvense* and *E. telmateia*, reveals a significant accumulation of PTE in their underground parts. Notably, the concentrations of the investigated elements, except for As and Mn, were considerably higher in the underground plant parts (Table II) compared to the corresponding EDTA-available element concentrations in the substrates (Table I). Consequently, this disparity led to their BCFs > 1 (Table III). Both *E. arvense* and *E. telmateia* exhibited the highest bioconcentration factors for Fe and Ni, followed by Zn and Cu. Generally, *E. arve*nse demonstrated higher BCFs compared to *E. telmateia*, with Cu and Ni showing a 1.7-fold and 4.5-fold higher BCFs in *E. arvense*. Both *Equisetum* species efficiently retained and immobilized accumulated PTE in their underground parts, manifesting low transfer rates to shoots. This was detected through significantly lower concentrations of the elements in the shoots, accompanied by TFs < 1 (Table III). However, an exception was noted only for Mn (TF = 1.24) in *E. telmateia*. The overall results indicate that both species possess a substantial bioaccumulation capacity and tolerance to elevated concentrations of PTE in their underground parts. Their metal tolerance is attributed to complex and efficient PTE detoxification systems in rhizomes that could be also associated with typically high silicon content in *Equisetum* that is not simply beneficial, but essential mineral element.[27-28] It is well documented that Si alleviates heavy metal stress in horsetails and some other plants by being involved in external and internal mechanisms of Si-mediated alleviation of metal toxicity, as a part of their biochemistry.[14,29-33] Previous studies have shown that horsetails are often behaving as extremophiles regarding their substrate properties. Thus, *E. arvense* was found to tolerate nitrogen deficiency and specific elemental composition in volcanic tephra and flotation tailings, therefore being the most or among the most successful and dominant herbaceous species in such specific disturbed habitats.[34-36] Also, *E. palustre*, *E. ramosissimum* and *E. ramosisti* were among the first plant colonizers in natural succession of the mine and flotation tailings.[37-40] Furthermore, owing to its metal tolerance *E. hyemale* was efficiently used in the removal of Pb and Cr from the leachate in the wastewater treatment biotechnology.[41]

Table II. PTE concentrations in underground parts and shoots of *E. telmateia* and *E. arvense* grown in the flotation tailings (mg kg^{-1})

		E. telmateia	*E. arvense*	Upper concentration limits[20]
underground parts	As	18 ± 1^{a}	23 ± 0.7^{b}	/
	Cd	5.0 ± 0.1^{a}	9.3 ± 0.3^{b}	/
	Cu	51.6 ± 3.3^{a}	117 ± 8^{b}	/
	Fe	711 ± 6^{a}	842 ± 15^{b}	/
	Mn	93.9 ± 3.3^{a}	318 ± 15^{b}	/
	Ni	13.8 ± 0.5^{a}	44.2 ± 2.8^{b}	/
	Pb	65.4 ± 2.4^{a}	232 ± 24^{b}	/
	Zn	389 ± 14^{a}	633 ± 33^{b}	/
shoots	As	35.5 ± 2.6^{b}	10 ± 0.4^{a}	5-20
	Cd	1.3 ± 0.1^{a}	3.1 ± 0.1^{b}	5-30
	Cu	10.5 ± 0.7^{b}	8.0 ± 0.3	20-100
	Fe	618 ± 4^{b}	380 ± 4^{a}	/
	Mn	116 ± 3.6^{a}	270 ± 6^{b}	400-1000
	Ni	6.5 ± 0.3^{b}	5.9 ± 0.4	10-100
	Pb	26.2 ± 0.8^{b}	24.3 ± 0.6	30-300
	Zn	317 ± 14^{b}	235 ± 4	100-400

Table III. Bioconcentration (BCF) and translocation factor (TF) for two horsetail species grown in flotation tailings

	BCF		TF	
	E.telmateia	*E. arvense*	*E.telmateia*	*E. arvense*
Cd	1.43	2.66	0.26	0.33
Cu	2.06	4.68	0.20	0.07
Fe	14.51	17.18	0.87	0.45
Mn	0.29	0.91	1.24	0.85
Ni	1.62	5.20	0.47	0.13
Pb	0.33	1.16	0.40	0.10
Zn	2.54	4.14	0.81	0.37

Even though *Equisetum* species typically form extensive colonies on wetlands, they have some properties that can be helpful in substrates that appear dry on the surface. One such trait is the presence of an extensive underground rhizome system that can penetrate up to a depth of one meter, allowing them to access water from deeper soil layers.[12] This morphological adaptation proves particularly valuable in colonising substrates with unfavourable granulometric structure and water conditions, such as flotation tailings.

CONCLUSION

The current study demonstrates the ability of wetland species *Equisetum arvense* and *E. telmateia* to successfully establish themselves in heavily metal-polluted flotation tailings. Despite absorbing substantial concentrations of various potentially toxic elements (As, Cd, Cu, Pb and Zn) in their underground parts, these plants exhibit no adverse effects from the elevated levels of these elements. Remarkably, the concentrations of PTE in the shoots remain consistently low, indicating that the PTE tolerance of the two investigated horsetail species relies primarily on their capacity to exclude these elements. The findings provide further evidence that the PTE tolerance observed in both species is supported by efficient adaptive mechanisms, enabling the accumulation, effective immobilization, and detoxification of PTE within the underground plant parts.

Furthermore, the significant availability of potentially toxic elements (PTE) within the flotation tailings, containing multiple metals, highlights the potential for secondary extraction of residual metals from this type of waste material. Reprocessing the tailings would not only reduce metal leaching that are precious for industry, but also mitigate their detrimental environmental impact. Although PTE-tolerant horsetail plants could be suitable candidates for metal extraction from the rhizosphere, the collection of their underground parts from flotation tailings presents technical challenges. However, their vital ecological role in such technosols primarily lies in increasing organic matter content through the decomposition of old underground and aerial parts. This, in turn, enhances the substrate's capacity to retain PTE. Over the long term, this process facilitates gradual improvements in the physical, chemical, and biological properties of the substrate and promotes natural ecological succession by other metal-tolerant plant species and soil microorganisms.

Acknowledgements: This work was supported by the Serbian Ministry of Education, Science and Technological Development (Grant No. 451-03-68/2022-14/ 200178 and 451-03-68/2022-14/ 200019).

Compliance with Ethical Standards: Conflict of Interest: The authors declare that they have no conflict of interest.

ИЗВОД

Акумулација потенцијално токсичних елемената код две самоникле врсте рода *Equisetum* на одлагалишту флотационе јаловине

ГОРДАНА АНДРЕЈИЋ[1], МИЛИЈАНА КОВАЧЕВИЋ[2], ЖЕЉКО ЦЕЛЕТОВИЋ[1], УРОШ АЛЕКСИЋ[1], ИСИДОР ГРДОВИЋ[2] И ТАМАРА РАКИЋ[2]

[1]Универзитет у Београду, Инстиут за примену нуклеарне енергије, Банатска 31б, 11080 Београд, Србија и [2]Универзитет у Београду, Биолошки факултет, Студентски трг 16, 11000 Београд, Србија

Резултат вишедеценијских рударских активности су знатне количине флотационе јаловине која се одлаже на велике површине стварајући наносе дебљине неколико десетина метара. Јаловина се карактерише дефицитом органске материје и макронутријената, садржи хемикалије пореклом из технолошког процеса и високу концентрацију потенцијално токсичних елемената (ПТЕ). Последично, површина јаловишта изузетно дуго остаје без вегетације и подложна је флувијалној и еолској ерозији. *Equisetum arvense* и *E. telmateia* се појављују као пионирске врсте на одлагалишту флотационе јаловине рудника Pb-Cu-Zn у Србији који је истраживан у овој студији. Свака биљка је узоркована заједно са супстратом из зоне ризосфере. Псеудоукупне и приступачне концентрације As, Cd, Cu, Fe, Mn, Ni, Pb, Zn у супстрату и концентрације у биљним ткивима одређене су атомском апсорпционом спектрофотометријом. Резултати показују да су механизми толеранције засновани на ефикасној акумулацији, имобилизацији и детоксификацији ПТЕ у подземним биљним деловима. Ове две врсте раставића имају неизоставну улогу у повећању садржаја органске материје што постепено побољшава физичка, хемијска и биолошка својства супстрата, а тиме и подржава природне еколошке сукцесије другим биљним врстама и земљишним микроорганизмима отпорним на метале.

(Примљено 13. јануара; ревидирано 21. јуна; прихваћено 1. јула 2023.)

REFERENCES

1. J. S. Adiansyah, M. Rosano, S. Vink, G, Keir, *J. Cleaner Prod.* **108** (2015) 1050 (https://doi.org/10.1016/j.jclepro.2015.07.139)
2. Y. Liu, F Du, L. Yuan, H. Zeng, S. Kong, *J. Hazard. Mater.* **178** (2010) 999 (https://doi.org/10.1016/j.jhazmat.2010.02.038)
3. C. Bayliss, M. Bertram, K. Buxmann, B. de Gelas, S. Jones, L. Wu, Global primary aluminium industry 2010 life cycle inventor, in Energy Technology 2012: Carbon dioxide management and other technologies, M.D.Salazar-Villalpando, N.R.

Neelameggham, D. P. Guillen, S. Pati, G. K. Krumdick (Eds.), Wiley-TMS, Canada, p. 85-92

4. J. Escarré, C. Lefèbvre, S. Raboyeau, A. Dossantos, W. Gruber, J. C. Cleyet Marel, H. Frérot, N. Noret, S. Mahieu, C. Collin C, F. van Oort F, *Water Air Soil Pollut.* **216** (2011) 485 (https://doi.org/10.1007/s11270-010-0547-1)
5. R. Rezaei, M. Massinaei, A. Z. Moghaddam, *Miner. Eng.* **119** (2018) (https://doi.org/10.1016/j.mineng.2018.01.012)
6. J. V. Kalinović, S. M. Šerbula, A. A. Radojević, J. S. Milosavljević, T. S. Kalinović, M. M. Steharnik, *Environ. Monit. Assess.* **191** (2019) 15 (https://doi.org/10.1007/s10661-018-7134-0)
7. G. Andrejić, J. Šinžar-Sekulić, M. Prica, Ž. Dželetović, T, Rakić. *Environ. Sci. Pollut. Res.* **26** (2019) 34658 (https://doi.org/10.1007/s11356-019-06543-7)
8. R. A. Crane, D. E. Sinnett, P.J. Cleall, D. J. Sapsford, *Resour. Conserv. Recycl.* **123** (2017) 117 (https://doi.org/10.1016/j.resconrec.2016.08.009)
9. R. Ginocchio R, P. León-Lobos, E. C. Arellano, V. Anic, J. F. Ovalle, A. J. M. Baker, *Environ. Sci. Pollut. Res.* **24** (2017) 13484 (https://doi.org/10.1007/s11356-017-8894-8)
10. M. T. González, V. Á. López, Á. P. Fernández, B. R. Garrido, C. T. Cepeda, M. Mench, M. Puschenreiter, C. Q. Sabarís, F. M. García, P. S. Kidd, *J. Environ. Manage.* **168** (2017) 301 (https://doi.org/10.1016/j.jenvman.2016.09.019)
11. C. Husby, *Bot. Rev.* **79** (2013) 147 (https://doi.org/10.1007/s12229-012-9113-4)
12. R. L. Hauke, *A taxonomic monograph of the genus Equisetum, subgenus Hippochaete* Nova Hedwigia 8. Stuttgart, 1963, p. 1-123. (https://western.marmot.org/Record/.b2346849x)
13. H. L. Cannon, H. T. Shacklette, H. Bastron, *Geological Survey Bulletin* 1278-A, United States government printing office, Washington, USA, 1968.
14. D. Pant, V. Sharma, P. Singh, *Toxicol. Rep.* **2** (2015) 716 (https://doi.org/10.1016/j.toxrep.2015.04.006)
15. A. Channing, A. Zamuner, D. Edwards, D. Guido, *Am. J. Bot.* **98** (2011) 680 (https://doi.org/10.3732/ajb.1000211)
16. L. P. van Reeuwijk, *Procedures for soil analysis*, FAO/ISRIC, Wageningen, 2002, p. 1-120 (https://www.isric.org/sites/default/files/ISRIC_TechPap09.pdf)
17. U.S. EPA 3051: Microwave assisted acid digestion of sediments, sludges and oils (1998).
18. M. Pansu, J. Gautheyroy, *Handbook of soil analysis. Mineralogical, organic and inorganic methods,* Springer, Berlin, 2006, p.1-993 (https://doi.org/10.1007/978-3-540-31211-6)
19. A. J. Baker, *J. Plant Nutr.* **3** (1981) 643 (https://doi.org/10.1080/01904168109362867).
20. V. Stanković, V. Milošević, D. Milićević, M. Gorgievski, G. Bogdanović G, *Chem. Ind. Chem. Eng. Q.* **24** (2018) 333 (https://doi.org/10.2298/CICEQ170817005S)
21. D. Kasowska, K Gediga, Z. Spiak, *Environ Sci Pollut Res* **25** (2018) 824 (https://doi.org/10.1007/s11356-017-0451-y)
22. A. Karczewska, K. Milko, *Ecological Chemistry and Engineering. A* **17** (2010) 395
23. W. Khalir, M. Hanafiah, S. So'ad, W Ngah, *Pol. J. Chem. Technol.* **13** (2012) 84 (https://doi.org/10.2478/v10026-011-0054-1)
24. L. Zheng, P. Meng, *J Taiwan Inst Chem Eng* 58 (2016) 391 (http://dx.doi.org/10.1016/j.jtice.2015.06.017)

25. N. Osmolovskaya, V. V. Dung, L. Kuchaeva, *Bio. Comm.* 63 (2018) 9 (https://doi.org/10.21638/spbu03.2018.103)
26. A. Kabata-Pendias, *Trace elements in soils and plants,* CRC Press, London, 2011
27. E. Epstein, *Annu. Rev. Plant Physiol*. **50** (1999) 641 (https://doi.org/10.1146/annurev.arplant.50.1.641)
28. V. García-Gaytán, E. Bojórquez-Quintal, F. Hernández-Mendoza, D. K. Tiwari, N. Corona-Morales, Z. Moradi-Shakoorian Z. *J. Chil. Chem. Soc.* **64** (2019) 4298 (http://dx.doi.org/10.4067/s0717-97072019000104298)
29. K. M. Cocker, D. E. Evans, M. J. Hodson, *Physiol. Plant.* **104** (2002) 608 (https://doi.org/10.1034/j.1399-3054.1998.1040413.x)
30. C. Zhang, L. Wang, Q. Nie, W. Zhang, F Zhang, *Environ. Exp. Bot.* **62** (2008) 300 (https://doi.org/10.1016/j.envexpbot.2007.10.024)
31. M. Sahebi, M. M. Hanafi, A. Siti Nor Akmar, M. Y. Rafii, P. Azizi, F. Tengoua, J. Nurul Mayzaitul Azwa, M. Shabanimofrad, *Biomed Res. Int.* **2015** (2015) 396010 (https://doi.org/10.1155/2015/396010)
32. J. A. Bhat, S. M. Shivaraj, P. Singh P, D. B. Navadagi, D. K. Tripathi, P. K. Dash, A. U. Solanke, H. Sonah, R. Deshmukh, *Plants* **8** (2019) 71 (https://doi.org/10.3390/plants8030071)
33. S. M. Zargar, R. Mahajan, J. A. Bhat, M. Nazir, R. Deshmukh, *3 Biotech* **9** (2019) 73 (https://doi.org/10.1007/s13205-019-1613-z)
34. T. Morishita, J. K. Boratynski, *J. Soil Sci. Plant Nutr.* **38** (1992) 781 (https://doi.org/10.1080/00380768.1992.10416712)
35. A. A. Meharg, J. Hartley-Whitaker J. *New Phytol.* **154** (2002) 29 (https://doi.org/10.1046/j.1469-8137.2002.00363.x)
36. A. Clark, T. Hutchinson. Enhancing natural succession on Yukon mine tailings sites: a low-input management approach, in: Mining Environment Research Group Report 2005-3, Geoscience Information and Sales, Indian and Northern Affairs, Whitehhorse, Canada, 2005
37. H. Deng, Z. H. Ye, M. H. Wong, *Environ. Pollut.* **132** (2004) 29 https://doi.org/10.1016/j.envpol.2004.03.030
38. I. W. R. Young, C. Naguit, S. J. Halwas, S. Renault, J. H. Markham, *Restor. Ecol.* **21** (2013) 498 (https://doi.org/10.1111/j.1526-100X.2012.00913.x)
39. J. May, Q. Yang, Y. Zhang, X. Zeng, Y. Zhong, D. Liu, *MATEC Web of Conferences* **100** (2017) 04030, https://doi.org/10.1051/matecconf/201710004030
40. D. Ranđelović, N. Mihailović, S. Jovanović, 2019 *Int. J. Phytorem.* **21** (2019) 707 (https://doi.org/10.1080/15226514.2018.1556590)
41. E. Kurniati, T. Imai, T. Higuchi, M. Sekine, Lead and chromium removal from leachate using horsetail (*Equisetum hyemale*). *Journal of Degraded and Mining Lands Management* **1(2)** (2014) 93 ISSN: 2339-076X.