



HAL
open science

Five Years of Leaching Experiments to Evaluate Land Spreading of a Modified Bauxite Residue Before and After Treatment of Acid Mine Drainage: Sand or Soil Capping and Revegetation

Patricia Merdy, Alexandre Parker, Chen Chen, Pierre Hennebert

► **To cite this version:**

Patricia Merdy, Alexandre Parker, Chen Chen, Pierre Hennebert. Five Years of Leaching Experiments to Evaluate Land Spreading of a Modified Bauxite Residue Before and After Treatment of Acid Mine Drainage: Sand or Soil Capping and Revegetation. *Minerals*, 2024, 14, pp.1210. 10.3390/min14121210 . hal-04807603

HAL Id: hal-04807603

<https://hal.science/hal-04807603v1>

Submitted on 27 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Article

Five Years of Leaching Experiments to Evaluate Land Spreading of a Modified Bauxite Residue Before and After Treatment of Acid Mine Drainage: Sand or Soil Capping and Revegetation

Patricia Merdy ^{1,*}, Alexandre Parker ¹, Chen Chen ¹ and Pierre Hennebert ²

¹ Université de Toulon, Aix Marseille Univ., CNRS, IM2NP, CEDEX 9, 83041 Toulon, France; salexandre.parker@orange.fr (A.P.); chen.83400@gmail.com (C.C.)

² Ineris (French National Institute for Industrial Environment and Risks), BP 2, 60550 Verneuil-en-Halatte, France; pierre.hennebert@gmail.com

* Correspondence: patricia.merdy@univ-tln.fr

Abstract: The global generation of bauxite residue necessitates environmentally responsible disposal strategies. This study investigated the long-term (5-year) behavior of bauxite residue whose pH was lowered to 8.5, called modified bauxite residue (MBR), using lysimeters to test various configurations: raw MBR or used MBR (UMBR) previously applied for acid mine drainage remediation, sand or soil capping, and revegetation. Throughout the experiment and across all configurations, the pH of the leachates stabilized between 7 and 8 and their salinity decreased. Their low sodium absorption ratio (SAR) indicated minimal risk of material clogging and suitability for salt-tolerant plant growth. Leaching of potentially toxic elements, except vanadium, decreased rapidly after the first year to low levels. Leachate concentrations consistently remained below LD50 for *Hyalella azteca* and were at least an order of magnitude lower by the experiment's end, except for first-year chromium. Sand capping performed poorly, while revegetation and soil capping slightly increased leaching, though these were negligible given the low final leaching levels. Revegetated MBR shows promise as a suitable and sustainable solution for managing bauxite residues, provided the pH is maintained above 6.5. This study highlights the importance of long-term assessments and appropriate management strategies for bauxite residue disposal.

Keywords: red mud; toxic elements; environmental protection; remediation; lysimeters; acid mine drainage



Citation: Merdy, P.; Parker, A.; Chen, C.; Hennebert, P. Five Years of Leaching Experiments to Evaluate Land Spreading of a Modified Bauxite Residue Before and After Treatment of Acid Mine Drainage: Sand or Soil Capping and Revegetation. *Minerals* **2024**, *14*, 1210. <https://doi.org/10.3390/min14121210>

Academic Editors: Jasminka Alijagić and Srećko Stopic

Received: 14 October 2024

Revised: 15 November 2024

Accepted: 25 November 2024

Published: 27 November 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Bauxite residue, also known as red mud, is a byproduct of processing bauxite ore to produce alumina (Al₂O₃) through the Bayer process. This process involves heating bauxite in caustic soda (NaOH) at a high temperature and pressure to form sodium aluminate. The residual material consists of about 4% liquor and 55% solid, ranging from 0.3 to 2.5 tons per ton of Al₂O₃ produced. Worldwide, approximately 120 million tons of bauxite residue are generated annually. Primary concerns about bauxite residue disposal include salinity, alkalinity, physical properties, and the presence of potentially toxic metals, posing significant environmental hazards [1–3]. Therefore, it is crucial to explore methods for repurposing this waste and rehabilitating existing disposal sites.

The pH of the bauxite residue is alkaline, between 10 and 13, a consequence of the caustic soda used in the Bayer process. The elevated salinity and sodicity induce toxic effects on plants and animals. Consequently, if revegetation is contemplated, the neutralization of bauxite residue becomes a priority. Rai et al. [1] have explored various techniques, including the use of mineral acids, acidic waste, superphosphate and gypsum, coal dust, CO₂, silicate material, and seawater. Concerning their physical properties, bauxite residues exhibit low structural stability, rendering spreading deposits impermeable to rainwater

percolation and hindering the development of vegetation root systems. This is attributed to their silty nature and the salinity that impedes particle aggregation [2]. In terms of mineralogical and chemical composition, bauxite residue varies across refinery plants but typically contains elevated concentrations of Fe oxides (goethite, hematite, magnetite) in addition to undissolved alumina, and Ti oxide (anatase, rutile, perovskite). The major elements in bauxite residue are Fe (20%–45%), Ti (5%–30%), Al (10%–22%), Si (20%–45%), and to a lesser extent Mn, Ca, Na, Cr, V, La, Sc, and Y [3]. Other elements are present at trace levels, such as As, Be, Cd, Cu, Gl, Pb, Hg, Ni, Th, U, V, Zn, Ce, Nd, and Sm. Some of these elements, like Sc and REE rare earths, are recoverable [4]. Non-metallic and non-metalloid elements such as P and S may also be present [5]. Regarding radioelements, bauxite residue exhibits radioactive activity around 0.03 to 0.06 Bq g⁻¹ due to ²³⁸U and 0.03 to 0.76 Bq g⁻¹ due to ²³²Th, both originating from the ore [5]. This may limit the use of bauxite residue as building material [6] or can be a source of danger in red mud dams [7].

Due to the substantial volumes of bauxite residue and the adverse environmental impact associated with simple disposal methods like ocean dumping, landfilling, or settling ponds, numerous efforts have been undertaken to explore environmentally sustainable and economically viable approaches for bauxite residue management. Reuse applications, including building materials, recovery of valuable chemicals, cement production, road and levee construction, and environmental remediation [8–12] have been proposed, potentially consuming more than 500,000 t y⁻¹ [13]. While this volume is substantial, it falls short of addressing the entirety of residues generated annually, necessitating consideration of alternative disposal methods. Landspreading has historically been a cost effective and widely employed disposal technique. However, a crucial condition for its application is to facilitate the successful revegetation of the spreading area [14,15], thereby mitigating the risk of wind and water erosion on the surface. Various techniques have been implemented to enhance revegetation, primarily focusing on reducing pH and improving the physical properties of the residue, resulting in a modified bauxite residue (MBR). Common practices include washing with a filter press [16], gypsum amendment [17–19], or the addition of coarse materials such as sand [20]. Even in areas where MBR deposits have been successfully revegetated through spreading, concerns persist regarding major elements and particularly toxic trace elements such as Cd, necessitating ongoing monitoring of leaching by groundwater.

Bauxite residue exhibits the capability to immobilize elements that may be mobile in aqueous solutions, encompassing both cationic and anionic species. Examples include phosphate from used water [21] and potentially toxic metal cations in applications such as remediating acid mine tailings (AMT) or addressing acid mine drainage (AMD). Acid mine drainage forms when sulfides in AMT oxidize upon exposure to air and water, generating sulfated acidic solutions with a pH below 6, resulting in various environmental problems [22,23]. Conventionally, alkaline chemicals like CaO or calcite are introduced to neutralize AMD [24]. Interestingly, bauxite residue can serve the same purpose and can also be mixed with AMT to inert it and foster revegetation.

There have been many studies on the possibility of revegetation and ecological restoration of bauxite residue spreading. Some rely on the extrapolation of characterization or laboratory experiments such as column leaching [25]. Regarding studies in an outdoor environment, in situ or using field-scale lysimeters, most of these consider the properties of the spreading at the time of their installation or at a single moment after it [26], temporal monitoring over one year being already considered a long time [27]. However, it is imperative that the ecological relevance of spreading be evaluated over the long term. Here, we propose, for the first time, a study in an outdoor environment with temporal monitoring over 5 years.

In a prior study, we explored this process by examining the long-term behavior of a mixture comprising modified bauxite residue (MBR) and acid mine tailings (AMT) [28]. In the current study, our focus is directed towards delineating the impact of the design of MBR spreading on the leaching of potentially toxic elements, with or without revegetation,

with a sand or a soil capping. We also characterized the leaching from a previously utilized MBR (UMBR), which had been employed in the depollution of acid mine drainage (AMD). Utilizing nine lysimeters established for a duration of five years, we systematically examined the leaching of sulfate and 12 potentially toxic elements in aqueous solutions from both MBR and UMBR.

2. Materials and Methods

2.1. Modified Bauxite Residue (MBR) and Used Modified Bauxite Residue (UMBR)

All chemical reagents were provided by VWR-advantora company (Rosny-sous-Bois, France) at analytical purity. An experimental flow diagram is given in Figure 1. Bauxaline[®] from ALTEO (Gardanne, France) is bauxite residue washed and partially dried in a filter press. The MBR used in the present study is Bauxaline[®] treated with atmospheric CO₂, to which 5% gypsum was added in order to reduce the pH to 8.5 with precipitation of CaCO₃. Soluble Na₂SO₄ remained. The MBR has a variable composition depending on the ore. Table 1 gives the usual range of major and potentially toxic elements in the Bauxaline and the values for the MBR used in this study, which are for most metal and metalloids above the limits for admission to inert waste storage facilities (IWSF) or non-hazardous waste storage facilities (NHWSF) [29]. The UMBR used in this study is the MBR described above, which was used to bind contaminants from acid mine drainage rich in As, Pb, Cd, Cr and Zn [30].

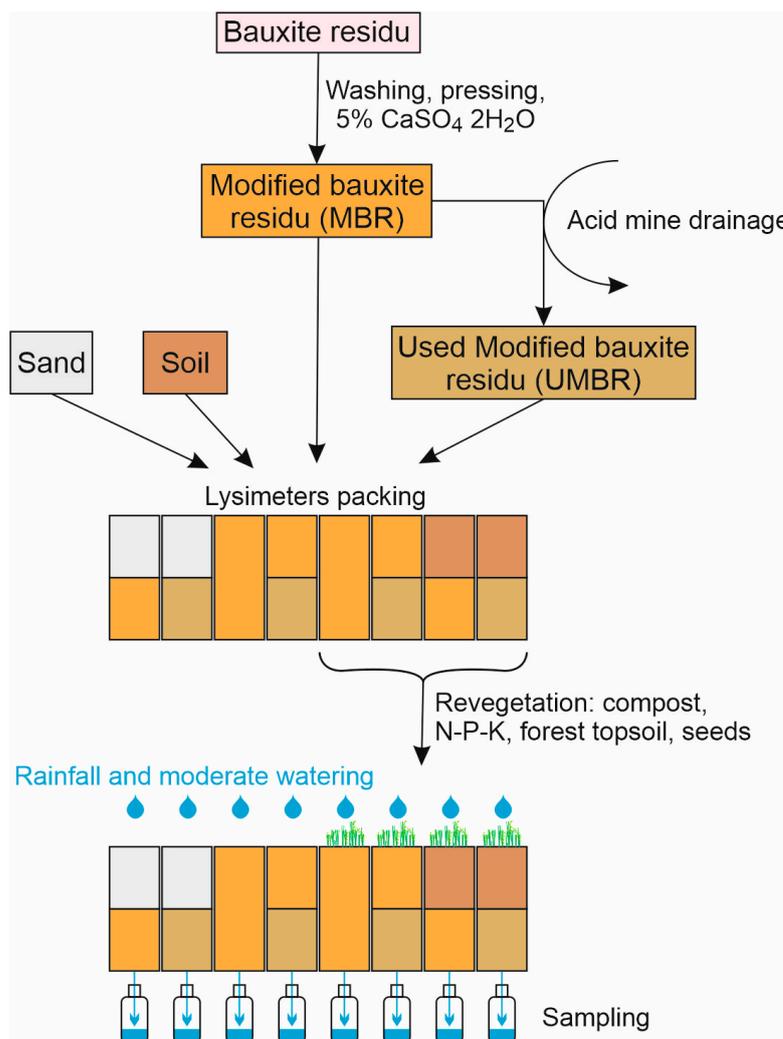


Figure 1. Experimental flow diagram.

Table 1. Usual range of major and potentially toxic elements in the Bauxaline[®] and composition of the Bauxaline[®] used in the present study. IWSF and NHWSF: concentration limits of leachable elements for admission to an inert waste storage facility and non-hazardous waste storage facility, respectively.

	Major Elements (%)		Trace Elements (ppm)				
	Usual Range	Present Study	Usual Range	Present Study	IWSF	NHWSF	
Al	1.6–8.1	7.9	As	10–200	18	0.5	2
Ca	1.4–4.8	4.3	Cd	<0.5–10	0.8	0.04	1
Fe	21.0–38.0	32.2	Co	1–75	35		
Na	1.5–3.0	3.0	Cr	200–2000	1638	0.5	10
Si	0.9–3.9	3.3	Hg	<1.5–2	0.2		
Ti	1.8–5.4	6.0	Ni	5–50	18	0.4	10
			Pb	10–100	42	0.5	10
			Se	<1.5–50	<6	0.1	0.5
			V	200–1500	968		
			Zn	<20–500	115	4	50

Two pilot trials were conducted to treat the highly contaminated acid mine drainage (AMD) from Saint-Félix (pH 2.2, As 57 mg L⁻¹, Cd 1.05 mg L⁻¹, Zn 117 mg L⁻¹) using 50 kg each of granulated MBR as metal binding. The trials involved treating 30 L of AMD per kg of MBR with a residence time of one hour. The decontamination efficiencies achieved were 99.89% and 99.63% for the two trials, respectively. The loading of contaminants in the MBR, calculated from the difference between influent and effluent concentrations, was 1710 mg kg⁻¹ for As, 38 mg kg⁻¹ for Cd, and 4100 mg kg⁻¹ for Zn.

2.2. Lysimeter Conception and Management

Eight 40-L lysimeters (hand-made from large plastic containers) were employed in this study, with varying content, including MBR, UMBR, silicate sand, and soil, with a total thickness of around 44 cm, as depicted in Figure 2. Lysimeters #1 to #4 remained unvegetated, while lysimeters #5 to #8 underwent a revegetation process. Additionally, a larger 700-L lysimeter (#16) filled with 66 cm (1087 kg) of MBR was subjected to the same revegetation process, aiming to more accurately simulate real MBR storage conditions (Figure 1). This last lysimeter was started a year after the others. To ensure technical and financial feasibility, we prioritized the collection of dense time series data over an extended period, without repetition. Repetition would have necessitated either sparse time series data or a shorter experimental duration. In this context, the consistency in the evolution of various variables over time ensures the validity of the results. Additionally, the comparison of the nine lysimeters further reinforces the robustness of the findings.



Figure 2. Lysimeters experimental setup. Left: 40-L lysimeters, view and diagram of filling and revegetation; center and right: 700-L lysimeter, shown from the side and from above, respectively.

The revegetalization was made using *Dactylis glomerata* (orchardgrass) and *Onobrychis sativa* (common sainfoin). The revegetation procedure encompassed the introduction of compost (1% *w/w* in the top 20 cm layer), N-P-K fertilizer, forest topsoil (1% *w/w* in the upper 22 cm layer) in lysimeters #5 and #6, which had no soil capping, and seeds. To address trace element requirements of carbonate-rich soils, an additional soluble manganese (MnSO_4) was added in the second and third years. Additionally, an annual application of N-P-K fertilizer, matching the initial dose, was conducted. Lysimeters #5, #6, and #16 underwent an initial watering prior to seeding to facilitate seedbed desalination.

Autumn, winter and spring rains were sufficient for plant growth. During the summer months, a moderate watering was conducted to sustain plants in a vegetative state. This approach facilitated their swift recovery once rainfall resumed, all while preventing runoff. It is noteworthy that the unvegetated lysimeters underwent the same watering regimen.

In years 4 and 5 of the study, a supplement of fresh forest plant litter was introduced onto the topsoil. Lysimeters #5 to #8 received 5 g each, while lysimeter #16 received 15 g. This deliberate addition aimed to foster the colonization of decomposing organisms, as organic matter had accumulated on the surface, forming a cohesive mat.

Notably, the revegetation efforts proved successful for each lysimeter where it was implemented.

2.3. Sample Collection and Analysis

After each rainfall event, drainage samples were systematically collected, acidified with ultrapure acid, and then stored at 2 °C. Each year, an annual composite sample was created, proportional to the annual drained volumes of the raw samples. For each sample, measurements of pH, electrical conductivity, and redox potential were recorded (VWR phenomenal MD8000L instrument, VWR-advantors company, Rosny-sous-Bois, France). However, redox potential measurements were not used because field tests have shown that the measured redox value was likely to be modified within a few minutes after contact with the atmosphere at the lysimeter outlet. Major and trace element analyses were performed using ICP-AES and ICP-MS at the Eurofins-certified laboratory.

Each sample volume was quantified by weighing, allowing for the calculation of the liquid/solid (L/S) ratio in liters per kilogram of residue. This ratio represents the volume of the leachate divided by the mass of the residue. Concentration is given in mg L^{-1} , while quantity data are given in mg kg^{-1} by multiplying the concentration by the sample L/S ratio. Cumulative quantities correspond to the sum of the quantities of each sample over the duration of the experiment.

There are no international standards for element concentrations in landfill leachates. Existing regulations vary by country and type of filing. As toxicity is a key determinant of the ecological safety of leachates, we used an exposure test using the freshwater amphipod *Hyalella azteca*, chosen for its adaptability to the salinity of some of the leachates [31]. The method used is that described by ISO 16303 [32].

To assess the risk of clay dispersion presented by leachate salinity, we calculated the SAR (sodium absorption rate) using the formula

$$\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{\frac{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}{2}}}$$

where $[\text{Na}^+]$, $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ are expressed in mmol L^{-1} [33].

3. Results and Discussion

3.1. Effect of Sand or Soil Capping on MBR Leaching

This topic was addressed by the results of lysimeters #1 (22 cm of MBR covered by 22 cm of sand), #3 (unvegetated 44 cm of MBR), #5 (vegetated 44 cm of MBR), #7 (22 cm of MBR covered by 22 cm of vegetated soil) and #16 (vegetated 66 cm of MBR).

3.1.1. Hydraulic Properties

The cumulative volumes over the experimental time of water input and drainage, expressed in mm of water height (equivalent to $L m^{-2}$), the drainage/water input ratio and the L/S ratio (litre per kg of MBR) are given in Figure 3 and Table 2.

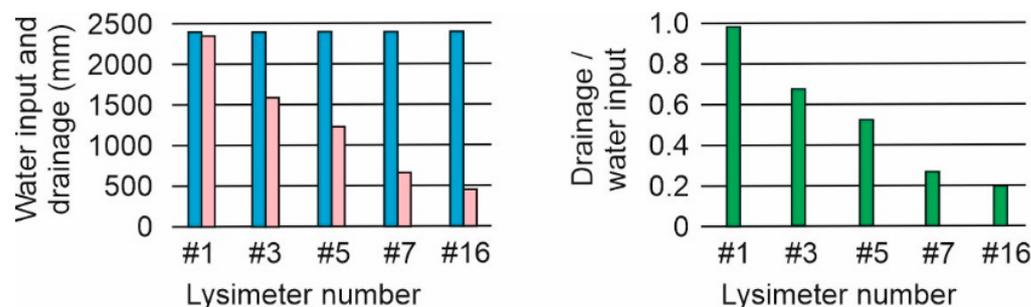


Figure 3. Cumulative water input (rainfall + watering) (blue columns), drainage (pink columns) and drainage/water input ratio (green columns) of lysimeters #1, #3, #5 and #16.

Table 2. Cumulated L/S ratio ($L kg^{-1}$ of MBR) of lysimeters #1, #3, #5, #7 and #16.

	#1	#3	#5	#7	#16
Year 1	2.68	1.16	0.88	1.02	-
Year 1 to 2	3.85	1.45	1.02	1.08	0.09
Year 1 to 3	5.12	1.85	1.33	1.60	0.26
Year 1 to 4	6.67	2.22	1.46	1.72	0.30
Year 1 to 5	8.89	2.99	2.31	2.48	0.46

A drainage-to-water input ratio of 99% was observed for lysimeter #1, suggesting that the sand capping significantly reduced evaporation. Conversely, lysimeters #3 and #5 exhibited ratios of 67% and 52% respectively. This reduction in drainage showed that revegetation increased evapotranspiration. The ratio was even lower for vegetated soil capping (26%), indicating that the soil capping improved water storage or evapotranspiration. The ratio was even lower, by only 20%, for lysimeter #16. Compared to lysimeter #5, the greater thickness of material in lysimeter #16 enabled the augmentation of water storage, thereby increasing the quantity of water available for evapotranspiration.

The potential for leaching of elements towards the depth is possibly higher when the L/S value is high, this will be commented on below (Section 3.1.3). Here, this value decreased with the presence of plant cover and with soil capping (Table 2). The values were nearly identical between lysimeters 5 (vegetated MBR) and 7 (vegetated soil capping), despite the quantity of MBR being half in the latter case, highlighting the effectiveness of soil capping.

3.1.2. pH and Salinity

During the first year of the experiment, the pH levels of leachate remained consistently above 8. Over the subsequent years, there was a gradual decrease, with pH values nearing 7 for lysimeters #1 and #3, and approximately 8 for lysimeters #5 and #16 in the last year (Figure 4). These pH variations align with the changes observed in electrical conductivity, which decreased from the beginning to the end of the experiment (see Figure 4). This indicates a decrease in the alkaline reserve in the soil solution. The latter was in equilibrium with the atmosphere, which explains the decrease in pH. At pHs of the order of 6.5 to 8, Al, Cr, V, Mo, and As exhibit minimal solubility in water, while Pb and Cu exhibit solubility below $10^{-5} mol L^{-1}$ [34,35].

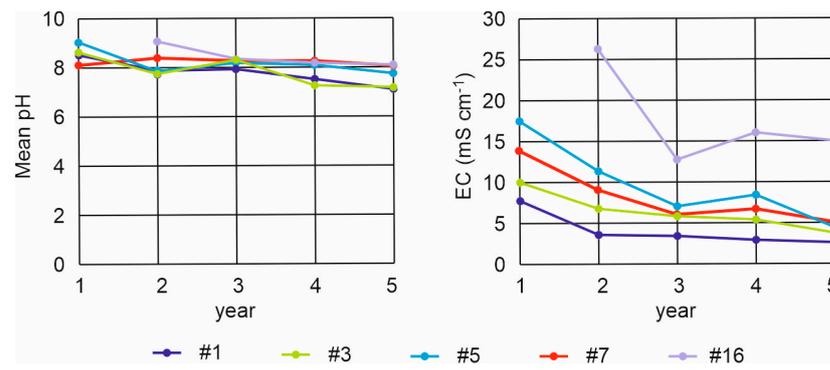


Figure 4. pH and electrical conductivity (EC) of lysimeters #1, #3, #5, #7 and #16.

The differences among lysimeters can be attributed to the cumulative L/S ratios, as shown in Table 2. Lower ratios indicate less solution passing through the lysimeter material, thus reducing the leaching of highly soluble salts that remained at higher concentrations at the end of the experiment. This resulted in higher conductivity and pH levels in the leachates at the end of the experiment. This was particularly clear for lysimeter #16.

3.1.3. Elements in Leachates

Figure 5 gives the temporal variation of the annual leaching per kg of MBR of the elements most likely to pose environmental hazards, such as Na and S, due to salinity or sulfation issues for plants and soils, as well as potentially toxic metals or metalloids. Data for all analyzed elements are provided in the Supplementary Materials Section. Figure 6 presents the cumulative leaching from each lysimeter for all analyzed elements over the entire experimental period (5 years for lysimeters #1 to #7 and 4 years for lysimeter #16).

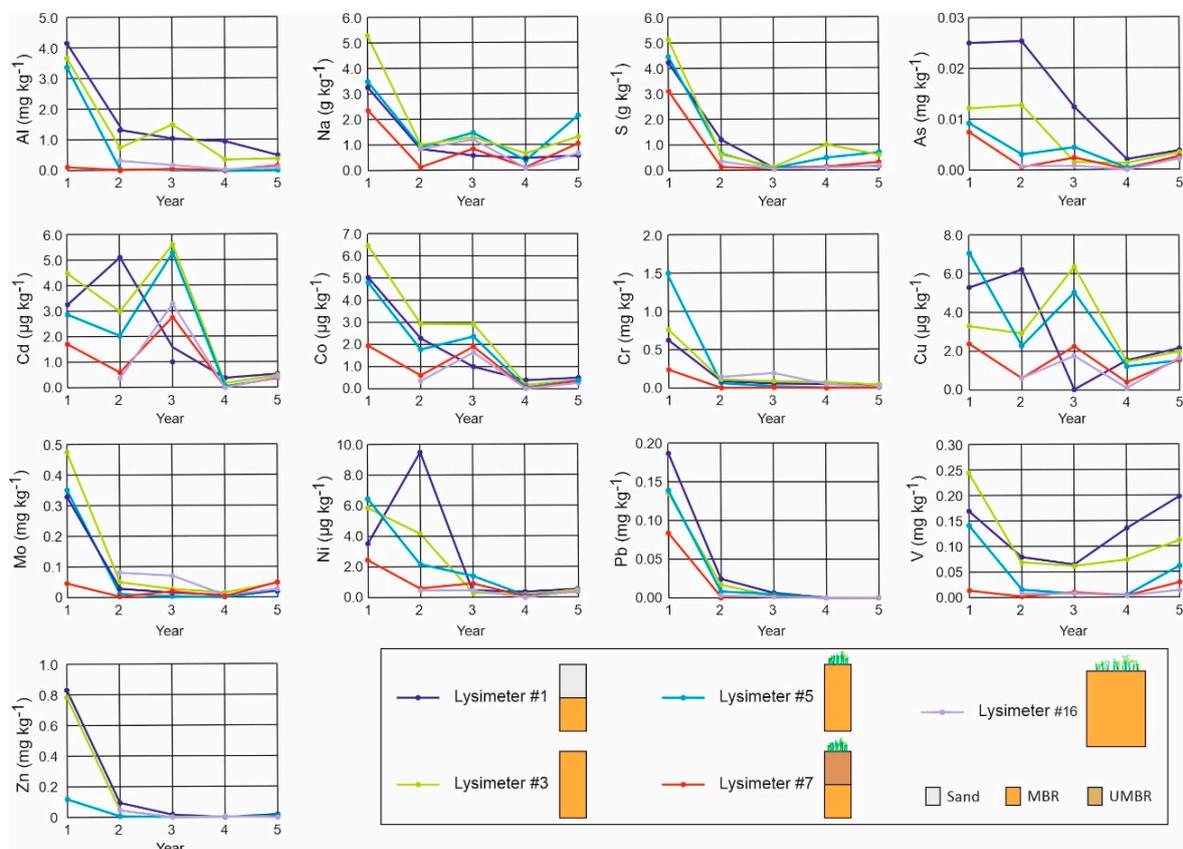


Figure 5. Variation of element leaching over time of some selected elements (Al, Na, S, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn) in mg kg⁻¹ of MBR. Sketch of lysimeters, see Figure 2.

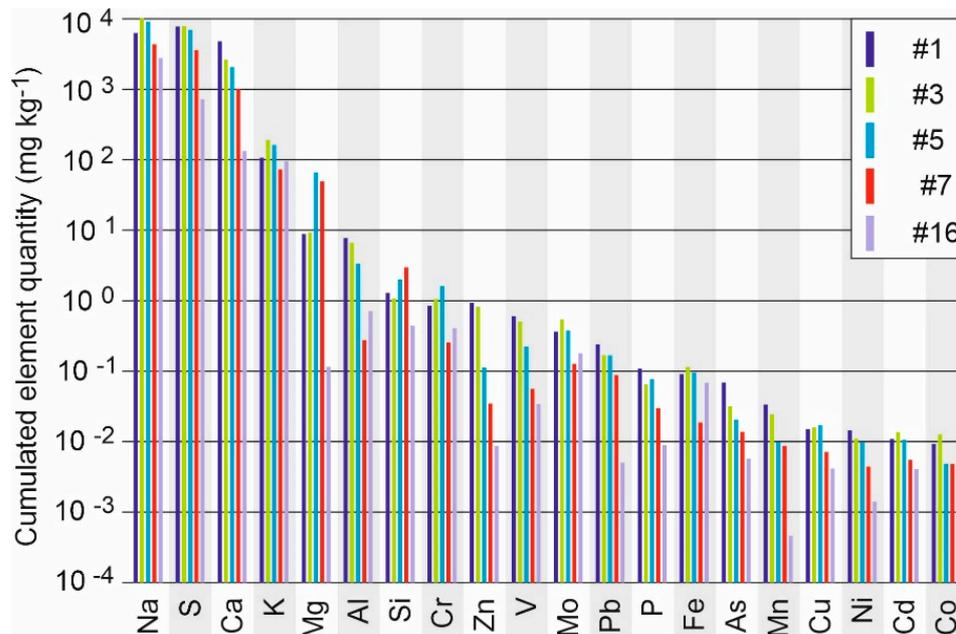


Figure 6. Cumulated element quantity (mg kg^{-1} of MBR) leached by the lysimeters during the 5-year experiment for #1, #3, #5, and #7 and the 4-year experiment for #16.

For most elements in all lysimeters, leaching decreased over time, and for most elements, most of the decrease was observed in the first two years. This trend is primarily influenced by the quantity and availability of a soluble stock that is depleting. The slight increase in leaching between years 4 and 5 can likely be attributed to an intense rain event during year 5, where 72 mm of rainfall occurred following 54 mm of cumulative rainfall during the previous four days. This event saturated the lysimeters with water, facilitating diffusive transfer throughout their entire volume and likely temporarily lowering the material redox state, potentially leading to changes in species of the redox-sensitive elements such as As, Fe or V [36].

For most elements, leaching in lysimeters #1, #3 and #5 was higher than in lysimeters #7, and significantly higher than in lysimeter #16 (Figures 5 and 6). The latter difference can be attributed to the significantly lower L/S ratio in lysimeter #16 compared to other lysimeters. Lysimeter #7 had an L/S ratio similar to that of lysimeter #5 (Table 2); its lower element leaching was, therefore, due to soil capping. It should be noted that soil capping reduces the concentration peak observed in the first year of the experiment. Identifying the processes responsible for the better retention of leachable metals would require a dedicated study; however, one hypothesis is the production of non-leachable complexing organic matter in the soil, which could promote the immobilization of metals.

Average annual leachate concentrations are depicted in Figure 7. Consistent with annual leaching, concentrations for most elements were lower for lysimeters #7 and #16 compared to lysimeters #1, #3 and #5, respectively. Ca, Mg and P exhibited higher concentrations in all lysimeters during the final year compared to the first year of the experiment. The increase in Ca and Mg concentrations can be attributed to a pH decrease over the course of the experiment, as the solubility of these elements is highly pH sensitive. The increase in P concentrations is likely due to added fertilizer. Conversely, the concentrations of all other elements were lower in the final year compared to the first year, except for Si, V, Fe, As, Mn and Co in lysimeter #16, which exhibited higher concentrations in the final year. As previously mentioned, this can be due to an exceptional waterlogging period during the final year.

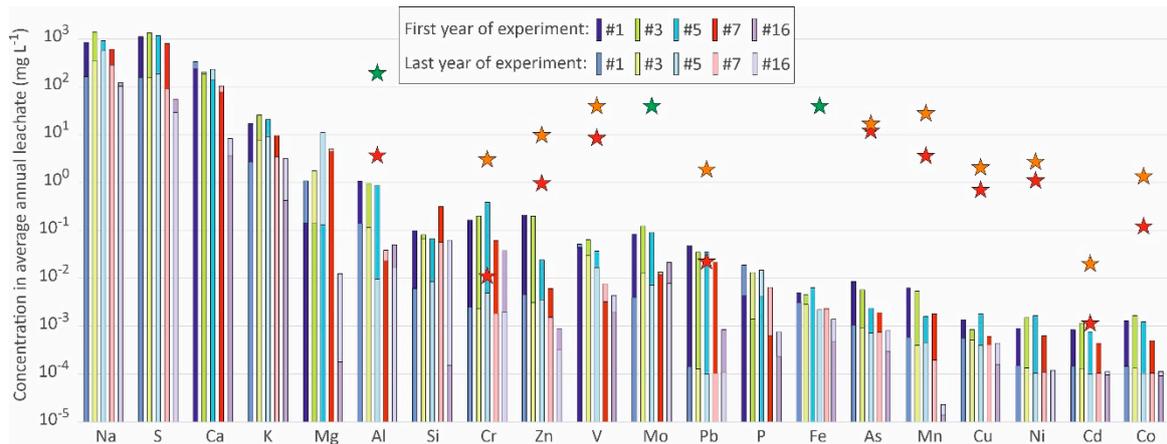


Figure 7. Concentrations in average annual leachate for the first year and the final year of the experiment. Stars indicate the LD50 concentrations for *Hyalella azteca* in soft freshwater (hardness 18, red stars) and hard freshwater (hardness 124, orange stars); green stars indicate that the LD50 concentration is over the star value [31].

Regarding the toxicity test carried out with *Hyalella azteca*, all observed concentrations remained below the LD50 level, except for Cr at the beginning of the experiment. Cd concentration was very close to the LD50 level at the beginning of the experiment. Concentrations of all elements remained under the LD50 values at the end of the experiment, especially knowing that the leachate water is hard (orange stars in Figure 7).

While the element concentrations in the leaching at the end of the experiment were low regardless of the experimental conditions, the quantities leached during the first years were lower for the vegetated soil capping configuration (#7) for all elements except Si.

Leachates contain high concentrations of Na that could cause the clay to disperse into the material underlying the spreading, leading to clogging of the porosity and making it impermeable [33,37]. The consequence would be the clogging of the spread materials and, therefore, a risk of death of vegetation, surface erosion by runoff and modification of the Eh conditions and, therefore, of the mobility of elements likely to change their oxidation state. SAR and EC values for the first and final years of the experiment are given in Figure 8. All points are plotted in the area, indicating no clay dispersion problems. All leachates, however, remained strongly saline with regard to plant growth.

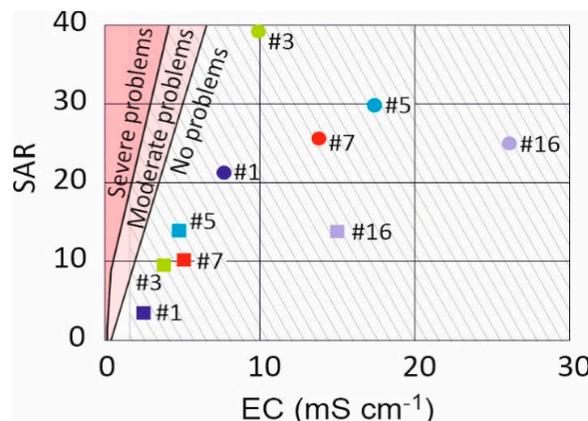


Figure 8. SAR and electrical conductivity (EC) of lysimeters #1, #3, #5, #7 and #16. Circles and squares give first and final-year values, respectively. Areas related to clay dispersion problems were drawn after Hanson et al. [38]. Hatched area represents high and very high salinity with regard to plant growth [39].

In summary, for all potentially toxic metals but V (Al, As, Cd, Co, Cr, Mo, Ni, Pb, Zn), element leaching was very low after 5 years regardless of the design, and concentration in leachates was an order of magnitude or lower than the LD50 toxicity level for *Hyaella azteca*. V leaching was relatively less reduced, but concentrations remained well below the toxicity threshold considered. This finding indicates efficient immobilization of these elements at final pH, whether by precipitation of oxides or adsorption on the active surfaces of clays or oxides.

3.1.4. Effect of Revegetation on MBR or UMBR Leaching

The impact of revegetation on element leaching was evaluated by comparing lysimeters #5 versus #3 (solely MBR) and #6 versus #4 (MBR over UMBR) (Figure 9). Overall, revegetation led to a decrease in leaching of most metals or metalloids investigated, except for Cr in both MBR-only and MBR/UMBR lysimeters, as well as to a small extent Cu in MBR-only lysimeter and Pb in MBR/UMBR lysimeter.

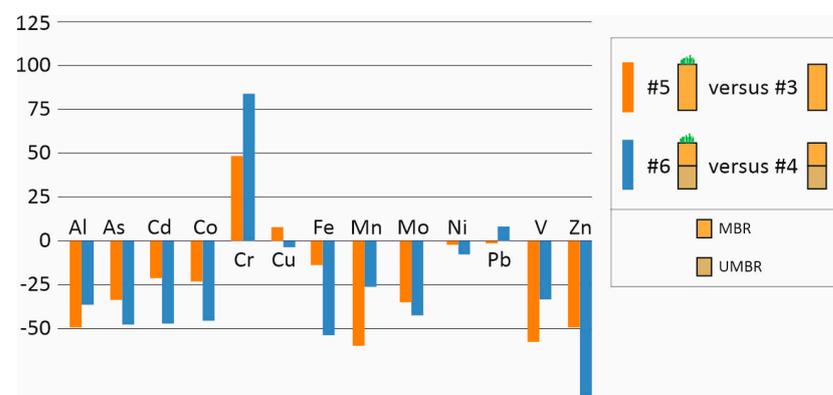
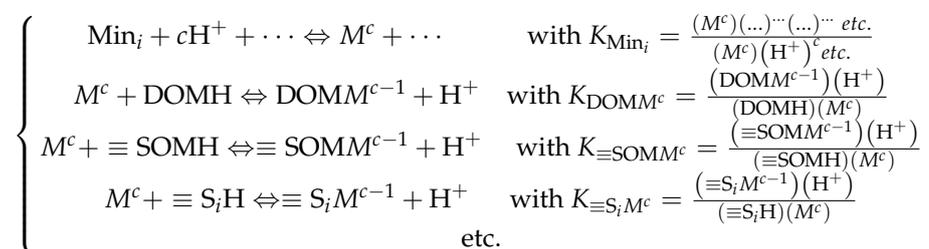


Figure 9. Element leaching from vegetated lysimeter (#5 and #6) as a % of the element leaching from the corresponding non-vegetated lysimeter (#3 and #4, respectively). Cumulative leaching during the 5 years of experimentation.

The mobility in leachates of the ionic species of a given metal M with charge c depends on the solubility of the metal-bearing minerals $Min_1, Min_2, etc.$, its complexation with mobile dissolved organic matter (DOM), and its adsorption on solid surfaces, whether organic (solid organic matter, SOM) or mineral, $S_1, S_2, etc.$ (e.g., oxides or clays). These interactions can be formally described by a set of equations such as the following, where the activities of the adsorbed species are calculated using the site density on the solid related to the solid/soil solution ratio and where K_i is the stability constant of the corresponding reaction:



Parametrizing and solving such an equation system requires the use of a geochemical model such as PHREEQC [40,41] and would be the subject of a further study.

Biological activity associated with vegetation produces organic matter that can form stable organometallic complexes with metals or metalloids [42–46]. For instance, the complexation constants of a typical dissolved organic matter (DOM), as defined in the MinteqA2 database [47], vary for different metals: Al (5.2), Cd (3.3), CrIII (15.2), CuII (4.9), FeIII (7.7), Ni (3.3), Pb (5.2), and Zn (3.5). However, DOM enhances the mobility of an element only if its complexation constant is sufficiently high to facilitate the element

desorption from solid matter, soil organic matter (SOM), or minerals. In this study, most elements exhibited lower leaching in the presence of vegetation, suggesting that their complexation constants with the available DOM were not high enough to promote mobility. In other words, the elements generally remained bound to the solid matter, SOM, or minerals despite the presence of DOM.

Chromium showed the opposite trend to most other elements, with higher leaching in vegetated lysimeters. This behavior can be attributed to different processes, such as oxidation of Cr^{III} to highly mobile Cr^{VI} species [48] or lower adsorption constants of Cr^{III} on solid surfaces than on DOM. It is noted that the Cr-DOM complexation constant given in the MinteqA2 database is particularly high (15.2). Further complementary studies would be necessary to fully elucidate this behavior.

3.2. Immobilization of Potentially Toxic Metals by UMBR That Has Depolluted Acid Mine Drainage

This topic was addressed by the results of lysimeters #2 (22 cm of UMBR covered by 22 cm of sand), #4 (22 cm of UMBR covered by 22 cm of MBR), #6 (22 cm of UMBR covered by 22 cm of MBR), and #8 (22 cm of UMBR covered by 22 cm of vegetated soil) (Figure 2).

3.2.1. Hydraulic Properties

The drainage/water input ratio (Figure 10) as well as the cumulated L/S ratio (Table 3) for lysimeters #2, #4, #6, and #8 were almost identical to those observed for lysimeters #1, #3, #5, and #7, respectively, leading to the same observation as for the latter lysimeters: sand capping limited evaporation, revegetation increased evaporation and reduced drainage, soil capping improved water storage or evapotranspiration.

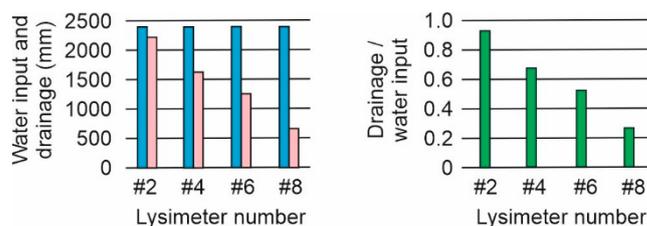


Figure 10. Water input (rainfall + watering) (blue columns), drainage (pink columns) and drainage/water input ratio (green columns) of lysimeters #2, #4, #6 and #8.

Table 3. Cumulated L/S ratio (L kg⁻¹ of MBR) of lysimeters #2, #4, #6 and #8.

	#2	#4	#6	#8
Year 1	2.55	2.39	2.20	0.85
Years 1 to 2	3.68	2.99	2.53	0.89
Years 1 to 3	4.95	3.74	3.19	1.40
Years 1 to 4	6.38	4.55	3.37	1.51
Years 1 to 5	8.39	6.15	4.76	2.54

Lysimeters with the same coverage had very similar L/S ratios. Revegetation of the MBR cover (lysimeters #5 and #6) have reduced the drainage volume, without reaching the reduction observed for the revegetated soil capping (lysimeters #7 and #8).

3.2.2. pH and Salinity

Compared to lysimeters #1, #3, #5 and #7, lysimeters #2, #4, #6 and #8 leachates showed slightly lower pHs and lower ECs at the beginning of the experiment, and almost identical pHs and ECs at the end of the experiment (Figures 4 and 11). This can be related to the fact that the more soluble salts had already been leached in the UMBR material during the acid mine treatment, resulting in pHs already below 8 and ECs already below 10 at the start of the experiment.

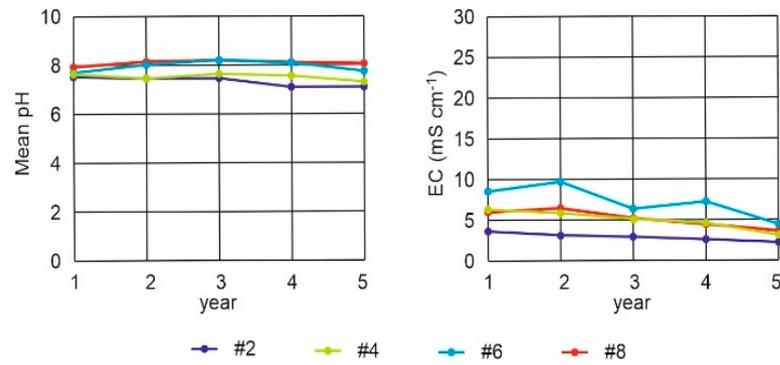


Figure 11. pH and electrical conductivity (EC) of lysimeters #2, #4, #6 and #8.

3.2.3. Effect of UMBR on Elements Leaching

Figure 12 shows the temporal variation of the annual leaching per kg of MBR or MBR+UMBR of potentially toxic metals or metalloids. Data for all analyzed elements are provided in the Supplementary Materials Section. In lysimeters with UMBR, the behavior of the elements is similar to that observed in lysimeters without UMBR, with leaching decreasing over time to reach very low values in the fifth year, with the exception of vanadium, as previously commented.

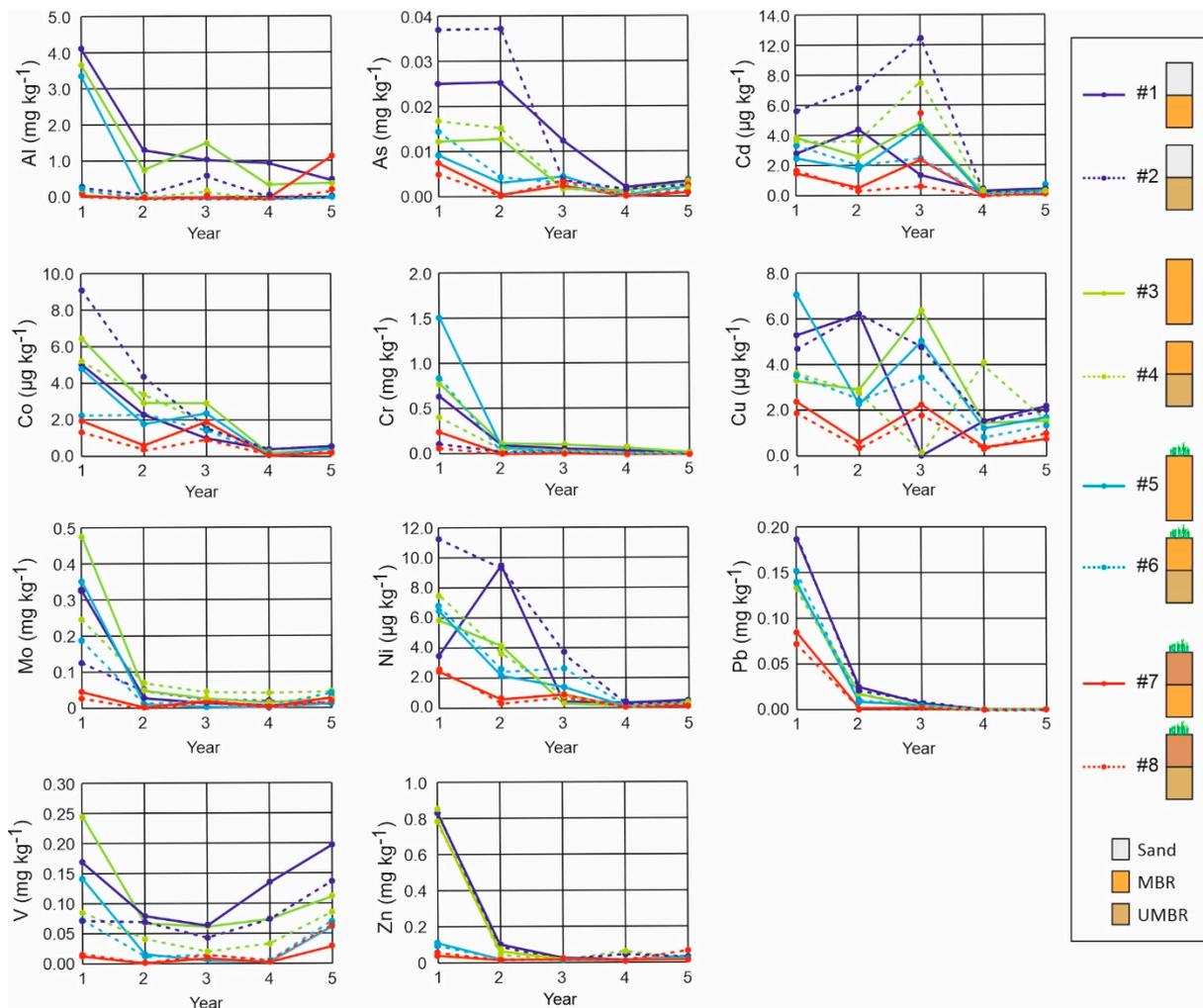


Figure 12. Variation of leaching over time of potentially toxic elements (Al, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn) in mg kg⁻¹ of (MBR+UMBR). Sketch of lysimeters, see Figure 2.

Figure 13 illustrates the variation in cumulative leaching between lysimeters with and without UMBR. There was no clear trend in the difference in leaching between lysimeters with and without UMBR. The presence of UMBR led to varying retention and leaching patterns for different elements: some elements, such as Al, Cr, and Mo, were more retained, while others, like As, Mn, and Ni, were more emitted. Additionally, the retention or leaching of certain elements varied depending on the lysimeter design: sand capping increased leaching for Cd, Co, Cu, Fe, and Ni, whereas soil capping led to higher leaching for Fe, Mn, V, and Zn. Interestingly, despite the higher As, Pb, Cr, and Zn contents in UMBR, lysimeters with UMBR did not consistently show higher leaching for these elements throughout the experiment. This indicates the effectiveness of UMBR in retaining these elements.

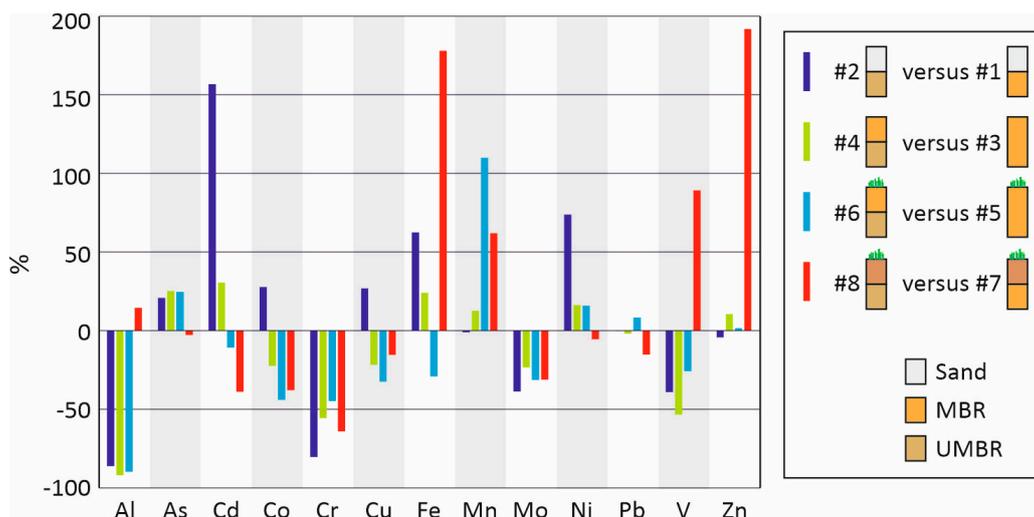


Figure 13. Element leaching from lysimeter with UMBR as a % of the element leaching from the corresponding lysimeter without UMBR. Cumulative leaching during the 5 years of experimentation.

As explained above, many parameters and mechanisms may be involved in the mobility of elements and their transfer into leachates. The treatment of AMD by UMBR led to a drop in pH; it could also have led to the precipitation of other mineral forms, modified the specific surfaces of the minerals or released sorption sites by the leaching of major mobile elements such as Ca or Mg. The precise determination of the mechanisms involved would require the fine characterization of the mineral phases present, the evaluation of their specific surfaces, in situ redox and pH monitoring in the lysimeters, the determination of the species present in the leachates and conceptual modeling.

Despite the observed variations, annual average concentrations remained below the LD50 values for all elements except Cr during the first year of the experiment, as previously mentioned.

4. Conclusions

Over the course of the 5-year experiment and across all configurations tested—raw, sand capping, soil capping, and revegetation—the pH of the leachates stabilized between 7 and 8, and their salinity gradually decreased. Although the salinity remained significant in the final year, ranging from 3 to 5 mS cm⁻¹, the SAR stayed well below the values that could cause clay dispersion and material clogging. Therefore, in all cases, the material remained suitable for the growth of plants compatible with the observed salinity.

Except for V, the leaching of potentially toxic elements from the modified bauxite residue (MBR), whether or not it was used to remediate acid mine drainage, rapidly decreased after the first year, reaching low levels. Except for Cr in the first year, the concentrations in the leachates always remained below the LD50 values and reached levels at least one order of magnitude lower than the LD50 by the end of the experiment. Among the different designs studied, soil capping and revegetation significantly reduced the

leaching of elements. Soil capping, in particular, reduces the concentration peak observed in the first year of the experiment.

As a recommendation, in the climatic conditions of the test, which do not lead to soil acidification, spreading MBR, or an MBR previously used for AMD decontamination, with revegetalization after soil capping is the best environmental practice, which avoids the dispersion of dust and is not accompanied by the worry about leaching of potentially toxic elements. It will be necessary to check the composition of the residue before spreading, to verify that the contents of potentially toxic elements do not exceed the usual values as defined above, in particular vanadium. Under climatic conditions more conducive to soil acidification, for example, with high rainfall, the pH of the spreading should be controlled, not falling below 6.5, and adjusted if necessary by liming. Future research should establish content thresholds for the different potentially toxic elements in MBR-type matrices.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min14121210/s1>, Table S1. Annual leachate emission (mg/kg of MBR).

Author Contributions: Conceptualization, P.M. and P.H.; methodology, P.H.; validation, P.M. and P.H.; investigation: P.M., P.H., C.C. and A.P.; writing—original draft preparation: P.M.; writing—review and editing, P.M. and P.H.; resources, P.H.; project administration, P.H.; funding acquisition, P.H. All authors have read and agreed to the published version of the manuscript.

Funding: Funding was provided by the BauGeste (also called Bauxaline Technologies) project (ADEME, Rhône-Mediterranean-Corsica Water Agency (AERMC agreement 2012/0547) and ALTEO) and the Bauxite+ project (ECCOREV-OHM).

Data Availability Statement: Data are given in Supplementary Materials.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Rai, S.; Wasewar, K.; Agnihotri, A. Treatment of alumina refinery waste (red mud) through neutralization techniques: A review. *Waste Manag. Res.* **2017**, *35*, 563–580. [CrossRef] [PubMed]
2. Newson, T.; Dyer, T.; Sharp, S. Effect of structure on the geotechnical properties of bauxite residue. *J. Geotech. Geoenviron. Eng.* **2006**, *132*, 143–151. [CrossRef]
3. Samal, S. Utilization of Red Mud as a Source for Metal Ions—A Review. *Materials* **2021**, *14*, 2211. [CrossRef] [PubMed]
4. Botelho Junior, A.B.; Espinosa, D.C.R.; Tenório, J.A.S. Characterization of bauxite residue from a press filter system: Comparative study and challenges for scandium extraction. *Mining Metal. Explor.* **2021**, *38*, 161–176. [CrossRef]
5. Gu, H.; Wang, N.; Liu, S. Radiological restrictions of using red mud as building material additive. *Waste Manag. Res.* **2012**, *30*, 961–965. [CrossRef]
6. Gu, H.; Wang, N.; Yang, Y.; Zhao, C.; Cui, S. Features of distribution of uranium and thorium in red mud. *Physicochem. Probl. Miner. Proc.* **2017**, *53*, 110–120. [CrossRef]
7. Kovács, T.; Sas, Z.; Jobbágy, V.; Csordás, A.; Szeiler, G.; Somlai, J. Radiological aspects of red mud disaster in Hungary. *Acta Geophys.* **2013**, *61*, 1026–1037. [CrossRef]
8. Liu, Y.; Naidu, R. Hidden values in bauxite residue (red mud): Recovery of metals. *Waste Manag.* **2014**, *34*, 2662–2673. [CrossRef]
9. Klauber, C.; Gräfe, M.; Power, G. Bauxite residue issues: II. options for residue utilization. *Hydrometallurgy* **2011**, *108*, 11–32. [CrossRef]
10. Verma, A.S.; Suri, N.M.; Kant, S. Applications of bauxite residue: A mini-review. *Waste Manag. Res.* **2017**, *35*, 999–1012. [CrossRef]
11. Kim, S.Y.; Jun, Y.; Jeon, D.; Oh, J.E. Synthesis of structural binder for red brick production based on red mud and fly ash activated using Ca(OH)₂ and Na₂CO₃. *Constr. Build. Mater.* **2017**, *147*, 101–116. [CrossRef]
12. Rivera, R.M.; Ulenaers, B.; Ounoughene, G.; Binnemans, K.; Van Gerven, T. Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching. *Miner. Eng.* **2018**, *119*, 82–92. [CrossRef]
13. International Aluminium Institute. *Bauxite Residue Management: Best Practice*; IAI: London, UK, 2015; pp. 1–31.
14. Mishra, T.; Pandey, V.C.; Singh, P.; Singh, N.B.; Singh, N. Assessment of phytoremediation potential of native grass species growing on red mud deposits. *J. Geochem. Explor.* **2017**, *182*, 206–209. [CrossRef]
15. Mishra, T.; Singh, N.B.; Singh, N. Restoration of red mud deposits by naturally growing vegetation. *Int. J. Phytoremed.* **2017**, *19*, 439–445. [CrossRef]
16. Kinnarinen, T.; Lubieniecki, B.; Holliday, L.; Helsto, J.-J.; Häkkinen, A. Enabling safe dry cake disposal of bauxite residue by deliquoring and washing with a membrane filter press. *Waste Manag. Res.* **2015**, *33*, 258–266. [CrossRef]
17. Lindsay, W.L. *Chemical Equilibria in Soils*; John Wiley and Sons Ltd.: Hoboken, NJ, USA, 1979.

18. Barrow, N.J. Possibility of using caustic residue from bauxite for improving the chemical and physical properties of sandy soils. *Aust. J. Agric. Res.* **1982**, *33*, 275–285. [CrossRef]
19. Wong, J.W.C.; Ho, G.E. Use of waste gypsum in the revegetation on red mud deposits: A greenhouse study. *Waste Manag. Res.* **1993**, *11*, 249–256. [CrossRef]
20. Courtney, R.G.; Timpson, J.P. Reclamation of fine fraction bauxite processing residue. red mud) amended with coarse fraction residue and gypsum. *Water Air Soil Pollut.* **2005**, *164*, 91–102. [CrossRef]
21. Pradhan, J.; Das, J.; Das, S.; Thakur, R.S. Adsorption of Phosphate from Aqueous Solution Using Activated Red Mud. *J. Colloid Interface Sci.* **1998**, *204*, 169–172. [CrossRef]
22. Elghali, A.; Benzaazoua, M.; Taha, Y.; Amar, H.; Ait-khouia, Y.; Bouzahzah, H.; Hakkou, R. Prediction of acid mine drainage: Where we are. *Earth-Sci. Rev.* **2023**, *241*, 104421. [CrossRef]
23. Sarmiento, A.M.; Rodriguez-Perez, A.M.; Davila, J.M.; de la Torre, M.L. Effect of acid mine drainage on the mechanical properties of AISI 1020 carbon steel and AW6060 aluminium. *J. Mat. Res. Technol.* **2024**, *32*, 541–549. [CrossRef]
24. Kalin, M.; Fyson, A.; Wheeler, W.N. The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Sci. Total Environ.* **2006**, *366*, 395–408. [CrossRef]
25. Wu, Y.; Li, X.; Jiang, J.; William, H.; Zhu, F.; Xue, S. Integrating column leaching experiments and geochemical modelling to predict the long-term alkaline stability during erosion process for gypsum amended bauxite residue. *J. Environ. Manag.* **2021**, *289*, 112479. [CrossRef] [PubMed]
26. Jiang, Y.; Huang, S.; Zhu, F.; Guo, X.; Zhang, X.; Zhu, M.; Zhang, Y.; Xue, S. Long-term weathering difference in soil-like indicators of bauxite residue mediates the multifunctionality driven by microbial communities. *Sci. Total Environ.* **2023**, *890*, 164377. [CrossRef] [PubMed]
27. Scullett-Dean, G.; Stockwell, K.; Myers, L.; Nyeboer, H.; Santini, T.C. Accelerating soil formation in bauxite residue: A solution for long-term tailings management and storage. In Proceedings of the Mine Closure 2022: 15th International Conference on Mine Closure, Brisbane, Australia, 4–6 October 2022; Australian Centre for Geomechanics: Crawley, Australia, 2022; pp. 1027–1036. [CrossRef]
28. Merdy, P.; Parker, A.; Chen, C.; Hennebert, P. 5-year leaching experiments to evaluate a modified bauxite residue: Remediation of sulfidic mine tailings. *Environ. Sci. Pollut. Res.* **2023**, *30*, 96486–96498. [CrossRef] [PubMed]
29. European Communities. Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. *Off. J. Eur. Commun.* **2003**, *11*, 27–49. Available online: <https://eur-lex.europa.eu/LexUriServ.do?uri=OJ:L:2003:011:0027:0049:EN:PDF> (accessed on 12 October 2024).
30. Jacukowicz-Sobala, I.; Ociński, D.; Kociołek-Balawejder, E. Iron and aluminium oxides containing industrial wastes as adsorbents of heavy metals: Application possibilities and limitations. *Waste Manag. Res.* **2015**, *33*, 612–629. [CrossRef]
31. Borgmann, U.; Couillard, Y.; Doyle, P.; Dixon, D.G. Toxicity of sixty-three metals and metalloids to *Hyalella azteca* at two levels of water hardness. *Environ. Toxicol. Chem. Int. J.* **2005**, *24*, 641–652. [CrossRef]
32. ISO 16303:2013; Determination of Toxicity of Fresh Water Sediments Using *Hyalella azteca*. International Standardization Organization: Geneva, Switzerland, 2013. Available online: <https://www.iso.org/obp/ui/#iso:std:iso:16303:ed-1:v1:en> (accessed on 12 October 2024).
33. Rengasamy, P. Irrigation water quality and soil structural stability: A perspective with some new insights. *Agronomy* **2018**, *8*, 72. [CrossRef]
34. Cherfouh, R.; Lucas, Y.; Derridj, A.; Merdy, P. Metal speciation in sludges: A tool to evaluate risks of land application and to track heavy metal contamination in sewage network. *Environ. Sci. Pollut. Res.* **2022**, *29*, 70396–70407. [CrossRef]
35. Rocha, L.; Rodrigues, S.M.; Lopes, I.; Soares, A.M.V.M.; Duarte, A.C.; Pereira, E. The water-soluble fraction of potentially toxic elements in contaminated soils: Relationships between ecotoxicity, solubility and geochemical reactivity. *Chemosphere* **2011**, *84*, 1495–1505. [CrossRef] [PubMed]
36. Rinklebe, J.; Antoniadis, V.; Shaheen, S.M. Redox Chemistry of Vanadium in Soils and Sediments: Biogeochemical Factors Governing the Redox-Induced Mobilization of Vanadium in Soils. In *Vanadium in Soils and Plants*; CRC Press: Boca Raton, FL, USA, 2022; pp. 95–111. [CrossRef]
37. Cherfouh, R.; Lucas, Y.; Derridj, A.; Merdy, P. Long-term, low technicality sewage sludge amendment and irrigation with treated wastewater under Mediterranean climate: Impact on agronomical soil quality. *Environ. Sci. Pollut. Res.* **2018**, *25*, 35571–35581. [CrossRef] [PubMed]
38. Hanson, B.; Grattan, S.R.; Fulton, A. Agricultural salinity and drainage. In *Water Management Series Publication 3375*; University of California: Davis, CA, USA, 2006.
39. Wilcox, L.V. *Classification and Use of Irrigation Water (No. 969)*; U.S. Department of Agriculture: Washington, DC, USA, 1955.
40. Johnson, J.; Anderson, G.; Parkhurst, D. *Database Thermo.com.V8.R6.230, Rev 1.11*; Lawrence Livermore National Laboratory: Livermore, CA, USA, 2000; Volume 995.
41. Merdy, P.; Gamrani, M.; Montes, C.R.; Rezende Filho, A.T.; Barbiero, L.; Ishida, D.A.; Silva, A.R.C.; Melfi, A.J.; Lucas, Y. Processes and rates of formation defined by modelling in alkaline to acidic soil systems in Brazilian Pantanal wetland. *Catena* **2022**, *210*, 105876. [CrossRef]
42. Caporale, A.G.; Violante, A. Chemical processes affecting the mobility of heavy metals and metalloids in soil environments. *Curr. Pollut. Rep.* **2016**, *2*, 15–27. [CrossRef]

43. Merdy, P.; Guillon, E.; Aplincourt, M.; Duomonceau, J. Interaction of metallic cations with lignins. Part 1: Stability of iron (III), manganese (II) and copper (II) complexes with phenolic lignin model compounds: Coumaric, ferulic and sinapic acids and coniferyl alcohol. *J. Chem. Res.* **2000**, *2000*, 76–77. [[CrossRef](#)]
44. Merdy, P.; Lucas, Y.; Coulomb, B.; Melfi, A.J.; Montes, C.R. Soil organic carbon mobility in equatorial podzols: Soil column experiments. *Soil* **2021**, *7*, 585–594. [[CrossRef](#)]
45. Merdy, P.; Meunier, J.D.; Ziarelli, F.; Lucas, Y. Evidence of humic acid-aluminium-silicon complexes under controlled conditions. *Sci. Total Environ.* **2022**, *829*, 154601. [[CrossRef](#)]
46. Dobran, S.; Zagury, G.J. Arsenic speciation and mobilization in CCA-contaminated soils: Influence of organic matter content. *Sci. Total Environ.* **2006**, *364*, 239–250. [[CrossRef](#)]
47. Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J. *MinteqA2/ProdefA2, a Geochemical Assessment Model for Environmental Systems, Database of Computer Programme; Version 3.0*; U.S. Environmental Protection Agency: Athens, GA, USA, 1991.
48. Pansar-Kallio, M.; Reinikainen, S.P.; Oksanen, M. Interactions of soil components and their effects on speciation of chromium in soils. *Anal. Chim. Acta* **2001**, *439*, 9–17. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.