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Use of selected amendments for reducing metal mobility and ecotoxicity in contaminated bottom sediments

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Abstract

The aims of the study were 1) to assess the suitability of selected amendments for reducing the mobility of metals in sediments by evaluating their effects on metal sorption capacity, and 2) to assess the ecotoxicity of sediment/amendment mixtures. Three different amendments were tested: cellulose waste, biochar, and dolomite. The efficiency of metal immobilization in mixtures was dependent on pH, which increased with concentrations of amendment. The higher negative charge observed for dolomite and cellulose waste corresponded with greater attraction of cations and enhanced metal sorption. For cellulose waste, the highest values of the Q parameter were attributed to the presence of OH groups, which corresponded with the highest immobilization of metals. Biochar reduced the negative surface charge, which highlights the importance of additional factors such as high specific surface area and volume of pores in metal immobilization. All amendments increased the SSA and V_{N2}, indicating a higher number of sorption sites for metal immobilization. Most bioassays established a reduction of the ecotoxicity for amendments. Mixtures with dolomite (25%, 45% doses) and biochar (45% dose) were low toxic. Mixtures with cellulose waste were toxic or highly toxic. The mobility of metals from contaminated sediments can be limited by reused industry side products, which could contribute to further closing the circular economy loop.

Keywords: metal fractionation, industry side products, immobilisation, sorption capacity, biotest

1. Introduction

Metal contamination of bottom sediments poses a significant ecological risk. Metals can persist in sediments for decades, and they can easily enter the food chain, posing a threat to all levels of the biosphere (Peng et al., 2018; Baran et. al., 2023). Metal contamination also limits the options for using dredged sediments outside of their original waterbody, such as for agriculture, reclamation, and civil engineering projects (Renella, 2021). Because of the threat to the aquatic environment, contaminated sediments require remediation. However, this is a complex issue due to the variety in physical and chemical properties of sediments. Therefore, there is an urgent need to conduct remediation studies to develop effective and sustainable solutions (Peng et al., 2018; Polrot et al., 2021).

Metal immobilization is a simple, efficient, and widely used remediation method for metal-contaminated bottom sediments (Palansooriya et al., 2022; Wang et al., 2021). It involves changing the physical and chemical properties of the sediments to make the metals less mobile. This is done by modifying the sorption complex of the substrate by adding materials that improve the physicochemical parameters responsible for metal immobilization (Zhang et al., 2015; Peng et al., 2018; Martínez-Nicolás et al., 2020). The goal is to move metals from mobile to less mobile forms or to immobilize them completely. It is important to note that immobilization does not reduce the total metal content of the sediments, but it does make the metals less accessible and less harmful.

To remediate metal-contaminated bottom sediments, it is important to consider not only the total metal content, but also the forms and fractions of the metals present. This is because the mobility of metals in the environment depends on their form. Soluble and exchangeable metal forms are considered to be mobile, potentially bioavailable, and toxic (Wojtkowska and Bogucki, 2022). The mobility of metals in bottom sediments is governed by the properties of the sediment, the environmental conditions, and the type and form of the metals (Wojtkowska, 2013, Peng et al., 2018). Strong and relatively permanent binding of metals occurs in combination with carbonates, phosphates, sulfates, and sulfides. Incorporation into the lattice structure of minerals can also occur as a result of coagulation, flocculation, precipitation, or co-precipitation into insoluble forms (Wojtkowska, 2013; Zhang et al., 2014). In contrast, the colloid and organic matter contents of sediments are key factors influencing the ecologically most important type of interaction with metals, which is exchangeable sorption. This process is reversible and depends on pH, redox potential, ionic strength, and the structure and content of organic matter. Under unfavorable conditions, metals may re-mobilize and become more toxic (Boguta et al., 2016). In the case of bottom sediments, sorption processes can also be mediated by the presence of dissolved natural organic matter, including humic and fulvic acids (Boguta et al., 2016). The mobility/immobility of metals in sediments also shows a direct relationship with some physical parameters, such as porosity and the surface area available for adsorption. These parameters are a function of sediment granulometry (Brito et al., 2020; Otunola and Ololade, 2020).

Metal immobilisation is a widely studied and promising approach for remediating metal-contaminated bottom sediments (Peng et al., 2018; Ma et al., 2019; Wikström et. al., 2021). While various materials have been investigated for metal immobilization, environmentally friendly solutions are constantly being sought, and materials of natural or waste origin are increasingly promoted (Lwin et al., 2018; Palansooriya et al., 2019; Wang et al., 2021). Metal immobilization in bottom sediments involves using materials with good sorption properties that can affect pH and form hardly soluble compounds with metal ions. According to the literature, metal immobilization can be achieved by introducing into bottom sediments various substances that permanently or temporarily bind metal contaminants, such as limestone, gypsum, zeolites, phosphorus compounds, lignite, and natural minerals (Lwin et al., 2018). Recently, industrial side products have shown promise as amendments for further reducing the mobility and bioavailability of metals in soil/sediments (Lwin et al., 2018; Wang et al., 2021). Industrial by-products have been widely used beneficially in agriculture and reclamation, and most have alkaline properties that can increase soil pH, reduce bulk density, increase aggregate stability and water holding capacity, and add basic soil cations. They also contain many macro and micronutrients with useful properties for enhancing soil quality (Lwin et al., 2018; Antonkiewicz et al., 2019). To effectively reduce metal solubility while preserving the physicochemical properties suitable for a bottom sediment substrate, it is important to match the distinct properties of the sediment and amendment. An important factor determining the success of metal immobilization processes is the effectiveness of the substance used to immobilize metal ions. However, there is a lack of data on the effective modification of the properties of contaminated bottom sediments by the application of industrial by-products characterized by the potential to immobilize many metals and reduce their ecotoxicity.

The goals of the study were 1) to assess the suitability of selected amendments (cellulose waste, biochar, and dolomite) for reducing the mobility of metals in sediments by evaluating their effects on metal sorption capacity, and 2) to assess the ecotoxicity of sediment/amendment mixtures. Evaluating the relationships between sorption capacity, metals mobility and ecotoxicity is useful for managing contaminated bottom sediments and reducing the risk of introducing metals to the environment.

2. Materials and methods

2.1. Materials and experimental setup

Bottom sediment was collected from one of the contaminated zones (dam zone) of the Chechło reservoir. Using an Ekman sampler, five sediment samples within a 30-meter radius were collected from a depth of 0 to 15 centimeter and stored at 4°C for transport. In the laboratory, the samples were combined, air-dried, and ground.

Three amendments were tested: cellulose waste (CW), biochar (BC), and dolomite (DL). Cellulose production waste was acquired from the Paper and Cardboard Factory Beskidy S.A. in Wadowice, Poland (Antonkiewicz et al., 2018). Cellulose waste with code 030310 includes “fibre rejects, fibre-, filler- and coating sludges from mechanical separation”. It belongs to chapter 03 of the European waste Catalogue concerning “wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard”, from sub-chapter 03 on “wastes from pulp, paper and cardboard production and processing” (European Commission, 2014). The biochar came from the company Fluid SA in Sędziszów, Poland. Biochar was made of renewable resources, i.e. plants, wood production residue in sawmills, or specifically grown energy willow and miscanthus, through FLUID technology. As opposed to the classical pyrolysis process, this technology is an innovative method of thermal treatment of every type of plant biomass and biomass residues in an oxygen-free atmosphere, at temperatures below 300°C. Dolomite was obtained from Kopalnia Józefka Sp. z o.o. in Górno, Poland. This waste material is a byproduct of grinding dolomite for use as aggregate in the construction industry. Amendments were air dried prior to the experiment, ground (0-0.2 mm) and homogenized.

Before the experiment started, a chemical analysis of the sediments and materials was preformed (Table 1). Bottom sediment was characterised by an acidic pH, whereas cellulose waste, dolomite and biochar were alkaline. The highest pH value of the cellulose waste resulted from technological processes where calcium compounds are used for hygienisation of this waste. Biochar had the highest content of total organic carbon (TOC). A high content in Cd, Zn and Pb were found in the bottom sediments, whereas biochar had the highest content in Cr , Ni and Cu.

The experimental design covered 4 treatments with a combination of 95%, 75%, 55% bottom sediment and 5%, 25%, 45% of each waste material respectively, and a control sample which was only bottom sediment (100%). The proportion of sediment and amendments was calculated based on their dry weight. Each mixture was placed in a 500 cm^3 propylene container and mechanically mixed for 24 hours until homogeneous blending (36 rpm). Next, mixtures were hydrated to 45% maximum water holding capacity, and kept in the dark at 20℃ for 116 days. Water losses were supplemented with distilled water once a week. The incubation experiment was conducted in triplicate for each mixture.

2.2. Physico-chemical analysis

In the bottom sediment, in the additives, as well as in the developed mixtures, pH was determined potentiometrically with a pH meter in 1 mol KCl/dm^3 after 24 h in a 2:5 suspension of material and distilled water. TOC was measured with a CNS analyser (Vario EL Cube, Elementar Analysensysteme, Germany).

Fourier-transform infrared spectroscopy (FTIR) was performed on all mixtures prepared as a thin, pressed pellet containing 1 mg of sample, dried at 105°C and homogenized with 200 mg of KBr. Spectra were recorded using a Tensor 27 FTIR spectrometer (Bruker Optics, Germany) in the spectral range of 400-4000 cm^{-1}, with resolution of 256 scans at 2 cm^{-1}.

Negative surface charge (Q) and distribution function of dissociation constants f(pKapp) were calculated from the raw data of potentiometric titration according to Szatanik-Kloc et al. (2009). Potentiometric titration was performed using an automated Titrino 702 SM instrument (Metrohm, Switzerland) in a pH range from 3.0 to 10.0 using 0.1 *M* NaOH based on 0.1 M NaCl as a titrant. Samples were prepared as suspensions of 100 mg of the dried solid mixture in 25 ml of 0.1 M NaCl, adjusted to pH 3.0, left on 24h and readjusted (if necessary) to pH 3.0 on the next day.

Pore size distributions from 0.003 to 360 µm were measured on an Autopore IV 9510 mercury porosimeter (Micromeritics, Norcross, GA, USA). The equivalent pore diameter was estimated from Washburn's equation: $D_{MIP} = -4\sigma_m\cos\theta_m / P_m$, where D_{MIP} is the pore diameter, σ_m is the mercury surface tension (0.485 J m^{-2}), θ_m the mercury contact angle (assumed 130 degs) and P_m the external pressure (Pa). From the obtained pore size distributions, the total pore volume (V_{MIP}, $cm^3\ g^{-1}$), total pore area (S_{MIP}, $m^2\ g^{-1}$) and average pore diameter (D_{MIP}, nm) were calculated. The samples' total porosity (P_c) was estimated according to the formula: $P_c = V_{MIP}\ \rho_D\ 100\%$, where V_{MIP} is the total pore volume, and ρ_D is the sample bulk density defined as the ratio of the sample dry mass to its volume (including pores) measured at 0.51 psia.

Sorption on nitrogen was measured on a 3Flex device (Micromeritics, Norcross, GA, USA). Before the measurement, samples were heated to 105 °C and kept under a vacuum overnight. From the experimental data, the specific surface area (SSA), volume of pores (V_{N2}) and average pore diameter (D_{N2}) were calculated. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models were adopted to estimate SSA and pore characteristics, respectively. The SSA was estimated in a relative pressure range from 0.05 to 0.35. Pore characteristics (VN2 and DN2) were calculated in the capillary condensation range in mesopores from the desorption curve. The area of the nitrogen molecule was assumed to be 0.162 nm^2 at 77 K.

The pseudo-total content of metals (Cd, Cr, Ni, Zn, Pb, Cu, Cr) in the bottom sediment, additives and mixtures was determined after *aqua regia* digestion (HNO_3 (65%) and HCl (30%) acids (3:1 v/v) (suprapure, MERCK, Germany)), using a dedicated microwave system at 180°C and 1200 W for 20 minutes (Mars 6, CEM, NC, USA).

Fractions of metals (Cd, Cr, Ni, Zn, Pb, Cu) in the sediment/amendment mixtures were assessed using the BCR sequential extraction procedure (Rauret et al., 1999). Four fractions of metals are distinguished: F1 fraction – acid extractable (CH_3COOH at 0.11 mol/L and pH = 2); F2 fraction – reducible (extractable with $NH_2OH.HCl$ at 0.5 mol/dm^3 and pH = 1.5); F3 fraction – oxidisable, (extractable with hot 30% H_2O_2, and then re-extracted with CH_3COONH_4 at 0.5 mol/dm^3 and pH = 2); fraction F4 – residual (digested using a hot mixture of HNO_3 and HCl (3:1 v/v)).

The metal content in each fraction was determined using an inductively coupled plasma optical emission spectrophotometer – PerkinElmer ICP-OES Optima 7300 DV (PerkinElmer, Inc., Waltham, MA USA) while total metal content was assessed with an iCAP 7400DUO ICP-OES from Thermo Fisher Scientific (MA, USA). The certified reference materials CRM020 Sandy loam 2 trace element (MERCK, Germany) and BCR-701 (fractions) (LGC Standards, UK) were used for quality control. Recoveries with reference to the certified concentrations were 95% for Zn, 98% for Cu, 105% for Pb, 98% for Cr, 86% for Cd, 113% for Ni (total content) and 93% for Zn, 93% for Cu, 86% for Pb, 119% for Cr, 89% for Cd, 98% for Ni (BCR fractions).

2.3. Ecotoxicological analysis

Ecotoxicity of the mixtures was assessed through three biotests: Phytotoxkit, Ostracodtoxkit F, and Microtox. In the Phytotoxkit test three plants were used: *Sinapis alba*, *Lepidium sativum*, and *Sorghum saccharatum.* The inhibition of root lengths of each plants were measured after incubation in the dark for 72 hours at 25 °C. In the Ostracodtoxkit F, the crustacean *Heterocypris incongruens* was used as test organism (Ostracodtoxkit F, 2001). After 6 days of incubation of *H. incongruens* with tested samples on multi-well plates at 25 °C in the dark, mortality and inhibition of growth were evaluated. Luminescent bacteria

Alivibrio fischeri as test organisms was used in the Microtox. Inhibition of luminescence was measured before and after 15 minutes of incubating the bacteria with the tested sample. Microtox M500 Analyzer was used for the test (MicrobicsCorporation, 1992).

All tests were conducted according to the procedures developed by the manufacturer (Microbics Corporation, 1992; Ostracodtoxkit, 2001; Phytotoxkit, 2004). The mixture ecotoxicity was assessed using toxicity classes, based on the percentage effect (PE) of growth inhibition: class I (PE ≤ 20%, non-toxic sample); class II (20% < PE ≤ 50%, lowly toxic sample); class III (50% < PE < 100%, toxic sample); class IV (PE = 100% for at least one test, very toxic sample), class V (PE = 100% for all tests, very toxic samples) (Persoone et al., 2003).

2.4. Statistical analysis

The significance of differences between mean values of parameters were analysed using one way ANOVA and post-hoc Tukey's test at a significance level of 0.05. All statistical analyses were conducted using Microsoft Excel 2016 and the Statistica 13 software package.

3. Results

3.1. Properties of mixtures

Selected physico-chemical properties of the mixtures are shown in Table 2. Amendment of mineral and organic materials to acid bottom sediment resulted in a significant increase in pH in all treatments compared to the control. The pH, depending on the treatment, was 3.58 in the bottom sediment and between 4.16 to 12.3 in the mixtures. Mixtures with cellulose waste were alkaline, with a pH as high as 12.3 for the highest dosage (45%). Slightly acidic (DL 5%), neutral (DL 25%) and alkaline (DL 45%) conditions were witnessed in the mixtures of bottom sediment and dolomite. The mixtures of bottom sediment and biochar were acidic to neutral (BC 45%). The additives affected the TOC, which ranged from 6.37 to 18.73%,content of the mixtures differently. TOC increased significantly in mixtures with biochar (all doses) and dolomite (doses of 25 and 45%). The mixtures based on biochar contained from 10 to almost 60% more TOC compared with the control treatment. Dolomite increased the TOC content in mixtures by 2 to 18%. In contrast, the addition of CW reduced the TOC content by 9% on average.

The FTIR spectra of the bottom sediment (Figure 1) shows the contribution of both organic and mineral compounds in the studied material. Applied additives modified the structure of the BS at some conditions. Cellulose waste addition caused a significant increase in the absorption band at ~1425 cm^{-1} that is assigned to vibrations in aliphatic C-H, aromatic C=C, and C=O (in case of CW – to CH_2 bonds) (Oh et al., 2005; Liu et al., 2013; Boguta et al., 2022), alongside a decrease in the band at ~1090 cm^{-1}, attributed to vibrations of Si–O–Si and C-O-C of ethers (Kovač et al., 2005). Decrease in this band at the highest CW content revealed another one at 1039 cm^{-1} attributed to primary alcoholic OH and CO polysaccharide vibrations (Boguta et al., 2022). Addition of the biochar decreased the absorbance at ~3441 cm^{-1} related to decrease in O-H stretching vibrations of carboxylic acids, phenols, alcohols, and water, N-H bonds, H-bonded OH and intermolecular bonded OH (da Silva et al., 2018). BC additions also contributed to a decrease in the ~1630 cm^{-1} band, attributed to C=O stretching vibrations of deprotonated COO^-, C–O and C-N stretching in amides, and vibrations of –C=C– on benzene rings (da Silva et al., 2018). BC, similarly to CW, decreased the band at ~1090 cm^{-1}; this drop was however not as marked. Increasing dolomite fractions caused a reduction in bands at ~3441 cm^{-1}, ~1630 cm^{-1} and at ~1090 cm^{-1}. As in the case of CW, the addition of DL increased the intensity of absorbance at ~ 1425 cm^{-1}. All additives lowered the signal height at ~ 780 cm^{-1}, 530 cm^{-1} and 470 cm^{-1}, derived mainly from vibrations of Si-O-Si and aromatic C-H structures. This was less noticeable with the addition of BC. The data obtained show that the application of BC, DL and CW additives clearly influenced both the organic and inorganic matrix of the BS resulting mainly in the decrease of the contribution of siloxane, polysaccharide and alcoholic structures.

The potentiometric titration of the bottom sediment revealed the presence of various functional groups generating negative surface charge (Q) at different pH conditions (Figure 2). The highest increment in Q was observed in the lower pH range, indicating the importance of acidic functional groups such as the carboxyl group (Skic et al., 2016). The increase in Q was less pronounced in neutral pH ranges, before proportionally rising again in the alkaline ranges, which indicated the contribution of e.g. OH groups (Sokołowska et al., 2011). The additives influenced the Q value in different ways. Treatments CW 25% and 45% increased this parameter and the strongest effect was observed above pH 6.0. The Q values for both CW 5% and BC 5% additives did not differ from the control sample, BS. Interestingly, successive increasing concentration of the biochar from 25 to 45% caused a decrease in Q as compared to treatment BS. This reduction concerned the charge generated in the lower pH ranges. The addition of dolomite seemed to decrease the Q value, especially at low pHs ranges, but no clear trend could be observed with this amendment.

Distribution function of dissociating constants (f(pKapp)) of the bottom sediment (Figure 3) showed that the most abundant population includes the functional groups dissociating at pK_a ~ 3.5, as well as these that dissociate under alkaline conditions (broader spectrum of dissociating constants). The clearest influence of amendments was noted when adding cellulose waste at 25%, where a shift of the “acidic” maximum to the pK_a value of ~6.25 was observed, alongside an increase in an “alkaline” maximum, indicating important changes in acidic species for the enriched samples. Interestingly, the increase in biochar in the mixtures caused flattening of the distribution curve of dissociation constants in the entire range of pK_a values, indicating a fairly similar share of functional groups over a wide spectrum of dissociation constants. The addition of dolomite at 5% resulted in a decrease in the signal at pK_a 4.75, while higher amounts of DL caused an additional shift of the main fraction of dissociation constants to pK_a of about 6.0.

The differential and cumulative mercury intrusion porosimetry (MIP) curves obtained for mixtures of bottom sediment with cellulose waste, biochar, and dolomite are shown in Figure 4. All cumulative curves are s-shaped with a rapid increase in volume at a pore diameter of about 6 µm. Noticeably, biochar increased the pore volume of the analysed mixtures proportionally to amendment rates, while dolomite, in contrast, reduced it significantly. The effect of cellulose waste was equivocal, showing a decrease in the pore volume only for low and medium concentrations. The differential pore size distributions show unimodal patterns, with the main peaks observed around 0.02 to 6 µm. In the case of BC mixtures, the peak size increased with amendment concentrations. It is also slightly shifted towards pores of a greater diameter. In contrast, a higher concentration of DL diminished peak height.

The effects of additives on pore characteristics measured by MIP and N_2 adsorption methods are presented in Table 2. Total porosity (P_c) ranged from about 47.8% to over 55.3%. The highest average value was noticed for treatments BC 25% and 45%, while the lowest was for DL 45%. Addition of biochar lowered the pore surface area (S_{MIP}) and bulk density (ρ_D) to respectively 7.2 $m^2 \cdot g^{-1}$ and 0.83 $g \cdot cm^{-3}$ at the mixture 45%. In turn, dolomite increased bulk density and diminished the total pore area compared to the control. S_{MIP} was highest, at 21.5 $m^2 \cdot g^{-1}$, for cellulose waste (CW 45% variant). The value of D_{MIP} ranged from about 473 nm to over 1225 nm and was higher than the control for higher concentrations of biochar. In treatments CW 5% and 45%, D_{MIP} was lower, whereas D_{MIP} was similar to the control for mixtures with dolomite. The N_2 adsorption results revealed that all amendments had a significant impact on the BET surface area (SSA) and cumulative pore volume (V_{N2}). These generally increased compared to the bottom sediment, except for the highest dose of dolomite. It is worth noting that the patterns were not always consistent with increasing additive dose. For example, the average pore diameter (D_{N2}) was usually lower in the mixtures than in the control, but this difference was statistically insignificant in most cases ($\alpha=0.05$).

3.2. Content and mobility of metals in mixtures

The total content of metals in the treatments depended on the metal, type of additive, and its dose (Table 3). It was found that the contents of all metals decreased with the addition of cellulose waste and dolomite. One of the possible explanations for this relationship could logically be attributed to a dilution of the metal content during mixing, coincidentally accompanied by alkalinisation due to high amendment pH. Treatments with 45% cellulose waste and dolomite had the lowest metal content, 1.4 to 2.4 times lower than the control. Mixtures with biochar had different effects, significantly reducing Cd, Zn, and Pb, but increasing Ni, Cu, and Cr by 1, 9, and 28%, respectively. The BC 45% mixture had the highest content of these latter elements.

However, relying solely on the total metal content in the mixtures does not allow to reliably assess metal mobility and risks of release into the environment. Metal fractionation and speciation provides a more accurate picture. Information on the most mobile, easily available metal fractions is particularly relevant (Wang et al., 2021). BCR sequential extraction is an essential tool in this context. It is commonly assumed that the following three metal form categories are distinguished based on the results of: (a) easily mobile/bioavailable (F1), (b) potentially mobile/bioavailable (F2 and F3) and (c) biologically unavailable metals (F4) (Devi and Saroha, 2014). Other authors reported that metals in the exchangeable fraction (F1) are more mobile and bioavailable, while the potential mobile fraction of metal fractions F1, F2 and F3 (∑F1-3), are more bioavailable than the residual (F4) (Baran et al., 2019).

Metals fraction F4 are stable, bound within a structure of some primary and secondary minerals, and can therefore not impact organisms. In contrast, metal forms found in fraction F1 are easily interchangeable, water- and acid-soluble, and carbonate-bounded. It happens that the metals in this latter fraction are easily bioavailable, rendering this fraction this most risky to the environment (Liang et al., 2017). As mentioned above, the purpose of the additives introduced into the contaminated bottom sediments was to immobilise metals through the reduction of their mobility.

The F1 fraction differed considerably for the different tested metals under the influence of amendments (Table 3, Figure 5). Cadmium was the most mobile element among the analysed metals, as evidenced by its very high share in fraction F1 in the unprocessed sediment (75%). The share of cadmium in the remaining fractions, depending on the treatment, was average or small and ranged from 14 to 37% (F2), from 4 to 45% (F3) as well as from 1 to 25% (F4) of the total content. All amendments decreased this fraction, with varying efficiency. Treatments with cellulose waste seemed the most effective, with the F1 share impressively dropping as low as 1% for the 45% dose, corresponding to a 60 times lowering compared with the control. Furthermore, CW 25% dosage resulted in a significantly lower Cd fraction in F1 than for 45% of either biochar or dolomite. Interestingly, treatments with these two other materials still reduced the % share of Cd in F1 by a factor 1.3 to 1.7. Decreases in F1 were accompanied by increases in the three other fractions, most notably F3 and F4. In treatments with 5% share of CW, BC and DL, the reduction in Cd mobility was insignificant.

Patterns for Zn were similar. Also for this element, the F1 fraction in the sediment was high. Cellulose waste was again the most effective amending material, impressively lowering the F1 fraction from 71% in the control to 5% for the 45% amendment rate. Additionally, significant decreases of 1.8 and 1.9 times were achieved with 45% BC and DL, respectively. Diminished F1 fraction were mostly accompanied by increases in F3 and F4.

Nickel displayed a relatively lower F1 fraction in the unprocessed sediment, which was still as high as 26%. All amendments demonstrated significant efficiencies for reducing this fraction, with fairly similar values (2.6 to 3.7 times lowering) for all mixtures at 25 and 45%. Both cellulose waste and dolomite even performed significantly well at 5% dosage already (2.2 and 2.6 times lowering, respectively). Decreases in F1 were mostly accompanied by increases in fractions F3 and F4. F2 was even decreased as well (below 1%) for DL treatment at 25 and 45%. Overall, only the BC 5% treatment did not seem to show any immobilizing effect.

It is widely considered that Pb, Cu and Cr have a rather low mobility and they occur dominantly in fractions 3 and 4. This was witnessed here as well, these metals being much less present in fraction F1 in the unprocessed sediments (1 to 8%). Fraction F2 was also lower for Cu and Cr than for other metals. The influence of amendments was less marked than for other metals. For Cu and Cr, a significant reduction in the F1 fraction could be achieved for all amendment dosages except for cellulose waste 5% (Cr) and biochar 5% (Cu, Cr). This decrease was less marked than for Cd or Zn, and dolomite seemed the most effective material. As for previously discussed metals, this was accompanied by enrichments in fractions F3 and F4, less noticeable than for the others given how predominant these fractions were initially. For Pb, finally, amendments led to various patterns in fraction distributions. In contrast with other metals, no reduction in F1 could be achieved; this fraction remained limited however, ranging from 1 to 3%. Immobilization seemed the most effective under DL treatments, whereby 25% and 45% led to a reduction in F2 and F3, accompanied by a higher share in F4. A notable enrichment in fraction F2 was noticed for BC treatments, but this seemed less marked at 45% (1.5 times increase) than at 5% (2.6 times increase). Cellulose waste irregularly led to an enrichment in F3, with a high 80% at 45% dosage.

3.3. Assessment of metal immobilisation with indices

The effectiveness of these additives for metal immobilisation was further assessed using three factors (Table 3): Risk Assessment Code (RAC), Individual Contamination Factor (ICF) (Liang et al., 2017; Baran et al., 2019; Matabane et al. 2021) and Ecological Risk Factor (ERF) (Tytła and Kostecki 2019). In RAC, the percentage share of the metals associated with fraction F1 is considered relatively to their total content. ICF was calculated by dividing the sum in potentially mobile fractions (∑F1-3) by the residual fraction (F4), while ERF was calculated based on dividing the sum of metal contents in fractions F1 and F2 by their contents in fractions F3 and F4. A common characteristic of all 3 factors is that the lower their value, the less mobile and bioavailable a given metal will be. From then, different classes of risks have been defined based on these indices. Value ranges for these classifications are provided under Table 3.

From the RAC classification, it appears that cellulose waste decreased metal mobility significantly more than dolomite or biochar, for a variety of elements and doses. Treatments with CW at 25% and 45% doses led respectively to a moderate and low risk of releasing Cd. In contrast, other mixtures were associated with a very high (BS, CW 5% dose, BC at all doses, DL 5 and 25% doses) to high (DL 45%) risk regarding the mobility of this metal. A similar trend was seen for Zn, with 25% and 45% CW treatments resulting in moderate and low risks, while others were linked with high (CW 5%, BC 25% and 45% doses, DL 25 and 45% doses) or very high (BS, BC 5%, DL 5%) risks. For Ni, a high risk relating to the mobility of this metal was determined only in the 5% BC mixture, and a moderate risk was found in the BS and CW 5% mixture, with a low risk for other treatments. Regardless of the treatments, Cu was characterised by a low risk. The risk of release of Pb in the majority of the treatments was low; mixing with 25 and 45% cellulose waste even resulted in no risk. Chromium was the least mobile element, with no risk observed for all mixtures expect the original sediment and treatments with CW and BC at 5% dosage (low risk).

The individual contamination factor (ICF) is used to assess the ability of an element to be released from the sediment/soil samples under different environmental conditions (Naji and Sohrabi, 2015). Different physicochemical properties of a sediment or a mixture may cause differences in ICF values. On average, it seemed that amendments led to a decrease in ICF when compared with the control, pointing out a decrease in their mobility. However, DL performed seemingly better than the other. In fact, BC treatments were the least effective in reducing ICF, even showcasing increases for Cd at 5% dose. The above relationship was also found for Pb in treatments with 45% CW and BC, and for Cu in treatments with 25% and 45% cellulose waste (Table 3, Figure 5). Higher ICF values in these treatments indicate a higher tendency to release bioavailable metals to the environment relative to the control. Due to the fact that ICF reflects the risk of metal pollution samples exhibited a very high and considerable contamination for Cd (except CW 25%, DL 45%), Zn (except CW 45% , DL 45%), Pb only for CW 45%. Moderate contamination degree was recorded for Ni (except DL 25%, DL 45%, CW 5%), Cu (except CW 5%), Pb (except DL 25%, DL 45%, CW 45%), and for Cd (CW 25%, DL 45% and Zn (CW 45%, DL 45%). Low contamination rate observed for Cr (all treatments), Ni (CW5%, DL 25%, DL45%), Cu (CW 5%), and Pb (DL 25%, DL 45%).

The above observations were partially confirmed by ERF that, similar to ICF, pointed out that the additives and their increasing doses generally reduced the value of this factor relative to the control treatment (Table 3). Lower ERF values indicate the increase in the metal contents in less mobile fractions F3 (associated with organic matter) and F4 (residual fraction), and thus the reduction of the risk of their release to the environment. This relationship was not demonstrated for Pb in the treatments with BC (all doses), CW and DL (in 5% dose), as well as for Cd in the treatments with 5% share of CW and DL, and for Ni and Cu in the treatments with 5% dose of BC. For Cd (except CW45%) and Zn (all doses of CW), most study treatments showed a high risk of mobility of these metals in the environment. For Cd (except CW45%) and Zn (all doses of CW) most study treatments showed a high risk to the mobile of the environment. The remaining treatments had a moderate or low risk relating to the release of the analysed metals (Table 3). Given the average ERE values, the highest effectiveness in decreasing the mobility of the metals (excluding Pb) with respect to the control (BS) was found in BS+CW mixtures, then in BS+DL mixtures, and the lowest effectiveness was determined in BS+BC mixtures.

3.4. Ecotoxicity of mixtures

The amendments significant reducted ecotoxicity of the sediment/amendment mixtures in most cases. Responses varied importantly according to the amendment, dose, and test organism (Table 4). The highest reduction in toxicity for plants was obtained with dolomite, for which stimulation of *S. saccharatum* root growth was even observed at 25% and 45% doses. It was noticeable that CW seemed to alleviate toxicity at lower doses (5 and 25%), only for the toxicity to increase again for the 45 % rate. The Ostracodtoxkit test revealed most of the mixtures were toxic to *H. incongruens*, with a lower toxicity achieved for treatments CW 25%, BC 45% and DL 25 and 45%. Finally, the inhibition of luminescence of *A. fischeri* showed the widest spectrum in sensitivity, with PE ranging from -30 to 100%. Treatments BC 45% and DL 25 and 45% performed best again, even leading to stimulation of the luminescence. Interestingly, DL could already reduce toxicity 2.4 times at 5 % dosage. In contrast, CW barely alleviated toxicity, the 45 % dose being as highly toxic as the control (PE = 100%).

These various responses among test organisms can be further visualized in Figure 6. Mixtures based on cellulose waste seemed to trigger more toxicity in *A. fischeri* than other treatments. Contrastingly, treatments with biochar and dolomite proportionnaly led to more toxicity to *H. incongruens*, and to a certain extent to *S. alba* (for DL in particular). Among plants, monocotyledons *S. saccharatum* turned out to be the less sensitive species, and *S. alba* the most. The majority of the treatments were non-toxic or of low toxicity to the former (similarly as for *L. sativum*), while they were deemed lowly toxic to toxic for the latter. Another studies also showed that on the substratum with different wastes *S. alba* was the plant most sensitive to the effect of chemical substances in these wastes, and *Sorghum saccharatum* was less sensitive (Baran and Antonkiewicz, 2017; Antonkiewicz et al., 2019). In the studies of Szara et al. (2020) and Gondek et al. (2023) *H. incongruens* was the most sensitive organism to the substance present in the tested mixtures based on bottom sediment or diatomite different waste. *H. incongruens* is a very attentive organism to the acid pH, and, the oral ingestion is the main route of exposure of this organism to toxic substances (Mariani et al., 2022). Differences in sensitivity of the test organisms were related not only to their species or trophic group, but also to the method of exposure to toxic substances (Szara et al., 2020; Heise et al., 2020; Gondek et al., 2023). In the Phytotoxkit and Ostracodtoxkit biotests, the organisms are exposed to both soluble and contaminants absorbed on the solid particles of the mixtures, while the exposure of *A. fischeri* (Microtox) are limited to bioavailable, easy-soluble compounds.

The 5 tests considered altogether, a lower toxicity class could be achieved in all treatments except for cellulose waste 45%. This latter mixture, like the unprocessed sediment, were deemed highly toxic (class IV), and would pose serious threats in the environment. In contrast, mixtures of bottom sediment with dolomite (in 25% and 45% doses) and biochar (in 45% dose) were assigned to toxicity class II, meaning that these samples present a low toxicity. The remaining mixtures (DL 5%, BC 5 and 25%, and CW 5 and 25%) were assigned to class III, which means their toxicity would still represent an environmental threat.

4. Discussion

4.1. Impacts of the amendments on metal immobilisation

The metal content in the residual fraction (F4) generally increased with increasing dolomite rates. One possible reason for this is that the low and medium dolomite doses increased the number of binding sites for metals, as evidenced by the increase in SSA and V_{N2} compared to the bottom sediment control. In contrast, the decrease in P_c and V_{MIP} could be attributed to the filling of the bottom sediments' skeletal pores with fine particles of high density dolomite (Gruszecka-Kosowska et al., 2017). In accordance with Chen et al. (2007), the specific surface area was the key factor determining Cu(II) adsorption onto the surface of acid-activated dolomite. Salameh et al. (2010) suggested that one of the mechanisms involved in As(V) adsorption was the rough surface of dolomite, which provides contact points for chemisorption at low metal concentrations. In line with Emami et al. (2016) and Qui et al. (2015), dolomite surfaces are rough and irregular, show significant porosity, and provide functional groups capable of metallic species complexation. Our studies also showed that the highest dose of dolomite caused a marked decrease in SSA and V_{N2}. Diwan et al. (2020) observed a similar effect when studying the adsorptive removal of uranium from an aqueous phase with dolomite. They observed enhanced removal efficiencies up to a specific dolomite dose, followed by a decrease in removal capacity, attributed to a reduction in total surface area due to partial aggregation of adsorbent particles. The decrease in Q values after adding the lowest dose of DL (5%) was possibly due to the blocking of O-containing functional groups on the BS by the Mg and Ca ions of the DL (Figure 2C). The highest doses of DL caused an increase in the Q relative to the 5% DL treatment (Table 2), which could be due to the higher contribution of HCO_3^- and CO_3^{2-} ions. This increase in Q could also be partly due to the increase in the dissociation of the biochar functional groups with increasing pH of the mixtures. A higher negative charge on the surface of functional groups reduces competition for active sites between metal and protons, making it easier to attract cations, thus enhancing metal sorption. This immobilizing effect at DL 25% and 45% doses was observed for all analysed metals, as evidenced by the increased F4 fraction (Figure 5). Indeed, related studies show that the main mechanism for metal retention in systems with dolomite can be precipitation of carbonates (Radziemska, 2018).

In certain conditions, a further increase in the pH can adversely affect sorption processes due to the weakening of electrostatic attraction forces resulting from the increasing conversion of metal cations to hydrolysed species (Diwan et al., 2020). Additionally, negatively charged forms, such as chromate (VI), have less opportunity to sorb due to increased repulsion of negatively charged ions (Khoshraftar et al., 2023). The importance of controlling the pH was also confirmed by Pehlivan et al. (2009) in studies on adsorption of Cu and Pb on dolomite, in which the highest efficiency of cation removal via surface complexation and ion exchange was observed at pH 5, while these processes were reduced above pH 6 due to hydrolysis.

The addition of cellulose waste significantly increased the surface properties SSA and V_{N2}. The fraction of metals associated with organic matter (F3) also increased, suggesting that metals were immobilized on the outer surface of the cellulosic material, including the walls and/or mouths of small pores (Boguta et al., 2022). Hydroxyl groups on the outer surface of cellulose increases its ability to adsorb and react with various chemical moieties (Godage and Gionfriddo, 2020). The lowest dose of cellulose waste raised the pH of the mixture to 7.84, a value at which dissociation of phenolic OH groups is still limited (pK_a ca. 8.2–8.3; Su et al., 2013). An earlier study of the sorption properties of cellulose waste confirmed the relatively low efficiency of the OH groups of cellulose materials in metal binding at lower pH (Jamshed et al., 2017). This is because more protons compete with metal cations for active sites at lower pH. Moreover, at lower pH, the number of active sited is reduced because of the overall reduced netto negative surface charge.

In our cases, the higher additions of cellulose waste increased the pH of the materials to 8.96 and 12.3, promoting the dissociation of organic OH groups. Indeed, the cellulose waste amendment, especially at dose of 25%, caused an increase in Q values (Figure 2a). This change was attributed to the presence of OH groups, as evidenced by the shift of the maxima of the distribution function of dissociation constants toward the higher contribution of the charge generated in alkaline pH ranges (Figure 3a) (Szatanik-Kloc et al., 2019). The highest values of Q for the cellulose waste treatment 25% treatment corresponded to the highest immobilization of Cd, Pb and Zn in F4 fraction, which suggests that OH groups are involved in metal binding. At the pH of this treatment (pH=8.96), the above metals reveal positively charged forms: Cd^{2+}, $Cd(OH)^{+}$, Pb^{2+}, $Pb(OH)^{+}$, Zn^{2+}, $ZnOH^{+}$, which are readily attracted to negative surface charges. Under these conditions, there is also the possibility of precipitating metals as hydroxides, for example, $Zn(OH)_2$. Such forms could also be a reason for enrichment in stable forms. The immobilization of Cd and Pb for cellulose waste 45% in F4 was lower as compared to cellulose waste 25%, which is likely due to the presence of a higher number of negatively charged forms of metals, such as $Cd(OH)_3^-$ and $Pb(OH)_3^-$, at strongly alkaline conditions (pH=12.3) and their repulsion with dissociated OH groups of the cellulose waste.

Biochar interacts with metals in various ways, including outer-sphere complexation, inner-sphere complexation, electrostatic interactions, surface precipitation, and ion exchange (Shaheen et al., 2019; Wang et al., 2021). In our studies, the gradual decrease in Q values upon addition of the BC was likely due to the increase in the number of structures poor in oxygen functional groups, which to a large extent undergo thermal degradation during biochar production at temperatures above 300°C. At the same time, biochars derived from high-temperature biomass exhibit an increased content of non-volatile cations (Wang et al., 2015). These cations can attach to bottom sediment functional groups, blocking the negative charge. The decrease in the value of Q with the simultaneous decrease in the content of metals in the most mobile fraction (F1), except Pb, and the increase in metals in F4 show that metals are bound in more stable forms, and immobilization does not have to be dependent on binding by groups generating a negative charge.

Considering the well-developed surface area of biochar, which was observed in the mixtures, it is likely that this mechanism depends to some extent on adsorption onto the porous biochar structure. The outer surface of biochar, followed by the interior pores, may cause the cation exchange capacity to shift and enhance element retention (Ahmad et al., 2014). This is also supported by other studies on the sorption of metals with the use of biochars (Inyang et al. 2012; Kim et al., 2013; Tomczyk et al., 2020). Simultaneously, the interaction and distribution of heterogeneous biochar particles in the bottom sediment matrix affected the structure of the prepared mixture. Biochar typically has a lower bulk density than soil and sediments, so it reduces the mixture density through a mixing or dilution effect (Blanco-Canqui, 2017). The specific surface area of biochar is comparable to or higher than that of clay minerals (Downie et al., 2009), so the use of biochar as an amendment generally resulted in a net increase in SSA and S_{MIP} compared to control bottom sediment. Additionally, the observed increase in total pore volume with a simultaneous decrease in bulk density suggests that biochar contained a significant proportion of macropores (Wildman and Derbyshire, 1991; Brewer et al., 2014). This group of pores may affect the transport processes within the bottom sediments (Boguta et al. 2022) and thus improve access to metal adsorption centers.

4.2. Impact of the amendments to ecotoxicity of mixtures

Combining different biotests (Phytotoxkit, Ostracodtoxkit, and Microtox) to polluted bottom sediments can be a useful tool for evaluating a range of environmental risks (Mierzwa-Hersztek et al., 2018; Heise et al. 2020; Baran et al. 2023). From an ecotoxicological point of view, bottom sediment proved to be the most toxic material, posing a severe environmental threat as demonstrated by its class IV toxicity. This high toxicity may be due to two factors: the acidic reaction of the sediment and its high content in Cd, Pb and Zn. The pH of the bottom sediment (3.58) is below the tolerance range for many organisms. Additionally, pH is one of the main factors determining the solubility and mobility of metals in the environment (Liang et al., 2017, Koniarz et al., 2022). The balance of sorption and desorption processes depends on the reaction of protons and metal cations. Metal solubility conditioned by exchangeable sorption processes is low in a range of neutral and alkaline pH, and increases with decrease in pH value (Kim et al., 2015). This increase in solubility in acidic environments is associated with the slow dissolution of iron, aluminum and manganese oxides and the release of metals from primary and secondary minerals. The acid pH of the bottom sediment may have increased the mobility and bioavailability of the tested metals to the test organisms, which is why bottom sediment was shown to be the most toxic material.

Despite a significant reduction in metal mobility, cellulose waste mixtures were highly toxic to test organisms. Studies by other authors also showed high ecotoxicity of substrates and mixtures containing cellulose production waste (Antonkiewicz et al., 2019; Szara et al., 2020). In the studies of Szara et al. (2020), the mixture of bottom sediment and cellulose waste (BS + CW) was assigned to toxicity class IV (toxic sample, high acute hazard). Wastes from cellulose production not only contain many valuable components, including organic compounds and macro- and microelements necessary for plants, but are also characterised by a significant content of toxic compounds (Baran and Antonkiewicz, 2017;

Antonkiewicz et al., 2019). Wastes from cellulose production not only contain many valuable components, including organic compounds and macro- and microelements necessary for plants, but also toxic compounds (Baran and Antonkiewicz, 2017; Antonkiewicz et al., 2019). For example, they may contain chlorinated organic compounds which are used to bleach paper and are highly toxic by causing carcinogenic, clastogenic, mutagenic and endocrine effects (Haq et al., 2022). Another factor contributing to ecotoxicity of cellulose waste is bleach residues in this material. Chemicals used to bleach paper include sodium hypochlorite, soda lye, and chloroacetic acid (MCAA), hydrogen peroxide, ozone, and molecular oxygen (Haile et al., 2021). Unfortunately, no specific analysis to detect toxic organic components could be performed during the current study. Additionally, it should be noted that the strong alkaline nature of the cellulose waste resulted in a high pH in mixtures, especially at 45% dosage (pH = 12.3). This is much above endurable values for living organisms, and this alkalinity very likely contributed to the ecotoxicity of the mixtures.

In recent years, there has been increasing interest in the use of biochar to immobilise metals in the environment (Wang et al., 2021; Palansooriya et al., 2022). The addition of biochar has been shown to reduce the toxicity of bottom sediments in a dose-dependent manner. Many studies have shown that biochar can stimulate the growth of organisms due to its potential content of macro- and micro-elements and the partial bioavailability of the carbon contained in its matrix. In addition, biochar has a porous structure and can be an excellent microenvironment for living organisms (Gondek et al., 2016; Palansooriya et al., 2019). On the other hand, biochar may contain various toxic compounds besides heavy metals, e.g. polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and dioxin, which may rather lead to ecotoxicity (Godlewska et al., 2021). Toxicity might also occur through specific physicochemical properties such as particle size, pH and/or salinity (Palansooriya et al., 2019; Godlewska et al., 2021). In our case, the pH of the mixtures was increasingly closer to ideal neutral values, which might be a reason why 25% and 45% doses reduced ecotoxicity significantly. Huang et al. (2017) observed that the most mobile fraction (F1) of Cd and Zn decreased when sediment was amended with biochar; however, a dosage rate as low as 50 mg kg^{-1} was shown to decrease enzymes activity and microbial abundance. It is worth noting that biotests allow not only for the detection of a toxic substance, but also for a full assessment of the interaction of all factors and substances, taking into account synergism or antagonism (Oleszczuk et al., 2013; Heise et al., 2020). Thus, even though no specific pollutant analysis could be carried out in our case, it can be reasonably assumed that BC was not contaminated to an extent that would result in toxicity.

Dolomite is the most common material used in agriculture for neutralizing soils as a mean to improve plant growth. It has also been assessed for the remediation of areas and materials contaminated with heavy metals (Khoshraftar et al., 2023; Gondek et al. 2023). In this study, the addition of dolomite to the contaminated sediments contributed to the highest reduction of the ecotoxicity of the mixtures for the test organisms, especially at 25 and 45% doses. Two test organisms even underwent a stimulating effect on root growth (*S. saccharatum*) and luminescence (*A. fischeri*) as compared to the control at 45% amendment rate. In the studies of Gondek et al. (2023), a reduction in the toxicity was also found under the influence of dolomite, as they witnessed a class I toxicity level for mixtures of diatomite and dolomite. This is consistent with earlier findings that demonstrated the high potential of dolomite to reduce the availability and toxicity of heavy metals in contaminated soils and water (Sidiri, 2018; Vrînceanu et al., 2019; Khoshraftar et al., 2023). In our case, dolomite helped achieving a near-neutral pH in all mixtures, which might be a main factor towards reducing ecotoxicity. It may also be that dolomite increased nutrient availability for microbes, or positively influenced plant nutrition as a source of magnesium and calcium (Baggs et al., 2010; Shaaban et al., 2017).

Research on living organisms is an important part of research on the toxicity of materials. Such analysis is complementary to chemical analysis and is therefore necessary for the proper assessment of risk related to the release of materials into the environment (Oleszczuk et al., 2013; Szara et al. 2020).

4.3. Implications for remediation

The effectiveness of the immobilisation process usually depends on the characteristics of the sediment and the materials used (Polrot et al., 2021). The interaction of the immobilisation agents with the metals and with the properties of the sediment is important as this will primarily determine the immobilisation efficiency and the short and long term environmental impact. Our studies found that amendments such as biochar, dolomite and cellulose waste can be recommended for the remediation of metal-contaminated sediments. Different doses of the products tested showed good efficacy as immobilising agents (especially for Cd, Zn and Pb) and often resulted in a significant reduction of the initial ecotoxicity. The materials significantly neutralised acidity of the bottom sediment (biochar, dolomite, cellulose waste) and biochar in addition contributed significant amounts of organic matter (biochar) to the sediment/amendment mixtures. These materials significantly improved the physico-chemical properties of the bottom sediments through an increase in pH improv sorption properties, and accordingly reduced mobility of metals. The industrial by-products also reduced the ecotoxicity of the amended bottom sediments. Other advantages can be added to these benefits, such as their quality as soil conditioners, low cost, convenient applicability, and economic competitiveness (Lwin et al., 2018). These three materials are processed industrial by-products that are produced in large amounts each year. Using these materials for bottom sediment remediation has the advantage of solving a waste disposal problem, preventing potential environmental pollution in the future (Lwin et al., 2018).

Industrial by-products may contain other hazardous substances in high concentrations. These can be of concern when the by-products are considered for use in remediation (Lehoux et al., 2020). Currently, Polish legislation lacks regulation about the use of bottom sediments in agriculture. This closest criteria for assessing the permissible content of metals would be existing restrictions on municipal sewage sludge (Cd – 20 mg/kg; Cu – 1000 mg/kg; Ni – 300 mg/kg; Pb – 750 mg/kg; Zn – 2500 mg/kg; Cr –500 mg/kg DM (Regulation 2015, 2015)). While most metals in the mixtures comply with these values in our case, Cd (and Zn, in most cases) does not. Valorization would then be restricted to non-agricultural purposes, compost production (Regulation 2015, 2015), or construction purposes.

There are not many single technologies that can remediate bottom sediments efficiently (Ma et al., 2019). Different remediation approaches should be adopted for different types of contaminated sediments. Our previous studies have attempted to remediate contaminated bottom sediments using physical and biological methods (thermal treatment processes and phytoremediation) (Koniarz et al.. 2022; Śliwa-Cebula et al., 2023). Further studies are needed to improve the environmental adaptability of remediation technologies in actual field conditions, and to develop a multistep remediation technology for heavy metal-contaminated sediments (Ma et al., 2019).

5. Conclusion

The impact of different amendments and their application rate on metal mobility and ecotoxicity in contaminated bottom sediments was assessed through various physicochemical analyses. These revealed a strong dependence of metal immobilization efficiency on on pH, which increased with all amendment additions. Dolomite and cellulose waste, with their high negative surface charge, caused an enhanced metal sorption. For cellulose waste, the presence of OH groups further contributed to its highest metal immobilization, as reflected by the highest Q value. Biochar, however, reduced the negative surface charge, suggesting the involvement of other factors like its high specific surface area and pore volume in metals immobilization. Most amendments increased the parameters SSA and V_{N2} compared to bottom sediments, indicating a higher number of binding sites for metals.

Most amendments reduced the ecotoxicity of the sediments. Mixtures with 25% and 45% dolomite and 45% biochar even achieved a low toxocity classification (class II). Cellulose waste, however, showed limited success. All mixtures remained classified as toxic (class III) or highly toxic (class IV), similar to the original sediment. Despite its superior performance in metal immobilization, its inability to mitigate toxicity significantly limits its potential reuse for sediment remediation.

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7. References

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Figures

Figure 1. FTIR spectra for mixtures of bottom sediment (BS) with increasing content of amendments: A) cellulose waste (CW); B) biochar (BC); C) dolomite (DL).

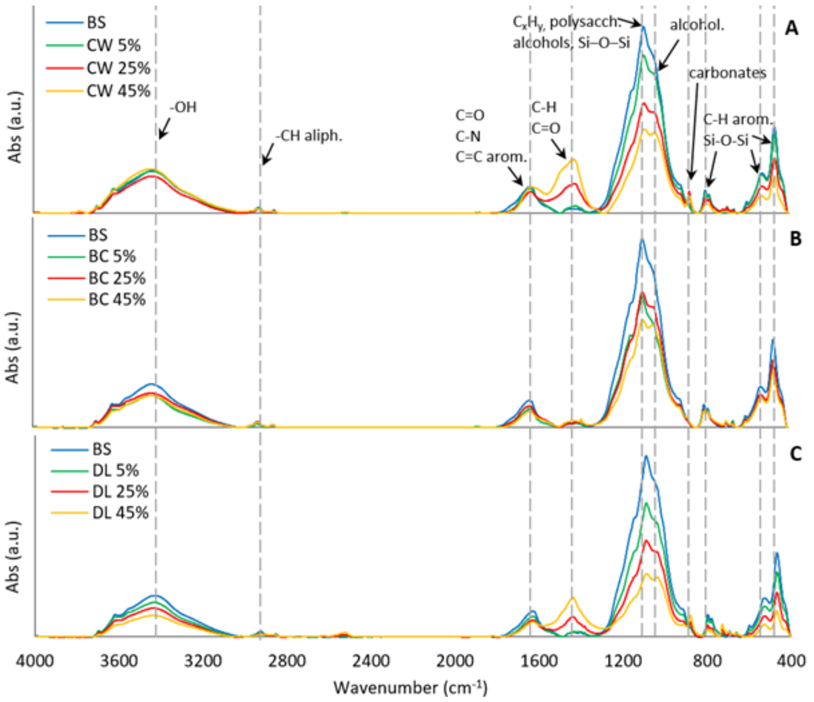

Figure 2. Cumulative negative surface charge (Q) of the bottom sediments (BS) in function of the pH and increasing content of additives: A) cellulose waste (CW); B) biochar (BC); dolomite (DL). Error bars represent standard deviation (n=30).

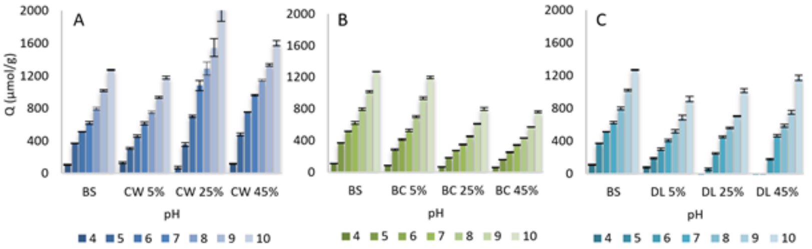

Figure 3. Distribution function of surface dissociation constants of the bottom sediment (BS) samples as a function of apKs and increasing content of additives: A) cellulose waste (CW); B) biochar (BC); dolomite (DL). Error bars represent standard deviation (n= 30).

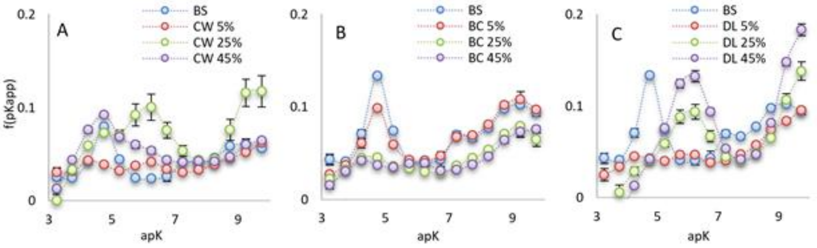

Figure 4. Cumulative (left) and differential (right) pore size distribution (0.003–360 μm) determined by mercury intrusion porosimetry for bottom sediment (BS) and mixtures with increasing concentration of cellulose waste (CW), biochar (BC), and dolomite (DL)

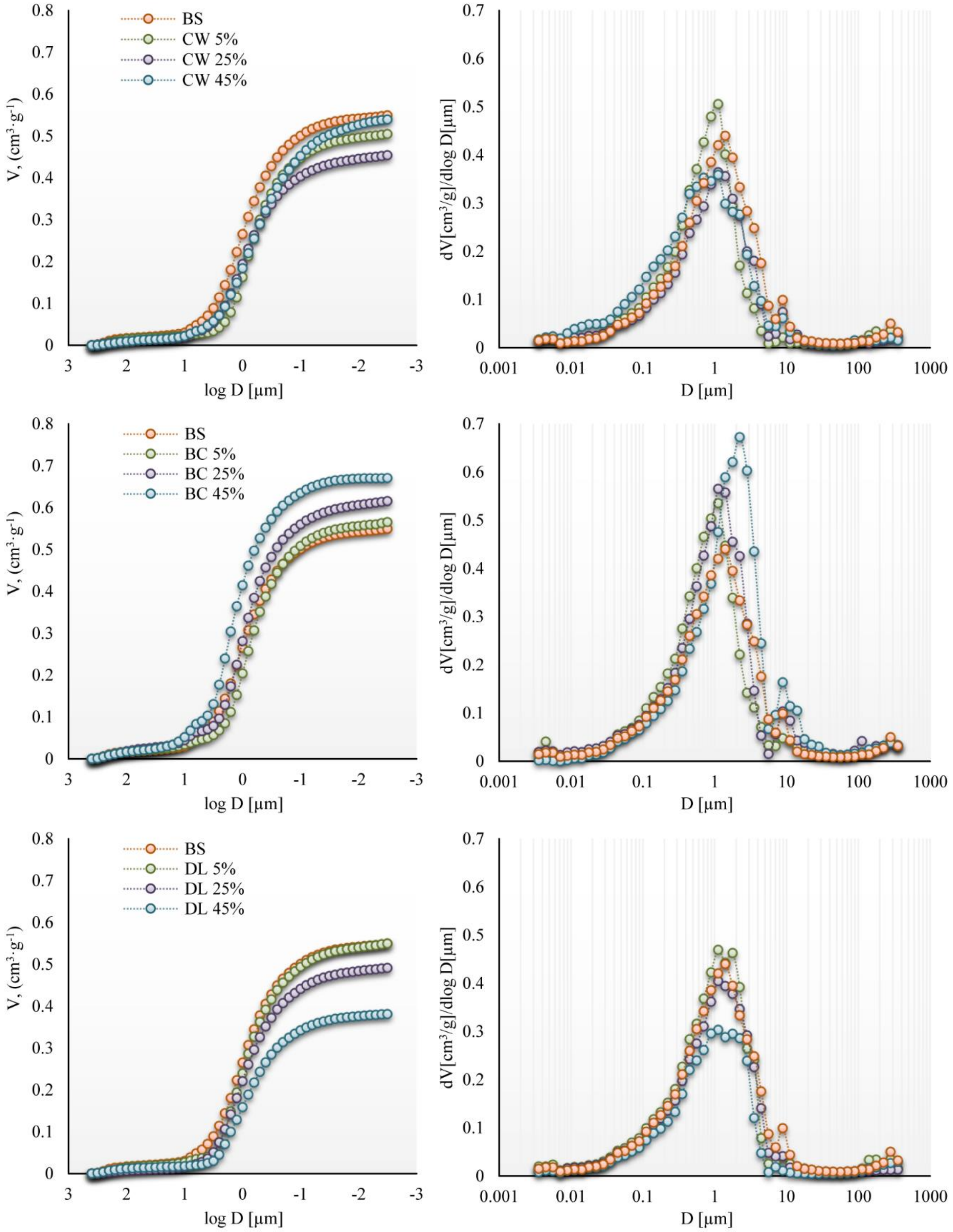

Figure 5. Metal fractionation according to the BCR sequential extraction scheme in bottom sediments (BS) and mixtures with cellulose waste (CW), biochar (BC), and dolomite (DL)

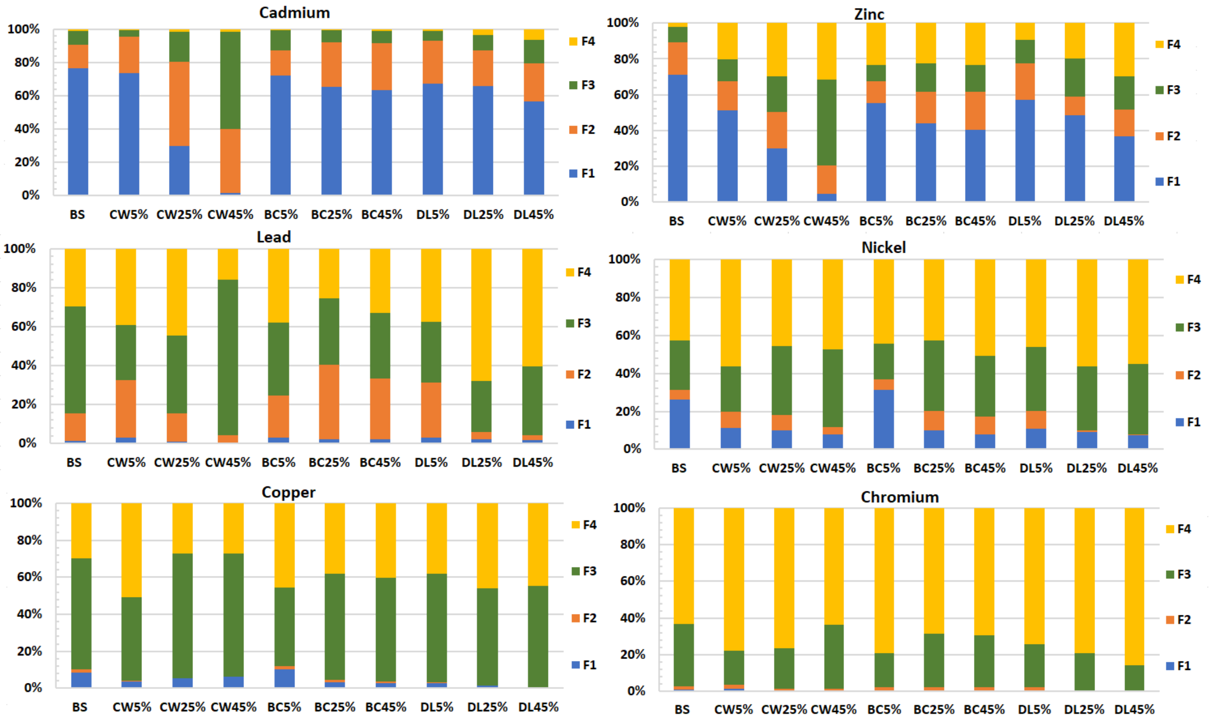

Figure 6. Share of the different biotests in the cumulated toxic response for the bottom sediments (BS) and mixtures with cellulose waste (CW), biochar (BC), and dolomite (DL)

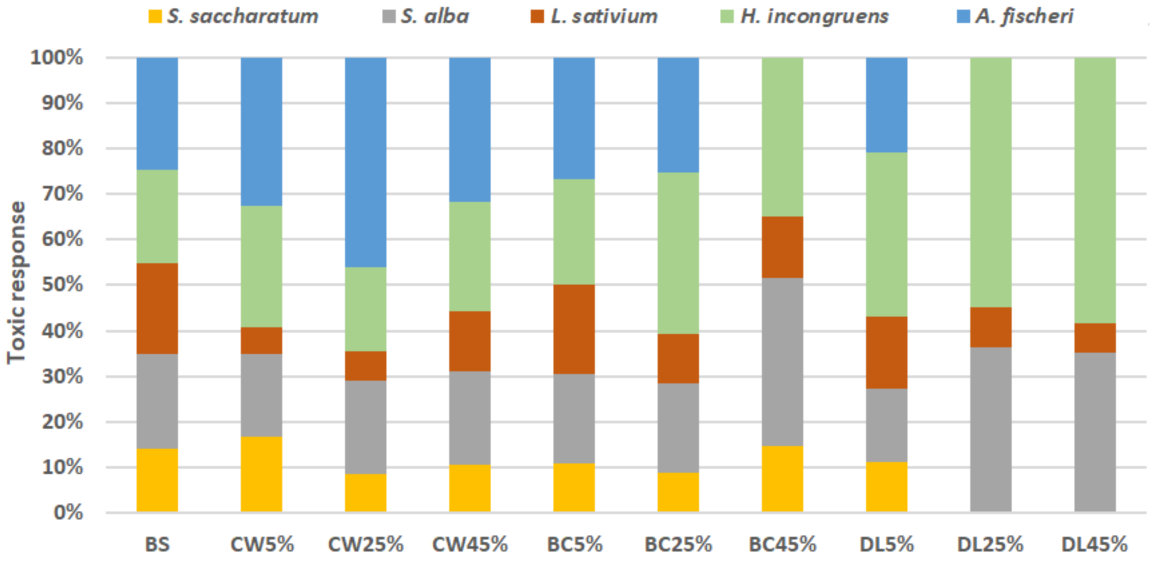

Table 1. **pH, total organic carbon (TOC), and selected metal contents of the bottom sediment and amendments used in the mixtures**

Parameter		BS*	CW	BC	DL
pH_{KCl}		3.55	12.50	7.31	8.53
TOC	g/kg dm	71.1±1.4	38.4±2.7	375±31	62.8±5.8
Cd	mg/kg dm	54.1±8.5	0.17±0.04	0.50±0.03	0.45±0.15
Cr		35.5±16.7	56.5±10.5	87.2±6.9	6.0±0.8
Ni		30.6±3.2	20.6±5.8	24.4±1.3	3.9±0.1
Zn		4409±75	51.6±6.7	219±31	46.6±1.7
Pb		279±21	2.6±0.3	28.1±3.9	3.3±0.2
Cu		68.0±16.9	8.9±0.2	43.8±10.5	15.4±0.9

*BS – bottom sediment, CW– cellulose waste, BC – biochar, DL – dolomite

Table 2. Selected chemical and sorption properties of bottom sediments and mixtures

Treatments	pH_{KCl}	TOC	**Q7**	**Q10**	**P_c**	**ρ_D**	**D_{MIP}**	**S_{MIP}**	**V_{MIP}**	**SSA**	**V_{N2}**	**D_{N2}**
		g/kg dm	µmol/g		%	g/cm^3	nm	m^2/g^1	cm^3/g	m^2/g	mm^3/g	nm
BS	3.58 a^1	76.3 a	622 e	1268 d	53.4 cd	0.97 c	835d	13.2 c	0.55 e	7.9 b	26.6 ab	10.3 bc
CW 5%	7.84 d	72.2 a	617 e	1177 d	52.6 c	1.04 de	541ab	15.6 cd	0.51 cd	11.4 c	26.4 a	9.0 ab
CW 25%	8.96 e	71.5 a	1080 g	2044 f	50.1 b	1.10 f	653 abcd	14.2 cd	0.45 b	15.1 d	37.6 c	9.3 ab
CW 45%	12.3 f	63.7 a	962 f	1600 e	53.7 cd	0.99 cd	473 a	21.5 e	0.54 de	17.6 e	42.8 de	8.8 ab
BC 5%	4.16 ab	85.1 b	528 d	1197 d	54.3 cd	0.96 c	626abc	16.6 d	0.57 e	17.8 e	42.8 de	8.6 ab
BC 25%	6.19 b	136.8 d	350 a	796 ab	55.3 cd	0.90 b	792 cd	16.3 d	0.62 f	14.7 d	31.6 b	7.9 ab
BC 45%	7.04 c	187.3 e	343 a	763 a	55.3 cd	0.83 a	1225 e	7.2 a	0.67 g	17.6 e	38.0 cd	7.8 ab
DL 5%	6.48 b	77.8 a	406 b	914 bc	54.3 cd	0.99 cd	682 bcd	15.7 cd	0.55 e	21.5 f	45.5 e	7.4 a
DL 25%	7.23 cd	86.2 cb	450 bc	1016 c	52.3 c	1.06 ef	661 abcd	13.6 c	0.49 bc	25.5 g	60.2 f	8.3 ab
DL 45%	7.35 d	92.8 c	464 c	1172 d	47.8 a	1.25 g	658 abcd	9.9 b	0.38 a	5.9 a	24.1 a	12.3 c

[1] Means followed by different letters indicate significant differences at $\alpha \le 0.05$ according to Tukey's test. BS – bottom sediment; CW – cellulose waste; BC – biochar; DL – dolomite. TOC – total organic carbon; Q7 and Q10 – negative surface charge at pH 7 and 10; P_c - total porosity; ρ_D – bulk density; D_{MIP} – average pore diameter; S_{MIP} – total pore area; V_{MIP} – cumulative volume of pores; SSA – specific surface area; V_{N2} – cumulative volume of pores measured by nitrogen adsorption method; D_{N2} – average pore diameter measured by N_2 method

Treatments	**Cd**	**Zn**	**Pb**	**Ni**	**Cu**	**Cr**
Total content (mg/kg dm)						
BS	54.1 d[1]	4409 d	279 d	30.6 cd	68.0 bcd	35.5 cd
CW 5%	47.5 cd	3858 c	252 cd	29.5 cd	66.7 bcd	35.2 cd
CW 25%	33.8 b	2782 ab	176 b	21.4 b	57.2 ab	26.4 ab
CW 45%	22.9 a	1935 a	120 a	16.0 a	48.2 a	19.2 a
BC 5%	48.4 cd	3986 cd	267 cd	31.3 cd	75.4 d	41.5 cd
BC 25%	32.1 b	2747 ab	184 b	27.5 cd	71.7 cd	49.0 de
BC 45%	29.6 b	2638 ab	181 b	33.8 d	76.2 d	57.4 e
DL 5%	49.3 cd	3974 cd	261 cd	29.6 cd	66.8 bcd	34.2 cd
DL 25%	43.7 c	3293 bc	235 c	24.7 c	58.4 bc	32.7 cd
DL 45%	30.1 b	2517 a	164 ab	20.0 b	45.0 a	23.6 ab
RAC (% in total content metals bound to F1)[2]						
BS	75.0 d	70.8 c	1.0 a	26.0 b	7.8 c	0.9 b
CW 5%	70.1 d	49.7 bc	3.2 b	11.7 a	2.7 ab	0.7 b
CW 25%	21.3 b	30.2 b	0.8 a	9.7 a	5.0 ab	0.0 a
CW 45%	1.2 a	5.0 a	0.1 a	8.2 a	6.1 b	0.0 a
BC 5%	71.1 cd	54.1 bc	2.8 b	31.6 b	9.6 c	1.1 b
BC 25%	62.4 cd	44.9 b	1.8 ab	10.2 a	3.2 ab	0.0 a
BC 45%	55.6 c	40.1 b	2.0 ab	7.0 a	3.0 ab	0.0 a
DL 5%	67.0 cd	56.3 bc	3.3 b	10.0 a	2.9 ab	0.0 a
DL 25%	58.2 cd	49.2 b	2.2 ab	8.2 a	2.1 ab	0.0 a
DL 45%	42.9 c	36.7 b	2.0 ab	6.9 a	0.8 a	0.0 a
ICF (∑F1-F3)/F4 [3]						
BS	97.0 d	48.0 d	2.36 c	1.30 b	2.35 c	0.59 b
CW 5%	19.0 b	3.89 ab	1.55 b	0.86 a	0.96 a	0.28 ab
CW 25%	2.46 ab	3.36 ab	1.24 b	1.20 ab	2.69 c	0.31 ab
CW 45%	5.23 ab	2.18 a	5.24 d	1.11 ab	2.68 c	0.57 b
BC 5%	98.0 d	3.30 ab	1.62 b	1.25 ab	1.20 ab	0.26 ab
BC 25%	16.1 b	3.44 ab	2.95 c	1.33 ab	1.61 b	0.46 ab
BC 45%	6.69 ab	3.29 ab	2.05 c	1.09 ab	1.48 ab	0.44 ab
DL 5%	49.0 c	9.90 c	1.67 b	1.18 ab	1.64 b	0.35 ab
DL 25%	5.67 ab	4.00 b	0.47 a	0.81 a	1.17 ab	0.26 ab
DL 45%	2.77 a	2.37 a	0.65 a	0.82 a	1.23 b	0.16 a
ERF (F1+F2)/(F3+F4)[4]						
BS	9.89 cd	8.35 c	0.18 b	0.46 c	0.12 b	0.03 b
CW 5%	10.59 cd	2.07 b	0.48 c	0.26 abc	0.04 a	0.03 b
CW 25%	1.37 ab	1.00 ab	0.18 b	0.22 abc	0.06 a	0.01 ab
CW 45%	0.52 a	0.25 a	0.04 a	0.13 ab	0.07 a	0.01ab
BC 5%	6.62 b	2.08 b	0.33 bc	0.58 d	0.14 b	0.02 ab
BC 25%	6.86 b	1.62 ab	0.68 d	0.25 abc	0.05 a	0.02 ab
BC 45%	4.17 ab	1.62 ab	0.50 c	0.24 abc	0.04 a	0.02 ab
DL 5%	11.86 d	3.46 ab	0.45 c	0.25 abc	0.03 a	0.02 ab
DL 25%	3.30 ab	1.44 ab	0.06 a	0.11 ab	0.02 a	0.00 a
DL 45%	1.66 ab	1.06 ab	0.04 a	0.09 a	0.01 a	0.00 a

Table 3. Content of metals in mixtures and assessment of their mobility

[1] Means followed by different letters indicate significant differences at α ≤ 0.05 according to Tukey's test. BS – bottom sediment; CW – cellulose waste; BC – biochar; DL – dolomite. , [2]RAC ≤1% no risk, 1% < RAC ≤ 10% low risk, 10% < RAC ≤ 30% medium risk, 30% < RAC ≤ 50% high risk, 50% < RAC very high risk, [3]ICF ≤1 low contamination, 1 < ICF ≤ 3 moderate contamination, 3 < ICF ≤ 6 considerable contamination, ICF > 6 very high contamination, [4]0 < ERF ≤ 0.4 low risk, 0.4 < ERF ≤ 1 medium risk, 1 < ERF high risk

Table 4. Ecotoxicity of mixtures based on the response of test organisms and classification of their toxicity

Treatments	SsRI	SaRI	LsRI	HiGI	AfLI	Class of toxicity[3]
	Percentage effect (PE, %)					
BS	57 d	84 d	80 e	83 cd	100 e	IV
CW 5%	43 cd	47 b	15 abc	69 bc	84 d	III
CW 25%	17 ab	40 ab	13 abc	36 a	91 d	III
CW 45%	33 bc	65 c	41 d	76 bc	100 e	IV
BC 5%	40 cd	72 cd	71 e	85 cd	98 e	III
BC 25%	22 b	49 bc	27 bc	89 d	63 c	III
BC 45%	15 ab	38 ab	14 abc	36 a	-30 a	II
DL 5%	22 b	32 a	31 c	71 bc	41 b	II
DL 25%	-32 a	33 a	8 ab	50 a	-16 a	II
DL 45%	-7 a	27 a	5 a	45 a	-3 a	II

[1] Means followed by different letters indicate significant differences at α ≤ 0.05 according to Tukey's test. BS – bottom sediment; CW – cellulose waste; BC – biochar; DL – dolomite. [2]SsRI – *Sorghum saccharatum*, roots growth inhibition, LsRI – *Lepidium sativum*, root growth inhibition, SaRI – *Sinapis alba*, roots growth inhibition; HiGI – *Heterocypris incongruens*, growth inhibition; AfLI – *Allivibrio fischeri*, luminescence inhibition. [3]Toxicity classes: class I (PE ≤ 20%, non-toxic sample); class II (20% < PE ≤ 50%, lowly toxic sample); class III (50% < PE < 100%, toxic sample); class IV (PE = 100% for a single test, very toxic sample), class V (PE = 100% for all tests, very toxic samples)