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Corncob and rice husk biochar mitigate potentially toxic elemental mobility in flooded-paddy-mine-contaminated soils

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Abstract

Redox-induced changes in soils via flooding influence the solubility and mobility of potentially toxic elements (PTEs) and, by extension, trigger an upsurge of their transport into surrounding ecosystems. We simulated an anaerobic paddy field environment through flooding of amended artisanal-gold mine-contaminated soils in an 85-day pot incubation experiment. We studied the redox-induced changes that occurred in these amended soils treated with 5% rates of compost, corn-cob biochar, rice husk biochar (RB), and poultry manure (PM) whilst under rice cultivation. The biogeochemical drivers that may influence PTE mobilisation under dynamically changing redox conditions, such as those in paddy soils, were then investigated. Slurry samples were collected from each flooded pot with a syringe after the 85-day incubation period for laboratory analysis of seven PTE concentrations, including As, Cd, Cu, Fe, Mn, Pb, and Zn. We employed linear regression models to identify the variables controlling the mobilisation and release of these PTEs from the multi-element mine-contaminated sites. The study identified Eh as the dominant control on PTE mobilisation, with temperature acting as a secondary but important driver. The influence of temperature was particularly evident in regulating the behaviour of As, Fe, and Mn,

suggesting that temperature-dependent redox and biogeochemical processes contribute substantially to PTE mobilisation. In contrast, pH exerted a comparatively limited influence, indicating that PTE mobilisation was governed more strongly by redox conditions and temperature than by pH. These findings highlight the potential of corncob and rice husk biochar to mitigate elemental mobility in flooded mine-contaminated soils.

Keywords: *Artisanal and small-scale mining; formalization; sustainability; mercury; galamsey.*

1.0 Introduction

Flooding at abandoned gold mining sites poses a critical yet often overlooked environmental concern: the mobilization of potentially toxic elements (PTEs) in soils, sediments, and water bodies. During flooding, the dynamics of PTEs change when a PTE-contaminated site is completely submerged by excess water from either prolonged rainfall or river overbank flooding (Kelly et al., 2020; Ponting et al., 2021; Indraratne & Kumaragamage, 2017). Anaerobic conditions caused by prolonged inundation affect the mobility of PTEs and their spread into nearby natural resources such as farmland, surface water bodies, and groundwater. Such anaerobic environments usually cause deprotonation and result in an increased pH in acidic soils, which reduces the mobility of cationic PTEs such as Cu, Cd, Pb, and Zn while facilitating the solubility of anionic PTEs such as As, Se, Cr, and Mo (Mensah et al., 2025). Redox-induced changes via flooding influence the speciation, solubility, and mobility of these PTEs, often increasing their release into the soil solution and enhancing their transport into surrounding environment (Bunquin et al., 2017). Consequently, flooding not only transforms the physical environment but also modifies the chemical behavior and ecological risks associated with soil contaminants.

As floodwaters spread across contaminated landscapes, dissolved and particulate contaminants can be redistributed into agricultural fields, wetlands, rivers, groundwater, and urban water supplies (Maliszewska-Kordybach et al., 2013). Regardless of their origin, floodwaters saturate the soil profile and fill soil macropores with water, drastically reducing oxygen diffusion and creating redox conditions (Holden, 2019). As oxygen is depleted through microbial respiration, soil redox potential declines, creating reducing (anaerobic) conditions that fundamentally alter soil biogeochemical processes. A large proportion of PTEs naturally exist in the soil profile (i.e., attached to rock particles and sequestered in clays, minerals, and colloids) in locked or immobilized forms; however, they may become unstable under changing environmental conditions during flooding (Ali et al., 2019; Shaheen et al., 2013; Kabata-Pendias, 2011). Consequently, these PTEs can become available and mobile in the environment and may contaminate the food chain through their release into the ecosystem.

Additionally, changes in Fe concentrations relative to PTE levels in waterlogged areas, expressed in terms of the Fe:PTE ratio, influence the mobility of PTEs into groundwater resources via deep

percolation and may cause contamination. Because of the high sorption capacity of iron oxides or oxyhydroxides, high concentrations of Fe in soils under prolonged inundation can immobilize anionic PTEs and reduce their transport to groundwater. Similarly, some cationic PTEs are immobilized by high Fe concentrations through surface complexation and co-precipitation (Mensah et al., 2025). In light of the foregoing, once the prevailing anaerobic conditions change temporarily and oxygen levels increase sufficiently to cause acidification, the biogeochemistry may change and result in secondary pollution by cationic PTEs that were previously co-precipitated or adsorbed via surface complexation (Ponting et al., 2021).

This increases the likelihood of contamination of crops, drinking water sources, and aquatic ecosystems, thereby extending the impacts of flooding beyond its commonly recognized role as a natural disaster. These trace elements may originate from both natural geological sources and anthropogenic activities such as gold mining. This occurs, for instance, when former mining sites are left abandoned without reclamation or any form of protection. Numerous studies (e.g., Boakye et al., 2025; Emon et al., 2023; Milošković & Simić, 2023; Zahran et al., 2025; Mensah et al., 2025; Thalassinos et al., 2023), along with assessments by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO), have demonstrated that elevated concentrations of these elements in soil, water, and food crops pose significant risks to human health, agricultural productivity, and environmental quality.

Although both large-scale commercial mining and artisanal and small-scale mining (ASM) exist in Ghana, unregulated and illegal activities perpetrated by ASM operators disproportionately contribute to PTE pollution and environmental degradation in the country (Basu et al., 2015; Rajaee et al., 2015). Some of their problematic activities, such as mining and washing in water bodies, the use of mercury for amalgamation, abandonment of open pits after mining operations, and inappropriate disposal of tailings, accelerate environmental degradation. For example, Mensah et al. (2025) found that abandoned gold-mining sites in a mining district in Ghana were contaminated with several PTEs, including As, Cd, Md, Ni, Cu, Pb, and Fe, whose concentrations even exceeded internationally acceptable thresholds. As these polluted sites are abandoned and not remediated, they are susceptible to erosion and can subsequently cause non-point-source contamination of nearby ecosystems (Karaca et al., 2018; Hudson et al., 2018; Venkateswarlu et al., 2016).

The incorporation of organic soil amendments, such as biochar, compost, and poultry manure, could influence the dynamics of PTE (im)mobilization under flooded conditions. Mensah et al. (2025), in their study investigating the mobilization of PTEs in flood-contaminated soils affected by the addition of soil amendments reported that poultry manure and biochar mobilized Pb and As, whereas compost immobilized Cd. According to some studies (e.g., Moore et al., 2023; Aftabtalab et al., 2022), microbial activities can also reduce Fe(III) and Mn(IV) oxides, allowing adsorbed PTEs (e.g., As) to become mobile again under waterlogged conditions. Microorganisms can also immobilize PTEs through bioaccumulation, biosorption, and biomineralization (Abo-Alkasem et al., 2023; Nnaji et al., 2023). Further, time could also influence the aforementioned variability in PTE dynamics under waterlogged conditions in abandoned gold-mining sites, as observed in floodplains by some researchers (e.g., Ponting et al., 2021; Kelly et al., 2020). Yet, to the best of our knowledge, no study has investigated how PTE immobilization under prolonged inundation evolves in remediated, abandoned gold-mining sites cultivated with rice.

Although Mensah et al. (2025) sought to determine how PTE mobility in soils under flooding conditions could be mitigated through the incorporation of organic soil amendments, their 28-day incubation study was not long enough to fully unravel these potential dynamics. Hence, this study aims to analyze the dynamics of PTE mobility in mine tailings under flooding conditions following the incorporation of organic soil amendments over time and rice cultivation. This study will provide insight into the timely remediation of PTE-contaminated mine sites using organic soil amendments. Our study makes the following assumptions: the various soil biogeochemical variables that regulate PTE release patterns do not change over time under flooded conditions in metal-contaminated sites; soil variables such as pH, redox potential, Al, Fe and Mn, electrical conductivity, soil resistivity, and soil temperature are not affected by the addition of soil amendments; and the addition of soil amendments to mine-contaminated sites does not affect PTE mobilization and release dynamics. To this end, our study seeks to answer the following research questions:

I. How do the various soil parameters regulating the release dynamics of PTEs in amended mine-contaminated sites change over time under flooded paddy conditions?

II. How do the various soil-governing parameters, such as pH, redox potential, and the chemistry of Al, Fe, and Mn, regulate the mobilization of PTEs in flooded amended, contaminated paddy fields?

III. How does the addition of soil amendments such as biochar, compost, and manure affect the release and mobilization dynamics of PTEs in flooded, contaminated paddy field?

2.0 Materials and methods

2.1. Study site characteristics

The study was conducted in a greenhouse at the CSIR-Soil Research Institute (SRI) in Kumasi, in Ghana's Ashanti Region. To mimic real-world conditions, temperature and light were not controlled in the greenhouse, which was exposed to ambient temperature and sunlight. Tailing samples were collected from five (5) different abandoned gold-mining sites in Nsiana (6° 2921.2 ″ N, 1° 49′ 8.8″ W; 6° 28′ 8.9″ N, 1° 48′ 49.2″ W; 6° 28′ 14.2″ N, 1° 48′ 29″ W; 6° 28′ 46.9″ N, 1° 49′ 12.2″ W; 6° 28′ 48.3″ N, 1° 49′ 12.9″ W) near Antoakrom in the Amensie West District of the Ashanti Region. Sekyi-Annan et al. (2021) indicate that the district is located in the semi-deciduous forest agroecological zone, which is distinguished by a bimodal rainfall pattern. The major rainy season lasts from March to July, while the minor rainy season lasts from September to November. The district has an area of approximately 1,364 km² and is known for its artisanal and small-scale gold mining. Degraded lands left after mining operations are commonplace.

Mine tailings at abandoned sites are either in heaps or spread out on the ground as a result of erosion. Sandy loam is the most common soil type found on abandoned mining sites. The area is also known for crop production (Wongnaa et al., 2024). According to Ghana's Ministry of Food and Agriculture (MoFA), the district's major crops are rice, maize, cassava, plantain, cocoyam, and yam. It is worth noting that the majority of these abandoned gold-mining sites in the study district were once croplands (Wongnaa et al., 2024).

2.2. Sample collection and preparation

Samples of mine tailings were collected from the 0–20 cm horizon at five (5) randomly selected abandoned gold-mining sites in the study district. Three (3) sampling points were identified at each of the five (5) sampling sites to capture site-specific heterogeneity, and tailing samples were collected from those locations using a shovel. The soil samples collected from the three locations were combined, stored in plastic sacks, and labeled appropriately. The composite samples were transported, air-dried, and sieved (<2 mm) for laboratory analysis.

2.3. Determination of physicochemical properties of the tailing samples

The analyses were conducted using conventional analytical techniques, as detailed below. The hydrometer approach, as outlined by Bouyoucos (1962), was employed to determine particle-size distribution. Soil bulk density and initial volumetric moisture content were determined using the core and gravimetric methods, respectively (Al-Shammary et al., 2018). The pressure-plate method described by Karkanis (1983) was used to measure soil moisture at saturation, field capacity, and wilting point. Soil pH was measured in a 1:2.5 suspension of soil and water using an HI9017 microprocessor pH meter calibrated with buffer solutions of pH 7, 9, and 4. The Thermo Scientific EC electrode Orion 013605MD was used to determine electrical conductivity (EC). Organic carbon was quantified using a modified Walkley–Black method, as outlined by Nelson and Sommers (1982).

Total nitrogen was quantified using the Kjeldahl digestion and distillation methods, as outlined by Bremner and Mulvaney (1982). Exchangeable bases, including calcium, magnesium, potassium, and sodium, in the soils were quantified using a 1.0 M ammonium acetate (NH_4OAc) extract (Black, 1986). Exchangeable acidity (H + Al) was determined in a 1.0 M KCl extract according to the methodology outlined by Page (1982). Calcium and magnesium in the extract were quantified using EDTA titration, while potassium and sodium were measured using flame photometry. Effective cation exchange capacity (ECEC) was determined by summing the exchangeable bases (calcium, magnesium, potassium, and sodium) and exchangeable acidity (hydrogen and aluminum). Available phosphorus was determined using the Bray-1 method, as outlined by Bray and Kurtz (1945). The PTEs (Zn, Cu, Mn, Fe, Cd, Pd, As, and Hg) were quantified in an EDTA extract by atomic absorption spectrophotometry. Soil anion contents (sulfates and carbonates) were analyzed using the procedures outlined by FAO (2008).

2.4. Production and determination of physicochemical properties of the organic soil amendments

This study utilized rice husk biochar (RB), corncob biochar (CCB), poultry manure (M), and compost (Com) as soil amendments. The RB and CCB were sourced from rice- and maize-processing facilities in Ghana, respectively and subjected to charring for one hour in a muffle furnace using a gradual pyrolysis method at 550°C. The compost used in this investigation was produced by the Soil Microbiology Division of CSIR-SRI using maize stover and damp poultry manure over a period of four (4) months through an experimental composting method akin to that employed by Alfano et al. (2011). Following a 48-hour air-drying period, the amendments were pulverized, homogenized, and passed through a 2-mm mesh sieve. Subsequently, their pH, organic carbon, total nitrogen, phosphorus, potassium, calcium, and magnesium contents were determined. Metallic elements, including arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), and mercury (Hg) in the amendments were also determined.

2.5. Treatments and experimental design

This study examined five (5) treatments, comprising sieved tailing samples mixed with four (4) organic soil amendments, along with an unamended control group. Tailing samples weighing 6 kg were measured into a basin and thoroughly mixed with 300 g of soil amendment yielding a total weight of 6.3 kg for each amended treatment. The control had a mass of 6 kg since no organic soil amendment was added. The 300 g of soil amendment represented 5% of the tailing sample weight based on Alhar et al. (2021), who indicated that incorporating 5% organic soil amendment (i.e., biochar) into soil significantly increased the dry matter yield of ryegrass cultivated on contaminated mined sites in the UK. Subsequently, the homogenized tailing-amended samples for each treatment and the control were placed in cylindrical plastic pots with a diameter of 20 cm and a height of 18 cm, and appropriately labeled.

This study utilized a randomized complete block design (RCBD) with three replications. The five treatments (four soil amendments and one control) each with three replications, resulted in fifteen pots. The treatment pots were arranged on a concrete table (length = 3.91 m; width = 1.55 m; height = 0.82 m) in the greenhouse according to the previously described experimental design, with 42-cm inter- and intra-row spacing.

2.6. Flooded incubation, data collection, laboratory determination of soil PTEs, data treatments and statiscal analyses

The flooded incubation experiment was based on previous studies (e.g., Indraratne and Kumaragamage, 2018; Jayarathne et al., 2016). In this investigation, all treatments were required to maintain a water depth of at least 2 cm above the surface of the samples in the pots. This was essential to provide an anaerobic environment for examining the behavior of the PTEs during the incubation period. The quantity of water applied for ponding the treatments in the pots was determined based on the laboratory-measured volumetric moisture contents of the tailing samples at field capacity (20.7%) and saturation (43.5%) as described in detail by Mensah et al. (2025). Consequently, 2,000 liters of water were applied to each treatment resulting in a moisture content of 31.7% and a water depth of ≥2 cm.

The incubation experiment was conducted between 8 November 2024 and 31 January 2025. Every two weeks, a handheld water quality meter (YY-1010) (Mensah et al. 2025) was used to monitor and measure soil physicochemical properties, including pH, electrical conductivity (EC), redox potential, salt content, salinity, soil temperature, fertility, and resistance. Additional soil slurry samples were collected using a syringe for the analysis of PTEs (As, Cd, Cu, Zn, Cr, Ni) via aqua regia digestion. In total, five batches of soil slurry samples were collected, representing weeks 1–5. Thus, 75 samples were analyzed. The slurry samples in the syringes were transferred into Falcon tubes and centrifuged at a constant speed for five (5) minutes to separate the supernatant solution from the mixture. The slurry samples were filtered using 0.45-µm membrane filters before analysis. An Agilent 200 Atomic Absorption Spectrophotometer (AAS) was used to analyze the metal elements in the solution.

All collected and measured variables were subjected to both descriptive and inferential statistics. Descriptive statistics such as the mean, minimum value, median, maximum values and standard deviations were computed for all data collected. Tables were used to present the summary results. Inferential statistics were run to test for hypotheses used in our study. Here, we first tested for normal distribution of our data using Shapiro Wilk tests. Further, we run mean comparison tests among the different treatments using Tukey tests and used different letters to indicate where means among treatments significantly differ at $p < 0.05$. Same letters indicated that no statistical

significance existed among the treatments. Finally, we run spearman correlation and linear regression models to demonstrate biogeochemical influence of the measured soil variables on the mobilisation of the PTEs. All data analyses were carried out using ORIGIN PRO 2026 Version.

3.0 Results and Discussion

3.1 Study area demographics, soil physico-chemical properties, and amendments characterization

The basic characteristics of the mine soil and that of the soil amendments used are earlier published by Mensah et al. (2025). The site had a bulk density of 1.5 g cm^{-3} and primarily dominated by sandy loam composed of sandy material accounting for 69% of the total soil particle-size composition, while clay and silt contents were 17% and 14%, respectively. The observed bulk density is indicative of moderate soil compaction. For such unreclaimed soils as was observed in the study area, the bulk density is relatively high. An initial volumetric water content of 14% was recorded indicating a relatively dry moisture condition given the moisture content of the tailings at field capacity, wilting point, and saturation was 21%, 12%, and 44%, respectively. Such moderately high bulk density and dry moisture conditions are characteristic of degraded mining site owing to the removal of vegetation. Oduro Appiah & Larbie (2025) reported similar moisture conditions for a post-mining degraded landscape. They indicated that bare soils experience dryer moisture conditions than land covered with vegetation. Cao et al. (2021) affirm our findings when they observed that volumetric moisture content of 14% for mine tailings in China. The pH (5.58) of the soil at the site was moderately acidic. The electrical conductivity of 40 µS cm^{-1} indicated that the soil at the mine site was saline. This was supported by the established base saturation content of 60%. The levels of organic carbon, organic matter, and total nitrogen measured at the site were all low. Exchangeable bases were generally low, with a total cation exchange capacity of 1.34 meq per 100 g and an effective cation exchange capacity of 2.24 meq per 100 g.

For the soil amendments used, poultry manure contributed the most calcium, while corncob biochar contributed the least. The percentage distribution of calcium among the soil amendments ranged from 0.3% to 2.7%. Similarly, poultry manure contributed the most magnesium, whereas the other soil amendments had values of 0.5% for compost and 0.2% each for CCB and RB. Poultry

manure provided the largest percentage of potassium (5%), followed by RB (2.2%). Generally, the levels of total phosphorus were low. Due to the application of poultry manure, the nitrogen content was 2%. The nitrogen content was lowest in CCB and RB. Exchangeable acidity was low for all amendments.

3.2 Changes in Soil Physico-chemical Properties as Affected by Incubation Time and Addition of Soil Amendments

3.2.1 Electrical Conductivity (EC) and Salinity

Soil electrical conductivity and salinity are closely related, indicating the presence of solutes or salts in the soil solution. Both salinity and EC followed a similar pattern, with an increase during the initial flooding phases and a gradual decrease near the end of the experiment (Fig. 1). Peak EC values were measured in the control during the second week of incubation, indicating mineral-phase dissolution and the release of charged ionic species under anaerobic conditions during the early flooding period. The direct relationship between EC and soil salinity is well established (Nordio et al., 2025; Regia et al., 2025; Awoke et al., 2025). The rise in soil salinity and EC during the early stages of flooding is in line with earlier research by He et al. (2023), Regia et al. (2025), and Su et al. (2024). For instance, during a brief flooding period, Regia et al. (2025) found that flooding increased volumetric water content, which in turn raised EC and salinity levels. These findings were confirmed by Awoke et al. (2025). Nordio et al. (2024) attributed the increase in EC and salinity during the short flooding period to evapotranspiration. This process raises salinity by absorbing freshwater while leaving salt behind, resulting in pore-water salinity in the shallow soil layer (Yu et al., 2021). As a result, accumulated salts are further dissolved by floodwater, raising EC and salinity (Cox et al., 2018).

The changes in the soil EC, salinity and the other soil basic properties during the entire experimental-incubation trial is shown in Table 1. Throughout the incubation period, salinity levels in the unamended control were consistently higher than those in the amended treatments, indicating that the amendments reduced ion release and, by extension, PTE release while increasing their retention (Gao et al., 2024). Corncob biochar reduced salinity due to its high calcium content, as reported in other findings (e.g., Mensah and Frimpong, 2018; Huang et al.,

2023). This soil property can facilitate ion exchange and the precipitation of carbonate compounds (Tack, 2010). Metal-carbonate complexes may limit metal mobility and toxicity in soils by converting free, bioavailable metal phases into more geochemically stable forms (Lwin et al., 2018). Thus, the lower EC and salinity values associated with rice husk biochar, corncob biochar, and compost indicate that these amendments have potential for PTE remediation in the contaminated mine tailings.

3.2.3 Soil Electrical Resistance

Soil resistivity is a measure of how strongly a given volume of soil opposes the flow of electric current, expressed in ohm-meters (Ω·m) or ohm-centimeters (Ω·cm). Moisture regimes generally disrupt bonds in soil minerals and colloids and weaken their resistance to electrical conduction through the soil solution. Concomitantly, the soil's buffering capacity to resist changes in electrical conductivity decreases, increasing the susceptibility to release sequestered, adsorbed, or co-precipitated PTEs. Soil electrical resistance declined markedly during the early stages of flooding, inversely mirroring the increase in EC and salinity (Fig. 1). This initial decline could also be due to the higher solubility of organic solutes available to soil microbes because of their increased activity at the beginning of flooding (e.g., Mensah et al., 2022; Beiyuan et al., 2020). The most pronounced reductions in resistance were observed in the control treatment, whereas amended soils, particularly corncob biochar and rice biochar, maintained comparatively higher resistance throughout the incubation. The recalcitrant nature of biochar treatments enhanced their resistance-buffering capacity (e.g., Beiyuan et al., 2017; 2020). This suggests that amendment-mediated control of ion release not only influences salinity and EC, but also affects the bulk conductive properties of the flooded soil matrix. Flooding impacts soil structure and aggregation by altering the resistance of soil to slaking (e.g., Falcão et al., 2026), which occurs when aggregates are not strong enough to withstand internal stresses caused by rapid water uptake. The disruption of soil aggregates (e.g., Shah et al., 2024) can enhance soil erosion and sediment transport during flooding events (e.g., Kerr et al., 2016) and contribute to the sedimentation of water bodies and the degradation of aquatic ecosystems (e.g., Pittelkow et al., 2017).

3.2.4 Soil Temperature

Soil temperature exhibited natural diurnal and seasonal fluctuations during the incubation period, ranging from approximately 21 to 30°C (Fig. 1). The addition of amendments did not significantly alter soil temperature, suggesting that temperature variation was predominantly governed by ambient climatic and environmental conditions rather than amendment-induced soil chemical processes. Nevertheless, temperature was retained as an important covariate in subsequent correlation analyses because it regulates microbial activity and the kinetics of biogeochemical reactions occurring in soils, including those associated with redox transformations under waterlogged conditions (Kaur et al., 2020; Kögel-Knabner et al., 2010). Under anaerobic conditions, the progressive depletion of oxygen promotes the sequential use of alternative electron acceptors, including nitrate, Mn(IV), Fe(III), sulfate, and CO_2, with many of these reduction processes being microbially mediated (Kögel-Knabner et al., 2010). Consequently, temperature variation within the observed range may influence the rates of Mn and Fe reduction and associated geochemical transformations. This is particularly relevant to PTE dynamics because Fe and Mn (hydr)oxides are important sorbents and host phases for trace elements, and their reductive dissolution under reducing conditions can release sorbed or co-precipitated PTEs into soil solution (Ponting et al., 2021). Thus, although temperature was not directly affected by the amendments, its variation during incubation may have contributed to temporal differences in microbial activity, redox processes, and PTE mobilization.

3.2.5 Soil pH and Redox Potential (Eh)

In the unamended control, pH rose from initially slightly acidic values to near-neutral or mildly alkaline conditions within the first two weeks of incubation (Fig. 2). This is a well-documented phenomenon attributed to the consumption of protons during reductive processes such as the reduction of Fe(III) and SO_4^{2-} and the production of alkalinity through microbial metabolism (e.g., Lukasz et al., 2014; Mensah et al., 2022, 2025; Shaheen et al., 2018). We also observed a sharp decline in Eh, from oxidative values (above +200 mV) to strongly reducing conditions (below −100 mV), consistent with observations made in a similar study by Mensah et al. (2022). This shows that as the amount of oxygen in the soil water decreased, anaerobic conditions gradually developed. Under these conditions, oxygen depletion may compel microorganisms to transition from aerobic to anaerobic metabolism, during which Fe^{3+} is reduced to Fe^{2+} and Mn(IV) to Mn^{2+}. The pH rises as a result of reduction and anaerobic reactions that consume H^+ and cause negatively

charged species, such as hydroxyl ions (OH^-), to predominate in the soil solution (Frohne et al., 2011). Lima et al. (2026) observed that soil pH increased from 4.5 to 6.0 following a 65-day flooding period in rice-field management experiments in southern Brazil.

It was also observed that the most pronounced and sustained increase in pH relative to the control occurred with corncob biochar, consistent with its high calcium carbonate content and liming capacity. The rice biochar treatment also elevated pH relative to the control, consistent with the alkaline nature of rice biochar (e.g., Shen et al., 2019; Shi et al., 2019). In contrast, the compost treatment tended to buffer pH at slightly lower values than corncob biochar and rice biochar, reflecting the competing effects of organic acid production during decomposition. Eh trends were broadly similar across treatments, although the amended soils generally exhibited slightly less negative Eh values, suggesting that the amendments modulated the intensity of reducing conditions.

3.3.2 Iron (Fe) and Manganese (Mn) Dynamics

The reductive dissolution of iron and manganese oxides is a central process governing the mobilization of PTEs under flooded conditions. We observed that both Fe and Mn concentrations in the soil solution increased markedly following the onset of flooding (Fig. 3). They then reached peak values at intermediate sampling time points before stabilizing or declining. Reducing conditions were sustained, and secondary phases began to precipitate. Manganese peaked earlier in the incubation than Fe across all treatments, confirming the greater sensitivity of manganese oxides to redox conditions compared with iron oxides (Maguffin et al., 2020). This observation also indicates that Mn dissolution during the anaerobic phase was faster than that of Fe. Maguffin et al. (2020) made similar observations in their study on the influence of manganese abundance on Fe and As solubility in rice paddy soils. They observed that Mn oxides were proportionally about 20-fold more dissolved than Fe oxides. The compost treatment stimulated Mn reduction during the early incubation phase, possibly because of enhanced microbial respiration from labile organic substrates in the compost. This may also have led to faster oxygen and nitrate depletion during the onset of Mn-reducing conditions.

In the control, peak dissolved Fe concentrations were considerably higher than in the amended treatments. This suggests that the capacity of Fe to hold and stabilize contaminants against their

release is reduced in flooded ecosystems that are left without protection (e.g., soil amendments or vegetation). In such settings, Fe dissolution can occur readily, and PTEs that are precipitated, co-precipitated, or adsorbed onto surfaces can be released. Corncob biochar suppressed the reductive dissolution of Fe-bearing minerals, possibly by raising pH, which stabilizes Fe(III) oxides at higher Eh, or by enhancing sorption capacity. Thus, the addition of soil amendments offers some stability to Fe and Mn and consequently enhances their sequestration capacity. In this context, Mensah (2024) observed that the addition of manure to iron oxide enabled ryegrass to increase its phytostabilization potential for metals. Consequently, phytostabilization of Co, Hg, Mo, and Ni by ryegrass reduced multi-metal environmental concerns and associated human health threats.

3.4 Flood induced changes on the content of element-to-iron ratios

The control provides the reference trajectory against which each amendment should be evaluated. Relative to the control, rice biochar most clearly altered Cu, Cd, As and Pb relationships: Cu/Fe increased, while Cd/Fe, As/Fe and Pb/Fe decreased over time. This mixed response demonstrates that Rice Biochar cannot be characterized as uniformly immobilizing or mobilizing all PTEs. Compost reduced the relative As/Fe and Pb/Fe trajectories while increasing Cu/Fe and Cd/Fe. This is consistent with the dual role of compost-derived organic matter documented in the literature: organic ligands can bind metals strongly, but soluble organic complexes may also enhance transport. Corncob Biochar produced very high overall As/Fe and Zn/Fe ratios, but the temporal As/Fe trajectory was strongly negative. This distinction is important: a high overall treatment mean does not necessarily mean that the ratio increased during the experiment. It may reflect an initially high ratio followed by a decline. Manure produced high overall As/Fe and Pb/Fe values, together with decreasing As/Fe and Pb/Fe trajectories. This suggests that the amendment changed the relative element–Fe relationship substantially. Manure and compost should not be assumed equivalent because their organic matter composition, mineral content, pH and dissolved organic matter chemistry can differ considerably. The broader literature confirms that amendment composition and soil conditions govern immobilization efficiency (Palansooriya et al., 2020; Gao et al., 2023).

3.5 Flood-Induced Changes in Soil PTEs with Time and Amendment Addition

3.5.1 Copper (Cu), Cadmium (Cd), Zinc (Zn), and Lead (Pb)

Table 2 presents the number of the PTEs that were measured in our study and indicated that As, Cd, Hg, and Pb were particularly of concerns. These four elements exceeded the safe limits as per Ghana EPA, EU and WHO guidelines. Flooding led to significant temporal changes in the dissolved concentrations of Cu, Cd, Zn, and Pb in all treatments. In the control, the concentrations of these elements increased during the initial anaerobic phase as reductive dissolution of their associated carrier phases (principally Fe and Mn oxides) released them into solution. Cadmium and zinc, being more soluble across a wider range of pH conditions than lead and copper, exhibited particularly pronounced increases in dissolved concentrations during the early flooding period. Lead concentrations also increased, albeit less markedly, consistent with its tendency to form stable sulfide complexes under reducing conditions, which can limit its mobility even at low Eh values.

The amendment addition substantially modified these dynamics. Corncob biochar reduced dissolved Cd, Zn, and Pb concentrations most effectively, attributable to pH elevation, which promoted precipitation as hydroxides and carbonates and enhanced adsorption to newly formed calcite surfaces (Tack, 2010). Rice biochar also reduced PTE mobility, consistent with its well-established capacity to adsorb heavy metals through surface complexation, ion exchange, and electrostatic attraction (Mensah et al., 2025). The compost treatment showed intermediate effects, reflecting the competing influences of organic-ligand complexation, which may enhance PTE solubility, and pH buffering, which may suppress it (e.g., Lwin et al., 2018). Copper behaved somewhat differently from the other PTEs, with elevated dissolved concentrations persisting for long in the control because of its affinity for organic complexation and its release from organic matter decomposition during anaerobic incubation.

3.5.2 Arsenic (As)

Arsenic showed a distinctive mobilization pattern under flooding conditions, with dissolved As concentrations increasing markedly as Eh declined, consistent with reductive dissolution of As-bearing Fe(III) oxides and desorption of As(V) from oxide surfaces under reducing conditions. This is consistent with earlier observations in similar mine-contaminated tailings in Ghana (Mensah et al., 2022) and in As-contaminated coastal areas in the USA (Lemonte et al., 2017). In

the control treatment, As concentrations continued to rise throughout much of the incubation period, reflecting sustained reducing conditions and the progressive dissolution of As-rich iron phases. In contrast, the rice biochar and compost treatments significantly suppressed As mobilization, with the rice biochar treatment showing particularly strong As retention, likely because of its high surface area and the presence of iron-rich biochar surfaces capable of adsorbing arsenate and arsenite.

3.6 Changes in Soil PTEs in the Inundated Soils as Affected by pH

This study used within-treatment Spearman correlations to explore the relationships between soil pH and PTE concentrations across the five amendment treatments (Fig. 10). The results from Fig. 10 show that, overall, pH was a relatively weak and inconsistent predictor of PTE mobilization when assessed within individual treatment groups. The majority of predictor–PTE pairs retained statistically insignificant correlations. These findings suggest that although pH is a well-recognized master variable governing PTE solubility in soil chemistry, other controlling variables may override its predictive capacity within individual treatment groups. Only a few treatment–element combinations exhibited significant pH–PTE relationships.

Among these few treatment–element combinations, the corncob biochar treatment showed a significant negative correlation between pH and Cu ($\rho = -0.548$, $p = 0.034$). This suggests that as pH was elevated by biochar addition, Cu concentrations declined, consistent with increased adsorption of Cu onto mineral surfaces and precipitation at higher pH. Similarly, pH was negatively correlated with As in the manure treatment ($\rho = -0.530$, $p = 0.042$) and with Pb in the corncob biochar treatment ($\rho = -0.528$, $p = 0.043$), both reflecting pH-driven increases in anion adsorption and cation precipitation.

3.7 Changes in Soil PTEs in the Inundated Soils as Affected by Eh

Redox potential (Eh) was the most consistent predictor of PTE mobilization in the data. There was a significant negative correlation between Eh and multiple PTEs in the control treatments and several amended treatments (Fig. 8). As Eh declined, the concentrations of Cu, Cd, Zn, As, Pb, Fe, and Mn in the soil solution generally increased in the unamended control. This is consistent with reductive dissolution of their carrier phases. In a similar incubation study, Rinklebe et al. (2020)

found that the release of arsenic (As), cobalt (Co), nickel (Ni), selenium (Se), and zinc (Zn) increased under reducing acidic conditions during flooding. These releases were facilitated by the dissolution of iron (Fe)–manganese (Mn) oxides caused by redox reactions (Rinklebe et al., 2020). Metals and metalloids sequestered on the surfaces of Al, Mn, and Fe sesquioxides can be released under anaerobic conditions because these carrier phases become reduced. Reductive dissolution of organic matter can also lead to the release of bound PTEs. Similarly, dissolution of Mn- and Fe-oxyhydroxides associated with organic matter can affect PTE mobility. These processes ultimately cause the release of PTEs that were previously adsorbed on the outer or inner surfaces of Al/Fe/Mn phases and/or co-precipitated with organic matter on mineral surfaces.

Among the amended treatments, the compost treatment retained several significant Eh–PTE relationships, including Zn ($\rho = -0.681$, $p < 0.01$), As ($\rho = -0.893$, $p < 0.001$), Pb ($\rho = -0.927$, $p < 0.001$), Fe ($\rho = -0.599$, $p < 0.05$), and Mn ($\rho = -0.736$, $p < 0.01$). This suggests that, despite the addition of organic amendments, the compost-amended soil still exhibited strong redox control over PTE mobilization, potentially because compost stimulated microbial activity and accelerated the establishment of reducing conditions. The rice biochar treatment showed significant Eh–As ($\rho = -0.794$, $p < 0.001$), Eh–Fe ($\rho = -0.676$, $p < 0.01$), and Eh–Mn ($\rho = -0.646$, $p < 0.01$) relationships, indicating that biochar did not fully decouple As and Fe/Mn dynamics from redox control. In contrast, the corncob biochar and manure treatments showed no significant Eh–PTE correlations, suggesting that these amendments most effectively disrupted the direct Eh dependence of PTE mobilization.

3.8 Changes in Soil PTEs in the Inundated Soils as Affected by Temperature

The study shows that temperature was a moderately significant predictor of PTE mobilization in the selected treatment–element combinations. The results in Fig. 8 indicate that a significant positive correlation was identified, particularly in the control and rice biochar treatments. This suggests that higher temperatures may accelerate microbial metabolic rates, increase the rates of Fe and Mn reduction, and enhance the dissolution of mineral phases, thereby promoting PTE mobilization. In the control treatment, temperature was positively correlated with Cu ($\rho = 0.537$, $p < 0.05$), Cd ($\rho = 0.578$, $p < 0.05$), As ($\rho = 0.618$, $p < 0.05$), and Fe ($\rho = 0.627$, $p < 0.05$), consistent with temperature-enhanced reductive dissolution and microbial activity. These findings deepen

our understanding of how recent temperature increases associated with climate change can stimulate redox reactions and subsequently increase the rates at which PTEs are dissolved and released. In this regard, Yu et al. (2025) argued that climate change could alter rainfall patterns and increase temperatures, thereby stimulating microbial activity and influencing metal and contaminant release in aquatic environments.

The rice biochar treatment showed a broader range of significant temperature–PTE relationships, including Cu ($\rho = 0.575$, $p < 0.05$), Zn ($\rho = 0.643$, $p < 0.01$), Fe ($\rho = 0.651$, $p < 0.01$), and Mn ($\rho = 0.698$, $p < 0.01$). The observed pattern suggests that, in biochar-amended soil, the role of temperature is more pronounced in driving PTE mobilization than in the control. This may be because biochar stimulates specific microbial communities that are more sensitive to temperature fluctuations, or because biochar alters the activation-energy barriers for key geochemical reactions. In contrast, the corncob biochar, manure, and compost treatments showed few significant temperature–PTE correlations, suggesting that amendment application in these cases effectively buffered the soil chemical system against temperature-driven fluctuations in PTE availability.

3.9 Changes in the soil PTEs as Affected by the Addition of Fe and Mn

From Fig. 7, we can observe that the co-variation of Fe and Mn with PTEs reflects the role these redox-active metals play as carriers and vectors of trace-element mobility in flooded soils. From the model, we can observe that as Fe and Mn oxides undergo reductive dissolution during flooding, and thus associated PTEs such as Cu, Cd, Zn, Pb, and As are released into the soil solution. The model revealed a strong positive correlation between dissolved Fe and dissolved PTE concentrations, and the result reflects the dissolution-linked release of PTEs from Fe oxide surfaces.

Typically, manganese precedes iron in the onset of reduction but then displays a weaker PTE correlation overall. This is due to the Mn oxides, which, while highly reactive sorbents, constitute a smaller fraction of the total sorbed PTE inventory compared with Fe oxides in the studied soils. The observed divergence between Fe and Mn as PTE predictors across the amendment treatments shows that the two metals occupy partially distinct ecological niches in the redox cascade. Fe plays a more quantitatively important role in PTE cycling under the moderately to strongly anaerobic conditions achieved in the study. In treatments where Fe dissolution was suppressed, notably with

corncob biochar, PTE mobilization was correspondingly reduced, reinforcing the mechanistic link between Fe cycling and PTE availability.

3.10 Changes in element-to-iron ratios and PTE mobility in the inundated soils

A lower E/Fe ratio can be consistent with stronger relative association with Fe or lower elemental concentration relative to Fe; a higher E/Fe ratio can be consistent with weaker relative Fe association or increased elemental concentration. For cationic PTEs such as Cd, Cu, Zn and Pb, amendments can reduce mobility through cation exchange, electrostatic attraction, complexation and precipitation. Biochar reviews consistently identify these processes, while also noting that amendment properties and soil chemistry determine their effectiveness (Sachdeva et al., 2023; Mei & Wang, 2025). For As, Fe oxide chemistry is particularly important. Arsenate is commonly retained by Fe and Al oxides under oxidizing conditions, whereas changes in pH and redox can alter arsenic speciation and adsorption. Findings as per Mensah et al. (2022) demonstrated that As adsorption depends strongly on pH, speciation and competing ions, and that redox conditions determine the relative stability of arsenite and arsenate. For organic amendments, the direction of change is not uniform. Compost-derived dissolved organic matter can either immobilize metals through strong complexation or mobilize them by producing soluble metal–organic complexes. Recent evidence therefore supports a maturity-dependent interpretation: humified, high-molecular-weight DOM tends to favour sequestration, whereas labile DOM can enhance mobility (Liu et al., 2026).

4.0 Conclusions and future research

Flooding of abandoned gold-mine tailings triggered rapid, redox-driven mobilization of Cu, Cd, Zn, Pb, and As, and mediated principally by the reductive dissolution of Fe- and Mn-oxides. Eh was the dominant control on PTE release, followed by temperature, while pH exerted a weaker and more amendment-specific influence. Among the four organic amendments tested, corncob biochar was the most consistently effective at limiting PTE mobilization, primarily through liming-driven pH elevation and enhanced sorption, while rice biochar was particularly effective against arsenic release. These findings indicate that organic amendments, particularly corncob biochar, offer a practical, low-cost strategy for reducing PTE mobility in flood-prone and mine-

contaminated soils. Future work should extend monitoring beyond 85 days incorporate direct speciation of methylmercury, and evaluate amendment performance under field-scale, naturally fluctuating flood regimes.

Declarations

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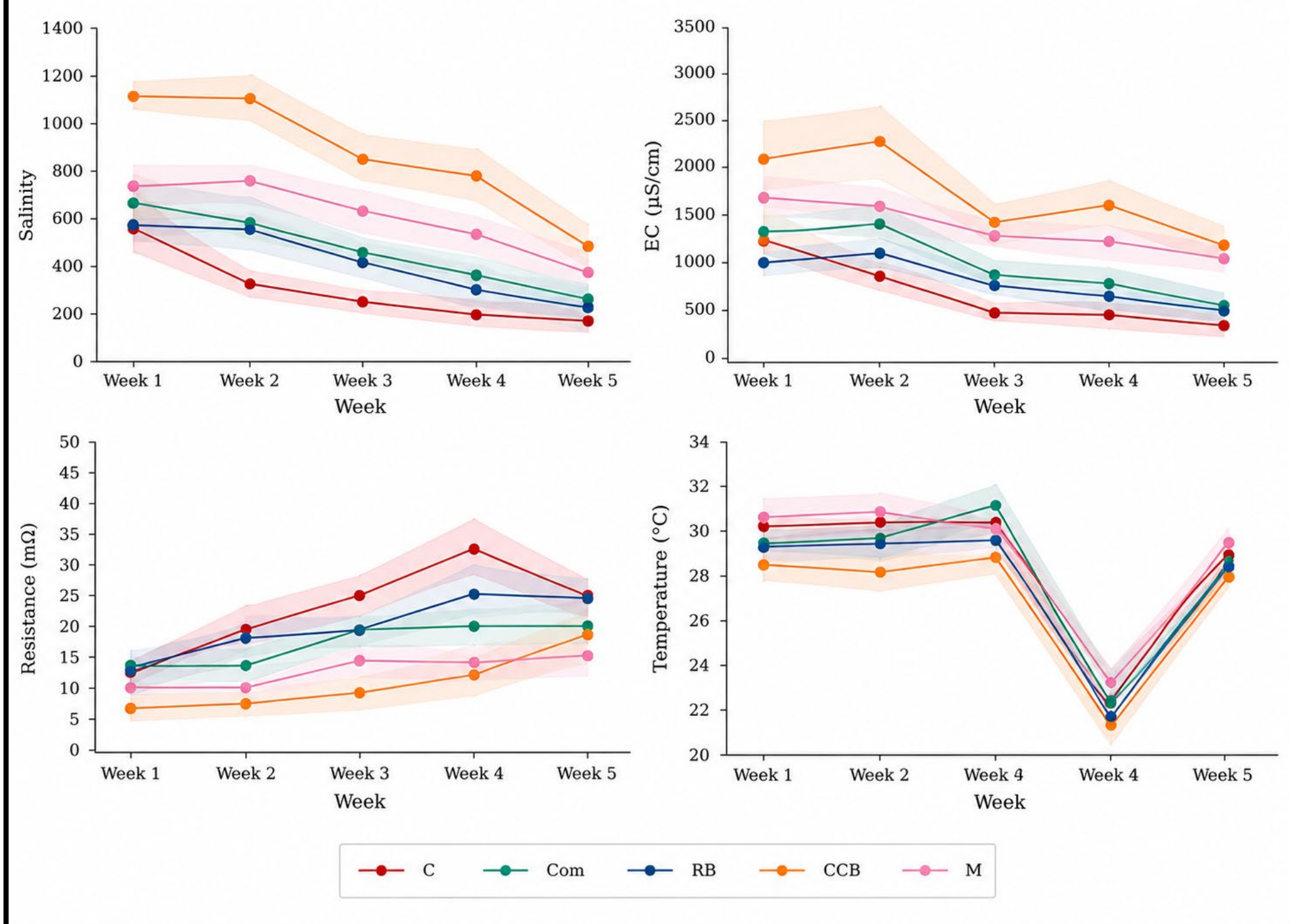

Salinity
1400
1200
1000
800
600
400
200
0
Week 1
Week 2
Week 3
Week 4
Week 5
Week
EC (µS/cm)
3500
3000
2500
2000
1500
1000
500
0
Week 1
Week 2
Week 3
Week 4
Week 5
Week
Resistance (mΩ)
50
45
40
35
30
25
20
15
10
5
0
Week 1
Week 2
Week 3
Week 4
Week 5
Week
Temperature (°C)
34
32
30
28
26
24
22
20
Week 1
Week 2
Week 4
Week 4
Week 5
Week
C
Com
RB
CCB
M

Fig. 1

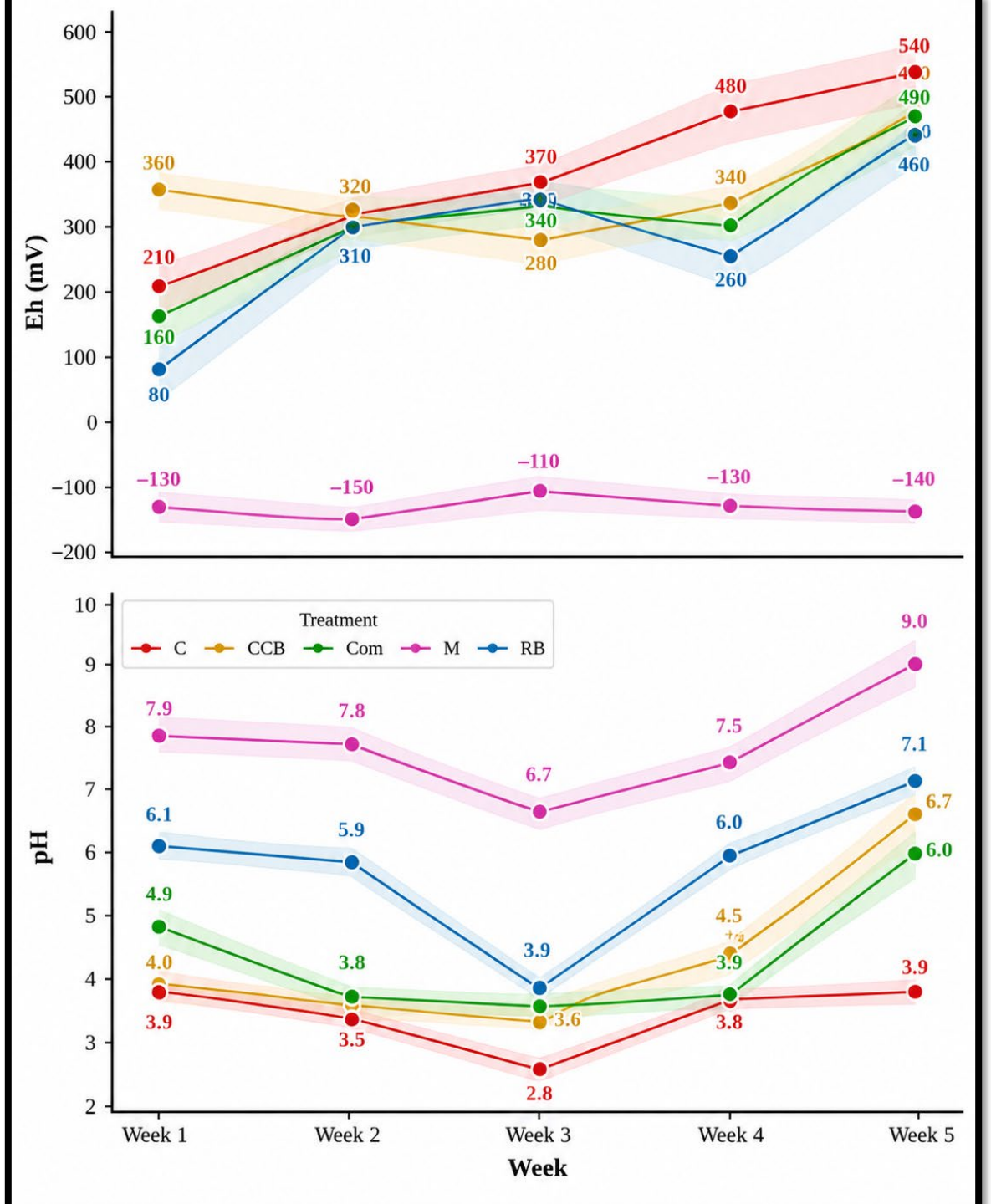
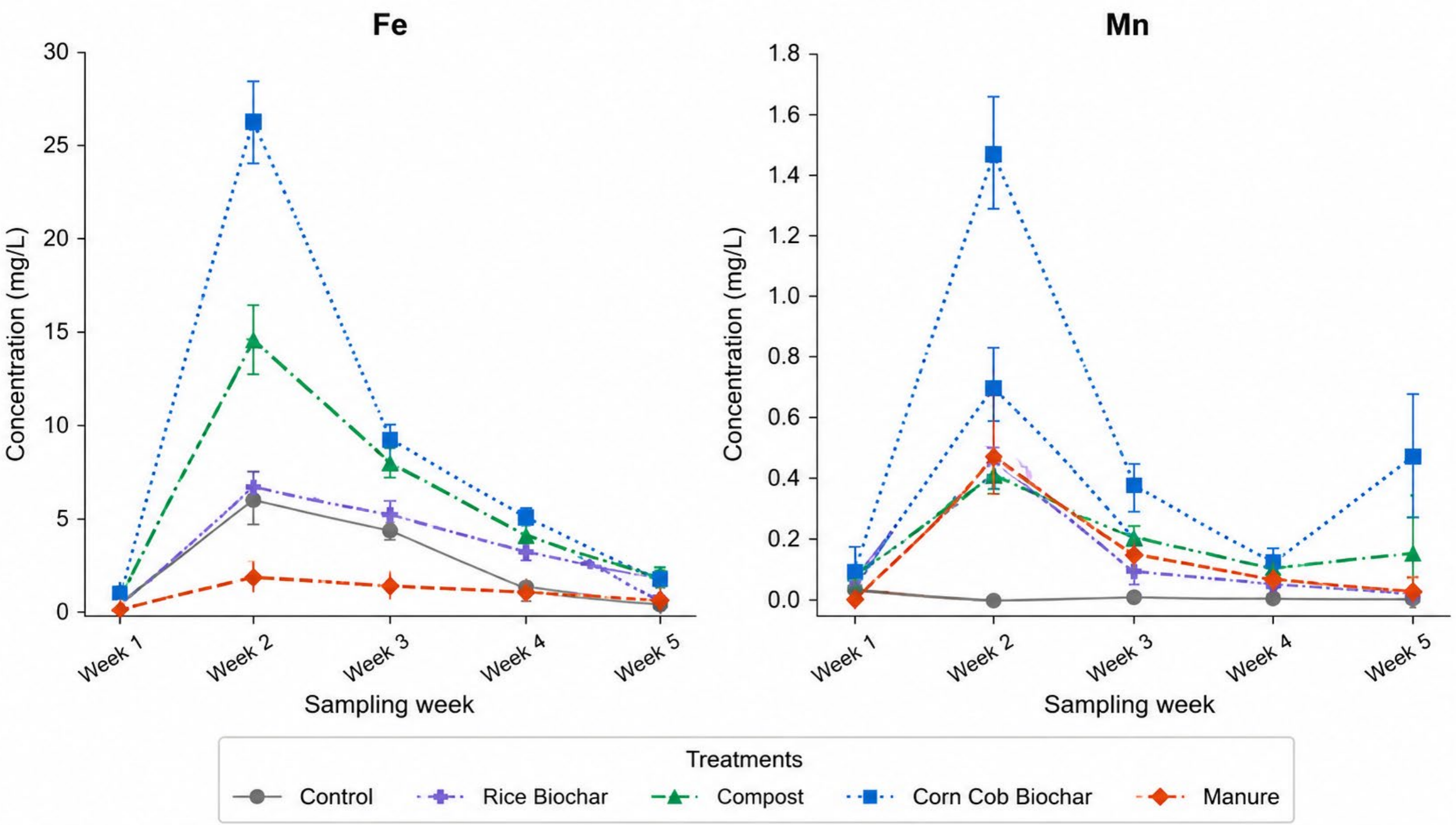
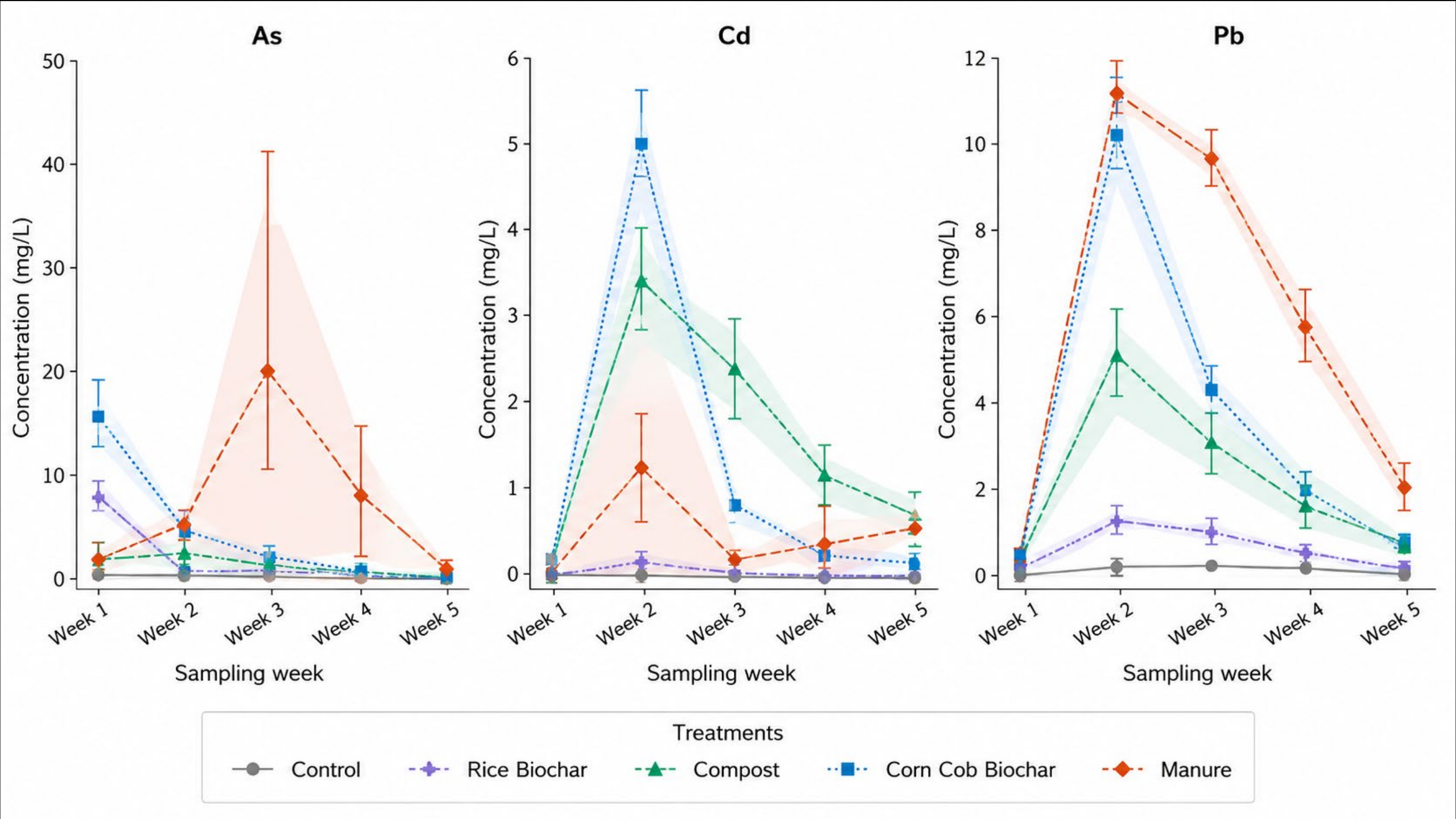

Eh (mV)
600
500
400
300
200
100
0
−100
−200
540
480
490
460
370
360
320
340
340
310
280
260
210
160
80
−130
−150
−110
−130
−140
pH
10
9
8
7
6
5
4
3
2
Treatment
C
CCB
Com
M
RB
9.0
7.9
7.8
7.5
7.1
6.7
6.1
5.9
6.0
6.7
6.0
4.9
4.5
4.0
3.8
3.9
3.9
3.9
3.6
3.5
3.8
2.8
Week 1
Week 2
Week 3
Week 4
Week 5
Week

Fig. 2


Fe
Mn
Concentration (mg/L)
Sampling week
Week 1
Week 2
Week 3
Week 4
Week 5
Treatments
Control
Rice Biochar
Compost
Corn Cob Biochar
Manure


As
Cd
Pb
Concentration (mg/L)
Sampling week
Week 1
Week 2
Week 3
Week 4
Week 5
Treatments
Control
Rice Biochar
Compost
Corn Cob Biochar
Manure

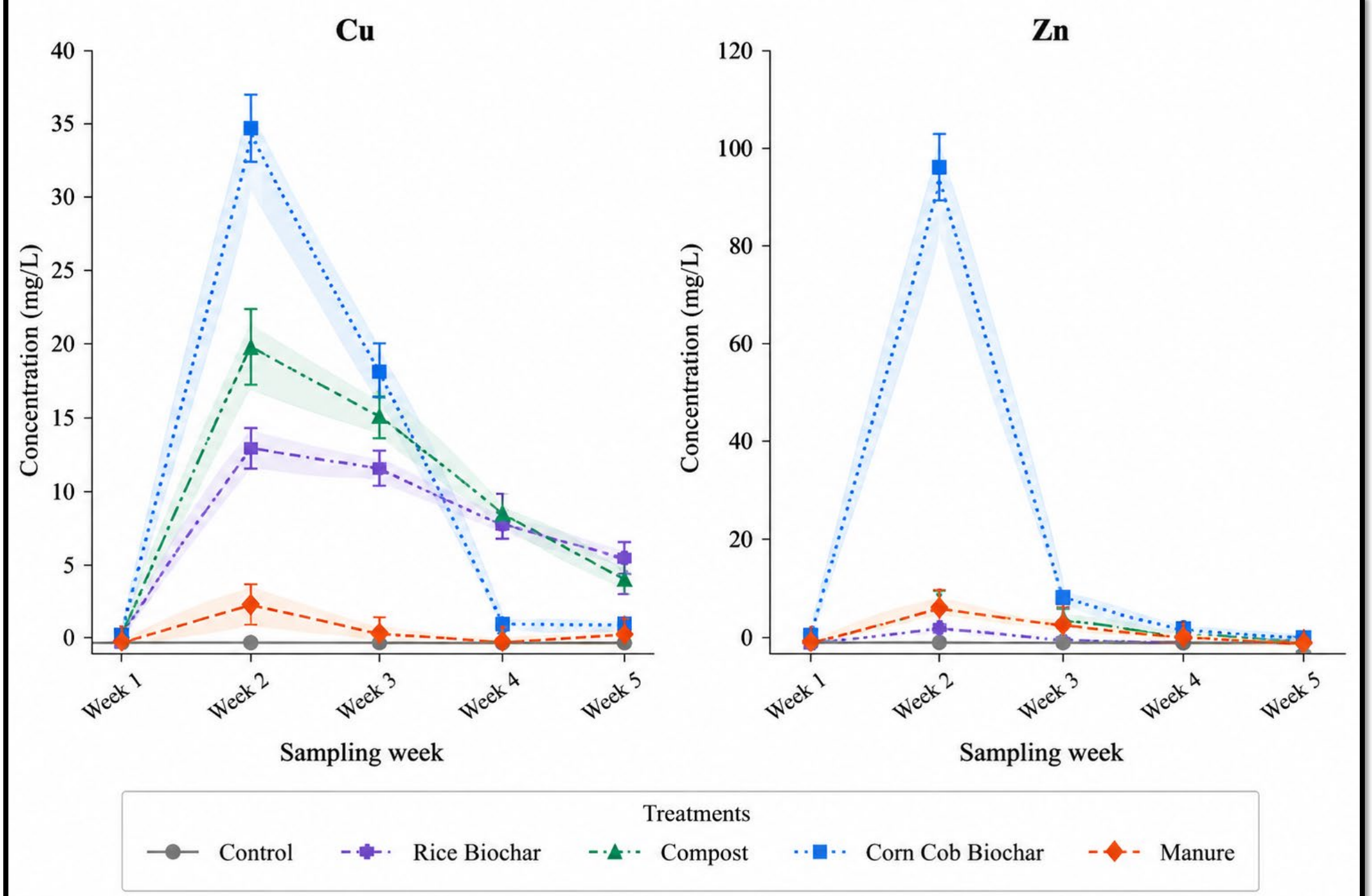

Cu
Zn
Concentration (mg/L)
Sampling week
Week 1
Week 2
Week 3
Week 4
Week 5
Treatments
Control
Rice Biochar
Compost
Corn Cob Biochar
Manure

Fig. 5

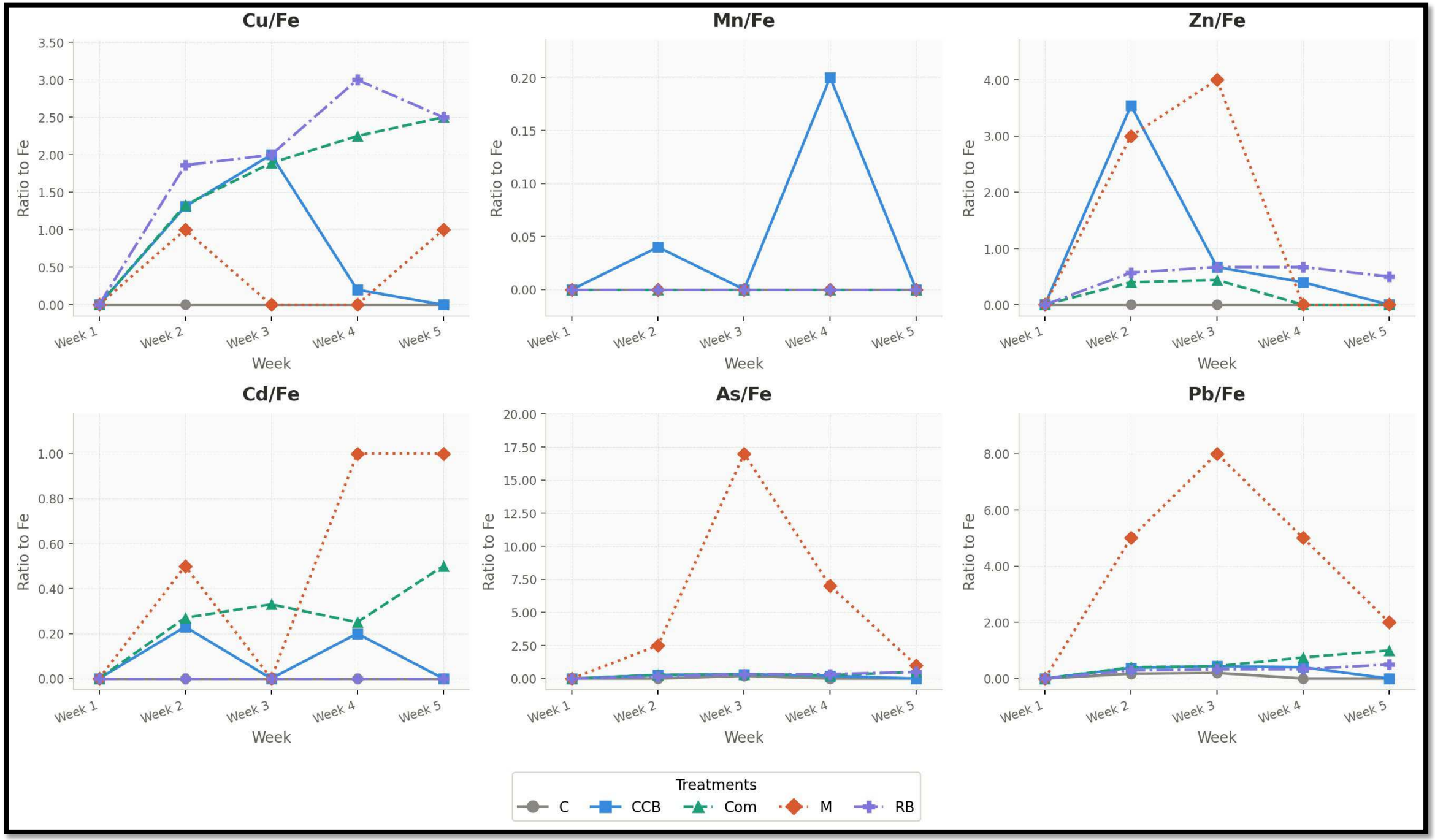
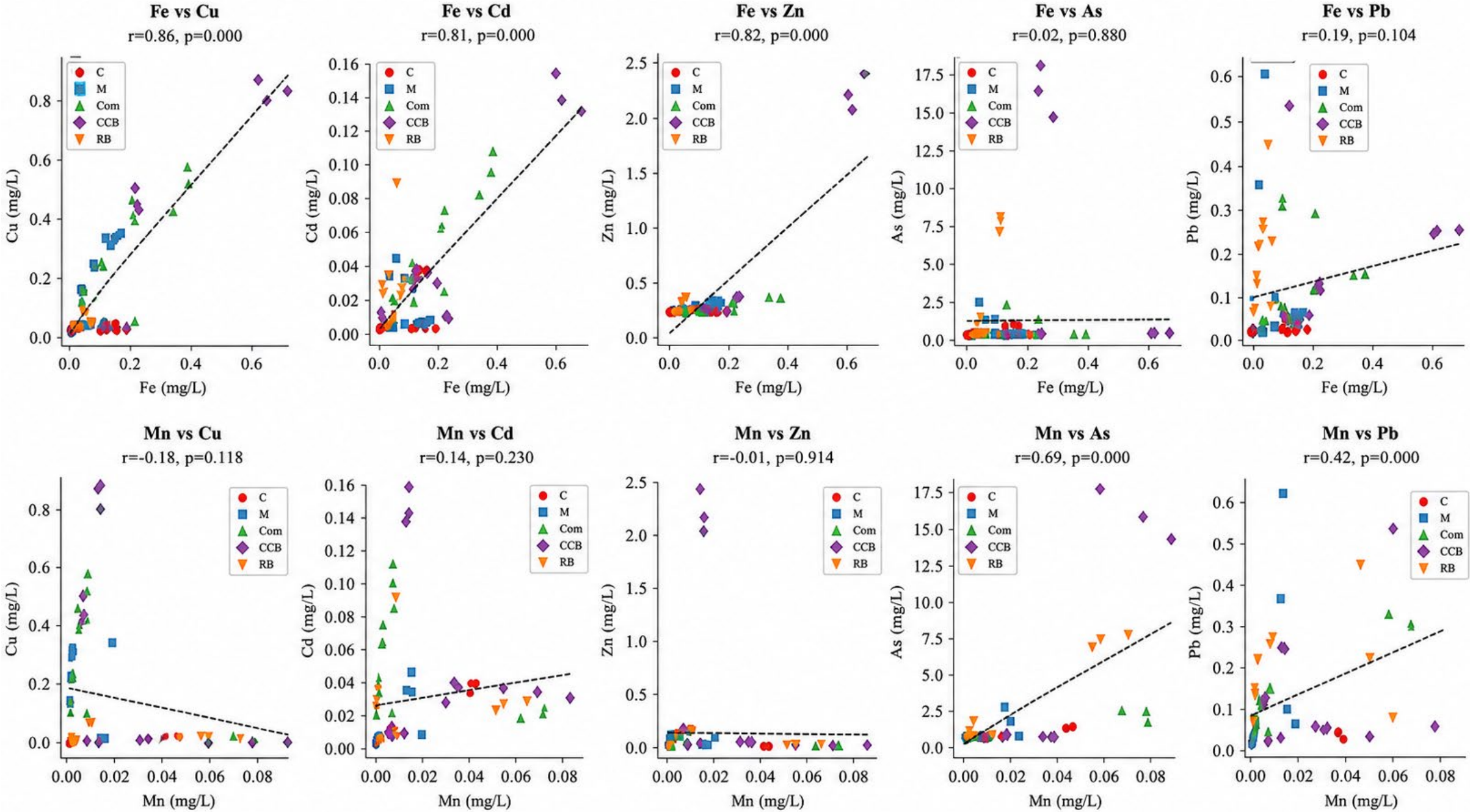
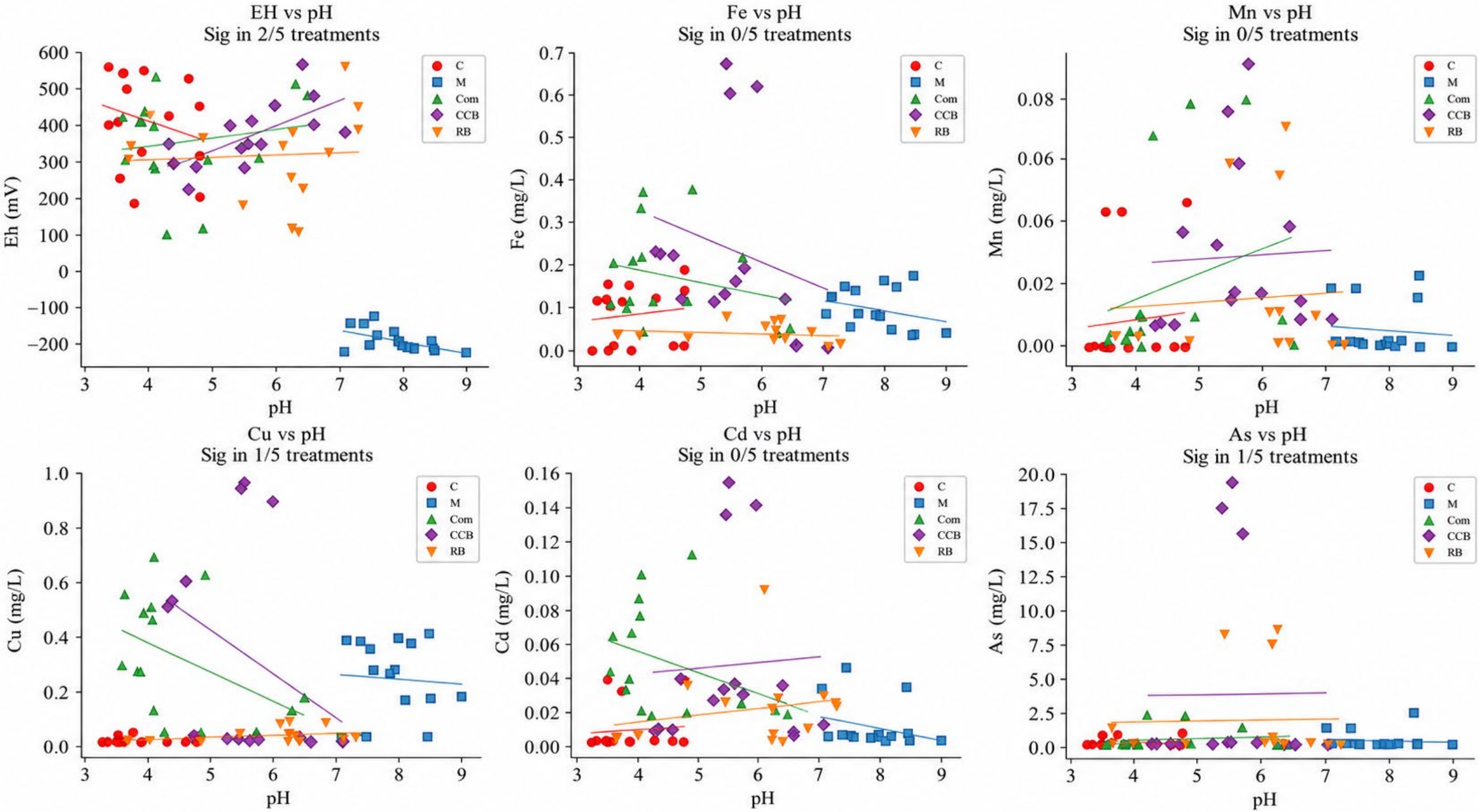

Cu/Fe
Mn/Fe
Zn/Fe
Cd/Fe
As/Fe
Pb/Fe
Ratio to Fe
Week
Week 1
Week 2
Week 3
Week 4
Week 5
Treatments
C
CCB
Com
M
RB

Fig. 6


Fe vs Cu
r=0.86, p=0.000
Fe vs Cd
r=0.81, p=0.000
Fe vs Zn
r=0.82, p=0.000
Fe vs As
r=0.02, p=0.880
Fe vs Pb
r=0.19, p=0.104
Mn vs Cu
r=-0.18, p=0.118
Mn vs Cd
r=0.14, p=0.230
Mn vs Zn
r=-0.01, p=0.914
Mn vs As
r=0.69, p=0.000
Mn vs Pb
r=0.42, p=0.000
C
M
Com
CCB
RB
Cu (mg/L)
Cd (mg/L)
Zn (mg/L)
As (mg/L)
Pb (mg/L)
Fe (mg/L)
Mn (mg/L)


EH vs pH
Sig in 2/5 treatments
Eh (mV)
pH
Fe vs pH
Sig in 0/5 treatments
Fe (mg/L)
pH
Mn vs pH
Sig in 0/5 treatments
Mn (mg/L)
pH
Cu vs pH
Sig in 1/5 treatments
Cu (mg/L)
pH
Cd vs pH
Sig in 0/5 treatments
Cd (mg/L)
pH
As vs pH
Sig in 1/5 treatments
As (mg/L)
pH
C
M
Com
CCB
RB

	Potentially Toxic Element (PTE)						
Predictor	**As**	**Cd**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
Eh	**3/5**	**1/5**	**1/5**	**3/5**	**3/5**	**2/5**	**2/5**
Temp	**1/5**	**1/5**	**2/5**	**2/5**	**2/5**	**1/5**	**1/5**
pH	**1/5**	**0/5**	**1/5**	**0/5**	**0/5**	**1/5**	**0/5**

Table 1: PTE contents in our water slurry compared against WHO, EU, and Ghana EPA limits

Element	Mean (mg/L)	WHO	EU	Ghana EPA	Status
Cu	0.04	2	2	2	✅ Safe
Mn	0.06	0.08	0.05	0.4	Slightly exceeds EU
Fe	0.2	0.3	0.3	0.3	✅ Safe
Zn	0.04	5	5	5.0*	✅ Safe
Cr	1.54	0.05	0.05	0.05	Exceeds all
Ni	0.12	0.07	0.02	0.02	Exceeds all
Cd	0.05	0.003	0.005	0.003	Exceeds all
As	0.899	0.01	0.01	0.01	Exceeds all
Hg	0.36	0.006	0.001	0.001	Exceeds all
Pb	0.041	0.01	0.01	0.01	Exceeds all

Table 1: General summary statistics (mean, standard deviation, minimum, median, and maximum values) during the 5 weeks of data collection

Variable	mean	std	min	median	max
Week	4.0	NA	2.0	4.0	6.0
Treatment	NA	NA	C	NA	RB
pH	5.564	1.617	3.26	5.47	9.0
EC (µs/cm)	1102.64	560.153	237.0	992.0	3043.0
EH (mV)	256.187	250.694	-228.0	332.0	568.0
Salt content (%)	0.051	0.025	0.02	0.05	0.13
Salinity	547.227	264.081	72.0	483.0	1307.0
Temp (◦C)	28.177	3.15	21.0	29.3	32.3
Res(mΩ)	16.639	6.726	6.397	15.218	38.35
Cu mg/L	0.151	0.215	0.002	0.028	0.88
Mn mg/L	0.017	0.024	0.0	0.005	0.094
Fe mg/L	0.127	0.136	0.001	0.104	0.684
Zn mg/L	0.135	0.447	0.0	0.018	2.508
Cd mg/L	0.027	0.034	0.002	0.017	0.156
As mg/L	1.141	3.442	0.004	0.04	18.15
Pb mg/L	0.111	0.128	0.01	0.056	0.63

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- APPENDIXA11.05.26.pptx