EFFECT OF DRY AND WET ALTERNATION ON THE TRANSFORMATION OF HEAVY METAL FORMS IN BIORETENTION SYSTEMS

by

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Urban stormwater runoff pollution has emerged as a pressing concern, with heavy metals emerging as a primary contaminant. This poses a significant threat to the ecological environment and human health. As an effective management measure, heavy bioretention systems are often subject to different degrees of wet and dry alternation, resulting in changes in the accumulation patterns of heavy metals in the system. In this study, a simulation system was constructed and experimental groups with varying dry and wet alternation cycles were established. We then proceeded to analyze the morphological transformations of Cd^{2+} and Pb^{2+} using the continuous extraction method, thereby unveiling the mechanism behind changes in the bioefficacy of heavy metals under dry and wet alternation. The results demonstrated that wet-dry alternation significantly altered the morphological distribution of heavy metals. Specifically, the exchangeable states of Cd^{2+} and Pb^{2+} decreased by 3%-7% and 2%-3%, respectively, during the drought period. However, these metals increased by 1%-4% after rewatering. The bioavailability of Cd and Pb exhibited an increase in response to short-term wet-dry alternation, while long-term drought resulted in a decrease. This study elucidates the regulatory principles that govern the alterations in the morphology and bioavailability of heavy metals under conditions of wet and dry alternation. This provides a theoretical basis for controlling heavy metal pollution in urban stormwater and optimizing bioretention systems.

Key words: *bioretention systems, wet/dry alternation, heavy metal morphology, bioeffectiveness*

Introduction

In recent years, China's urbanization has continued to advance, leading to an increase in the proportion of impervious surfaces in cities and a growing prominence of non-point source pollution caused by rainfall runoff [1]. Heavy metals are the primary pollutants in urban runoff and pose a threat to the ecological environment and human health due to their non-degradable and bioaccumulative properties [2]. Bioretention systems have been demon-

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strated to be an efficient measure for purifying stormwater, exhibiting remarkable removal efficiency for heavy metals in runoff through the interaction of plants, fillers, and microorganisms [3]. However, precipitation in natural environments is characterized by seasonality and randomness, which frequently result in wet-dry cycles for bioretention systems. These cycles alter the operational environment of the systems. The impact of wet-dry cycles on the transformation of heavy metal speciation and bioavailability in bioretention systems is not yet fully understood [4].

These wet-dry cycles have the potential to disrupt the internal physical, chemical, and biological processes of the systems, thereby affecting the behavior of heavy metals. Research has demonstrated that wet-dry cycles have the capacity to modify the physical and chemical properties of soil, thereby influencing processes such as the adsorption and desorption of heavy metals, as well as their precipitation and dissolution. These processes have the potential to induce alterations in the speciation of heavy metals and their bioavailability [5, 6]. However, the mechanisms by which wet-dry cycles affect the transformation of heavy metal speciation and bioavailability in the complex bioretention system remain unclear. It is imperative to comprehend these mechanisms to enhance our comprehension of the variations in the purification efficiency of bioretention systems for heavy metal pollution. This theoretical framework is expected to provide essential support for the scientific design and long-term stable operation of these systems. Furthermore, the practical implications of this framework are significant for improving the urban water environment and ensuring ecological security.

Experimental design and methods

Experimental design

The experiments were conducted in pots using morning glory as the research material. The pots were fabricated from polyvinyl chloride (PVC), had a diameter of 15 cm, and a height of 20 cm. They were filled with 2.5 kg of sandy soil collected from the riverbank. The background values of heavy metals in this soil were 0.036 mg/kg for cadmium (Cd) and 4.21 mg/kg for lead (Pb). The experiment comprised four treatments: a blank control, a single Cd treatment (0.3 mg/L), a single Pb treatment (3 mg/L), and a compound Cd+Pb treatment (0.3 mg/L + 3 mg/L). Each treatment was meticulously divided into five groups, with each group comprising three biological replicates. The simulation of drought stress was achieved by withholding water, thereby reducing the soil water content. The simulation of rainfall was conducted on days 7, 14, 21, 28, and 35 of the drought period, as illustrated in tab. 1. The simulated rainfall was prepared using cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$] and lead nitrate [$Pb(NO_3)_2$]. The rainfall intensity was 3 mm per hour, and the total volume of precipitation was 1 mm. For the experimental groups exhibiting severe symptoms of long-term drought, an additional 1 mm of heavy-metal-free simulated rainfall was supplied during the drought period.

Table 1. Simulated rainfall concentrations and drought settings

Treatment group	Blank control					Cd					Pb					Pb, Cd				
Concentration [mgL^{-1}]	0					0.3					3					0.3 + 3				
Drought [days]	7	14	21	28	35	7	14	21	28	35	7	14	21	28	35	7	14	21	28	35

Experimental method

The process of sample collection was executed in accordance with the drought and rewetting cycles. Immediately preceding and following each drought treatment, rhizosphere and non-rhizosphere soil samples were collected. Three days after the completion of the simulated rainfall rewatering process, corresponding samples were collected once more. The modified BCR method was employed to analyze the speciation of heavy metals in the soil and categorize them into exchangeable, reducible, oxidizable, and residual fractions. The bioavailability of heavy metals was calculated based on the speciation distribution. This calculation was used to systematically explore the transformation patterns of heavy metal speciation and changes in bioavailability during different drought periods and after rewatering.

Results and analysis

Effect of dry and wet alternation on the morphology of heavy metals style

The impact of drought stress on the speciation of Cd in both rhizosphere and non-rhizosphere soils was found to be significant, see figs. 1(a) and 1(b). During a brief (7-14 days) period of limited precipitation, the exchangeable fraction of Cd in rhizosphere soil exhibited a 3% increase. This phenomenon can be attributed to the incomplete transformation of ionic Cd following the application of the final heavy metal. In the case of a drought with a duration exceeding 21 days, the exchangeable and reducible fractions underwent a decline of 3%-7%, while the oxidizable fraction exhibited an increase of 3%-6%. This phenomenon is likely attributable to the augmented oxidative activity of Fe-Mn oxides, which were induced by the drought and promoted the decomposition of organic matter and its complexation with Cd to form oxidizable species. In the context of prolonged drought (duration $\geq$ 28 days), the residual fraction exhibited a modest increase, a phenomenon that may be attributable to the evolution of soil heavy metal distribution towards a stable state [7].

Following the rewatering process, the reducible fraction of Cd in the rhizosphere soil exhibited a decline, which may be attributable to the active uptake of Cd and Pb by plant roots via transport proteins, thereby facilitating recovery growth. Upon entering the roots, these heavy metals might be chelated or compartmentalized, thereby reducing the reducible fraction in the rhizosphere soil [8]. The exchangeable fraction exhibited a decrease ranging from 1% to 4%, indicating an enhancement in ion exchange reactions and dissolution processes. This phenomenon was attributed to elevated soil moisture levels, which promoted the release of exchangeable and carbonate-bound heavy metal ions into the soil solution. It is noteworthy that the oxidizable fraction exhibited significant changes exclusively during the initial phase of drought, with no substantial variations observed subsequently. This finding contradicts previous research and is attributed to the impact of drought-rewatering on the stability of soil organic matter, which causes fluctuations in the oxidisable fraction [9]. In non-rhizosphere soil, the speciation of cadmium followed a trend that was consistent with the observations made in rhizosphere soil. However, in this instance, the exchangeable fraction accounted for a smaller proportion of the total, a phenomenon that can be attributed to the presence of rhizosphere metabolites that promote Cd activation [10].

In both rhizosphere and non-rhizosphere soils, Pb was predominantly found in the residual (77%-84%) and oxidisable fractions, figs. 1(c) and 1(d). Drought had a weaker effect on the speciation distribution of Pb than Cd. Drought caused a 2%-3% decrease in the exchangeable fraction, which was associated with elevated soil pH inhibiting Pb ion desorption [11].

The reducible fraction increased due to enhanced soil aeration under drought conditions, which promoted Fe-Mn oxide oxidation. Meanwhile, the oxidisable fraction increased due to the strengthened complexation capacity of organic matter under neutral to alkaline conditions. After rewatering, soil water saturation caused a decline in pH, leading to an increase in exchangeable Pb due to enhanced ion exchange. The reducible fraction decreased due to the reductive dissolution of Fe-Mn oxides, with the released Pb possibly transforming into the exchangeable form [12]. In non-rhizosphere soil, the residual and oxidisable fractions of Pb were insensitive to wet-dry alternation. However, the proportions of the exchangeable and reducible fractions in rhizosphere soil remained higher than in non-rhizosphere soil, which confirms the regulatory role of root activities in Pb speciation.

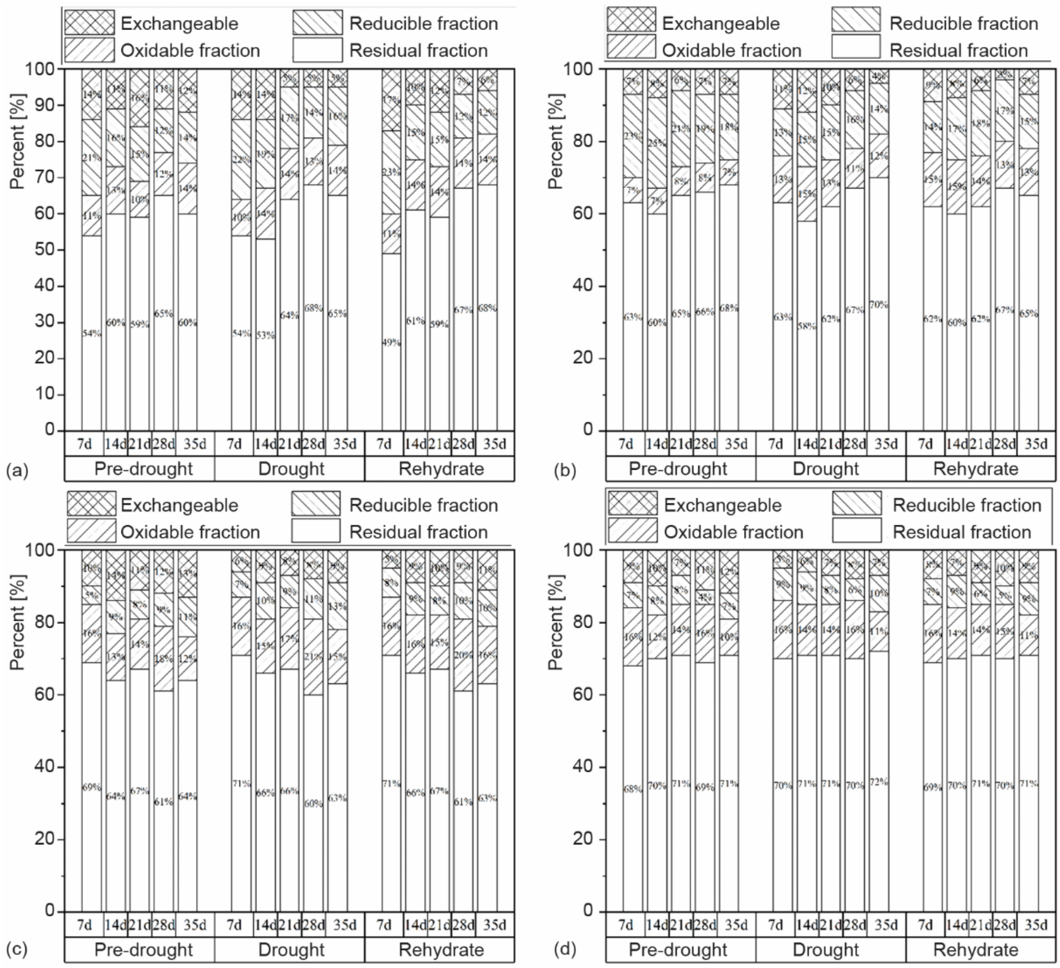

Figure 1. Morphological distribution of inter- and non-inter-root heavy metals Cd and Pb under different wet and dry alternations; (a) morphological distribution of inter-root heavy metals in Cd treatment group, (b) morphological distribution of non-inter-root heavy metals in Cd treatment group, (c) morphological distribution of inter-root heavy metals in Pb treatment group, and (d) morphological distribution of non-inter-root heavy metals in Pb treatment group

During the drought-rewatering cycle, Cd speciation in the composite treatment exhibited marked discrepancies from the single-treatment group: the oxidisable fraction was lower than in the single Cd treatment, while the reducible fraction was higher, fig. 2. This is primarily due to the distinct competitive adsorption behavior between Pb^{2+} and Cd^{2+} in soil. In soils with high organic matter content in particular, Pb^{2+} demonstrates stronger competitive superiority over Cd^{2+} for adsorption sites. As the concentration of Pb^{2+} increases, it occupies the adsorption sites on soil particles and organic matter preferentially, thereby reducing the adsorption of Cd^{2+}. This results in Cd^{2+} migrating from an adsorbed state to active forms, such as the reducible fraction [13].

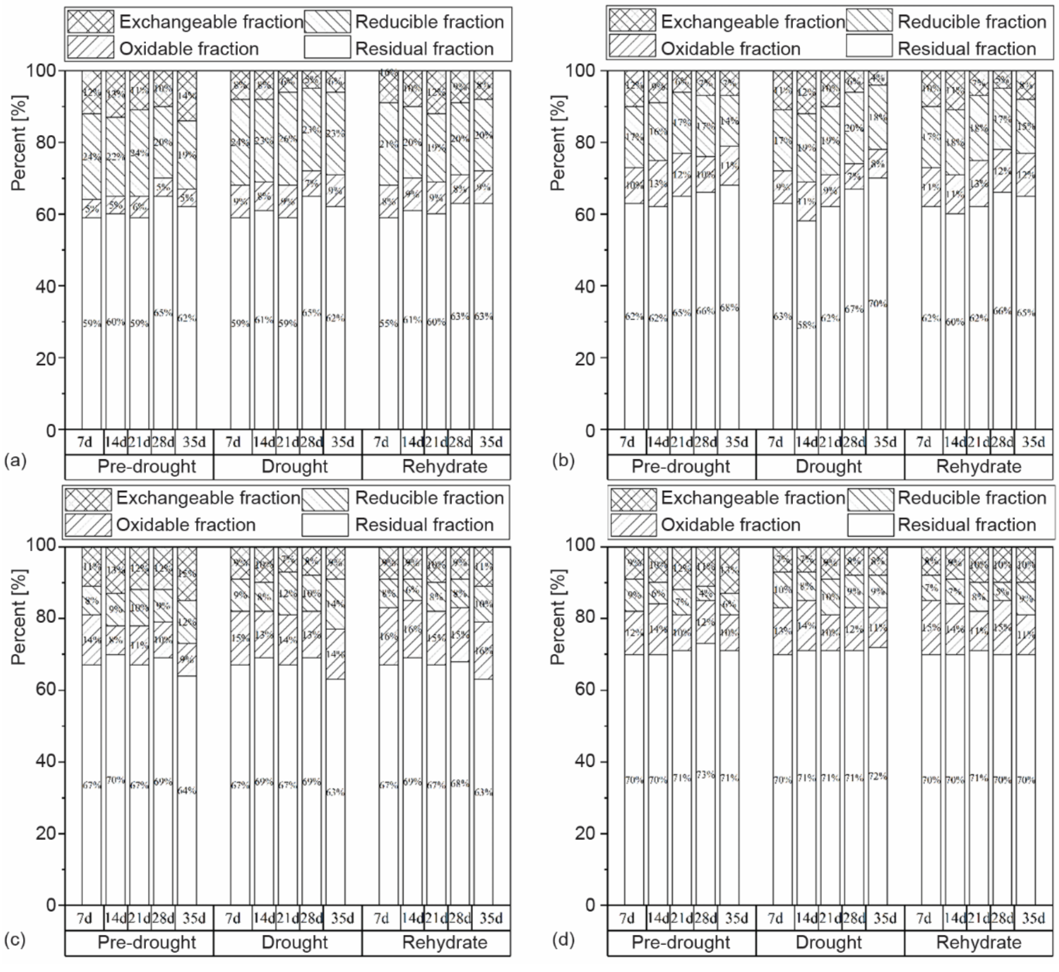

Figure 2. Morphological distribution of heavy metals in composite treatment groups; (a) morphological distribution of inter-root Cd heavy metals in composite treatment, (b) morphological distribution of non-inter-root Cd heavy metals in composite treatmen, (c) morphological distribution of inter-root Pb heavy metals in composite treatment, and (d) morphological distribution of non-inter-root Pb heavy metals in composite treatment

For Pb speciation, the composite treatment generally followed the same trend as the single treatment. However, the oxidisable fraction decreased and the exchangeable fraction increased in some treatment groups. Specifically, the presence of Cd increased the exchangeable Pb content due to competitive adsorption. Additionally, the interaction between Pb and Cd may promote speciation transformation. Pb tends to form precipitates with sulfides, whereas Cd preferentially binds to Fe-Mn oxides. These discrepancies exacerbate the complexity of heavy metal speciation under composite stress [14].

Effect of dry and wet alternation on the bioefficacy of heavy metals

Bioavailability reflects the fact that the forms of heavy metals readily taken up by plants and involved in biological interactions are primarily in exchangeable and reducible states. This study found that an increase in exchangeable state content resulted in a significant increase in the bioavailability of Cd^{2+} and Pb^{2+}. Specifically, in the group subjected to a 7 days drought treatment, the bioavailability of Cd^{2+} increased from 28% to 35% compared to the pre-alternation stage, while that of Pb^{2+} rose from 22% to 27%. This is due to wet-dry alternation promoting the decomposition of degradable components in dissolved organic matter, thereby altering its molecular composition and influencing the binding and release of heavy metals.

However, as wet-dry alternation continued, heavy metals gradually transformed into more stable forms, leading to a decrease in the bioavailability of both Cd^{2+} and Pb^{2+}. This phenomenon is analogous to the behavior of Cl^- in aggregated concretes [15]. After 28-35 days of alternation treatment, the bioavailability of Cd^{2+} decreased by 8%-15% and that of Pb^{2+} by 6%-12%. This indicates that prolonged drought drives the transformation of Cd^{2+} and Pb^{2+} from highly bioavailable forms to more stable ones that are difficult for organisms to absorb, significantly reducing their bioavailability. This process involves the complexation or precipitation of heavy metals with soil organic matter, carbonates or phosphates to form insoluble compounds that are less available for uptake by plants and other organisms in bioretention systems. These dynamic changes in bioavailability are closely linked to the transformations in the speciation of heavy metals under wet-dry alternation. This further confirms the importance of considering both the speciation of heavy metals and their bioavailability when evaluating the environmental behavior of heavy metals in bioretention systems.

Conclusions

This study systematically investigated the effect of wet-dry alternation on the morphological transformation and bioavailability of heavy metal markers in a bioretention system. It was determined that wet-dry cycles significantly altered the morphological distribution of cadmium, Cd^{2+}, and lead, Pb^{2+}. During the drought period (7-35 days), enhanced complexation of organic matter resulted in a decrease in the exchangeable fraction and an increase in the oxidisable fraction of Cd^{2+} and Pb^{2+}. The restoration of the exchangeable fraction is achieved through enhanced ion exchange, while fluctuations in organic matter stability result in a concurrent decrease in the oxidizable fraction. Bioavailability is known to increase under conditions of short-term drought and gradually decrease during prolonged drought (> 21 days), as the metals are converted into stable residual forms.

Secondly, the Cd+Pb composite treatment exhibited different dynamics in the transformation of heavy metals compared to single treatments. Competitive adsorption between Pb^{2+} and Cd^{2+} has been demonstrated to promote the transport of Cd^{2+} to the reducible fraction, thereby exacerbating fluctuations in bioavailability.

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