

Stability of Lead Immobilization by Hydroxyapatite and Biochar in a Typical Brown Soil (Haplic Cambisol)

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Abstract

Soil contamination with lead remains an acute geoecological problem, necessitating effective in situ immobilization methods. This study aimed to evaluate the efficiency and temporal stability of biochar, hydroxyapatite (HAP), and their combination in reducing lead mobility in a typical brown soil (Haplic Cambisol, southern Primorsky Krai). The intrinsic sorption capacity of the soil for lead ions was found to be 24.3–25.0 mg/g; according to X-ray diffraction (XRD) analysis, the binding occurs predominantly via reversible mechanisms on clay minerals, without the formation of distinct Pb-containing phases. Hydroxyapatite exhibited a sorption capacity ($q_m = 1095$ mg/g) nearly 45 times higher than that of the soil. In the incubation experiment, HAP ensured a stable, non-diminishing over time reduction of lead mobility at moderate and high contamination levels—by 18.5–59.1% in the water-soluble fraction and by 8.6–46.4% in the exchangeable lead fraction. This reduction was achieved without significant alkalization of the medium (pH shift of + 0.06 to + 0.17), which enables the direct application of HAP in acidic soils without liming. Low-ash biochar demonstrated a temporally unstable effect comparable in magnitude to the intrinsic capacity of the soil. In the model binary system, it precluded an unambiguous assessment of synergism with HAP due to the substantially more rapid lead binding by hydroxyapatite. The obtained results suggest that hydroxyapatite serves as an effective and stable long-term barrier against mobile forms of lead in acidic Haplic Cambisols, whereas the role of biochar in such a system is limited to the improvement of soil structure.

1. Introduction

Lead contamination of soil ecosystems remains one of the most acute problems in global and regional geoecology (Ponizovskii & Mironenko, 2001; Sipos et al., 2005). Lead is considered a priority anthropogenic pollutant due to its high toxicity and tendency for irreversible accumulation in upper humus-accumulative soil horizons (Ponizovskii & Mironenko, 2001; Sipos et al., 2005; Diagboya et al., 2015). This problem becomes particularly critical in urbanized territories and areas influenced by the mining and metallurgical industries, including the southern regions of Primorsky Krai.

An excess of free Pb^{2+} ions in the soil solution induces pronounced phytotoxic stress: inhibition of chlorophyll synthesis enzymes, disruption of photosynthesis, generation of reactive oxygen species, and damage to cellular membrane structures (Zulfiqar et al., 2019; Rahman et al., 2024; Gupta et al., 2024). The uptake of lead by plants from the soil solution leads to its inevitable incorporation into food chains. Subsequent bioaccumulation of the heavy metal at higher trophic levels poses a direct threat to human and animal health. This dictates the necessity of adhering to strict sanitary and hygienic standards: in the Russian Federation, the maximum permissible concentration (MPC) of mobile lead forms extracted with an ammonium acetate buffer solution (pH 4.8) is limited to a threshold of 6.0 mg/kg. For acid-soluble forms of this element in soils, tentative permissible concentrations (TPC) have been established, the values of which depend on the soil particle size distribution and pH (SanPiN 1.2.3685-21, 2021).

Mandatory environmental monitoring is conducted annually in various regions of Russia, during which the content of pollutants in the soil is assessed and their concentrations are compared with MPC and TPC values. To achieve safe lead concentrations in the soil, various in situ immobilization methods are traditionally employed; however, most of them have limitations. For instance, liming is effective at the initial stage, but the created alkaline barrier is reversible over time and carries the risk of lead remobilization by dissolved organic carbon at $\text{pH} > 6.5$ (Sipos et al., 2005; Saleh et al., 2026). Unmodified organic amendments bind the metal predominantly via the ion exchange mechanism, which is reversible and susceptible to the physicochemical aging of the material (Long et al., 2024). Mineral sorbents, in turn, may demonstrate a decrease in selectivity for the Pb^{2+} ion in the presence of competing Ca^{2+} and Mg^{2+} cations due to the predominant ion-exchange nature of retention and pronounced sensitivity to ionic strength fluctuations and the complex composition of the actual soil solution (Liu et al., 2019; Velarde et al., 2023). It is also necessary to consider the high heterogeneity of soil conditions, including the composition and properties of organic matter (primarily the content of humic acids) and the composition of soil-forming rocks, which may contain elements such as Ca and Fe, potentially influencing lead sorption by soils.

These drawbacks dictate the need to develop multicomponent sorbents (composites) where the influence of soil conditions will be minimal. One of the actively used sorbents for heavy metals in soils in recent times is biochar. Biochar can act as a basic structure-forming matrix [12, 13]. Its primary immobilization capacity is provided by a combination of mechanisms: mineral precipitation, complexation on oxygen-containing groups, ion exchange with cations of the ash fraction, cation- π interactions, and electrostatic attraction (Lu et al., 2012; Zhou et al., 2022). At the same time, the actual carbon matrix accounts for less than 1% of the total Pb^{2+} capacity, while more than 99% is controlled by precipitation on inorganic ash (Xu et al., 2014; Han et al., 2024). The ash content of biochar is determined mainly by the type of feedstock rather than the pyrolysis temperature. Wood consistently yields the lowest ash content, typically less than 10%, whereas manure- and algae-derived biochars contain 40–50% ash (Mukome et al., 2013; Tomczyk et al., 2020). It is the inorganic ash components that make the primary contribution to Pb binding on biochar, whereas the isolated carbon matrix binds Pb extremely weakly (Han et al., 2024). Therefore, low-ash wood biochars have a systemic limitation in sorption capacity.

The problem is exacerbated by the fact that the physicochemical properties of biochar change over time under the influence of soil and climatic factors (field aging) (Wang et al., 2020; Long et al., 2024). Although in certain soil types long-term aging can intensify Pb^{2+} fixation due to matrix oxidation (Chen et al., 2024), in low-ash systems this process is often accompanied by the leaching of ash alkalinity, a decrease in local surface pH, and the risk of the formation of colloidal particles that artificially overestimate metal lability (Cui et al., 2024; Tiberg et al., 2025). Consequently, pure biochar is incapable of functioning as a universal, long-term geochemical barrier, playing predominantly an agronomic role (as a structural modifier and water-regulating agent) rather than serving as an independent capacity reserve.

Considering these limitations, ensuring the irreversible fixation of lead requires the introduction of a specific component capable of converting the labile metal into thermodynamically stable phases. The most promising agent for this purpose is hydroxyapatite (HAP), which initiates the crystallization of secondary minerals of the pyromorphite group ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$ and $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) (Ma et al., 1994; Xu & Schwartz, 1994; Mavropoulos et al., 2002). The reaction proceeds through the dissolution of apatite and the release of phosphate ions, forming a continuous solid solution series (Motyka et al., 2015; Zhu et al., 2016; Guan et al., 2018). At the same time, the use of HAP as a standalone ameliorant is also associated with its own independent limitations. During the reaction, newly formed lead phosphate precipitates rapidly coat the surface of HAP particles, blocking access to the remaining active sites, which leads to diffusion limitations and a decrease in the overall efficiency of the sorbent over time (Zhang & Ryan, 1999; Li et al., 2017). Furthermore, in highly acidic soils ($\text{pH} \leq 5.0$), excessive dissolution releases Ca^{2+} , which is capable of desorbing lead from the soil exchange complex before the crystallization of pyromorphite occurs (Ponizovsky & Tsadilas, 2004), whereas in neutral media, dissolution is conversely kinetically delayed (Zhang & Ryan, 1999).

Thus, both ameliorants possess significant but fundamentally different limitations. The combined application of these components can be motivated not by the expectation of their chemical synergism, but by the necessity of functional separation. Since low-ash biochar binds Pb^{2+} primarily through reversible ion exchange, it cannot serve as a reliable long-term barrier. Among other things, the gradual degradation of biochar in soils due to the activity of the soil microbiome must also be considered. The application of HAP, on the contrary, provides irreversible fixation and exceeds the sorption capacity of biochar by approximately two orders of magnitude (Chen et al., 2007; Zhou et al., 2022; Novikova et al., 2025). Simultaneous application aims to separate functions: biochar acts as a soil structure modifier, while HAP assumes the role of the primary long-term binding reserve, even accounting for the risks of its own gradual passivation.

The design of the present study is based on the previously investigated properties of the utilized ameliorants. It has been shown that the intrinsic sorption capacity of birch biochar is comparable to the retention potential of the soil itself (Egorin et al., 2025), whereas the efficiency of pure HAP under actual soil conditions reaches an optimum at doses of 1–2% (Novikova et al., 2025).

Based on these data, a fixed dose of biochar (1%) was applied in the present study. This approach limits the contribution of biochar to the overall sorption capacity of the system, assigning the function of the primary chemical barrier to HAP, and the function of a structural soil matrix to biochar. The proposed experimental design is aimed at an overall assessment of the nature of the ameliorants' interaction (additivity of contributions or the presence of a synergistic effect).

The humus horizon of a typical brown soil (Haplic Cambisol) (Deckers et al., 1998) was selected as the experimental model. This soil lacks a carbonate buffer. It is characterized by an acidic medium reaction ($\text{pH} 4.83$) and a high organic carbon content (8.24%). In general, these soils can be characterized as acidic heavy loam soils. The properties of individual ameliorants have already been quite

comprehensively described in the literature. However, their combined effect on lead mobility at various contamination levels within the same soil remains poorly investigated. In addition, the temporal stability of this effect and the specific mechanisms of pollutant fixation at the mineralogical level have been insufficiently studied.

Based on the identified gaps, the aim of the present work is to evaluate the efficiency and temporal stability of biochar, hydroxyapatite, and their combination in reducing lead mobility in a typical brown soil (Haplic Cambisol).

2. Experimental Section

2.1. Study Objects and Basic Materials

The following chemically pure (c.p.) grade chemical reagents were used in this study: lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), potassium nitrate (KNO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), nitric acid (HNO_3), and potassium hydroxide (KOH), manufactured by NevaReaktiv LLC (Russia).

A typical brown soil (Haplic Cambisol, IUSS WRB) (Deckers et al., 1998) served as the object of study. A soil profile was established in the area of Russky Island (southern part of Primorsky Krai; 43.02526079° N, 131.88571221° E) under a broadleaf-forb forest on granite eluvium. Samples were collected from the humus-accumulative AY horizon (0–23 cm) in accordance with GOST 28168-89 (1990); the morphological description was conducted according to GOST 17.4.2.03-86 (1987). The soil particle size distribution was determined by the pipette method according to Kachinsky (1958), which is methodologically analogous to ISO 11277 (2020). The obtained fractions were subsequently converted to the USDA textural classification system (Sand, Silt, Clay) using logarithmic interpolation of the cumulative curve.

Acid-base properties were measured potentiometrically according to GOST 26423-85 (1986). Organic carbon was determined by the Tyurin method (an analogue of the Walkley–Black method, Walkley & Black, 1934); total nitrogen was determined using the Kjeldahl method (equivalent to ISO 11261, 1995); available phosphorus was measured spectrophotometrically; and exchangeable potassium was analyzed by flame photometry (Mehlich, 1984) (using a PFA-378 flame photometer, UNICO-SYS LLC, St. Petersburg, Russia). The total Pb content was indicatively assessed by the pXRF method (using a SciAps X-555 portable X-ray fluorescence analyzer, SciAps Inc., USA).

Synthetic hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and slow-pyrolysis birch wood biochar (500°C, 0.3–0.5 mm fraction) were used as ameliorants. The baseline sorption characteristics of this biochar for Pb^{2+} have been detailed by the authors previously ($q_m = 14.21$ mg/g according to the Langmuir model, ion-exchange mechanism, two-stage kinetics, $S_{\text{BET}} = 73.25$ m²/g) (Egorin et al., 2025).

2.2. Evaluation of Sorption Capacity (Isotherms, Kinetics, and Model Binary System)

The sorption capacity of the soil was evaluated using the isotherm method under static conditions (following the general principles of OECD 106 (OECD, 2000)) at liquid-to-solid (LS) ratios of 1000 and 50 mL/g in a 0.01 M KNO₃ background solution (initial pH 5.0). The range of initial Pb²⁺ concentrations was from 10 to 600 mg/L, with an exposure duration of at least 48 hours. The sorption kinetics by the soil were studied at an LS ratio of 1000 mL/g and C₀ = 40 mg/L.

Similarly, the isotherm and kinetics of Pb²⁺ sorption by pure HAP were investigated under static conditions. For the isotherm, the range of initial Pb²⁺ concentrations varied from 10 to 2000 mg/L, with an exposure duration of no less than 48 hours. The kinetics were evaluated at concentrations of 40 and 400 mg/L (LS = 1000 mL/g).

The experimental data were fitted using the Langmuir and Sips isotherms, as well as pseudo-first-order and pseudo-second-order kinetic models, and the Elovich equation. The model parameters were calculated using non-linear least squares (NLLS) regression (Levenberg–Marquardt algorithm); the mathematical framework and formulas are provided in Online Resource 1 (Section S4.5).

To verify the synergism or antagonism of the components, an additional model binary system was utilized: 0.01 M KNO₃, pH 5.0, a fixed biochar dosage of 0.2 g, and a variable HAP addition (initial Pb concentrations of 10 and 100 mg/L, *n* = 3).

2.3. Incubation Experiment Design, Mineralogical Analysis, and Analytical Methods

The ameliorants were applied to the soil individually and in combination at a dose of 1% by mass. The choice of the HAP dose is based on data regarding its maximum specific efficiency (1–2%) established for related soil types (Novikova et al., 2025). The biochar dose was equalized with that of HAP for direct comparability of the treatments and falls within the typical range for heavy metal immobilization (0.5–10% by mass) (Palansooriya et al., 2022). The experiment was implemented with the simultaneous application of the ameliorants and a Pb(NO₃)₂ solution in a 0.01 M KNO₃ background at three contamination levels (low – 5, moderate – 22, high – 27 mg Pb/g soil), with a liquid-to-solid (LS) ratio of 1.5:1 mL/g. The incubation was carried out without strict thermostatic control.

Upon completion of the incubation periods (8, 46, and 90 days), sequential extraction was performed on a single sample: water-soluble fraction (distilled water, 60 min) and exchangeable fraction (0.01 M Ca(NO₃)₂, 120 min), in accordance with the conservative levels of the international hierarchy for assessing pollutant bioavailability (ISO 17402, 2008; ISO 17586, 2016; ISO 21268-1, 2019; ISO 21268-2, 2019). The LS ratio during extraction (20 L/kg) corresponds to the US EPA 1311/1312 methodology (US EPA Method 1311, 1992; US EPA Method 1312, 1994) and falls within the parameters of the BCR scheme (Ure et al., 1993; Rauret et al., 1999) and ISO 21268 (ISO 21268-1, 2019; ISO 21268-2, 2019).

Although a 0.01 M CaCl₂ solution is widely standardized for the routine assessment of heavy metal bioavailability (Houba et al., 2000), the use of 0.01 M Ca(NO₃)₂ is a recognized methodological alternative for evaluating the pool of exchangeable metals, including in soils subjected to amelioration (Meers et al., 2009; Wang et al., 2025). This extractant was deliberately selected to preserve the high displacing ability of the Ca²⁺ cation while eliminating the distortion of results caused by chloride complexation. It is known that in chloride extracts, the fraction of the soluble PbCl⁺ complex can reach 31% of the total pool of extracted lead (Du et al., 2023), leading to an artificial overestimation of its mobility, particularly in alkaline or carbonate media (Wasay et al., 2002). Unlike chlorides, the nitrate ion acts as an inert background electrolyte, allowing for an accurate assessment of the exchangeable Pb fraction driven by cationic displacement. This makes Ca(NO₃)₂ the preferred extractant for investigating the fundamental mechanisms of immobilization, eliminating the risks of secondary chemical mobilization of lead by the extractant. (The methodological justification is provided in Online Resource 1, Section S4).

The mineralogical composition of the initial soil and its transformation upon Pb saturation were investigated using powder X-ray diffraction (XRD). Powder diffractograms of the ground and sieved samples were recorded on a STADI P diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with a copper anode, a nickel K β filter (CuK α radiation, λ = 1.541874 Å), and a MYTHEN2 1D detector (DECTRIS). Data collection was performed at room temperature in the 2 θ angle range from 5 to 80° with a step of 0.012°. Quantitative phase analysis was conducted using the full-profile Rietveld method (details of the refinement procedure are provided in Online Resource 1, Section S6).

The Pb²⁺ concentration in the extracts was determined potentiometrically using an ion-selective electrode based on a crystalline PbS membrane (ELIT-231, ESR-10101 reference electrode, "Ekspert-001" instrument). Prior to measurement, the samples were filtered through nylon membranes with a pore size of 0.45 μ m, and the equilibrium pH value was measured using a Hanna Instruments HI2215 meter. To ensure optimal operating conditions for the ion-selective electrode, the pH of the filtrates was adjusted, if necessary, to 5.0 $\pm$ 0.2 using a 1 M KOH or HNO₃ solution. Following this, the ionic strength of the analyzed solution was fixed at 0.1 M by adding a background electrolyte (1 M KNO₃ solution) to stabilize the activity coefficients and minimize potential drift. The measurement uncertainty was evaluated using the uncertainty budget method (Type B); the full budget and criteria for statistical significance are presented in the Supplementary Materials (Sections S1–S3).

3. Results and Discussion

3.1. Soil Analysis

The *Haplic* qualifier indicates a weakly differentiated Cambisol profile, lacking signs of clay illuviation, stagnant waterlogging, or secondary carbonate accumulation; the profile is formed via *in situ* weathering of aluminosilicates, resulting in the formation of a metamorphic Bm horizon. According to the USDA

particle-size classification, the soil is dominated by the silt fraction (0.05–0.002 mm), which accounts for 55%. The contents of sand (2.0–0.05 mm) and clay (< 0.002 mm) are 22% and 23%, respectively. Based on this ratio, the soil is classified as a silt loam (Table 1).

Table 1
Basic physicochemical properties of the
initial Haplic Cambisol

Parameter	Value
Physical properties	
Sand (2.0–0.05 mm), %	22
Silt (0.05–0.002 mm), %	55
Clay (< 0.002 mm), %	23
Textural class (USDA)	Silt loam
Chemical properties	
pH (H ₂ O)	4.83
pH (KCl)	4.01
Soil organic carbon (SOC), %	8.24
Total nitrogen (TN), %	2.80
C/N ratio	2.94
Available P ₂ O ₅ , mg/100 g	8
Available K ₂ O, mg/100 g	7.55

The soil is characterized by an acidic medium reaction, which is typical for Cambisols in the humid landscapes of the southern Russian Far East. A high organic carbon content is observed alongside a narrow C/N ratio (Table 1), reflecting an intensive input of fresh litter. Concurrently, the acidic reaction of the medium likely limits microbial transformation, leading to decelerated humification processes as well as a low supply of available phosphorus forms and exchangeable potassium.

According to the pXRF screening analysis, the background Pb content was 22 mg/kg, which does not exceed the regional clarke values (Vinogradov, 1962) and falls within the typical background range for uncontaminated soils (12–50 mg/kg) (Kabata-Pendias, 2000; Senila, 2014), indicating the absence of initial anthropogenic contamination at the site.

At a soil pH of 4.83, the carboxyl groups of organic matter (pKa 3–6) are only partially dissociated, whereas the phenolic sites (pKa 7–10) are almost completely protonated (Giannakopoulos et al., 2009; Shi et al., 2016; Mahler et al., 2021). Thus, despite the high SOC content, the potential sorption capacity

of the organic matter for lead is not fully realized. Under these conditions, the constant structural charge of the mineralogical matrix begins to play a key role in cation retention.

According to the X-ray diffraction (XRD) analysis, the mineralogical matrix is represented by an association of plagioclase, illite, quartz, and vermiculite (Table 2). The dominance of plagioclase over quartz indicates a moderate stage of weathering of the parent rock. Despite its low content, it is vermiculite that possesses the highest cation exchange capacity among the identified phases and plays a decisive role in the fixation of heavy metals.

Table 2
Quantitative mineralogical composition of the control sample (Rietveld method)

Mineral phase	Content, wt. %
Andesine (plagioclase)	44,08
Illite (hydromica)	28,62
Quartz	26,35
Vermiculite	0,95

3.2. Sorption Capacity and Mechanisms of Pb2 + Fixation by Native Soil

Both obtained sorption isotherms (LS = 1000 and 50 mL/g) are described by the Langmuir equation (the Freundlich model is inapplicable due to pronounced saturation; the Sips model did not provide a significant improvement) (Fig. 1, Table 3).

Table 3
Parameters of the Langmuir equation for Pb²⁺ sorption by the Cambisol

LS (mL/g)	q _m (mg/g)	K _l (L/mg)	R ²
1000	24,32	0,98	0,78
50	24,96	0,47	0,88

The q_m value is virtually identical for both systems despite the 20-fold difference in the LS ratio, indicating a stable intrinsic property of the Cambisol. The values are in good agreement with independent estimates of the capacity of Cambisols and similar acidic forest soils (Sipos et al., 2005; Pokrovsky et al., 2012). At the same time, the affinity constant (K_l) decreased by almost half upon transition to a dense suspension, which is explained by the mutual screening of soil particles.

The observed pattern aligns with the concept that for the studied heavy loamy acidic soils, the sorption and retention of Pb are primarily determined by pH, cation exchange capacity, the content of iron and

manganese oxides, and the clay fraction; comparative studies have shown that Pb is bound more strongly compared to Cd (Shaheen, 2009; Cerqueira et al., 2015). Among the mineral phases identified in the studied Cambisol (Table 2), vermiculite primarily acts as the main Pb-binding component, despite its low content (0.95%).

At equilibrium Pb concentrations above 100 mg/L (LS = 50 mL/g, 0.45 μ m filtrate), the formation of a flocculent precipitate was recorded, likely representing Pb complexes with dissolved organic matter (humic and fulvic acids). The most probable mechanism involves the neutralization of the charge of organic macromolecules by Pb²⁺ cations, followed by polymer cross-linking (Ai et al., 2020).

The kinetics of Pb²⁺ sorption demonstrates a clear temporal separation of functions at different LS ratios. In a dense suspension (LS = 50 mL/g), equilibrium is reached in 15–30 min (pseudo-second order, $q_e = 2.11$ mg/g). In a diluted system (LS = 1000 mL/g), equilibrium is established over three days; the pseudo-second-order model ($q_e = 22.41$ mg/g, $R^2 = 0.77$) provides a better fit than the Elovich equation ($q_e = 22.41$ mg/g) and is in good agreement with the independent estimation of the maximum capacity derived from the Langmuir isotherm (Fig. 2). The pseudo-first-order model was not considered substantively adequate, given that binding by the soil is predominantly determined by chemisorption on the functional groups of organic matter and clay minerals, rather than by physisorption under conditions of excess free sites (Chien & Clayton, 1980; Ho & McKay, 1999).

The sorption kinetics reflects the behavior of the system under different loads. The dense suspension ensures rapid binding of the incoming Pb, whereas the diluted system clearly manifests the maximum capacity of the soil itself (22–25 mg/g), the attainment of which requires a prolonged time. When the amount of lead exceeds this limit, the exchange complex of the Cambisol exhausts its resource. Under such conditions, the use of HAP as an additional capacity reserve for the irreversible fixation of lead is fundamentally important.

To establish the mechanism of lead fixation by the native soil, the X-ray diffractograms of the initial control were compared with a series of progressive saturation (low, moderate, and high saturation levels) (Fig. 3).

In the low-angle region (5–20° 2 θ), encompassing the basal reflections of vermiculite (6.10°) and illite (8.8° and 19.67°), the relative scattering intensity progressively decreases as the Pb concentration increases. This is consistent with data on Pb²⁺ sorption onto vermiculite, where binding proceeds via an outer-sphere complexation mechanism and is accompanied by a reduction of interatomic distances in the interlayer space, which is detectable by XRD (Rehman et al., 2021).

Direct quantitative data on the degree of contraction specifically upon Pb²⁺ saturation were not found in the available literature; for this reason, the estimation to ~ 11.0 Å is provided by analogy with the dehydrational collapse of the interlayer space by weakly hydrated cations, exemplified by data for Cs⁺ as a model weakly hydrated cation with a similar final d-spacing (Dzene et al., 2015).

The gradual nature of the transformation is explained by the partial aluminization of soil vermiculites in Cambisols. Polymeric interlayers of Al and Fe hydroxides in the interlayer space (hydroxy-interlayering) act as structural props and prevent the complete collapse of the lattice (Karathanasis, 1988; Meunier, 2007; Lanson et al., 2015; Dietel et al., 2019).

In the diffraction profiles of the lead-saturated samples, a weak reflection appears at $2\theta = 41.54^\circ$ ($d \approx 2.17 \text{ \AA}$), which is absent in the control (Fig. 3). Its intensity increases already at the initial stage of saturation and subsequently reaches a plateau without further growth with increasing Pb concentration. The absence of a dose-dependent increase precludes the interpretation of this reflection as a distinct crystalline Pb phase or a microprecipitate. The reflection can be interpreted as the result of a local substructural rearrangement in the packing of the clay fraction upon Pb^{2+} fixation at a limited number of highly active sorption sites of vermiculite. The plateauing is consistent with the low initial content of this mineral (0.95%), as its capacity is exhausted already at the initial stage of saturation.

Thus, lead binding by the native Cambisol is realized predominantly through reversible mechanisms: cation exchange and sorption on the surface of clay minerals, without the formation of distinct crystalline Pb-containing phases. This determines the potential lability of lead fixed in this manner and, irrespective of the incubation experiment results, justifies the expediency of additional immobilizing agents that convert the metal into thermodynamically more stable forms. Thereby, this result serves as a mineralogical justification for the role of HAP in the system.

3.3. Adsorption Characteristics of HAP

The isotherm exhibits a shape close to the H-type according to the Giles classification: a sharp initial rise followed by a transition to a plateau at minimal equilibrium concentrations. The profile is statistically better described by the Sips model than by the Langmuir equation ($R^2 = 0.96$ versus 0.93). The calculated maximum capacity is $q_m = 1095 \text{ mg/g}$, with $K_s = 4.65 \text{ L/mg}$, which is 45 times higher than the capacity of the native Cambisol.

This value falls within the range reported for synthetic HAPs of various morphologies: 100–150 mg/g for microcrystalline forms (Hashimoto & Sato, 2007), 330–714 mg/g for powder and nanoscale materials (Sandrine et al., 2007; Chen et al., 2010; Mobasherpour et al., 2011), and up to 625–1304 mg/g for purposefully designed porous and lamellar architectures [83, 84]. The HAP utilized in this study was not subjected to such morphological optimization; therefore, the observed capacity serves as an additional argument in favor of its practical applicability.

The steep nature of the isotherm is consistent with the dissolution-reprecipitation mechanism established by XRD, FTIR/Raman, and HRTEM methods (Xu & Schwartz, 1994; Mavropoulos et al., 2002; Motyka et al., 2015): upon reaching the solubility product of the secondary phase, Pb ions almost entirely transition into the solid phase, forming a continuous solid solution series of $\text{Pb}_{10-x}\text{Ca}_x(\text{PO}_4)_6(\text{OH})_2$ (Xu & Schwartz, 1994; Mavropoulos et al., 2002; Zhu et al., 2016), up to virtually pure hydroxypyromorphite at high loads (Mavropoulos et al., 2002).

At 40 mg/L, the immobilization is almost instantaneous (> 99% in 1.5 min). At 400 mg/L, the kinetics are biphasic: over 60% of Pb is extracted within 5–10 min, followed by a slow stage lasting up to 38 hours, reaching a plateau at approximately 400 mg/g. Both stages are satisfactorily described by both the pseudo-second-order model ($q_e = 383.0$ mg/g, $R^2 = 0.93$) and the Elovich equation ($R^2 = 0.94$), indicating the energetic heterogeneity of the process.

The two-stage nature aligns with the estimates of the activation energy for Pb sorption on carbonate HAP ($E_a \approx 11.9$ kJ/mol (Xu et al., 2008)), which are characteristic of diffusion-limited rather than kinetically-limited processes: the formation of a new phase on the surface creates steric resistance and shifts the rate-limiting step to intraparticle diffusion through the reaction product layer (Mavropoulos et al., 2002; Xu et al., 2008).

Hydroxypyromorphite is 22 orders of magnitude less soluble than the initial HAP (Scheckel & Ryan, 2002; Zhu et al., 2015); however, the binding is not unconditionally irreversible: during the leaching of chloropyromorphite, up to 21% of Pb is released in 1 hour at pH 2.0, whereas only 0.17% is released over a year at pH 6.0 (Scheckel & Ryan, 2002). The pH value of the studied soil (4.01–4.83) is far from the extremely acidic conditions under which rapid leaching occurs. This allows concluding that for soils within this acidity range, HAP will maintain its practical efficiency as a long-term immobilizing barrier. The increasing solubility of unreacted HAP at $\text{pH} \leq 5.0$ (Sjoberg, 2000), conversely, promotes further release of Ca^{2+} and PO_4^{3-} , intensifying the precipitation reaction rather than causing the dissolution of the pyromorphite phase.

3.4. Compatibility of HAP and Biochar in a Model Binary System

To test the hypothesis regarding potential chemical or kinetic interaction between the components, a model "biochar + HAP" binary system was investigated in the absence of a soil matrix.

At $C_0 = 100$ mg/L, biochar in the absence of HAP bound 67.7% of Pb. The addition of HAP in an amount of 2.4% of the total mixture mass increased the binding degree to 99.2%. A further increase in the HAP proportion yielded only a marginal increment (99.7–99.8%). At $C_0 = 10$ mg/L, biochar alone bound over 95% of the introduced Pb; therefore, the addition of HAP operates on a nearly depleted pool, and the specific capacity of the mixture logically decreases with an increase in the total dosage due to the dilution effect (Fig. 6a).

It is impossible to unambiguously partition the total mass of bound Pb between the contributions of biochar and HAP based solely on the equilibrium concentration in the solution: the result depends on the assumption regarding the nature of their interaction in the mixture. The lower estimate of the specific capacity of HAP corresponds to the assumption of complete additivity (biochar in the mixture retains the same capacity as in the isolated system). Concurrently, the upper boundary assumes the complete suppression of biochar, wherein all the Pb bound by the mixture is associated with HAP (Online Resource

1, Section S7). For $C_0 = 100$ mg/L, both estimates differ by a factor of 3.1–6.6 depending on the HAP dose and are shown in Fig. 6b.

The choice between these boundaries is determined by the ratio of the rates of the two processes. The precipitation of hydroxypyromorphite on HAP occurs almost instantaneously (over 99% binding in 1.5 min at 40 mg/L, over 60% in the first 5–10 min at 400 mg/L). Conversely, Pb binding by biochar is realized through ion exchange, the driving force of which is the equilibrium concentration of Pb^{2+} in the solution, and is established on a substantially larger time scale. Given this ratio of rates, HAP apparently intercepts the bulk of free Pb^{2+} faster than biochar. The actual capacity of HAP in the mixture in this case will be closer to the upper boundary of the specified range in Fig. 6b.

The absence of a pronounced negative influence of the components on each other at the level of the total mixture capacity does not imply an absence of interaction between them at the level of individual contributions. It is more accurate to speak not of the additivity of contributions, but of the kinetic redistribution of Pb in favor of the faster and thermodynamically more capacitive sorbent, whereby the actual contribution of biochar in the presence of HAP is likely lower than its isolated capacity. The practical conclusion remains unchanged: the total capacity of the mixture remains high and predictable even at low HAP doses (99.2–99.9% binding), which confirms the chemical compatibility of the components and renders the synthesis of a unified composite material (e.g., biochar purposefully modified with HAP during the synthesis stage) impractical. Since the primary contribution to binding is provided specifically by HAP, the separate application of the components does not result in noticeable efficiency losses compared to a hypothetical co-synthesis.

3.5. Dynamics of the Incubation Experiment and the Role of pH

3.5.1. Dynamics of Mobile Lead Forms in the Incubation Experiment

The proportion of water-soluble (Fig. 7) and exchangeable (Fig. 8) Pb relative to the applied dose for three contamination levels across three incubation periods (8, 46, and 90 days) is presented below. (Numerical data are provided in Online Resource 1, Section S5).

At the low contamination level, no statistically significant effect was observed for any of the ameliorants (Figs. 7, 8). The material balance indicates that the intrinsic exchange complex of the Cambisol independently retains over 99% of the lead dose applied at this level; the absence of a visible effect reflects the efficiency of the soil's natural capacity at a low contamination level. This is in full agreement with the sorption isotherm, according to which the intrinsic capacity of the Cambisol ($q_m = 24.3$ – 25.0 mg/g) is sufficient to bind lead at a low contamination level, regardless of the introduced additives.

As the contamination level increases, the soil's intrinsic capacity becomes insufficient, and the contribution of the ameliorants to Pb^{2+} retention becomes substantial. The significance of this threshold is corroborated by XRD data, which demonstrate that the soil binds lead predominantly via reversible mechanisms on clay minerals. Moreover, the fraction of Pb retained by the soil upon the exhaustion of its intrinsic capacity maintains partial lability. The reduction of the water-soluble and exchangeable fractions upon HAP application is accompanied not merely by the redistribution of lead, but by its transition into a form resistant to reverse mobilization to a significantly greater extent than that provided by the soil itself.

The impacts of biochar and HAP additions on the reduction of water-soluble and exchangeable lead forms differ. Specifically, HAP demonstrates a stable and non-diminishing over time reduction in lead mobility at moderate and high contamination levels across both fractions throughout the entire experiment (Figs. 7, 8). In the exchangeable fraction, which can be considered an indirect indicator of potential Pb bioavailability to plants, the reduction relative to the control amounted to 8.6–46.4%. The absolute Pb content in the treatments with HAP decreases monotonically throughout the entire experiment.

In contrast, biochar exhibits an ambiguous efficiency that does not increase over time. The significant effect varied from 9.2% to 24.1% in the water-soluble fraction, whereas in the exchangeable fraction it fluctuated from a statistically indistinguishable zero to 21% without a clear temporal trend (Figs. 7, 8). This behavior is expected; given that the intrinsic capacity of this biochar is comparable to the capacity of the soil itself (Egorin et al., 2025), it provides only a limited additional binding reserve. Under high load, this reserve is exhausted relatively quickly and is subjected to the same competitive processes of reversible ion-exchange desorption as the intrinsic exchange complex of the Cambisol.

The combination of HAP and biochar outperforms both individual components at moderate and high contamination levels on the 8th and 46th days of the experiment. However, by the 90th day, pure HAP begins to slightly surpass the combined treatment. The dynamics of the combined system (HAP + biochar) do not reveal a stable trend toward enhanced immobilization. Taking into account the proven absence of chemical synergism, the observed fluctuations in efficiency reflect a simple additive superimposition of two independent processes. The binding mechanisms do not mutually enhance each other, and their contributions vary differently depending on the conditions and duration of incubation. It is possible that this unevenness is partly related to the lack of strict thermostatic control during incubation (April–August, the actual temperature was determined by the laboratory room temperature): temperature is capable of modulating the mobility of reversibly bound forms of heavy metals in the soil (Cornu et al., 2016; Bai et al., 2020). It should be noted that verifying this effect was not among the objectives of the present study. This is because it does not affect the main conclusion regarding the stable efficiency of HAP, as the fluctuations solely concern the magnitude of the additional advantage in combination with biochar.

Overall, upon HAP application, the reduction of the water-soluble fraction is more pronounced than that of the exchangeable fraction: 18.5–59.1% versus 8.6–46.4% at the same levels and incubation durations. This is consistent with the mechanism of HAP action, where free Pb^{2+} ions are more effectively precipitated during the formation of hydroxypyromorphite. The exchangeable fraction decreases less effectively as it is determined by the process of desorption from the surface of soil particles.

At moderate and high contamination levels, the effect of HAP intensifies over time. This aligns with the slow, diffusion-limited kinetics of hydroxypyromorphite formation, where in a model aqueous system the attainment of a plateau at high Pb concentrations takes up to 38 hours, and the two-stage nature of the kinetics itself is associated with mass transfer limitations through the forming hydroxypyromorphite phase. In the soil matrix, where Pb adsorption onto HAP is constrained by additional factors, such as solid-phase dilution and the presence of competing ions, the process of irreversible binding may be significantly prolonged, which likely explains the primary increase in efficiency by the 90th day rather than in the initial days of incubation. The increasing Pb binding efficiency over time indicates the practical suitability of HAP, which, even at a dose of 1%, noticeably reduces the bioavailable fraction of lead at moderate and high contamination levels.

3.5.2. Equilibrium pH of Extracts

At the low contamination level, the pH of the water and exchangeable extracts corresponds to the initial soil value (Table 1) or slightly exceeds it, regardless of the incubation duration. Moderate and high contamination levels induce persistent acidification of the medium, which intensifies by the 90th day. The nature of this dependence is identical for both fractions, with the only difference being a shift in the absolute values. The differences between the treatments (control, biochar, HAP, and combination) at each time point and level do not exceed the measurement error, whereas the differences between contamination levels and incubation periods substantially exceed it. This indicates that the acidification of both extracts is determined by the applied dose of Pb, rather than the presence of ameliorants.

The observed effect cannot be explained by the direct hydrolysis of the lead cation in solution ($\text{Pb}_{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$, $\text{pK}_a1 = 7.7$). Within the working pH range of 3.7–5.0, this equilibrium is almost completely shifted toward the free ion. The most probable cause of acidification is the specific inner-sphere sorption of lead cations onto the edge sites of variable-charge clay minerals. It is known that, in addition to the formation of outer-sphere complexes on the planar sites of vermiculite and related phyllosilicates, an independent pathway for cation binding exists. It occurs via deprotonated silanol and aluminol groups ($\equiv \text{SiO}^-$, $\equiv \text{AlO}^-$) at the particle edges, which are predominantly protonated under highly acidic conditions ($\text{pH} < 4.0$) (Malandrino et al., 2006). It is hypothesized that the coordination of lead ions at such sites is accompanied by the release of a proton into the pore solution ($\equiv \text{MeOH} + \text{Pb}^{2+} \rightarrow \equiv \text{MeO}-\text{Pb}^+ + \text{H}^+$, where Me is Al or Si). A surface hydrolysis process of a sorbed metal, acting as a proton source and analogous in nature, has been previously confirmed by the XAFS method for iron oxides (Bargar et al., 1997).

Unlike ion exchange on basal surfaces, this mechanism depends on the reaction of the medium and is limited by the number of edge sites. This premise is supported by the analysis of the initial diffractograms. The appearance and rapid plateauing of the reflection at $2\theta = 41.54^\circ$, caused by the structural rearrangement of the clay fraction packing during lead fixation at the active sites of vermiculite, indicates a limited number of such sites. The fact that pH dynamics do not depend on the presence of ameliorants confirms the determining role of lead interaction with the native mineralogical matrix of the soil rather than with the applied amendments.

The dynamic amphotericity of phyllosilicate edge surfaces, consisting in their ability to exchange protons with the solution depending on the local pH, finds independent confirmation in the results of molecular dynamics simulations of montmorillonite (Feng et al., 2026).

The average pH shift of the extracts upon HAP application relative to the control is practically zero in the exchangeable fraction (mean value of + 0.06), despite the decrease in the proportion of the exchangeable Pb fraction. This rules out the classical liming mechanism (where a pH increase causes a rise in cation exchange capacity and indirect immobilization) and confirms that the primary binding pathway is specific chemical precipitation with the formation of hydroxypyromorphite.

In the water-soluble fraction, the pH shift is somewhat more noticeable (+ 0.17), but it is also less than the typical liming effect (Figs. 9, 10). The practical significance of this result is that HAP in soil systems can operate directly in the native weakly acidic medium of the Cambisol (extract pH 3.7–5.7) without the need for concomitant correction of the medium reaction via liming.

The minimal intrinsic contribution of biochar to the pH of the extracts ($\Delta\text{pH} + 0.11$ in the water-soluble and + 0.03 in the exchangeable fraction) indicates the absence of an alkalizing mechanism contribution to its action in this system, contrary to the hypothesis of co-alkalization by biochar and the apatite component formulated by analogy with an independent study (Vuong et al., 2022). This is supported by independent physicochemical characterization of the same biochar, whose ash content is $9.27 \pm 1.98\%$ (Egorin et al., 2025), corresponding to the value typical for wood biochars (usually less than 10%) and an order of magnitude lower than that of manure and seaweed biochars (40–50%) (Mukome et al., 2013; Tomczyk et al., 2020). A weak intrinsic contribution to pH, therefore, is an expected consequence of the confirmed low ash content of the used biochar. It is reasonable to consider low-ash biochars predominantly as an agronomic additive (improving soil structure and water-air regime) rather than as an independent tool for lead immobilization, either through sorption capacity or pH shift.

4. Conclusions

The studied humus horizon of the typical brown soil (Haplic Cambisol) possesses an intrinsic but limited capacity for lead retention: the maximum sorption capacity is 24.3–25.0 mg/g. According to the X-ray diffraction (XRD) analysis, the binding is accompanied by structural changes in vermiculite without the formation of distinct crystalline phases, which indicates the potential lability of lead fixed in this manner. As long as the applied lead dose does not exceed approximately 20% of this capacity (low

contamination level, 5 mg/g), the soil independently manages the binding, and the application of ameliorants yields no significant effect. As the dose approaches the limit of the intrinsic capacity (about 90% at the moderate level, 22 mg/g) and exceeds it (about 110% at the high level, 27 mg/g), the absorption resource of the soil is exhausted, and the contribution of the ameliorants becomes substantial.

Under these conditions, hydroxyapatite exhibited a sorption capacity ($q_m = 1095$ mg/g) nearly 45 times higher than that of the soil. In the incubation experiment, this manifested as a stable and non-diminishing over time reduction in lead mobility at moderate and high contamination levels—by 18.5–59.1% in the water-soluble fraction and by 8.6–46.4% in the exchangeable fraction; moreover, the efficiency with respect to the exchangeable fraction did not decrease by the 90th day, but rather increased.

It is particularly noteworthy that this effect is achieved without noticeable alkalization of the medium: the average pH shift of the extracts upon HAP application was only + 0.06 in the exchangeable fraction and + 0.17 in the water-soluble fraction, which is decidedly less than the typical liming effect. Consequently, HAP is capable of reducing lead mobility directly in the native weakly acidic medium of the Cambisol (pH 3.7–5.7), without requiring prior or concomitant lime amelioration of the soil.

The role of low-ash biochar in this system proved to be different. Its effect on lead mobility was temporally unstable, did not increase by the 90th day, and remained comparable in magnitude to the intrinsic capacity of the soil. In the model "biochar + HAP" binary system, it was not possible to partition the contribution of the components based solely on the equilibrium concentration in the solution: since Pb binding by hydroxyapatite kinetically significantly outpaces binding by biochar, its actual contribution in the presence of HAP is likely lower than its intrinsic capacity, making the assessment of their mutual influence difficult. At the same time, the total capacity of the mixture increases even at low HAP doses, which indicates, at the very least, the absence of mutual suppression of the components.

The totality of these results allows for the functional separation of the ameliorants within the system. Hydroxyapatite, even at a dose of 1% of the soil mass, acts as an effective and temporally stable barrier against mobile forms of lead, requiring no liming of acidic soils. Low-ash wood biochar does not perform this role and, in the given system, can be considered primarily as an agronomic additive that influences the structure and water-regulating function of the soil, rather than as an independent tool for lead binding.

Thus, both components can be utilized in the remediation of lead-contaminated soils, but in a phased manner: first, applying HAP for lead binding, and subsequently applying biochar as a soil conditioner in soils experiencing excessive moisture.

Declarations

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Data Availability: The datasets generated and analyzed during the current study, including full numerical data for the incubation experiment, uncertainty budgets, and Rietveld refinement details, are provided as Online Resource 1 accompanying this article.

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