

Influence of Soil pH, Organic Matter, and Clay Content on Environmentally Available Lead in Soils: A Case Study in Muncie, Indiana, USA

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Abstract

Due to historical and ongoing industrial practices, lead contamination in urban soils presents substantial health risks, primarily due to its capacity to readily migrate from the soil to humans. This research focused on the influence of soil pH, organic matter, and clay content on extractable lead amounts. Sixty-four soil samples from Muncie, Indiana, were analyzed, revealing that the examined factors accounted for 21.71% of the Pb mg/Kg-dry variable variance (p < 0.002). A significant inverse correlation was observed between Pb and clay content (r = -0.4, p < 0.001), with XRD and FTIR analyses confirming the binding affinity of clay minerals with lead. In contrast, no significant relationships were found between Pb concentrations and soil pH (r = 0.07; p = 0.59) or organic matter content (r = 0.12; p = 0.34). Elucidating the interactions between lead, clay minerals, and other soil constituents is crucial for addressing lead-contaminated soils and reducing environmental and health impacts.

Keywords

Soil Acidity/Alkalinity, Lead Leaching, Lead Solubility, Health Risks, Lead Mobility

1. Introduction

Lead-contaminated soil remains a potent public health hazard, reflecting sustained increases in lead (Pb) levels in fertile and uncultivated soils and posing severe risks to humans and animals [1]. The widespread prevalence of Pb pollution means many soils, especially upper horizons, likely contain high concentrations of this metal [2] [3]. For instance, significant transfers of Pb from polluted soil to individuals, particularly in industrially affected regions, have been welldocumented [4] [5]. Lead contaminations in soil, deriving mainly from industrial and mining activities, have long been recognized, with, for instance, Pb isotope analyses revealing medieval workshops as significant sources of Pb in French soils [6].

Present guidelines from agencies such as the California Department of Toxic Substances Control and the EPA have stipulated actionable lead levels in soils and areas to curb Pb exposure and its consequent health risks [7] [8]. The persistence and high environmental availability of Pb, denoting its potential for interaction and transport in various environmental media, underlines the urgency of these regulatory interventions [9].

The repercussions of lead exposure are numerous and significant, with no safe blood lead concentration levels identified [10] [11]. The CDC emphasizes immediate public health interventions for blood lead levels exceeding five μ g/dL, citing enduring health impacts from early exposure [12]. Pb's physiological and physicochemical aspects, including its absorption through the gastrointestinal tract and its presence in various forms, accentuate its toxicity and the diverse health risks it poses [13] [14].

The interactions and accumulations of Pb in soil are largely dictated by varying soil properties and the nature of Pb minerals [1] [15] [16]. The roles of soil properties like pH, organic matter, cation exchange capacity, and content of clay minerals in the adsorption and desorption of heavy metals, in turn, control their mobility and availability [5] [17] [18] [19].

Among the soil properties, pH significantly impacts the solubility, movement, and bioavailability of metals in soil, influencing ion pair and complex formation, surface charge, and organic matter solubility [20] [21]. Changes in pH values notably alter the proportions of readily mobile lead forms and the exchangeable Pb, affecting Pb bioavailability [22] [23].

Additionally, soil organic matter (O.M.) and its content also play vital roles in heavy metal availability, influencing the adsorption of heavy metals onto soil and the immobilization of Pb in soil [15] [24] [25]. The solubility of soil organic matter and the formation and dissolution of organic Pb complexes are pH-dependent, impacting Pb solubility and O.M. content in varying pH ranges [26] [27].

Lastly, the content and type of clay in soil play pivotal roles in the mobility of heavy metals. Clay-rich soils are typically characterized by higher retention capacities, and the specific clay minerals present in soil act as crucial indicators of soil quality and the bioavailability of heavy metals in soil [15] [28] [29] [30] [31].

This study aims to explore the intricate relationship between soil properties and the availability and mobility of Pb in soil to elucidate the environmental concentration of Pb in soils. By comprehending the influential factors of availability and mobility of Pb, the study could provide substantial insights into the risks of lead-contaminated soil and propose significant implications for future studies in this domain.

2. Methods and Materials

2.1. Sample Preparation

The study focused on soil samples obtained from Muncie, Indiana (**Figure 1**). The selection of field sites revolved around the vicinity of the old battery factory and the surrounding parks and streets. In total, sixty-four composite samples were collected using a soil sampler probe. The sampling process specifically targeted accessible locations without impervious surfaces or tree/shrub cover. To ensure the integrity of the samples, the soil sampler probe was meticulously cleaned before and after each use with deionized water. Five subsamples were gathered and combined at each site to form an aggregate soil sample weighing approximately 150 g. The collected soil samples underwent a series of preparation steps to ensure consistency and uniformity. First, the samples were air-dried to remove any excess moisture. Subsequently, they were sieved with a 2 mm mesh size to remove larger debris and achieve a standardized particle size. Finally, the sieved samples were homogenized to create a consistent and representative soil composition for further analysis.

2.2. Soil Analysis

The sieved samples were analyzed for environmental Pb concentration, soil pH, organic matter content, and soil texture. The pH was determined according to EPA method 9045D (SW-846 Test Method 9045D: Soil and Waste pH), an electrometric procedure for measuring pH in soils and waste samples [32] [33]. The



Figure 1. The study area, Muncie, Delaware County, IN USA.

soil texture was determined by the Bouyoucos-hydrometer method [34]. Organic matter content was determined by the loss on ignition method used to estimate the organic matter content following [35] and [36]. Environmental Pb concentration in soil samples was determined using microwave-assisted acid digestion following US EPA SW-846 Test Method 3050B [37], with analysis by inductively coupled plasma-optical emission spectrometry following US EPA SW-846 Method 6010D [38].

2.3. Statistical Analysis

Correlation analysis and regression analysis are suitable for evaluating the relationship between soil properties and the availability and mobility of Pb in soil. Correlation analysis helps determine the strength and direction of the relationship between two variables, such as the correlation between soil properties and Pb availability. It provides information on the degree of association between variables [39]. Regression analysis, particularly multiple regression analysis, allows for examining the impact of multiple independent variables (e.g., soil properties) on a dependent variable (e.g., Pb availability). It helps quantify the relationship and assess the contribution of individual variables [40].

2.4. Geographic Information System (GIS)

The study used a Geographic Information System (GIS) to create Inverse Distance Weighting (IDW) maps for representing the values of soil properties and concentrations of Pb in soil. Firstly, the spatial distribution of properties and Pb concentrations were visualized using GIS software. The IDW interpolation technique was employed to estimate values at unsampled locations based on the proximity of neighboring sample points. This method assigns higher weight to closer points, resulting in a smooth surface of predicted values. In interpolating soil properties using IDW, a power of 2 was applied, considering the 12 nearest points from a total of 64 soil samples. These maps are valuable tools for understanding spatial patterns in soil properties and potential contamination hotspots of Pb, aiding in environmental management and decision-making processes.

2.5. Analytical Methods for Confirming Clay Minerals in Soil

X-ray Diffraction (XRD) analysis is a technique that determines the crystal structure and composition of materials like clay minerals. It involves exposing a powdered sample to X-rays, which produce a diffraction pattern. By analyzing the pattern, the mineralogical composition can be determined. On the other hand, Fourier Transform Infrared (FTIR) analysis identifies the chemical composition of materials, including clay minerals, by measuring the absorption of specific wavelengths of infrared light. This reveals characteristic peaks related to functional groups in the minerals. Combining XRD and FTIR analyses confirm the presence of clay minerals in a soil sample, providing insights into their crystal structure, mineralogical composition, and chemical characteristics. Clay minerals

neralogy identification did not include Mg-, Ca-, K-saturation, heat, or glycolated treatments due to instrumental limitations.

This study analyzed samples with varying clay content using XRD and FTIR. For XRD, the samples were oven-dried, finely ground, and mounted onto appropriate holders before being scanned over a typical 2θ angle range for clays. The resulting diffractograms were interpreted to identify mineralogical compositions. For FTIR analysis, the dried samples were ground and pressed into transparent pellets. The sample spectra were collected. The resulting FTIR spectra, highlighting specific vibrational modes, were then compared against reference databases to elucidate the organic and inorganic components.

3. Results and Discussion

3.1. Environmental Pb Concentrations, Soil pH Values, Organic Matter, and Clay Contents

The values of environmental Pb concentration, pH, organic matter content, and clay fraction of 64 composite soil samples are shown in **Table 1**. The lead concentrations of Muncie's soils were determined in this study, and there was a distinct difference among sampling locations. In detail, lead content ranged from 17.08 to 623 mg/kg-dry. The soil pH ranged from 5.1 to 7.9, mostly alkaline. Organic matter contents of all soil samples ranged from 3% to 14%. The clay fraction ranged from 5% to 37%. These results indicated that the sampled soils covered a wide pH, organic matter content, and clay fraction. **Figure 2** illustrates the spatial variability (IDW), highlighting the differences in patterns for soil Pb, soil pH, organic matter, and clay content across the study area. This variety is suitable for studying the influence of soil pH, organic matter, and clay content on mobility of lead in soil in Muncie's soils.

3.2. Effects of Soil pH, Organic Matter, and Clay Content on Environmental Pb in Soils

A multiple linear regression analysis was performed to examine the influence of soil pH, O.M., and clay variables on the Pb mg/Kg-dry variable. The regression model showed that the variables explained 21.71% of the variance from the variable Pb mg/Kg-dry. The model found that the effect is statistically significant, with R2 = 0.22, F = 5.55, p = 0.002.

A Pearson correlation analysis was performed to test whether there was an association between the environmental Pb mg/Kg-dry and soil pH, O.M., and clay content. Correlation analysis showed that the environmental Pb concentrations were strongly correlated with clay content (r = -0.4, p < 0.001). The result showed no significant correlation (r = 0.07, p = 0.59) between the environmental Pb concentration between organic matter content and the environmental Pb concentration (r = 0.12; p = 0.34), suggesting that there was meaningful relationship between these two variables in the dataset (**Table 2**).





Figure 2. (a) The maps show IDW estimates of the values of environmental Pb concentration in soil from Muncie; (b) The maps show IDW estimates of the soil pH value in soil from Muncie; (c) The maps show IDW organic matter content % in soil from Muncie; (d) The maps show IDW estimates of clay content in soil from Muncie.

Table 1.	Descriptive	statistics of	f soil pH	I value,	organic	matter	content,	clay	content,	and
lead cond	centrations i	n the Munc	ie soil s	amples.						

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 Table 2. Correlation coefficients and significance between soil properties and extractable

 the environmental lead concentrations in soil.

		Pb mg/ Kg-dry	Soil pH	Organic Matter Content	Clay %
Pb mg/Kg-dry	Correlation	1	0.07	0.12	-0.46
	р		0.599	0.342	< 0.001
Soil pH	Correlation	0.07	1	-0.34	-0.05
	р	0.599		0.007	0.686
Organic Matter Content	Correlation	0.12	-0.34	1	-0.31
	р	0.342	0.007		0.012
Clay %	Correlation	-0.46	-0.05	-0.31	1
	р	< 0.001	0.686	0.012	

3.3. Discussion

The study area's soil was found to be mostly alkaline (Figure 3(a)). In alkaline



Figure 3. Scatterplot graphs showing the relationships between soil Pb and (a) soil pH level, (b) organic matter content, and (c) clay content.

conditions, the solubility of lead tends to decrease. A high soil pH may precipitate Pb as insoluble lead compounds, such as lead hydroxide (Pb (OH)₂) or lead carbonate (PbCO₃), which have lower solubility and are less mobile in the soil solution [41]. Increasing acidity may increase the Pb solubility, but this mobilization is usually slower than the accumulation in the organic-rich layer of soils. While our study observed no statistical correlation between soil pH and environmental lead concentrations (**Table 2**), it is noteworthy to mention a discernible increase in extractable Pb levels at higher soil pH values (**Figure 3(a)**). This implies that as the soil pH increased, there was a direct rise in the Pb absorption, indicating that the behavior of Pb in the soil might be more complex than simple linear correlations can capture. Such an observation is consistent with [42] and [43] findings.

Delving further into this phenomenon, Harter (1983) conducted a study where he noticed a substantial retention of four metals, including Pb, when the soil pH was raised beyond 7.0 to 7.5. Intriguingly, up to 75% of most of these metals were extractable. Harter's findings not only shed light on the presence of specific adsorption sites in soil for lead but also highlight a potential limitation to using pH management as a sole strategy for immobilizing heavy metals. Even with pH adjustment, significant amounts of Pb were still extractable when treated with a 0.01M HCl solution. These outcomes emphasize the multifaceted nature of Pb behavior in soils. The interactions are intricate, and while pH is a significant factor, it might not always directly translate to predictable Pb mobility trends, especially when considering diverse soil types and conditions [44].

There was not a significant correlation between organic matter content and Pb concentration (r = 0.12; p = 0.342) (Figure 3(b); Table 2). Several factors could contribute to the lack of a significant correlation between O.M. content and Pb concentration in soils, even though O.M. is known to play a role in metal sorption. All O.M. is not the same, as the type of organic compounds (e.g., humic and fulvic acids) and their molecular structures can affect metal binding capacity [45]. Soils that are anthropogenically transformed often exhibit a deficiency in organic matter, such as humic substances, thereby reducing their effectiveness as a natural barrier [46]. In addition, sites with high contamination typically exhibit low levels of O.M. content and diminished microbial activity [47]. Also, organic matter's intricate and multifaceted role may affect Pb adsorption. Lo, (1992) reveals the intricate interplay between soil organic matter, specifically humic and fulvic acids, and Pb adsorption [48]. An increase in O.M. typically leads to more functional groups that can bind Pb, but their effectiveness is mainly localized at the soil/aqueous interfaces. This, along with the observed soil particle aggregation and formation of clay-humus complexes at higher organic content levels, diminishes the specific surface area and reduces the availability of functional groups, mitigating overall Pb adsorption efficiency. Consequently, a heightened level of O.M. does not necessarily equate to increased Pb adsorption due to these complex interactions and modifications within diverse soil matrices. Organic matter significantly determines the availability and mobility of Pb in soils in two

ways. One is that O.M. could reduce the availability of Pb in soils by adsorption or forming stable complexes with humic substances. Second, it can also facilitate the transport of this element in soils via forming soluble complexes with O.M. [49] [50]. Humus is a dark, intricate combination of organic materials transformed from their original organic tissue. This substance, synthesized by diverse soil organisms, resists additional microbial breakdown [51]. Halim et al. (2003) found that introducing humic acid reduced the amount of extractable heavy metals in soils high in heavy metal content. Conversely, O.M. contributes to the soil solution by providing organic chemicals that can act as chelates, potentially improving the accessibility of metals to plants [25] [52]. The capability of O.M. to mobilize or immobilize metals depends on the nature of the O.M., pH, redox, and competing ions and ligands. Another study yielded comparable findings; Sauve (1998) observed that soluble organic O.M. complexes accounted for 30 to 50% of dissolved Pb in contaminated orchard soil treated with leaf compost at low pH. However, this percentage increased significantly to 80% - 99% when the pH reached 7. The reason behind this phenomenon is attributed to the promotion of organo-Pb complex formation and dissolution at higher pH levels, subsequently enhancing Pb solubility [26].

The absence of statistical significance in a correlation between variables does not necessarily indicate a lack of relationship between them. Instead, it signifies that the observed variability in the data is too insignificant to confirm or reject the presence of a correlation with a predetermined level of certainty [53]. These observations reinforce the idea that multiple factors beyond pH and O.M. alone influence Pb dynamics in soil. It is worth noting that while soil pH can influence lead availability, other factors, such as soil composition and specific minerals, can also play a crucial role. These additional factors might contribute to the lack of a strong correlation observed between pH and O.M. in these analyses.

Correlation analysis showed that the environmental Pb concentrations were strongly correlated with clay content. The result of the Pearson correlation reveals that the variable clay has the most significant influence on the variable Pb mg/Kg-dry (r = -0.4, p < 0.001) (Figure 3(c); Table 2). Therefore, we conducted another analysis using XRD and FTIR analyses to find out what kind of clay minerals are present in the soil, which may affect the availability of lead. In our investigation, XRD analysis was used to clarify the mineralogical composition of the studied samples (Figure 4). The results manifested characteristic diffraction patterns, which can be substantiated to infer the presence of montmorillonite, illite, and kaolinite in the samples. Remarkably, the detected diffraction peaks correspond closely with the spectrum data [54], and the congruence in peak positions and intensities provides a reliable comparison basis.

Furthermore, FTIR analyses were performed to determine the vibrational frequencies of the constituent minerals (**Figure 5**). Notably, kaolinite showcased distinctive absorption bands in the 3500 to 3750 cm⁻¹ range, reflecting the stretching frequencies of O.H. groups. Frost and Kristof (2004) denoted reliable diagnostic bands for kaolinite at approximately 3695, 3666, 3650, and 3630 cm⁻¹,



Figure 4. XRD patterns of clay minerals for the study area.



Figure 5. Extracts of representative FITE spectra from the study samples.

corroborating our findings [55]. In addition, absorption bands discerned between 1200 and 955 cm⁻¹ are considered indicative of the clay minerals under study, as per the findings of Robinson, Robertson *et al.* (2015). The spectral bands observed in our analysis exhibit significant alignment with the documented spectrum data, substantiating the presence of the inferred clay minerals [56].

Our findings align with those of Jiang (2010), who similarly demonstrated the capacity of Kaolinite clay, mainly a blend of kaolinite and illite clays from Longyan, China, to adsorb heavy metal ions like Pb (II) from wastewater [57]. The study highlighted the process's effectiveness in significantly reducing lead concentration from 160.00 to 8.00 mg/L in natural wastewater, particularly at higher pH levels, achieving peak adsorption within a short span of 30 minutes [57]. To clarify more, the association of Pb and other metals in mineral soil components generally follows the sequence: clay > silt > sand. Clay minerals, such as montmorillonite, illite, and Kaolinite, are recognized for their capability to trap heavy metals within their layers through ion exchange reactions [58]. Clay mineralogy additionally plays a role in influencing the sorption of Pb in soils. The geochemical properties of Pb²⁺ share similarities with divalent alkaline-earth group elements, enabling its substitution for K, Ba, Ca, and Sr within minerals and sorption sites [59]. Adsorption of Pb²⁺ is favored over Ca²⁺ on model clay minerals, *i.e.*, montmorillonite, illite, and Kaolinite which is the most preferred [60]. Also, the pH-dependent edge charge on Kaolinite becomes increasingly negative as pH increases [43]. Due to these factors, the lead concentrations were strongly affected by the clay from the soils of the study area, where the clay content was high, and the soil pH ranged between 5.5 and 7.5. These factors likely made for strong lead-kaolinite bonds, resulting in less lead extraction in the samples with higher clay content.

4. Conclusions

This research undertook an in-depth exploration of the interactions between environmental lead concentrations and various soil properties. Central to this investigation were the roles of different clay minerals, soil pH, and organic matter content in determining the lead extraction potential and mobility within the soil matrix.

Main Findings:

Significant Variations: The study confirmed significant variations in environmental lead concentrations based on specific soil properties.

Role of Clay Minerals: The most notable findings pertained to clay. XRD and FTIR analyses revealed the presence of montmorillonite, illite, and kaolinite clay minerals in the soil samples. These minerals, especially kaolinite, had a robust affinity for lead, limiting its extraction in clay-rich samples. The binding capacity of kaolinite to lead increased with pH, owing to its pH-dependent edge charge.

Soil pH and Lead Solubility: Alkaline soil conditions decreased lead solubility. High pH values precipitated lead as an insoluble compound, reducing its mobility within the soil.

Association with Organic Matter: While the study did not establish a statistically significant correlation, it identified a positive, albeit non-significant, association between environmental lead concentration and soil's organic matter content. Organic matter's role is intricate; on the one hand, it can reduce lead availability through adsorption or complex formation, and on the other, it can facilitate lead transport by forming soluble complexes.

Call for a Multifaceted Approach: The intricate interactions between lead, organic matter, and other soil components underscore adopting a comprehensive approach when studying lead in soils. Practical strategies for addressing lead contamination challenges will only emerge once these complexities are fully understood.

Recommendations for Future Research: Further studies, especially those covering diverse contexts and environments, are imperative to deepen our understanding of the intricate relationships between soil properties and lead. Such endeavors will enhance our knowledge, ultimately aiding in the efficient management of lead-contaminated soils and mitigating associated environmental and health risks.

While this study sheds light on the known theoretical relationships between soil components and lead, the practical and applied nuances demand further exploration. The observed non-significant yet positive associations underline the need for more intensive research in this field.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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