land

MDPI

Article

Predictive Modeling of Zinc Fractions in Zinc Chloride-Contaminated Soils Using Soil Properties

Edyta Nartowska [1,*], Anna Podlasek [2], Magdalena Daria Vaverková [2,3], L'ubica Kozáková [4] and Eugeniusz Koda [2]

[1] Faculty of Environmental Engineering, Geomatics and Renewable Energy, Kielce University of Technology, 25-314 Kielce, Poland
[2] Department of Sustainable Construction and Geodesy, Institute of Civil Engineering, Warsaw University of Life Sciences, Nowoursynowska 159, 02-776 Warsaw, Poland; anna_podlasek@sggw.edu.pl (A.P.); magdalena_vaverkova@sggw.edu.pl (M.D.V.); eugeniusz_koda@sggw.edu.pl (E.K.)
[3] Department of Applied and Landscape Ecology, Faculty of AgriSciences, Mendel University in Brno, Zemědělská 1, 613-00 Brno, Czech Republic
[4] Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Kosice, Letna 9, 042 00 Kosice, Slovakia; lubica.kozakova@tuke.sk
* Correspondence: enartowska@tu.kielce.pl

Abstract

The combined effects of soil properties, zinc (Zn), and chloride ion (Cl^-) concentrations on Zn distribution across soil fractions are poorly understood, even though zinc chloride ($ZnCl_2$) contamination in industrial soils is a major source of mobile Zn and poses significant environmental risks. This study aimed to (1) assess how the soil type, physicochemical properties, and Zn concentration affect Zn distribution in Community Bureau of Reference (BCR)-extracted fractions; (2) evaluate the impact of Cl^- on Zn mobility; and (3) develop predictive models for mobile and stable Zn fractions based on soil characteristics. Zn mobility was analyzed in 18 soils differing in Zn and Cl^-, pH, specific surface area (SSA), organic matter (OM), and texture (sand, silt, clay (CLY)), using a modified BCR method. Zn fractions were measured by atomic absorption spectroscopy (AAS). Analysis of Covariance was used to assess Zn distribution across soil types, while Zn fractions were modeled using non-linear regression (NLR). The results showed that mobile Zn increased with the total Zn, and that the soil type and Zn levels influenced Zn distribution in soils contaminated with $ZnCl_2$ (Zn 304–2136 $mg \cdot kg^{-1}$ d.m.; Cl^- 567–2552 $mg \cdot kg^{-1}$; pH 3.5–7.5; CLY 11–22%; SSA 96–196 $m^2 \cdot g^{-1}$; OM 0–4.8%). Although Cl^- enhanced Zn mobility, its effect was weaker than that of Zn. Predictive models based on the total Zn, SSA, and CLY accurately estimated Zn in mobile and stable fractions ($R > 0.92$), whereas the effects of the pH and OM, although noticeable, were not statistically significant.

Keywords: soil pollution; predictive models; salinity; potentially toxic metals; zinc; chloride ions; sequential extraction; clay fraction; specific surface area

check for updates

Academic Editor: Gregorio García

Received: 18 August 2025
Revised: 3 September 2025
Accepted: 5 September 2025
Published: 7 September 2025

Citation: Nartowska, E.; Podlasek, A.; Vaverková, M.D.; Kozáková, L.; Koda, E. Predictive Modeling of Zinc Fractions in Zinc Chloride-Contaminated Soils Using Soil Properties. *Land* **2025**, *14*, 1825. https://doi.org/10.3390/land14091825

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Soil contamination with zinc (Zn) remains a serious and widespread environmental problem worldwide [1]. Although Zn is essential in small amounts for proper plant growth, excess disrupts natural biochemical processes and becomes toxic [2]. Toxic effects have been identified at total Zn concentrations ranging from 100 to over 1000 $mg \cdot kg^{-1}$ dry mass (d.m.) [3]. Zn contamination can also lead to the deterioration of soil physicochemical

properties and, consequently, to a decline in its engineering quality [4,5]. In the soil environment, Zn occurs in various chemical forms that differ in mobility and bioavailability. Zn adsorption onto clay particles likely involves complex mechanisms. These include rapid ion exchange and ion uptake by diffusion into mineral structures or interlayer binding. Additionally, organic matter (OM) can retain 1–10% of the dry mass of heavy metals such as Zn, Cu, Pb, and Ni [6]. As a result of these mechanisms, Zn may be present in soil in (1) water-soluble form, (2) OM-bound form, (3) exchangeable form, (4) form associated with metal oxides and clay minerals, and (5) form bound within primary minerals [7]. To determine the proportions of these forms and their potential mobility, fractionation methods are used. The most commonly applied method is the modified BCR protocol (Bureau of Chemical Regulation). It divides zinc into four fractions based on bioavailability: F_I—acid-soluble—the most mobile form (exchangeable and carbonate-bound), F_{II}—reducible—associated with Fe and Mn oxides (mobilized by changes in pH or redox potential), F_{III}—oxidizable—associated with OM and sulfides (potentially stable), and F_{IV}—residual—permanently bound within mineral structures (the least mobile) [8].

In industry, zinc(II) chloride ($ZnCl_2$) is often produced as waste, particularly during textile recycling, electroplating, and dry battery production [9,10]. Zn concentrations in soils from industrial sites and closed mining areas have been reported to range from 18 to 10,638 mg·kg^{-1} d.m., depending on soil type [11–13]. The application of biosolids—including sewage sludge, manure, and compost—as organic fertilizers can also enrich soils with zinc (Zn) and chloride ions (Cl^-), originating from industrial processes, detergents, and water treatment agents [14]. According to Wuana and Okleimen [11], the main anthropogenic pathways of Zn and Cl^- into soils include fertilizers containing Zn (e.g., zinc sulfate or zinc chloride), historical use of Zn-containing pesticides, and biosolid application. Industrial or airborne emissions from metallurgy, electroplating, battery production, textile recycling, fossil fuel combustion, tire wear, and engine oils also contribute significantly. These pathways are typical in industrialized and urbanized regions, contributing to local Zn accumulation in soils and potential migration to groundwater. Due to its high solubility, $ZnCl_2$ constitutes a significant source of mobile Zn in soils, while Cl^- influence Zn speciation and mobility. Although Cl^- have a weak affinity for the soil solid phase [15], they can indirectly affect Zn mobility, for the appearance of chloro-complexes. Lommelen et al. [16] demonstrated that the decrease in Zn extraction efficiency at high Cl^- concentrations is not caused by competition with HCl_2^- but rather by the appearance of more highly hydrated Zn complexes with greater charge density. Additionally, Cl^- may slightly lower the pH and affect the amount of dissolved OM [17,18]. It can also indirectly influence the soil structure and mineral interactions. For example, in soils rich in Zn and Cl^-, secondary minerals such as simonkolleite may form, which can impact Zn stability in the environment [5]. Acosta et al. [19] reported that salinity promotes metal mobility. They studied soils with Zn concentrations ranging from 34 to 401 mg·kg^{-1} d.m., pH 7.8–8.17, and a high calcium carbonate content, treated with NaCl, $MgCl_2$, and $CaCl_2$ solutions at different concentrations (0.006 mol·dm^{-3}, 0.03 mol·dm^{-3}, and 0.3 mol·dm^{-3}, respectively). In these conditions, Zn mobility was relatively low—up to 0.18% of the total Zn content—compared to other metals: Cu (1.1%), Pb (2.1%), and Cd (40%). Zn mobility increased depending on the type of dominant cations in the following order of increasing mobility: Na > Mg > Ca. The authors indicated that the main mechanism of Zn mobilization is competition with calcium ions (Ca^{2+}), while chloro-complex formation is the least significant. Other possible mechanisms include competition with magnesium (Mg^{2+}) and/or sodium (Na^+) ions. In summary, Zn behavior in the presence of Cl^- in soil results from complex and still not fully understood interactions. This behavior depends on multiple factors, including the following: (1) soil type and properties, (2) type and concentration of Cl^-, (3) Zn concentration, (4) pH, and

(5) soil chemistry, including the presence of other ions and carbonates. Due to the complexity of soil systems and the variability in physicochemical conditions in which the studies are conducted, further analyses are required to better evaluate the role of Cl^-.

Zn contamination can change the physicochemical properties of soils. Additionally, high salinity (presence of Cl^-) may influence the chemical behavior of Zn [5]. Angelaki et al. [20] observed that in clay-rich soils (CLY, 58%) lacking Cl^-, Zn contamination caused structural changes in the soil, resulting in an increased filtration coefficient. Such changes were not observed in sandy soils. Bai et al. [21] reported higher Zn concentrations in soils with elevated CLY, silt (SIL), and OM contents, accompanied by a decrease in Cl^- levels. Similarly, Nartowska et al. [4], studying clay soils without free Cl^- ions, showed that lower CLY favored increased mobile Zn fractions. Rutkowska et al. [22] found that the activity of free Zn^{2+} in soil solutions was higher in sandy soils and lower in clay-rich ones. However, CLY alone did not prove to be a significant predictor of Zn mobility. The authors emphasized that the main factors contributing to elevated concentrations of free Zn ions are higher total Zn levels and lower soil pH (pH = 4). Likewise, Makuch-Pietraś and Wójcikowska-Kapusta [23] concluded that the share of potentially mobile Zn fractions depends primarily on the soil type, OM content, and environmental conditions such as the pH and urbanization degree. Nartowska et al. [17], analyzing the total Zn concentrations across various soil types, demonstrated that the behavior of $ZnCl_2$-contaminated soils can be explained by variations in the CLY content, pH, and specific surface area (SSA). Studies conducted on source clays without free Cl^- showed that potentially stable Zn fractions (BCR fractions III–IV) increase with a rising silt content (SIL) and, to a lesser extent, with an increasing SSA [4]. Current research confirms that Zn mobility and retention in soils depend on a complex interplay of factors. These include the soil type, CLY and SIL content, OM, pH, and salinity (Cl^- content). Although high CLY may promote Zn retention, its role is not straightforward and appears to depend on other variables such as Cl^- and the SSA. It is also suggested that the total Zn concentration and low pH are the primary drivers of increased mobile Zn fractions. However, most existing studies rely on total Zn measurements or were conducted under physicochemical conditions different from those in $ZnCl_2$-contaminated soils. This limits their applicability to highly saline systems.

Moreno-Lora and Delgado [24] emphasize that soil properties related to Zn adsorption should be considered in Zn uptake model estimation. In the literature, there are predictive models for free Zn ion activity based on the total Zn concentration, pH, and CLY. These models were developed for soils with Zn concentrations ranging from 42 to 320 $mg \cdot kg^{-1}$ d.m., pH from 4 to 6, and CLY between 7 and 13%, with a maximum coefficient of determination R^2 = 72.3% ($p < 0.001$) [22]. The authors note that including CLY in the model did not improve its effectiveness. The activity of free Zn^{2+} ions in the soil solution was determined using the MINTEQA2 software. Predictive models concerning Zn's mobile and stable fractions are valuable tools for rapid environmental risk assessment. They eliminate the need for costly and time-consuming laboratory analyses, which is particularly important in post-industrial land reclamation. However, the number of available models is limited, and existing approaches have been developed for various soil types under differing physicochemical conditions, highlighting the need for further research in this area. One of the key shortcomings of previous analyses is the lack of consideration of the effect of Cl^- on Zn speciation. However, the presence of these ions can significantly enhance Zn mobility and influence its interactions with various soil components. Understanding these mechanisms in the context of diverse soil types and salinity levels is crucial for reliable risk assessment and effective contamination management. The novelty of this study lies in the simultaneous consideration of soil physicochemical properties, variable metal concentrations, and different salinity levels (Cl^- content) on the distribution of Zn into mobile and

non-mobile fractions. Additionally, for the first time, predictive models were developed to predict the Zn content in individual extractable fractions (F_I–F_{IV}), incorporating both the total Zn concentration and key soil properties.

The objectives of the study were to (1) determine the influence of the soil type and its physicochemical properties—such as the SSA, CLY, OM, pH, and metal concentration—on the distribution of Zn in BCR fractions (F_I–F_{IV}) in soils contaminated with $ZnCl_2$; (2) assess the effect of Cl^- on the mobility of Zn; and (3) develop empirical equations for predicting the Zn content in BCR fractions for environmental and engineering applications.

The following research hypotheses were formulated: H_1: CLY, OM, pH, and SSA significantly influence the distribution of Zn in BCR fractions (F_I–F_{IV}) in soils contaminated with $ZnCl_2$; H_2: the presence of Cl^- increases Zn mobility in soil; and H3: predictive models based on the soil physicochemical properties and total Zn concentration can accurately estimate the distribution of Zn in BCR extractable fractions (R^2 > 90%).

2. Materials and Methods

2.1. Materials

The research material consisted of six soils from the Świętokrzyskie Voivodeship (Poland), which differ in physicochemical properties (Table 1). This variability is crucial for a more accurate assessment of the role of soil characteristics in influencing Zn mobility. Soil samples were collected from unused land to avoid significant alterations resulting from anthropogenic activities. Detailed information on the criteria for site selection is provided in the study by Nartowska et al. [17]. The physicochemical and mineralogical characteristics are presented in Tables 1 and A1.

Table 1. Physicochemical and mineralogical characteristics of soils prior to modification with $ZnCl_2$.

Types of Soils and Locations $^{\epsilon}$	Type of Soil Acc. Classification		Mineralogical Composition $^{\pm}$	PI §	CLY *	SIL *	SSA $^{\varepsilon}$	pH_{KCl} $^{\approx}$	Zn	Cl **
	USDA $^{\sigma}$ [25]	Moreno-Maroto et al. [26]	[-]		[%]		[$m^2 \cdot g^{-1}$]	[-]	[$mg \cdot kg^{-1}$ d.m.]	[$mg \cdot kg^{-1}$]
a 50.88666° N, 20.79222° E	silt loam	silt loam	Albite, $NaAlSi_3O_8$ Kaolinite, $Al_2Si_2O_5(OH)_4$ Microcline, $KAlSi_3O_8$ Muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$ Quartz, SiO_2 Sodalite, $Na_8Al_6Si_6O_{24}Cl_2$ Tridymite, SiO_2 Vermiculite, $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$ Montmorillonite, $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ $^{\Diamond}$	7.0	15.94	75.54	99.8	3.69	53.0 ± 0.5	141.8
b 50.88596° N, 20.79231° E	silt loam	silt loam		6.4	19.98	72.59	105.7	3.75	65.7 ± 0.6	70.9
c 50.9226° N, 21.42749° E	silt loam	silty clay/clay		20.2	18.84	68.17	114.5	4.22	62.5 ± 0.5	425.4
d 50.9234° N, 21.42515° E	silt	clay		20.3	8.00	86.67	184.5	7.21	108 ± 0.9	283.6
e 50.97516° N, 21.25893° E	silt loam	silty clay		14.9	9.24	78.22	86.8	7.55	79.1 ± 0.4	354.5
f 51.06555° N, 21.08708° E	silt loam/silt	silty clay		18.5	12.91	83.44	138.8	6.72	127.7 ± 1.1	567.2

Notes: $^{\epsilon}$ letters (a–f) are conventional symbols for the different soil types. $^{\sigma}$ United States Department of Agriculture classification; $^{\pm}$ X-ray diffraction (XRD) in the Bragg–Brentano geometry (Table A2); $^{\Diamond}$ present only in soils e and f; § PI—plasticity index (it helps determine how the soil will behave under the influence of water—a higher PI indicates greater plasticity; PI = LL (liquid limit) − PL (plastic limit)) (PN-EN ISO 17892-12 [27]); * clay, silt, sand—laser diffraction method [28]; $^{\varepsilon}$ specific surface area of soil—the water vapor sorption test acc. to Stępkowska [29]; $^{\approx}$ acc. to ISO 10390:2021 [30]; ** concentration of chloride ions—Mohr method (PN-ISO 9297:1994) [31].

To simulate Zn and Cl^- contamination, $ZnCl_2$ (Chempur, Piekary Śląskie, Poland, CAS No. 7646–85-7) was added to each soil type at three molar concentrations (0.02, 0.05, and 0.08 mol·dm^{-3}). To minimize the risk of secondary contamination, sample preparation was carried out in a specific sequence—beginning with those containing the lowest concentration of metal chloride (0.02 mol·dm^{-3}) and concluding with those with the highest concentration (0.08 mol·dm^{-3}). Each soil type was analyzed in triplicate using analytical-grade reagents. The applied Zn concentrations reflect levels commonly found in contaminated soils [12,13]. $ZnCl_2$ was preferred over other chloride salts (e.g., $MgCl_2$, $CaCl_2$, NaCl) to isolate the specific effects of Zn on soil properties while minimizing interference from competing cations such as Mg, Ca, and Na [19].

Before contamination, soil samples were air-dried, ground, and passed through a 2 mm sieve. The volume of $ZnCl_2$ solution applied to each soil type was determined based on its SSA and plasticity characteristics (PI)—to ensure complete absorption and homogeneity. A detailed description of the experimental procedure is provided in Table A2.

The physicochemical properties of the soils after contamination were characterized (Table 2) according to the methodology outlined in the authors' previous work (Table A3) [17].

Table 2. Physicochemical properties of soils after contamination with $ZnCl_2$.

Type of Soil [€]	CLY *	SIL *	SA *	SSA [ε]	pH_{KCl}	OM [§]
	[%]			[$m^2 \cdot g^{-1}$]	[-]	[%]
a	17.70 ± 0.68	72.97 ± 3.04	9.33 ± 3.48	98.77 ± 3.77	3.56 ± 0.02	0.0 ± 0.0
b	18.58 ± 1.07	69.01 ± 0.82	12.41 ± 1.88	108.93 ± 0.80	3.68 ± 0.04	0.0 ± 0.0
c	21.20 ± 0.38	70.11 ± 1.61	8.69 ± 1.76	131.13 ± 7.51	4.22 ± 0.06	4.8 ± 0.0
d	14.05 ± 0.38	81.69 ± 0.29	4.27 ± 0.19	189.43 ± 6.04	6.42 ± 0.42	1.2 ± 0.0
e	11.42 ± 0.64	76.71 ± 0.36	11.87 ± 0.42	104.93 ± 10.49	7.34 ± 0.15	0.0 ± 0.0
f	14.87 ± 1.55	80.90 ± 1.19	4.23 ± 2.20	145.87 ± 9.37	6.21 ± 0.41	1.0 ± 0.0

Notes: [€] letters indicate soil types as classified in Table 1. The mean value for samples contaminated with 0.02, 0.05, and 0.08 mol·dm^{-3} $ZnCl_2$ was calculated ± standard deviation; * clay, silt, sand—laser diffraction method [28]; [ε] specific surface area of soil SSA—water sorption test method [29]; [§] organic matter—loss on ignition method (ASTM D 2974-87 (Method C)) [32].

2.2. Methods

2.2.1. Community Bureau of Reference (BCR) Procedure

The study was conducted using a modified three-step sequential extraction Tessier and Campbell procedure [33] as proposed and validated by the BCR (Community Bureau of Reference) [8], with a modification in the mineralization process of the residual fraction —specifically, aqua regia was used in accordance with the EN ISO 15587:2002 standard [34]. This method is widely used to assess the distribution of potentially toxic metals in contaminated soils [35,36]. A detailed description of the BCR procedure is provided in Table A4. The individual steps of the BCR extraction were carried out using appropriate chemical reagents:

- F_I—acid-soluble fraction—bound to carbonate (mobile fraction); 40 mL of 0.11 mol·dm^{-3} CH_3COOH (CAS No. 64-19-7) for 16 h at 22 °C ± 5 °C.
- F_{II}—reducible fraction—bound to Fe and Mn oxides (potentially mobile fraction); 40 mL of 0.5 mol·dm^{-3} NH_2OH-HCl (CAS No. 5470-11-1) added HNO_3 (CAS No. 7697-37-2) (pH = 2) for 16 h at 22 °C ± 5 °C.
- F_{III}—oxidizable fraction—bound to OM and sulfides (potentially stable fraction); 10 mL of 8.8 mol·dm^{-3} H_2O_2 (CAS No. 7722-84-1) at 85 °C (1 h) then 1 mol·dm^{-3} CH_3COONH_4 (CAS No. 631-61-8) adjusted to pH = 2 with concentrated HNO_3 (CAS No. 7697-37-2) for 16 h at 22 °C ± 5 °C.

- F_{IV}—residual—strongly associated with the crystalline structures of minerals (stable fraction); 25 mL of HNO_3-HCl (CAS Nos. 7697-37-2 and 7647-01-0) 3:1, aqua regia.

Based on the determinations, the metal stability index (I_r) was calculated using Equation (1).

$$I_r = \sum \frac{i^2 \cdot F_i}{k^2} \quad (1)$$

where i—the next step of sequential extraction; k = 4; F_i—percentage of metal in the i-th chemical form.

A separate analysis was performed to compare the results of the BCR sequential extraction (ΣF_I–F_{IV}) with those obtained via aqua regia digestion [34]. A blank sample served as a control. The methodology followed the procedures described by Larner et al. [37] and Rao et al. [38]. The extraction efficiency ranged from 95% to 105%, meeting the established quality control criteria.

2.2.2. Metal Concentration Analysis

The concentrations of Zn in the soils were measured using a Thermo Scientific ICE 3000 Series atomic absorption spectrometer (AAS) (Waltham, MA, USA). Before analysis, the instrument was calibrated with AAS elemental standards from AppliChem GmbH, traceable to certified reference materials from the National Institute of Standards and Technology (NIST). Calibration curves were constructed using standards of known concentrations [39], allowing for precise quantification of the target elements. This method is well-established and has been successfully applied in numerous previous studies [39,40].

2.2.3. Statistical Treatments

Statistical analyses were performed using Statistica 12 (StatSoft Inc., Tulsa, OK, USA). Data normality was assessed with the Kolmogorov–Smirnov test, and relationships between Zn fractions and soil properties were evaluated using Pearson's correlation. The correlation coefficient (R) was used to evaluate the strength and direction of relationships between variables, while the coefficient of determination (R^2) assessed the model's goodness of fit. To analyze the effect of the soil type on Zn distribution (mg·kg^{-1} d.m.) Analysis of Covariance (ANCOVA) was performed. A Dunnett post hoc test was used to compare treatment groups with the control. The mobile and stable Zn fractions were modeled using non-linear regression (NLR).

3. Results and Discussion

3.1. The Content of Zn in BCR Chemical Fractions in Soils Contaminated with $ZnCl_2$

Table 3 shows the proportion of the main metal (Zn) in each soil sample across the individual BCR chemical fractions.

Table 3. The content of Zn ions in BCR fractions depending on the soil type and molar concentration (M) of $ZnCl_2$ and Cl^-.

Type of Soil €	$ZnCl_2$	Cl^- *	Σ F_I–F_{IV} (Total Zn)	Zn Content in BCR Fraction				Potentially Mobile Fractions	Non-Mobile Fractions	I_r (Stability Index)
				F_I	F_{II}	F_{III}	F_{IV}			
	[mol·dm^{-3}]	[mg·kg^{-1}]	[mg·kg^{-1} d.m.]						[%]	
a	0.02	850.9	303.9 ± 2.6	98.5 ± 0.9	98.8 ± 0.9	28.1 ± 0.3	78.5 ± 0.7	64.92	35.08	0.41
a	0.05	1134.5	546.9 ± 8.5	157.2 ± 2.5	225.4 ± 3.5	53.8 ± 0.8	110.5 ± 1.7	69.94	30.06	0.38
a	0.08	1701.7	962.1 ± 4.6	477.6 ± 3.8	315.2 ± 2.5	65.3 ± 0.5	104.1 ± 0.8	82.39	17.61	0.26
b	0.02	709.1	306.5 ± 3.0	98.9 ± 1.8	86.8 ± 1.6	29.3 ± 0.5	91.6 ± 1.7	60.57	39.43	0.44
b	0.05	992.7	611.1 ± 4.4	210.6 ± 2.7	249.7 ± 3.2	56.3 ± 0.7	94.5 ± 1.3	75.33	24.67	0.33
b	0.08	1843.6	1087.8 ± 13.3	501.9 ± 10.2	398.7 ± 8.1	67.4 ± 1.4	119.7 ± 2.4	82.80	17.20	0.27

Table 3. *Cont.*

Type of Soil €	$ZnCl_2$	Cl^- *	Σ F_I–F_{IV} (Total Zn)	Zn Content in BCR Fraction				Potentially Mobile Fractions	Non-Mobile Fractions	I_r (Stability Index)
				F_I	F_{II}	F_{III}	F_{IV}			
	[mol·dm^{-3}]	[mg·kg^{-1}]	[mg·kg^{-1} d.m.]						[%]	
c	0.02	567.3	412.8 ± 3.3	113.0 ± 2.7	123.7 ± 2.9	61.7 ± 1.5	114.4 ± 2.7	57.35	42.65	0.45
c	0.05	1134.5	922.2 ± 7.6	372.1 ± 4.8	325.6 ± 4.5	91.4 ± 2.4	133.1 ± 2.9	75.66	24.34	0.31
c	0.08	1559.9	1538.1 ± 11.4	829.2 ± 8.4	449.8 ± 6.2	129.1 ± 3.3	129.9 ± 3.3	83.16	16.84	0.24
d	0.02	850.9	593.6 ± 5.1	132.6 ± 2.4	230.4 ± 3.2	101.4 ± 2.1	129.3 ± 2.4	61.14	38.86	0.42
d	0.05	1701.7	1102.0 ± 10.9	316.8 ± 5.8	422.0 ± 6.7	224.0 ± 4.9	139.2 ± 3.9	67.03	32.97	0.35
d	0.08	2552.6	2136.1 ± 13.5	813.9 ± 8.3	902.2 ± 8.8	273.9 ± 4.8	146.1 ± 3.5	80.34	19.66	0.27
e	0.02	921.8	543.3 ± 3.1	180.6 ± 1.8	214.0 ± 1.9	66.5 ± 1.1	82.3 ± 1.2	72.63	27.37	0.34
e	0.05	1985.4	1255.5 ± 7.9	768.6 ± 6.2	305.3 ± 3.9	62.8 ± 1.8	118.8 ± 2.4	85.53	14.47	0.22
e	0.08	2127.2	1972.7 ± 7.0	1006.2 ± 5.0	682.4 ± 4.1	153.2 ± 1.9	130.8 ± 1.8	85.60	14.40	0.23
f	0.02	850.9	571.6 ± 3.7	192.7 ± 2.1	224.9 ± 2.3	47.6 ± 1.1	106.3 ± 1.6	73.06	26.94	0.35
f	0.05	1418.1	1187.0 ± 15.6	435.3 ± 9.5	546.4 ± 10.5	89.6 ± 4.3	115.8 ± 4.9	82.70	17.30	0.28
f	0.08	2552.6	1745.2 ± 8.2	845.4 ± 5.7	684.1 ± 5.1	104.9 ± 2.0	110.8 ± 2.1	87.64	12.36	0.23

Notes: € letters indicate soil types as classified in Table 1; F_I—exchangeable and weak acid-soluble fraction. F_{II}—reducible fraction. F_{III}—oxidizable fraction. F_{IV}—residual fraction determined by BCR method using atomic absorption spectroscopy (AAS); potentially mobile fractions—sum of F_I and F_{II}; non-mobile fractions—sum of F_{III} and F_{IV}; I_r—stability index acc. to Formula (1); ± standard deviation; * concentration of chloride ions.

The results of ANCOVA showed that the molar concentration and soil type significantly affected the Zn content in various fractions, with the molar concentration influencing F_I–F_{III} (p = 0.000) and F_{IV} (p = 0.002), while the soil type had a significant effect on F_I (p = 0.011), F_{II}–F_{III} (p = 0.000), and F_{IV} (p = 0.004) (Table 4).

Table 4. Univariate tests of significance (ANCOVA) for the molar concentration of $ZnCl_2$ and soil type on the BCR fractions of Zn (F_I–F_{IV}) and post hoc Dunnett test.

Source Variation	Sum of Square (SS)	Degrees of Freedom (df)	Mean Square (MS)	Calculated F-Ratio	Sig. of Remark F (p-Value)	Post Hoc Dunnett
			F_I Zn [mg·kg^{-1} d.m.]			
Intercept	27,324	1	27,324	2.06961	0.178099	No significant difference when control group is d
Molar concentration $	1,115,075	1	1,115,075	84.46077	0.000002 *	
Type of soil §	336,920	5	67,384	5.10397	0.011538 *	
Error	145,225	11	13,202			
			F_{II} Zn [mg·kg^{-1} d.m.]			
Intercept	1324.4	1	1324.4	0.14769	0.708075	a—0.009156 *
Molar concentration	501,762.4	1	501,762.4	55.95531	0.000012 *	b—0.018342 *
Type of soil	242,229.8	5	48,446.0	5.40257	0.009442 *	c—0.060792 d—control group e—0.449451 f—0.989741
Error	98,639.2	11	8967.2			
			F_{III} Zn [mg·kg^{-1} d.m.]			
Intercept	3346.78	1	3346.78	4.10848	0.067606	a—0.000205 *
Molar concentration	17,581.53	1	17,581.53	21.58298	0.000710 *	b—0.000228 * c—0.003488 *
Type of soil	45,685.80	5	9137.16	11.21672	0.000505 *	d—control group e—0.003513 * f—0.001420 *
Error	8960.62	11	814.60			
			F_{IV} Zn [mg·kg^{-1} d.m.]			
Intercept	31,371.37	1	31,371.37	312.4328	0.000000	a—0.001807 *
Molar concentration	1612.86	1	1612.86	16.0628	0.002058 *	b—0.004075 * c—0.448952
Type of soil	3472.75	5	694.55	6.9172	0.003760 *	d—control group e—0.024031 * f—0.025788 *
Error	1104.51	11	100.41			

Notes: * results are statistically significant at the 0.05 level; $ zinc(II) chloride (0.02; 0.05; 0.08 mol·dm^{-3}). § acc. to Moreno-Maroto et al. [26] classification—6 types of soil acc. to Table 1. a,b—silt loam; c—silty clay/clay; d—clay; e,f—silty clay; modified 3-step BCR method [8]. F_I—exchangeable and poorly acid-soluble fractions. F_{II}—reduction fraction. F_{III}—oxidizable fraction. F_{IV}—residual fraction.

A Dunnett's post hoc test was performed (Table 4) to identify which soil types showed significant differences in Zn content across the F_I–F_{IV} fractions. The control group was clay (soil d), which had the highest SSA.

3.1.1. Mobile Fraction (F_I) of Zn

The post hoc analysis (Table 4) did not reveal significant differences in mobile Zn content between clay (soil d) and the other soil types (silty loams a, b, silty clays c–f), suggesting that the specific surface area (SSA) alone is not the sole determinant of mobile Zn in soils. When silt clay (soil e) was used as the control group in Dunnett's test, statistically significant differences in the F_I Zn content were found between soil e and soils a, b (Table 5).

Table 5. F_I-Zn dynamics and soil properties across soil types.

Soil Type [€]	Trend/Observation
Silt loams (a, b)	• Mobile Zn is lower (98.5 ± 0.9–501.9 ± 10.2 mg·kg^{-1} d.m.) compared to silt clay e, despite similar SSA (a = 99.8 m^2·g^{-1}; b = 105.7 m^2·g^{-1}; e = 86.8 m^2·g^{-1}). • Higher CLY (a = 15.94%, b = 19.98%) and lower total Zn concentrations (303.9 ± 2.6–1087.8 ± 13.3 mg·kg^{-1} d.m.), limit Zn mobility. • Dunnett's test shows significant differences with soil e (p = 0.004 (a); p = 0.007 (b)).
Silt clay (e)	• Mobile Zn is higher (180.6 ± 1.8–1006.2 ± 5.0 mg·kg^{-1} d.m.) due to lower CLY (10.93–12.15%) and higher total Zn concentrations (543.3 ± 3.1–1972.7 ± 7.0 mg·kg^{-1} d.m.). • SSA is low (86.8 m^2·g^{-1}), so SSA alone does not restrict mobility. • pH = 7.55 favors Zn immobilization.
Silty clay/clay (c, d, f)	• At lower total Zn (~413 mg·kg^{-1} d.m.), mobile Zn is low, similar to silt loams. • At higher Zn (>571 mg·kg^{-1} d.m.), higher SSA (c = 114, d = 184, f = 140 m^2·g^{-1}) reduces mobile Zn even when CLY is lower (c = 18.9%, d = 8%, f = 12.9%). • Total Zn and SSA together influence mobility.

Notes: [€] letters indicate soil types as classified in Table 1.

In summary, higher total Zn concentrations increase Zn mobility, potentially leading to a greater proportion of the mobile Zn fraction (F_I). However, Zn mobility is not dictated solely by the total content—physicochemical soil properties, such as CLY and SSA, are also key, with different soil types responding differently to these factors. In silt loams, higher CLY content results in lower F_I Zn values, whereas in clay and silty clay soils, increased SSA is associated with reduced Zn mobility. At high Zn concentrations, sorption sites can become partially saturated, leading to increased Zn mobility regardless of the CLY or SSA content.

Previous studies [22] have shown that the soil structure influences the Zn concentration in the soil solution, with sandy soils (CLY = 7%) having a lower sorption capacity and containing more active Zn forms compared to soils with a higher clay fraction (CLY = 13%). Moreover, the total Zn concentration and pH significantly affect Zn solubility. Our findings extend this knowledge by demonstrating the importance of the SSA and soil type in shaping these relationships. Additionally, while the pH significantly influenced the total Zn concentrations [17], its effect on F_I was less pronounced.

3.1.2. Potentially Mobile Fraction (F_{II}) of Zn

Silt loam soils (samples a and b) generally exhibited lower F_{II} Zn values compared to silty clay/clay soils (samples c–f) (Table 4). This trend is likely related to differences in the physical and chemical properties, such as the CLY, SSA, and total Zn, which influence the soil's capacity to retain or release Zn (Table 6).

Table 6. Summary of F_{II} Zn trends and key factors across soil types.

Soil Type [€]	Trend/Observation
Silt loams (a, b)	• Lowest total Zn (303.9 ± 2.6 mg·kg^{-1} d.m. and 306.5 ± 3.0 mg·kg^{-1} d.m.), limits the proportion of F_{II}. • Low SSA (99.8–105.7 m^2·g^{-1}) reduces the number of sorption sites. • CLY supports Zn retention—even with low SSA.
Silty clays/clay (c, d, f)	• F_{II} Zn increases (123.7 ± 2.9 → 902.2 ± 8.8 mg·kg^{-1} d.m) with total Zn (412.8 → 2136.1 mg·kg^{-1} d.m. across successive $ZnCl_2$ concentrations).
Silty clay (e)	• Despite the lowest SSA (86.8 m^2·g^{-1}) and high total Zn (543.3 → 1972.7 mg·kg^{-1} d.m.), F_{II} Zn is lower than expected (214.0 → 682.4 mg·kg^{-1} d.m.). • Higher pH (7.41) limits Zn mobility, reducing the proportion of F_{II}.

Notes: [€] letters indicate soil types as classified in Table 1.

The results (Tables 5 and 6) indicate that the main mechanisms determining the content of the F_I Zn and F_{II} Zn fractions are the following:

(1) Specific sorption reactions, primarily controlled by the Zn concentration and pH, which dominate in clay and silty clay soils.
(2) Nonspecific sorption via ion exchange, mainly occurring on clay mineral surfaces (related to CLY), and weakly influenced by the pH. In silt loam soils, both mechanisms appear to play important roles.

These findings are generally consistent with those of Mertens and Smolders [3], who reported that at Zn concentrations above 200 mg·kg^{-1} d.m., precipitation of secondary Zn minerals may occur. However, no clear evidence of such precipitation was observed in the present study. Therefore, specific and nonspecific sorption remain the primary processes controlling Zn mobility, with their relative importance depending on the soil type.

3.1.3. Potentially Stable Fraction (F_{III}) of Zn

The results of Dunnett's post hoc test (Table 4) indicate that the F_{III} Zn fraction content differs significantly in all analyzed soils compared to the control soil d, which had the highest SSA and nearly twice the F_{III} Zn content. This highlights the significant role of the SSA in affecting this fraction. Data in Tables 1 and 3 show a clear increasing trend in F_{III} Zn with both the SSA and total Zn concentration. The statistical significance of these relationships is supported by the correlation coefficients: F_{III} Zn with the total Zn (R = 0.74) and F_{III} Zn with the SSA (R = 0.77). Although the relationship appears linear, more detailed analysis shows that the mechanisms governing Zn retention in the F_{III} form are complex and influenced by multiple factors simultaneously (Table 7).

In clay soils, a higher SSA and total Zn content enhance F_{III} Zn binding. In silty clays, the pH, CLY, and OM also contribute to Zn retention alongside the SSA. In silt loams, even with a low SSA, F_{III} Zn increases with the total Zn, indicating sorption on clay particles.

Table 7. Observed trends in F_{III} Zn fraction in relation to soil types and physicochemical parameters.

Soil Type [€]	Trend/Observation
Silt loams (a, b)	• The F_{III} Zn content increased with total Zn (from 303.9 ± 2.6 to 1087.8 ± 13.3 mg·kg^{-1} d.m.) and the SSA. • Despite the relatively low SSA (99.8–105.7 m^2·g^{-1}), Zn was likely retained on CLY. • The SSA did not change significantly with increasing Zn concentrations (0.02–0.05–0.08 M).

Table 7. *Cont.*

Soil Type [€]	Trend/Observation
Silty clays/clay (c, e, f)	• The F_{III} Zn content was not determined solely by the SSA and total Zn concentration. • Soil e, with the lowest SSA (86.8 $m^2 \cdot g^{-1}$) and the highest total Zn (1972.7 ± 7.0 $mg \cdot kg^{-1}$ d.m.), had the highest F_{III} Zn (153.2 ± 1.9 $mg \cdot kg^{-1}$ d.m.), likely due to its elevated pH (7.55) promoting Zn immobilization. • Soil c (F_{III} Zn = 129.1 ± 3.3 $mg \cdot kg^{-1}$ d.m.) contained more F_{III} Zn than soil f (104.9 ± 2.0 $mg \cdot kg^{-1}$ d.m.) despite its lower SSA (114.5 vs. 138.8 $m^2 \cdot g^{-1}$) and lower total Zn (1538.1 vs. 1745.2 $mg \cdot kg^{-1}$ d.m.), probably due to higher OM (4.8% vs. 1%), higher CLY content (19% vs. 13%), and lower pH (4.2 vs. 6.7).
Clay (d)	• The F_{III} Zn content increased with the total Zn (from 593.6 ± 5.1 to 2136.1 ± 13.5 $mg \cdot kg^{-1}$ d.m.) and SSA (from 184.5 $m^2 \cdot g^{-1}$ before saturation to 196.4 $m^2 \cdot g^{-1}$ after $ZnCl_2$ 0.08 $mol \cdot dm^{-1}$ saturation). • Zn in this soil was primarily bound by the SSA, which directly enhanced the retention capacity of the fraction.

Notes: [€] letters indicate soil types as classified in Table 1.

3.1.4. Stable Fraction (F_{IV}) of Zn

The stable Zn fraction (F_{IV}) is mainly controlled by the total Zn concentration and the SSA (Tables 2 and 3). The F_{IV} content generally increases with the increasing Zn concentration and SSA. At lower Zn concentrations (306.5 ± 3.0 to 593.6 ± 5.1 $mg \cdot kg^{-1}$ d.m.), this increase shows a strong correlation with the SSA (R = 0.92). At higher Zn concentrations, the upward trend persists; however, a lower correlation coefficient indicates that additional factors, such as CLY and pH, may also contribute to predicting the F_{IV} content. In most of the studied soils (a,c–f), the CLY content increased following $ZnCl_2$ saturation, regardless of its concentration in the range of 0.02–0.08 M, compared to the initial soil.

Soil type also proved to be a statistically significant factor ($p < 0.05$; Table 4). Post hoc tests revealed significant differences in the F_{IV} fraction content between silt loam soils (a, b) and silty clay soils (e,f) compared to clay (d), while no significant differences were observed between clay (d) and clay/silty clay (c) soils. The analysis of the data presented in Tables 1–4 enabled the identification of the trends in fraction IV changes depending on the soil type, which are summarized in Table 8.

Zn retention in F_{IV} follows the same sorption-based mechanisms as F_I–F_{III}, but is reinforced by a high SSA, CLY, and pH, resulting in the strongest immobilization. Previous studies by Nartowska et al. [17] also emphasized the importance of these parameters in assessing environmental risk in soils contaminated with $ZnCl_2$. As the Zn concentrations increased (up to approximately 2000 $mg \cdot kg^{-1}$ d.m.), a general upward trend in the F_{IV} Zn content was observed, although the intensity of this trend varied depending on the soil properties. The highest F_{IV} Zn values (above 130 $mg \cdot kg^{-1}$ d.m.) were observed in clay (d) and silty clay/clay (c) soils—associated with the highest SSA (184.5 $m^2 \cdot g^{-1}$ in soil "d") and high CLY (18.84%) and OM (4.8%) content in soil c. In silt loam soils, an increase in F_{IV} was also observed, even with a constant or decreasing SSA, indicating the significant role of CLY (~18–20%) in Zn retention as also confirmed by the findings of Hanif et al. [41]. In silty clay soils (e, f), F_{IV} increased with the rising Zn concentration and SSA; however, in soil f, a decrease in F_{IV} was observed at the highest Zn concentration, which may be attributed to a reduction in the CLY content and lower pH.

The main trends in the contents of Zn fractions I–IV are summarized in Figure 1.

Table 8. F_{IV} Zn dynamics and soil properties across soil types under increasing Zn levels.

Soil Type [€]	Trend/Observation
Silt loams (a, b)	• F_{IV} Zn increases with rising Zn concentrations, from 78.5 ± 0.7 to 104.1 ± 0.8 mg·kg^{-1} d.m. in soil a and from 94.5 ± 1.3 to 119.7 ± 2.4 mg·kg^{-1} d.m. in soil b. • The SSA decreases slightly in soil a (103 > 97.5 m^2·g^{-1}) and remains constant in soil b (109.5 m^2·g^{-1}). • CLY remains high (~18–20%), likely supporting Zn retention.
Silty clays (e, f)	• F_{IV} Zn generally increases with the Zn concentration and SSA. • In soil e, F_{IV} Zn rises from 82.3 ± 1.2 to 130.8 ± 1.8 mg·kg^{-1} d.m., the SSA increases from 96.9 to 116.8 m^2·g^{-1}, and CLY slightly decreases (12.15 > 11.19%). • In soil f, F_{IV} Zn increases from 106.3 ± 1.6 to 115.8 ± 4.9 mg·kg^{-1} d.m. but slightly decreases to 110.8 ± 2.1 mg·kg^{-1} d.m. at the highest Zn, while the SSA continues increasing (136.2 < 154.9 m^2·g^{-1}) and CLY decreases (14.96 > 13.28%). • The decrease in CLY in soil f limits the further increase in F_{IV} Zn, despite the rising SSA and Zn concentrations. • Soil pH varies (6.72(f)–7.55(e)), influencing Zn immobilization through enhanced sorption onto mineral surfaces.
Clay (d) and silty clay/clay (c)	• F_{IV} Zn remains high across all $ZnCl_2$ treatments (0.02–0.08 mol·dm^{-3}). • In soil d, this is primarily due to very high SSA (184.5 m^2·g^{-1}). • In soil c, moderate SSA (114.5 m^2·g^{-1}) is compensated by high CLY (18.84%) and OM (4.8%). • These properties collectively support strong Zn retention.

Notes: [€] letters indicate soil types as classified in Table 1.

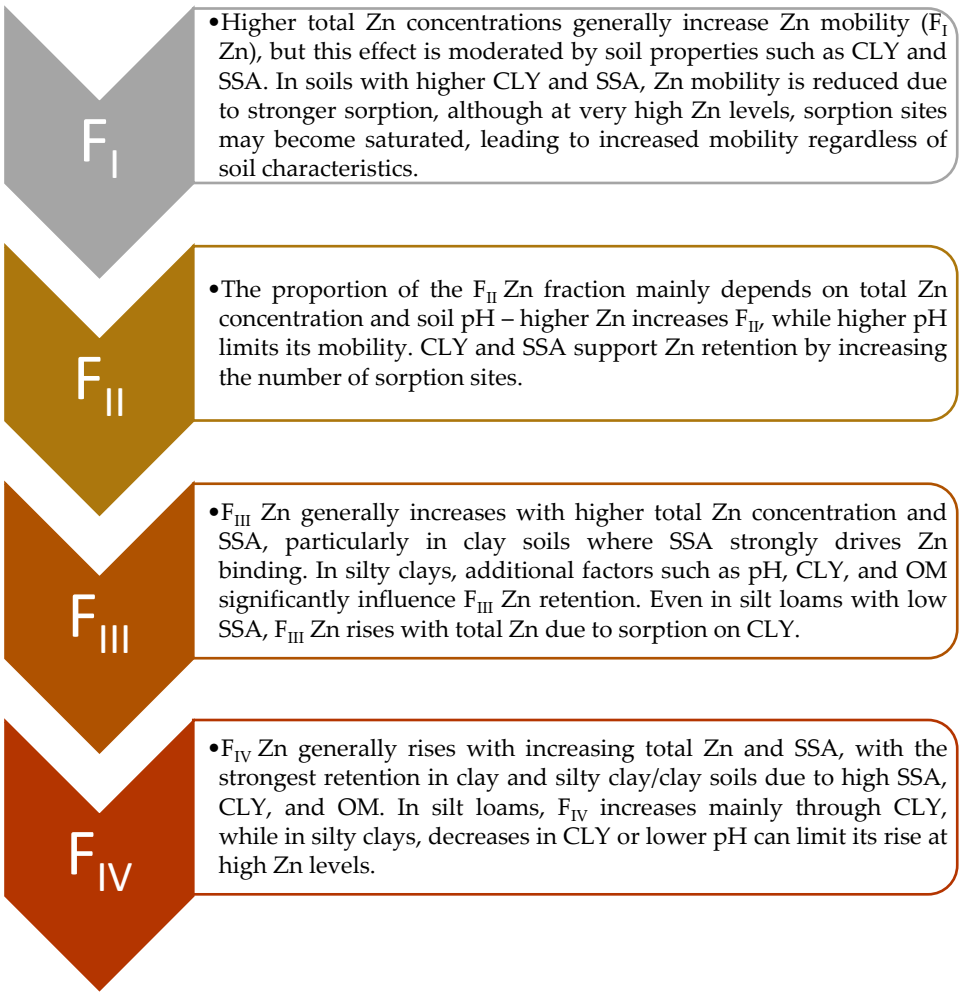


Figure 1. Main trends in soil Zn fraction distribution (I–IV).

3.2. The Effect of Chloride Ions

The Cl^- ion is among the most prevalent anions in salinized soils. It exhibits limited affinity for binding to the soil solid phase and can significantly influence the mobility of Zn [15]. The mobility of Zn increases with rising Cl^- concentrations, and these changes are statistically significant. Regression analysis of the dependent variable F_I Zn + F_{II} Zn and Cl^- yielded R = 0.79 ($p < 0.05$) (Table 9).

Table 9. Regression analysis of the total concentration of Zn and Cl^- and the proportion of potentially mobile (F_I + F_{II}) fractions of this metal in soils to total sum of fractions.

	The Standardized Beta (ß)	Std. Error ß	The Unstandardized Beta (B)	Std. Error B	*t* Test Value	*p*-Value	Significance
Independent variable: Zn total							
Dependent variable: F_I Zn + F_{II} Zn							
R = 0.79 R^2 = 0.59 adj. R^2 = 0.57 Std. error of estimate: 6.32							
Intercept			61.96	3.06	20.21	0.000	
Zn total	0.77	0.16	0.01	0.00	4.82	0.000	***
Independent variable: Cl^- concentration							
Dependent variable: F_I Zn + F_{II} Zn							
R = 0.79 R^2 = 0.63 adj. R^2 = 0.61 Std. error of estimate: 6.00							
Intercept			57.49	3.61	15.93	0.000	
Cl	0.79	0.15	0.01	0.00	5.24	0.000	***

Notes: N = 18, significant at the *** 0.001 level; F_{I+II} (%).

This increase may be attributed to several mechanisms, including (1) the formation of soluble Zn–Cl^- complexes, which reduce the metal's affinity for the solid phase and enhance its presence in the soil solution [41]. Additionally, (2) ion exchange processes between Zn ions introduced with salts and those already bound to soil colloids may promote Zn desorption, particularly when competing cations are displaced [19,42]. (3) The Cl^- ion can also indirectly influence Zn mobility by altering key soil physicochemical parameters—such as lowering the pH, increasing the ionic strength, and modifying the redox potential—which, in turn, affect the binding capacity of soil constituents such as clay minerals and organic matter [17,43]. These effects collectively enhance Zn mobility under saline conditions.

Despite this, both the proportion of potentially mobile Zn fractions (F_I and F_{II}) and the more stable fractions (F_{III} and F_{IV}) appear to be more strongly influenced by the total Zn concentration than by Cl^-. Linear relationships between the total concentrations of Zn and Cl^- in soils and their distribution among the BCR chemical fractions showed varying degrees of fit (R^2) (Figures 2 and A1).

Strong correlations were observed for Total Zn vs. F_I Zn (R^2 = 0.90) and F_{II} Zn (R^2 = 0.91), and for Cl^- vs. F_I Zn (R^2 = 0.79) and F_{II} Zn (R^2 = 0.78). Weaker correlations were found for the more stable fractions: Total Zn vs. F_{III} Zn (R^2 = 0.55) and F_{IV} Zn (R^2 = 0.45); Cl^- vs. F_{III} Zn (R^2 = 0.41) and F_{IV} Zn (R^2 = 0.28) (Figure 2).

The stronger correlations of Zn with Cl^- in fractions F_I and F_{II}, compared to F_{III} and F_{IV}, can be explained by the fact that salinity enhances Zn mobility primarily through the formation of soluble Zn–Cl^- complexes [19]. In contrast, Cl^- has a limited effect on strongly bound forms of Zn—specifically, Zn associated with Fe and Mn oxides (F_{III}) and Zn structurally incorporated into mineral matrices (F_{IV}). These forms exhibit very low mobility, as they are not readily subject to desorption, dissolution, or ion exchange processes.

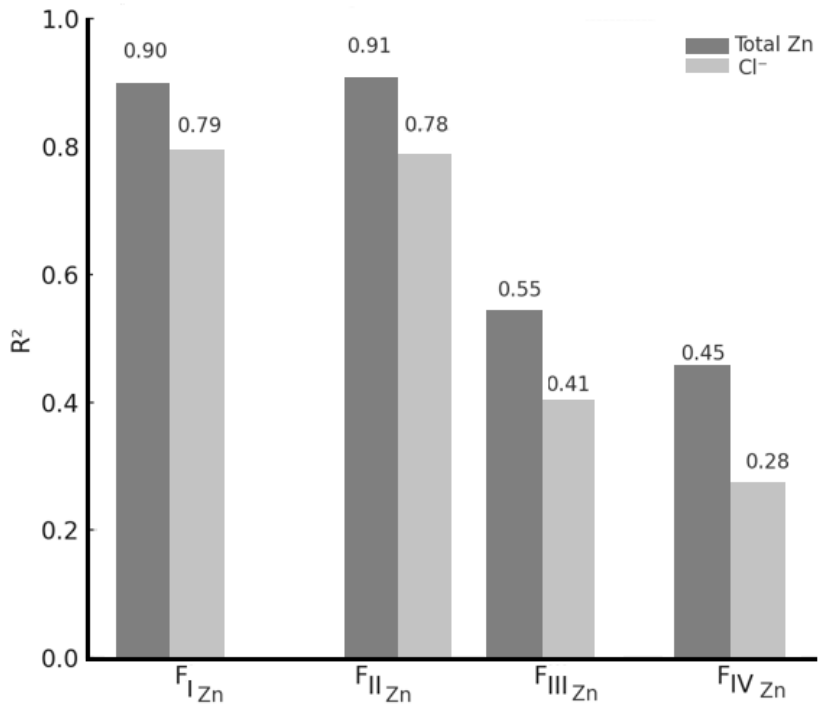


Figure 2. Correlation (R^2) between Cl^- concentrations, Total Zn, and Zn BCR fractions ($F_{I–IV}$) ($mg \cdot kg^{-1}$ d.m.) in saline soils.

The effect of Cl^- on Zn mobility in soils contaminated with $ZnCl_2$ turned out to be weaker than initially expected, which can be explained by several factors.

Firstly, the total Zn content in the soil determines the number of Zn ions that are actually available for interactions with mineral surfaces, participation in ion exchange processes, or complexation with OM and Cl^- anions. Therefore, the total Zn concentration is the main factor controlling the mobility of this metal. Previous studies [17] also indicated that changes in soil physicochemical properties, such as the SSA and CLY, induced by $ZnCl_2$ contamination, explain Zn behavior in the soil system to a greater extent than the presence of Cl^-. This is due to the fact that Zn has a much higher affinity for the solid phase than Cl^-, which directly affects the sorption–desorption balance. This interpretation is supported by our results, which show weak correlations between the Cl^- concentration and Zn content in the more stable fractions (F_{III} and F_{IV}, Figure 2), suggesting a limited role of Cl^- in controlling Zn mobility in these fractions.

Secondly, the weaker-than-expected effect of Cl^- is also related to the presence of other cations in the soil environment (Table A1), which compete with Zn for sorption sites on clay minerals and for the ability to form complexes with Cl^-. According to Acosta et al. [19], Zn mobility was primarily controlled by Ca, and to a lesser extent by Mg and Na, which significantly limited the role of Zn–Cl^- complexes in determining Zn mobility. Similarly, Nartowska et al. [17] reported that Cl^- also competes with other potentially toxic metals (e.g., Cu, Ni), whose concentrations increase due to their displacement from sorption complexes by large amounts of Zn introduced in the form of $ZnCl_2$. Such multi-ion competition further reduces the contribution of Cl^- to Zn mobility.

The main conclusion is that the total Zn content in soil, rather than changes in the Cl^- concentration, primarily controls Zn migration, ion competition, the soil's ability to retain the metal, and Zn distribution among BCR fractions. Therefore, analyzing the soil's physicochemical parameters is essential for understanding the factors influencing Zn behavior and its interactions in contaminated soils.

3.3. Prediction of Mobile, Potentially Mobile, and Stable Fractions of Zn Using Empirical Equations

The results suggest complex mechanisms that require a non-linear approach to fully understand the causes of the observed variability in Zn fractions. In this research, as well as in previous studies [17], using multivariate techniques (factor analysis), CLY, SSA, Zn, and Cl^- were identified as among the most important factors influencing the behavior of soils contaminated with $ZnCl_2$. These observed relationships formed the basis for developing empirical equations applicable in engineering practice, enabling the estimation of the proportion of individual BCR fractions—an aspect of significant importance for environmental risk assessment and for designing interventions aimed at improving soil quality.

Analogous to the models proposed for soils contaminated with copper(II) chloride [44,45], new prediction models for the Zn content in the mobile fraction (F_I) (2), potentially mobile fraction (F_{II}) (3), and potentially stable and stable fraction ($F_{III} + F_{IV}$) (2a) were estimated based on the total Zn concentration and the soil's SSA or CLY.

$$\log(F_I Zn) = a \cdot \log(totalZn) + b \cdot \log(SSA) \quad (2)$$

where a, b—empirical parameters, a = 1.42065, b = −0.78789. Notes: F_I—mobile BCR fraction; SSA (soil's specific surface area—water sorption test).

$$\log(F_{III} Zn + F_{IV} Zn) = a \cdot \log(totalZn) + b \cdot \log(SSA) \quad (2a)$$

where a, b—empirical parameters, a = 0.328471, b = 0.634608. Notes: F_{III+IV}—potentially stable BCR fraction, SSA (soil's specific surface area—water sorption test).

$$\log(F_{II} Zn) = a \cdot \log(totalZn) + b \cdot \log(CLY) \quad (3)$$

where a, b—empirical parameters, a = 0.96568; b = −0.28969. Notes: F_{II}—potentially mobile BCR fraction; CLY (clay fraction—laser diffraction method).

Table 10 presents the model estimation parameters, and Figure 3 illustrates the relationships between the actual Zn contents and the Zn contents predicted by the models.

Table 10. Parameter estimates and overall characteristics of the models given by Equations (2), (2a) and (3).

Parameter	Estimate	Standard Error	*t*-Statistic	*p*-Value	Confidence Limits	
					Lower	Upper
Model according to Equation (2) F_I Zn						
a	1.42065	0.05736	24.76836	0.00000 **	1.29906	1.54224
b	−0.78789	0.08002	−9.84663	0.00000 **	−0.95753	−0.61827
Model according to Equation (2a) F_{III} Zn + F_{IV} Zn						
a	0.328471	0.064656	5.080275	0.000111 **	0.191406	0.465536
b	0.634608	0.090199	7.035655	0.000003 **	0.443395	0.825821
Model according to Equation (3) F_{II} Zn						
a	0.96568	0.04479	21.55821	0.00000 **	0.87072	1.06064
b	−0.28969	0.10902	−2.65720	0.01721 *	−0.52081	−0.05858

Notes: ** Statistically significant at $p < 0.001$; * statistically significant at $p < 0.05$. For Equation (2), $R = 0.98$; $n = 18$ and standard errors of the estimate (SEEs) F_I Zn = 59.48 mg·kg^{-1} d.m. For Equation (2a), $R = 0.915$; $n = 36$ and standard errors of the estimate (SEEs) F_{III} + F_{IV} Zn = 35.42 mg·kg^{-1} d.m. For Equation (3), $R = 0.95$; $n = 18$ and standard errors of the estimate (SEEs) F_{II} Zn = 69.02 mg·kg^{-1} d.m.

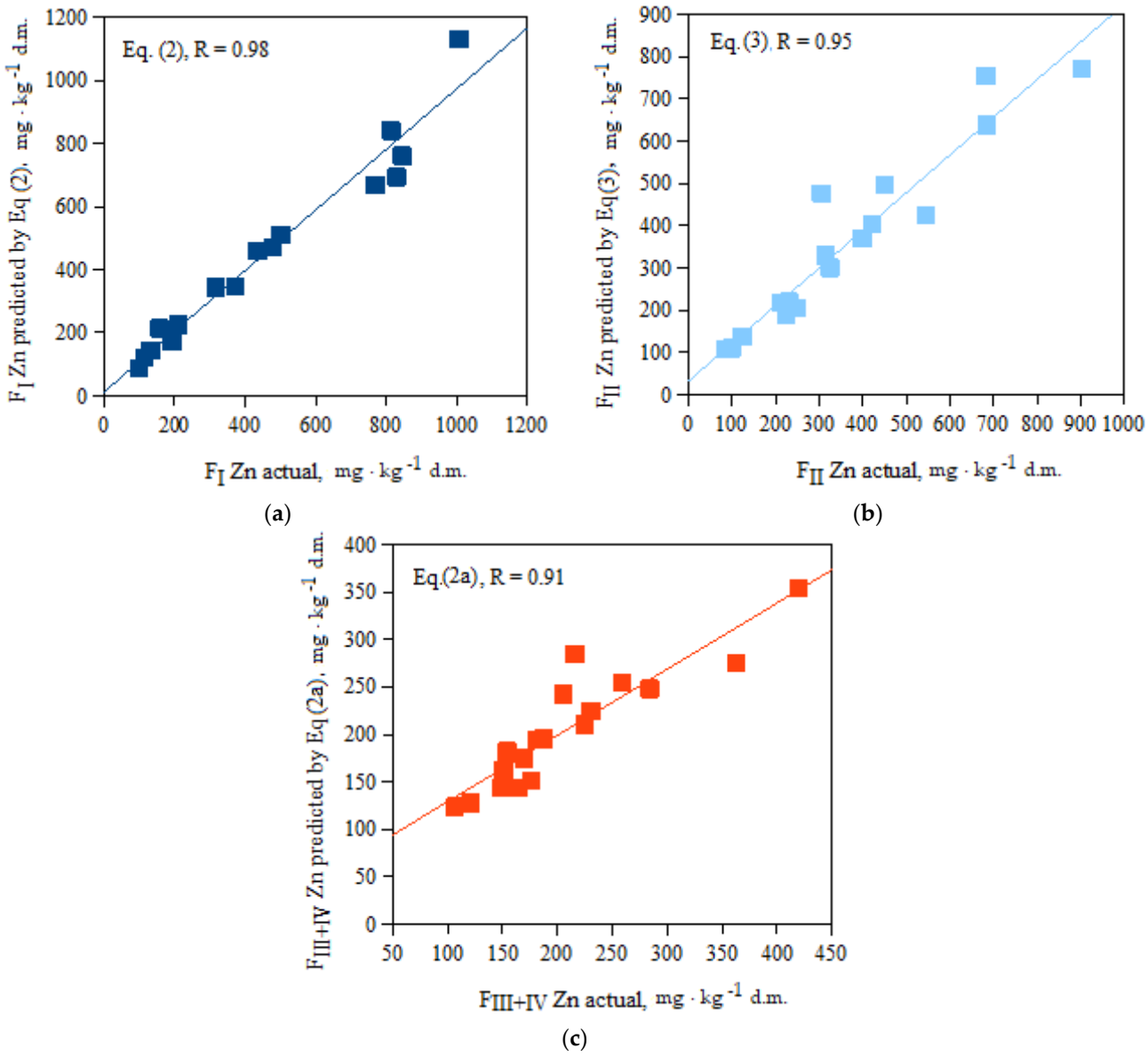


Figure 3. Agreement plot among actual and predicted BCR Zn fraction: (**a**) F_I Zn acc. to Equation (2); (**b**) F_{II} Zn acc. to Equation (3); (**c**) F_{III} + F_{IV} Zn acc. to Equation (2a). Notes: F_I acc. to modified Tessier and Campbell 3-step BCR method [33] with a modification in the mineralization process of the residual fraction (aqua regia—in accordance with the EN ISO 15587:2002 standard [34]). F_I—exchangeable and poorly acid-soluble fractions (mobile); F_{II}—reduction fraction (potentially mobile); F_{III}—oxidizable fraction (potentially stable); F_{IV}—residual fraction (stable).

The developed models (2), (2a) and (3) effectively predict Zn fractionation (R = 0.92–0.98), as confirmed by their close agreement with the observed empirical data (Table 10, Figure 3).

In the empirical models (2) and (3), soil SSA was selected as the physical parameter and was determined using the water vapor sorption test (WST). The standard BET-N_2 method may not capture changes in the surface area in soils where metal ions, e.g., Zn, accumulate within interlayer spaces of clay minerals, nor does it account for micropores accessible to water [5]. In contrast, the WST method measures the surface area available to water, which better reflects natural soil–water conditions and enables a more accurate assessment of metal ion availability and fractionation [5,17]. A direct conversion of the WST results into BET values is difficult, as these methods are based on different measurement principles and often yield different absolute values. Although attempts at comparison have

been reported in the literature [5], no universal conversion factors have been established. Therefore, in our models, we deliberately emphasized the use of the SSA determined by the WST as the parameter most appropriate for assessing metal mobility in soils.

The developed models are empirical and rely on a minimal number of parameters, which enhances their simplicity and practical applicability. Their main limitation, however, is the exclusion of the pH and organic matter, which in other soil systems may substantially influence Zn mobility. Importantly, within the range of physicochemical conditions examined, the models performed very well and provided reliable predictions of Zn fractions. In the soils examined, contaminated with $ZnCl_2$ (Zn 304–2136 $mg \cdot kg^{-1}$ d.m.; Cl^- 567–2552 $mg \cdot kg^{-1}$; pH 3.5–7.5; CLY 11–22%; SSA 96–196 $m^2 \cdot g^{-1}$; OM 0–4.8%), the effect of these factors was limited as follows: increases in the total Zn did not cause statistically significant changes in the pH, the F_I Zn–pH correlation was weak ($R^2 = 0.11$), and the contribution of OM in low-organic soils was negligible. Therefore, their omission did not compromise the model's predictive performance. Nevertheless, when extrapolating the model to other soil types—particularly those richer in OM or with different pH ranges—this limitation should be carefully considered.

The results of this study indicate that the mobility and stability of zinc in soils contaminated with zinc(II) chloride depend not only on the total amount of the metal but also on fundamental soil properties such as the texture, specific surface area, organic matter content, and pH. This knowledge is of considerable importance for land management and environmental protection, enabling the development of targeted remediation strategies and the prevention of further contamination of groundwater and crops. The predictive approach developed in this work can be adapted to other metals and contamination scenarios, providing a practical tool for anticipating long-term environmental risks and supporting sustainable land use policies.

4. Conclusions

Considering the complex interactions between $ZnCl_2$ contamination and soil properties, this study uses the modified Community Bureau of Reference (BCR) sequential extraction to show the following:

1. Zinc mobility depends on the total Zn concentration and soil properties. Mobile Zn forms (F_I and F_{II}) are governed by physicochemical and exchangeable sorption, with a high specific surface area (SSA) in silty clay and clay soils limiting mobility, while the clay content (CLY) enhances sorption in silt loam soils.
2. Stable Zn forms (fractions F_{III} and F_{IV}) are stabilized through specific sorption, complexation with organic matter (OM), and favorable pH conditions. In clay soils, the SSA is critical for Zn retention in less mobile forms, while in silty clay and silt loam soils, the combined effects of the SSA, pH, CLY, and OM further enhance stabilization.
3. The influence of Cl^- ions on Zn mobility is noticeable but weaker than the effect of the total Zn concentration and soil physicochemical properties. Its impact is mainly limited to fractions F_I and F_{II}, potentially facilitating Zn transport through soluble complex formation.
4. Regression models using the total Zn, SSA, and CLY accurately predict the Zn BCR fractions ($R = 0.92–0.98$) and are useful for assessing retention across soils.
5. Practical implications: Management of $ZnCl_2$-contaminated soils should focus on maintaining a high SSA and favorable pH in clays, and increasing CLY in silt loams, to enhance Zn sorption and stabilization.
6. Future studies should explore interactions with other ions and extend predictive models to more metals and soil conditions.

Author Contributions: Conceptualization, E.N.; methodology, E.N. and A.P.; software, E.N.; validation, E.N. and A.P., formal analysis, E.N.; investigation, E.N., A.P., and L.K.; resources, E.N. and E.K.; data curation, E.N. and M.D.V.; writing—original draft preparation, E.N.; writing—review and editing, E.N., A.P., E.K., M.D.V., and L.K.; visualization, E.N. and M.D.V.; supervision, E.N.; project administration, E.K. and E.N.; funding acquisition, E.K. and E.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Faculty of Environmental Engineering, Geomatics, and Renewable Energy of the Kielce University of Technology No. 05.0.12.00/1.02.001/SUBB.IKGT.25.002. The APC received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article/Appendix A. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

Zn	Zinc
Cl^-	Chloride ion concentration
SSA	Specific surface area of soil
CLY	Clay fraction ($d \leq 0.002$ mm)
SIL	Silt fraction (0.002 mm $< d \leq 0.063$)
SA	Sand fraction (0.063 mm $< d \leq 2.00$ mm)
OM	Organic matter
BCR	Community Bureau of Reference-extracted fractions
AAS	Atomic absorption spectrometry
ANCOVA	Analysis of Covariance
NLR	Non-linear regression

Appendix A

Table A1. Chemical and physical characteristics of soils prior to modification with $ZnCl_2$.

Type of Soil *	Ca &	Mg &	Na &	K &	Cu &	Ni &	Pb &	SA **	OM §
	[mg·kg^{-1} d.m.]							[%]	
a	15.1 ± 0.1	20.2 ± 0.1	21.5 ± 0.2	11.3 ± 0.1	8.1 ± 0.1	13.4 ± 0.1	3.7 ± 0.0	8.52	0
b	55.0 ± 0.5	19.3 ± 0.1	8.9 ± 0.1	14.0 ± 0.1	6.8 ± 0.1	8.6 ± 0.1	3.8 ± 0.0	7.43	0
c	90.4 ± 0.7	59.9 ± 0.4	6.7 ± 0.1	32.9 ± 0.3	8.2 ± 0.1	13.6 ± 0.1	6.3 ± 0.1	12.99	4.80
d	53.6 ± 0.4	8.1 ± 0.1	21.9 ± 0.1	70.9 ± 0.5	10.9 ± 0.1	14.1 ± 0.1	8.9 ± 0.1	5.33	1.20
e	67.94 ± 0.6	41.2 ± 0.3	6.5 ± 0.1	28.5 ± 0.2	6.5 ± 0.0	8.0 ± 0.1	4.8 ± 0.0	12.54	0
f	141.8 ± 1.2	56.8 ± 0.3	7.7 ± 0.1	17.9 ± 0.1	7.5 ± 0.1	12.6 ± 0.1	5.5 ± 0.1	3.65	1.00

Notes: * depending on the geographical location as classified in Table 1; & AAS method, limit of detection 0.01 mg·L^{-1}, ±SD (Standard deviation); ** sand—laser diffraction method; § organic matter—loss on ignition method at 440 ± 10 °C (ASTM D 2974-87 (Method C)) [32].

Table A2. Characteristics of the research material and description of the experimental procedure.

Type of Soil [€]	No. Soil	Sampling Depth [m]	w * [%]	LL ** [%]	PL ** [%]	m [$] [g]	$ZnCl_2$ [mL]	M [±] [mol·dm^{-3}]
a	1	0.7	19.1	23.3	16.3	120	25	0.02
	2							0.05
	3							0.08
b	4	0.7	16.2	20.8	14.4	120	25	0.02
	5							0.05
	6							0.08
c	7	1.5	15.0	40.4	20.2	100	30	0.02
	8							0.05
	9							0.08
d	10	1.5	25.5	39.9	19.3	90	35	0.02
	11							0.05
	12							0.08
e	13	1.5	29.8	30.8	15.9	70	25	0.02
	14							0.05
	15							0.08
f	16	0.7	38.8	39.0	20.5	90	30	0.02
	17							0.05
	18							0.08

Notes: * the natural moisture content defined as the mass of water to the mass of the soil skeleton (dried at 105 °C); ** LL—liquid limits (it is the moisture content at which the soil stops being plastic and begins to exhibit liquid properties); PL—plastic limits (the lowest moisture content at which the soil retains its plastic properties); [$] mass of air-dry soil used in the experimental procedure; [±] molar concentration of $ZnCl_2$ solution. [€] letters indicate soil types as classified in Table 1.

Table A3. Methods used to determine the physicochemical and mineralogical properties of soils.

Parameters	Methods
SSA	Water vapor sorption was measured following the method of Stępkowska [29]. About 3 g of soil (dried at 105 °C for 24 h) was placed in a desiccator over a saturated $Mg(NO_3)_2$ solution and equilibrated for 10 days. After sorption, the samples were dried at 220 °C for 24 h, and sorption moisture at $p/p_0 = 0.5$ (w_{50}) was determined. The specific surface area (SSA) was then calculated using the formula: $SSA = 6 \cdot (w_{50} \cdot 5.85)$.
pH_{KCl}	Soil pH was determined potentiometrically using a CPR-411 multifunctional meter (Elmetron, Zabrze, Poland) at 21 °C. A 1:5 (m:v) soil suspension in 1 mol·dm^{-3} KCl was prepared according to ISO 10390:2021 [30].
OM	Soil organic matter was determined by the loss on ignition method at 440 ± 10 °C, following ASTM D2974-87 (Method C) [32], using ~5 g of soil previously dried at 105 °C.
Cl^-	Chloride content was determined by the Mohr method (PN-ISO 9297:1994) [31]. Soil samples (2 g) were shaken for 24 h in 20 mL of distilled water (conductivity 0.06 µS·cm^{-1}) and then filtered through Whatman paper to obtain a clear extract.
CLY, SIL, SA	Particle size distribution was analyzed using the laser diffraction method with a HELOS/BF SUCELL (Sympatec GmbH, Clausthal-Zellerfeld, Germany) equipped with a wet dispersion unit. Soil paste (3 g) was dispersed in 50 mL of distilled water, and sample concentration in the test chamber was kept below 25%.
Plasticity parameters	Plasticity characteristics were determined according to EN ISO/TS 17892-12 [27] using Casagrande's cup for the liquid limit (LL) and the rolling test for the plastic limit (PL). The plasticity index (PI) was calculated as PI = LL − PL.
Mineralogical composition	X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer with a Johansson-type monochromator (CuKα1 radiation, λ = 1.5406 Å) and a LynxEye detector. Scans were collected over 4.51–70° 2θ with 0.02° steps at 3.54 kV and 530 mA. Mineral phases were identified using the PDF-4+ database (ICDD, Newtown Square, PA, USA).

Table A4. Modified four-step BCR procedure.

Fractionation	Solution
Step 1—extraction of exchangeable and/or carbonate-bound metals (exchangeable and poorly acid-soluble fraction (mobile fraction)—F_I).	A 2 g dry soil sample was mixed with 40 cm^3 of 0.11 $mol \cdot dm^{-3}$ CH_3COOH (CAS 64-19-7) in a 100 cm^3 rotary tube and shaken for 16 h at 22 °C. The extract was separated by centrifugation (10 min, 4000 rpm), and the content of the most mobile metals, adsorbed on soil surfaces and bound to carbonates, was determined.
Step 2—extraction of metals that are combinations of metals with amorphous Fe and Mn oxides (reduction fraction (potentially mobile fraction)—F_{II}).	Soil samples were treated with 40 cm^3 of 0.5 $mol \cdot dm^{-3}$ $NH_2OH \cdot HCl$ (CAS 5470-11-1, pH 2), with HNO_3 (CAS 7697-37-2) used to adjust the pH. The samples were shaken and centrifuged as in step one, and metals of fraction II, considered partially mobile, were determined in the extract.
Step 3—extraction of metals bound to organic matter and sulfides (oxidizable fraction (potentially stable fraction)—F_{III}).	The soil residues from step 2 were treated with 10 cm^3 of 8.8 $mol \cdot dm^{-3}$ H_2O_2 (CAS 7722-84-1) and heated in a water bath at 85 °C until evaporation. The cooled samples were then mixed with 50 cm^3 of 1 $mol \cdot dm^{-3}$ CH_3COONH_4 (CAS 631-61-8, pH 2 after HNO_3 correction, CAS 7697-37-2), shaken for 16 h, and centrifuged. Metals of fraction III, considered immobile, were determined in the extract.
Step 4—extraction involving the metal binding to primary and secondary minerals (residual fraction (stable fraction)—F_{IV}).	The remaining soil sediment was dried at 105–110 °C to constant weight. A 1 g sample was treated with 7.5 cm^3 concentrated HCl (CAS 7647-01-0) and 2.5 cm^3 concentrated HNO_3 (CAS 7697-37-2), heated to dryness, and then dissolved in 25 cm^3 HCl (1 + 5). The solution was transferred to a 50 cm^3 volumetric flask, diluted with distilled water, filtered, and metals of fraction IV, considered immobile, were determined in the filtrate.

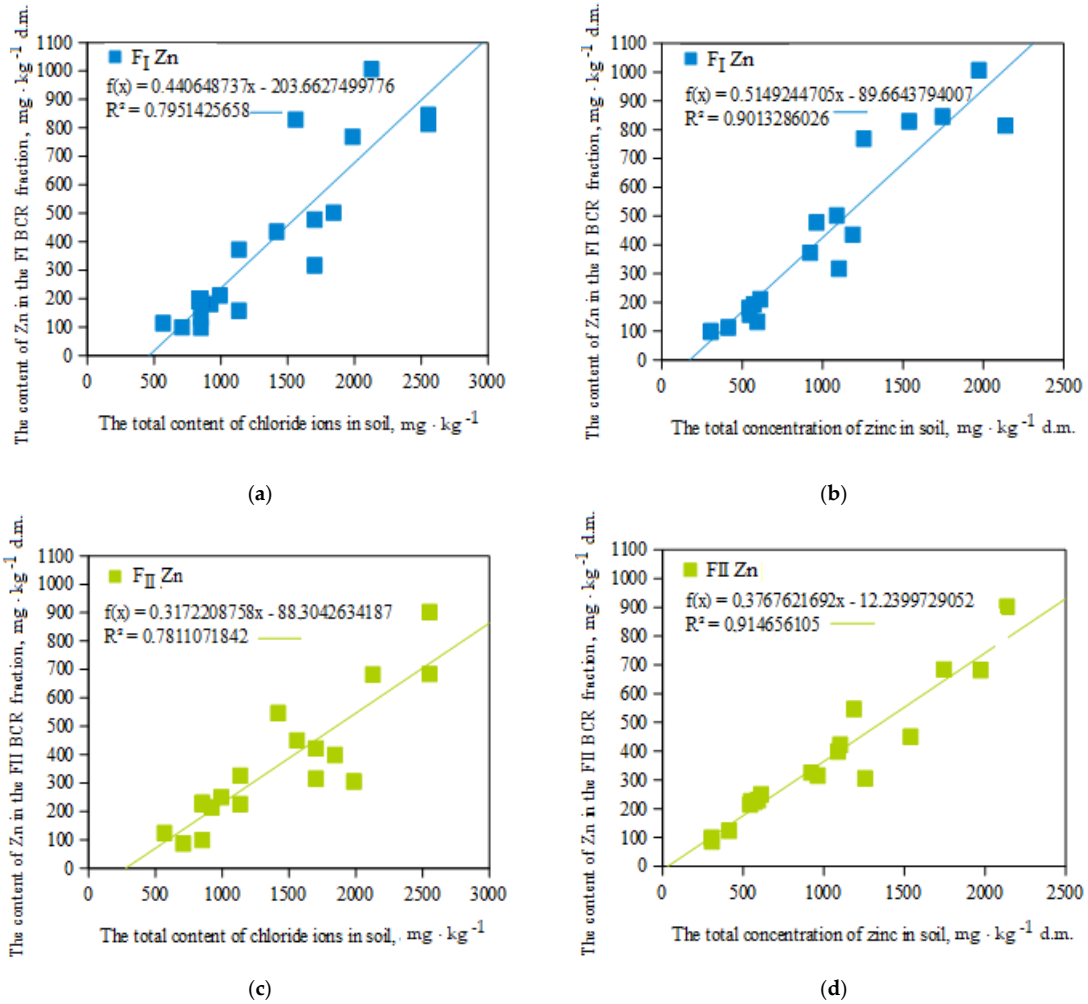


Figure A1. *Cont.*

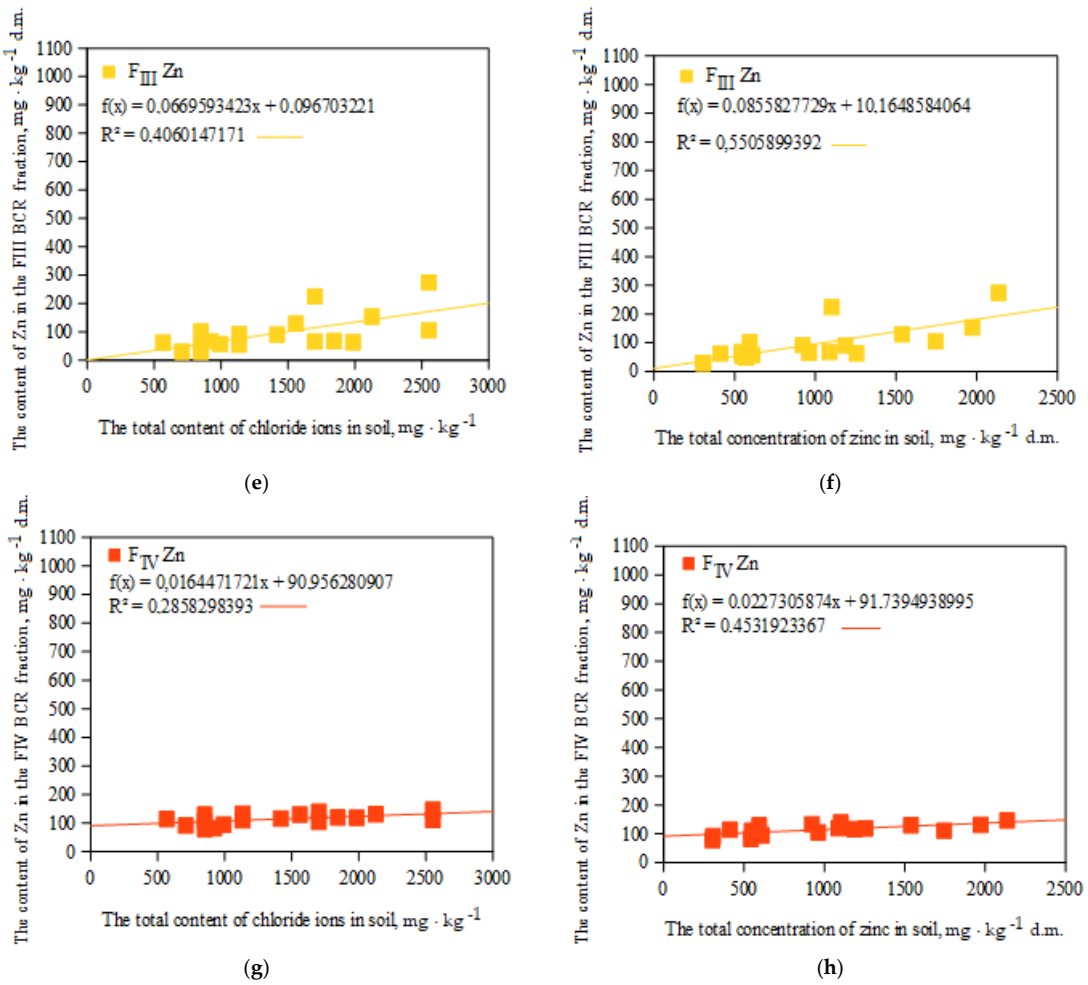


Figure A1. The relationship between the total concentration of zinc and chloride ions in soil and their content in the BCR chemical fractions. (**a**,**b**)—F_I (exchangeable and poorly acid-soluble fractions); (**c**,**d**)—F_{II} (reduction fraction); (**e**,**f**)—F_{III} (oxidizable fraction); (**g**,**h**)—F_{IV} (residual fraction).

References

1. Rouhani, A.; Gutiérrez, M.; Newton, R.A.; Al Souki, K.S. An overview of potentially toxic element pollution in soil around lead–zinc mining areas. *Environ. Rev.* **2025**, *33*, 1–16. [CrossRef]
2. Hussain, S.; Khan, M.; Sheikh, T.M.M.; Mumtaz, M.Z.; Chohan, T.A.; Shamim, S.; Liu, Y. Zinc essentiality, toxicity, and its bacterial bioremediation: A comprehensive insight. *Front. Microbiol.* **2022**, *13*, 900740. [CrossRef]
3. Mertens, J.; Smolders, E. Zinc. In *Heavy Metals in Soils*; Alloway, B., Ed.; Springer: Dordrecht, The Netherlands, 2013; Volume 22. [CrossRef]
4. Nartowska, E.; Podlasek, A.; Vaverková, M.D.; Koda, E.; Jakimiuk, A.; Kowalik, R.; Kozłowski, T. Mobility of Zn and Cu in bentonites: Implications for environmental remediation. *Materials* **2024**, *17*, 2957. [CrossRef]
5. Nartowska, E.; Stępień, P.; Kanuchova, M. Impact of zinc(II) chloride contamination on bentonites: Formation of simonkolleite and effects on porosity and chemical composition. *Materials* **2025**, *18*, 2933. [CrossRef]
6. Bourg, A.C.M.; Filby, R.H. Adsorption isotherms for the uptake of Zn^{2+} by clay minerals in a freshwater medium. In Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems, Ottawa, ON, Canada, 1–3 May 1974; Volume II, pp. 1–18.
7. Kaur, H.; Srivastava, S.; Goyal, N.; Walia, S. Behavior of zinc in soils and recent advances on strategies for ameliorating zinc phyto-toxicity. *Environ. Exp. Bot.* **2024**, *220*, 105676. [CrossRef]
8. Ure, A.M.; Quevauviller, P.H.; Muntau, H.; Griepink, B. Speciation of heavy metals in soils and sediments: An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151. [CrossRef]
9. Bågenholm-Ruuth, E.; Sanchis-Sebastiá, M.; Hollinger, N.; Teleman, A.; Larsson, P.T.; Wallberg, O. Transforming post-consumer cotton waste textiles into viscose staple fiber using hydrated zinc chloride. *Cellulose* **2024**, *31*, 737–748. [CrossRef]

10. Sun, W.-J.; Tang, Q.-T.; Lu, T.-H.; Fan, R.-D.; Sun, G.-G.; Tan, Y.-Z. Adsorption performance of bentonite and clay for Zn(II) in landfill leachate. *Geoenviron. Disasters* **2024**, *11*, 4. [CrossRef]
11. Wuana, R.A.; Okieimen, F.E. Heavy metals in contaminated soils: A review of sources, chemistry, risks, and best available strategies for remediation. *ISRN Ecol.* **2011**, *2011*, 402647. [CrossRef]
12. Oyourou, J.-N.; McCrindle, R.; Combrinck, S.; Fourie, C.J.S. Investigation of zinc and lead contamination of soil at the abandoned Edendale mine, Mamelodi (Pretoria, South Africa) using a field-portable spectrometer. *J. S. Afr. Inst. Min. Metall.* **2019**, *119*, 55–62. [CrossRef]
13. Pietrzykowski, M.; Antonkiewicz, J.; Gruba, P.; Pająk, M. Content of Zn, Cd and Pb in purple moor-grass in soils heavily contaminated with heavy metals around a zinc and lead ore tailing landfill. *Open Chem.* **2018**, *16*, 1143–1152. [CrossRef]
14. Janaszek, A.; Silva, A.F.d.; Jurišević, N.; Kanuchova, M.; Kozáková, Ľ.; Kowalik, R. The assessment of sewage sludge utilization in closed-loop economy from an environmental perspective. *Water* **2024**, *16*, 383. [CrossRef]
15. White, P.J.; Broadley, M.R. Chloride in soils and its uptake and movement within the plant: A review. *Ann. Bot.* **2001**, *88*, 967–988. [CrossRef]
16. Lommelen, R.; Vander Hoogerstraete, T.; Onghena, B.; Billard, I.; Binnemans, K. Model for metal extraction from chloride media with basic extractants: A coordination chemistry approach. *Inorg. Chem.* **2019**, *58*, 12289–12301. [CrossRef]
17. Nartowska, E.; Podlasek, A.; Vaverková, M.D.; Koda, E.; Kanuchova, M.; Jakimiuk, A.; Gawdzik, J. Identification of factors affecting the properties of soils contaminated with Zn(II) and Cu(II) chlorides. *J. Soils Sediments* **2025**, *25*, 1175–1200. [CrossRef]
18. Ziegler Rivera, F.R.A.; Prado Pano, B.; Guédron, S.; Palomino, L.M.; de León, P.; Hill, C.; Grabach, C.S. Impact of the change in irrigation practices from untreated to treated wastewater on the mobility of potentially toxic elements (PTEs) in soil irrigated for decades. *J. Soils Sediments* **2023**, *23*, 2726–2743. [CrossRef]
19. Acosta, J.A.; Jansen, B.; Kalbitz, K.; Faz, A.; Martínez-Martínez, S. Salinity increases mobility of heavy metals in soils. *Chemosphere* **2011**, *85*, 1318–1324. [CrossRef]
20. Angelaki, A.; Dionysidis, A.; Sihag, P.; Golia, E.E. Assessment of contamination management caused by copper and zinc cations leaching and their impact on the hydraulic properties of a sandy and a loamy clay soil. *Land* **2022**, *11*, 290. [CrossRef]
21. Bai, J.; Zhao, Q.; Wang, W.; Wang, X.; Jia, J.; Cui, B.; Liu, X. Arsenic and heavy metals pollution along a salinity gradient in drained coastal wetland soils: Depth distributions, sources and toxic risks. *Ecol. Indic.* **2019**, *96*, 91–98. [CrossRef]
22. Rutkowska, B.; Szulc, W.; Bomze, K.; Gozdowski, D.; Spychaj-Fabisiak, E. Soil factors affecting solubility and mobility of zinc in contaminated soils. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 1687–1694. [CrossRef]
23. Makuch-Pietraś, I.; Wójcikowska-Kapusta, A. Differences in the content of Zn fractions in the profiles of soils from allotment and domestic gardens in south-eastern Poland. *Land* **2021**, *10*, 886. [CrossRef]
24. Moreno-Lora, A.; Delgado, A. Factors determining Zn availability and uptake by plants in soils developed under Mediterranean climate. *Geoderma* **2020**, *376*, 114509. [CrossRef]
25. Soil Survey Manual. Agriculture Handbook No. 18, United States Department of Agriculture. 2017. Available online: https://www.nrcs.usda.gov/sites/default/files/2022-09/The-Soil-Survey-Manual.pdf (accessed on 29 June 2024).
26. Moreno-Maroto, J.M.; Alonso-Azcárate, J.; O'Kelly, B.C. Review and critical examination of fine-grained soil classification systems based on plasticity. *Appl. Clay Sci.* **2021**, *200*, 105955. [CrossRef]
27. *EN ISO 17892–12:2018/Amd2:2022*; Geotechnical Investigation and Testing—Laboratory Testing of Soil—Part 12: Determination of Liquid and Plastic Limits. International Organization for Standardization: Geneva, Switzerland, 2022.
28. *Sympatec Guidelines*; Sympatec GmbH: Clausthal-Zellerfeld, Germany, 2017. Available online: https://tecnos.ro/cloud/document/files/HELOS_1737381638541.pdf (accessed on 9 June 2024).
29. Stępkowska, E.T. Simple method of crystal phase water, specific surface and clay mineral content estimation in natural clays. *Stud. Geotechn.* **1973**, *4*, 21–36.
30. *ISO 10390:2021*; Soil, Treated Biowaste and Sludge—Determination of pH. International Organization for Standardization: Geneva, Switzerland, 2021. Available online: https://www.iso.org/standard/75243.html (accessed on 9 June 2024).
31. *PN ISO 9297:1994*; Water Quality—Determination of Chloride—Silver Nitrate Titration with Chromate Indicator (Mohr's Method). Polish Committee for Standardization: Warsaw, Poland, 1994.
32. *ASTM D 2974–87*; Standard Test Method for Ash in the Analysis of Biomass Fuels (Method C). ASTM International: West Conshohocken, PA, USA, 1987.
33. Tessier, P.G.C.; Campbell, M.B. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51*, 844–851. [CrossRef]
34. *EN ISO 15587:2002*; Water Quality—Digestion for the Determination of Selected Elements in Water—Part 1: Aqua Regia Digestion. International Organization for Standardization: Geneva, Switzerland, 2002. Available online: https://www.iso.org/standard/31354.html (accessed on 9 June 2024).
35. Golia, E.E.; Tsiropoulos, N.G.; Dimirkou, A.; Mitsios, I. Distribution of heavy metals of agricultural soils of central Greece using the modified BCR sequential extraction method. *Int. J. Environ. Anal. Chem.* **2007**, *87*, 1053–1063. [CrossRef]

36. Pueyo, M.; Mateu, J.; Rigol, A.; Vidal, M.; López-Sánchez, J.F.; Rauret, G. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environ. Pollut.* **2008**, *152*, 330–341. [CrossRef]
37. Larner, B.L.; Seen, A.J.; Townsend, A.T. Comparative study of optimised BCR sequential extraction scheme and acid leaching of elements in the certified reference material NIST 2711. *Anal. Chim. Acta* **2006**, *556*, 444–449. [CrossRef]
38. Rao, C.R.M.; Sahuquillo, A.; López-Sánchez, J.F. Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. *Anal. Chim. Acta* **2010**, *662*, 128–136. [CrossRef] [PubMed]
39. García, R.; Báez, A.P. Atomic absorption spectrometry (AAS). In *Atomic Absorption Spectroscopy*; Farrukh, M.A., Ed.; Intech: Rijeka, Croatia, 2012; pp. 1–14. [CrossRef]
40. Senesi, G.S.; Dell'Aglio, M.; Gaudiuso, R.; De Giacomo, A.; Zaccone, C.; De Pascale, O.; Miano, T.M.; Capitelli, M. Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium. *Environ. Res.* **2009**, *109*, 413–420. [CrossRef] [PubMed]
41. Hanif, M.; Bullen, J.; Plancherel, Y.; Kirby, M.; Kirk, G.; Weiss, D. Significant effect of salinity on zinc adsorption on tropical coastal and floodplain soils. *Eur. J. Soil Sci.* **2024**, *75*, e13575. [CrossRef]
42. Wu, Z.; Chen, Y.; Yang, Z.; Liu, Y.; Zhu, Y.; Tong, Z.; An, R. Spatial distribution of lead concentration in peri-urban soil: Threshold and interaction effects of environmental variables. *Geoderma* **2023**, *429*, 116193. [CrossRef]
43. Meers, E.; Unamuno, V.R.; Du Laing, G.; Vangronsveld, J.; Vanbroekhoven, K.; Samson, R.; Diels, L.; Geebelen, W.; Ruttens, A.; Vandegehuchte, M.; et al. Zn in the soil solution of unpolluted and polluted soils as affected by soil characteristics. *Geoderma* **2006**, *136*, 107–119. [CrossRef]
44. Nartowska, E.; Podlasek, A.; Vaverková, M.D.; Koda, E. Copper mobility in chloride-contaminated soils: Empirical models considering surface area and concentration. *J. Soils Sediments* **2025**, *25*, 1280–1301. [CrossRef]
45. Sereni, L.; Guenet, B.; Lamy, I. Mapping risks associated with soil copper contamination using availability and bio-availability proxies at the European scale. *Environ. Sci. Pollut. Res.* **2023**, *30*, 19828–19844. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.