

RESEARCH ARTICLE

Significant effect of salinity on zinc adsorption on tropical coastal and floodplain soils

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Abstract

Rising sea levels due to climate change are causing increased salinisation of low-lying coastal and floodplain soils, and the impact of this process on the bioavailability of plant nutrients needs to be understood as mitigation strategies are adapted. Zinc (Zn) is an element of particular importance due to its function as a micronutrient for plants including rice and other staple foods. In the current study, our aim was to investigate the effects of salinisation on zinc adsorption onto soils representing at-risk coastal and floodplain environments, addressing in particular our knowledge gap concerning the roles that solution chemistry and soil composition play. To this end, we conducted batch adsorption experiments in the laboratory and ran geochemical models in saline solutions up to 0.7 mol L^{-1} ion strength incorporating both (i) a multi surface model (MSM) for surface reactions containing three phases, that is iron hydroxides, organic matter and phyllosilicate clays, and (ii) aqueous-phase complexation to dissolved organic and inorganic ligands. Surface reactions were modelled using the diffuse double layer model, the NICA–Donnan model and an ion exchange model using the Gaines–Thomas convention. We combined the experimentally determined mass composition of surface phases with generic modelling parameters taken from the literature. We first show that increasing salinity enhances the formation of aqueous Zn-chloride complexes in the presence of dissolved organic matter and bicarbonate, thereby decreasing the availability of free Zn^{2+} and suppressing the partitioning of zinc to the adsorbed phase. We demonstrate using batch adsorption experiments with a calcareous hydraquent and a tropaequept, that salinity decreases zinc adsorption strongly in the pH range between 3 and 6. Satisfactory agreement between experiments and model calculations was achieved with root-mean-square errors ranging for different salinities between 2.88% and 2.92% for the hydraquent and between 4.59% and 2.74% for the tropaequept soil. Model predictions of adsorption were slightly inferior at low salinity for the hydraquent soil and at high salinity for the tropaequept soil, pointing possibly to an incomplete

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geochemical model or to a need to parametrise surface adsorption models at higher ionic strengths. Present surface models have been largely parametrised at lower ionic strength. We lastly apply the MSM to examine zinc adsorption in five endoaquepts soils, representing soil series from Bangladesh. We show that increasing salinity decreases zinc adsorption to the soil organic matter and the clay fractions. We conclude from our findings that increased soil salinity due to rising sea levels and climate change will have a significant impact on zinc cycling and possibly other micronutrients in areas where coastal soils and floodplain soils overlap, such as deltas and estuaries. In particular, we predict a decrease in zinc adsorption in acidic to neutral soils. The availability of zinc for biouptake through the roots of crop plants including rice will be significantly disturbed following salinisation, most likely affecting crop production. Our study demonstrates the potential that geochemical modelling combined with experimental data has to improve our capability to assess the effects of salinity due to rising seawater levels in vulnerable regions of the world.

KEYWORDS

adsorption, Bangladesh, endoaquept, geochemical modelling, hydraquent, multi-surface model, parametrisation, salinity, speciation, tropaquept, Visual Minteq, zinc

1 | INTRODUCTION

Rising sea levels due to climate change cause the salinisation of soils and groundwater aquifers in low-lying areas around the world (Dasgupta et al., 2015). This process is likely to change trace element cycling in affected soils, influencing consequently plant growth and ecosystem functions. At present, around 20% of coastal agricultural lands are affected by varying levels of salinity (Corwin, 2021) and predictions suggest this will increase to around 50% impacted by severe salinisation by 2050 (Shahid et al., 2018). This scenario is alarming for low-lying countries such as Bangladesh where about 30% of cultivable land is located in coastal areas (Ahmed et al., 2010; Dasgupta et al., 2015; Haque, 2006).

Reactions at the solid/solution interface, including adsorption and precipitation, control trace metal concentrations and speciation in soils, affecting mobility and plant bioavailability (Bradl, 2004). Sodium (Na^+) and chloride (Cl^-) are the dominant ions in seawater and their concentrations in soil solutions increase following saltwater intrusion. They directly impact adsorption processes by (i) increasing the formation of Cl complexes reducing thus the amount of free Zn^{2+} in solution, (ii) compressing the electric double layer (Barrow et al., 1981; Barrow & Hartemink, 2023; Barrow & Whelan, 1998; Meegoda et al., 2019), (iii) competing for access to vacant adsorption sites on soil surfaces (Paalman et al., 1994) and (iv) forming additional surface complexes, for example ternary

Highlights

- The impact of salinisation on zinc adsorption processes in tropical wetland soils is assessed.
- The study combines laboratory and modelling work, using a state of the art multi-surface model.
- Salinity reduces zinc adsorption mainly in acidic and neutral pH soils. Mainly clay and soil organic matter affected.
- Salinity will have a significant impact on zinc cycling in coastal tropical soils. Existing multi-surface models can have an important role in predicting the extent and identifying vulnerable regions.

surface complexes (Bradl, 2004; Lumsdon et al., 1995; Stietiya, 2010; Strawn, 2021). Accurate identification of metal speciation in dissolved and solid phases is critical to predict transport processes in soils (Shaheen et al., 2014), but the experimental quantification of the partitioning of adsorbed metals between different surface phases, as per a complex soil mixture, is challenging due to limitations of analytical techniques. To this end, our understanding of the adsorption of metals onto complex surfaces is increased when supported by modelling approaches (Bonito et al., 2018;

Bullen et al., 2022; Bullen, Kenney, et al., 2020; Bullen et al., 2024; Davis et al., 1998; Pierrot & Millero, 2017; Tepavitcharova et al., 2011; Turney et al., 2023).

Soils are complex natural systems with a wide range of chemically distinct organic and inorganic sorbent phases, for example soil organic matter (SOM), iron (hydr)-oxides (HFO) and clay. Geochemical speciation codes enable us to construct so-called multi surface models (MSM), with different surface components (see for example Khai et al., 2008), each with their own surface reaction modelling equations to represent the distinctive chemical mechanisms (e.g. surface complexation versus ion exchange). MSMs have indeed been successfully used to predict surface reaction processes in systems containing soils with variable solid phases and solutions with changing chemical compositions and ionic strengths (Groenenberg & Lofts, 2014). These models have been critically important in the deconvolution of complex adsorption processes in soils and other multi-phase systems (Bullen, Kenney, et al., 2020; Bullen, Landa-Consiglio, et al., 2020; Dijkstra et al., 2004; Groenenberg & Lofts, 2014; Weng et al., 2001).

The parameterisation of surface reaction models used to build MSMs is challenging (Barrow & Hartemink, 2023; Barrow & Whelan, 1998) because of various effects requiring nuance in modelling equations and parameter sensitivity. One example is the compression of the electrical double layer (EDL) at solid/solution interfaces that typically requires accounting for in a surface complexation model (SCM). Early work by Barrow and Bowden (1987) demonstrated, for example, that the constant capacitance model (CCM), one type of SCM, does not describe experimental data well regarding zinc adsorption on iron oxides when pH and the concentration of adsorbate both vary. The use of the diffuse double layer (DDL) model is generally preferred. Conditional equilibrium constants ($\log K^{\text{cond}}$) are calculated by taking the intrinsic equilibrium constants ($\log K^{\text{int}}$) valid at ion strength (I) = 0 from the literature database and modifying by an exponential term, which incorporates the surface potential of the adsorbent surface, using the EDL model correction, whether it is the CCM, DDL or another. The surface potential is calculated from the balance of positive and negatively charged surface species, of which the pH-dependent protonation of surface hydroxyls is a major contributor. The DDL model incorporates the ionic strength of the solution to determine the thickness of the DDL, and at higher ionic strength greater surface charge can be developed. More advanced SCM/EDL models such as triple layer model (TLM) or the CD-MUSIC model have been developed. Surface models used in multi surface models have been largely parametrised at lower ionic strength below 0.5 mol L^{-1} (Duffner et al., 2014; Fisher-Power et al., 2016;

Mizutani et al., 2017; Weng et al., 2001; Zhang et al., 2018), yet in a range of cases, the DDL model has been used successfully to predict metal adsorption onto iron oxides in seawater matrices (Gao & Mucci, 2001, 2003; Mercer & Tobiasson, 2008). Early work in soils showed that the influence of pH on surface reactions (the so-called pH adsorption edge) is less steep for mixed solid phase systems than for pure substances (Barrow & Whelan, 1998). This is explained by the fact that each surface phase component in a soil has its own unique pH adsorption edge, rising at a different pH and the dramatic curvature is lost when these edges are aggregated and overlap, as per a mixed surface soil. The experimentally observed adsorption profile of mixed-phase systems can be recreated using component additive modelling, that is the linear combination of independently acting single-phase surface components, with each phase weighted according to its surface mass fraction (Bullen et al., 2020; Bullen et al., 2024; Davis et al., 1998; Di Bonito et al., 2024).

Zinc (Zn) plays a dual role in the plant-soil environment. Whilst zinc deficiency is one of the most important micronutrient challenges for staple foods including rice and wheat (Brown et al., 2002; Impa & Johnson-Beebout, 2012; Weiss et al., 2021; Wissuwa et al., 2006), it is also toxic at concentrations anywhere above $0.01\text{--}0.5 \text{ mg L}^{-1}$, reducing plant growth and making plants vulnerable to disease (Alloway, 2008; Briffa et al., 2020). Zinc-deficient foods lead to zinc-deficient humans (Harrington et al., 2022) and a recent study linked stunting in 41% of children under the age of five in Bangladesh to inadequate zinc consumption (Rahman et al., 2016). One strategy to prevent zinc deficiency is the application of micronutrient-containing fertilisers (agronomic biofortification) (Praharaj et al., 2021; Singh et al., 2023); however, micronutrients such as zinc in applied fertiliser products can be lost as runoff when mobilised, and it is thus important to understand soil mobility of zinc from both environmental and anthropogenic sources (Zhang et al., 2003; Islam, Karim, Zheng & Li, 2018). Despite the huge importance that zinc deficiencies play in global agriculture, our knowledge regarding the effects that salinisation and flooding have on the interface processes of zinc in tropical coastal and floodplain soils is inadequate (Weiss et al., 2021). Findings from the limited studies to date have been contradictory, and often lacking mechanistic details. Acosta et al. (2011) and Shuman (1986) for example reported that increasing salinity does not significantly affect the adsorption of zinc in temperate soils, whilst Linde et al. (2007) and Chu et al. (2015) reported that zinc adsorption decreases with increasing salinity. Given the conflicting or missing information and the importance of soils in tropical coastal and floodplain environments for plant production, further studies are clearly warranted.

The objective of the present study was to investigate the impact of salinisation on zinc adsorption onto soils representing the characteristics of both coastal and floodplain environments. To this end, we first used geochemical modelling to identify the speciation of zinc in saline aqueous solutions, with a special focus on the role bicarbonate and dissolved organic carbon (DOC) play due to their significant abundance in floodplain and coastal soils. We next conducted batch adsorption experiments in the laboratory using two chemically different soils (a hydraquent and a trophaquent) and consequently validated a multi-surface model (MSM) consisting of three previously parametrised surface models. This MSM was subsequently applied to explore the effect of salinisation on zinc adsorption in endoaquent soils from coastal and floodplain areas in Bangladesh.

2 | MATERIALS AND METHODS

2.1 | Study design

2.1.1 | Chemical composition of aqueous solutions

The chemical composition of the soil solutions used during batch adsorption experiments and geochemical modelling contained Na^+ and Cl^- concentrations ranging between 0.1 and 0.7 mol L⁻¹, bicarbonate (HCO_3^-) concentrations ranging between 2 and 8 mmol L⁻¹, DOC concentration at 40 mg L⁻¹ and Zn concentrations at 0.08 mmol L⁻¹. This choice was based on the following considerations. Salinity in coastal soils typically ranges between 4 and 15 dS m⁻¹ (Dasgupta et al., 2015). In flooded soils, concentrations of dissolved CO_2 and hence bicarbonate (HCO_3^-) are typically high because CO_2 formed in soil microbial respiration escapes from the soil slowly (Affholder et al., 2017; Kirk et al., 2019). In calcareous soils, dissolution of carbonates further raises aqueous bicarbonate concentrations (Ahmed et al., 2020; Zuo et al., 2007). Dissolved organic carbon concentrations in coastal and floodplain soils are significant and typically range between 10 and 40 mg L⁻¹ (Ayers et al., 2016). For the adsorption experiments, we used a moderate initial zinc concentration of 0.08 mmol L⁻¹.

2.1.2 | Soil selection and characterisation

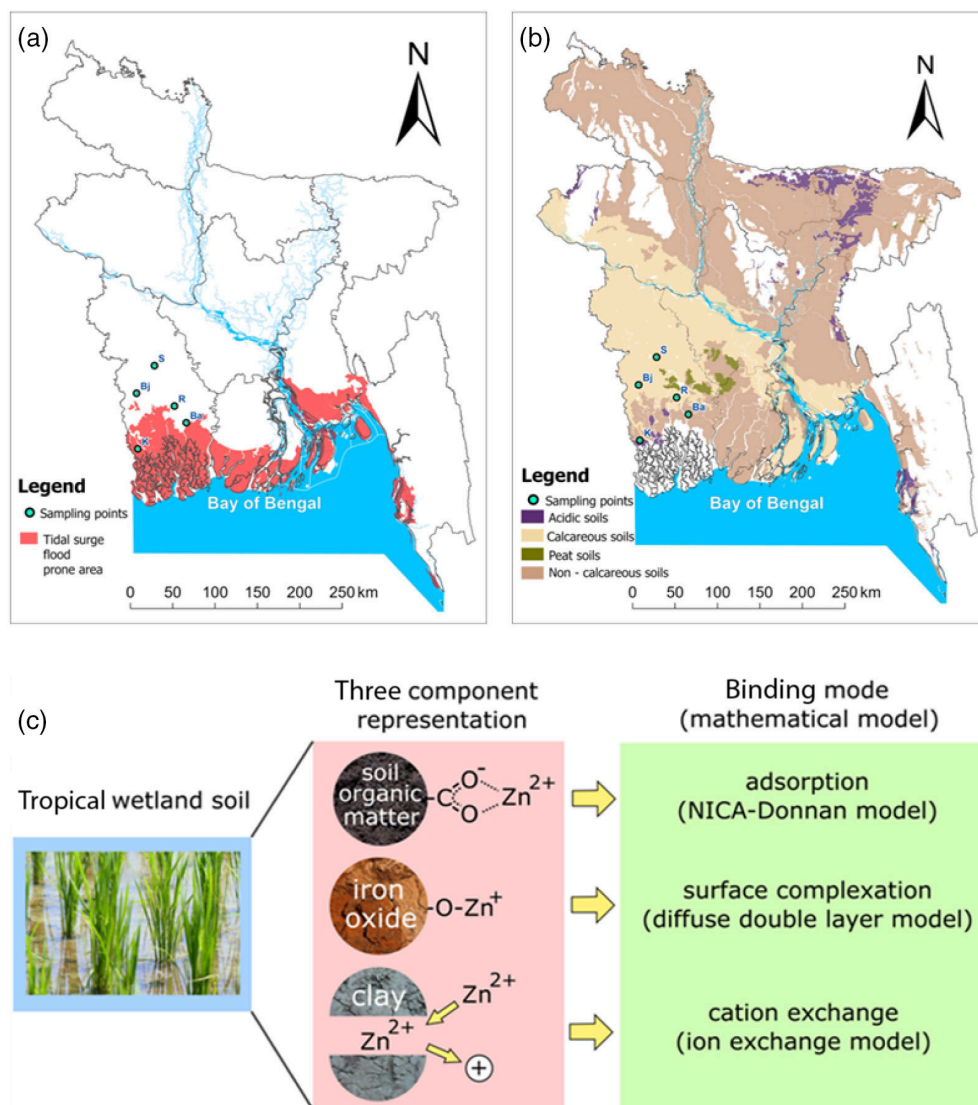
The soils used in the laboratory batch adsorption experiments were from non-saline lowland rice fields in the Philippines, a trophaquent from Bay, Laguna, and a calcareous hydraquent from Tiaong, Quezon, both denoted as experimental soils in this study. Trophaquents include

non-acidic to moderately acidic soils with organic matter content typically around 1.3%–1.9% by weight and hydraqunts develop under wet conditions in areas with sufficient moisture (USDA Soil Taxonomy, 1999). These soil types are common in coastal and floodplain areas in the tropics including Bangladesh (Brammer, 1972; Huq & Shoaib, 2013) and are crucial for agriculture, particularly for growing crops such as rice and vegetables, due to their fertility and proximity to water sources. The pH, clay content, cation exchange capacity (CEC), soil organic carbon content and carbonate content were determined during a previous study by our group (Izquierdo et al., 2016). Amorphous iron (hydr)oxides and the reactive major cations (Ca^{2+} , Mg^{2+} and K^+) were determined during the current study using ammonium oxalate (McKeague & Day, 1966) and nitric acid extraction with a solid: liquid ratio of 1:10 and shaking samples for 2 h (Groenenberg et al., 2017). X-ray diffraction (XRD) analysis showed that the dominant mineral phases were smectite, plagioclase and quartz, with no crystalline iron (hydr)-oxides (Figures S1 and S2, Table S1). Elemental analysis of both soil samples was conducted using X-ray fluorescence (XRF) (Table S2). The amount of zinc adsorbed on the soil was determined using ICP-MS following a leaching experiment with 0.43 mol L⁻¹ nitric acid (Groenenberg et al., 2017), and concentrations were very low, that is 0.05 mmol kg⁻¹.

The soils simulated during the geochemical modelling included five endoaquents soils located within the Ganges Tidal Floodplain region of Bangladesh, each representative of a distinct soil series (Figure 1). There is moderately deep flooding during monsoon seasons and mainly shallow flooding at high tide. We term the soils in this work as calcareous, non-calcareous and acidic following the classification scheme used in Bangladesh (Huq & Shoaib, 2013). The Kamalkathi soil series is acidic, the Barisal soil series is non-calcareous, and the Bajoa, Ramgati and Sara soil series are calcareous alkaline. The properties of the soils of Bangladesh were extracted from a reconnaissance soil survey report and from published data (Brammer, 1972; Brammer, 1996; Islam & Lotse, 1986; Moslehuddin et al., 1999; Rabbi et al., 2005; Rahman et al., 2005; SRDI, 2010). The CEC of clay was set to 0.4 mol kg⁻¹ for all soils during model analysis.

Table 1 gives the properties of the two soils from the Philippines (Bay, Tiaong) used during the batch adsorption experiments and of the five soils from the Ganges Floodplain in Bangladesh used during the geochemical modelling. The Bay and Tiaong soils were chosen because they are well characterised and judged to be representative entisols and inceptisols for coastal and flooded areas, allowing us therefore to extrapolate the experimental data to the Bangladesh soils (and beyond) via geochemical modelling.

FIGURE 1 Maps of (a) tidal surge flood risk (redrawn from Bangladesh Agricultural Research Council [BARC]/GIS Project, BGD/95/006) and (b) soil types in Bangladesh (redrawn from https://en.banglapedia.org/index.php/Bangladesh_Soil) indicating the location of the five endoaquepts soil profiles studied. Plot (c) shows the design of the MSM and the modelling concept, representing the adsorption of zinc onto tropical wetland soils as the linear addition of zinc adsorbing independently onto soil organic matter, iron oxide and clay surface phases, according to the component additive approach (Bullen et al., 2022, 2024; Davis et al., 1998).



2.1.3 | Chemical equilibrium calculations

To conduct the chemical equilibrium calculations, we used the software Visual MINTEQ ver. 3.1 and the database thermo.vdb (Gustafsson, 2019). To represent the formation of aqueous zinc species, we used thermodynamic stability constants recommended more recently following a critical literature assessment (Powell et al., 2013). The intrinsic equilibrium constants ($\log K^{\text{int}}$) for $I = 0 \text{ mol L}^{-1}$ from both literature sources are presented in Table S3.

2.1.4 | Multi-surface model (MSM)

The MSM used in this study was successfully applied to soils in previous work (Duffner et al., 2014; Khai et al., 2008; Weng et al., 2001; Zhang et al., 2018), albeit at low ionic strength only, and is composed of three

reactive surfaces to account for the adsorption behaviour of zinc (iron oxide, SOM and clay). Calcite was not included because its role in zinc adsorption is minor following the small specific surface area (Antoniadis et al., 2018; Duffner et al., 2014; Selim et al., 2013; Trehan & Sekhon, 1977; Zachara et al., 1988). Crystalline phases containing Fe and Al and amorphous aluminium were not detected in the experimental soils (Table S1) using XRD and XRF and therefore were not included in the geochemical model set-up. They are known to be largely absent in Bangladeshi soils (Islam & Lotse, 1986).

The surface components within the MSM used the following binding modes (mathematical models): (i) the NICA–Donnan model for SOM, (ii) the DDL model for iron hydroxide and (iii) the ion exchange model with the Thomas Gaines convention for clays. A linear combination of non-interacting single-phase surfaces was used to account for the three individual phases to represent the

TABLE 1 Properties of the two soils (Bay and Tiaong) from the Philippines and of the five soils representing soil series of the Ganges Tidal Floodplain in Bangladesh.

Soil	USDA classification	Reaction with 10% HCl	pH	Clay %	CEC cmol _c kg ⁻¹	SOC %	Free carbonate %	Amorphous Fe-oxide mg kg ⁻¹	Extractable		
									Ca cmol kg ⁻¹	Mg cmol kg ⁻¹	K mmol L ⁻¹
Bay	Tropaquept	Non-calcareous	7.3	49.9	10.6	5.43	0.16	80	25.0	4.3	0.6
Tiaong	Hydraquept	Calcareous	8.5	42.2	9.0	7.28	9.59	60	48.5	3.6	0.5
Kamalkathi	Typic Endoaquepts	No reaction	4.60	38.97	25.37	2.04	—	50	6.76	5.08	0.46
Barisal	Typic Endoaquepts	Non-calcareous	6.52	44.00	28.69	1.60	0.20	50	26.32	6.76	0.34
Bajoa	Typic Endoaquepts	Calcareous	8.02	30.00	21.73	1.30	6.00	50	20.4	6.01	0.44
Ramgati	Typic Endoaquepts	Calcareous	8.15	17.71	20.0	1.00	6.60	50	12.28	3.32	0.37
Sara	Aeric Endoaquepts	Calcareous	7.70	24.02	6.06	1.35	2.38	50	3.40	1.13	0.32

Note: The soils of Bangladesh are classified in this study as calcareous, non-calcareous and acidic following the classification scheme used in Bangladesh (Huq & Shoaib, 2013) and are presented with their series names. The Kamalkathi soil series is acidic, the Barisal soil series is non-calcareous, and the Bajoa, Ramgati and Sara series are calcareous alkaline soils. The exact locations of the sampling sites are 22.79722° N/89.44584° E for Bajoa, 22.64452° N/89.51864° E for Barisal, 22.6591° N/89.10258° E for Kamalkathi, 22.69375° N/89.52899° E for Ramgati and 22.93588° N/89.47106° E for Sara. The properties of the soils of Bangladesh were extracted from a reconnaissance soil survey report and from published data (Brammer, 1972; Islam & Lotse, 1986; Moslehuddin et al., 1999; Rabbi et al., 2005; Rahman et al., 2005; SRDI, 2010). During the modelling, the concentration of dissolved organic carbon (DOC) was set to 40 mg L⁻¹ and the cation exchange capacity (CEC) of clay was set to 0.4 mol kg⁻¹.

adsorption of zinc on the soil (Bullen, et al., 2020; Bullen et al., 2024; Davis et al., 1998; Di Bonito et al., 2024). This simple component additivity concept means that zinc adsorption to various surfaces is calculated separately and then summed to determine total adsorption. Interactions between different surfaces and their effects on metal ion adsorption are neglected (Bonten et al., 2008). The component additive approach has been used successfully to predict the behaviour of composite adsorbent systems, including natural systems, as a linear combination of pure surface phase (Bullen et al. 2020; Bullen, Landa-Consiglio, et al., 2024; Davis et al., 1998; Di Bonito et al., 2024; Fisher-Power, Shi & Cheng, 2019). Figure 1 displays the MSM design and the modelling concept.

2.2 | Batch adsorption experiments

The batch adsorption experiments were conducted over the pH range from 3 to 10 and with solution salinities ranging from 0.1 to 0.7 mol L⁻¹ using NaCl as electrolyte. In triplicate, 49 mL solution of the desired ionic strength was added to 0.5 g soil in 50 mL polypropylene Falcon centrifuge tubes, capped and shaken on a VWR orbital shaker at 25°C and 300 rpm for 24 h to equilibrate. After shaking, 1 mL of zinc stock solution was added to give an initial concentration in the solution of 0.08 mmol L⁻¹. The pH was adjusted by adding small volumes of 1 mol L⁻¹ of HCl or NaOH. The tubes were capped and shaken again for 24 h. After shaking, the tubes were centrifuged, and the pH of the supernatant was immediately measured using a ion selective electrode (Metrohm pH meter model 826). The supernatant was passed through a 0.45 µm nylon syringe filter to remove fine soil particles. The collected filtrates were acidified with 2% (v/v) HNO₃ and analysed for zinc using ICP-MS (Agilent 7900 quadrupole ICP-MS with a helium collision cell). At least five concentrations of zinc were prepared from a single-element zinc standard to obtain a calibration curve (Merck, 1000 µg mL⁻¹). Indium was used as an internal standard solution to correct for changes in the sensitivity of the detector during analysis. The amount of zinc adsorbed to the soil was calculated by the difference between the total added zinc and the zinc remaining in the filtrate. Within the 24 h time frame of the zinc adsorption experiments, the dissolution of Fe(OH)₃ is very limited and any dissolved iron will have an insignificant effect on zinc adsorption (Fisher-Power et al., 2016; Shi et al., 2007, 2013). For quality control, blank samples, consisting only of NaCl and MilliQ water, were analysed and blank contributions determined were insignificant.

2.3 | Speciation modelling of aqueous solutions

The Davies activity model was used during speciation calculations of the aqueous phase (Bonito et al., 2018; Gustafsson, 2019; Northover et al., 2021, 2022). The Davies activity model is a variant of the Debye-Hückel activity model that can be carried to higher ionic strengths, that is above 0.2 mol L⁻¹ (Northover et al., 2021, 2022; Stumm & Morgan, 1995). The Davies activity model provides a more accurate description than the original Debye-Hückel theory for ionic strengths up to about 0.5 mol L⁻¹ and the specific ion interaction (SIT) theory is typically used for solutions with higher ionic strengths, usually between 1 and 3 mol L⁻¹. To this end, prior to our modelling experiments, we conducted a comparison of speciation calculations using the Davies and SIT activity models to assess the accuracy of our model calculations at 0.7 mol L⁻¹. We find good agreement between both speciation calculations (Figure S3). Between pH 6 and 8, the abundance of free Zn²⁺ is approximately 5% lower than that of ZnCl⁺ and ZnCl₂ is approximately 5% higher when using the Davies activity model. Similar level of deviations calculating free ion activities in seawater using different activity models have been observed by Stockdale et al. (2015).

To identify and quantify the zinc species in soil solutions following salinisation and to study the effect of bicarbonate and DOC on zinc speciation, we set up our modelling experiment as follows. First, we determined zinc species in saline systems in the presence of DOC, termed thereafter as Zn-NaCl-DOC system. We varied the NaCl concentration between 0.1 and 0.7 mol L⁻¹. We used the NICA-Donnan model for the complexation of zinc with DOC with previously determined generic parameters (Gustafsson & Kleja, 2005; Milne et al., 2003; Gustafsson, Pechova & Berggren, 2003), assuming 83 wt % of DOC composed of reactive fulvic acid with a carbon content of 50%. The dissolved organic matter to DOC ratio was 1.65. Second, we added bicarbonate (HCO₃⁻) to the Zn-NaCl-DOC system as it is an important inorganic ligand complexing with zinc in environmental aqueous solution (Powell et al., 2013). The bicarbonate concentrations used, 2 and 8 mmol L⁻¹, are representative of submerged tropical wetland soils (Ahmed et al., 2020; Kirk et al., 2019).

2.4 | Surface adsorption models for clays, soil organic matter and hydrous iron oxides

We used three reactive surfaces within the MSM to account for the adsorption behaviour of the soil

TABLE 2 Model parameters used in the MSM during this study. This includes parameters used in (i) the NICA–Donnan model for the complexation of metals to soil organic matter (SOM), including solid and dissolved SOM for fulvic acid and dissolved SOM for humic acid (Gustafsson & Kleja, 2005; Milne et al., 2003), (ii) the diffusive double layer (Dzombak & Morel, 1990) for the complexation of metals with HFO and (iii) an ion exchange model using the Thomas Gaines convention. Intrinsic stability constants ($\log K^{\text{int}}$) for the formation of surface complexes on HFO include strong and weak binding surface sites (Dzombak & Morel, 1990). The surface area of HFO were set to $600 \text{ m}^2 \text{ g}^{-1}$ and site concentrations were 0.056 nm^{-2} for strong and 2.255 nm^{-2} for weak sites.

Soil organic matter (SOM): NICA—Donnan model								
Model parameters								
Parameter			Carboxylic type site		Phenolic type site			
Site density, $Q_{\text{max,H}}$ (mol kg ^{−1})			3.15		2.55			
Heterogeneity, p			0.62		0.41			
Electrostatic Donnan b value			0.49					
Fixed V_{D} for solid HA only			1					
Ion-specific parameters								
Cation	Humic acid				Fulvic acid			
	Carboxylic type site ^a		Phenolic type site ^b		Carboxylic type site ^a		Phenolic type site ^b	
	Affinity log K_1	Non-ideality n_1	Affinity log K_2	Non-ideality n_2	Affinity log K_1	Non-ideality n_1	Affinity log K_2	Non-ideality n_2
Ca ²⁺	−1.37	0.78	−0.43	0.75	−2.13	0.85	−3.0	0.80
Mg ²⁺	−0.6	0.77	0.6	0.59	−2.1	0.77	−2.4	0.59
Zn ²⁺	0.11	0.67	2.39	0.27	−3.84	0.67	−0.73	0.61
H ⁺	2.93	0.81	8.00	0.63	2.34	0.66	8.60	0.76
Hydroxide iron oxides (HFO):Diffuse double layer (DDL) model								
Model parameters								
Surface area		600 m ² g ^{−1}						
Site concentration (strong)		0.056 nm ^{−2}						
Site concentration (weak)		2.255 nm ^{−2}						
Surface species								
Surface species strong site		log K^{int}		Surface species weak site		log K^{int}		
≡Fe-OH		0		≡Fe-OH		0		
≡Fe-OH ₂ ⁺		7.29		≡Fe-OH ₂ ⁺		7.29		
≡Fe-O [−]		−8.93		≡Fe-O [−]		−8.93		
≡Fe-OHCa ²⁺		4.97		≡Fe-OCa ⁺		−5.85		
≡Fe-OZn ⁺		0.99		≡Fe-OZn ⁺		−1.99		
≡Fe-OMg ⁺		nd		≡Fe-OMg ⁺		−4.6		
≡Fe-SO ₄ [−]		7.78		≡Fe-SO ₄ [−]		7.78		
≡Fe-OHSO ₄ ^{2−}		0.79		≡Fe-OHSO ₄ ^{2−}		0.79		
≡Fe-CO ₃ [−]		12.78		≡Fe-CO ₃ [−]		12.78		
≡Fe-CO ₃ H		20.37		≡Fe-CO ₃ H		20.37		

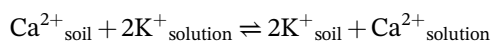
TABLE 2 (Continued)

Clay: ion exchange model (Gaines–Thomas convention)					
Model parameter					
CEC of clay = 0.4 mol kg ⁻¹					
Surface species					
Species name	Selectivity coefficient (<i>K</i> -sel)	Charge	Stoichiometry of first component	Stoichiometry of second component	Stoichiometry of third component
Ca + 2D	1	2	Ca + 2	H + 1D	H + 1
Zn + 2D	1	2	Zn + 2	H + 1D	H + 1
K + 1D	1	1	K + 1	H + 1D	H + 1
Mg + 2D	1	2	Mg + 2	H + 1D	H + 1
Na + 1D	1	1	Na + 1	H + 1D	H + 1

^aLow affinity.^bHigh affinity.

building upon previous work (Khai et al., 2008). Table 2 gives relevant thermodynamic and model parameters.

(i) Binding to phyllosilicate clay minerals was modelled using an ion exchange model using the Gaines–Thomas convention (Khai et al., 2008). The model uses equivalent fraction for activity of the exchangeable cations. The potassium-calcium exchange equilibrium for example can be represented by:



According to the convention, the thermodynamic equilibrium constant of this exchange is given by:

$$K = (g_K N_K)^2 (\gamma_{\text{Ca}} M_{\text{Ca}}) / (g_{\text{Ca}} N_{\text{Ca}}) (\gamma_K M_K)^2$$

where g_K and g_{Ca} are the adsorbed activity coefficient of the K and Ca ions, N_K and N_{Ca} are the respective equivalent fraction of K^{+} and Ca^{2+} on the exchanger and γ_{Ca} and γ_K are the activity coefficient of K^{+} and Ca^{2+} on the equilibrium solution and M_K and M_{Ca} are the K^{+} and Ca^{2+} molarities in the equilibrium solution (mol L⁻¹). The selectivity coefficient is set to unity for all cations. The CEC for clay during this study was 0.4 mol kg⁻¹ (McBride, 1994) since XRD analysis showed that the two experimental soils were rich in smectite (Figure S2, Table S1).

(ii) Binding to iron(hydr)oxide used the DDL model (Dzombak & Morel, 1990). This model is the most widely applied SCM for metal oxides, with equilibrium constants reported for surface complexes formed by the most significant environmental species. The

recommended specific surface area of 600 m² g⁻¹ was used to calculate site concentrations (Dijkstra et al., 2004). The DDL accounts for the effect of salt concentration on the EDL as apparent equilibrium constants are calculated taking intrinsic equilibrium constants and modifying them by an exponential term which incorporates the surface potential (Ψ_i) of the adsorbent surface (Bullen et al., 2024), for example, for the formation of a surface complex with +1 charge from a neutral >SOH surface hydroxyl site:

$$K^{\text{cond}} = K^{\text{int}} e^{(-F\psi/RT)}$$

where K^{int} is the intrinsic equilibrium constant, K^{cond} is the conditional constant at the particular ionic strength, ψ is the potential at surface (V), F is the Faraday constant (C mol⁻¹), R is the universal gas constant (J K⁻¹ mol⁻¹), and T is the temperature (K). The surface potential is calculated from the balance of positive and negatively charged surface species, of which the pH-dependent protonation of surface hydroxyls is a major contributor (Bullen et al., 2023; Goldberg, 2014; Kanematsu et al., 2013). The DDL model thus incorporates the ionic strength of the solution to determine the thickness of the DDL.

(iii) Binding to SOM uses the non-ideal competitive adsorption Donnan (NICA–Donnan) model assuming that 46% is active generic humic acid (Groenenberg & Lofts, 2014; Weng et al., 2001). The derivation of the NICA–Donnan model is discussed thoroughly elsewhere (Kinniburgh et al., 1999; Milne et al., 2003). The NICA equation describes the specific binding of cations to the humic reactive sites. The expression of the consistent

NICA model for multicomponent competitive binding states that the amount bound, Q , of a component i , at solution concentration c_i , is given by

$$Q_i = \frac{n_{i1}}{n_{H1}} Q_{\max 1, H} \times \frac{(K_{1i} c_i)^{n_{i1}}}{\sum (K_{1i} c_i)^{n_{i1}}} \times \frac{[\sum (K_{1i} c_i)^{n_{i1}}]^{p_1}}{1 + [\sum (K_{1i} c_i)^{n_{i1}}]^{p_1}} + \frac{n_{i2}}{n_{H2}} Q_{\max 2, H} \times \frac{(K_{2i} c_i)^{n_{i2}}}{\sum (K_{2i} c_i)^{n_{i2}}} \times \frac{[\sum (K_{2i} c_i)^{n_{i2}}]^{p_2}}{1 + [\sum (K_{2i} c_i)^{n_{i2}}]^{p_2}}$$

Thus, the total binding of a component is given by the sum of two identical binding expressions, one for each of the two site distributions considered by the NICA. Four parameters are characteristic of the humic material in question, that is $Q_{\max 1, H}$ and $Q_{\max 2, H}$ describe the maximum proton site density of the humic material for each distribution (in mol kg⁻¹), p_1 and p_2 represent the widths of the distributions and encapsulate the intrinsic heterogeneity of the humic material. For each component considered, four ion-specific parameters, K_{i1} , K_{i2} , n_{i1} and n_{i2} , are used to describe the median affinities, and non-idealities of the ion binding to each distribution. The generic proton-binding parameters of Gustafsson and Kleja (2005) were used, which consider a stronger salt effect for solid-phase humic acid (HA) and fulvic acid (FA).

The performance of the combined MSM is evaluated from the root-mean-square error (RMSE) calculated as:

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=0}^n (C_i - C'_i)^2}$$

where C_i and C'_i are the i -th measured and modelled adsorbed zinc values, respectively, and n is the total number of values. We used the RMSE as it is the classic error function outside of a simple linear regression, used to evaluate most SCMs. We calculated the RMSE using the absolute difference between experimental observations and model predictions for the percentage of zinc adsorbed at each pH value. Table 2 lists the model parameters used in the MSM during the study.

3 | RESULTS AND DISCUSSION

3.1 | Zinc speciation in saline solutions in the presence of dissolved organic matter and bicarbonate

The first central question we address is how DOC, carbonate and salinity influence the relative concentration of free Zn²⁺ in the soil aqueous phase, seeking to understand the impact that aqueous-phase complexation will

have on the availability of free Zn²⁺ as the reactant in soil adsorption equilibria.

3.1.1 | Speciation in the Zn–NaCl–DOC system

Figure 2a–c shows the Zn–NaCl–DOC system and the abundance of different zinc species as a function of pH in solutions with different salinities.

In the pH range between 4 and 7, speciation calculations for the 0.1 mol L⁻¹ NaCl solution show a distribution of total aqueous zinc with relative abundances of between 87% and 79% for free Zn²⁺, between 4% and 12% for Zn–DOC complexes, and approximately 8% for ZnCl⁺. Increasing the salinity to 0.7 mol L⁻¹, the abundance of free Zn²⁺ and Zn–DOC complexes decreases, whereas the abundance of Zn–chloride complexes increases. Zn–chloride complexes have relatively low association constants and thus require high chloride concentrations to form. At low chloride concentrations (0.1 mol L⁻¹), ZnCl⁺ is the only chloride complex to form. Other Zn–chloride complexes, that is ZnCl₂, ZnCl₃⁻ and ZnCl₄²⁻, are observed only at higher salinities, that is 0.3 and 0.7 mol L⁻¹. The relative importance of the Zn–chloride complexes in saline solutions follows the order of ZnCl⁺ > ZnCl₂ > ZnCl₃⁻ > ZnCl₄²⁻. At pH 7, the abundance of Zn–chloride complexes increases with increasing salinity and the abundance of free Zn²⁺ decreases from 80% to 54%. Above pH 8, Zn–carbonate and Zn–hydroxide complexes start to form. Zn–chloride, Zn–carbonate and Zn–hydroxide complexes make up 50% of the total zinc. In the pH range between 9 and 10, Zn–carbonate complexes, that is Zn(CO₃)₂ and ZnCO₃ are major species. The formation of Zn–DOC complexes lowers the abundance of Zn²⁺.

The abundance of Zn–DOC complexes decreases as the ion strength increases. Contributing to this effect is not just the competition between chloride and DOC for the complexation with zinc (Raspor et al., 1984; Weng et al., 2002), but also the suppression of the electrostatic interactions between zinc and DOC by screening charged sites (Northover et al., 2021). Speciation calculations using NaNO₃ as the electrolyte (see Figure S4) shows for example that like in the NaCl solution, the abundance of Zn–DOC complexes decreases as the ionic strength is increasing. NaNO₃ increases the ionic strength but the NO₃⁻-ligand does not complex with Zn²⁺. It should be noted that accurate electrostatic interactions used in ion binding models such as NICA–Donnan, WHAM Model VII and the Stockholm Humic Model are still discussed, especially for small-sized organic matter particles such as fulvic acids (Town et al., 2019).

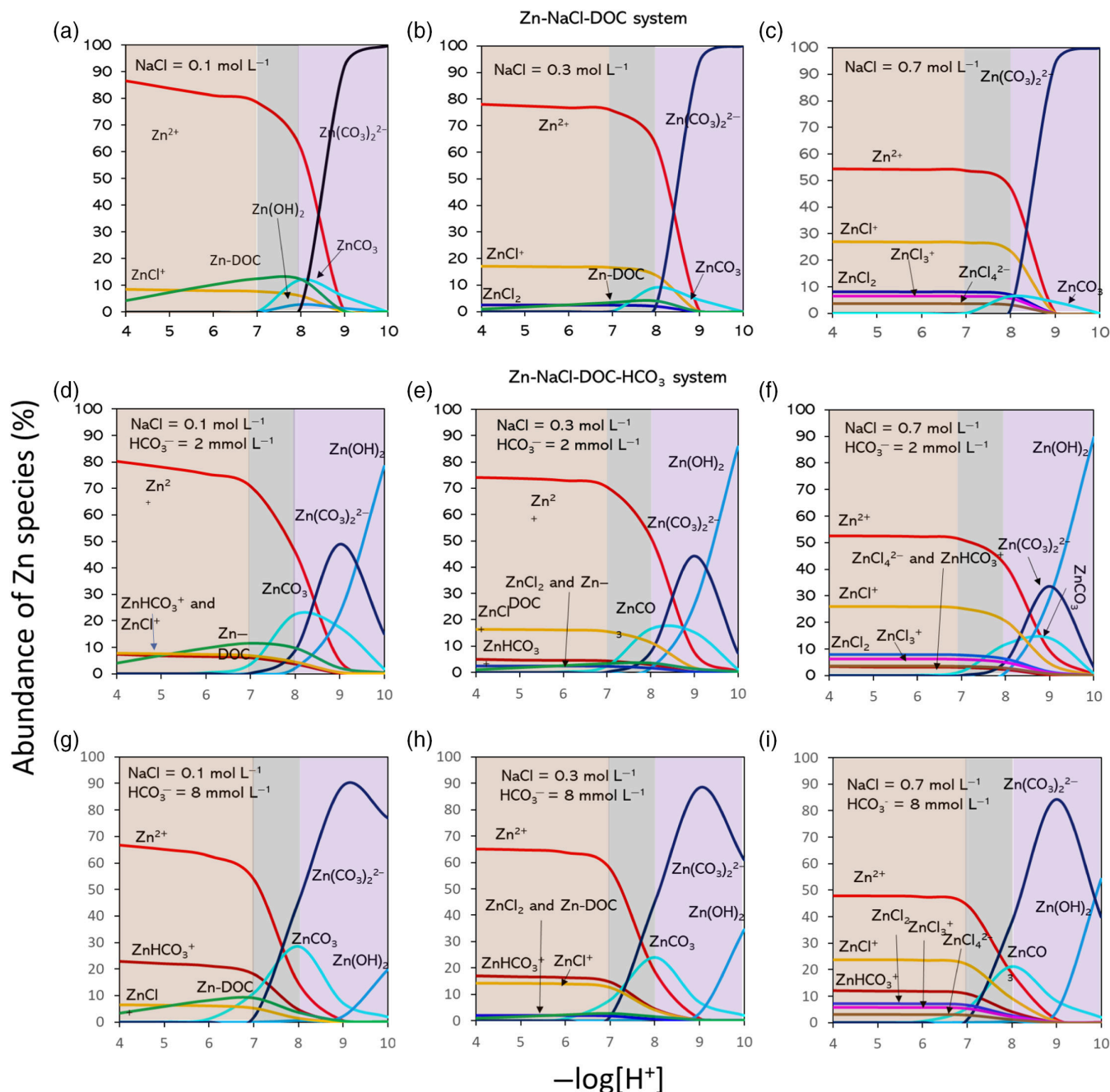


FIGURE 2 Speciation diagram of zinc in the Zn-NaCl-DOC and Zn-NaCl-DOC- HCO_3^- system with $[\text{Zn}] = 0.08 \text{ mmol L}^{-1}$ and $[\text{DOC}] = 40 \text{ mg L}^{-1}$. (a) $[\text{NaCl}] = 0.1 \text{ mol L}^{-1}$; (b) $[\text{NaCl}] = 0.3 \text{ mol L}^{-1}$; (c) $[\text{NaCl}] = 0.7 \text{ mol L}^{-1}$; (d) $[\text{NaCl}] = 0.1 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 2 \text{ mmol L}^{-1}$; (e) $[\text{NaCl}] = 0.3 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 2 \text{ mmol L}^{-1}$; (f) $[\text{NaCl}] = 0.7 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 2 \text{ mmol L}^{-1}$; (g) $[\text{NaCl}] = 0.1 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 8 \text{ mmol L}^{-1}$; (h) $[\text{NaCl}] = 0.3 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 8 \text{ mmol L}^{-1}$; (i) $[\text{NaCl}] = 0.7 \text{ mol L}^{-1}$ and $[\text{HCO}_3^-] = 8 \text{ mmol L}^{-1}$. Three distinct pH areas are distinguished, that is between pH 4 and 7 (orange), pH 7 and 8 (light grey), and pH 9 and 10 (purple). In the Zn-NaCl-DOC system, the systems were in equilibrium with the open atmosphere (partial pressure of CO_2 was $3.8 \times 10^{-4} \text{ atm}$).

3.1.2 | Speciation in the Zn-NaCl-DOC- HCO_3^- system

Figure 2d-i shows the abundance of zinc species as a function of pH in solutions with different salinities for the Zn-NaCl-DOC- HCO_3^- system.

In the pH range between 4 and 7, the bicarbonate ion, HCO_3^- , forms complexes with Zn^{2+} (ZnHCO_3^+ and ZnCO_3) and there is less free Zn^{2+} than when carbonate is absent. The decrease in the abundance of free Zn^{2+} due to the addition of HCO_3^- is greater in solutions with lower salinity and in solutions with higher HCO_3^- .

concentrations. In solutions with a salinity of 0.1 mol L^{-1} , the abundance of free Zn^{2+} decreases by 5% and 18% following the addition of 2 and $8 \text{ mmol L}^{-1} \text{ HCO}_3^-$, respectively. In solutions with salinity of 0.3 mol L^{-1} , the decrease is 4% and 13%, and in solution with salinity of 0.7 mol L^{-1} the decrease is 2% and 7%. The abundance of Zn-chloride complexes in the pH range between 4 and 7 is similar in the Zn-NaCl-DOC and Zn-NaCl-DOC- HCO_3^- systems after addition of 2 mmol L^{-1} of bicarbonate but different after addition of 8 mmol L^{-1} of bicarbonate. The abundance of Zn-DOC complexes is slightly lower following the addition of bicarbonate. At pH 8, zinc carbonate complexes, that is ZnCO_3 and $\text{Zn}(\text{CO}_3)_2^{2-}$, are abundant and the concentration of free Zn^{2+} decreases drastically following the addition of bicarbonate. In the pH range between 9 and 10, Zn-carbonate complexes, that is $\text{Zn}(\text{CO}_3)_2^{2-}$ and ZnCO_3 , and $\text{Zn}(\text{OH})_2$, are abundant. Precipitation of $\text{Zn}(\text{OH})_2$ is observed at pH 10 in the NaCl-DOC- HCO_3^- system.

The observed decrease in free Zn^{2+} following the addition of bicarbonate in the Zn-NaCl-DOC system has been also inferred previously from modelling and experimental work (Heijerick et al., 2002, 2003; Hyne et al., 2005; Millero & Hawke, 1992; Powell et al., 2013; Tepavitcharova et al., 2011, 2014). ZnHCO_3^+ is abundant in acidic to neutral solutions and ZnCO_3 in alkaline solutions in the pH range between 8 and 10. The abundance of ZnHCO_3^+ and ZnCO_3 is higher in solutions with a salinity of 0.1 mol L^{-1} compared to solutions with salinity of 0.7 mol L^{-1} .

3.1.3 | pH edges for zinc adsorption onto tropaept and hydraquent soils in saline solutions

Having established the influence of salinity, DOC and carbonate on the availability of free Zn^{2+} for adsorption, we assessed the role of salinity on zinc adsorption onto soils through a combined experiment-modelling approach. We used experimental pH adsorption edges to validate a multi-surface model (MSM) developed by combining the characterisation of the soil samples with generic model parameters.

Figure 3 shows the experimentally determined percentage of zinc adsorbed on both soils studied, that is the hydraquent (Tiaong) and the tropaept (Bay) soils, as a function of pH in solutions with increasing salinities. The pH-dependent evolution curve for the zinc adsorption is similar for both soil types. Adsorption is low at pH 3, increases sharply between pH 3 and 6, then increases gradually between pH 6 and 7 and finally plateaus at pH 8 when adsorption is quantitative (essentially all zinc is removed from solution). Increasing salinity from 0.1 to 0.3 mol L^{-1} significantly decreases zinc adsorption onto both soils in the pH range between 3 and 7. Under these conditions, up to 20% of total zinc moves from the adsorbed phase to the aqueous phase. We do not observe any macroscopic salinity effect in the pH range above 8, since adsorption is quantitative. Increasing salinity from 0.3 to 0.7 mol L^{-1} reduces zinc adsorption slightly more in the tropaept soil, suggesting possibly an important control of the soil type.

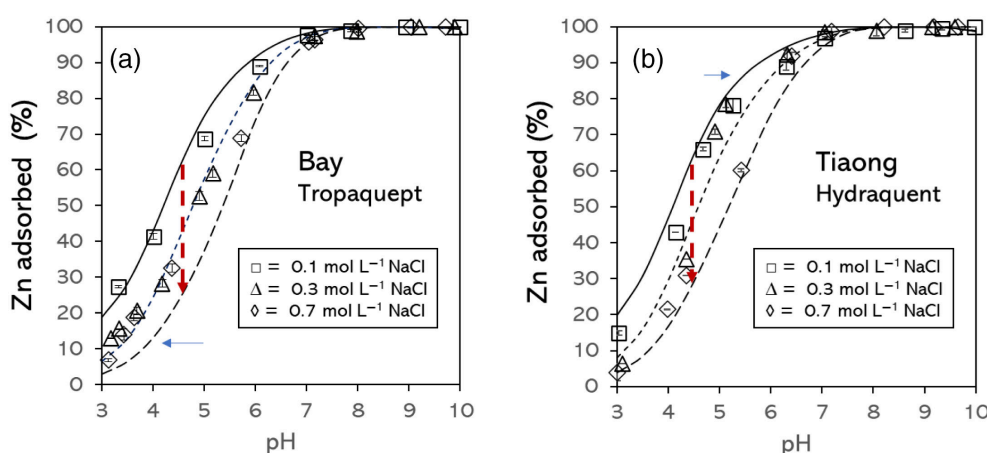


FIGURE 3 Zinc adsorbed (in %) on Bay (a) and Tiaong (b) soil as a function of pH in solutions with 0.1 ($\square$), 0.3 (Δ) and 0.7 ($\diamond$) mol L^{-1} NaCl and $[\text{Zn}] = 0.08 \text{ mmol L}^{-1}$. Models are represented by the solid (0.1 mol L^{-1}), short-dashed (0.3 mol L^{-1}) and long-dashed lines (0.7 mol L^{-1}), respectively. Model calculations included all major background cations. Standard errors of means were calculated from triplicate experiments and were smaller than the data symbols. All the model parameters used are listed in Table 2. Note the decrease in zinc adsorption at higher salinities (red dashed arrows). The model fits are inferior at low salinity for the hydraquent soil and at high salinity for the tropaept soil (blue arrows).

Likely reasons for the reduced adsorption at higher salinity (0.7 mol L^{-1}) include (i) the increased formation of less positively charged Zn–chloride complexes in the aqueous phase (i.e. ZnCl^+ and ZnCl_2), which consequently adsorb less on the mainly negatively charged sorption sites of clay minerals and SOM (Khai et al., 2008; Weng et al., 2001), (ii) neutral-to-positive surface charge at these pH values, increasing with rising salinity, resulting in unfavourable electrostatics for adsorption of zinc cations, (iii) the dissociation of SOM and clay leading to increased shielding of surface charge on SOM, clay and zinc species, reducing therefore electrostatic interactions between adsorbent surfaces (Acosta et al., 2011; Gustafsson & Kleja, 2005; Renkou et al., 2009; Wang & Harrell, 2005).

The role of Na^+ is likely insignificant due to its less competitive nature for adsorption sites compared with Zn^{2+} (Jalali & Zinli, 2012; Wang & Harrell, 2005). Sodium cations form outer-sphere complexes with clay minerals and are at a greater distance from the surface so cannot displace zinc from sorption sites (Acosta et al., 2011). Na^+ binds only electrostatically in the NICA–Donnan model, so competition between Na^+ and Zn^{2+} that mainly binds to the functional groups of the humic is also expected to be limited. Furthermore, organic matter plays a critical role as it blocks or neutralises charged sites on clay and iron oxide minerals at low pH. The importance of associations between organic matter and iron oxides on metal sorption in soils are widely reported in the literature, for example humic acids form complexes with iron oxide surfaces, especially at acidic pH and cause iron oxides to become largely negative and

non-responsive to pH, resulting in the absence of a measurable isoelectric point (Carlson & Kawatra, 2013; Jalali & Zinli, 2012; Ramos-Tejada et al., 2003).

The MSM model applied using pre-defined parameters shows a good fit to experimental data as shown in Figure 3. The overall RMSE range for different salinities between 2.88% and 2.92% for the hydraquent and between 4.59% and 2.74% for the tropaquept soil. RMSE values are lower in the alkaline and larger in the acidic regions, that is for the latter 4.04%, 3.63% and 8.88% for hydraquent soil and 6.09%, 3.57% and 4.50% for tropaquept soil for solutions with 0.1, 0.3 and 0.7 mol L^{-1} salinity. An alternative assessment of the model performance is possible using Figure 4, where the MSM predicted concentration of free Zn^{2+} in solution is plotted against the experimental determination of dissolved zinc using ICP-MS. We find that model and experiment differ especially at low concentrations, which correspond to higher pHs when sorption is greatest. The deviation is also greater in the calcareous hydroquent soil. The model fits are lower for experiments at high salinity for the hydraquent soil. Possible reasons for discrepancies observed at higher pH include the plausibly greater role speciation plays, that is ternary surface complexes with Zn–Cl are missing in the SCM model for iron hydroxides (see Table 2). The failure to predict dissolved zinc activities at higher salinity could suggest that using parameters developed at lower ion strengths is not fully adequate. Indeed, the NICA–Donnan model is known to be less accurate at higher salinities (Avendano et al., 2016) due to electrostatic interactions poorly accounted for by the present Donnan model (Gustafsson & Kleja, 2005). Metal

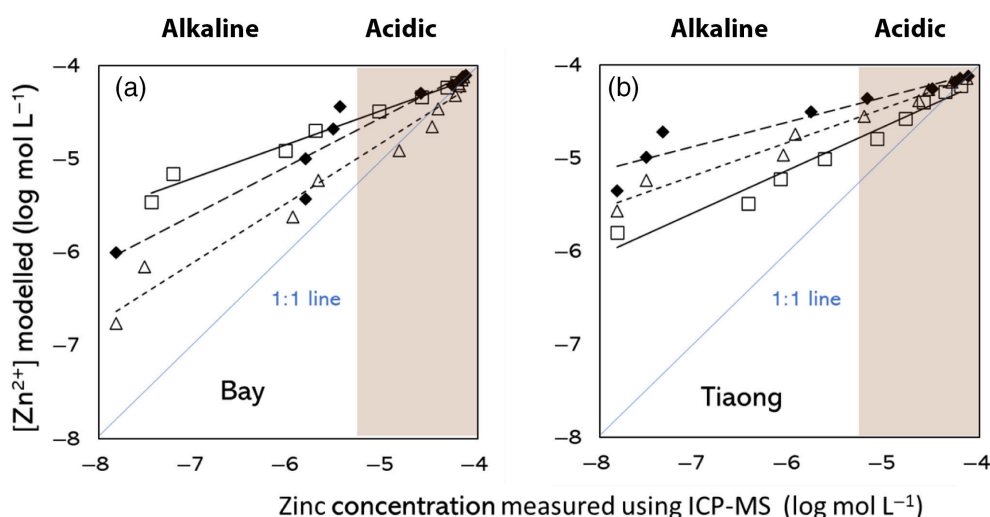


FIGURE 4 Comparison of measured total zinc concentration and predicted free Zn^{2+} concentration in solutions with 0.1 ($\square$), 0.3 (Δ) and 0.7 ($\blacklozenge$) mol L^{-1} NaCl for Bay (a) and Tiaong (b) soils. Standard errors of means calculated from triplicates are smaller than the data symbols. The model fits are represented by the solid (0.1 mol L^{-1}), short-dashed (0.3 mol L^{-1}) and long-dashed lines (0.7 mol L^{-1}), respectively. Shown is also the 1:1 line in blue and the shaded region highlights the acidic pH region.

binding parameters used to derive the model parameters for the NICA–Donnan model have been obtained mostly from adsorption studies in a 1:1 electrolyte at a concentration of 0.1 mol L^{-1} (Groenenberg et al., 2010; Milne et al., 2001). Analytical uncertainties measuring these small concentrations of aqueous zinc may also play a role. Finally, the model assumption of atmospheric CO_2 pressure might be wrong as possibly the true CO_2 pressure is greater, leading therefore to an over-estimation of free Zn^{2+} concentrations.

The pH effect on cation adsorption on soils is in general less dramatic compared with single-phase sorbents (Barrow & Whelan, 1998). This is due to the overlap, and thus convolution, of multiple adsorption edges, one for each surface phase present (Bullen et al., 2020; Davis et al., 1998). The MSM deals with this problem using a component additive approach, that is adsorption onto the soil is predicted by adding up zinc adsorption onto non-interacting, independent surface components (HFO, SOM, clay) (Bullen et al., 2020; Davis et al., 1998). We used generic model parameters from the literature, combined with experimental characterisation data for the unique composition of each soil, in terms of its iron oxide, SOM and clay contents. This component additive approach shows that as pH increases from 3 to 6, the observed pH adsorption edge is essentially entirely due to the contribution of SOM (Figure 5). The contribution of

the HFO surface phase to the observed, convoluted pH adsorption edge only begins from pH 6 onwards. Whilst total zinc adsorption is quantitative from pH 7 onwards, we observe that the contribution of HFO towards total adsorption increases from pH 7 to 8, with Zn partitioning from the SOM surface to the HFO surface. The ratio of adsorbed zinc between HFO and SOM surface phases reaches a maximum at pH 8, before zinc repartitions to the HFO surface at pH 9–10 (Figure 5). The MSM explains the experimental observation that soil pH adsorption edges are softer than pH edges for single-phase adsorbents and highlights insights gained through component additive modelling that are typically unavailable even when using state-of-the-art surface-sensitive analytical techniques such as X-ray photoelectron spectroscopy (XPS) or low-energy ion scattering (LEIS), where data remain convoluted (Bullen et al., 2020).

3.2 | Impact of salinity on zinc partitioning in soils in coastal and floodplain areas

The distributions of zinc within the different soil phases (aqueous and solid) predicted using the MSM are shown for the tropaquept and hydraquent in Figure 5 and for the Bajoa, Barisal, Kamal, Ramgati and Sara soils

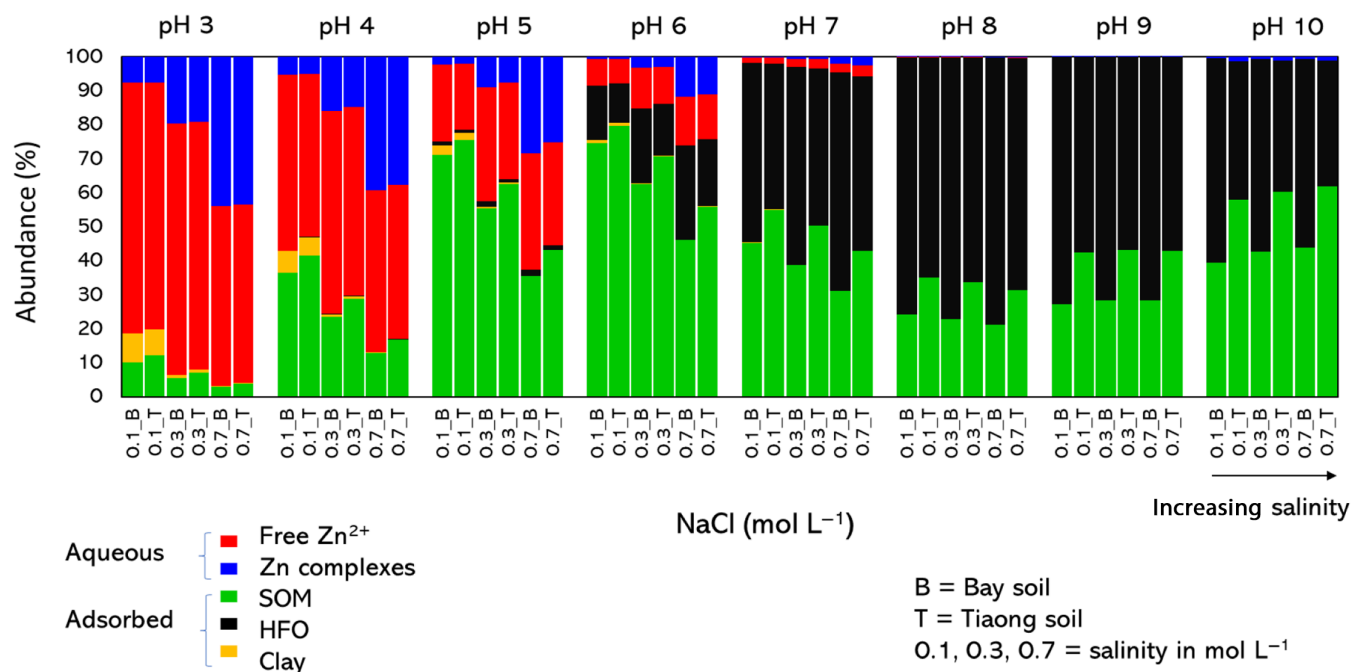


FIGURE 5 Abundance of zinc (in %) in the solid (clay, HFO and soil organic matter [SOM]) and aqueous (free Zn^{2+} and Zn complexes) phases in soil systems with 0.1, 0.3 and 0.7 mol L^{-1} NaCl. $[\text{Zn}] = 0.08 \text{ mmol L}^{-1}$. 0.1_B = Bay soil, 0.1 mol L^{-1} NaCl; 0.3_B = Bay soil, 0.3 mol L^{-1} NaCl; 0.7_B = Bay soil, 0.7 mol L^{-1} NaCl; 0.1_T = Tiaong soil, 0.1 mol L^{-1} NaCl; 0.3_T = Tiaong soil, 0.3 mol L^{-1} NaCl; 0.7_T = Tiaong soil, 0.7 mol L^{-1} NaCl. The calculations were performed with the inclusion of the major background cations. Zinc complexes include Zn-chlorides, $\text{Zn}(\text{OH})_2$ and ZnCO_3 .

representing endoaquepts in the Ganges Floodplain region of Bangladesh in Figure 6. Shown are the abundances of free Zn^{2+} , complexed zinc in solution and zinc

adsorbed to each surface phase (SOM, hydrous iron oxides and clays). In Bangladesh, entisols cover about 20%–30% of the land area and inceptisols about 60%. Both soil orders are commonly found along major rivers like the Ganges and Brahmaputra, as well as in the coastal regions of the Bay of Bengal.

We find that for the tropaequept and hydrquent soils (Figure 5), zinc adsorption in acidic solutions is controlled by SOM and at neutral and alkaline pH by SOM and iron (hydr)oxide. These observations are in line with findings from experimental and modelling studies including a wide range of soil types with low and high zinc content (Duffner et al., 2014), sandy soils (Weng et al., 2001), natural sediments (Fisher-Power et al., 2016) and contaminated soils (Ren et al., 2017). The contribution of clay to zinc absorption is minimal and constrained to acidic solutions. This reflects the role of major cations present in solutions such as Ca^{2+} and Mg^{2+} occupying the clay's permanently negatively charged sites. Clay minerals adsorb metal cations in solutions with low pH, low organic matter content and low cation concentrations (Weng et al., 2001).

In all Bangladesh soils (Figure 6), we find that increasing salinity leads to the increased formation of zinc complexes with chloride and bicarbonate in agreement with the speciation calculations conducted in Section 3.1. Zn-chloride complexes become particularly more abundant in the acidic and non-calcareous soil series compared with alkaline soil series where most zinc is adsorbed. A small concentration of Zn-DOC complexes is observed in the acidic Kamalthaki soil system, at low salinity only (0.1 mol L^{-1}). In both the acidic Kamalthaki and non-calcareous Barisal soil series, the abundance of free zinc (Zn^{2+}) increases in solutions with salinities ranging from 0.1 to 0.3 mol L^{-1} and decreases in solutions with salinity of 0.7 mol L^{-1} . In the acidic Kamalthaki soil series, SOM is the main adsorbing phase, whilst

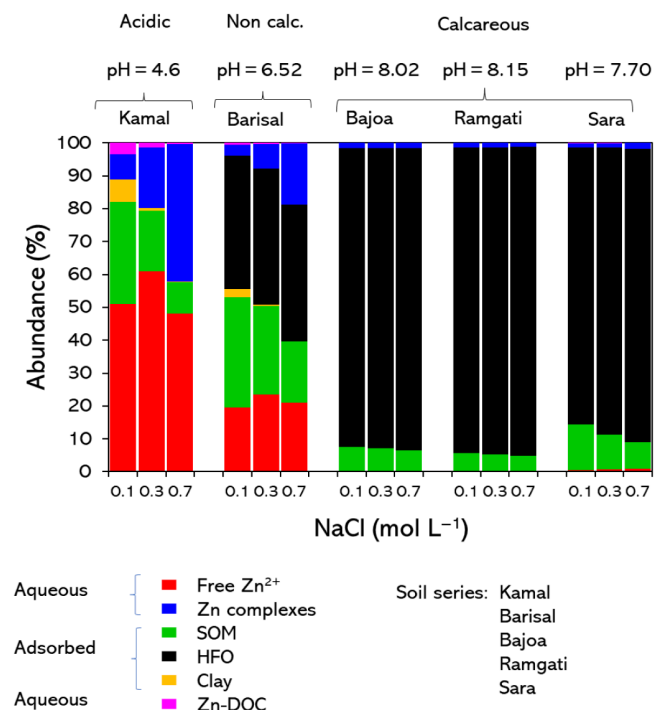
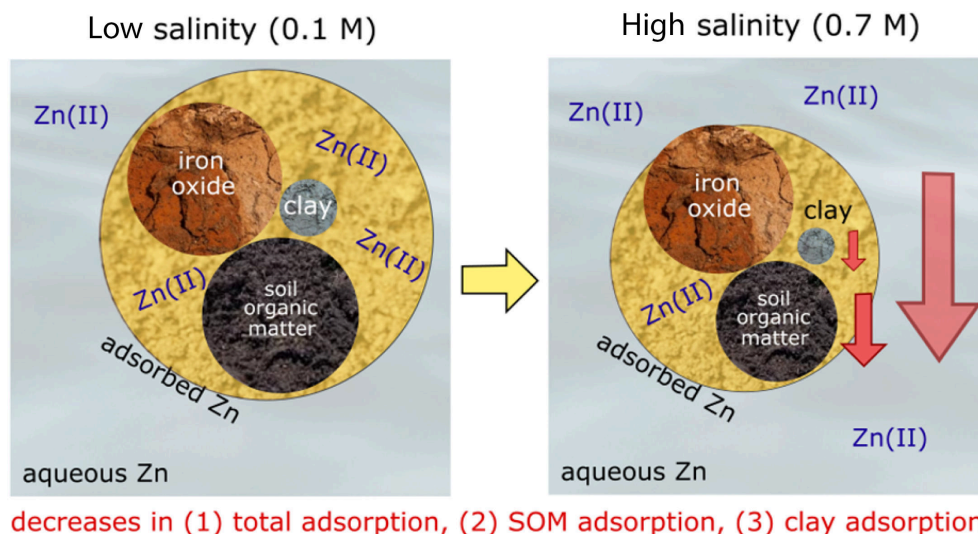


FIGURE 6 Abundance of zinc (in %) in the solid (clay, HFO and soil organic matter [SOM]) and aqueous (Zn-DOC, free Zn^{2+} and Zn complexes) phases in soils of the Ganges Floodplain in Bangladesh with solutions of 0.1, 0.3 and 0.7 mol L^{-1} NaCl. The classification of the soils is acidic for the Kamalthaki soil series, non-calcareous for the Barisal soil series and calcareous for the Bajoa, Ramgati and Sara soil series. The calculations were performed with the inclusion of the major solution anions and cations. Zinc complexes include Zn-chloride complexes, $\text{Zn}(\text{OH})_2$ and ZnCO_3 . Zn-DOC complexes are separate. The locations are shown on the map in Figure 1. See Table 1 for details on model input and parameters.

FIGURE 7 Summary schematic of the major influences of increasing salinity on zinc adsorption. Total zinc adsorption decreases with increasing salinity, primarily due to a reduction in zinc adsorption onto soil organic matter (SOM) (and to a lesser extent, clay also). Adsorption into iron oxides appears little changed.



in the non-calcareous Barisal soil series, both SOM and iron oxides are significant adsorbing phases. In both soil series, zinc adsorption to SOM decreases with increasing salinity, whilst adsorption to iron oxides in the Barisal soil series is little affected. In both soils, the clay phase plays a minor role in adsorption, and only at low ionic strength (0.1 mol L^{-1}). In the alkaline Bajoa, Ramgati and Sara soil series, iron oxides are important zinc adsorption sites and we observe only a small salinisation effect. The iron oxide negative surface charge at higher pH promotes the adsorption of zinc cations (Chesne & Kim, 2014) and SOM plays a minor role in zinc adsorption only in these alkaline soils. Overall, the pH of the soil series has a major role in determining both the extent of zinc adsorption, and susceptibility to impact by increasing salinisation: Acidic Kamalkathi soil (pH 4.6) shows limited zinc adsorption, reliant upon SOM and decreasing with rising salinity; near neutral Barisal soil (pH 6.5) shows moderate zinc adsorption, using both SOM and iron oxide, with SOM adsorption only decreasing with rising salinity; alkaline calcareous soils (pH 7.7–8.2) show high zinc adsorption, primarily using the iron oxide phase and potentially less impacted by rising salinity. This trend is not dissimilar to the pH adsorption edge observed for individual soils (Figure 5). The major changes in zinc adsorption with increasing salinity are summarised schematically in Figure 7.

4 | CONCLUSIONS

The current study presents the results of a combined experimental and modelling investigation into effects of salination on zinc speciation and adsorption in soil systems relevant to tropical coastal and floodplain environments. Our main conclusions are:

1. Increasing salinity enhances the formation of aqueous Zn–chloride complexes in the presence of dissolved organic matter and bicarbonate, decreasing the chemical potential towards surface complexation. Zinc speciation in saline solutions up to 0.7 mol L^{-1} is well represented using the Davies ion activity model. In the presence of NaCl, bicarbonate and DOC, zinc interactions with Cl^- and DOC are most significant at pH between 4 and 7. In the presence of DOC and HCO_3^- , the abundance of Zn–bicarbonate complexes decreases with increasing salinity. Zn–DOC complexes are more abundant in low-salinity solutions and decrease with increasing salinity. Overall, increasing salinity decreases the activity of Zn^{2+} , which will influence the adsorption equilibria mass expression.
2. Laboratory batch experiments using a hydraquent and a tropaquept soil, show a significant decrease in zinc adsorption in solutions with salinities between 0.1 and 0.3 mol L^{-1} in the pH range between 3 and 6. We attribute this mainly to the increased formation of Zn–chloride complexes at higher salinity and its effect on electrostatic interactions.
3. Geochemical modelling applying a multisurface model containing three surface phases, that is iron hydroxides, SOM and phyllosilicate clays, represented using the DDL model, the NICA–Donnan model and ion exchange equation with pre-determined parameters from the literature show good agreement with experimental data. The error between model and experiment increases at low salinity for the hydraquent soil and at high salinity for the tropaquept soil. Possible reasons for discrepancies observed include (i) incomplete representation of surface complexes (e.g. ternary surface complexes) in the DDL model, (ii) the parameters developed at lower ion strengths might not be fully adequate and (iii) modelling assumptions of atmospheric CO_2 pressure may be incorrect (the true CO_2 pressure may be greater). There is a need to parametrise multi-surface adsorption models and zinc complexes with DOC at higher ionic strengths to improve the accuracy of our present multi-surface model.
4. The MSM developed provides insights into the changes in zinc partitioning following salinisation in one hydraquent and one tropaquept soil from the Philippines and in five endoaquept soils from Bangladesh. We gain insights into not just solution-surface partitioning but partitioning between surface phases also. We find that iron hydroxides are the most important sorbent phases in the alkaline soil series, whereas SOM is the dominant sorbent phase for near-neutral and acidic soils. Increasing salinity decreases zinc adsorption to the SOM and clay fraction. The most significant findings are summarised schematically in Figure 7.
5. We conclude that climate change leading to increasing sea levels and hence salinisation of coastal and floodplain soils will have a significant impact on zinc cycling in these ecosystems. We predict a decrease in zinc adsorption in particular in acidic to neutral soils, with alkaline soils comparatively less affected. Consequently, the availability of zinc in the soil water available for biouptake through the roots of crop plants such as rice will be affected, and there is a greater risk that zinc amendments applied via fertiliser products is lost to runoff, hence negatively impacting crop production in acidic and neutral soils.

AUTHOR CONTRIBUTIONS

Md. Hanif: Conceptualization; data curation; formal analysis; visualization; writing – original draft; methodology; funding acquisition. **Jay Bullen:** Formal analysis; investigation; supervision; writing – review and editing. **Yves Plancherel:** Supervision; project administration; writing – review and editing. **Matthew Kirby:** Methodology; writing – review and editing. **Guy Kirk:** Supervision; writing – review and editing. **Dominik Weiss:** Conceptualization; supervision; project administration; writing – review and editing; funding acquisition; resources.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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