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Optimizing multi-surface modelling of available cadmium as measured in soil pore water and salt extracts of soils amended with compost and lime: The role of organic matter and reactive metal

Yuwei Qin [a,b,*], Jan E. Groenenberg [a], Yoann Viala [b], Sheila Alves [b], Rob N.J. Comans [b]

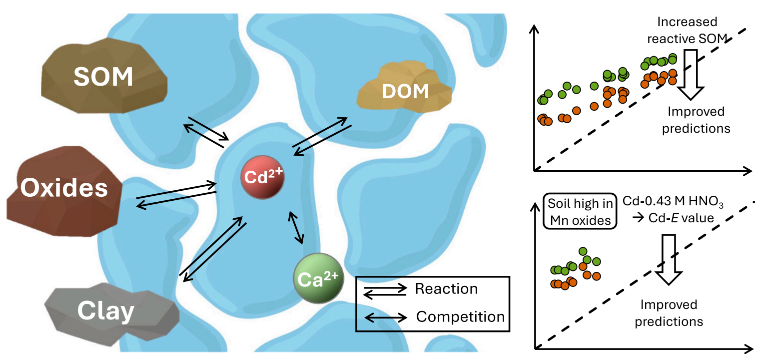
[a] Chair Group Soil Chemistry and Chemical Soil Quality, Wageningen University, Wageningen University & Research (WUR), P.O. Box 47, 6700, AA, Wageningen, the Netherlands

[b] Teagasc, Crops Research Centre, Oak Park, Carlow R93 XE12, Ireland

HIGHLIGHTS

- Incomplete extraction of humic substances resulted in overprediction of dissolved Cd by multi- surface models.
- 1 mM $Ca(NO_3)_2$ extraction is a suitable proxy for soil pore water in terms of dissolved Cd concentration and speciation.
- Residuals between modelled and measured Cd increase with pH suggesting uncertainties in the generic NICA-Donnan parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

The effectiveness of strategies to reduce cadmium (Cd) availability for crop uptake can be assessed using various measures of Cd availability, such as Cd concentration in pore water and Cd extracted with salt solutions. This study evaluated the performance of multi-surface modelling (MSM) to predict dissolved Cd in two Irish tillage soils treated with lime, zinc (Zn) and spent mushroom compost (SMC). Predictions were assessed against Cd measured in three solution media, i.e., 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$ extractions, as well as in soil pore water. Results indicate that reactive soil organic matter (SOM) may be underestimated using a single 0.1 M NaOH extraction in the investigated soils, leading to substantial overestimation of dissolved Cd by MSM, particularly at higher pH. Repeating the 0.1 M NaOH extraction three times substantially improved model predictions. Additionally, using reactive Cd determined by isotopic dilution instead of 0.43 M HNO_3 improved model predictions for one of the soils that was rich in manganese (Mn) oxides, revealing a possible role of Mn oxides in determining the reactive Cd fraction. After optimizing reactive SOM and reactive Cd, residuals between predicted and measured Cd showed an increasing trend along with increasing solution pH and decreasing dissolved Cd. This is likely related to Cd binding to high affinity sites due to uncertainties in the binding parameters for these sites

* Corresponding author at: Chair Group Soil Chemistry and Chemical Soil Quality, Wageningen University, Wageningen University & Research (WUR), P.O. Box 47, 6700, AA, Wageningen, the Netherlands.
E-mail address: yuwei.qin@wur.nl (Y. Qin).

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and/or to slow desorption kinetics for Cd bound to these sites. Despite significant variations in solution properties, including higher dissolved Ca and reactive dissolved organic matter (DOM), 1 mM $Ca(NO_3)_2$ extracts exhibited similar extractable Cd levels, model performance, and Cd speciation compared to soil pore water especially at higher pH. Thus, 1 mM $Ca(NO_3)_2$ can be a reliable proxy for soil pore water in assessing Cd availability for crop uptake in soils with circumneutral to alkaline pH.

1. Introduction

Cadmium (Cd) is a toxic metallic trace element that can be found in the edible parts of terrestrial crops (European Food Safety Authority, 2012). Cd is a non-essential element to humans that may cause health effects; therefore, several countries have set limits for Cd in foodstuffs (McLaughlin et al., 2021). It is well known that crop metal uptake is often poorly reflected by the total metal concentrations in soils (Meers et al., 2007). However, there is no consensus on a standard measurement that indicates soil available Cd for plant uptake (Sauvé et al., 2000). Soil pore water is the primary medium from which plants take up metals, making Cd concentrations in soil pore water an important measure of the available Cd for crop uptake (Alloway, 2013). Due to practical constraints in collecting soil pore water, weak salt extracts are often used as a proxy (Houba et al., 2000; Degryse et al., 2003; Regelink and Koopmans, 2021). However, Cd is usually depleted near the root surface as a result of its rapid uptake (Degryse et al., 2006; Degryse et al., 2012; Degryse and Smolders, 2012; Smolders et al., 2020). Consequently, the fraction of Cd in the soil solid phase which can replenish the pore water Cd concentration is an important factor for crop uptake (Lin et al., 2015). This may explain Cd measured in a stronger salt extraction, 0.1 M $CaCl_2$, has been found to correlate well with potato tuber Cd concentrations, where other reagents failed so (Alves et al., submitted).

The concentration of Cd available for crop uptake can also be assessed by process-based multi-surface modelling (MSM) (Groenenberg and Lofts, 2014; Di Bonito et al., 2024). By simulating metal binding to soil reactive surfaces, such as soil organic matter (SOM), metal oxides and clay minerals under equilibrium conditions, MSM utilizes concentrations of total reactive metal in soils to predict its partitioning between the soil solid phase and a designated solution medium representing the soil dissolved phase, as well as its chemical speciation in that solution medium (Bonten et al., 2008). The amount of the soil reactive surfaces and solution pH, concentrations of the major cations and anions are required as model input. As soil Cd measured in various solution media can be associated with crop Cd concentrations, it is important to investigate their differences in terms of Cd extractability and crucial properties such as pH and dissolved organic matter (DOM), as well as to evaluate the performance of MSM to predict Cd solubility and speciation in these solution media.

Cd in soils is mainly present adsorbed to the solid phase, where it is primarily bound to SOM (Christensen and Haung, 1999; Gustafsson et al., 2003; Dijkstra et al., 2004). The binding of Cd onto SOM is largely influenced by soil pH (Sauvé et al., 2000). Applying organic and/or inorganic amendments may reduce soil Cd availability for plant uptake by shifting its partitioning towards the solid phase without changing total Cd concentrations (Kirkham, 2006; Loganathan et al., 2012). For example, soil liming is a common practice to raise soil pH through the dissolution of hydroxide ions, and consequently enhances the sorption of metal ions onto SOM (Hamid et al., 2019; He et al., 2021). On the other hand, application of organic amendments may also increase Cd binding by providing additional adsorption sites (Bolan et al., 2003). During such amelioration processes, various chemical changes are induced in soils, including changes in soil pH, the concentration and composition of both SOM and DOM, leading to changes in Cd solid solution partitioning and speciation (Kirkham, 2006; Loganathan et al., 2012; Khan et al., 2017; Hamid et al., 2019). While MSM has been previously used to predict dissolved Cd in diverse soils with varying properties and total Cd (Zhang et al., 2018; Zhu et al., 2018; Gao et al., 2022), its applicability to predict dissolved Cd in soils as a result of amelioration treatments remains largely unexplored. By accurately simulating dissolved Cd in different solution media (e.g. soil pore water and salt extracts) in the presence of one or more amendments, MSM is potentially a valuable tool for optimizing crop Cd amelioration strategies.

In the concept of advanced ion-binding models for ion binding to SOM, humic acids (HA) and fulvic acids (FA) are considered as the primary components in SOM to which metals adsorb, and the MSM is parameterized for these substances (Tipping, 1998; Kinniburgh et al., 1999; Gustafsson and Van Schaik, 2003). Therefore, we consider the sum of the HA and FA fractions as the reactive fraction of SOM. The quantity of reactive SOM may range from 31 % to 87 % in different soils, and has been identified as one of the important sources of model uncertainty in ion binding models (Groenenberg et al., 2012; Groenenberg and Lofts, 2014). Preliminary experiments from this study also showed that MSM-modelled dissolved Cd was highly sensitive to variations in the quantity of reactive SOM. The quantity of reactive SOM can be experimentally determined by a rapid batch procedure, which involves measuring the concentrations of HA and FA in the 0.1 M NaOH-extractable humic substances (HS) (Van Zomeren and Comans, 2007). This approach has been used in multiple studies involving MSM by Dijkstra et al. (2009), Van Eynde et al. (2022), Gao et al. (2022) and others.

Based on the above, the aims of this study were: (1) to assess the performance of the MSM in predicting dissolved Cd in soil pore water and extracts with 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$, which received applications of one or more amendments; (2) to gain insights into variation between different solution media used to assess available Cd with regards to their Cd dissolution properties and speciation, as well as modelled Cd concentration and speciation. Dissolved Cd concentrations of soils samples collected from a pot experiment, with amendments of compost, lime and Zn, were predicted in and assessed against dissolved Cd measured in in-situ collected soil pore water and 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$ extracts. We optimized model inputs based on additional measurements and critically evaluated deviations between predicted and measured dissolved Cd in the three different solution media.

2. Materials and methods

2.1. Origin of the soil samples

Soil samples used in this study were obtained from a potato pot experiment designed to study the effectiveness of three amendments in reducing potato tuber Cd concentration: spent mushroom compost (SMC), zinc and lime. A detailed description of the pot experiment setup and sampling can be found in the Supplementary Information (S1). In short, the treatments comprise two Irish tillage soils (Grange and Backweston, coded as GR and BW, respectively), three incubation treatments (untreated, acidified, limed) for soil GR and one incubation treatment (untreated) for soil BW. Under each incubation treatment, a combination of two zinc application rates (0 and 45 kg ha^{-1}) and four SMC application rates (0, 15, 30 and 60 t ha^{-1}) were applied. The application rates of SMC were chosen to assess the response of SMC application at half and double the maximum allowable rate according to the EU Nitrates Directive (European Commission, 2008), which is 30 t ha^{-1} based on the estimated available N and P contents of this material. Applying Zn at 45 kg ha^{-1} was relatively large compared to common Zn application rates of <10 kg ha^{-1} (Montalvo et al., 2016). This higher rate was chosen to amplify and further investigate its potential in reducing tuber Cd levels. In total, this resulted into 32 different treatments.

2.2. Soil analysis

All soil samples were dried at 40 °C and sieved (<2 mm) before analysis.

2.2.1. Soil properties

Soil pH was determined in a suspension of soil and water (1:5 soil to solution ratio) using a pH meter (ORION STAR A211, Thermo Fisher Scientific) after shaking for 1 h and settling for 1 h (ISO:10390, 2005). Soil cation exchange capacity (CEC) at actual soil pH was measured by the hexamminecobalt (III) chloride extraction method (ISO:23470, 2018). SOM content was determined gravimetrically in oven-dried soil samples (105 °C), by ignition at 550 °C in a muffle furnace, and the value corrected for structural water loss from clay (Hoogsteen et al., 2015). Clay content was determined by the pipette method (Gee et al., 1986). Poorly crystalline Fe, Al and Mn oxides were determined by extracting the soils with a solution of ammonium oxalate (AO) and oxalic acid (ISO:12782–3, 2012). Fe, Al and Mn in the extracts were measured with Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES, iCAP 6500 DUO, Thermo Fisher Scientific) Pseudo-total Cd, Cu and Zn content was determined by microwave assisted aqua-regia digestion for soil samples (HNO_3/HCl). The elements in the extract were measured with ICP-OES. Total reactive Cd, Cu and Zn were extracted using a 0.43 M HNO_3 solution at a solid-to-liquid (SL) ratio of 0.1 (Groenenberg et al., 2017). The extraction involved a shaking period of 4 h, followed by centrifugation at 3000 rpm for 10 min. The supernatants were then filtered through a 0.45 μm membrane filter (Aqua 30/0.45 CA, Whatman) and the Cd, Cu and Zn concentrations were subsequently measured by ICP-OES.

2.2.2. Salt solution extraction procedures

Concentrations of Cd, Cu, Zn, K, Mg, Mn, P, Na and Ca were determined in two salt extracts: 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$. All salt extractions were carried out at a soil-to-solution ratio of 1:10 and the suspensions were shaken horizontally at 180 beats per minute for 2 h (1 mM $Ca(NO_3)_2$) or 3 h (0.1 M $CaCl_2$) and centrifuged at 3000 rpm for 10 min (Klinkert and Comans, 2020; Alves et al., submitted). pH was measured in a portion of the soil suspensions before centrifugation. Concentrations of the aforementioned elements were then quantified in the 0.45 μm-filtered (Aqua 30/0.45 CA, Whatman) supernatants using ICP-OES for the elements K, Mg, Mn, P, Na and Ca or High Resolution - Inductively Coupled Plasma - Mass Spectroscopy (HR-ICP-MS, Element 2, Thermo Fisher Scientific) for the elements Cd, Cu and Zn. Additionally, dissolved organic carbon (DOC) was measured in those supernatants using a Segmented Flow Analyzer (SFA-TOC, San ++, Skalar).

2.2.3. Soil pore water collection and analysis

Soil pore water was collected using Rhizon samplers with a 0.15 μm pore size (model MOM, Rhizosphere Research Products B.V., Wageningen, the Netherlands) and characterized in terms of pH, elemental concentrations (Cd, Cu, Zn, K, Mg, Mn, P, Na and Ca) and DOC as described for soil extracts in 2.2.2.

2.2.4. Isotopic dilution

In addition to the 0.43 M HNO_3 extraction which was used for all treatments to determine reactive Cd, the reactive Cd concentration (i.e., *E* value) of the two original soils was also determined with isotopic dilution following the principles of Marzouk et al. (2013) and modifications by Wiersma et al. (In preparation). Here we used ^{111}Cd as the spike isotope and ^{114}Cd as the reference isotope. In short, soils were suspended in 1 mM $Ca(NO_3)_2$ solution at a soil-to-solution ratio of 1:10 and shaken on an end-over-end shaker at 40 rpm for 72 h. Thereafter the suspensions were spiked with 0.1 mL of ^{111}Cd (97.21 % purity, ISOFLEX) at 1 (GR) or 2 (BW) mg L^{-1} and the suspensions were again shaken on an end-over-end shaker at 50 rpm for 72 h. After centrifuging at 3000 rpm for 10 min, Cd isotopes were determined in the filtered supernatants (< 0.45 μm) using ICP-MS. Based on the quantified spike and reference isotope counts per second in the spiked and non-spiked suspensions, reactive Cd (*E*-value) was calculated based on the formula in (Marzouk et al., 2013).

2.2.5. Fractionation of SOM and DOM by a rapid batch procedure

SOM and DOM of soil samples of the 0 and 60 t ha^{-1} SMC treatments in each incubation group at 0 kg ha^{-1} Zn application were fractionated, assuming Zn application did not change SOM and DOM composition. NaOH-extractable SOM and 1 mM $Ca(NO_3)_2$-extractable DOM, as well as DOM in soil pore water were fractionated into HA, FA, hydrophilic acid (Hy) and hydrophobic neutral organic matter (HON) fractions. These fractions were determined using the rapid batch procedure (Van Zomeren and Comans, 2007). A detailed description of the procedure is given in S 2. The concentrations of the HA, FA, dissolved HA (DHA) and dissolved FA (DFA) were used as input in the MSM.

2.3. Multi-surface modelling

The MSM was implemented in the JAVA environment modelling platform ORCHESTRA (Meeussen, 2003). The MSM includes three submodels: (1) the NICA-Donnan model to describe the binding of protons and metal cations to SOM and DOM (modelled as HA and FA) (Kinniburgh et al., 1999; Milne et al., 2001; Milne et al., 2003); (2) the generalized two-layer model (GTLM) to describe metal adsorption to both Fe- and Al- (hydr)oxides (Dzombak, 1990), (3) a Donnan model to describe the electrostatic adsorption of metals onto the planar surfaces of clay minerals, assuming a charge density of 0.25 eq kg^{-1} and a fixed Donnan volume of 1 L kg $^{-1}$ (Weng et al., 2001). In section 3.4, the binding of Cd to Mn oxides is included in one of the discussed model scenarios (including Mn oxides in the solid phase), in which the GTLM with binding parameters from Tonkin et al. (2004) was used. Model inputs include: (1) reactive Cd, Cu and Zn, extracted with 0.43 M HNO_3; (2) measured pH and total dissolved concentrations of K, Mg, Mn, P, Na, Ca, PO_4, Cl and NO_3; (3) concentrations of the different reactive surfaces (see Table S1), and (4) generic parameters for the sub-models in the cited references without modifications, except for the parameters of Fe^{3+} binding to FA which were taken from Hiemstra and van Riemsdijk (2006). Further details of the model inputs and their corresponding measurements, calculations and assumptions (if applicable) are listed in Table S1.

3. Results and discussion

3.1. The obtained dataset

Selected properties of the two Irish tillage soils are listed in Table 1. The two soils had comparable levels of CEC, SOM and clay content, as well as oxalate extractable Fe and Al, while the pH-H_2O of soil BW was higher than soil GR. Soil BW had nearly twice the amount of pseudo-total Cd and reactive Cd measured in 0.43 M HNO_3, as well as the *E*-value, were also higher for BW than those for GR. BW had 2.6 times the amount of AO-extractable Mn compared to soil GR.

With the two soils, three incubation treatments, four doses of SMC and two doses of Zn application, 32 treatments were created, varying in SOM, reactive Cd and Zn, pH, DOC, and dissolved Cd and Ca. The minimum, average and maximum values for each property in each solution medium are given in Table 2.

While reactive Cd measured by 0.43 M HNO_3 remained relatively constant among different treatments of the two soils (1.7–2.6 % variation for the two soils), pH, DOC (concentration and composition), dissolved Cd and Ca showed considerable variation among the treatments,

Table 1
Selected properties of the two original soils used in this study. See section 2.2 for measurement details.

Soil	pH-H_2O	CEC[a]	SOM[b]	Clay[c]	Al_{ox}[d]	Fe_{ox}[d]	Mn_{ox}[d]	Cd-total[e]	Cd-0.43 M HNO_3[f]	Cd-*E* value[g]
		cmol kg^{-1}	%		mmol kg^{-1}			mg kg^{-1}		
GR	6.10 ± 0.04	11.1 ± 0.2	4.4 ± 0.3	22.3 ± 1.0	48.7 ± 0.5	121.0 ± 1.1	11.2 ± 0.1	1.25 ± 0.05	0.75 ± 0.02	0.67
BW	6.90 ± 0.02	12.4 ± 0.2	4.2 ± 0.2	19.5 ± 2.2	49.0 ± 0.4	102.0 ± 1.3	29.0 ± 0.2	2.19 ± 0.04	1.18 ± 0.01	0.82

[a] CEC measured by hexamminecobalt trichloride extraction.
[b] SOM content measured by LOI, corrected for structural water loss from clay minerals.
[c] Clay content measured by the pipette method.
[d] AO-extractable Fe, Al and Mn determined by ICP-OES.
[e] Total Cd, Cu and Zn content determined by ICP-OES in the digests of aqua regia (HNO_3/HCl) for soil samples.
[f] Reactive Cd measured in the 0.4 M HNO_3 extraction.
[g] *E*-values of the reactive Cd determined by the isotopic dilution method.

Table 2
Overview of the range of properties of the 32 treatments measured in the three solution media. Ranges of SOM, and reactive Cd and Zn measured in the 0.43 M HNO_3 extraction are also given (see section 2.2 for measurement details). The percentage of each humic substance fraction in samples receiving 15 and 30 t ha-1 SMC application were linearly interpolated by the difference between those of samples receiving 0 and 60 t ha-1 SMC application, as explained in Table S1.

Dissolved phase property								
Property		Medium	Soil GR			Soil BW		
			Min	Mean ± STD	Max	Min	Mean ± STD	Max
pH		Soil pore water	5.0	6.4 ± 1.2	8.6	7.4	7.5 ± 0.2	8.0
		1 mM $Ca(NO_3)_2$	5.5	6.4 ± 0.7	7.5	6.8	6.9 ± 0.1	7.0
		0.1 M $CaCl_2$	4.9	5.7 ± 0.7	6.7	6.2	6.1 ± 0.1	6.4
DOC	mg C L^{-1}	Soil pore water	8.4	20.0 ± 9.8	42.2	7.8	15.0 ± 6.9	26.4
		1 mM $Ca(NO_3)_2$	28.7	36.6 ± 5.9	52.4	20.0	28.1 ± 11.5	54.3
		0.1 M $CaCl_2$	33.5	43.6 ± 5.7	56.6	20.6	26.6 ± 5.4	35.1
Reactive DOM[a]	%	Soil pore water	69.4	84.9 ± 13.4	104.8	68.6	81.8 ± 18.7	95.1
		1 mM $Ca(NO_3)_2$	37.2	41.2 ± 3.6	46.9	44.4	40.8 ± 5.1	49.3
Dissolved HA (DHA)	mg C L^{-1}	Soil pore water	1.2	1.6 ± 0.4	2.1	0.9	1.0 ± 0.1	1.1
		1 mM $Ca(NO_3)_2$	0.7	0.9 ± 0.2	1.1	0.6	0.60 ± 0.04	0.7
Dissolved FA (DFA)	mg C L^{-1}	Soil pore water	6.5	14.5 ± 7.2	27.9	7.0	12.0 ± 7.1	17.0
		1 mM $Ca(NO_3)_2$	8.3	10.3 ± 2.0	12.0	5.6	7.4 ± 2.5	9.1
Hy	mg C L^{-1}	Soil pore water	1.1	5.1 ± 3.6	11.1	0.4	3.7 ± 4.6	7.0
		1 mM $Ca(NO_3)_2$	14.5	16.6 ± 3.6	19.1	8.5	9.7 ± 1.7	10.9
Cd	ug L^{-1}	Soil pore water	0.1	2.8 ± 3.4	9.5	0.0	0.1 ± 0.1	0.2
		1 mM $Ca(NO_3)_2$	0.1	0.8 ± 0.6	2.1	0.2	0.3 ± 0.1	0.4
		0.1 M $CaCl_2$	9.4	28.8 ± 14.2	47.0	19.1	23.1 ± 2.4	26.1
Ca	mg L^{-1}	Soil pore water	132.0	429.0 ± 214.7	859.0	98.4	238.2 ± 94.1	348.0
		1 mM $Ca(NO_3)_2$	47.3	86.9 ± 26.4	157.0	46.9	75.4 ± 26.1	116.0

Solid phase property							
Property		Soil GR			Soil BW		
		Min	Mean ± STD	Max	Min	Mean ± STD	Max
SOM	%	4.3	4.9 ± 0.4	5.8	4.2	4.7 ± 0.5	5.6
SHA	mg C L^{-1}	374.8	512.4 ± 97.8	624.6	491.5	570.8 ± 108.6	694.5
SFA		128.9	146.4 ± 78.7	171.9	184.1	191.8 ± 9.1	201.8
Reactive Cd	mg kg^{-1}	0.74	0.77 ± 0.02	0.84	1.18	1.21 ± 0.02	1.24
Reactive Zn		9.9	29.0 ± 16.6	55.9	11.2	24.2 ± 12.3	39.7

[a] Calculated as the sum of the DHA and DFA fractions measured in the rapid batch procedure in relation to total DOM, assuming 50 % of DOM consisted of DOC. A value exceeding 100 % was the result of the recovery rate.

as well as for the same treatments across different solution media (Table 2). For the same treatment, soil pore water demonstrated the largest variation in pH and DOC, followed by 1 mM $Ca(NO_3)_2$, while 0.1 M $CaCl_2$ showed the smallest variation. Soil pore water had a lower average total DOC concentration, but with a higher fraction of HA and FA compared to 1 mM $Ca(NO_3)_2$. The overall higher DOC in the two salt extracts may be attributed to the soil oven-drying and re-wetting process, which has been reported to significantly increase the Hy fraction which is likely due to microbial cell lysis (Koopmans and Groenenberg, 2011; De Troyer et al., 2014). This is further confirmed by the dominance of the Hy fractions in the DOM of 1 mM $Ca(NO_3)_2$, while DOM in soil pore water mainly consisted of FA. The composition of DOM in 1 mM $Ca(NO_3)_2$ extracts found in our study is in agreement with the results of Groenenberg et al. (2010), Ren et al. (2015) and Gao et al. (2022), who also found the Hy fractions to be dominant in 2 mM and 10 mM $Ca(NO_3)_2$- extractable DOM in previously dried soil samples.

Remarkably, >4 times higher dissolved Ca was present in soil pore water compared to that in 1 mM $Ca(NO_3)_2$ extracts, possibly due to the SL ratios of soil pore water (on average SL = 3.1) compared to that in batch salt extractions (SL = 0.1). Despite the differences in pH, DOC (both concentration and composition) and dissolved Ca for the same treatments, dissolved Cd concentrations measured in 1 mM $Ca(NO_3)_2$ were comparable to those in soil pore water. On the other hand, 0.1 M $CaCl_2$ extracted on average two orders of magnitude higher Cd than the other two solution media. Overall, these samples compose a unique dataset for a systematic assessment of important variables that codetermine Cd solubility and speciation, i.e. the SL ratio, solution pH, Ca and Cl concentration, DOM concentration and composition, but with limited or no variation in reactive metal contents and mineral properties of the soil. This makes this set very useful to assess MSM performance in relation to these solution phase properties.

3.2. Predictions of dissolved Cd by MSM

MSM predictions of dissolved Cd in the three solution media are shown in Fig. 1. When using the standard scenario for determining HA + FA in soil (noted as reactive-SOM_{1st}), good correlations were found between the logarithm of the measured and predicted dissolved Cd across three solution media for soil GR ($R^2 > 0.94$), while those for soil BW were weaker. For both soils, MSM consistently overpredicted dissolved Cd across all solution media, with predictions for soil GR generally outperforming those for soil BW, as evidenced by the logarithm of the root meat square error ($\log_{10}$ RMSE) (see Fig. 1).The strong correlations between measured and predicted dissolved Cd for soil GR suggest that MSM was able to predict the trends of dissolved Cd in response to amendment-induced chemical changes. However, the consistent deviation of the slopes from one indicates the accuracy to decrease with decreasing dissolved Cd. The accuracy of the predictions is somewhat inferior to the model accuracy reported in other studies with median logRMSE usually between 0.3 and 0.5 (Groenenberg and Lofts, 2014). Possible reasons for the systematic overprediction of dissolved Cd are an underestimation of Cd binding to the soil solid phase due to: (1) underestimation of the amount of reactive surface; (2) binding of Cd to other reactive surfaces considered in the modelling; (3) model parameters resulting in a too low affinity for binding Cd. Another reason could be the overestimation of reactive Cd with the 0.43 M HNO_3 extraction. These possible reasons will be further analysed in the following sections.

3.3. Overprediction of dissolved Cd: The possible role of underestimating reactive SOM

Because Cd is primarily adsorbed to SOM, the prediction of dissolved Cd is expected to be most sensitive to an underestimation of reactive SOM. It has been reported previously that a single 0.1 M NaOH extraction step as frequently applied in fractionation schemes for HS may result in an incomplete extraction (Stevenson, 1994; Li et al., 2003; Song et al., 2011). To evaluate a possible incomplete extraction of HS we choose to extend the standard batch procedure with repeated 0.1 M NaOH extractions. In addition to the sequential extraction with 0.1 M HCl and 0.1 M NaOH, identical to the standard rapid batch procedure, the residual soil was extracted again with 0.1 M NaOH for a second and a third time, in which we measured total organic carbon. No further analysis in fractionation between the HA, FA, Hy and HON fractions was employed in the extended extraction procedure.

The initial base extraction yielded 10.7 ± 0.6 and 9.1 ± 0.4 g C kg^{-1} soil from GR and BW, respectively (Table S2). The subsequent second and third base extractions additionally yielded 3.1 ± 0.3 and 1.0 ± 0.0 g

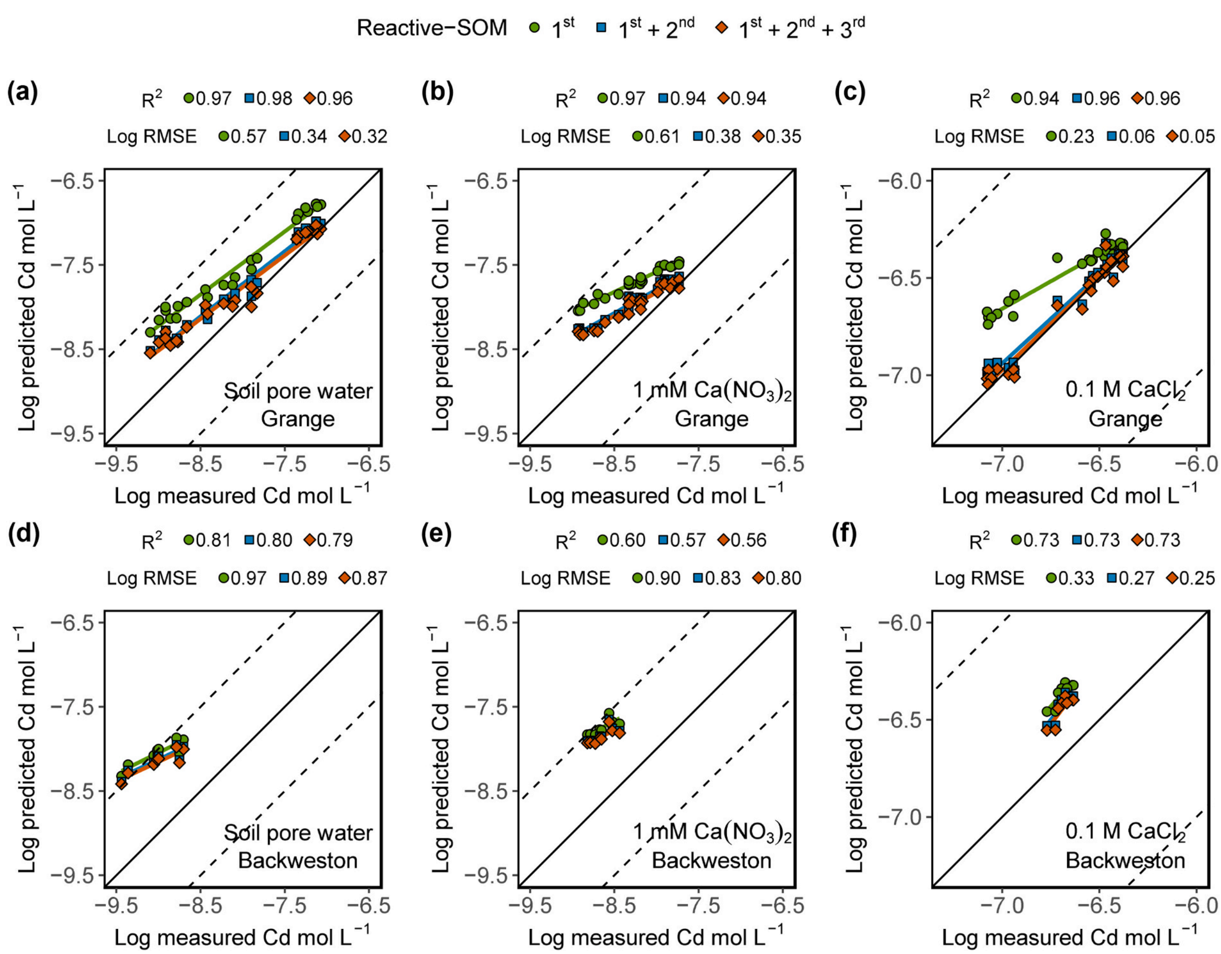

Fig. 1. Comparison of MSM predicted dissolved Cd with measured dissolved Cd (both on a $\log_{10}$ scale) in soil pore water (a,d), 1 mM $Ca(NO_3)_2$ (b,e) and 0.1 M $CaCl_2$ (c,f) for predictions with model inputs of cumulative soil extracted HA and FA after 1 (standard, green circles), 2 (blue squares) and 3 (orange diamonds) subsequent 0.1 M NaOH extractions in the batch fractionation procedure. Coloured solid lines indicate linear regressions between the logarithm of measured Cd and predicted Cd for each scenario, black solid lines indicate 1:1 lines with black dashed lines representing ±1 $\log_{10}$ unit (notice that graphs for 0.1 M $CaCl_2$ have different scales).

C kg^{-1} soil for GR, leading to cumulative increases of 26.9 % and 35.7 % in total acid + base extractable HS compared to the standard procedure with a single base extraction. For BW, the corresponding values were 1.9 ± 0.2 and 0.7 ± 0.0 g C kg^{-1} soil, representing cumulative increases of 19.5 % and 26.9 %, respectively.

With the successive base extractions, the percentage of the total extractable HS (including the first acid extraction) increased from 52.4 % to 66.5 % and further to 71.1 % for soil GR. Similarly, but to a somewhat lesser extent, the percentage of the total extractable HS of BW increased from 46.4 % to 55.4 % and further to 58.5 %. The composition of extracted HA has been shown to change with subsequent base extractions by Li et al. (2003) based on elemental composition, functional group composition and ^{13}C NMR determined in eight subsequent base extractions of peat. However, in their study, the chemical characteristics in the first three fractions were more similar and clearly distinct from the HA extracted in the last five base extractions. Moreover, Song et al. (2011) found similar ^{13}C NMR spectra in the material extracted in a second extraction with 0.1 M NaOH +6 M urea, to that of the initial base extraction. Assuming the HA and FA percentages in extracted HS remained the same as in the original fractionation described in 2.2.5, we calculated the amount of HA and FA in the 2nd and 3rd base extraction. From this we calculated the percentages of reactive SOM (the sum of HA and FA) to be 52.9 % for GR and 41.0 % for BW, which are in the range as reported percentages of reactive SOM in a review paper on MSM by (Groenenberg and Lofts, 2014) based on experimental data or model optimisation.

After incorporating cumulative reactive SOM as quantified by HA + FA in the first and second extraction (reactive-$SOM_{1st+2nd}$), substantial improvement in model predictions was observed for soil GR (Fig. 1), with a further marginal improvement upon applying cumulative reactive SOM in all three extractions (reactive-$SOM_{1st+2nd+3rd}$). The obtained model improvement for soil GR supports our approach of conducting the base extraction three times, which appears to be sufficient to recover the majority of the reactive SOM in soils without introducing notable chemical heterogeneity among the extracted HS fractions as discussed before. For soil BW, however, minimal improvement was observed in model predictions when applying reactive-SOM including the additional extractions. For soil GR which covers a wider dissolved Cd range, model predictions appear to be most sensitive to the model input of reactive SOM in the range of low dissolved Cd. Despite the improvement in model predictions when applying reactive-$SOM_{1st+2nd+3rd}$, the deviations between predicted and measured dissolved Cd remained larger at low dissolved Cd.

3.4. Overprediction of dissolved Cd: The potential role of Mn oxides

It was discussed in section 3.3 that the model predictions of dissolved Cd for soil BW were still unsatisfactory compared to soil GR after optimizing the reactive SOM in the input, despite the two soils having comparable levels of pH, CEC, and content of SOM, clay, and AO-extractable Fe and Al (Table 1). Remarkably, soil BW had a 2.6 times higher AO-extractable Mn content than soil GR. Including Mn oxides in the MSM did, however, not substantially change the predicted dissolved Cd concentrations for soil BW (Fig. S1), but slightly shifted the solid phase speciation of Cd bound to SOM, clay and Al, Fe-oxides to Mn oxides bound Cd (Table S3) in agreement with findings of Van Eynde et al. (2022) for Cu and Zn.

Although including Mn oxides did not improve the model predictions for soil BW, the high Mn content of soil BW might still be associated with the relatively poor model predictions for this soil. Another substantial difference between the two soils is their reactive Cd content measured by isotopic dilution (Cd-*E* value) relative to that measured by the 0.43 M HNO_3 extraction (Cd-0.43 HNO_3). For soil GR, Cd-*E* value is 0.67 mg kg^{-1}, only 10.7 % less than Cd-0.43 M HNO_3, whereas for soil BW, Cd-*E* value is 0.82 mg kg^{-1}, which is 33.3 % less than Cd-0.43 M HNO_3 (Table 1). Using Cd-*E* value as reactive Cd in the model input instead of 0.43 M HNO_3 extracted Cd, the log RMSE values for soil BW reduced by 0.20 unit for the three solution media, whereas minimal improvements (pore water and 1 mM $Ca(NO_3)_2$) or even a worsened prediction (0.1 M $CaCl_2$) were found for soil GR (Fig. S2). Mn oxides in soils consist of basic MnO_6 octahedron units, which can form tunnel or layer structures (Post, 1999). In the latter, part of the adsorbed Cd can be present in between the layer sheets and having a slower desorption rate than Cd adsorbed to the exterior surface. We hypothesize that this intralayer fraction of Cd was not or only partly desorbed in the time frame of the isotopic dilution method, yet extractable in 0.43 M HNO_3. This suggests that, for soils with high Mn oxides content, 0.43 M HNO_3 extraction might overestimate the total reactive Cd content and consequently lead to overestimation of dissolved Cd by MSM. Our hypothesis is strengthened by the slower desorption of Cd bound to Mn oxides compared to other surfaces as found by Wang et al. (2009), comparing Cd desorption from various oxide surfaces, and by Covelo et al. (2007), comparing desorption of Cd from clay minerals, Fe- and Mn- oxides and SOM. However, as our datasets only consist of soils from two origins, further research is required to compare the two methods and assess the model performance on soils varying in Mn oxides content.

3.5. Trend of residuals: Implications for equilibrium multi surface modelling

Although substantial improvement in the model predictions was achieved through optimizing the model input of reactive SOM and reactive Cd, residuals still persist with a clear trend in relation to dissolved Cd and solution pH (Fig. 2), and not with other soil properties, such as SOM and DOM (results not shown). As solution pH increases from around 5 to above 8 and the measured Cd concentrations decreases from around $10^{-6.5}$ to $10^{-9.5}$ M, the residuals between the logarithm of predicted and measured Cd concentrations consistently increase for both soils and all three solution media.

Overprediction of dissolved Cd by humic ion binding models at low Cd concentration or at high pH have been reported in other studies. Gustafsson et al. (2003) reported overprediction of dissolved Cd to be related to the total soil Cd content which was varied for two soils, with higher overprediction for the low concentrations of total soil Cd. Their case, however, differs from ours as they observed this overprediction in the full pH range of their experiments (acidic to near neutral pH) whereas our overpredictions are limited to the higher pH range. Moreover, their overprediction was dependent on the total Cd concentration whereas in our case total reactive Cd, as measured with 0.43 M HNO_3, was relatively constant over the treatments (Table 2). Both reactive Cd determined with 0.43 M HNO_3 and the *E*-value are not expected to vary with changing pH of the soil (Yada and Kawasaki, 2008; Groenenberg et al., 2017). Dijkstra et al. (2004) reported systematic overprediction of dissolved Cd towards higher pH values in a pH-stat leaching experiment and attributed this to a possible underestimation of the amounts of reactive surfaces or contribution of other binding mechanisms than those considered in the MSM.

A possible missing mechanism in the used MSM setup is Cd binding to thiol groups in soils. Thiol-type functional groups can form strong complexes with Cd, although their abundance is much smaller in soils compared to HA and FA (Smith et al., 2002; Fan et al., 2020). Karlsson et al. (2007) obtained *LogK* values for Cd binding to thiolate groups of 11.2–11.6 at pH 3.1–4.6, which is substantially higher than that for carboxyl groups (*LogK*= 3.2) as determined in the same study. In a recent study of Gustafsson et al. (2024), the addition of high-affinity thiol sites to SOM in the Stockholm Humic Model substantially decreased the overpredictions of dissolved Cd in four out of the five tested soils. However, while the absence of the thiol-type functional groups may explain the lack of binding mechanisms in some studies, the binding of Cd to thiolate groups is only important at lower pH (< 6) in Gustafsson et al. (2024) and therefore, cannot explain the increasing overprediction of dissolved Cd towards high pH as we observed

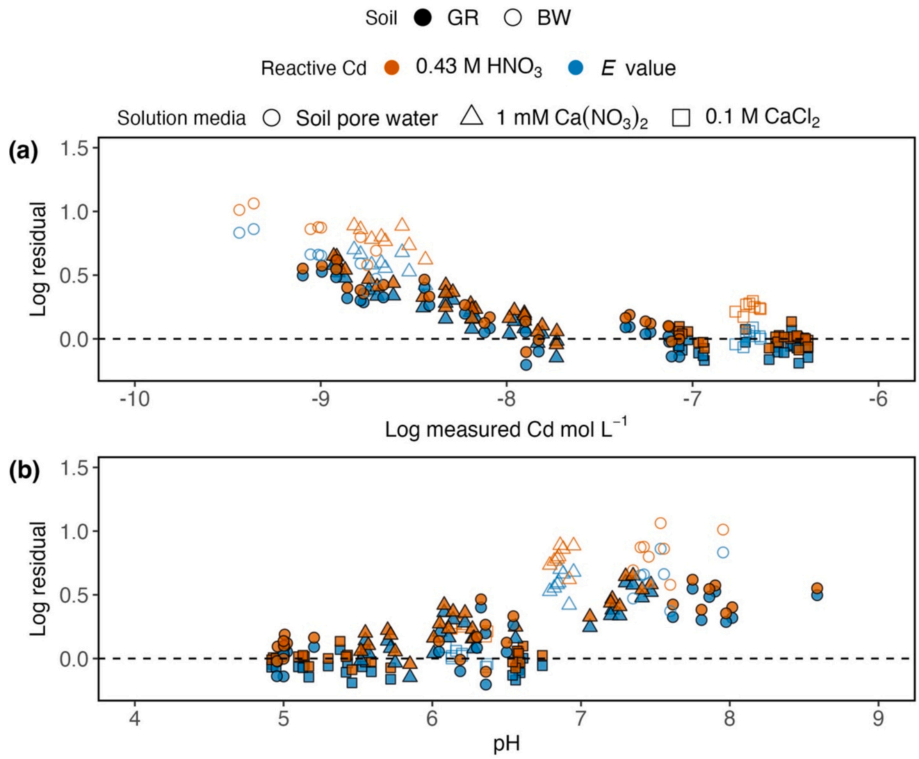

Fig. 2. Residuals between the logarithm of predicted and measured dissolved Cd in the three solution media (soil pore water, 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$) as a function of (a) the logarithm of measured dissolved Cd and (b) pH measured in the respective solution medium. The residuals are shown for two scenarios both with optimized reactive SOM but with different model inputs for reactive Cd: reactive Cd measured by 0.43 M HNO_3 extraction (red) and by isotopic dilution (blue).

(Fig. 2b). For the higher pH range, the phenolic groups become more important due to their higher $LogK_H$ (i.e. dissociate at higher pH). A higher $LogK_{Cd,phenolic}$ value (i.e. the median affinity of Cd binding to the phenolic type sites) or a lower $n_{Cd,phenolic}$ value (i.e. the nonideality of the Cd binding to the distribution) could potentially reduce the over-prediction of dissolved Cd in the lower pH range. Therefore, the increasing trend of errors we observed towards high pH might be linked to uncertainties in the model parameter of Cd binding to phenolic type high affinity sites. Another explanation may be slow desorption kinetics for Cd strongly bound to these high affinity sites of organic matter as desorption rates decrease with the apparent binding strength which increases with increasing pH (Shi et al., 2016), possibly leading to a non- or pseudo-equilibrium status between the solid and solution phase of the soil.

3.6. Comparison of the three solution media in terms of modelled solid-solution distribution and speciation of Cd

Using the optimized model input (i.e. reactive-SOM$_{1st+2nd+3rd}$ for both soils and reactive Cd-*E* value for soil BW, including Cd binding to Mn oxides for both soils), the modelled solid-solution partitioning as a function of the solution pH in the three solution media is shown in Fig. 3 for all 32 samples. Dissolved Cd in the pore water of soil GR constitutes <0.5 % of the total reactive Cd, while in soil BW it is even <0.03 %. This is followed by 1 mM $Ca(NO_3)_2$, in which up to 3.0 % of total reactive Cd is predicted to be dissolved and the difference between the two soils is smaller. On the other hand, 13.3–68.4 % of the Cd is present in dissolved form in 0.1 M $CaCl_2$. Although the percentage of the dissolved Cd varies by several orders of magnitude across the three solution media, it consistently increases with decreasing pH.

In the partitioning of Cd between the soil solid phase and all three solution media, Cd in the solid phase is primarily bound to HA (Cd_SHA) for both soils (70.8–91.7 % in soil pore water, 70.5–86.6 % in 1 mM Ca $(NO_3)_2$ and 62.8–87.3 % in 0.1 M $CaCl_2$), followed by FA (Cd_SFA, 4.7–27.4 % in soil pore water, 10.9–27.1 % in 1 mM $Ca(NO_3)_2$ and 11.5–36.1 % in 0.1 M $CaCl_2$), and <8.0 % to clay (Cd_clay) and metal (hydr)oxides (Cd_HFO and Cd_HMO, Fig. 4). As solution pH increases from 5 to almost 9, the changes in Cd speciation are similar for the three solution media. From solution pH 5 to 9, Cd_SHA gradually becomes more important, while Cd_SFA decreases. Cd_Clay, which is only significant at pH levels below 7, decreases as the solution pH increases from 5 to 7. In parallel, Cd_HFO becomes important, and continues to increase from pH 7–9. Compared to soil GR, more Cd is bound to Mn oxides (Cd_HMO) in the BW soil. As observed for Cd_HFO, the contribution of HMO becomes more important towards higher pH.

As observed for the solid phase, the speciation of Cd is also similar in the dissolved phase for soil pore water and 1 mM $Ca(NO_3)_2$ (Fig. 5). At solution pH below around 6, the majority of the Cd is present as free ions (Cd_free) in both soil pore water and 1 mM $Ca(NO_3)_2$, up to 90.2 % in soil pore water at pH around 5. As solution pH increases from 6 to 9, Cd is increasingly bound to DFA (Cd_DFA) and DHA (Cd_DHA), with a prevalence for DFA. On the other hand, inorganic complexes (Cd_InorgComplex), specifically Cd—Cl complexes, dominated Cd speciation in the dissolved phase in 0.1 M $CaCl_2$ (by up to 96.2 %), resulting in the observed shift of the Cd partitioning from mostly being adsorbed to the dissolved phase for both soils (Fig. 3). The high concentration of the dissolved Cd in 0.1 M $CaCl_2$, both measured and modelled, was the result of both a high concentration of Ca^{2+} ions and Cl^- ions. The former competes with Cd^{2+} for adsorption, while the latter forms strong soluble complexes with Cd^{2+} (Van der Sloot et al., 1996). Cd_DHA complexes are not present in the modelled speciation in 0.1 M $CaCl_2$ because the concentration of DHA was set to zero considering the suppression of DHA at the high Ca concentration (Weng et al., 2002).

Overall, despite distinct extraction conditions (e.g. SL ratio, equilibrium time) and differences in the ranges of measured pH, reactive DOM, and dissolved Ca and Cd (Table 2), soil pore water and 1 mM Ca $(NO_3)_2$ were comparable with regard to extractable Cd (Table 2), modelled speciation of Cd in the solid and dissolved phase (Fig. 4 and

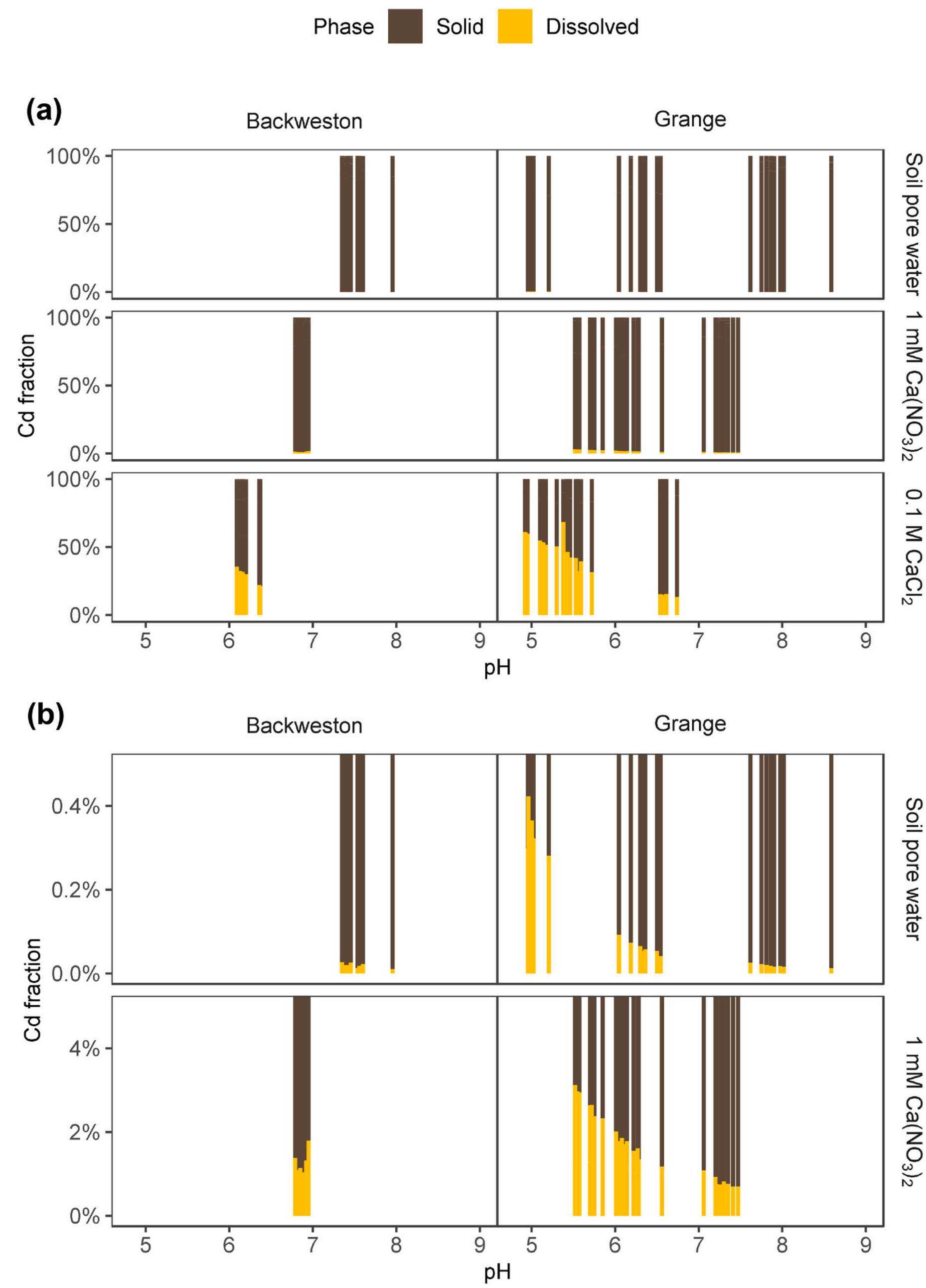

Fig. 3. (a) Partitioning of Cd between soil solid and dissolved phase in three solution media (soil pore water, 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$) as a function of pH. (b) zoomed-in y-axis for soil pore water and 1 mM $Ca(NO_3)_2$.

Fig. 5), as well as with regard to model performance (Fig. 1). The higher reactivity of the DOM in soil pore water compared to 1 mM $Ca(NO_3)_2$ was the result of the smaller Hy fractions, while the absolute concentrations of the reactive DOM (i.e. sum of the DHA and DFA fractions) of the two solution media were less distinct (Table 2), leading to their similar modelled predictions and speciation of Cd. However, over the same treatments, solution pH in soil pore water did exhibit larger variation than in 1 mM $Ca(NO_3)_2$ extracts, especially in the non-neutral pH range (Fig. 3, Fig. 4 and Fig. 5), leading to the observed differences in the measured dissolved Cd concentrations in the higher Cd concentration range (Table 2). Therefore, we suggest that 1 mM $Ca(NO_3)_2$ can be a suitable proxy to soil pore water to assess soil dissolved Cd concentration and speciation in circumneutral to alkaline pH-water range, but less so in the acidic range.

The 0.1 M $CaCl_2$ solution composition was very different from the other two solution media in terms of the order of magnitude of the extracted Cd (Table 2), and modelled partitioning and speciation of Cd (Fig. 3, Fig. 4 and Fig. 5). From the comparison of the absolute contribution of each Cd fraction in the solid phase to the partitioning of Cd in 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$ (Fig. S3), it can be further concluded that the 0.1 M $CaCl_2$ extraction primarily desorbed part of the Cd_SHA, and less so for Cd_SFA, to the dissolved phase. The model performance of the MSM is clearly better for the 0.1 M $CaCl_2$ extraction than for the other two solution media. This can be partly explained by the maximum pH measured in the 0.1 M $CaCl_2$ extracts to be below pH 7, i.e. the pH from which we observed the increasing deviation between model predictions and measurements. In addition, model predictions for a system with a more evenly distribution of the partitioning between the soil solid and solution phase, as is the case for the 0.1 M $CaCl_2$ extraction will be less uncertain, than in those cases where the Cd is almost entirely in the solid phase (>97 % in both the pore water and 1 mM $Ca(NO_3)_2$), where a small change in predicted adsorbed Cd leads to a relative large change in

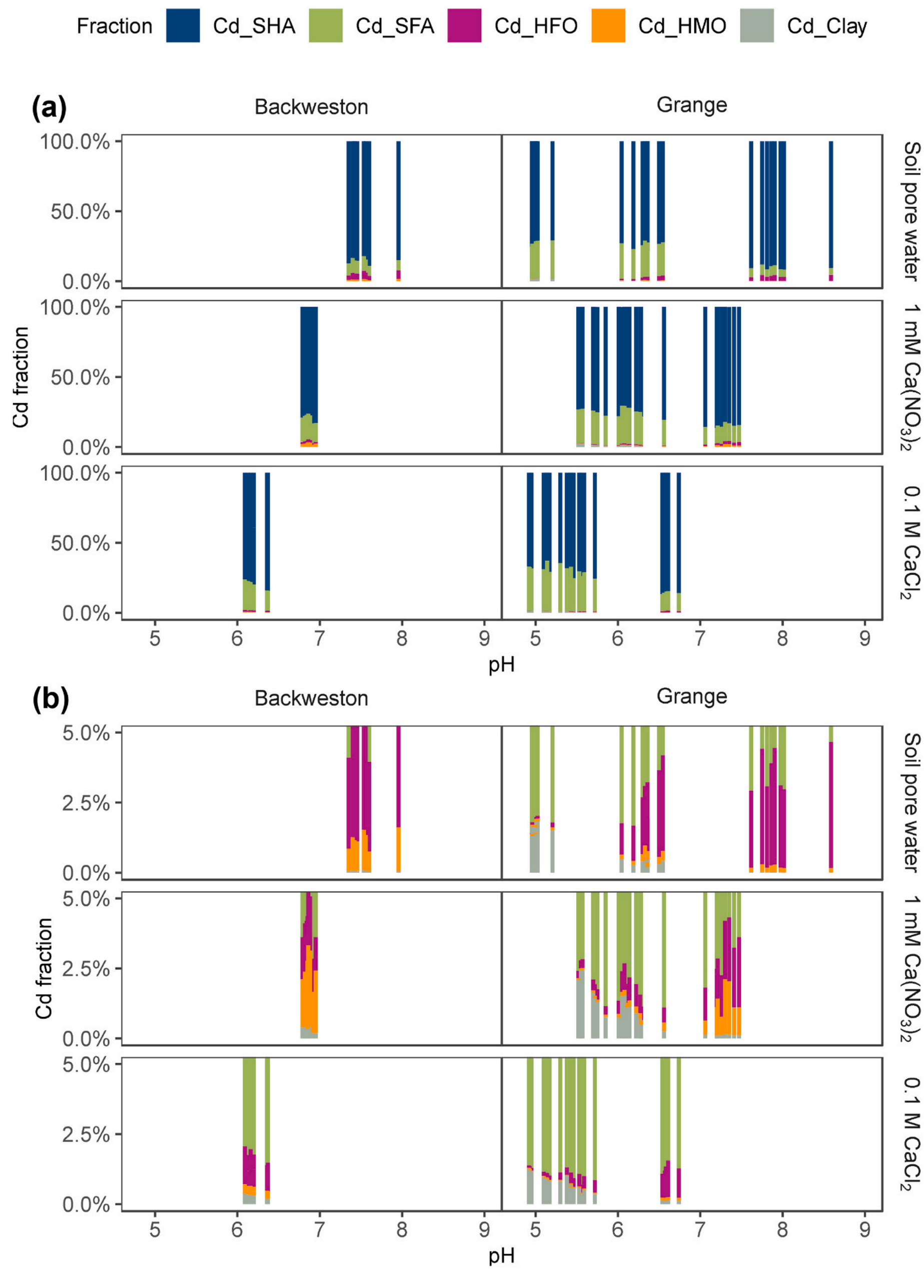

Fig. 4. (a) Speciation of Cd in the solid phase modelled in the three solution media (soil pore water, 1 mM $CaNO_3$ and 0.1 M $CaCl_2$) as a function of solution pH. (b) zoomed-in y-axis for all three solution media.

predicted dissolved Cd.

4. Conclusions

In the present study, we assessed the performance of the MSM in predicting dissolved Cd concentrations in soils receiving amendment applications in three different solution media: soil pore water, 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$. The incomplete extraction of HS by a single 0.1 M NaOH extraction step led to a substantial overestimation of dissolved Cd in the clay-rich soils by MSM in our study, highlighting the importance of reactive SOM in the model input. The 0.43 M HNO_3 extraction to quantify reactive Cd, might result in an overestimation of the reactive Cd in the presence of high levels of Mn oxides and further research on our hypothesis on the role of Mn oxides on the reactive fraction of Cd is needed. Increasing overprediction of dissolved Cd at pH above pH 7 is thought to be related to Cd binding to the high affinity phenolic groups due to uncertainties in generic NICA parameters for these groups and/or by slow desorption kinetics for Cd bound to these high affinity sites and needs further investigation. We demonstrated that the 1 mM $Ca(NO_3)_2$ extraction can be used as a proxy for soil pore water in terms of dissolved Cd and Cd speciation because of the similar levels of dissolved Cd, model performance and Cd speciation. Overall, we have demonstrated the potential of MSM in predicting dissolved Cd in soils receiving various forms and doses of amendments and can serve as a valuable tool for evaluating amelioration strategies.

CRediT authorship contribution statement

Yuwei Qin: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jan E. Groenenberg:** Writing – review & editing, Supervision, Methodology. **Yoann Viala:** Writing – review & editing, Supervision.

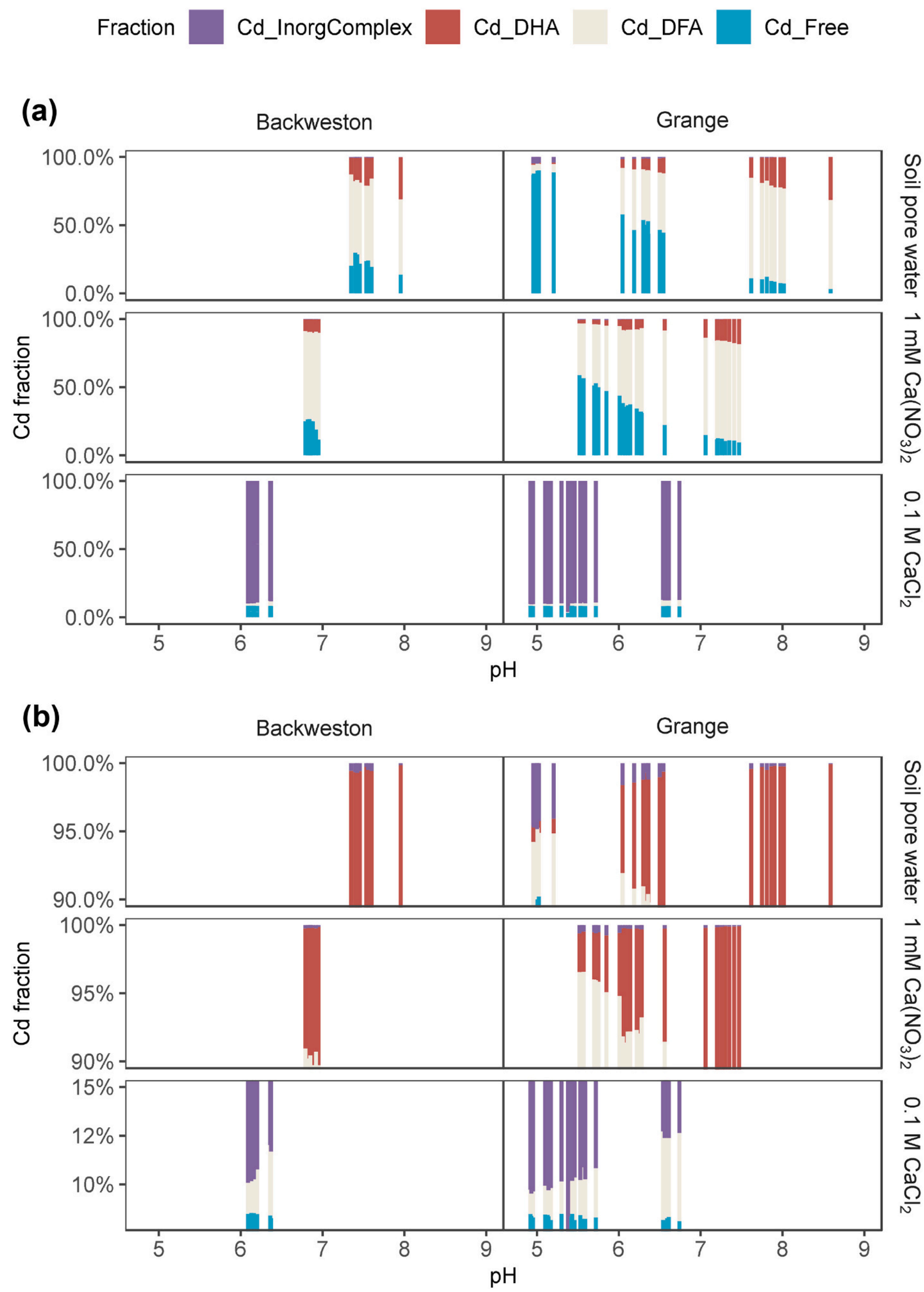

Fig. 5. (a) Speciation of Cd in the dissolved phase the in three solution media (soil pore water, 1 mM $Ca(NO_3)_2$ and 0.1 M $CaCl_2$) as a function of solution pH. (b) zoomed-in y-axis for all three solution media.

Sheila Alves: Writing – review & editing, Supervision, Funding acquisition. **Rob N.J. Comans:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177769.

Data availability

Data will be made available on request.

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