Solid-solution partitioning of micronutrients Zn, Cu and B in tropical soils: Mechanistic and empirical models

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ABSTRACT

Trace elements such as zinc (Zn), copper (Cu) and boron (B) are important micronutrients for crop production. Their bioavailability is essential to crops yield quantity and quality in many tropical soils. Nutrient bioavailability depends partly on the soil nutrient status, and in particular on the reactive and soluble fractions. Adsorption/desorption and precipitation/dissolution processes control the partitioning of the reactive pool over the solid and solution phase. However, so far the solid-solution partitioning of trace elements has mostly been studied in temperate and often contaminated soils. We studied, therefore, the solid-solution partitioning of Zn, Cu and B for 172 soils from Burundi, Rwanda and Kenya, using extensive soil characterization in combination with multi-surface modelling and two types of empirical Freundlich type partition relations. Our aim was to enhance the understanding of the soil chemical processes that control the solid-solution partitioning of the three micronutrients in these soils from the tropics with a multi-surface model, and to use this knowledge as benchmark to develop partition relations that require less input data and are more convenient tools for predicting the concentration in solution based on existing soil data. We show that the generic multi-surface model applied to these tropical soils performs similarly for Zn and Cu as in previous studies on temperate and contaminated soils. The Zn and Cu speciation was dominated by adsorption to soil organic matter, with an increased importance of metal (hydr)oxides with increasing pH. Given its generally low concentrations in these soils, dissolved organic matter was found to be important only for the solution speciation of Cu. The adsorption of B was mainly to metal (hydr)oxides at low pH, and with increasing pH soil organic matter became more important. The multi-surface model overestimated the dissolved B concentration for most soil samples, which we attributed to an inaccurate estimation of reactive B. Interestingly, the variation in observed and modeled solid-solution partitioning expressed as K_d of Cu and B among the soils was relatively small ($\sim$1 log L kg^{-1}), and the concentration in solution was consistently mainly controlled by the reactive concentration. Generally, the optimized partition relations resulted in a smaller prediction error compared to the multi-surface models. The partition relations in which the concentration in solution was optimized, resulted generally in an overestimation for the lowest observed concentrations, and an underestimation for highest concentrations of all three elements. Partition relations with optimized Freundlich parameters K_f and n resulted in more robust predictions since the prediction error was not related to the actual measured concentration. The partition relations from this study are easy-to-use tools for predicting the dissolved concentrations of Zn, Cu and B in soils from the tropics with low contents of these micronutrients and can therefore enhance the use of current existing soil information data for Sub-Saharan Africa.

1. Introduction

There is increasing awareness that micronutrients can play an important role in reducing crop yields and hampering yield responses to regular NPK-fertilizer in Sub-Saharan Africa (SSA) (Kihara et al., 2017).

Among the micronutrients, the bioavailability of especially zinc (Zn), but also copper (Cu) and boron (B) is low in SSA soils (Kihara et al., 2020; Sillanpää, 1990). Low soil levels of micronutrients such as Zn also lead to inadequate intake of these nutrients by humans via the consumption of crops, which can lead to severe health issues (Alloway,

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2009; Black et al., 2013; Gregory et al., 2017).

Soils usually contain substantial total amounts of micronutrients. A large part that is present in the solid phase is however inert and not readily available for crop uptake, because it is occluded in the matrix of soil constituents such as (hydr)oxides and clay minerals (de Vries et al., 2005; Groenenberg et al., 2017). This fraction is assumed to be released from the soil matrix only by very slow weathering processes. More relevant is the labile, reactive or potentially available pool that is distributed over the solid and solution phase, through sorption/ desorption and precipitation/dissolution (Groenenberg et al., 2017). A fraction of this reactive pool is present in the soil solution and is therefore directly available for plant uptake. Several chemical processes affect the speciation and the partitioning of the reactive pool between the solid and solution phase. Ions can be in the solid phase when adsorbed to mineral and organic reactive surfaces (i.e. clay particles, organic matter, metal (hydr)oxides) and precipitated as minerals, or in the solution phase as free ion or in the form of inorganic and organic complexes. The solid-solution partitioning of Zn and Cu has been used to assess the risk for leaching (Bonten and Groenenberg, 2008; Dijkstra et al., 2004) or toxicity or deficiency towards crops (Catlett et al., 2002; Degryse et al., 2009). In the context of plant nutrition, the difference in solid-solution partitioning has been used to explain why certain soil tests are more successful in predicting crop response to fertilization than others. For example, soil tests that approximate the dissolved concentration have been found to be better in predicting the crop growth response to phosphate fertilization in tropical soils, while soil tests that approximate the reactive pool work better for soils from temperate regions because phosphate adsorbs more strongly in tropical than in temperate soils (Nawara et al., 2017).

Different methods exist for assessing, understanding and predicting the solid-solution partitioning of elements in soils. One approach is geochemical multi-surface models that use thermodynamic constants for inorganic speciation together with an assembly of specialized models that describe ion adsorption to reactive surfaces in soils, such as clay, metal (hydr)oxides and organic matter (Groenenberg and Lofts, 2014). Next to predicting the solid-solution partitioning of various elements, these models also provide insight in which soil chemical processes are most relevant in controlling solid-solution partitioning. These models have contributed to our understanding of the behavior of trace elements such as Zn and Cu, often in polluted soils (Dijkstra et al., 2009, 2004; Groenenberg et al., 2012; Gustafsson et al., 2003; Gustafsson and Tiberg, 2015; Tiberg et al., 2018; Weng et al., 2001) but have also been successfully applied to model the free Zn activity in a limited set of low Zn soils (Duffner et al., 2014).

A generalized composite approach has been mainly used to model B adsorption behavior in soils, in which the soil is considered as a single plane for adsorption reactions (Goldberg, 2004, 1999). This modelling approach does not take into account the specific characteristics (i.e. binding capacities, affinities, heterogeneity of surface sites) of each of the reactive surfaces, and does not give insights into the relative importance of the different reactive surfaces that control B speciation in soils. In a recent contribution, we applied successfully a multi-surface model for assessing the B speciation and extractability in a limited set of temperate and tropical soils (Van Eynde et al., 2020b).

The application of geochemical multi-surface models on soil systems requires modelling parameters such as the thermodynamic constants and generic adsorption parameters. In addition, there are a number of decisions to be made regarding the input variables, which results in a certain conditionality of the multi-surface model. For example, the reactive content of the elements of interest is required as input. Examples for measuring the reactive pool are the 0.43 M HNO_3 soil extraction (Groenenberg et al., 2017) or the isotopically exchangeable fraction (Mao et al., 2017). Secondly, the multi-surface model requires the fraction of soil organic matter (SOM), in the form of humic substances, that is reactive towards ion adsorption in the solid and solution phase (Groenenberg et al., 2012). In previous modelling studies, this fraction

has either been estimated (Groenenberg et al., 2012), calculated based on the CEC and clay content (Duffner et al., 2014), fitted during the modelling calculations (Tiberg et al., 2018) or measured by fractionation schemes (Klinkert and Comans, 2020). In general, for soils from the tropics, little is known about the reactivity of SOM for ion adsorption in comparison with soils from temperate regions, while isotopic measurements or 0.43 M HNO_3 extractions are not routinely performed and consequently hardly available. Previous fractionation studies suggest the existence of a lower fraction of humic and fulvic acids of SOM in tropical soils compared to soils from temperate regions (Xu et al., 2018), while others have found opposite results (Wei et al., 2020). Since it has been shown that soil organic matter is an important reactive surface for the adsorption of Zn, Cu and B (Duffner et al., 2014; Groenenberg et al., 2012; Van Eynde et al., 2020b), the fraction of reactive organic matter in the solid and solution phase will have great implications on the concentration in solution and speciation of these micronutrients.

Another method for calculating the solid-solution partitioning of elements are partition relations in which the distribution of elements between the solid and solution phase is empirically related to soil properties. In this approach, the mechanistic soil chemical processes that are explicitly described in the multi-surface model, are lumped into empirical equations in the form of regression functions. A major advantage of such models is that they generally require less input data and less assumptions, making them suitable for large-scale applications and when limited data are available (de Vries et al., 2005; van der Perk et al., 2018). For SSA countries, partition relations have the potential to use micronutrient soil information based on currently available soil data which includes Mehlich-3 extraction data as proxy for the reactive concentration (Hengl et al., 2017, 2015), for the formulation of site-specific micronutrient fertilizer recommendations. Previously, relations have been derived for the solid-solution partitioning of trace elements such as Zn and Cu, often for contaminated soils from temperate regions (De Groot et al., 1998; Degryse et al., 2003; Groenenberg et al., 2012; Impellitteri et al., 2003; Nolan et al., 2005; Tipping et al., 2003). These partition relations vary in their specific mathematical form, in the choice of independent and dependent variables and in their methodological specifications (Degryse et al., 2009; Groenenberg et al., 2010b). Relations for the solid-solution partitioning of Zn and Cu do not yet exist for soils from the tropics, with their frequently relatively low background levels. To the best of our knowledge, no partition relations exist for B. For tropical soils, the reactivity of the soil surfaces may differ, thereby changing the solid-solution partitioning and partition relations in comparison with temperate soils. In addition, the micronutrient levels are expected to be lower in tropical soils compared to temperate soils, and may thus not be part of the experimental window for which previously calibrated partition relations were derived. The macronutrient levels may also differ, thereby affecting the partition relations for tropical and temperate soils. Particularly phosphate may enhance the adsorption of cationic metals (Van Eynde et al., submitted) while it competes with boron (Van Eynde et al., 2020a), which may result in different empirical binding parameters for temperate and tropical soils.

Based on the above, the first aim of this study was to improve the understanding of soil chemical processes that control the solid-solution partitioning of Zn, Cu and B in soils from tropical regions and thus are relevant in terms of nutrient availability. Secondly, this knowledge was then used as benchmark to develop simplified partition relations to predict the dissolved concentrations of these micronutrients, approximated by a 0.01 M $CaCl_2$ extraction, based on general soil properties in combination with a measurement of the reactive pool. Previously derived partition relations based on temperate soils, were also used to test their ability to predict the concentrations of Zn, Cu and B in solution.

We collected for these objectives a set of Sub-Saharan African soils (n = 172). For the first aim, we applied a geochemical multi-surface model to calculate the speciation of the above mentioned micronutrients and identify which soil chemical processes control the solid-solution partitioning. With this modelling approach, we also aimed to

assess whether a generic multi-surface model works equally well for soils from the tropics for which it has not yet been used, compared to soils from temperate regions. Using these results as benchmark, we derived empirical partition relations for predicting the directly available pool of these micronutrients based on their concentration in the solid phase and soil properties.

2. Material and methods

2.1. Soil samples

We used 172 air-dried and sieved soil samples originating from Burundi (74), Rwanda (50) and Kenya (48). The Burundi soil samples included 59 samples that originated from 29 locations in the south of the country, where samples were taken at 0–20 cm and 20–40 cm depth. The other 15 samples were topsoils (0–20 cm) originating from different regions in the country. The Rwanda (50) and Kenya soil samples (48) were from the topsoil and spatially distributed all over the countries, resulting in a large variety of soil types (Fig. S1).

2.2. Soil chemical analyses

The solution concentration of B, Cu, Zn, Ca, Mn, Mg, K, Fe, P and Al, together with the total and inorganic carbon and pH were measured in soil extracts with 0.01 M $CaCl_2$ (Houba et al., 2000). Calcium chloride extractions have often been used as a proxy for the soil solution, and to validate multi-surface models or calibrate partition relations that aim to model the solid-solution partitioning of elements in soils (Degryse et al., 2003; Dijkstra et al., 2009; Groenenberg et al., 2012; Van Eynde et al., 2020a). A 0.01 M $CaCl_2$ solution was freshly prepared in a plastic volumetric flask, in order to avoid element contamination from glassware. A fixed volume of the $CaCl_2$ solution was added to the soil samples at a solution-to-solid ratio of 10 L kg^{-1} in polypropylene centrifuge tubes. The suspensions were equilibrated in a horizontal shaker at 180 oscillations $minute^{-1}$ for 2 h and were afterwards centrifuged for 10 min at 1800 g and filtered over a 0.45 μm membrane filter. The concentrations of Zn, Cu, B, Fe, and P were measured in the acidified (0.14 M HNO_3) subsample of the supernatant, using High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS, Element 2, Thermo Scientific). The concentrations of Al, Ca, Mg, K and Mn were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (Thermo Scientific iCAP6500). Blank samples were included throughout the analyses and the average concentrations with standard deviation of the micronutrients of interest in the sixteen blank samples were: −0.20 ± 0.14 μg B L^{-1}, 0.21 ± 0.04 μg Cu L^{-1} and 0.43 ± 0.36 μg Zn L^{-1}. In addition, the Zn, Cu and B concentrations of two reference samples were measured. The standard deviation among the eight measurements were 0.12/0.25 μg B L^{-1}, 0.17/0.06 μg Cu L^{-1} and 0.80/1.06 μg Zn L^{-1} for the two reference samples respectively. Samples with measured concentrations below the ICP-MS detection limit (0.3 μg Zn L^{-1}, 0.1 μg Cu L^{-1} and 0.8 μg B L^{-1}), were not included for the validation of the multi-surface model and for the calibration of the partition relations.

The pH was measured in the 0.01 M $CaCl_2$ using a glass electrode. The dissolved total carbon and dissolved inorganic carbon concentrations were measured in the supernatant with a Segmented Flow Analyzer (SFA-TOC, San++, Skalar) equipped with an IR detector that measures the amount of $CO_2(g)$ after an internal acidification and destruction step, and the dissolved organic carbon (DOC) concentrations were calculated as the difference between total and inorganic carbon.

The reactive pool of B, Cu and Zn were estimated by a 0.43 M HNO_3 extraction (Groenenberg et al., 2017). The samples were suspended in a freshly prepared extraction solution with 0.43 M HNO_3 at a solution-to-solid ratio of 10 L kg^{-1}. The suspensions were shaken for 4 h, centrifuged and filtered over a 0.45 μm membrane filter (ISO, 2016). Afterwards, the filtrates were analyzed for B, Cu and Zn using ICP-OES.

The clay content was measured by laser diffraction analysis (Konert

and Vandenberghe, 1997). Soils (0.5–1.5 g) were pre-treated three times with 10 ml H_2O_2 in 75 ml of H_2O, and once with a few mL of HCl, while standing in a warm water bath for half a day. Before analysis, the pre-treated samples were suspended in water (~200 ml) which was removed and replaced with fresh ultra-pure water for multiple times to remove excess of salts. The measured volume percentage of the fraction smaller than 2 μm was re-calculated to the mass percentage of clay using a particle density of 2.6 g cm^{-3} and a bulk density of 1.3 g cm^{-3}.

An ammonium oxalate (AO) extraction with a solution-to-solid ratio of 20 L kg^{-1} and an equilibration time of 4 h (ISO, 2012a) was used to measure micro-crystalline Fe and Al (Fe-AO, Al-AO). Iron (Fe-D) and Al (Al-D) were also measured in a sodium-dithionite extraction with a solution-to-solid ratio of 20 L kg^{-1} and an equilibration time of 3.5 h (ISO, 2012b), and crystalline Fe and Al were calculated as the difference between the Fe and Al measured in the dithionite and AO extraction. The Fe and Al in the ammonium oxalate and in the dithionite extractions were analyzed using ICP-OES.

Total SOC content in the soils was analyzed using a wet potassium dichromate oxidation method with concentrated sulphuric acid and subsequent colorimetric measurement of trivalent chromium formed from the oxidation of organic carbon with a spectrophotometer, according to the Kurmies procedure (Walinga et al., 2008). For a selection of soil samples, the humic and fulvic acid fractions of the organic matter in the solid phase (n = 19) and solution phase (n = 12) were measured following the procedure as described by Van Zomeren and Comans (2007). For the analysis of the solid organic carbon, the soils were first suspended with 0.1 M HCl (pH 1) and centrifuged, after which the pellet was re-extracted with 0.1 M NaOH (pH 12). This base solution was afterwards acidified to pH 1, followed by centrifugation. Subsequently, the supernatant of the acid extraction and the supernatant of the acidified base extract were combined and equilibrated with pre-cleaned DAX-8 resin. The fulvic acids were afterwards desorbed from the resin with 0.1 M KOH. The HA were measured by re-dissolving the pellet from the acidified base extract with 0.1 M KOH. A similar procedure (but without the initial 0.1 M HCl step) was followed for the fractionation of the dissolved organic carbon in the 0.01 M $CaCl_2$ extraction.

2.3. Multi-surface model

The multi-surface model included ion adsorption to organic matter, electrostatic adsorption to the planar surfaces of clay minerals and ion adsorption to Fe and Al (hydr)oxides. The aqueous speciation and corresponding thermodynamic constants can be found in Table S1. Modeling calculations were performed in ECOSAT, version 4.9 (Keizer and Van Riemsdijk, 1995). In order to calculate the solid-solution partitioning, the B, Cu and Zn concentrations measured in 0.43 M HNO_3 were used as input for the geochemically reactive concentration. To include competitive and synergistic adsorption effects from Fe^{3+}, Al^{3+}, Ca^{2+}, Cl^-, K^+, Mn^{2+}, Mg^{2+} and PO_4^{3-}, the measured concentrations of these elements in the 0.01 M $CaCl_2$ extractions were used as input of total dissolved concentrations (see specific calculation steps below). Preliminary calculations showed that the inclusion of Mg, Mn and K did not affect the calculated Zn, Cu and B speciation.

In the ECOSAT speciation software, total dissolved concentrations cannot be given as input, only the free ion concentration or activity in solution, or the total amount. Therefore, the calculation was carried out in two steps. Firstly, free ion concentrations of Fe^{3+}, Al^{3+}, Ca^{2+}, Cl^-, K^+, Mn^{2+}, Mg^{2+} and PO_4^{3-} were calculated based on the measured total element concentrations in the $CaCl_2$ extractions, considering pH, the Ca and Cl concentrations, and the adsorption to DOC. Secondly, the calculated free ion concentrations were used as fixed input together with pH, reactive B, Zn and Cu, and the reactive surfaces (including DOC), to model the solid and solution distribution of B, Zn and Cu. We corrected the total P measurements in the $CaCl_2$ for organic species by taking 20 % of total P as inorganic PO_4 (Mendez et al., 2020). This was found to be the average % of inorganic PO_4, measured by a segmented flow analyzer

applying a colorimetric molybdenum blue method (Murphy and Riley, 1962), relative to the total P measured in the 0.01 M CaCl$_2$ by ICP-MS (results not shown).

To test if mineral solubility controls the micronutrient concentration in the CaCl$_2$ extraction, the Zn, Cu and B activity in solution was calculated using ECOSAT based on the measured concentrations in the CaCl$_2$ extractions and compared with the activities that are expected based on the solubility of various Zn minerals (Duffner et al., 2014), Cu hydroxide (Lindsay, 1979) and various B minerals (Parks and Edwards, 2005). These calculations showed that the solubility of these minerals does not control the measured concentrations for the majority of soil samples, except for the Zn concentration measured in the soils with pH above 7 (Fig. S2).

2.3.1. Adsorption to organic matter

The adsorption to solid and dissolved organic matter was modelled with the Non Ideal Competitive Adsorption (NICA) model in combination with a Donnan model for electrostatic interactions (Kinniburgh et al., 1996). Based on the measurements of humic substances in selected soil samples, the average percentage of HA and FA relative to the total SOC and DOC was calculated, and these percentages were used to estimate the HA and FA concentrations for all soil samples in the dissolved and particulate phase. The adsorption to SOM was modelled assuming the reactive SOM being HA and FA based on their estimated concentration, and the adsorption to DOM was modelled assuming the reactive DOM being FA.

For the neutral B(OH)$_3^0$ ion, which is the dominant B species in the pH range of these soil samples (Table S1), there is no electrostatic attraction. Therefore, we did not include the B(OH)$_3^0$ present in the Donnan layer for calculating the total adsorbed B to SOM and DOM (Goli et al., 2019; Van Eynde et al., 2020b). Since there are only NICA parameters for B adsorption to HA and since there is generally a strong correlation between adsorption constants for HA and FA (Milne et al., 2003; Tipping, 1998), we considered the B adsorption to FA similar as the adsorption to HA and used the same adsorption parameters for both OM fractions (Goli et al., 2019).

The structural NICA-Donnan parameters for HA and FA were taken from Milne et al. (2003, 2001). Next to Zn, Cu and B, we included the specific adsorption of Fe, Al and Ca in the NICA-Donnan model to account for possible competitive effects. We used for these ions the parameters from Milne et al. (2003), except for Fe complexation to FA (Hiemstra and van Riemsdijk, 2006) and for B complexation to HA and FA (Goli et al., 2019). The adsorption parameters for the NICA-Donnan model are given in Tables S2 and S3.

2.3.2. Adsorption to clay

Cation adsorption to the planar surfaces of clay minerals due to the presence of a permanent negative charge was modelled with a Donnan ion exchange model. Illite was taken as a reference clay, with a constant Donnan volume of 1L kg^{-1}, and a surface charge of 0.25 eq kg^{-1} (Duffner et al., 2014; Weng et al., 2001). Using this approach, there will be no adsorption of B to the clay surfaces because of the neutral charge of the boric acid. However, we have shown previously by modeling that adsorption to clay does not play an important role for B speciation in soils (Van Eynde et al., 2020b). Although illite may not be representative for the dominant clay minerals in the soils of this study, preliminary calculations showed that the choice of clay surface charge did not affect the modeling calculations because of the minor contribution of clay to the Zn and Cu adsorption in the solid phase.

2.3.3. Adsorption to metal (hydr)oxides

The Charge Distribution (CD) model (Hiemstra and Van Riemsdijk, 1996) was used, in combination with a multi-site ion adsorption complexation (MUSIC) model (Hiemstra and Zhao, 2016) for calculating ion adsorption to the Fe and Al oxides.

The content of poorly crystalline oxides was calculated based on the

Al and Fe measured in the AO extraction. To transform the moles of Al and Fe in the AO extraction to the oxide mass, a molar mass of 95 g mol^{-1} Fe and 84 g mol^{-1} Al was used, which corresponds to particles with a specific surface of 600 m^2 g^{-1} (Hiemstra and Van Riemsdijk, 2009; Mendez et al., 2020). The amount of crystalline oxides were calculated as the difference between the Fe and Al in the sodium-dithionite extraction and the Fe and Al measured in the AO extraction, using a molar mass of 89 and 78 g mol^{-1} for Fe (goethite) and Al (gibbsite) respectively (Hiemstra et al., 2010). In case no Al was measured in the dithionite extraction, we did not include crystalline Al (hydr)oxides in the modelling. For the crystalline oxides, a specific surface area of 100 m^2 g^{-1} was assumed (Groenenberg et al., 2012).

Ferrihydrite (Fh) was used as model oxide for the natural oxide fraction of the soils (Mendez, 2020), using the structural parameters from Hiemstra and Zhao (Hiemstra and Zhao, 2016). The total Fh content was calculated by summing the mass of poorly crystalline and 1/6 of the mass of crystalline oxides (assuming a specific surface area of 100 m^2 g^{-1}), and in the modelling calculations a specific surface area of 600 m^2 g^{-1} was used for Fh. The CD-MUSIC parameters for modelling ion adsorption to Fh are given in Table S4.

Manganese (Mn) oxides have been suggested to be important for the adsorption of metal cations in soils (Cancès et al., 2003; Mossa et al., 2021; Ren et al., 2017). For the subset of Kenyan soils, the Mn concentration was also measured in the AO extraction to test its importance for the calculation of Zn and Cu speciation. The total Mn oxide content was calculated based on this Mn concentration in the AO extraction, using a molar mass of 86.9 g oxide mol^{-1} Mn (Tonkin et al., 2004). The adsorption of Zn and Cu to the Mn oxides was modeled with the General Two Layer Model (GTLM) using a specific surface area of 764 m^2 g^{-1} and the parameters from Tonkin et al. (2004) (Table S5).

2.4. Partition relations

Different forms of empirical models exist to describe the solid-solution partitioning of elements in soils. The most basic (linear adsorption) model uses a constant distribution coefficient:

$$K_d = \frac{Q}{C} \tag{1}$$

in which K_d = the distribution constant (L kg^{-1}), Q = the concentration in the solid phase (mol kg^{-1}) and C the concentration in the soil solution (mol L^{-1}). Since values of K_d can vary by different orders of magnitude among soil samples (Degryse et al., 2003), equation (1) is often extended with soil properties (X_i) to account for this variation (Sauvé et al., 2000):

$$\log K_d = \alpha_0 + \sum a_i \log X_i \tag{2}$$

with α_{0-i} being regression coefficients. In order to account for non-linear adsorption, Freundlich-type equations have been used as partition relations according to:

$$Q = K_f C^n \tag{3}$$

in which the exponential term n shows the deviation from linear adsorption (<1), and expresses the extent of decrease in bonding strength with increasing concentrations in solution.

Groenenberg et al. (2010) differentiated between three types of Freundlich-type partition relations (equation (3)), depending on which variable is optimized during the derivation of the partition relation. Most commonly, the concentration in solution is optimized as follows, with β_{0-i} regression coefficients (Nolan et al., 2003):

$$\log C = \beta_0 + \beta_1 \log Q + \sum \beta_i \log X_i \tag{4}$$

or the other way around, if Q is optimized instead of C (Elzinga et al., 1999). Less common is the optimization of the Freundlich constants K_f and n from equation (3), with γ_{0-i} being regression coefficients

(Groenenberg et al., 2010; Tye et al., 2003):

$$\log K_f = \log Q - n \log C = \gamma_0 + \sum \gamma_i \log X_i \qquad (5)$$

from which the concentration in solution can be calculated after optimization.

To assess the experimental variation in solid-solution partitioning of Zn, Cu and B, the K_d values were calculated according to equation (1), based on the concentrations measured in the 0.43 M HNO_3 and the $CaCl_2$ extracts. Next, the partition relations shown in equations (4) and (5) were derived. Input variables for the soil properties were SOM (%) based on the total carbon measurements and assuming that SOM consists of 50 % carbon, the clay content (%), $FeAl_{AO}$ as the sum of Fe and Al measured in the AO extraction (mmol kg^{-1}), the DOC measured in the 0.01 M $CaCl_2$ extraction (mg L^{-1}) and the pH measured in the 0.01 M $CaCl_2$ extract. All variables except for the soil pH were $\log_{10}$ transformed as input variable in the partition relations. We did not correct the reactive content for the concentration in solution to obtain Q (i.e. the nutrient concentration in the solid phase), since this is not practical for applications when only the reactive content is known. Preliminary calculations showed that such a correction did not improve the partition relations. The same soil properties were used as the ones that were used by Groenenberg et al. (2012) for the calibration of partition relations for Cu and Zn based on contaminated and non-contaminated soils from the Netherlands.

The coefficients in equation (4) were derived by multiple linear regression analysis, and the final model was selected based on the Akaike's Information Criterion (AIC) value (Webster and McBratney, 1989) using the dredge function from the MuMIn package (Barton, 2020).

For equation (5), the value of n and the coefficients of the regression model were optimized simultaneously. In R, the value of n was varied from 0.01 to 1, in steps of 0.01. For each n and corresponding K_f values, a linear regression model was calculated based on the soil properties. The final n was selected for the minimal sum of squared differences in K_f. Afterwards, the regression model for the particular n value was optimized in R with the dredge function from the MuMIn package (Barton, 2020) to select only the most important input variables for the final the equation.

The final regression equations were checked for multicollinearity between the independent variables, using the vif function from the car package in R (Fox and Weisberg, 2019). For the final models, the variance inflation factor (vif) for a specific independent variable was found never to be larger than 5. Interaction terms in the form of log X_i*pH, with X_i being one of the reactive surfaces for pH-dependent adsorption (i.e. DOC, SOM, metal (hydr)oxides), led to high vif values and did not result in better predictions, so these terms were not included in the final

models. The contribution of the variables to the total variance explained by the model was calculated using the calc.relimp function from the relaimpo package in R (Gromping, 2006).

The R software (version 4.0.2) was used for derivation of the partition relations, the visualization of the results and the calculation of the correlation table (R Core Team and R Development Core Team, 2020). The evaluation of the multi-surface model and the two different partition relations were done based on the mean error (ME: $mean(predicted - measured)$) and the root-mean-squared error (RMSE: $\sqrt{mean(predicted - measured)^2}$). The residuals of both model predictions were checked visually in relation with the independent and dependent variables.

3. Results and discussion

3.1. Soil characteristics

The concentrations of the micronutrients in the $CaCl_2$ and the HNO_3 extractions of the studied soils (Table 1) were relatively low, compared to previous measurements in temperate soils with natural background levels (Groenenberg et al., 2012). To illustrate, in the case for Zn, around 40 % of all samples had Zn concentrations in the $CaCl_2$ extraction below 1 µmol kg^{-1}, which is around the highest concentration for which Duffner et al. (2013) found a positive response of wheat biomass to Zn application in a pot experiment. For B, 52 % of all samples had measured B concentrations in the $CaCl_2$ extraction below 7 µmol kg^{-1}. The latter corresponds to 28 µmol kg^{-1} B measured by hot water extraction based on a previously derived relationship (Novozamsky et al., 1990) and is assumed to be a critical value associated with B deficiency for plant production (Kabata-Pendias and Pendias, 2001).

The Kenyan soil samples have the largest variation in soil properties and micronutrient concentrations (Table 1), which coincides with the largest variation in soil types compared to Burundi and Rwanda (Fig. S1).

As shown in Figs. S3-S4, the fractions of reactive SOC and DOC, as defined by the content of humic and fulvic acids, were on average 32 and 21 % of total SOC measured by the Kurmies method and DOC, respectively. These percentages were lower than the general assumptions that have been used before in multi-surface modelling studies (Groenenberg and Lofts, 2014) or that have been measured previously in temperate soils (Fest et al., 2008; Groenenberg et al., 2010a; Supriatin et al., 2015), especially for the DOC. These relatively low values will have implications for the micronutrient speciation calculated by the multi-surface modeling. As shown by Fig. S5, the data show a tendency that the fraction of reactive SOC decreases with increasing pH, and increases with metal (hydr)oxide content and total SOC. The latter is the opposite

Table 1
The median values and the range of soil properties, reactive concentrations (Q) measured in the 0.43 M HNO_3 extraction, and concentrations measured in the 0.01 M $CaCl_2$ extractions (solution-to-solid ratio of 10 L kg^{-1}) (C) for the soil samples from Burundi (n = 74), Rwanda (n = 50) and Kenya (n = 48).

	Burundi		Rwanda		Kenya	
	Median	Range	Median	Range	Median	Range
pH	4.4	3.9–5.3	4.9	3.9–6.2	6.9	4.0–8.8
DOC (mg L^{-1})	9.4	4.7–16.6	13.9	7.2–33.9	4.5	1.6–22.4
SOC (g kg^{-1})	18	7–50	16	9–50	10	2–67
Clay (g kg^{-1})	94	23–708	86	11–776	290	1–813
AO-Fe (mmol kg^{-1})	43	11–156	49	13–273	20	2–183
AO-Al (mmol kg^{-1})	76	34–314	50	14–459	31	6–832
DC-Fe (mmol kg^{-1})	536	261–995	459	124–919	245	16–1273
DC-Al (mmol kg^{-1})	88	34–328	50	14–459	58	7–832
Q-Zn (µmol kg^{-1})	15	3–171	28	5–273	37	8–1361
Q-Cu (µmol kg^{-1})	68	17–198	51	10–346	46	6–807
Q-B (µmol kg^{-1})	29	9–11	22	2–159	74	5–1748
C-Zn (µmol kg^{-1})	1.99	<0.2–14.19	1.53	0.26–13.65	0.08	<0.2–25.05
C-Cu (µmol kg^{-1})	0.17	0.05–1.62	0.13	0.08–0.43	0.13	< 0.04–1.08
C-B (µmol kg^{-1})	5.78	1.48–43.78	5.45	<0.2–22.05	13.26	<0.2–477.37

from what has been observed by Tipping et al. (2003) based on model fitting. However, these results were for specific upland soils with higher SOM levels. As shown by Fig. S6, the fraction of reactive DOC also increases with total DOC, but increases with increasing pH, and decreases with metal (hydr)oxide content. With increasing pH, the hydrophobic fractions of the soil organic carbon may become more soluble, thereby contributing a larger share of the DOC fraction. This may explain a higher fraction of dissolved FA and HA in soils with higher pH. The relations between the reactive organic carbon fractions and pH and metal (hydr)oxides, may also suggest the importance of adsorption to metal (hydr)oxides for SOC stabilization (Weng et al., 2007), resulting in a higher fraction of humic substances. Future studies with additional data are needed to confirm these trends and the underlying processes that explain the reactive organic matter fractions for ion adsorption in the particulate and solution phase.

3.2. Measured solid-solution partitioning

The experimental solid-solution partitioning of Zn, expressed as K_d (equation (1)) varied by a factor ~ 1000, and was mostly controlled by the soil pH (Fig. 1). For Cu, the K_d values varied less among the soils and were mostly related to the relative soil organic carbon fractions, expressed as the ratio of SOC over DOC (Fig. 1), showing that the interplay between these two organic matter pools controls the final Cu concentration in solution. The variance in K_d of Cu was generally less explained by soil properties than for Zn. For B, most K_d values were in the relatively narrow range between 10 and 100 (Fig. S7). These K_d values were low compared to Zn and Cu, pointing towards a relatively high mobility of B in soils (Kabata-Pendias and Pendias, 2001). In addition, there was no clear relation between the solid-solution partitioning of B and any of the soil properties (Fig. S7).

The correlation table in Fig. S8 confirmed the observed relations between K_d and soil properties. The strongest correlation for the Zn concentration in the CaCl$_2$ extract was found with soil pH (-0.83, p < 0.001), while the concentrations of B and Cu were mostly correlated with the reactive content (0.75 and 0.49 respectively, p < 0.001).

3.3. Multi-surface model calculations

The accuracy of the geochemical multi-surface model predictions for the concentrations in a 0.01 M CaCl$_2$ extract varied among Zn, Cu and B (Fig. 2). Based on the RMSE$_{logM}$, the model performed best for predicting the concentration in solution of Cu (0.30), followed by B (0.41) and Zn

(0.54). The RMSE$_{logM}$ values of Cu and Zn for these tropical soils were in line with previous multi-surface modelling studies for temperate soils (Groenenberg and Lofts, 2014), contaminated sites (Dijkstra et al., 2009; Mao et al., 2017), compost samples (Klinkert and Comans, 2020) and waste materials (Meima and Comans, 1998). This allows for the conclusion that these generic geochemical multi-surface models are performing equally well for soils from the tropics with lower levels of trace elements.

For B we first assumed its concentration in the 0.43 M HNO$_3$ extract represented the reactive B fraction. This resulted in an overprediction of soluble B for nearly all soils (Fig. S9). We have previously evaluated the use of three different extraction methods to estimate reactive B with a multi-surface model, for a limited set of tropical and temperate topsoils (Van Eynde et al., 2020b). The results suggested that the 0.43 M HNO$_3$ extraction may overestimate the reactive B content, due to (partial) dissolution of B containing minerals. The B measured in 0.05 M KH$_2$PO$_4$ was found to be a better estimation for the reactive B, based on modeling calculations. Based on the measurements of 10 soil samples, we found that the KH$_2$PO$_4$-extractable B was on average half of the concentration measured by the 0.43 M HNO$_3$ extraction (Fig. S10). So, in a next attempt to predict B concentration in solution (*i.e.*, the scenario shown in Fig. 2), we used half of the B concentration measured in the 0.43 M HNO$_3$ soil extracts as input for the multi-surface model. This approach still overestimated soluble B for most samples, resulting in a positive mean error of 0.26 log M (Fig. 2). Fig. S11 shows that the modeling error was not related to any of the soil variables. A possible explanation may be that the ratio between B measured in 0.43 M HNO$_3$ and actual reactive B varies among soil samples and may be larger in general, explaining the modeling deviation. For five soils, the B concentration in the CaCl$_2$ extract exceeded the HNO$_3$-extractable B (see Table 1), demonstrating that the HNO$_3$ extraction is not always adequate to estimate reactive B in soils .

For Zn, the multi-surface model tended to overestimate Zn concentration in solution with increasing pH, with increasing reactive content and with increasing Zn loading, expressed as the reactive Zn concentration per mass of reactive SOM or metal (hydr)oxides (Fig. S12). This resulted in an overall positive mean error of 0.26 log M (Fig. 2), suggesting an average overestimation of dissolved Zn by the model. These relations between modelling deviations for Zn and soil variables, have been observed in previous multi-surface modeling studies that focused on contaminated and non-contaminated soils from temperate regions and composts (Bonten and Groenenberg, 2008; Groenenberg et al., 2017; Klinkert and Comans, 2020; Mao et al., 2017), so these deviations
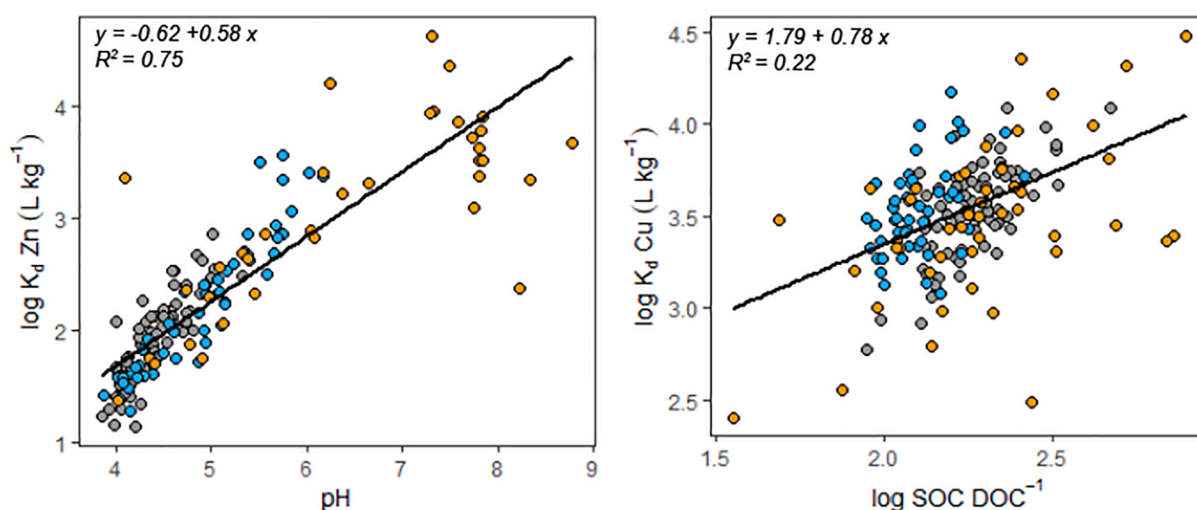

Fig. 1. Relation between the log K_d for Zn and pH (left) and for Cu and the ratio of soil organic carbon (SOC) over the dissolved organic carbon (DOC). The K_d value was calculated for soils from Burundi (grey makers), Kenya (yellow markers) and Rwanda (blue markers), based on the concentration measured in 0.43 M HNO$_3$ minus the concentration measured in 0.01 M CaCl$_2$ (mol kg^{-1}) divided by the concentration measured in the 0.01 M CaCl$_2$ (mol L^{-1}).
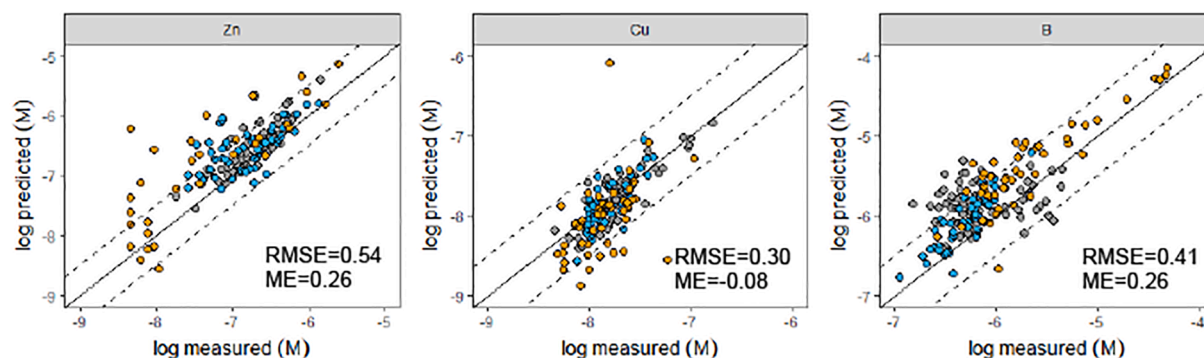
Fig. 2. Comparison between measured and predicted concentration in a 0.01 M CaCl₂ soil extraction, using multi-surface modelling for Zn (left), Cu (middle) and B (right) in soils from Burundi (grey markers), Kenya (yellow markers) and Rwanda (blue markers). The numbers given in the graphs represent the root mean squared error (RMSE) and the mean error (ME) in log M. The solid line is the 1:1 line, points within the dashed lines are within 0.5 log M deviation from the measured concentrations.

are not specific for soils from the tropics with low Zn concentration.

The aforementioned studies have given various explanations for this systematic deviation in multi-surface modeling calculations for Zn. For example, it has been shown that HNO_3-extractable Zn overestimates the exchangeable pool in neutral to alkaline soils due to dissolution of minerals from which the Zn is not isotopically exchangeable (Degryse et al., 2011; Groenenberg et al., 2017; Marzouk et al., 2013). Such an overestimation of reactive Zn as input may explain the over-prediction of Zn in solution in high pH soils by the multi-surface model as observed in this study, and in previous work (Bonten et al., 2008; Groenenberg et al., 2017). Mao et al. (2017) attributed the increased overprediction of soluble Zn with increasing pH to the simplification of the wide variety in metal (hydr)oxides to one single model oxide in the multi-surface model, resulting in a weak description of the ion adsorption processes to the different metal (hydr)oxides. The use of the CD model in this study is expected to better represent ion adsorption processes to metal (hydr)oxides compared to the models used in previous studies (Dijkstra et al., 2009; Groenenberg et al., 2017; Mao et al., 2017). Moreover, it has been shown recently that ferrihydrite nanoparticles are a good proxy for describing the metal (hydr)oxide surface reactivity, at least for phosphate, in temperate (Mendez et al., 2020) and tropical (Mendez et al., 2022) soils. In addition, by using the modeling parameters from Tonkin et al. (2004), our results for the subset of Kenyan soil samples do not suggest that the inclusion of other metal (hydr)oxides such as Mn oxides reduces this systematic modeling error (Fig. S14 and S15). Related to the adsorption processes to the metal (hydr)oxides and other reactive surfaces, one may question the validity of the concept of linear additivity that is assumed in this study and in previous studies that modeled trace element speciation in soils (Dijkstra et al., 2009; Groenenberg et al., 2017; Mao et al., 2017; Tiberg et al., 2018). The concept of linear additivity assumes that the different reactive surfaces in the multi-surface model do not interact in such a way that it affects ion adsorption processes (Groenenberg and Lofts, 2014). For cations, such as Cu and Ca, batch adsorption experiments have shown that the presence of organic matter compounds enhances the cation adsorption to metal (hydr)oxides such as goethite with increasing pH, due to electrostatic effects and the formation of ternary complexes (Weng et al., 2008). The interaction between SOM and metal (hydr)oxides, which was not included in the multi-surface model, may lead to more Zn adsorption. Finally, others have questioned the validity of the NICA-donnan parameters, especially the electrostatic model for fulvic acids (Benedetti et al., 1996; Hiemstra and van Riemsdijk, 2006; Klinkert and Comans, 2020) or the specific adsorption parameters for Ca (Town et al., 2019). Both aspects may have resulted in an overprediction of Ca competition on Zn adsorption, thereby leading to an overestimation of Zn concentration in solution by the model. Future research should confirm which of the above mentioned limitations is most important for explaining the

observed overprediction of soluble Zn, which is according to our results a general modeling error irrespective of Zn levels or soil types.

For Cu, the multi-surface model underestimated the dissolved Cu concentrations especially in soils with low Cu loadings (Fig. S13). Groenenberg et al. (2017) found similar results for a large set of Dutch soil samples and attributed this error to an incomplete recovery of Cu by the 0.43 M HNO_3 extraction at low Cu loadings due to very strong binding. The Cu concentration in solution is underestimated by the multi-surface model for the soils with low reactive and dissolved Cu concentrations. An alternative explanation for the prediction error for Cu may be that for these soils with low concentrations, the presence of organo-mineral colloids may enhance the measured Cu concentrations in the CaCl₂ extraction, while this process is not taken into account by the multi-surface model.

The speciation of Zn, Cu and B in the solid and solution phase according to the multi-surface model is shown in Fig. 3. In line with previous findings, soil organic matter was found to be the most important reactive surface for Zn and Cu adsorption in the solid phase (Groenenberg et al., 2017; Tiberg et al., 2018; Weng et al., 2001). However, with increasing pH, the metal (hydr)oxides start to play an important role. For Zn, this is already noticeable from pH 5.5–6, while for Cu above pH 7. Interestingly, for B, the opposite trend was found as shown by Fig. 3: the adsorption to metal (hydr)oxides dominates B adsorption in low pH soils, while soil organic matter becomes increasingly important with increasing pH. In the solution phase, Zn and B are mainly present as the free Zn^{2+} ion, and as $B(OH)_3$. Only for Cu, DOC was found to play an important role for the solution speciation.

3.4. Partition relations

Two different types of partition relations were derived for calculating the solid-solution partitioning of the three micronutrients: C-Q relations, in which the concentration in the 0.01 M CaCl₂ extraction was optimized based on soil variables and the reactive content (Eq. (4)) and K_f relations in which the two Freundlich parameters and regression coefficients were optimized simultaneously (Eq. (5)).

3.4.1. C-Q partition relations

The C-Q partition relations based on the tropical soils from this study for the three different micronutrients are shown in Table 2. The soil pH explained most variation (57%) in the Zn concentrations measured in the CaCl₂ extraction, with a negative coefficient. This is consistent with the previously observed relation between K_d and the concentration in the CaCl₂ extraction with pH (Fig. 1). For B and Cu, for which we found a less clear relation between K_d and soil properties, the reactive content appears to be most important variable to predict soluble B and Cu: respectively 49 and 25 % of the variance in the dissolved concentration
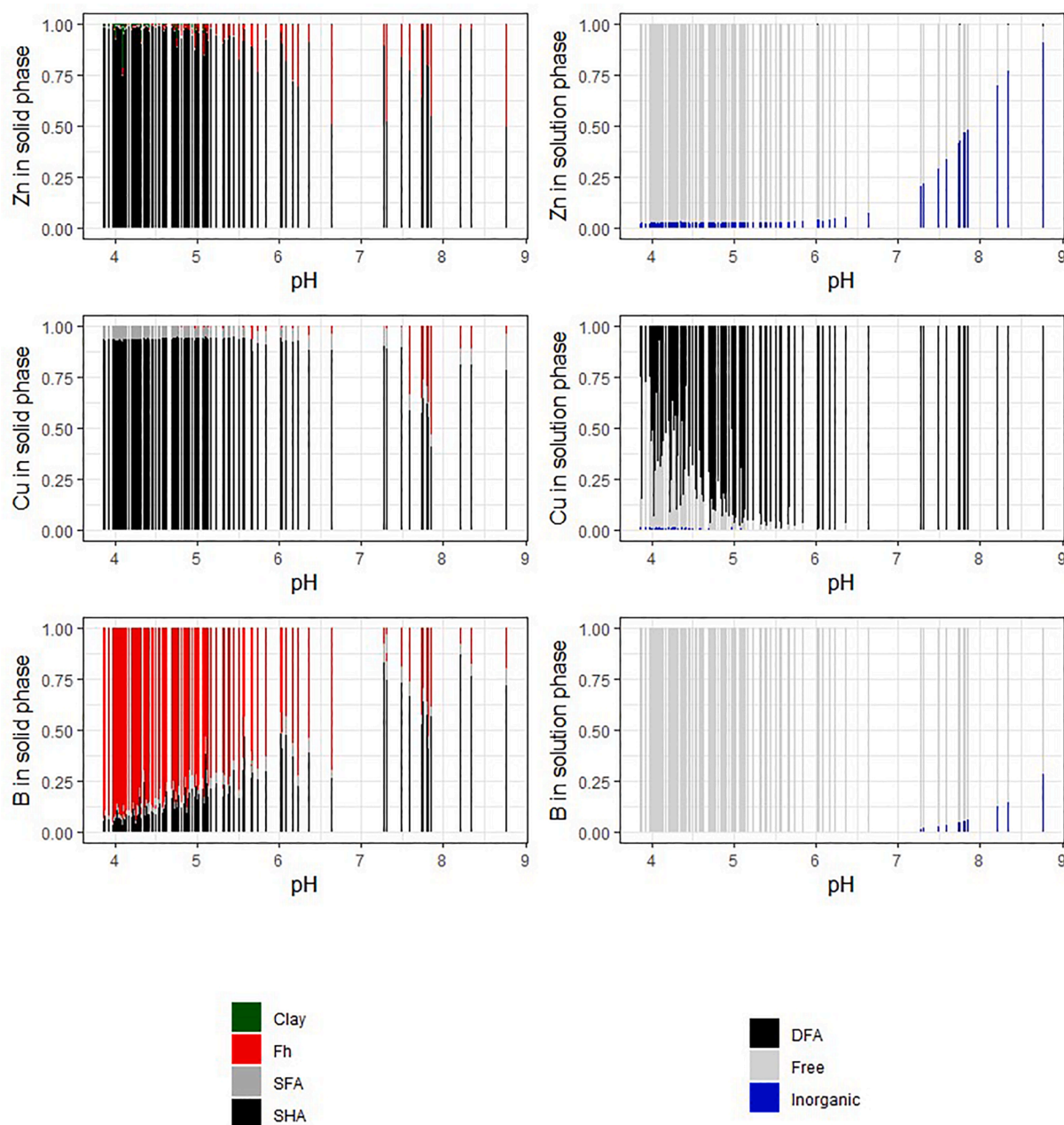
Fig. 3. The chemical speciation of Zn, Cu and B in the solid phase (left figures) and the solution phase (right figures) of all samples as it is predicted by the multi-surface model. The speciation is shown as a function of the soil pH measured in the 0.01 M $CaCl_2$. In the solid phase, the ions are adsorbed by clay, ferrihydrite (Fh), solid humic acids (SHA) and solid fulvic acids (SFA). In the solution phase, the elements are present as free ion (or in the case of B as $B(OH)_3$), inorganic complexes or adsorbed to dissolved fulvic acids (DFA).

was due to the variation in the reactive content (Table 2).

The partition relations, with their most important input variables and coefficients, were in agreement with the importance of the various reactive surfaces from the multi-surface modelling calculations (Fig. 3). For Zn and Cu, the multi-surface modelling calculations have shown that soil organic matter is the most important reactive surface for adsorption in the solid phase. In line with these results, SOM appears as a significant variable in both regression equations with a negative coefficient (Table 2). For Zn and B, we found a positive regression coefficient for clay in the C-Q relations, which is unexpected based on adsorption processes. For Zn, clay was found to be only slightly significant (p-value of 0.04), and the contribution to the variance in the dissolved Zn concentration was found to be only minor (0.8 %) as shown in Table 2.

Consistent with the prediction by the multi-surface model that

metals such as Zn and especially Cu in the $CaCl_2$ solution are present as a complex with DOC (Fig. 3), DOC concentration was found to be a significant variable with a positive coefficient explaining dissolved Cu and Zn in the partition relations (Table 2).

For B, the partition relation showed that the B concentration in solution is mainly governed by the reactive content (Table 2). Initially, a significant contribution of DOC was found for soluble B in these tropical soils, with a negative coefficient (results not shown). However, our multi-surface modeling calculations did not show an important role of DOC for B solubility (Fig. 3). The negative contribution of DOC on B solubility cannot be explained by soil chemical processes. The DOC concentrations were found to be strongly related to the SOC content (Fig. S8). As such, DOC may be a surrogate for SOC in the partition relation. When the partition relation was re-calibrated without DOC as

Table 2

The C-Q partition relations as shown in equation (4), derived based on # soil samples for predicting the concentrations of Zn, Cu and B in the 0.01 M CaCl$_2$ (logC, in M). The final model was selected based on the AIC value, with the following variables: the concentration measured in the 0.43 M HNO$_3$ of the specific element (Q), the pH (CaCl$_2$), the soil organic matter (SOM), the clay content, the sum of Fe and Al measured in the ammonium oxalate extraction (AO-FeAl) and the dissolved organic carbon concentration in the 0.01 M CaCl$_2$ extraction (DOC). For each soil variable, the coefficient in the model is given with the standard error between brackets, followed by the % of variation that is explained by the model and attributed to the particular variable. The coefficient of determination (R^2) is given to show the percentage of variation in logC that is explained by the model.

	α_0	pH	logQ	logSOM	logFeAl	logClay	logDOC	AIC	R^2	# samples
			mol kg^{-1}	%	mmol kg^{-1}	%	mg L^{-1}			
logC(Zn)	−0.95 ± 0.43	−0.54 ± 0.03	0.69 ± 0.06	−0.89 ± 0.17	–	0.13 ± 0.06	0.38 ± 0.13	35.8	0.80	159
		57%	8%	10%		0.8%				
							5%			
logC(Cu)	−5.77 ± 0.26	−0.04 ± 0.02	0.47 ± 0.05	−0.53 ± 0.11	–	–	0.42 ± 0.10	−25.52	0.35	172
		2%	25%	3%			4%			
logC(B)	−3.06 ± 0.26	–	0.68 ± 0.05	−0.20 ± 0.09	–	0.12 ± 0.06	–	64.7	0.62	169
			49%	6%		6%				

possible input variable, SOM was selected as a significant variable next to the reactive concentration (Table 2), and the negative coefficient for SOM is in line with the multi-surface modeling predictions that showed that SOM is an important reactive surface for B adsorption. The final model had the same R^2 and prediction error as the model with DOC.

The explained variance in dissolved Cu concentration by the partition relation (35%) was relatively low (Table 2), probably because of a too small variation in the experimental solid-solution partitioning. For B (62%) and Zn (80%), the explained variation was higher. However, the prediction error of the partition relations in the dissolved concentrations
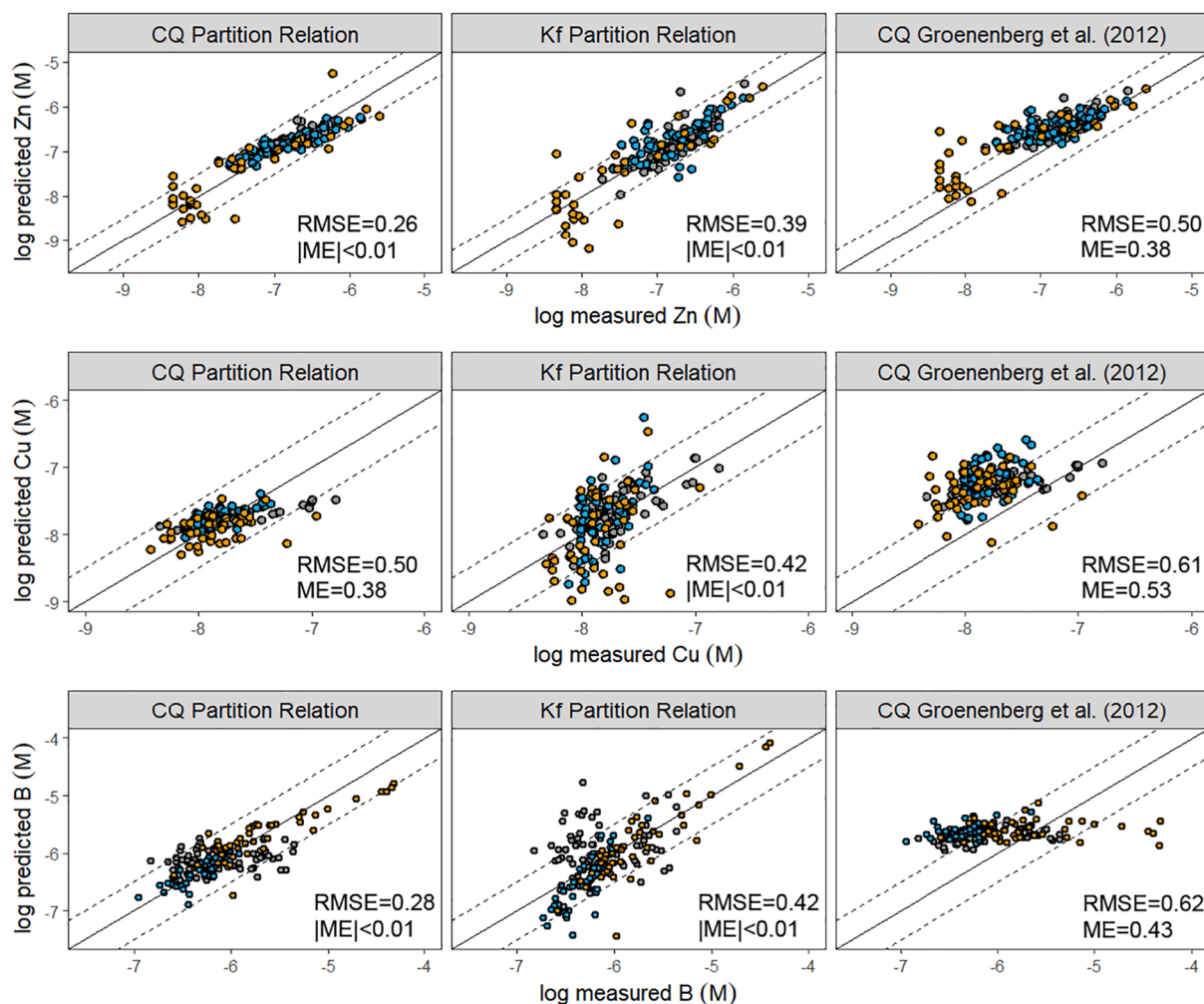
Fig. 4. The comparison between measured and predicted concentrations of Zn (upper), Cu (middle) and B (lower) in the 0.01 M CaCl$_2$ extraction, using CQ relations (left), K_f partition relations (middle) and the CQ partition relations from (Groenenberg et al., 2012). The numbers given in the graphs represent the root mean squared error (RMSE) and the mean error (ME) in log M. The solid line is the 1:1 line, points within the dashed lines are within 0.5 log M deviation from the measured concentrations.

was similar for all three elements, as illustrated by the respective RMSE (Fig. 4). Based on this observation, we can conclude that the partition relations are accurate prediction models of the soluble Zn, Cu and B concentrations measured in a 0.01 M CaCl$_2$ extraction for these soils from the tropics.

The prediction error of the C-Q partition relations for all three micronutrients was not related to any input variable (Figs. S11-S13), but it was related to the dependent variable namely the concentration measured in the CaCl$_2$ extraction: The dissolved concentrations are overestimated in the lower range, and underestimated in the higher range by the C-Q partition relation (Fig. 4). This modeling error becomes even more clear when using previously derived C-Q partition relations from (Groenenberg et al., 2012). These partition relations were calibrated based on a set of Dutch soils, with higher Zn, Cu and B concentrations in the CaCl$_2$ extract (Zn: $-7 - -3$ log M, Cu: $-8 - -6$ log M, B: $-6 - -4$ logM). For Zn and especially for B, using the partition relations from Groenenberg et al. (2012) also overestimates the dissolved concentrations at high values, and the opposite at low values. The dissolved concentrations in these tropical soils are lower than, or at the lower end of, the concentrations used for calibrating the partition relations from Groenenberg et al. (2012). As discussed in the next section, this systematic prediction error can be reduced when using K_f instead of C-Q partition relations. Using the partition relations from Groenenberg et al. (2012) results in a systematic overestimation of dissolved Cu concentrations in these tropical soils. Comparison of both C-Q partition relations shows that the effect of DOC and SOM on dissolved Cu is higher and lower, respectively, in the relations from Groenenberg et al. (2012) compared to the partition relations found in this study. Groenenberg et al. (2012) found larger fractions of reactive DOC (i.e. 50 %) for their multi-surface modeling calculations compared to this study, which may have resulted in a larger coefficient for DOC in their partition relations derived for the same set of temperate soil samples. In terms of SOC, these tropical soils have a lower Cu – SOC loading, which may result in a higher importance of high affinity sites for Cu adsorption, and therefore a larger coefficient of SOC in the partition relations for tropical soils.

3.4.2. K_F partition relations

For the derivation of K_f partition relations, the solid-solution partitioning itself was optimized instead of the concentration in solution, according to equation (5) (Groenenberg et al., 2010). The resulting equations are shown in Table 3. For Zn, this approach resulted in a partition relation that is similar to the C-Q relation. . Again, pH was the most important variable, similar as in the C-Q partition relation, explaining 69% of the variance in K_f. Compared to the C-Q partition relation, the total variance explained by the model is the same for the K_f relation (80%; Table 3), but the error in the Zn concentration is also slightly larger (see RMSE values in Fig. 4). More importantly, the

systematic underestimation of Zn in solution at highest concentrations and overestimation at lowest concentrations, as observed in the C-Q relation, disappeared when using a K_f partition relation (Fig. 4).

For Cu and B, a K_f partition relation resulted in a lower variance explained by the model, and a higher prediction error in the dissolved concentration compared to the C-Q relations. The K_f partition relation confirmed the previous result that the concentrations of Cu and B in the CaCl$_2$ extractions were mainly determined by the reactive content (Table 2), and that the experimental K_d values were slightly related to the soil organic matter pools in the case of Cu (Fig. 1), or not clearly to any soil property in the case of B (Fig. S7). As a result, optimization of the solid-solution partitioning in the form of K_f relations did not give good results for B and Cu.

3.5. Micronutrient availability in tropical soils

Micronutrient availability depends particularly on the reactive and soluble pools. We have shown that the solid-solution partitioning of Zn is mainly controlled by soil pH. When the reactive content is known, it is possible to make a reasonable estimation of the dissolved concentration based on easily obtainable soil parameters such as soil pH and soil organic matter. In acidic soils with pH $\sim$ 4, a large fraction of reactive Zn was found to be present in the solution phase. This implies that the buffering capacity of Zn in these soils is low, while the soluble concentration may be relatively high due to limited adsorption. As a consequence, the buffering capacity may limit uptake, and in these cases soil tests that approximate the reactive pool such as the 0.43 M HNO$_3$ extraction, may relate better to Zn uptake (Nawara et al., 2017). For B and Cu, the dissolved concentrations were mainly controlled by their reactive contents, the solid-solution partitioning was not related to soil properties. In terms of practical implications, measuring both nutrient pools instead of one may not give more information in terms of availability.

The correlation table in Fig. S8 shows that the reactive content of Cu and Zn in these soils is strongly related to the soil organic matter and metal (hydr)oxides content, which may be explained by the fact that these are the most important adsorption surfaces, thereby controlling the buffering capacity of both nutrients.

Our multi-surface modeling calculations for the large set of tropical soils in this study have confirmed the previous finding that the adsorbed amount of naturally present reactive B in soils is minor (Van Eynde et al., 2020b). As a consequence, it is expected that other processes than adsorption will be important for buffering the B concentration in the solution, such as precipitation, aerosol deposition, B originating from mineral weathering or from mineralization of soil organic matter (Gaillardet and Lemarchand, 2018; Park and Schlesinger, 2002; Su and Suarez, 2004). Reactive B content in these soils was found to be mostly

Table 3

The K_f partition relations as shown in equation (5), derived for predicting the Freundlich parameters for Zn, Cu and B concentrations in the 0.01 M CaCl$_2$ extract (logC, in M). The input variables were selected based on stepwise regression, using as possible input variables the concentration measured in the 0.43 M HNO$_3$ of the specific element (Q), the pH(CaCl$_2$), the soil organic matter (SOM), the clay content, the sum of Fe and Al measured in the ammonium oxalate extraction (AO-FeAl) and the dissolved organic carbon concentration in the 0.01 M CaCl$_2$ extraction (DOC). For each soil variable, the coefficient in the model is given with the standard error between brackets, followed by the % of variation that is attributed to the particular variable. The coefficient of determination (R^2) is given to show the percentage of variation in logK_f that is explained by the model.

	n	α_0	pH	logSOM	logFeAl	logClay	logDOC	R^2	AIC	# samples
					mmol kg^{-1}	%	mg L^{-1}			
logK_f(Zn)	0.64	-2.91 ± 0.16	0.49 ± 0.02	1.29 ± 0.12	–	–	-0.39 ± 0.11	0.80	22.30	159
			69%	8%			3%			
logK_f (Cu)	0.59	-0.11 ± 0.23	0.01 ± 0.02	0.54 ± 0.16	0.22 ± 0.10	0.10 ± 0.06	-0.44 ± 0.12	0.31	22.09	172
			1%	9%	10%	7%	4%			
logK_f (B)	0.53	-2.30 ± 0.13	0.19 ± 0.02	0.25 ± 0.09	–	–	–	0.40	16.7	169
			36%	4%						

related to clay content (Fig. S8). The correlation between reactive B or dissolved B concentration and clay content (correlation coefficients of 0.33 and 0.29 respectively) points towards the importance of chemical weathering for controlling the dissolved B concentrations in these tropical soils.

4. Conclusions

Micronutrient availability depends on the soil nutrient status, and in particular on the reactive and soluble pools. To improve the understanding of the processes that control the solid-solution partitioning of Zn, Cu and B in tropical soils, a multi-surface model was used to calculate the micronutrient speciation in a series of 172 soils samples from Burundi, Rwanda and Kenya. Next, partition relations were developed for predicting the soluble Zn, Cu and B concentrations based on general soil properties.

Most of the reactive Cu is present in the solid phase. Interestingly, we found that the solid-solution partitioning of Cu was rather constant among all 173 soil samples studied, and it was only partly explained by the soil organic matter in the solid and solution phase. The importance of soil organic matter (SOM) for Cu solid-solution partitioning was confirmed by the multi-surface model calculations, which showed that SOM was the dominant adsorbent for Cu, except for soils with pH larger than 7 in which the metal (hydr)oxides also start to play an important role. The weak relation between the rather constant Cu solid-solution partitioning and soil variables, resulted in partition relations in which the variation in soluble Cu was mainly explained by the reactive concentration. In comparison with the solid-solution partitioning of Cu in soils from temperate climates, lower Cu concentrations in solutions were found for the tropical soils in this study. We explained this phenomenon by the lower reactivity of dissolved organic matter that was measured in these tropical soils, and/or by the lower Cu:SOC ratio that was found, which may result in relatively higher Cu adsorption in the solid phase.

Similarly as for Cu, we found for B that the variation in soluble Cu was mainly explained by the reactive concentration. However, in contrast to Cu, these results for B can be explained by the weak interaction of B with the solid phase, which was shown by the relatively low solid-solution partitioning ratios and the multi-surface modeling calculations. Although small, the interaction of B with the solid phase is dominated by adsorption to metal (hydr)oxides in low pH soils, and to soil organic matter in soils with pH above ~ 6.

The solid-solution partitioning of Zn in the studied soils varied the most, and this variation was mainly explained by soil pH. The speciation of Zn in the solid phase was dominated by soil organic matter in low pH soils, but above pH 5.5–6, the metal (hydr)oxides started to play an important role. Due to the strong relation between the solid-solution partitioning of Zn and soil variables such as pH, the partition relations resulted in a higher explained variance of soluble Zn compared to Cu and B.

For B, the interaction with the solid phase is limited, resulting in a large fraction of the reactive pool being present in the solution. For B, differentiation between the reactive and soluble pool by soil tests may be less relevant due to the strong relation between both B concentrations, that was found by the C-Q partition relations.

Two types of partition relations have been derived that are reasonably good in explaining the variability of dissolved micronutrient concentrations. We have shown that partition relations in which the concentration in solution is optimized, may result in a systematic modelling deviation in relation to the measured concentration. This can be improved for Zn when models are calibrated in which the solid-solution partitioning itself is optimized. The partition relations from this study are easy-to-use tools for predicting the soluble concentrations of Zn, Cu and B in soils from the tropics with low contents of these micronutrients. These models can greatly enhance the usability of current existing soil information data for SSA and may thereby expand current soil information with data on micronutrient availability, thereby facilitating future decision support tools for micronutrient fertilization.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2022.115773.

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