

Evaluation of the Single Dilute (0.43 M) Nitric Acid Extraction to Determine Geochemically Reactive Elements in Soil

Jan E. Groenenberg,^{*,†,‡,§,||} Paul F. A. M. Römkens,^{||} André Van Zomeren,[⊥] Sonia M. Rodrigues,[#] and Rob N.J. Comans[†]

[†]Department Soil Quality, Wageningen University and Research, Wageningen, The Netherlands

[‡]CNRS, LIEC, UMR7360, 15 Avenue du Charmois, Vandoeuvre-lès-Nancy F-54501, France

[§]Université de Lorraine, LIEC, UMR7360, 15 Avenue du Charmois, Vandoeuvre-lès-Nancy, F-54501, France

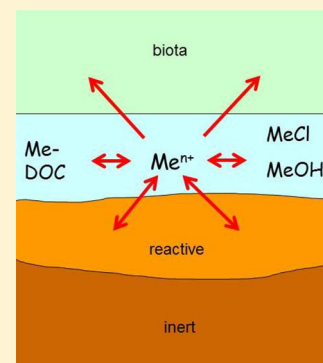
^{||}Environmental Research (Alterra), Wageningen University and Research, Wageningen, The Netherlands

[⊥]Energy Research Centre of The Netherlands, Petten, The Netherlands

[#]Centre for Environmental and Marine Studies (CESAM)/Departamento de Química, Universidade de Aveiro, Aveiro, Portugal

Supporting Information

ABSTRACT: Recently a dilute nitric acid extraction (0.43 M) was adopted by ISO (ISO-17586:2016) as standard for extraction of geochemically reactive elements in soil and soil like materials. Here we evaluate the performance of this extraction for a wide range of elements by mechanistic geochemical modeling. Model predictions indicate that the extraction recovers the reactive concentration quantitatively (>90%). However, at low ratios of element to reactive surfaces the extraction underestimates reactive Cu, Cr, As, and Mo, that is, elements with a particularly high affinity for organic matter or oxides. The 0.43 M HNO₃ together with more dilute and concentrated acid extractions were evaluated by comparing model-predicted and measured dissolved concentrations in CaCl₂ soil extracts, using the different extractions as alternative model-input. Mean errors of the predictions based on 0.43 M HNO₃ are generally within a factor three, while Mo is underestimated and Co, Ni and Zn in soils with pH > 6 are overestimated, for which possible causes are discussed. Model predictions using 0.43 M HNO₃ are superior to those using 0.1 M HNO₃ or Aqua Regia that under- and overestimate the reactive element contents, respectively. Low concentrations of oxyanions in our data set and structural underestimation of their reactive concentrations warrant further investigation.



■ INTRODUCTION

It is widely recognized that the availability of contaminants should be considered in environmental risk- and life cycle assessment and regulation.^{1–3} Similarly, the availability of micronutrients is of interest when evaluating whether sufficient levels of these elements are present in soil for uptake by biota.⁴ A prerequisite for elements present in the solid phase to be exchangeable with the solution phase and their subsequent mobility and uptake by biota is to be geochemically reactive. The geochemically reactive concentration, further briefly denoted as reactive concentration, is the amount in the solid phase that is available for interaction with the dissolved phase at short time scales of less than seconds up to days, through processes such as sorption/desorption and (surface) precipitation/dissolution reactions.^{5,6} The fraction of the total element concentration being reactive is related to their source and soil properties.^{7,8} The reactive concentration is also referred to as “labile” concentration⁹ or “potentially available” concentration particularly in bioavailability literature.¹⁰ The reactive concentration is considered potentially available for uptake by biota, thereby excluding the inert fraction which is incorporated in crystal lattices of minerals or occluded in particles (oxides, organic matter). In contrast to the potential

availability (i.e., the “reactive” concentration as defined in this paper) the actual availability is pH dependent and further determined by the concentration of reactive surfaces, competing ions and complexing ligands, species-specific physiology and kinetic constraints.^{8,10–12}

Various methods have been suggested to determine reactive concentrations in soils, including radioactive and stable isotopic dilution, single selective- and sequential extractions.^{9,13} Isotopic dilution is conceptually the most sound approach because of its mechanistic basis and conditions of minimal disturbance of the solid/liquid exchange processes.^{14,15} The choice of method depends on the objective of the particular study and may differ for scientific research, as opposed to more standardized investigations for risk-assessment and regulatory purposes that can be performed at relatively low cost and by less-specialized laboratories.¹⁶ Last year ISO published the ISO 17586:2016 standard¹⁷ “Extraction of trace elements using dilute nitric acid” which “specifies a method of extracting trace

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elements from soil at approximately pH 0.5–1.0 using a 0.43 M HNO_3 solution. Using this method the potential environmental available trace elements as defined in ISO 17402¹⁸ is extracted". Because the method is now standardized it is important to critically evaluate its performance to determine reactive element concentrations in soil.

The 0.43 M HNO_3 extraction, further denoted NA-extraction, was introduced in 1954 by Westerhoff¹⁹ to extract Cu in soil. The principle of the extraction is the dissolution of metal cations by competitive desorption with protons. Dissolution of oxyanions is due to their protonation at low pH and (partial) dissolution of hydrous oxides of Al, Fe and Mn to which the anions are adsorbed. The NA-extraction has been used for various elements to assess their leaching,^{5,20} bioavailability,^{10,21–23} and human bioaccessibility.²⁴ The applicability and comparability of the method in different laboratories in terms of repeatability and reproducibility, was established in an interlaboratory validation study.²⁵

In this study we aim at a thorough evaluation of this extraction and a better mechanistic understanding of acid extractions at different proton concentrations. Important questions are (1) is the proton activity of the extract high enough to fully desorb reversibly bound metal, (2) to which extent oxy-anions adsorbed to oxides are dissolved or remain adsorbed/readorb to not fully dissolved oxides and whether the (co)dissolved amount is geochemically reactive, (3) to which extent equilibration time determines extracted amounts and (4) whether trace metal bearing minerals dissolve or possibly precipitate in the extract. To obtain quantitative insight in the mechanism of the extraction, we have modeled the extraction of a large number of soil samples with varying soil properties and metal content using a mechanistic multisurface model. In a separate approach to evaluate the suitability of NA to extract reactive elements, we have assessed the performance of the model to predict dissolved concentrations, as measured in 0.01 M CaCl_2 -extracts of these soils, using nitric acid extractions with varying acidity, including 0.43 M HNO_3 , as alternative model-input. The results of this evaluation will enable the reader to make a well-considered choice for which purpose and under which conditions the method is appropriate to quantify the geochemically reactive concentration of specific elements.

MATERIALS AND METHODS

Data Sets Used for the Evaluation. Soil characteristics, element contents and ratios of NA:Aqua Regia (AR) extracted elements are summarized in Tables S1–S4 of the [Supporting Information \(SI\)](#).

Data Set NL1. contains 49 samples (0–20 cm depth) from The Netherlands of various types including sandy, peat and clay soils with metal contents ranging from background to heavily contaminated levels.²⁶ **Data set NL2** contains 69 soil samples from all diagnostic horizons down to 120 cm from 11 soil profiles in The Netherlands. Metal contents range from background to moderately elevated levels.²⁶ Element contents in both data sets were determined using NA (4 h extraction) and AR²⁷ for Al, Mn, Fe, V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, and P using archived soil samples. Additionally, NL 1 includes Cd, Cr, Cu, Ni, Pb, and Zn contents extracted with 0.01, 0.1, 0.43, 2 M HNO_3 , and 0.05 M Na_2EDTA and measured pH in these extracts. All soils were extracted with 0.01 M CaCl_2 (1:10 weight to volume ratio), in which pH, DOC and concentrations of Cd, Cu, Ni, Pb, and Zn were

measured. A subset of 70 samples from NL1 and NL2 was extracted with 0.01 M CaCl_2 in which dissolved As, B, Ba, Be, Co, Cr, Li, Mo, Sb, Se, Sn, V, and S were determined together with PO_4 , DOC, and pH.

Data Set PRT. contains 136 Portuguese soils (0–15 cm depth) including noncontaminated sites as well as fields impacted by industrial activities and mining practices.⁸ Soils were extracted with AR and NA (2 h extraction). A subset of 15 samples was extracted with 0.01 M CaCl_2 (1:10 weight to volume ratio) in which pH, dissolved concentrations and DOC were determined.²⁶

Data Set ECN. consists of five top-soil samples from sandy, peat and river-clay soils (see [Table S3 of the SI](#)) in The Netherlands. The soils were extracted in triplicate using 0.1, 0.43, 0.5, and 1.0 M HNO_3 (48 h extraction). The pH was measured in the filtered extracts.

Nitric Acid Extraction. Reactive concentrations in the four data sets were extracted with NA according to modified versions of the extraction procedure by Houba et al.²⁷ A general description of the NA-extraction is given below, details per data set are given in the [SI](#). The standard extraction time is 2 h. Because the applied extraction time varied among data sets, being 2, 4, or 48 h, we evaluated the effect of time by extracting a subset of the samples from all three data sets for each of the three applied extraction times.

General Description of the NA-Extraction. The sieved and air-dried soil sample (<2 mm) is extracted with 0.43 M HNO_3 at room temperature. The extraction solution is obtained by dilution of 30 mL concentrated HNO_3 (65%, analytical grade) in 1000 mL ultrapure water. The soil material together with the extracting solution at a 1:10 weight to volume ratio are shaken during 2 (standard), 4 or 48 h (see description per data set). After centrifugation and filtration dissolved concentrations in the filtrates are measured using ICP-AES and/or ICP-MS. The pH after extraction is usually between 0.5 and 1, which is required to extract the potential environmental available metals, as defined in ISO 17402.¹⁸ For calcareous soils, the final pH may be higher and should be adjusted by adding additional nitric acid. This is advised to be done using 0.2 mL of 5 M HNO_3 for each % of CaCO_3 in order to affect as little as possible the solid to solution ratio.²⁷ Because none of the samples in the evaluated data sets included calcareous soils, no additional nitric acid was added to any of the samples.

Effect of Extraction Time. A subset of 11 samples from the NL1, NL2 and PRT data sets was extracted during 2, 4, and 48 h. The samples were selected to resemble the variation in SOM, clay and Al/Fe-(hydr)oxide contents and pH of all samples. To minimize variation due to sample heterogeneity a single sample of each soil was used for the extraction and subsamples from solution were collected after each time. The change in the solid to solution ratio was minimized by extracting 10 g of soil with 100 mL 0.43 M HNO_3 and taking only 1 mL of the extract for analysis.

Geochemical Modeling. The geochemical model adopted from Dijkstra et al.²⁰ implemented in the ORCHESTRA software^{28,29} combines advanced models for ion binding, that is, the NICA-Donnan model³⁰ for particulate (SOM) and dissolved (DOM) organic matter, the generalized two layer model (GTLM)³¹ for Fe/Al(hydr)oxides and a Donnan model for clay together with selected mineral equilibria ([Table S5 of the SI](#)). We used the default model parameters included in ORCHESTRA, for elements for which no generic parameters

are available we used additional parameters from Dijkstra et al.²⁰ (see SI section 3).

The theoretical recovery of the extraction was evaluated by calculating the dissolved concentrations in the NA-extract, accounting for the binding capacity of the major reactive mineral and organic adsorbents in the soils, at a reactive concentration equal to that determined with NA. The recovery was then calculated according to

$$\text{recovery} = 100\% \times \frac{LS \times M_{\text{diss-model}}}{M_{\text{NA-extract}}} \quad (1)$$

With LS = the liquid to solution ratio (L.kg^{-1}); $M_{\text{diss-model}}$ = the total dissolved concentration calculated with the model (mol L^{-1}) and $M_{\text{NA-extract}}$ = the reactive concentration as determined with NA (mol.kg^{-1}). Sample specific inputs include (1) NA-extracted concentrations of the considered elements, competing ions Ca^{2+} , Mg^{2+} , Mn^{2+} , SO_4^{2-} and PO_4^{3-} (measured as S and P), (2) the pH of the NA-extract, (3) concentrations of the reactive surfaces (adsorbents): SOM, Al/Fe-(hydr)oxide and clay and (4) dissolved NO_3 set to 0.43 mol.L^{-1} . DOC was not measured in the NA-extracts and was set to the concentration measured in the CaCl_2 -extracts.²⁶ This concentration is likely a low estimate for DOC in the NA-extract because Dijkstra et al.²⁰ measured increasing DOC with decreasing pH below pH 4 in pH-static soil extractions. Ion binding to DOM and SOM was modeled with generic humic acid (HA)³² representing the binding to both humic- and fulvic acids^{20,26} with HA set to 50% of DOM/POM.^{20,26,33} The content of Al- and Fe-(hydr)oxides, which are partially dissolved, was calculated as the difference between oxalate and NA extracted Al and Fe. The pH was set at 0.9 based on the average pH in data sets NL1 and PRT. Results have to be interpreted with some care because this pH is below its range in the data used for the parametrization of the NICA-Donnan (pH > 3) and GTLM models (pH > 4). However, the mechanistic nature of the model together with adequately predicted dissolved concentrations at pH 2 in a previous study²⁰ give confidence using the model beyond the lower limit of its calibration domain. In addition, the use of the model under these low-pH conditions assumes that the considered mineral and organic surfaces have the same reactivity as in the pH-range where these models are generally applied.

The suitability of the 0.43 M HNO_3 and other nitric acid extracts of various concentrations and AR as alternative model input were evaluated by assessing predicted solution concentrations in 0.01 M CaCl_2 soil solution extracts against measurements. Sample specific model inputs include: (1) reactive element concentrations determined either with 0.1, 0.43, 2 M HNO_3 or AR of the considered elements and S, (2) concentrations of SOM, DOM, Al/Fe-(hydr)oxide and clay, (3) measured pH and dissolved concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and PO_4^{3-} in the CaCl_2 extract. The $\log\text{-pCO}_2$ was fixed at atmospheric pressure of -3.5 . The activities of Al^{3+} and Fe^{3+} in solution were assumed to be in equilibrium with Al- and Fe-hydroxide ($\log K_s$ of 8.5 and 2.5 respectively). The redox status of the soil (pe) was set to $\text{pH} + \text{pe} = 11$ being a representative value for aerobic soils.³⁴

RESULTS AND DISCUSSION

Geochemical Model Evaluation of the NA-Extraction. Model calculations for 248 samples of data sets NL1, NL2, and PRT give a median recovery by the NA-extraction of more than

90% for Co, Ni, Zn, Cd, Pb, Se, and Sb (Figure 1). Lower recoveries are predicted for Cu (69%), Cr (2%), and V (47%),

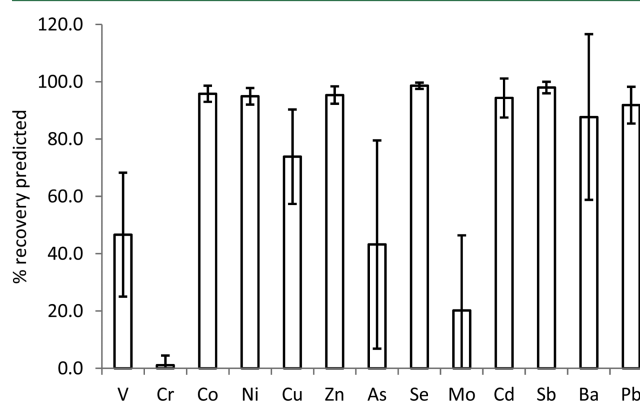


Figure 1. Average recovery of the 0.43 M HNO_3 -extraction according to eq 1 from dissolved concentrations in the extract calculated with the multisurface model for the soil samples of data sets NL1, NL2, and PRT, error bars indicate ± 1 standard deviation.

elements which share a very high affinity for binding to SOM. Chromium and V were assumed to be present in their trivalent (Cr^{3+}) and tetravalent (VO^{2+}) redox states under the ambient soil conditions.^{20,35,36} Similarly lower recovery is calculated for the oxyanions As (89%) and Mo (49%). For Cu a clear relation is found between the modeled recovery and the ratio of measured reactive Cu:SOM (Figure S1a, SI). Consistently, the measured ratio of NA and AR extracted Cu (NA:AR) as a function of Cu(NA):SOM (mol.kg^{-1}) declines toward low Cu:SOM ratios (Figure S1b, SI). These findings indicate that the NA-extraction is too weak to extract total reactive Cu at low Cu:SOM ratios, due to binding sites with a very high affinity for Cu even at the low pH of the extraction. The very low recovery of reactive Cr (2%) seems to be unrealistic since NA extracts 7% of that extracted by AR. The extremely low recovery of Cr is likely the result of poor model parametrization of Cr in the NICA-Donnan model.³⁷ The calculated recovery of reactive As and Mo varies strongly between soil samples ($p5 = 0.4\text{--}0.5\%$; $p95 = 99\%$). The recovery of the oxy-anions As and Mo is negatively correlated with the content of Al- and Fe-hydroxides not dissolved in the HNO_3 -extract (= oxalate minus NA extracted Al and Fe, Figure S2, SI) whereas the recovery of Se and Sb was invariably high. The oxy-anions As, Mo appear to remain partly adsorbed and/or are readsorbed to the remaining Al/Fe-hydroxides. This is likely due to strong specific sorption of these oxy-anions compared to Se and Sb. Although the hydrous oxides bear a strong positive charge at the low pH of the NA-extract, electrostatics are thought to play a minor role because, according to the model calculations, the oxy-anions are nearly completely present in their uncharged protonated form. The calculated recovery of reactive Ba is on average 88% but with large variation. Low recoveries ($p5 = 29\%$) occur in samples with high SO_4 -content for which oversaturation with Barite is calculated. Except for Barite, no oversaturation is calculated for any other mineral included in the model. Good correspondence between modeled and measured trends in fractions of metal extracted with 0.1 and 0.43 M HNO_3 relative to 2 M HNO_3 (Figure 2B), except for Cr, gives confidence in the used model approach.

Effect of Extraction Time on Extracted Metal Content. Extracted amounts increase with extraction time for all

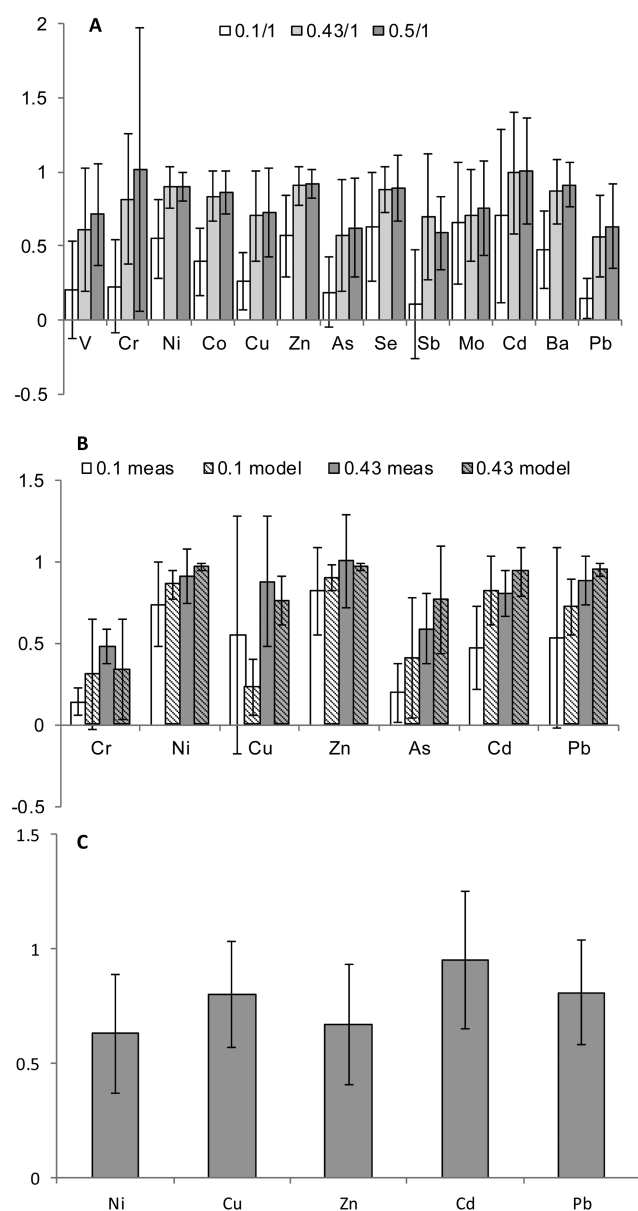


Figure 2. (A) Average fractions of elements extracted with 0.1, 0.43, and 0.5 M HNO₃ relative to the amount extracted with 1.0 M HNO₃ for the ECN data set; (B) average fractions of 0.1 and 0.43 M HNO₃ extracted metal relative to the amount extracted with 2.0 M HNO₃ as measured (0.1 meas and 0.43 meas) or modeled (0.1 model and 0.43 model) for data set NL1 error bars indicate standard deviations; (C) average fraction 0.05 M EDTA to 0.43 M HNO₃ extracted metal for data set NL1.

elements (Table 1). No data are available for Mo, Se, and Sb because their concentrations were below the limit of

quantification. The relative increase between 2 and 4 h is small with ratios <1.20 for most elements except Si (1.66), Fe (1.33), and Cr (1.32). The larger effect on Fe and Si indicates that especially the dissolution of Fe-(hydr)oxide and silicate minerals is rate limited. The large difference for chromium is likely due to the dissolution of Cr present in mixed Cr-Fe-hydroxides.³⁵ The time effect is notably small (ratio <1.05) for the elements Ba, Cd and Cu. The increase between 2 and 48 h is usually larger than a factor 1.2 except for Ba, Cd and Cu. The effect is again notably large for Si (ratio = 5.3), Fe (2.9) and Cr (3.17). Relatively large effects (1.5 < ratio < 1.9) are found for As which is generally associated with iron- and aluminum (hydr)oxides, and for Co, Ni, and Zn, elements which may form mixed metal-aluminum hydroxide surface precipitates or double layered hydroxides (DLH).^{38–41}

Effect of Acid Concentration on Extracted Amounts.

Iron and aluminum oxides are increasingly dissolved with increasing acidic concentration of the extracting solution as follows from the increasing ratio of NA-extracted to oxalate extracted Al and Fe (Table S6, SI). Model calculations indicate that at the final pH of the 0.1, 0.43, and 2 M HNO₃ extractions Al- and Fe-(hydr)oxides will be dissolved completely when chemical equilibrium is reached. However, none of the three concentrations HNO₃ dissolve oxalate-extractable Fe completely. This observation together with the large increase of extracted Fe with time indicates that incomplete dissolution of Fe-(hydr)oxides by NA is due to kinetic constraints. Conversely, the 0.43 and 2 mol·L⁻¹ extraction dissolved more Al than oxalate does. This is unlikely due to dissolution of clay minerals such as Illite of which less than 1% of the total Al content was released after 1 h by NA.⁴²

Extracted amounts increase with increasing HNO₃ concentration with the largest differences for the macro-elements Fe, Al, and P (Figure S3, SI). Large differences between 0.1 and 0.43 M HNO₃-extracted P, V, Cr, Cu, Sn, Sb, As, and Pb (Figure 2a and b) are consistent with their high affinity for Fe/Al-(hydr)oxides (PO₄³⁻, SbO₃⁻ and AsO₄³⁻/AsO₃³⁻ and Pb²⁺)³¹ and organic matter (cations VO²⁺, Cr³⁺, Cu²⁺, Pb²⁺).⁴³ The low solubility of Cr(III) may also be due to its presence in mixed Cr-Fe-hydroxides.³⁵ Small differences between 0.1 and 0.43 M HNO₃ were observed for Ni, Cd, and Zn, which have a medium affinity for organic matter.⁴³ Differences between 0.1 and 0.43 M HNO₃ are negligible for weakly binding Na, Mg, and K and indicates that these elements were already dissolved by 0.1 M HNO₃ and that 0.43 M HNO₃ does not substantially dissolve clay minerals, which contain significant amounts of Mg and K. This finding is in agreement with the small release of K (<1% of the total content after 1 h) from Illite in 0.43 M HNO₃.⁴² Generally the differences between the 0.43 and the 1 M (Figure 2a) and 2 M HNO₃ (Figure 2b) extraction are small except for strongly binding As, Sb (to Al/Fe-(hydr)oxide), Cr, Cu, Pb, and V (to

Table 1. Average Ratio (11 Samples) Of the Elements Extracted With 0.43 M HNO₃ After 4 and 48 h Equilibration Time Relative to the Amount Extracted After 2 h

time (hours)	Si	Na	Mg	Al	P	S	K	Mn	Fe	
4	1.66	1.04	1.06	1.15	1.08	1.06	1.02	1.15	1.32	
48	5.26	1.09	1.56	1.91	1.35	1.26	1.37	1.64	2.92	
	V	Cr	Co	Ni	Cu	Zn	As	Ba	Cd	Pb
4	1.18	1.32	1.21	1.13	1.04	1.11	1.14	1.05	1.02	1.10
48	1.88	3.17	1.93	1.92	1.14	1.52	1.54	1.17	1.07	1.37

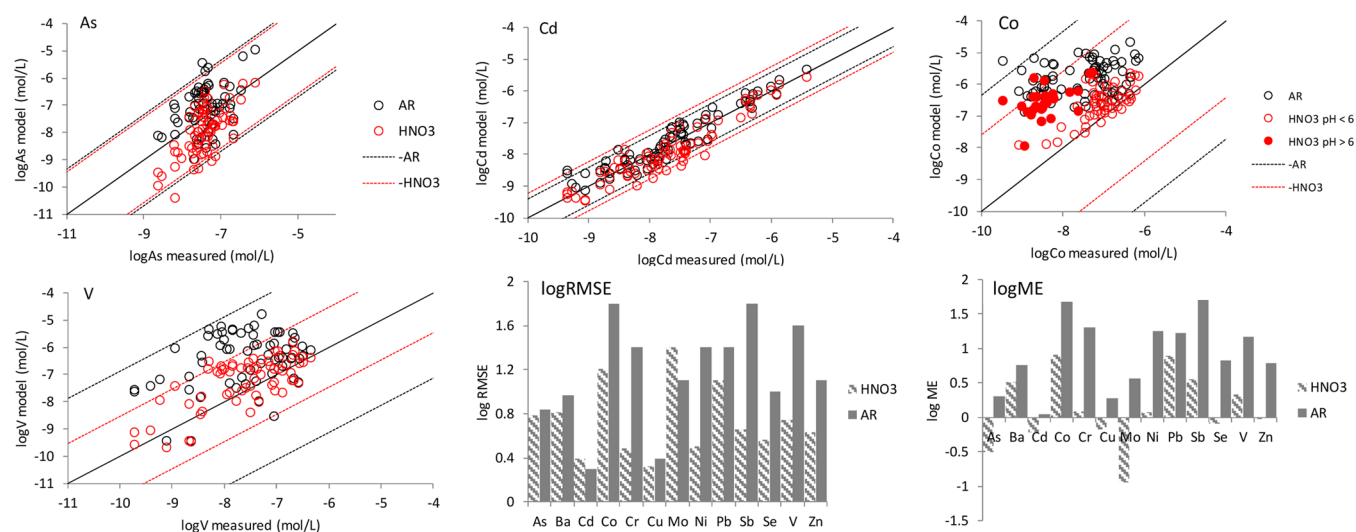


Figure 3. Assessment of modeled dissolved concentrations As, Cd, Co, and V in 0.01 M CaCl_2 -extracts against measured dissolved concentrations using either 0.43 M HNO_3 (red circles) or Aqua Regia (black circles) extracted metal as input to the geochemical model, dashed lines indicate $\pm 2 \times \log\text{RMSE}$ of the model calculations for AR (black) and 0.43 M HNO_3 (red) respectively. The $\log\text{RMSE}$ (bottom middle) and $\log\text{ME}$ (bottom right) of the modeled dissolved concentrations in the 0.01 M CaCl_2 extracts for all elements using either 0.43 M HNO_3 (red circles) or Aqua Regia (black circles) extracted metal as input to the model.

OM). Negligible differences were found between the 0.5 and 0.43 M HNO_3 extraction (Figure 2a).

Comparison of the 0.43 M HNO_3 Extraction with Other Methods. Statistical analysis of NA and 0.05 M EDTA extracted elements in data set NL1 shows strong correlation between methods with $r \geq 0.98$ for Cd, Cu, Zn, $r = 0.95$ for Pb and $r = 0.91$ for Ni and similar amounts extracted by both methods (Figure 2C). The NA-extraction appears to be somewhat stronger than EDTA for Cu, Pb, Ni, and Zn. The largest differences were found for Ni and Zn with strong variation in their ratios EDTA:NA (0.1–1.3) at $\text{pH} > 7$. Good correspondence between NA and EDTA for Cd, Cu, Pb, and Zn was also found by De Vries et al.⁴⁴ who found strong correlation between NA (1 h extraction) and 0.05 M Na_2EDTA (24 h extraction) extracted metal in 72 samples of Hungarian and Slovakian soils with a large range in metal concentration. The NA-extraction appeared to be somewhat weaker for Cd, Cu, and Pb (NA:EDTA = 0.8–0.9) but stronger for Zn (NA:EDTA = 1.3). Tipping et al.⁵ found very similar results for Cd, Cu, Pb, and Zn extracted with 0.1 M Na_2EDTA and NA (2 h equilibration) in 89 organic UK soils. Linear regression between the logarithm of concentrations extracted by both extractions had slopes not significantly different from one and intercepts not significantly different from zero. A few studies compared NA-extracted metal with that obtained by isotopic dilution. Results of Marzouk et al.⁴⁵ show that both methods compare well for Cd, Pb, and Zn in four acid to near neutral ($\text{pH} 3.5\text{--}6.4$) organic soils but show substantially larger values determined with NA in three calcareous soils for Cd (factor 2), Pb, and Zn (factor 5–15). Ren et al.⁴⁶ found comparable results for both methods for Cu in 9 soils ($4.8 \leq \text{pH} \leq 7.8$) and for Cd in 6 soils ($4.8 \leq \text{pH} \leq 6.64$), no Cd data were available for the higher pH soils because the Cd spike was too low to produce significant changes in isotopic ratios in the soil suspensions. Garforth et al.⁴⁷ found higher reactive metal determined with NA than by isotopic dilution, up to a factor three, for Cd, Cu, Ni, Pb, and Zn in four soils ($4.8 \leq \text{pH} \leq 7.4$). The results of these studies indicate that NA-extraction gives comparable results with isotopic dilution for Cu and for

Cd, Pb and Zn in acid to near neutral soils but may overestimate reactive Cd, Pb, and Zn in calcareous soils. The lower reactive concentration obtained by isotopic dilution may also be partly due to slow exchange between the isotopic spike and adsorbed metal,⁴⁶ while desorption is likely more rapid at low pH in 0.43 M HNO_3 .

Evaluation of Various Acid Extracts to Model Dissolved Metal Concentrations in CaCl_2 -extracts. *Aqua Regia and 0.43 M HNO_3 -Extraction.* Figure 3 shows the comparison between modeled and measured dissolved concentrations in 0.01 M CaCl_2 -extracts of As, Cd, Co, and V (see Figure S4 of the SI for the other elements) and model performance in terms of the Mean Error and Root Mean Square Error of the 10-log-transformed data (referred to as $\log\text{ME}$ and $\log\text{RMSE}$ respectively) for all elements using either AR or NA extracted element as model input. Model performance for Cd and Cu is about equal for both AR and NA. The most obvious differences in model performance are for Co, Ni, Pb, Zn, Co, Mo, Sb, Se, and V. For these elements, except Mo, the accuracy of the model calculations using NA is superior to those using AR as model input, based on both $\log\text{ME}$ and $\log\text{RMSE}$. Using AR results in considerable overprediction of dissolved Co, Ni, Pb, Zn, Sb, Se, and V ($0.6 < \log\text{ME} < 1.6$) whereas the calculations based on NA are closer to measurements ($-0.5 < \log\text{ME} < 0.5$) except for Co and Pb which are substantially overpredicted ($\log\text{ME} = 0.9$) but to a lesser extent compared with AR ($\log\text{ME} = 1.6$ and 1.2 respectively). The mismatch between modeled and measured Pb is likely due to limitations in the modeling of Pb binding to humics and Fe-oxides and binding of Pb to Mn-oxides not being included in the model.¹³ The substantial overprediction of dissolved Co (up to over 1 order of magnitude) is limited to samples with $\text{pH} > 6$ (Figure 3). Similarly dissolved Ni and Zn are substantially overpredicted for part of the samples with $\text{pH} > 6$. At neutral and more alkaline pH, Co, Ni, and Zn in soils may form mixed metal–aluminum hydroxide surface precipitates or double layered hydroxides (DLH).^{38–41} These precipitates are presumably at least partly dissolved by the NA-extract and are solubility-controlled but not geochemically

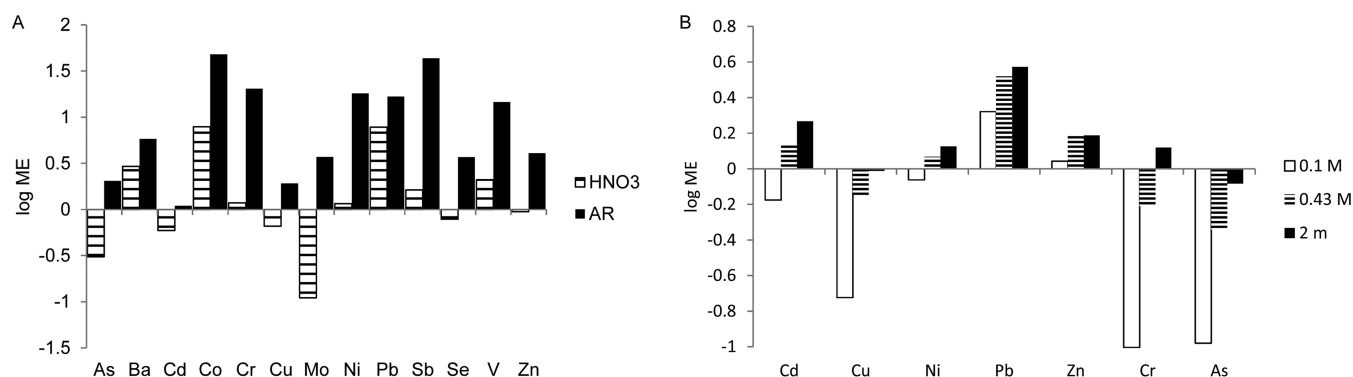


Figure 4. Log mean errors (log ME) of the modeled solution concentrations in the 0.01 M CaCl_2 -extracts using either 0.43 M HNO_3 or Aqua Regia extracted metal as input to the multisurface model (A, data sets NL1, NL2, and PRT) or various concentrations (0.1, 0.43, and 2 M) HNO_3 (B, data set NL1 only).

reactive under ambient conditions. Degryse et al. indeed established that Zn in such precipitates was not isotopically exchangeable.³⁸ Overprediction of dissolved Ni and Co is already observed at reactive concentrations as low as 0.1 mmol.kg^{-1} whereas dissolved Zn is overpredicted from 1 mmol.kg^{-1} onward. At these low concentrations, the presence of such precipitates is, however, less likely and overprediction may be due to overestimation of reactive Ni, Co, and Zn by (partial) dissolution of hydrous oxides together with elements entrained in these oxides.

Dissolved Mo is substantially underpredicted. This underprediction was also observed by Dijkstra et al.,²⁰ who therefore used the amount of Mo extracted at pH 10 as the reactive concentration, which substantially improved their model results. These findings indicate that NA is too weak to fully extract reactive Mo, which is in line with the modeled recovery of 40% (Figure 1). The good model performance for dissolved Cr based on NA ($\log\text{ME} = 0.07$) seems inconsistent with the extremely low recovery calculated using the same geochemical model. The generic NICA-Donnan parameters of Cr substantially overestimate the affinity for Cr to bind to humic substances.^{20,37} Due to the overestimated affinity the model calculates a substantial part of Cr to be bound to particulate organic matter, even at low pH ($\text{pH} = 0.9$) whereas Cr in solution is largely predicted to be present as free Cr^{3+} . At the higher pH of the CaCl_2 -extractions ($3.7 < \text{pH} < 7.3$) dissolved Cr is calculated to be largely present as Cr complexed with humic substances (>90%) and the solid solution partitioning of Cr in the CaCl_2 extracts is thus largely determined by the solid solution partitioning of organic matter. Model calculations of total dissolved Cr in these CaCl_2 extracts are therefore rather insensitive to the exact value of the model parameters.^{26,37}

Evaluation of the 0.1, 0.43, and 2 M HNO_3 Extraction. is limited to data set NL1 and the elements analyzed in these extracts, that is, Cd, Cu, Ni, Pb, Zn, Cr, and As. Model calculations based on 0.1 M HNO_3 lead to a clear underestimation of dissolved Cu, Cr, and As, that is, the elements with a high affinity for binding to SOM and/or Al/Fe-(hydr)oxides (Figure 4) and 0.1 M HNO_3 is therefore considered too weak to determine their reactive concentrations. Using 0.43 M HNO_3 the model adequately calculated dissolved concentrations of all elements ($-0.3 \leq \log\text{ME} \leq 0.3$) except Pb, and also resulted in lower logRMSE compared to 0.1 M HNO_3 . Differences between logME of the 0.43 and 2 M HNO_3 -extraction are small (0.03–0.26). Calculations using 0.43 M HNO_3 give somewhat better results for Cd, Ni, and Zn,

that is, the elements with relatively low affinity to bind to organic matter, whereas 2 M HNO_3 gives somewhat better results for Cu, which has a high affinity for organic matter, as well as for As with its high affinity for Al/Fe-(hydr)oxides.

Model performance using NA extracted reactive metal in relation to soil properties has been analyzed to get insight in specific causes of deviations, either being due to uncertainties in model inputs including the reactive metal or by specific limitations of the model. This analysis was performed by plotting the log transformed error ($\log[\text{Me}]_{\text{model}} - \log[\text{Me}]_{\text{measured}}$) against NA-extracted element, pH of the CaCl_2 -extract, SOM-, HFO- and clay content (Figure S5 of the SI). There are no specific trends in model performance in relation to soil properties for the elements Cd, Sb, Se, Ba, Pb, and V. Dissolved concentrations of both Cr and Cu are underpredicted at low pH ($\text{pH} < 5$). At higher pH, predicted Cr is too high whereas Cu is predicted well. The strongest underestimation of dissolved Cu and Cr is observed for samples with low reactive Cr or Cu ($\leq 1 \mu\text{mol.kg}^{-1}$) and/or high SOM contents (>10%). No such underprediction at low pH was observed for samples with manipulated pH in pH-static experiments.²⁰ This indicates that underprediction is due to incomplete recovery of reactive Cr and Cu by NA rather than to model limitations and agrees well with the low fraction reactive Cu (ratio NA:AR) at low Cu contents. Dissolved As is underpredicted at high pH, as was also found in pH-static experiments.²⁰ The deviation at high pH is therefore most likely due to limitations in the modeling of As, possibly related to inadequate description of competition with PO_4^{3-} and neglected competition with DOC.²⁰ Dissolved Mo is underpredicted at $\text{pH} < 6$. Strong underprediction is observed for samples below pH 5 together with high (>20%) SOM contents. Underprediction can be due to incomplete recovery of reactive Mo by NA as observed by Dijkstra et al.²⁰ In addition the underprediction at $\text{pH} < 5$ and high SOM can be due to overestimation of HFO, determined by oxalate because it also extracts Al and Fe bound to organic matter, which can be substantial in such samples.

Implications for the Use of the ISO Standard 0.43 M HNO_3 Extraction to Determine Reactive Elements in soil. Geochemical modeling of the NA-extraction shows that it quantitatively recovers (>90%) reactive elements when equilibrium conditions are met. However, at low reactive element to organic matter ratios reactive concentrations of elements with a particularly high affinity for organic matter, such as Cu, V, and Cr, may be underestimated. This may lead

to underestimation of reactive concentrations of micronutrients in the low concentration range at which they can be deficient for biota. The results of this study indicate that underestimation of reactive metal is unlikely at higher, possibly toxic, concentrations for all considered elements except Mo. A potential limitation of the method maybe overestimation of the reactive concentration by dissolution of hydrous oxides. Although this potential effect should be taken into consideration we observed it only for Co, Ni, and Zn in near neutral and higher pH soils (Figure 3 and SI Figure S4). Similarly the dissolution of carbonates may lead to the overestimation of the reactive concentration. Although our evaluation does not include calcareous soils, studies in which reactive concentrations were determined by isotopic dilution indicate overestimation of reactive Cd, Zn, and Pb in calcareous soils by NA-extraction. Both potential limitations of the NA-extraction discussed above will not lead to underestimation of environmental risks for metal cations. For those assessments that conclude unacceptable risk based on the NA-extraction, a more accurate assessment (e.g., isotopic dilution) can be used in a next tier.

The NA appears to be too weak to extract reactive Mo and also As in soils in which substantial amounts of amorphous iron are not dissolved by NA. Since the concentrations of these elements in our samples are low, we recommend to further investigate the performance of the NA-extraction using samples with higher (contaminated) levels of these elements, and to explore whether alkaline solutions are more adequate to extract reactive oxy-anion element concentrations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05151.

Information on soil characteristics, metal contents, and details on the 0.43 M HNO₃-extraction of the three data sets; model parameters of the geochemical model; additional figures as referenced in the main text (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone +31 624787354; e-mail bertjan.groenenberg@wur.nl.

ORCID

Jan E. Groenenberg: 0000-0002-3227-4052

Notes

The authors declare no competing financial interest.

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