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4

## Organic complexation of Al and Fe in acidic soil solutions: A comparison of DGT analyses with Model V and VI predictions\*

### Abstract

The last decade has seen important development of analytical and modeling tools to investigate the interactions in solution between metals and dissolved organic matter. We evaluated the internal consistency of the analytical method of diffusive gradients in thin films (DGT) and the speciation models Model V and Model VI for investigating organic complexation of Al and Fe in acidic sandy soil solutions. For this purpose we used our dataset obtained by DGT of the speciation of Al and Fe(III) between dissolved inorganic metal and soluble metal-DOM complexes in acidic soil solutions at pH = 3.5, 4.0 and 4.5 and different imposed metal/organic carbon (M/C) ratios in solution. We modeled this dataset with Model V and VI, using the default parameter values but optimizing the fraction of DOM that is inert with respect to metal binding (24%). The calculated speciation of Al by both Model V and VI was generally in good agreement with the DGT results. However, at low Al/C ratios the Al fraction measured by DGT was higher than the dissolved inorganic fraction calculated by the models, most likely due to the detection of small (<1000 Da), labile Al-DOM complexes by DGT. This discrepancy did not occur with Fe(III) probably because its complexes with DOM are not labile enough to be detected by DGT. The dissolved, inorganic Fe fractions calculated by Model V were in good agreement with the DGT results, especially considering the fact that extra uncertainty was introduced by the analytically determined Fe(II)/Fe(III) speciation in solution. Model VI calculated the trends in Fe binding well, but generally estimated a higher dissolved, inorganic Fe fraction than Model V and DGT. The Fe(III) binding constant in Model VI was recently modified to reflect stronger binding to DOM. Since both Model V and VI predicted the inorganic Fe in solution to consist mainly of Fe(II), we propose a similar critical evaluation of the Fe(II) binding constant in Model VI.

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## 4.1 Introduction

The complexation of Al and Fe with dissolved organic matter (DOM) in soil solutions is of great scientific interest because of its influence on the mobility of both metals through the soil column, which in turn affects such processes as pedogenesis and acidification (McBride, 1994). In addition, organic complexation of Al may alleviate toxicity for plants and soil organisms (Ma et al., 2001).

Interactions of Al and Fe with DOM are of special relevance for acidic, sandy soils where relatively high metal concentrations have been reported (Aran et al., 2001; Buurman, 1984; Petersen, 1976). The impetus for further research on Al- and Fe-DOM interactions in this type of system is given amongst others by the continued scientific debate about the mechanisms involved in podzolization. For instance, there is no consensus about the mechanisms responsible for the transport and accumulation at depth of Al, Fe and DOM in sandy soils (Farmer and Lumsdon, 2001; Gustafsson et al., 2001; Lundström et al., 2000; Mossin et al., 2002).

Because of the importance of metal-DOM interactions, a number of new analytical chemical techniques has been developed over the last decade (Tipping, 2002). Contemporary methods used for this purpose include equilibrium dialysis (Jansen et al., 2001), the quickly reaction Al method (Clarke and Danielsson, 1995) and the donnan-membrane technique (Temminghoff et al., 2000). Disadvantages of these methods include the amount of time needed per analysis in the donnan-membrane technique and equilibrium dialysis ( $\geq 48$  hours), and the impossibility to apply the quickly reacting Al method and to speciate Fe simultaneously. A promising alternative is the analytical method diffusive gradients in thin films (DGT), which can be used for simultaneous speciation of Al and Fe overnight (Jansen et al., 2001). DGT is based on the principle of diffusion of hydrated metal cations, as well as dissolved inorganic complexes and small, labile, organic complexes through a diffusion gel of known thickness, followed by immobilization on an chelating resin. The resin is subsequently removed and the metals are extracted by acid and detected (Zhang and Davison, 1995).

In addition to the development of analytical tools, considerable progress has been made with respect to the mathematical modeling of metal speciation in soils and water (Tipping, 2002). This has resulted amongst others in the development of Model V, which was recently succeeded by Model VI (Tipping, 1994; Tipping, 1998). Models V and VI are deterministic models, capable of predicting metal binding to organic matter taking into account multidentate binding, as well as site heterogeneity (Tipping, 1994; Tipping, 1998).

Both DGT and Models V and VI have been successfully used in several studies of the interactions of Al, Fe and DOM in acidic soil solutions (De Wit et al., 2001; Jansen et al., 2002; Jansen et al., 2003b; Lofts et al., 2001). However, so far little work has been done to compare analytical Al and Fe speciation data obtained using DGT with predictions by Model V and VI. Such an approach would allow for testing of the internal consistency of both methods and be helpful to further investigate their strengths and weaknesses. Ultimately this may lead to more insight in the interactions of Al, Fe and DOM.

The goal of this study was to evaluate the internal consistency of a combination of DGT and the speciation models Model V and VI for investigating organic complexation of Al and Fe in acidic sandy soil solutions and to gain more insight into the mechanisms involved in such complexation. We accomplished this by comparing Model V and VI calculations of the dissolved, inorganic Al and Fe fractions with DGT data obtained using soil extracts from the Oh horizon of a podzolic soil.

## 4.2 Materials and methods

### 4.2.1. Metal-DOM addition experiments

The dataset used in this study was obtained in a previous study and is described in detail elsewhere (Jansen et al., 2002). In short, we used a water extraction of the Oh horizon of a Fimic Anthrosol (FAO, 1988) to obtain a DOM solution. We divided this over three aliquots that we brought to pH = 3.5, pH = 4.0 and pH = 4.5, respectively. To each of these we added increasing amounts of  $\text{Al}(\text{NO}_3)_3$  or  $\text{Fe}(\text{NO}_3)_3$  stock solutions to obtain different metal to carbon (M/C)

ratios, adjusting the pH after each addition to keep it constant during the experiments. In order to prevent microbial degradation of the DOM and to maintain a constant background ionic strength during the experiments, we added sodium azide ( $\text{NaN}_3$ ) to obtain a final concentration of 0.01 M. The resulting relatively high ionic strength also prevented potential problems with DGT that have been reported to occur at very low solution ionic strengths (Alfaro-De la Torre et al., 2000). After each metal addition and subsequent pH adjustment, the solutions were shaken for 24 hours to allow for equilibrium to be reached (Yates and Von Wandruszka, 1999) after which they were sampled. In the samples, total concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , P and S were determined on a Perkin-Elmer Optima 3000XL ICP-OES. In addition, total concentrations of DOC were determined on a Skalar continuous flow automated analyzer and the Fe(II)/Fe(III) speciation was determined using 1,10-phenantroline in a colorimetric procedure (Begheijn, 1979). After sampling, DGT units were deployed in solution for 16 hours and the DGT concentrations of Al and total Fe (FeT) were determined. The experiments were conducted in triplicate.

#### 4.2.2 DGT

DGT can be used for speciation of dissolved metals in both water and soils at the  $\mu\text{M}$  level or below (Zhang and Davison, 1995; Zhang et al., 1998). Metal concentrations ( $C$ ) as estimated by DGT, are calculated using equations 1 and 2:

$$M = C_e(V_{\text{HNO}_3} + V_{\text{gel}})/f_e \quad (1)$$

$$C = M\Delta g/(DtA) \quad (2)$$

$M$ , the metal mass captured on the chelating resin, is calculated from the metal concentration in the elution sample ( $C_e$ ), the volume of the elution fluid ( $V_{\text{HNO}_3}$ ) and the volume of the chelating resin ( $V_{\text{gel}}$ ). In addition, an elution factor ( $f_e$ ) of 0.8 is needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From  $M$ , the DGT metal concentration is calculated by taking into account the thickness of the diffusion gel layer ( $\Delta g$ ), the diffusion coefficient

of the metals in the hydrogel (D), the deployment time (t) and the area of exposure to the sample solution (A).

In principle, a variety of hydrogels can be used in DGT analyses. We used the common APA hydrogel supplied by the manufacturer of DGT (DGT Research Ltd, UK). The diffusion coefficients in the APA hydrogel are similar to those in water, but vary slightly depending on the cross-linker used during the manufacturing of the hydrogel (Li and Gregory, 1974; Zhang and Davison, 1999). Accurate diffusion coefficients were supplied by the manufacturer.

The diffusion rate of larger organic complexes through the APA hydrogel is slow enough to appreciably limit diffusion, but small metal-DOM complexes are able to penetrate the hydrogel (Zhang and Davison, 1999). Small organic complexes that are labile enough for the metal ion to be liberated from the organic ligand and bind to the chelating resin, will be included in the DGT metal fraction. Therefore, in addition to hydrated metal cations and soluble (labile) inorganic metal complexes, DGT in combination with the APA hydrogel measures a portion of the smaller labile organic complexes. However, because DGT concentrations are calculated based on free metal diffusion coefficients, the concentrations of labile complexes measured by DGT will increasingly be underestimated with increasing molecular size and thus decreasing diffusion rates through the APA hydrogel (Zhang and Davison, 2000). Previously, we compared the results obtained with DGT in acidic forest soil solutions to those obtained with equilibrium dialysis using a membrane with a 1000 Da molecular weight cut-off (Jansen et al., 2001). We found no significant differences between the two methods in the measured dissolved inorganic Al and Fe(III) concentrations, indicating that the detection of Al/Fe-DOM complexes as dissolved inorganic metal by DGT, if happening at all, is limited to those complexes smaller than approximately 1000 Da. Nevertheless, the incomplete distinction between actual dissolved inorganic metals and small metal-DOM complexes represents a drawback of the DGT method for this application. Recently, a more restricted hydrogel was developed to resolve this problem (Zhang and Davison, 1999). However, even with this gel the separation cannot be perfect because complexes smaller than 1 nM are still able to diffuse through the gel at high enough rates to

reach the chelating resin and be detected as dissolved inorganic metal if labile enough (Zhang and Davison, 1999). Another disadvantage of DGT for laboratory studies is the relatively large minimum volume of sample solution needed (approximately 500 ml) as the bulk dissolved inorganic metal concentrations must remain large compared to the amount of metals immobilized on the chelating resin.

#### *4.2.3 Model V and VI*

Model V and VI are described and compared in detail elsewhere (Tipping, 1994; Tipping, 1998). Therefore, we only give a short highlight of the main features. Model V and VI are discrete site/electrostatic models of the interactions of protons, metals and their first hydrolysis products with fulvic and humic acids. Both models have been incorporated in a water and soil version called WHAM-W and WHAM-S respectively (Tipping, 2002). The water version consists of Model V or VI, combined with a full inorganic speciation model. In addition, the soil version includes a surface complexation model (Tipping, 2002). Since our experiments were carried out in solution, we used the WHAM-W versions of Model V and VI to model our data.

Both Model V and VI contain a maximum of six adjustable parameters. In our model applications we used published default parameter values, previously obtained by model fitting to several datasets (Tipping, 1998). In a recent study, Tipping et al. (Tipping et al., 2002) showed that new Al and Fe(III) data in freshwaters can be modeled adequately using Model VI and default model parameters, only optimizing the percentage of dissolved organic carbon (DOC) that actively partakes in metal binding.

There is a number of differences between Model V and VI. In both models proton dissociation is represented by 8 groups of different acid strengths. In Model V, the strength of binding of a metal to the different acidic groups is positively correlated to that for protons, whereas this is no longer the case in Model VI. Another difference is that Model VI takes into account a small number of high affinity sites, normally expected to be filled up in natural samples but thought to be important for the binding of trace metals (Tipping, 1998). Finally,

Model VI allows for a percentage of the binding sites to be involved in tridentate binding, in addition to permitting monodentate and bidentate binding. Model V allows for monodentate and bidentate binding only (Tipping, 1998). As a result of the differences, the metal binding constants are defined in a different way in Model VI than in Model V.

The main advantage of Models V and VI in addition to being two of the very few comprehensive metal-organic matter binding models, is the fact that they are discrete site models and it is reasonable to assume that the parameters in the model represent real physical entities (Tipping, 2002).

#### *4.2.4 Modeling and data analysis*

As input for the models we used the measured total concentrations in solution, both initially and after each metal addition, of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . For  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$  we used the initial concentrations in all cases, since the concentrations of these solutes were not determined during the experiments, as significant changes in their concentrations over the course of the experiments were not expected. Because  $\text{N}_3^-$  is not included as an input species in Model V and VI, we replaced it with an equal concentration of  $\text{NO}_3^-$  as we expected similar binding behavior to metals and organic matter for these two monovalent nitrogen anions. Similar to  $\text{Na}^+$  we used the initial concentrations for  $\text{N}_3^-$  for all data points. The concentration of  $\text{K}^+$  was not determined over the course of the experiments. However, since  $\text{K}^+$  will only bind weakly to DOM as compared to Al and Fe and was presumably present in much lower concentrations than  $\text{Na}^+$ , we did not include  $\text{K}^+$  in our model calculations as we did not expect a significant influence of its presence on the speciation of Al and Fe. The concentrations of  $\text{SO}_4^{2-}$  were based on the concentrations of total S as determined by ICP-OES. Probably this resulted in a slight overestimation, as some of the total S is represented by dissolved organic sulphur. However, sensitivity analyses showed that even a decrease of the  $\text{SO}_4^{2-}$  input concentrations by two orders of magnitude does not have a significant effect on the model output. All DOM was assumed to be present in the form of Fulvic Acid (FA). This variable, which has to be given in g/l of FA, was calculated using the DOC concentrations over the

course of the experiments and assuming 50% of the weight of FA to represent organic carbon (Tipping, 2002). In both Model V and VI we used the default parameter values provided with the model, except for the binding constant for Fe(III) to FA in Model VI where we used the optimized value derived in a recent study by Tipping et al. (2002) ( $\log K_{MA} = 2.6$ ).

We calculated the DGT Al and Fe fraction by dividing the measured DGT metal mass in solution by the total molar metal mass in solution. Similarly, we calculated the modeled dissolved inorganic Al and Fe fraction from the inorganic metal concentrations calculated by Model V and Model VI. Since DGT cannot distinguish between Fe(II) and Fe(III), we only determined the DGT total Fe (FeT) fraction. However, we did use the measured total Fe(II) and Fe(III) concentrations as input variables in Model V and VI and calculated the dissolved inorganic FeT fraction as the sum of the modeled dissolved inorganic Fe(II) and Fe(III) fractions. This allowed the models to take into account differences in binding strength between Fe(II) and Fe(III).

We compared the DGT metal fractions with the dissolved inorganic metal fractions calculated by both models using both correlation and linear regression analyses of the entire dataset for Al and Fe. As the number of observations was greater than 30 in all cases, we assumed that the observations were normally distributed and therefore used parametric statistical tests. We used a confidence interval of 0.05.

Previous modeling studies using Model V and VI (Lofts et al., 2001; Tipping et al., 2002) suggest that a considerable fraction of the DOC in surface waters and soil solutions consists of inert material with respect to metal binding. Therefore, we optimized the model data by changing the percentage of inert DOC to obtain a maximum  $r^2$  value for both the correlations and regression.

### 4.3 Results and discussion

In Table 1 we presented the total concentrations of DOC, Al, Fe(II) and Fe(III) in solution over the course of the experiments. For further details we refer to Jansen et al. (2002).

*Comparison of DGT analyses with Model V and VI predictions*

Table 1

Average total concentrations of Al, Fe(II), Fe(III) and DOC over the course of the Al and Fe addition experiments (metals in  $\mu\text{mol/l}$ , DOC in  $\mu\text{mol C/l}$ )

pH		Step								
		1	2	3	4	5	6	7	8	9 <sup>a</sup>
Al										
3.5	Al	20.1	21.6	23.3	35.1	69.6	80.9	145.8	325.3	
	DOC	3340	3549	3403	3356	3419	3508	3042	2357	
4.0	Al	19.7	21.5	23.1	35.7	67.7	79.9	103.0	251.3	
	DOC	3729	3711	3602	3651	3500	3565	2620	1723	
4.5	Al	19.7	21.2	23.1	36.0	68.2	79.5	86.6	98.1	
	DOC	3656	3699	3666	3612	3530	3574	2543	997	
Fe										
3.5	Fe(II)	4.2	4.8	4.5	5.5	9.6	11.7	16.6	32.6	0.0
	Fe(III)	4.8	4.0	4.4	6.3	10.0	14.1	22.7	30.6	98.7
	DOC	3486	3618	3547	3571	3581	3597	3552	2880	378
4.0	Fe(II)	3.6	3.5	3.3	3.7	14.8	7.7	14.9	39.1	0.0
	Fe(III)	4.8	5.3	5.9	8.9	7.9	19.1	32.3	39.9	50.8
	DOC	3448	3632	3594	3461	3422	3484	3465	2873	380
4.5	Fe(II)	2.6	2.1	2.6	3.3	8.9	5.6	17.2	42.0	0.0
	Fe(III)	5.6	6.5	6.3	9.1	13.3	20.8	28.1	35.5	36.6
	DOC	3528	3744	3720	3641	3528	3490	3532	3135	505

<sup>a</sup> Not performed due to problems with DGT (Jansen et al., 2002).

#### 4.3.1 Modeling 'free' Al

In Fig. 1 we plotted DGT Al as a fraction of total Al in solution against the Al/DOC ratio in solution. In addition, the non-optimized and optimized model results obtained by Model V and VI are provided. The best fit of the data for Al alone was obtained by assuming 21% of the DOM to be inert. However, when the Fe data was considered simultaneously, an overall optimization for both metals was obtained assuming 24% of the DOM to be inert. This value is of the same order of magnitude as the 30% inert DOM reported by Tipping et al. in their study of Al and Fe(III) binding to DOM in freshwaters (Tipping et al., 2002). The regression lines corresponding with the non-optimized and optimized model V

and model VI runs are presented in Fig. 2. The  $r^2$  values for both the linear regression and correlation are provided in Table 2.

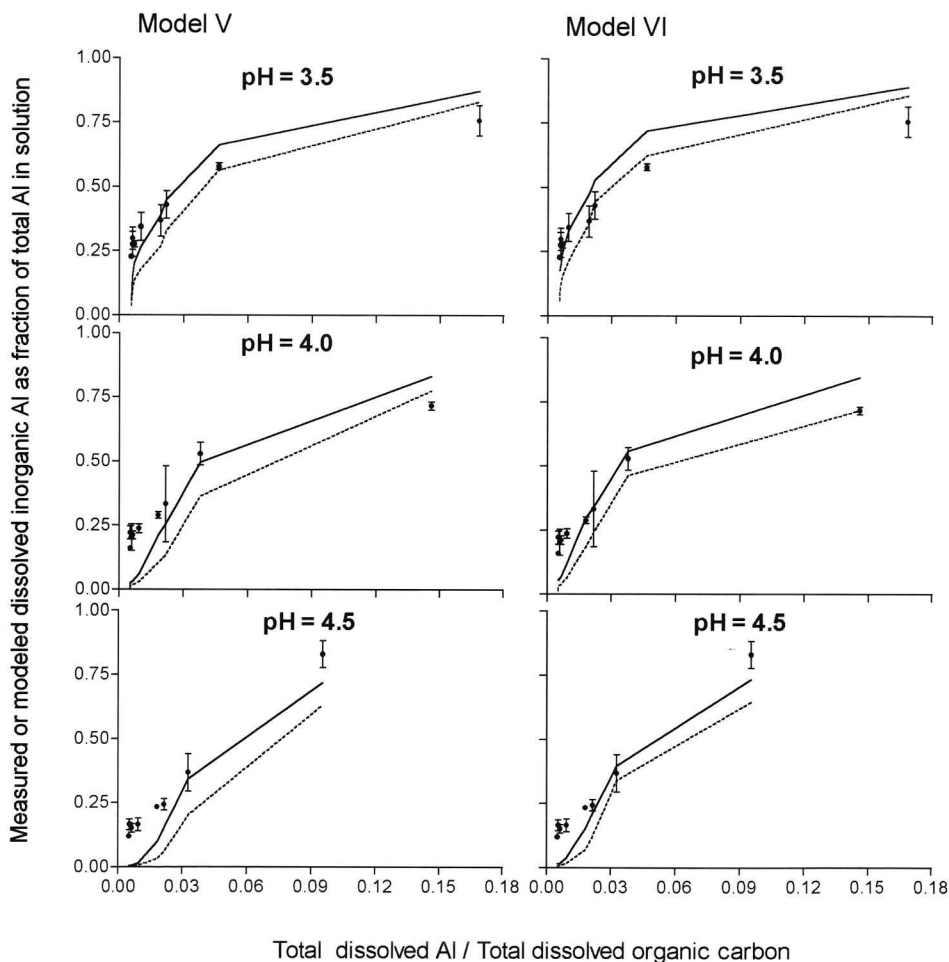


Fig. 1. Comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Al fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

It is clear from Fig. 1 that both Model V and VI are able to fit the DGT data reasonably well. Overall the predicted values by Model VI are somewhat higher than those by Model V, but the differences are only small. Recall that one of the main differences between Model V and VI is the presence of a small number of

sites with high binding affinity. The affinity of  $\text{Al}^{3+}$  for these sites is modified in the model by the distribution term  $\Delta\text{LK}_2$ , which is only small for Al (Tipping, 1998). Therefore, the similarities between the two models are in line with expectations.

Table 2  
 $r^2$  values for the linear regression and correlation between the DGT data and the Model V and VI results for Al and Fe.

	Model V Al	Model VI Al	Model V Fe	Model VI Fe
$r^2$ correlation non-optimized	0.9088	0.9267	0.8059	0.8650
$r^2$ correlation optimized	0.9288	0.9127	0.8258	0.8764
$r^2$ regression non-optimized	0.9034	0.9157	0.7987	0.8631
$r^2$ regression optimized	0.9247	0.9089	0.8207	0.8744

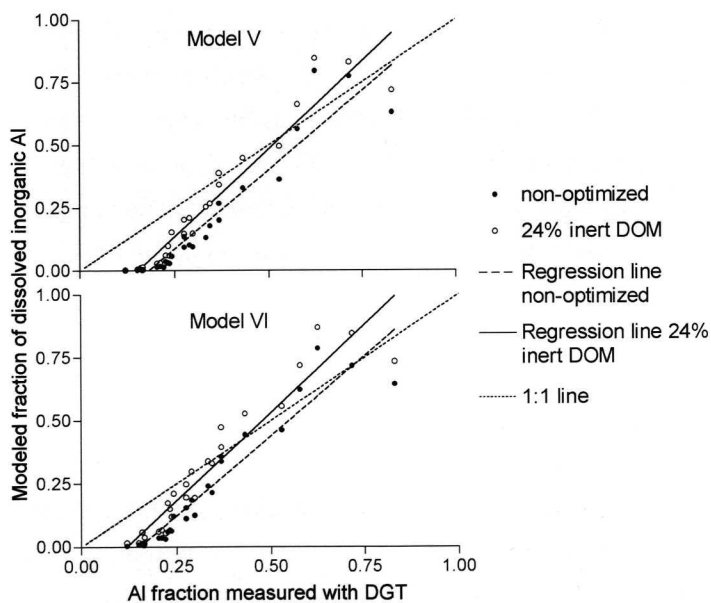


Fig. 2. Regression lines plotting the dissolved inorganic Al fraction calculated by Model V and Model VI against the Al fraction measured with DGT, using the non-optimized and the optimized models.

Even though the  $r^2$  values in Table 2 are indicative of a strong correlation between the Model predictions and DGT measurements, the regression lines

shown in Fig. 2 clearly deviate from the ideal 1:1 line, in slope as well as in absolute values. This is caused by a systematically lower predicted 'free' Al fraction at lower Al/C ratios than found by DGT. A plausible explanation for the discrepancy is an overestimation by DGT caused by the earlier mentioned penetration of small Al-DOM complexes through the diffusion gel and their subsequent detection as 'free' Al. Such complexes would have to be very small (< 1000 Da) (Jansen et al., 2001). Therefore, even if their functional group density is higher than on larger molecules, due to their limited size it is not unreasonable to expect their absolute number of functional groups to be relatively small. Consequently, they would be amongst the first to become saturated with Al and precipitate out of solution. As a consequence, at higher Al/C ratios in solution where precipitation of Al-DOM complexes starts to play a role, the overestimation of 'free' Al by DGT if caused by detection of very small Al-DOM complexes should diminish. The Al/C ratio that marks the onset of precipitation of Al-DOM complexes is approximately 0.03 (Nierop et al., 2002), which corresponds well with the point where the overestimation of DGT vanishes (Fig. 1). Another explanation for the overestimation of 'free' Al by DGT could be a shift in the complexation equilibrium towards decomplexation of Al from soluble complexes as a result of Al being removed from solution and immobilized in the DGT units. However, due to the relatively large solution volume used (750 ml) and the relatively short deployment time of the DGT units, this is unlikely.

#### *4.3.2 Modeling 'free' Fe*

DGT Fe as a fraction of total Fe in solution, as well as the model results obtained by non-optimized and optimized Model V and VI runs are presented in Fig. 3. For reasons of clarity separate graphs of the first few points were also plotted in Fig. 4. The best fit of the data for Fe alone could be obtained by assuming 30% of the DOM to be inert. However, again when both the Fe and Al data were considered an overall optimal fit for both metals was obtained by assuming 24% of the DOM to be inert. The regression lines corresponding with the non-optimized and optimized runs with model V and VI are presented in

Fig. 5. The  $r^2$  values for both the linear regression and correlation are again provided in Table 2.

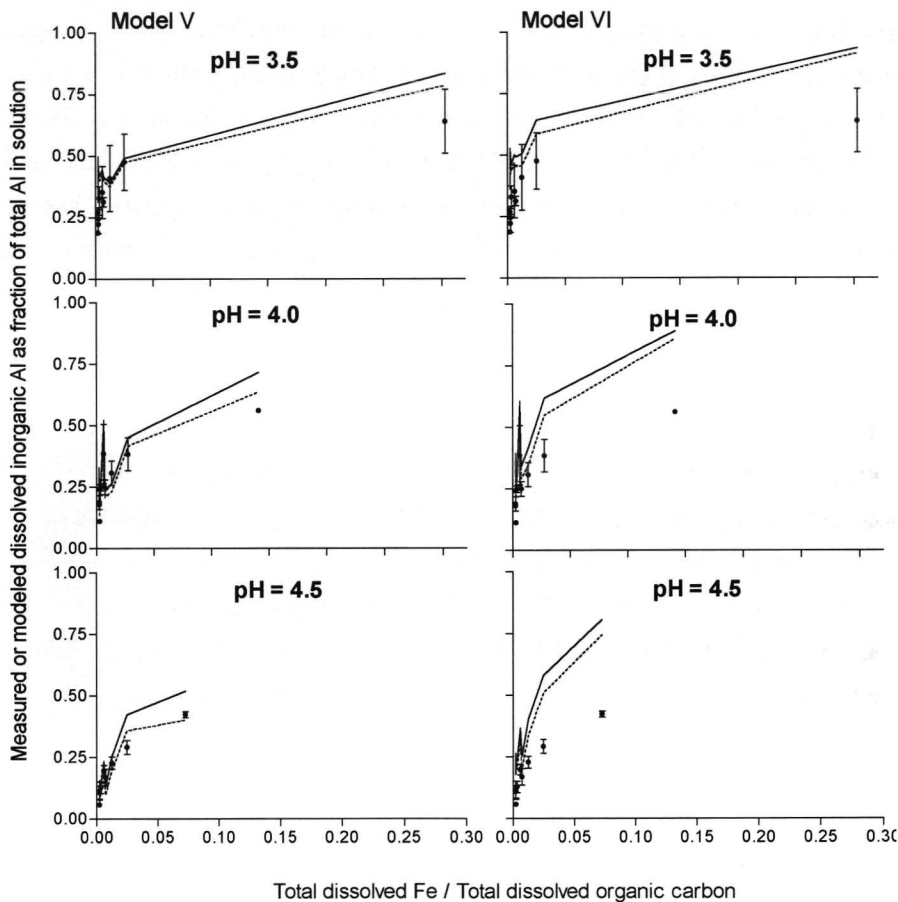


Fig. 3. Comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Fe fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

The  $r^2$  values for the regression and correlation using Model V and VI are lower for FeT than for Al. Yet they are remarkably high when one considers the fact that the modeled dissolved inorganic FeT fractions were based upon the sum of Fe(II) and Fe(III) binding. This introduces more uncertainty in the modeling results, as

two binding constants with their inherent uncertainty need to be used instead of one in the case of Al. In addition, the experimental speciation of Fe into total Fe(II) and Fe(III) concentrations, which are used as input for the model, introduces extra uncertainty in the model calculations. Both Model V and VI predict the majority of the Fe bound in DOM complexes to be present in the form of Fe(III) while Fe(II) dominates in the dissolved inorganic Fe fraction. This is in good agreement with the fact that in a previous study we found extensive complexation with DOM in experiments where Fe(III) was added, but only moderate complexation in experiments where Fe(II) was added (Jansen et al., 2002).

Table 3

Predicted 'free' Fe(II) and Fe(III) as fraction of total Fe(II) or Fe(III) in solution by Model V and VI for the optimal fit (24% inert DOM).

Step:	Model V						Model VI					
	pH = 3.5		pH = 4.0		pH = 4.5		pH = 3.5		pH = 4.0		pH = 4.5	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
0	0.86	0.000	0.64	0.000	0.36	0.000	0.92	0.04	0.85	0.03	0.73	0.02
1	0.91	0.001	0.77	0.000	0.50	0.000	0.94	0.04	0.93	0.03	0.91	0.03
2	0.91	0.001	0.74	0.000	0.48	0.000	0.94	0.03	0.92	0.03	0.90	0.02
3	0.91	0.001	0.76	0.000	0.49	0.000	0.94	0.03	0.92	0.03	0.91	0.03
4	0.91	0.001	0.77	0.000	0.49	0.000	0.94	0.05	0.93	0.05	0.92	0.05
5	0.90	0.001	0.80	0.000	0.59	0.000	0.94	0.08	0.93	0.06	0.92	0.06
6	0.92	0.001	0.81	0.001	0.61	0.000	0.95	0.12	0.94	0.11	0.93	0.11
7	0.92	0.002	0.83	0.001	0.67	0.001	0.96	0.18	0.95	0.17	0.94	0.19
8	0.95	0.005	0.91	0.006	0.78	0.002	0.97	0.30	0.96	0.28	0.96	0.30
9	0.00	0.835	0.00	0.716	0.00	0.519	0.00	0.93	0.00	0.92	0.00	0.91

The calculated regression lines are presented in Fig. 5. For both Model V and VI the slopes of the regression lines are very close to that of the 1:1 line. This suggests that contrary to Al there is no systematic difference between the DGT Fe fraction and the modeled dissolved inorganic Fe fraction in a specific Fe/C range. Fe(III) binds much stronger to DOM than Al, as evidenced amongst others by the very limited influence of proton competition on the binding to DOM even at pH values as low as 3.5 (Jansen et al., 2002). In all likelihood, contrary to Al,

complexes of  $\text{Fe}^{3+}$  with DOM are not labile enough for significant dissociation to occur in the DGT diffusion gel layer.

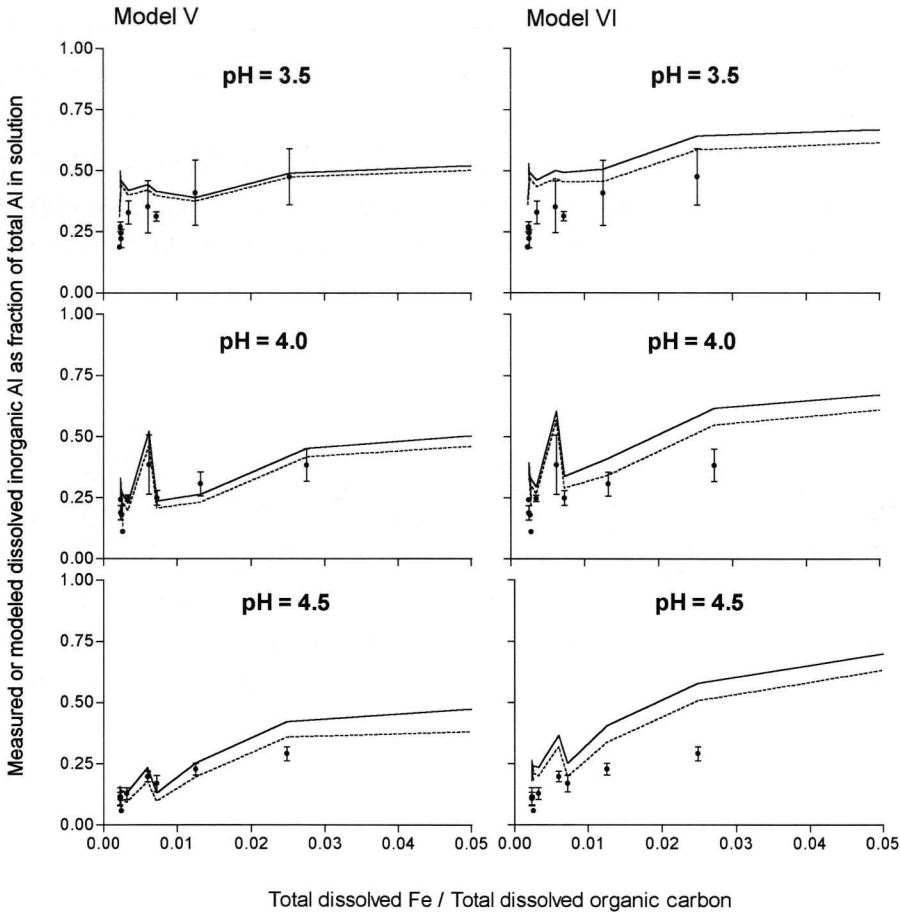


Fig. 4. A detailed representation of a comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Fe fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

In their study of the binding of Al and Fe(III) to DOM, Tipping et al. (Tipping et al., 2002) conclude that in the pH range of 4 – 9, Fe(III) will predominantly be bound as  $\text{FeOH}^{2+}$ . Model V and VI allow for binding of the first hydrolysis products of metals, using the same metal-DOM binding constants as for the free

metal cations (Tipping, 1998; Tipping et al., 1995). Therefore, Model V and VI will predict the same degree of complexation for Fe(III), regardless of whether it be bound in the form of  $\text{Fe}^{3+}$  or  $\text{FeOH}^{2+}$ . However, due to the lower net charge per molecule, we expect  $\text{FeOH}^{2+}$  to form complexes with DOM that are more labile than those of  $\text{Fe}^{3+}$ . Accordingly, if Fe(III) were predominantly bound to DOM in the form of  $\text{FeOH}^{2+}$ , analogous to Al one would expect a higher measured Fe fraction by DGT at lower Fe/C ratios than predicted by the models. Consequently, the lack of a systematic difference at a particular range of Fe/C ratios between the DGT Fe fraction and dissolved inorganic Fe fraction calculated by Model V and VI, leads us to believe that whereas Fe(III) not bound to DOM may have been predominantly present in solution in the form of  $\text{FeOH}^{2+}$ , Fe(III) bound to DOM occurred mostly in the form of  $\text{Fe}^{3+}$ .

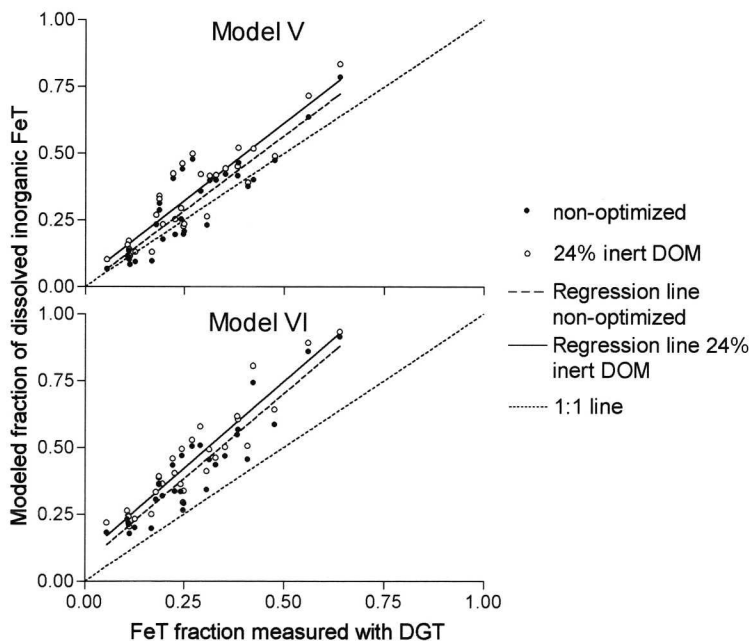


Fig. 5. Regression lines plotting the dissolved inorganic Fe fraction calculated by Model V and Model VI against the Fe fraction measured with DGT, using the non-optimized and the optimized models.

In addition, the lack of a systematic differences between DGT and Model V and VI at a particular range of Fe/C ratios, further strengthens our believe that the differences between the DGT Al fraction and calculated 'free' Al by Model V and VI at lower Al/C ratios was not caused by modeling uncertainty or a shift in the complexation equilibrium due to the removal of Al from solution by the DGT units. If that were the case, one would expect similar differences between the measured and modeled Fe fraction at lower Fe/C ratios.

While the slopes of the regression lines for both the Model V and VI predictions were very close the 1:1 line (Fig. 5), in the entire range of Fe/C ratios examined in the experiments, the dissolved inorganic FeT fraction computed by Model VI was significantly greater than the fraction measured by DGT. Surprisingly, we observed no such discrepancy between the Model V calculations and the DGT results.

As stated earlier, due to the differences in calculating metal binding to DOM, Model V and VI use different binding constants for metal binding to DOM. Because both Model V and VI calculations suggest that the majority of Fe(III) is bound to DOM (Table 3), the difference between the calculated 'free' FeT fractions are for a large part the result of differences in the binding constants of Fe<sup>2+</sup> between the two models. In addition, even with the modified Fe(III) binding constant according to Tipping et al. (2002) the modeled binding of Fe(III) to DOM by Model VI was lower than that by Model V. This further increased the differences in the results between both models. Contrary to Fe(III) the default binding constant of Fe(II) in Model VI has not yet undergone a critical evaluation. More extensive experiments using DGT may be useful for this purpose.

Despite the systematic discrepancy between the dissolved inorganic FeT fraction calculated by Model VI and the FeT fraction calculated by Model V and measured by DGT, it is promising that the trends in the organic FeT speciation are predicted so well. An example of the close correspondence of trends predicted by both models and DGT measurements, is the peak in the measured and modeled FeT fraction after the third metal addition in the cases of pH = 4.0 and 4.5 (Fig. 4). At the point of the peak, there was a higher fraction of total Fe in solution (both inorganic Fe and Fe-DOM complexes) present as Fe(II) than in the

preceding and following points (Jansen et al., 2002). The causes for this temporary shift in the total Fe(II)/Fe(III) ratio in solution are unclear. A possible cause is contamination of the Fe(III) stock solution used for the addition of Fe in this particular point with Fe(II). The same stock solution was used for all three replicates, explaining the occurrence of the peak in all replicates. Subsequent metal additions were done using a different stock solution. The addition of higher concentrations of a fresh, non-contaminated Fe(III) stock solution, explains the disappearance of the peak in the following points. Since Fe(II) binds more weakly to DOM than Fe(III), it is not surprising to find a higher 'free' FeT fraction in the point where the peak occurred (Jansen et al., 2002). Because DGT only measures FeT, the fact that the trend of the peak in the dissolved inorganic FeT was calculated well by both Model V and VI, indicates that it was not experimental error in the Fe(II)/Fe(III) determinations that caused it.

The fact that a combination of DGT with Model V and VI can predict the trends so well, seems to make it well suited to further examine Fe(II)/Fe(III) - DOM interactions in soil solutions. It would be even better if Model V or VI were capable of calculating redox equilibria, as this would make analytical determination of the Fe(II)/Fe(III) speciation unnecessary.

In a recent study Gimpel et al. (2003) compared DGT analyses of Fe in lakewater with predictions by Model V, using default model parameters and assuming 20% of the DOM to be inert to metal binding. Generally, they found reasonable agreement between the model calculations and the DGT results, but could not exactly reproduce them. They suggest that the binding constant for Fe<sup>3+</sup> to FA in Model V may be too high. This is in apparent contradiction with the good agreement between DGT results and Model V predictions found by us while using the default binding constant for Fe<sup>3+</sup>. However, instead of the acidic soil solutions considered here, Gimpel et al. (2003) studied lake water that in all but one case was at circumneutral pH. Furthermore, they did not analytically determine the speciation between Fe(II) and Fe(III) but assumed either all Fe to be present as Fe(II) or Fe(III). This makes direct comparison of our results difficult. Possibly, the discrepancy is caused by the increased influence of inorganic Fe(III) species and their binding to DOM at higher pH and lower DOC concentrations.

#### 4.4 Conclusions

In this paper dissolved inorganic Al and Fe fraction in solutions from an acidic sandy soil, as calculated with Model V and VI, were compared with analytical observations obtained with DGT. Both approaches have their merits and drawbacks and we found that a comparison helped shed light on the strengths and weaknesses of either approach for the study of the speciation of Al and Fe in acidic soil solutions.

This study suggest that the Al fraction measured by DGT with the conventional APA hydrogel is somewhat higher than the true dissolved inorganic Al fraction due to the detection of small (<1000 Da) labile Al-DOM complexes. This effect will be strongest in systems where Al concentrations are low and concentrations of DOM are high, so that a relatively large fraction of Al is organically bound. Binding of Fe(III) to DOM is considerably stronger than that of Al and it appears that Fe(III)-DOM complexes are not labile enough to be detected by DGT. Consequently, DGT seems to give good estimates of dissolved, inorganic Fe in solution, even at low Fe(III) concentrations and high DOM concentrations.

While in general the trends of metal binding to DOM as measured by DGT and calculated by Model V and VI agree surprisingly well, the systematically higher calculated dissolved inorganic Fe(II) fraction by Model VI warrants further investigation.

Finally, a welcome improvement of Model VI would be the inclusion of the redox equilibrium between Fe(II) and Fe(III), which would make it unnecessary to determine the redox speciation of Fe analytically if the redox potential and specific redox couples are known.

