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### The mobility of aluminium, iron and organic matter in acidic

Jansen, B.

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## Comparison of diffusive gradients in thin films and equilibrium dialysis for the determination of Al, Fe(III) and Zn complexed with dissolved organic matter\*

### Abstract

The distinction between 'free' metals and organically complexed metals in aqueous solutions is important for research involving the mobility or bioavailability of metals in the environment. In this study the applicability of equilibrium dialysis (Molecular Weight Cut-Off = 1000 Da) and Diffusive Gradients in Thin films (DGT) to determine 'free' Al, Fe(III), and Zn in four forest soil solutions was compared. The 'free' metals as measured by both methods, consist of hydrated metal cations and soluble inorganic metal complexes. In addition, dialysis measures any organic complexes < 1000 Da and DGT measures a portion of smaller labile organic complexes. The four soil solutions were prepared by water extraction of an organic soil horizon (H) from a Fimic Anthrosol, and contained either 20 or 75 mg C/l dissolved organic matter at pH = 4.0 and pH = 7.0. To test the performance of both methods and optimize experimental volume and time, experiments using metal nitrate solutions were carried out. In the solutions at pH = 4.0, no significant differences in average 'free' metal contents were found for Al, Fe(III) or Zn. This makes DGT a viable alternative for equilibrium dialysis for the study of the complexation of all three metals in acidic soils. At pH = 7.0, again no significant difference between both methods were found for Al and Fe(III), but the DGT results for Zn were significantly higher. This was likely caused by labile organic complexes that were only detected by DGT.

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## 2.1 Introduction

The interaction of metals with naturally occurring dissolved organic matter (DOM) plays an important role in determining the fate of those metals in soils. Not only does association with DOM influence the mobility of metals through the soil system (Fox, 1995; Sauvé et al., 2000), it also affects their bioavailability and toxicity (Lores et al., 1999; Simpson et al., 1997; Tam and McColl, 1990). In addition, metal-DOM interactions can affect the mobility of DOM itself in soils (Ares and Ziechman, 1988; Fox, 1995; Kaiser, 1998). Polyvalent metal cations are especially important, because of their capability of strong and specific binding to organic molecules (Stevenson, 1994; Tam and McColl, 1990; Tam and McColl, 1991).

In order to study metal-DOM interactions, several experimental methods have been developed to distinguish between organically complexed metals and 'free' metals (Saar and Weber, 1982; Simpson et al., 1997; Stevenson, 1994). These 'free' metals usually consist of a combination of hydrated metal cations and soluble inorganic metal complexes and are usually considered to represent the bioavailable metal fraction. A major pitfall with most of the existing experimental methods, such as voltammetry and the use of ion-selective electrodes, is that they are only applicable to a limited number of metals that do not include important metals like Al and Fe (Saar and Weber, 1982; Stevenson, 1994). Furthermore, the shifting of binding equilibria during the analysis of 'free' metals and the inability to use undisturbed samples are often a concern (Saar and Weber, 1982). One of the few techniques that do not suffer from these problems is equilibrium dialysis. This technique is based on the separation of the smaller hydrated metal cations and soluble inorganic complexes from the larger metal-DOM complexes by means of a dialysis membrane (Truitt and Weber, 1981) and has been used successfully in several studies of the binding of metals to DOM in natural systems (Hintelmann et al., 1997; Lores and Pennock, 1998; Lores et al., 1999; Truitt and Weber, 1981; Van Loon et al., 1992). However, there is a dilemma when using equilibrium dialysis. If a membrane with a relatively large pore-size (> 1000 Da) is used, the time before equilibrium is reached is relatively short but the

separation will be inaccurate. When a smaller pore size is used, the separation will be more complete but the time needed to reach equilibrium increases substantially, because the diffusive permeability of dialysis membranes is proportional to the square of the pore size (Kokubo and Sakai, 1998).

Recently, a new separation technique called Diffusive Gradients in Thin films (DGT) was developed (Zhang and Davison, 1995). DGT uses a chelating resin to immobilize metal cations and labile (in)organic complexes. 'Free' metal concentrations are calculated from the mass of metals collected on the resin (Zhang and Davison, 1995). The resin is covered with an ion-permeable hydrogel of defined area and thickness that allows free metals to pass at known rates. The diffusion rate of larger organic complexes through the commonly used APA hydrogel is slow enough to prevent significant diffusion, but smaller organic complexes will be able to penetrate the hydrogel to some extent (16% at 2400 Da) (Zhang and Davison, 1999). Therefore, in addition to hydrated metal cations and soluble (labile) inorganic complexes, DGT will measure a small portion of the smaller labile organic complexes.

Like equilibrium dialysis, DGT promises applicability to a wide range of metals and the ability to use undisturbed samples. Because metal concentrations are calculated from known diffusion rates through the hydrogel, the time needed for a given analysis can be very short (Zhang and Davison, 1995). DGT has already been used successfully to determine free concentrations of several metals in surface waters and specific trace metals, such as Cu, Zn and Cd, in soil solutions (Zhang and Davison, 1995; Zhang et al., 1998). However, problems may arise at the lower pH values ( $\text{pH} < 5$ ) common in many soils because of competition with protons for the exchange resin, especially when weakly binding metals are concerned (Zhang and Davison, 1995). Furthermore, the performance of DGT has not been tested thoroughly for many metals commonly encountered in soil solutions, such as Al that is a dominant metal cation in acidic soils.

In this study, the applicability of DGT to the determination of free metal concentrations in soil solutions was tested by comparison with results obtained by the established method of equilibrium dialysis. The soil under consideration is an acidic sandy forest soil in the temperate zone. In this type of soil the polyvalent

metals Fe(III) and Al are important, amongst others because of their relative abundance, their potential toxicity to soil organisms and their role in pedogenesis (McBride, 1994). Therefore, the detection of these two metals by DGT was tested. Because small, but significant amounts of the polyvalent and environmentally important metal Zn were found in the soil under study, this metal was also considered. Two water extracts at pH = 4.0 of the H horizon of the forest soil were used. These extracts contained either 20 mg C/l or 75 mg C/l, spanning the range of DOM concentrations usually found in sandy forest soils in the temperate zone. In addition, the same extracts brought to a pH of 7.0 were used for reference purposes, since no problems with DGT were expected at this pH value (Zhang and Davison, 1995).

## 2.2 Materials and methods

All chemicals used in the experiments were of analytical grade. To prevent metal contamination, all glassware was acid washed prior to the experiments. For the determination of metal content, a Perkin Elmer Optima 3000XL ICP-OES and a Varian Vista CCD simultaneous ICP-AES were used. The pH of samples analyzed on the ICP was adjusted to 1.0 by addition of a concentrated HNO<sub>3</sub> solution, to dissociate any metal complexes present. DOM content was measured as Dissolved Organic Carbon (DOC) by colorimetric determination on a Skalar continuous flow auto-analyzer.

### *2.2.1 Preparation of DOM solutions*

Soil material was collected from the H horizon ( $\text{pH}_{\text{H}_2\text{O}} = 3.8$ ) of a Fimic Anthrosol at the Buunderkamp location at the Veluwe, the Netherlands, and sieved without prior drying over 2 mm using a polyethylene sieve to avoid metal contamination. Two water extracts were prepared by adding 150 g and 400 g, respectively of the homogenized material per liter of doubly deionized water, shaking the resulting suspension for 16 hours, centrifuging at 3000 rpm and filtering the supernatant using a 0.45  $\mu\text{m}$  membrane filter. The extract prepared from 400 g of material per liter water was subsequently concentrated by a factor

of 1.2 by evaporation at 65 °C using a Rotavab vacuum evaporation device, because using a higher material to water ratio to obtain a higher DOM content proved impractical. The two DOM solutions were each divided over two aliquots, one of which was adjusted to pH = 4.0 and the other to pH = 7.0 by adding small quantities of a 1.0 M KOH solution. Samples were taken and analyzed to determine the initial metal and DOC contents of the four resulting solutions.

To all solutions 0.01 M NaN<sub>3</sub> was added to prevent microbial degradation of DOM (De Maagd et al., 1998). The pH was readjusted to compensate for the resulting rise in pH. To prevent osmosis during the dialysis experiments, the ionic strength of all solutions was adjusted by adding KNO<sub>3</sub> to obtain a concentration of 0.01 M.

### *2.2.2 Equilibrium dialysis experiments*

For the dialysis experiments, Spectra/Por Biotech CE dialysis membrane tubing with a Molecular Weight Cut-Off (MWCO) of 1000 Da was used. Glass containers were filled with the sample solution, referred to as the outside solution. In this outside solution a dialysis tube filled with doubly deionized water, referred to as the inside solution, was immersed. To minimize disturbance of metal-DOM binding equilibria in the sample as a result of metals migrating into the inside solution, the volumic ratio of outside to inside solution was set at 25:1 (Truitt and Weber, 1981). KNO<sub>3</sub> and NaN<sub>3</sub> were added to the inside solutions to match the concentrations in the outside solutions and the pH of the inside solutions was adjusted by adding small amounts of either 1.0 M KOH or 1.0 M HNO<sub>3</sub>. During the experiments, the closed containers were continuously shaken at a constant room temperature of 20 °C. At the beginning of the experiments, samples were taken from both the inside and outside solutions to determine initial DOC and total metal contents. After equilibrium had been reached, again samples were taken from both the inside and outside solutions and analyzed to allow calculation of the 'free' metal contents and DOM that possibly passed the membrane.

Two types of equilibrium dialysis experiments were performed. First, pilot experiments were carried out to determine the time needed to reach equilibrium over the membrane. Second, the main experiments using each of the four DOM

solutions were conducted, to determine the 'free' metal contents for comparison to those found with DGT. For the pilot experiments, aqueous solutions of the nitrate salts of the metals of interest were used. These solutions had the same metal concentrations as found in the DOM solutions. Since all metals are assumed to be in the 'free' metal form in the absence of DOM, equilibrium is reached when the concentrations in the inside and outside solutions are equal. The pilot experiments were started at the same time but were ended after different regularly spaced time periods to test for equilibrium. In addition, a pilot experiment using the 20 mg C/l DOM solution at pH = 4.0 was performed to test the attainment of equilibrium in the presence of DOM. This solution was spiked with 185  $\mu\text{M}$   $\text{Al}(\text{NO}_3)_3$  to assure significant complexation.

Based on the results of the pilot experiments, the experimental time in the main experiments was set at 400 hours. An outside solution volume of 300 mL, the smallest practical volume, was used. The main experiments were carried out in five-fold. At the same time, experiments containing the same DOM solutions without dialysis membranes were conducted, to test for fluctuations in metal and DOM contents in the course of the experiment due to other causes than the dialysis process.

### *2.2.3 DGT experiments*

Standard DGT units for metals were obtained from DGT Research Ltd, UK, and assembled according to the procedures described elsewhere (Zhang and Davison, 1995; Zhang et al., 1995). The units contained a Chelex 100 chelating resin in the  $\text{Na}^+$  form, covered with an APA hydrogel (Zhang and Davison, 1999) and a 0.45  $\mu\text{m}$  membrane filter. In the experiments, DGT units were suspended vertically halfway down glass containers filled with the initial sample solution. During the experiments, the closed containers were constantly shaken at a room temperature of 20 °C. At the beginning of the DGT experiments, samples from the sample solution were taken and metal and DOC contents were determined. At the end of the experiments, the metal content of the outside solution was determined to check for significant removal of metals from solution. In addition, the DGT units

were opened and metals were removed from the chelating resin using a 1.0 M HNO<sub>3</sub> solution, and subsequently analyzed (Zhang and Davison, 1995). The metal concentrations in the hydrogels were also measured to determine if the gel had retained significant amounts of metal.

First, pilot experiments were conducted to test the performance of DGT and determine the deployment time and sample volume needed, as DGT was primarily developed for use in large volumes (Zhang and Davison, 1995). Good performance of DGT in determining Fe, Zn, and Cd has been reported in several publications (Zhang and Davison, 1995; Zhang et al., 1998; Zhang et al., 1995). However, only limited data has been published about Al (Zhang and Davison, 1999). Therefore, more extensive tests using 10 μM Al(NO<sub>3</sub>)<sub>3</sub> solutions were performed. The pilot experiments were performed in a similar manner to those for equilibrium dialysis, with the exception that in addition to the metals of interest Cd(NO<sub>3</sub>)<sub>2</sub> was added as a performance reference.

Second, the main experiments using each of the four DOM solutions were conducted. Again the main experiments were carried out in five-fold. Based on the pilot experiments, a sample volume of 0.5 l and an experimental time of 16 hours were used in the main experiments.

#### *2.2.4 Calculation and comparison of the free metal fractions*

The performance of DGT was assessed by calculating the recovery, defined as the calculated 'free' metal concentrations divided by the total metal concentrations as measured in the bulk solutions. A recovery of 100% indicates all metal is present as 'free' metal.

For both the dialysis and DGT experiments the 'free' metal fraction in the main experiments was calculated as the mass of 'free' metal divided by the total metal mass present in solution. This total metal mass was calculated from the initial metal concentrations in the outside solutions.

For the equilibrium dialysis experiments, the 'free' metal mass was calculated from the metal concentrations measured in the inside solutions at the end of the experiments. For the DGT experiments the 'free' metal mass was calculated from

the amount of metal captured on the exchange resin, using the DGT formulas (Zhang and Davison, 1995).

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

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

M represents the metal mass captured on the chelating resin and is calculated from the metal concentration in the elution sample ( $C_e$ ), the volume of the elution fluid ( $V_{\text{HNO}_3}$ ) and the chelating resin ( $V_{\text{gel}}$ ), and an elution factor ( $f_e$ ) of 0.8 needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From M, the 'free' 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 ( $A$ ). 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. For the metals of interest at 20°C these are: Al:  $4.14 \times 10^{-6} \text{ cm}^2/\text{s}$ ; Fe:  $5.32 \times 10^{-6} \text{ cm}^2/\text{s}$ , Zn:  $5.29 \times 10^{-6} \text{ cm}^2/\text{s}$  and Cd:  $5.30 \times 10^{-6} \text{ cm}^2/\text{s}$  (used in the DGT performance tests).

The variance and means of the duplicate experiments for both DGT and dialysis were calculated and compared by use of F- and t-tests with  $\alpha = 0.05$ . If a significant difference in means was found an additional non-parametric test (Mann-Whitney test) was performed.

### 2.3 Results and discussion

The initial composition of the DOM solutions is provided in Table 1. Colorimetric tests confirmed that all Fe in the four DOM solutions was present as Fe(III).

**2.3.1 Equilibrium dialysis experiments**

The rate at which equilibrium was reached varied for the three metals and was slowest for Al and Fe(III). This difference in rate was most likely caused by slower passage of small soluble organic metal complexes, just small enough to penetrate the membrane. In addition, trivalent cations are surrounded by bulkier water shells and anion layers than divalent ions such as  $Zn^{2+}$ . This slows down their passage through the membrane. The approach to equilibrium for the pilot experiment using the Al-spiked 20 mg C/l solution at pH = 4.0 is presented in Fig. 1. The remaining differences between inside and outside solutions after equilibrium signify complexed metal, which is the highest for Al due to the spiking with Al. As a result of the much higher Al concentrations, we had problems detecting Zn on the ICP in this particular experiment, especially at the points before equilibrium. Therefore, Zn is not included in Fig. 1. Instead  $Mg^{2+}$ , which was present at higher concentrations, is included as a reference for the behavior of divalent cations. At the lower Al concentrations in the other pilot experiments we experienced no problems with the detection of Zn.

**Table 1**  
Characterization of the outside (bulk) soil solutions and the inside dialysis solutions

pH	DOC ( $\mu\text{mol C/l}$ )		Total Al( $\mu\text{mol/l}$ )		Total Fe(III) ( $\mu\text{mol/l}$ )		Total Zn ( $\mu\text{mol/l}$ )	
	Bulk	Inside <sup>a</sup>	Bulk	Inside <sup>a</sup>	Bulk	Inside <sup>a</sup>	Bulk	Inside <sup>a</sup>
4.1	1680	276	8.3	0.80	3.4	0.90	1.25	1.00
4.0	5920	1245	23.4	2.95	9.8	1.70	1.15	0.85
7.1	1770	198	8.0	0.30	3.6	0.15	1.10	0.10
7.0	6040	694	22.4	0.90	9.7	0.35	1.10	0.10

<sup>a</sup>Average of the five duplicate experiments, for explanation see text.

The final composition of the inside solutions in the main dialysis experiments is provided in Table 1. The amount of DOC that penetrated the membranes ranged from an average of 11.3 % for the experiments at pH = 7.0 to 18.6 % for the

experiments at pH = 4.0. The difference can be explained by the fact that the average size of DOM configurations decreases with decreasing pH, due to curling of the molecules (Conte and Piccolo, 1999). The metal composition of the outside solutions in the main dialysis experiments did not change significantly with respect to metal concentrations, when compared to solutions without a dialysis membrane. This indicates the volume ratio of inside to outside solutions was sufficient to prevent alteration of the association equilibrium between metals and DOM. A small decline in DOC concentrations in the outside solutions was found (< 6.0%), but this did not differ significantly from the decline in solutions without a dialysis membrane except for the 20 mg C/l, pH = 4.0 solution. The decline in DOC concentrations was probably caused by microbial degradation, in spite of the addition of  $\text{NaN}_3$ .

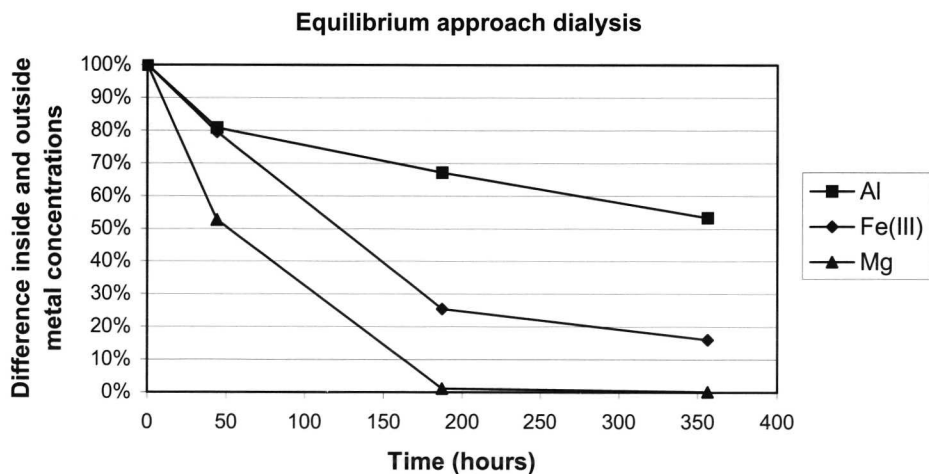


Fig. 1. Approach to equilibrium for dialysis pilot experiment with 20 mg C/l and spiked with 185  $\mu\text{M}$   $\text{Al}(\text{NO}_3)_3$ . A difference between metal concentrations of inside and outside solutions at equilibrium represents metal bound by DOM.

### *2.3.2 DGT experiments*

In the pilot experiments the recoveries of Cd, commonly used to test DGT units, were 94% (RSD = 2.0%) at pH = 4.0 and 99% (RSD = 7.0%) at pH = 7.0, indicating that the units were functioning properly. The recoveries in the pilot experiments for Al were 99.7% (RSD = 3.6%) at pH = 4.0 and 80.2% (RSD = 18.6%) at pH = 7.0. This indicates DGT detection of Al at pH = 4.0 worked well. The lower recovery, as well as higher variability for Al at pH = 7.0 can be explained by precipitation of  $\text{Al}(\text{OH})_{3(s)}$ . Calculations using the speciation code PHREEQC (Parkhurst, 1995) show that as much as 80% of Al may precipitate at pH = 7.0 in a solution without organic ligands. Such precipitation is usually slow and equilibrium will not have been reached in the course of the experiment. Because DOM complexation will dramatically shift the equilibrium away from precipitation by lowering 'free' metal contents, and significant complexation of Al was found in the main experiments, no precipitation of Al was expected in the main experiments.

In the main DGT experiments, the composition of the outside solution did not change significantly with respect to metal content during the experiments. This indicates the metal-DOM ratio in the bulk solution was not altered. The mass percentages of metals found in the gel layer covering the ion exchange resin in all cases were lower than 6.0 % of the total metal mass in solution.

### *2.3.3 Equilibrium dialysis versus DGT*

The percentages of 'free' metal as determined by both equilibrium dialysis and DGT are presented in Table 2 and Figs. 2 through 4. A total of eight experimental situations is presented: situations 1 and 3 represent the results of the equilibrium dialysis experiments at pH = 4.0, for respectively the 20 mg C/l and the 75 mg C/l DOM solutions. Situations 2 and 4 represent the same for DGT. Situations 5 and 7 represent the results for dialysis at pH = 7.0, for respectively the 20 mg C/l and the 75 mg C/l DOM solutions. Situations 6 and 8 represent the same for DGT. For each situation the results of all duplicate experiments are presented. Due to experimental problems (acid contamination), for situation 1 and 7 less than five measurements were available. In addition, systematic outliers were removed from

the Fe(III) and Al data of situation 5 and from the Zn data of situation 6. To allow comparison of the different metals, all figures were scaled to 100 % of 'free' metal.

Table 2

Average 'free' metal percentages and standard deviations of equilibrium dialysis and DGT analyses of the four soil extracts.

	20 mg C/l pH = 4.0		75 mg C/l pH = 4.0		20 mg C/l pH = 7.0		75 mg C/l pH = 7.0	
	dialysis	DGT	dialysis	DGT	dialysis	DGT	dialysis	DGT
Average 'free' <sup>a</sup>								
Al (%)	10.1	13.9	12.8	11.8	2.4	3.3	4.4	3.5
SD (%)	1.3	2.3	1.8	1.0	1.0	1.9	3.2	1.3
Average 'free' <sup>a</sup>								
Fe (%)	24.3	15.6	18.3	15.1	2.4	3.5	3.8	3.0
SD (%)	1.5	3.4	1.7	5.1	1.0	2.8	2.7	1.3
Average 'free' <sup>a</sup>								
Zn (%)	86.3	76.6	79.7	70.0	8.8	32.0	11.1	31.5
SD (%)	2.9	7.9	6.2	8.7	1.1	5.1	2.0	1.5

<sup>a</sup>Free' metal consists of hydrated metal cations and soluble inorganic complexes

For all metals the results showed a decrease of the 'free' metal fraction with increasing pH. This is consistent with observations from other studies and can be explained by a higher degree of dissociation of acidic groups at the DOM molecules, involved in metal binding (Martell et al., 1988; Tam and McColl, 1990). Furthermore, the results showed a larger degree of organic complexation of Al and Fe(III) on one hand and a smaller degree of organic complexation of Zn on the other, the difference being most pronounced at low pH values. This is in agreement with the fact that Zn is a weaker binding metal than Al and Fe(III) (Stevenson, 1994). Generally no significant difference in variance between dialysis and DGT was found (Table 2). However, a larger number of measurements may be necessary to draw proper conclusions on the precision of both methods.

Overall the variance of the Al and Fe(III) results were the lowest for both methods, due to their higher concentrations compared to Zn.

The results for Al and Fe(III) from the equilibrium dialysis and DGT experiments (Figs. 2 and 3) were similar for all four DOM solutions. Statistical tests confirmed that there was no significant difference in variance or mean for any situation, except for Fe(III) in the solution at pH = 4.0, containing 20 mg C/l. Here the mean 'free' metal percentage found in the equilibrium dialysis experiments was slightly higher than that obtained by DGT. The absence of differences between 'free' Al measurements at pH = 7.0 indicate that it was indeed precipitation of  $\text{Al}(\text{OH})_3(\text{s})$  that caused the underestimation by DGT in the pilot experiments without DOM and that DOM complexation indeed prevented such precipitation.

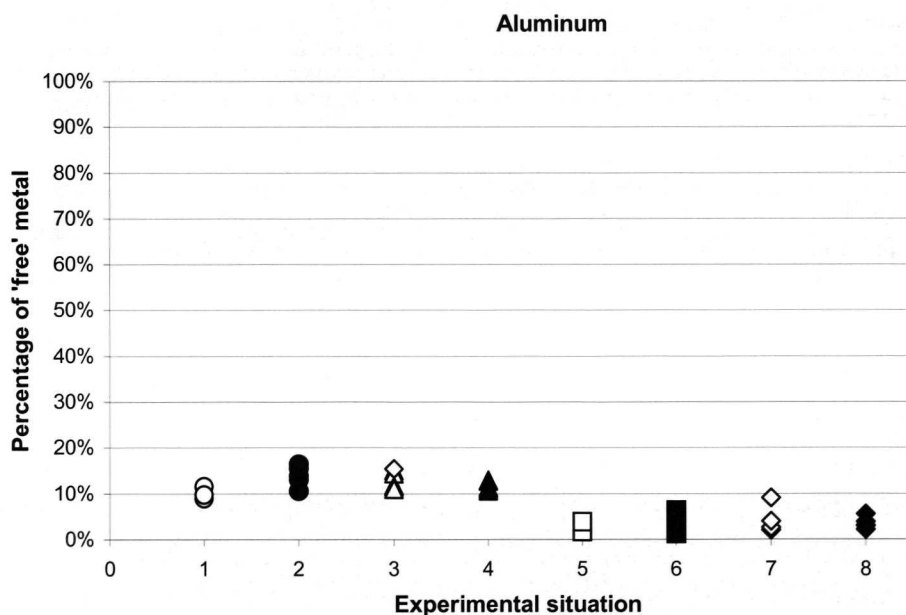


Fig. 2. Percentage of 'free' Al determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

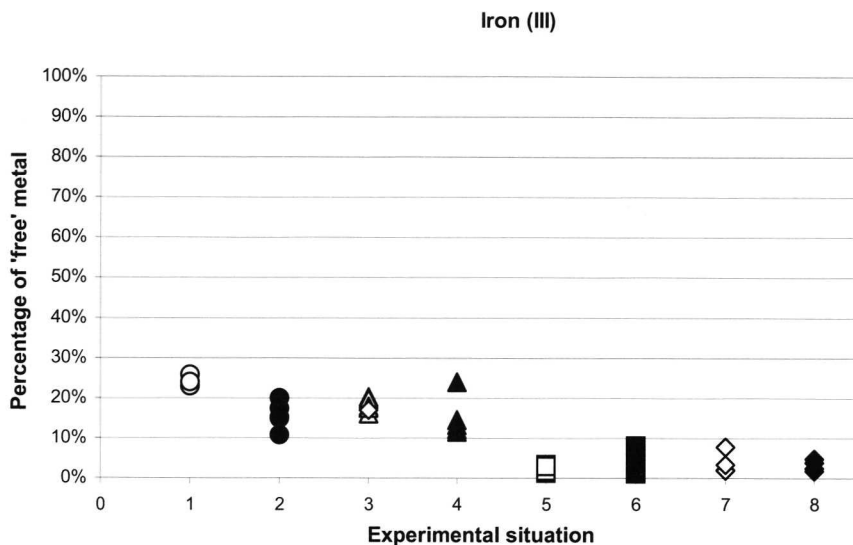


Fig. 3. Percentage of 'free' Fe(III) determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

Both Al and Fe(III) are believed to form strong, non-labile complexes with DOM. If this is the case, DGT will not detect any organic Al or Fe(III) complexes even if they are small enough to significantly penetrate the hydrogel. However, dialysis will measure any metal-DOM complexes < 1000 Da. Consequently, the differences between dialysis and DGT for Fe(III) at low pH and low DOC concentrations were most likely caused by a slight overestimation by equilibrium dialysis resulting from smaller metal-DOM complexes penetrating the dialysis membrane. As explained earlier, such penetration was found to be most pronounced at pH = 4.0. Research by Tam (Tam, 1987) shows that Al has a preference for association with larger DOM molecules. This explains why contrary to Fe(III), equilibrium dialysis did not overestimate the amount of 'free' Al present in the low DOC solution at pH = 4.0.

At pH = 7.0, calculations using the speciation code PHREEQC indicate that in solutions without DOM, over 90% of both Al and Fe(III) will be present as inorganic complexes. However, in the presence of DOM the actual amount of

inorganic complexes will be much lower because DOM in solution will quite effectively compete with inorganic ligands for the binding of Al and Fe(III). Due to their size, all dissolved inorganic complexes will be part of the 'free' metal as detected by dialysis. However, DGT will only measure labile inorganic complexes. Since only little 'free' Al and Fe(III) was found by both methods at pH = 7.0 and no significant difference was observed between DGT and equilibrium dialysis, either little inorganic complexation of Al and Fe(III) occurred in the presence of DOM, or all such complexes were labile.

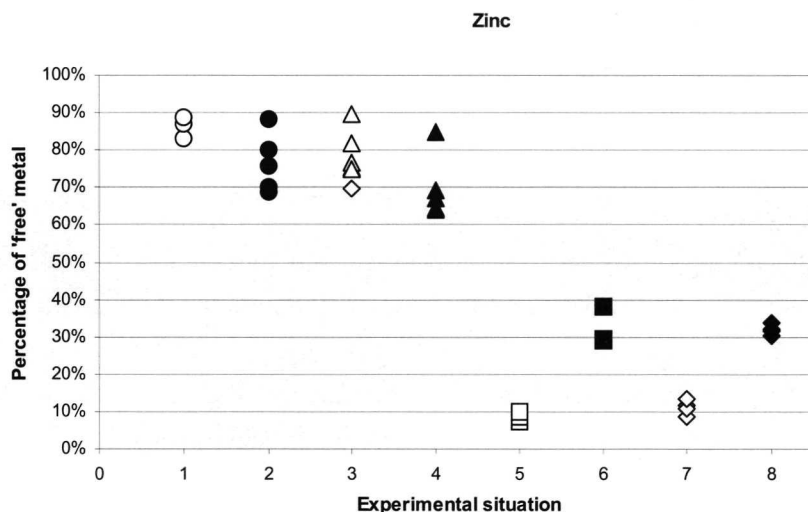


Fig. 4. Percentage of 'free' Zn determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

For Zn (Fig. 4), there was no significant difference between the equilibrium dialysis and DGT results at pH = 4.0, but the variance of the results was relatively large for both methods. This is the result of the very low Zn concentrations present in the initial solutions. As expected, at low pH most of the weaker binding Zn was found to be present in the 'free' metal form by both DGT and dialysis.

At pH = 7.0, the average 'free' metal percentages from the DGT experiments were higher than those from the equilibrium dialysis experiments. Because Zn is a weaker binding metal than Al and Fe(III), larger portions of the Zn-DOM

complexes will be labile. Therefore, small labile Zn-DOM complexes, still too large to pass the dialysis membrane, will have been measured by DGT and may explain the higher results as compared to equilibrium dialysis. Other studies by Lores and Pennock (Lores and Pennock, 1998), and Wells et al. (Wells et al., 1998) using DOM solutions from a leaf compost and seawater at pH values of 5.5 and 7.0 respectively, reported 'free' Zn percentages ranging from 30 to 55 %. These values are in the range of those found by us using DGT and would indicate a possible underestimation by dialysis. However, comparison with the data from other studies is difficult because the results strongly depend the detection method and experimental conditions that were used. Further research of the preference of Zn for a certain DOM size fraction and the lability of the complexes formed, is needed to clarify the differences between DGT and dialysis at pH = 7.0.

## 2.4 Conclusions

No significant differences were found between DGT and equilibrium dialysis (MWCO = 1000 Da) for the detection of Al, Fe(III) and Zn in both the 20 mg C/l and 75 mg C/l soil solutions at pH = 4.0. This shows that DGT is a viable alternative for equilibrium dialysis for the determination of 'free', and therefore bioavailable, Al, Fe(III) and Zn in soil solutions from acidic sandy forest soils. The fact that at pH = 7.0 again no significant differences between equilibrium dialysis and DGT were found for Al and Fe(III), further vindicates both methods for the detection of these two metals. Even though such high pH values do not occur in acidic sandy forest soils, the results are relevant for studies of other soil types.

For Zn the 'free' metal fractions as determined by DGT at pH = 7.0 were significantly higher than those measured by equilibrium dialysis. Due to the weaker binding of Zn, more labile organic complexes are formed than with Al and Fe(III). The observed difference is possibly caused by the detection of such labile complexes larger than 1000 Da by DGT.

In general the results indicate that in the case of strongly binding trivalent metals such as Al and Fe(III), the species measured by DGT and equilibrium

dialysis with a small MWCO are approximately the same under the circumstances tested. For weaker binding divalent (or monovalent) metals such as Zn, the measured species differ because of the detection by DGT of small labile complexes. The choice for either method would then depend on the species one is interested in.

