

Groundwater chemistry of Al under Dutch sandy soils: Effects of land use and depth

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Abstract

Aluminium has received great attention in the second half of the 20th century, mainly in the context of the acid rain problem mostly in forest soils. In this research the effect of land use and depth of the groundwater on Al, pH and DOC concentration in groundwater under Dutch sandy soils has been studied. Both pH and DOC concentration play a major role in the speciation of Al in solution. Furthermore, the equilibrium with mineral phases like gibbsite, amorphous Al(OH)₃ and imogolite, has been considered. Agricultural and natural land use were expected to have different effects on the pH and DOC concentration, which in turn could influence the total Al concentration and the speciation of Al in groundwater at different depths (phreatic, shallow and deep). An extensive dataset ($n = 2181$) from the national and some provincial monitoring networks on soil and groundwater quality was used. Land use type and groundwater depth did influence the pH, and Al and DOC concentrations in groundwater samples. The Al concentration ranged from $<0.4 \mu\text{mol L}^{-1}$ at $\text{pH} > 7$ to $1941 \mu\text{mol L}^{-1}$ at $\text{pH} < 4$; highest Al concentrations were found for natural-phreatic groundwater. The DOC concentration decreased and the median pH increased with depth of the groundwater. Natural-phreatic groundwater showed lower pH than the agricultural-phreatic groundwater. Highest DOC concentrations were found for the agricultural-phreatic groundwater, induced by the application of organic fertilizers. Besides inorganic complexation, the NICA-Donnan model was used to calculate Al³⁺ concentrations for complexation with DOC. Below pH 4.5 groundwater samples were mainly in disequilibrium with a mineral phase. This disequilibrium is considered to be the result of kinetic constraints or equilibrium with organic matter. Log K values were derived by linear regression and were close to theoretical values for Al(OH)₃ minerals (e.g. gibbsite or amorphous Al(OH)₃), except for natural-phreatic groundwater for which lower log K values were found. Complexation of Al with DOC is shown to be an important factor for the Al concentrations, especially at high DOC concentrations as was found for agricultural-phreatic groundwater.

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1. Introduction

Since the end of the 1970s, the chemistry of Al in the environment has received great attention. Elevated Al concentrations are an important result of

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acidification of forest soils (Cronan and Schofield, 1979; Ulrich et al., 1980; Johnson et al., 1981; David and Driscoll, 1984; Mulder et al., 1989). Increased Al concentrations can be toxic to aquatic biota and terrestrial vegetation (David and Driscoll, 1984) and these increased Al concentrations could therefore also be a potential risk for drinking water production.

Dissolution of Al from the soil matrix plays an important role in the buffering of acid deposition on soils (Berggren et al., 1998). In previous research the Al concentration in soil solutions and natural waters has been assumed to be controlled by equilibrium with gibbsite or some other forms of $\text{Al}(\text{OH})_3$ (Nordstrom and Ball, 1986; Gustafsson et al., 2001). However, it has often been shown that Al in soil solutions is frequently in disequilibrium with $\text{Al}(\text{OH})_3$ as well as with many other Al-minerals, e.g. jurbanite (AlSO_4OH) (Haag et al., 2001). Other research has shown that Al concentrations are controlled by complexation with soil organic matter (Cronan et al., 1986; Mulder et al., 1989; Walker et al., 1990; Berggren and Mulder, 1995; Wesselink and Mulder, 1995). Wesselink et al. (1996) concluded that organic matter controls Al activity in soils by complexation, but both organic matter complexation and kinetic controlled dissolution of inorganic Al will contribute to Al mobilization in soils. For example, Swiss forest soil samples are close to saturation with respect to amorphous Al hydroxides at $\text{pH} > 5.5$, but these soils show that $\text{Al}(\text{OH})_3$ is a poor predictor for Al^{3+} activity in soil below $\text{pH} 5.5$. Instead, the Al^{3+} activity is controlled by complexation with organic matter below $\text{pH} 5.5$ (Graf Pannatier et al., 2004). Van Hees et al. (2001) studied a large number of podzolic forest soils (Sweden) for their Al controlling mechanisms. The experimental results show that in the pH -range 4.0–6.2 no equilibrium with any mineral phase could explain the Al solubility in these soils and that for modeling purposes organic complexation models are best used for these soil samples.

Besides $\text{Al}(\text{OH})_3$ minerals, other studied Al controlling phases are hydroxyl-Al interlayered 2:1 minerals (Dahlgren et al., 1989), imogolite or the less ordered form proto-imogolite allophane (Farmer et al., 1980), 1:1 aluminosilicate like poorly crystalline kaolinite (Zysett et al., 1999) or feldspars (Mol et al., 2003). These potential controlling mineral phases show a 1–3 relation between pAl^{3+} and pH , except for the hydroxyl-Al interlayered 2:1 minerals. In contrast, when Al concentration is

regulated by equilibrium with organic matter a more or less 1–2 relation is found between pAl^{3+} and pH (Berggren and Mulder, 1995; Wesselink et al., 1996; Skjellberg, 1999). Similar to the disequilibrium between Al-hydroxide minerals and soil solutions, Al concentrations found in surface waters are not in equilibrium with mineral phases. Sullivan and Cosby (1998) found a relationship between pH and pAl^{3+} of close to 2:1 for lake waters. This is in contrast with the expected 3:1 relationship when the Al concentration is controlled by $\text{Al}(\text{OH})_3$. Cronan et al. (1986) concluded that Al-speciation in natural waters is controlled by equilibrium with a solid humic phase, instead of Al dissolution being kinetically constrained.

The Al chemistry of soil solutions and natural waters is very important in the context of acidification of aquifers. Several studies have been conducted on the effect of acidification of specific aquifers (Moss and Edmunds, 1992; Hansen and Postma, 1995; Kjeller et al., 2004) or the susceptibility of aquifers to acidification on national scales (Edmunds and Kinniburgh, 1986). The objective of this research was to study the effect of land use and depth of the sampled groundwater on Al speciation in groundwater under Dutch sandy soils. Here, depth is an indication for residence time, with a net discharge in the Netherlands of 250–300 mm a^{-1} . An extensive dataset of the Dutch groundwater and soil monitoring network ($n = 2181$), at a provincial and national scale was used. The speciation of Al was calculated taking DOC complexation into account. Furthermore, the relationship between pH and pAl^{3+} was studied for the different land use types and depths of the groundwater by regression analysis. Finally, with the $\log K$ values from the regression analysis the total Al concentration was calculated as a function of pH with and without taking DOC complexation into account.

2. Materials and methods

2.1. Monitoring networks

The groundwater data originated from various Dutch monitoring networks. A dataset was compiled on samples from sandy soils with agricultural and natural land use, since these 2 groups are the main land use types in the monitoring networks. Only samples with measurements of pH , DOC and Al were added to the dataset ($n = 2181$). First, the

dataset was divided into 2 groups based on land use (agricultural and natural). Furthermore both groups were subdivided by the depth of the sampled groundwater, phreatic (groundwater immediately below groundwater table), shallow (<10 m) and deep (>10 m). A schematization of the division of the dataset is shown in Fig. 1. The data on phreatic groundwater originated from the soil quality monitoring network Noord Brabant (Vander Grift et al., 2004). The data on shallow and deep groundwater originated from national (Van Duijvenbooden et al., 1985; Pebesma and De Kwaadsteniet, 1997) and provincial groundwater quality networks. Van der Grift et al. (2004) provide extended information on the monitoring networks and their results. A thorough description of the Dutch environmental monitoring systems is given by Mol et al. (2001).

The division between phreatic groundwater on one hand and shallow and deep groundwater on the other hand is based on the way the samples were taken. Phreatic groundwater was sampled for the first meter below the actual groundwater table in an open borehole. Shallow groundwater was sampled from permanent monitoring wells which have their well screen up to 10 m below surface, whereas deep groundwater was sampled from permanent monitoring wells which have their well screen between 10 and 25 m below surface. All samples were filtered through 0.45 µm filters and analyzed for elemental composition. Electrical conductivity and pH were immediately measured in the field. Samples were analyzed for HCO₃ by titration, for Cl and SO₄ by ion chromatography, for NO₃ and

NH₄ by auto-analyzer (AA3), for Al, Ca, Cu, Fe, K, Na, Ni, Mg, P, Pb and Zn by ICP-MS and for DOC by total organic carbon (TOC-500). The groundwater dataset included the replication of sampling over several years. The detection limits varied because different laboratories were involved in the measurements. To exclude uncertainties in measured Al concentrations, all measurements below 10 µg/L were ruled out (568 of 2749 samples). Data on shallow and deep groundwater were collected from 1990 to 1999 and data on phreatic groundwater were collected from 2002 to 2005.

2.2. Data handling and modeling

After the division of the data into the 6 groups, basic statistics were calculated per group. Furthermore, the relationship between the pAl^{3+} and pH was studied per group after calculation of the Al^{3+} concentration for every measurement. DOC complexation and competition with other cations was taken into account. The calculated concentrations of Al^{3+} were plotted versus pH. Linear regression was applied on the pAl^{3+} and pH data with SPSS (version 12.0.1), with a calculated and fixed slope. The linear regression was repeated for samples with $pH > 4.5$. Regression results were compared with solubility constants of various Al-(hydr)oxides. In addition, with the derived regression parameters the effect of DOC complexation on total dissolved Al was shown.

The speciation calculations for Al were performed with the chemical equilibrium program ECOSAT (Keizer and Van Riemsdijk, 1998) using the measured solution composition (Al, DOC, Ca, Cu, Fe, K, Mg, Mn, NH₄, Na, Ni, Pb, Zn, Cl, HCO₃, NO₃, PO₄ and SO₄). Complexation of cations with DOC was described with the NICA-Donnan model (Kinniburgh et al., 1999). The NICA-Donnan model has been used with good results in previous studies to describe metal complexation with DOC, e.g. (Temminghoff et al., 1997; Pinheiro et al., 2000; Oste et al., 2002; Weng et al., 2002a; Ge et al., 2005; Unsworth et al., 2005). Weng et al. (2002b) showed for a pH range between 3 and 7 that the NICA-Donnan model can describe Al complexation to HA reasonably well. For the studied pH range of the groundwater it was assumed that specific binding of hydrolyzed Al could be neglected.

The composition of DOC may vary for natural water, soil solution and groundwater. Since the exact composition of DOC was not known, assumptions

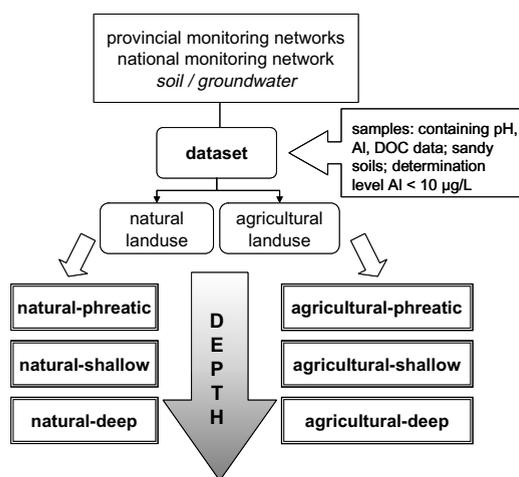


Fig. 1. Schematization of the division of the total dataset in different groups based on land use and depth of the groundwater.

Table 1

Stability constants for Al-containing minerals used in this study and other constants found in literature at $T = 298$ K

	Equilibrium reaction	log K
<i>Solubility constants used in this study (Fig. 4)</i>		
Amorphous $\text{Al}(\text{OH})_3$ 281 K ^a	$\text{Al}(\text{OH})_3 (\text{s}) + 3\text{H}^+ \leftrightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$	10.78
Gibbsite 281 K ^b		9.40
<i>Other reported solubility constants</i>		
Amorphous $\text{Al}(\text{OH})_3$ ^d	$\text{Al}(\text{OH})_3 (\text{s}) + 3\text{H}^+ \leftrightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$	9.66
Amorphous $\text{Al}(\text{OH})_3$ ^e		10.80
Gibbsite ^d		8.04
Gibbsite (crystalline) ^f		7.74
Gibbsite (synthetic) ^e		8.11
Gibbsite (natural) ^e		8.77
Gibbsite (microcrystalline) ^e		9.35
Gibbsite ^b		8.29
Imogolite ^c	$0.5(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH} (\text{s}) + 3\text{H}^+ \leftrightarrow \text{Al}^{3+} + 0.5\text{H}_4\text{SiO}_4^0 + 1.5\text{H}_2\text{O}$	6.05
Proto-imogolite sol ^g	$0.5(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH} (\text{s}) + 3\text{H}^+ \leftrightarrow \text{Al}^{3+} + 0.5\text{H}_4\text{SiO}_4^0 + 1.5\text{H}_2\text{O}$	7.02
Kaolinite ^d	$\text{Al}_2\text{SiO}_5(\text{OH}) + 6\text{H}^+ \leftrightarrow 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O}$	5.45
Kaolinite ^h		7.44

^a (Farmer, 1999).^b (Gustafsson et al., 1998).^c (Gustafsson et al., 2001).^d (Lindsay, 1979).^e (Johnson et al., 1981).^f (Palmer and Wesolowski, 1992).^g (Lumsdon and Farmer, 1995).^h (Stumm and Morgan, 1996).

had to be made about this composition. Assumptions in previous research vary from 100% FA (Christensen et al., 1999) to 50% FA and 50% inert (Lofts and Tipping, 2000; Tye et al., 2004; Guthrie et al., 2005). A DOC composition of 65% FA and 35% inert that has been used in several previous studies was chosen (Bryan et al., 2002; Weng et al., 2002a; Tipping et al., 2003; Ge et al., 2005; Guthrie et al., 2005). Low molecular weight organic acids (LMWOAs) could also play an important role in Al complexation, especially in organic and eluvial horizons of non-acidified podzolized soils. About 20–40% of Al can be complexed by these small LMWOAs. However, in this research, the LMWOAs are assumed to play a minor role since LMWOAs are not commonly present at greater depth (Holmström et al., 2005).

The K -values used to calculate the solubility of gibbsite and amorphous $\text{Al}(\text{OH})_3$ are shown in Table 1, as well as other reported solubility constants for Al minerals. Temperature has a significant effect on the K -values for these $\text{Al}(\text{OH})_3$ forms: Gustafsson et al. (1998) found a value for log K for gibbsite of 9.40 at 281 K whereas Lindsay (1979) reported a value of log K for gibbsite of 8.04 at 298 K. Also for amorphous $\text{Al}(\text{OH})_3$ the

log K value increased when temperature decreased (9.66 at 298 K (Lindsay, 1979) and 10.78 at 281 K (Farmer, 1999)). The temperature of Dutch groundwater is 283 K on a yearly average therefore a log K value of 9.4 for gibbsite and 10.78 for amorphous $\text{Al}(\text{OH})_3$ (281 K) were more suited for the studied groundwater data.

3. Results

In Table 2 median, 25 and 75 percentiles, minimum and maximum values are given for pH, Al concentration and DOC concentration. Results are shown for all 6 land use-groundwater combinations. The median of the groundwater pH increased with depth for each land use type, indicating that pH of the groundwater is buffered by the soil. For shallow and deep groundwater no difference existed in the median pH between the 2 land use types. However, the phreatic groundwater shows a clear difference in the median pH (>1 pH unit) between natural (4.25) and agricultural (5.46) land, which can be explained by the acidification of soils under natural vegetation and the adjustment of pH of agricultural sandy soils by liming. The range of the pH is larger for the deepest groundwater, ranging from 2.9 to

Table 2

Statistics (number of data points, median, 25% and 75% percentile, minimum and maximum) of the observed concentrations (pH, total Al concentration and DOC concentration) per group

<i>n</i>		Agri-phrea 311	Nat-phrea 151	Agri-shallow 801	Nat-shallow 271	Agri-deep 463	Nat-deep 184
pH	Median	5.46	4.25	5.70	5.60	6.10	5.89
	25% Percentile	4.90	4.15	5.03	4.85	5.64	5.50
	75% Percentile	5.97	4.48	6.39	6.50	6.74	6.62
	Minimum	3.55	3.68	2.80	3.10	2.90	3.34
	Maximum	6.96	6.56	7.90	7.96	8.05	8.50
Al-total ($\mu\text{mol L}^{-1}$)	Median	27	230	4.8	6.7	1.6	1.4
	25% Percentile	9.4	77	1.3	1.7	0.8	0.8
	75% Percentile	49	430	30	45	3.5	4.1
	Minimum	0.4 ^a	1.9 ^a	0.4 ^a	0.4 ^a	0.4 ^a	0.4 ^a
	Maximum	263	1941	295	546	641	587
DOC (mg L^{-1})	Median	24.3	5.4	5.2	2.7	2.6	1.8
	25% Percentile	13.8	3.5	2.7	1.8	1.4	1.1
	75% Percentile	38.2	9.3	9.5	4.7	4.6	3.2
	Minimum	2.5	0.8	0.0	0.0	0.0	0.0
	Maximum	88.6	33.0	57.0	50.0	121.0	18.1

Agri-phrea = agricultural-phreatic, nat-phrea = natural-phreatic, agri-shallow = agricultural-shallow, nat-shallow = natural-shallow, agri-deep = agricultural-deep, and nat-deep = natural-deep.

^a Detection limit of Al set at $10 \mu\text{g L}^{-1}$.

8.5. This implies that acidification of deeper groundwater and high Al concentrations could be expected. Because of the direct relation between Al^{3+} and pH, the natural-phreatic groundwater with a low median pH showed a higher median for Al than the other groups. The median of the Al concentration seemed to decrease with the depth of the groundwater (phreatic > shallow > deep). In addition, for shallow and deep groundwater no significant difference was found for Al concentration between the land use types. The highest DOC concentration was found for the agricultural-phreatic groundwater, which is even higher than the 75-percentiles of the other groups. For each groundwater depth, the median DOC concentration for agricultural land was higher than for natural land, even though the difference was rather small for the shallow and deep groundwater.

In Fig. 2 the measured total Al concentrations are plotted versus the pH and also the Dutch drinking water limit (VROM, 2001) is shown in the graphs. Most groundwater groups showed a big cloud of data points for the measured pH range, except the natural-phreatic group. For this group, most measurements were in the range between pH 3.5 and 4.5, and measured Al concentration showed a correlation with the pH in this range. This relationship is lacking for the other groups.

The Al concentration also depends on the DOC concentration and therefore the DOC concentrations are given in Fig. 3 versus the pH for all 6 groundwater groups. No correlation between DOC and pH was found. For all groups the 95% upper limit is shown (sum of the mean and twice the standard deviation). Highest DOC concentrations (61.4 mg L^{-1}) were found for the agricultural-phreatic group. Lowest DOC (6.8 mg L^{-1}) was found for the natural-deep group over the entire measured pH range. For the other groups the 95% upper limit was around 20 mg C l^{-1} .

The calculated pAl^{3+} by taking pH and DOC complexation into account, showed a good linear correlation with the pH (Fig. 4) and for most groups it perfectly matched the 1:3 relationship between pAl^{3+} and pH (at $\text{pH} > 4.5$) that is shown by the mineral equilibrium lines in Fig. 4. Most calculated data were close to equilibrium for gibbsite. Below pH 4.5 several measurements deviated from the 1 to 3 relationship (Fig. 4a, c–f). The relationship between pH and Al^{3+} was studied by linear regression on the data as plotted in Fig. 4. The regression was performed with a variable slope and a fixed slope of 3 for all measurements per group (Table 3a). Linear regression for this total dataset resulted in slopes from 2.10 to 2.69 and log *K* values from 4.61 to 7.24. For natural-phreatic groundwater a

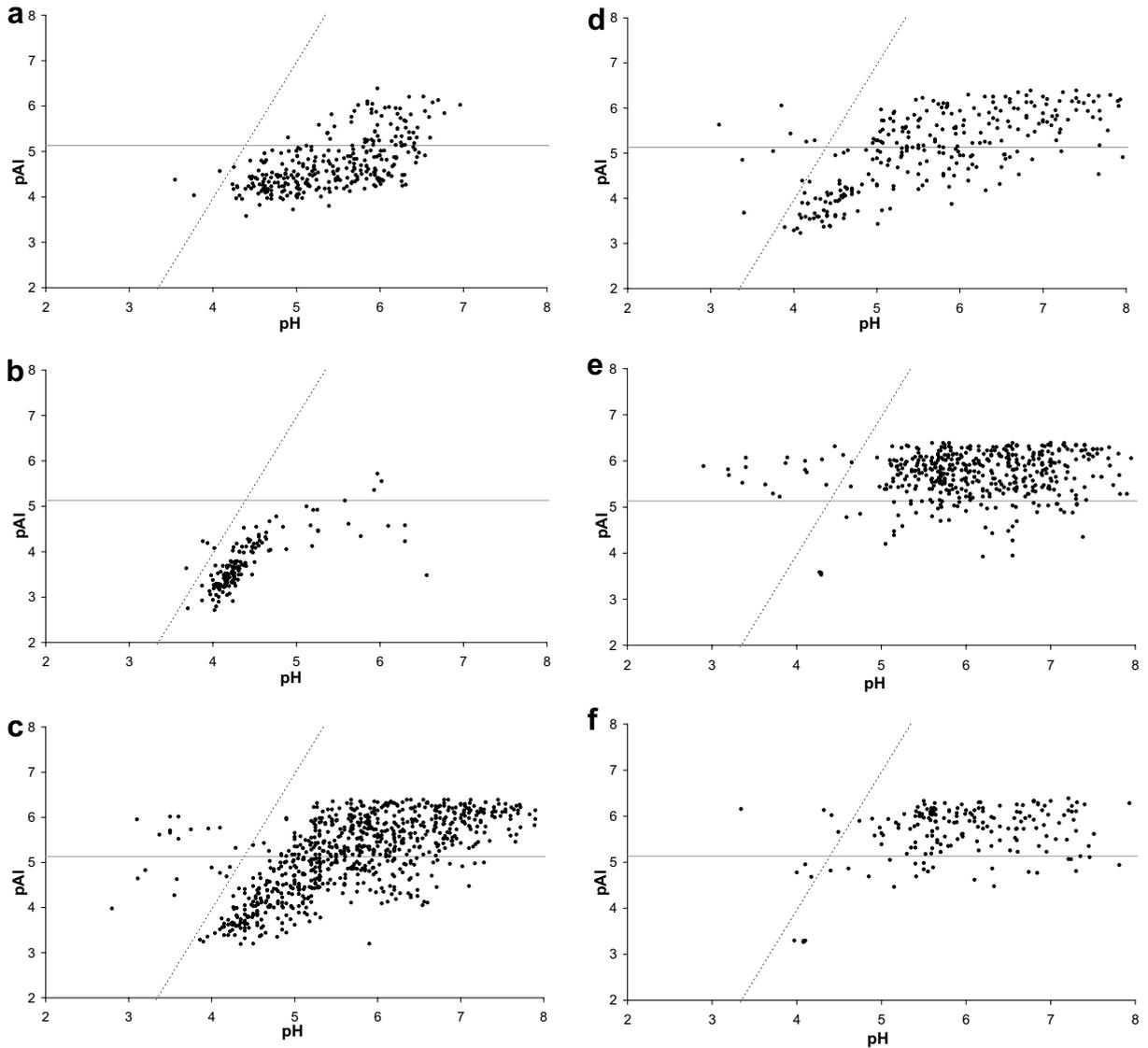


Fig. 2. Relationship between total Al (pAl) and pH (data points ●); (a) agricultural-phreatic; (b) natural-phreatic; (c) agricultural-shallow; (d) natural-shallow; (e) agricultural-deep; and (f) natural-deep; equilibrium line between pAl^{3+} and pH for gibbsite (---) and the Dutch drinking water limit for Al (VROM, 2001) (—) are plotted.

$\log K$ value of 4.84 and slope of 2.10 were found, indicating that no equilibrium with a mineral phase existed. Instead, Al concentrations in this group were assumed to be determined mainly by equilibrium with the organic phase. Other research (e.g., Berggren and Mulder, 1995; Wesselink et al., 1996; Skyllberg, 1999) has shown that equilibrium with the organic phase resulted in a slope around 2, which is in agreement with the value found for the natural-phreatic group. For the agricultural-deep group also a low $\log K$ value and slope were

found. Since this group showed a broad pH range (2.90–8.05), these regression results were thought to result from disequilibrium below pH 4.5. Since most groups show this disequilibrium with mineral phases below pH 4.5, leaving out the measurements below pH 4.5 lead to a better correlation (Table 3b). Regression analysis for $\text{pH} > 4.5$ was not performed for the natural-phreatic group, because the majority of the measurements lie below pH 4.5. The pAl^{3+} pH relations found in Table 3b (fixed and variable slope) are plotted in Fig. 4. Regression on the data

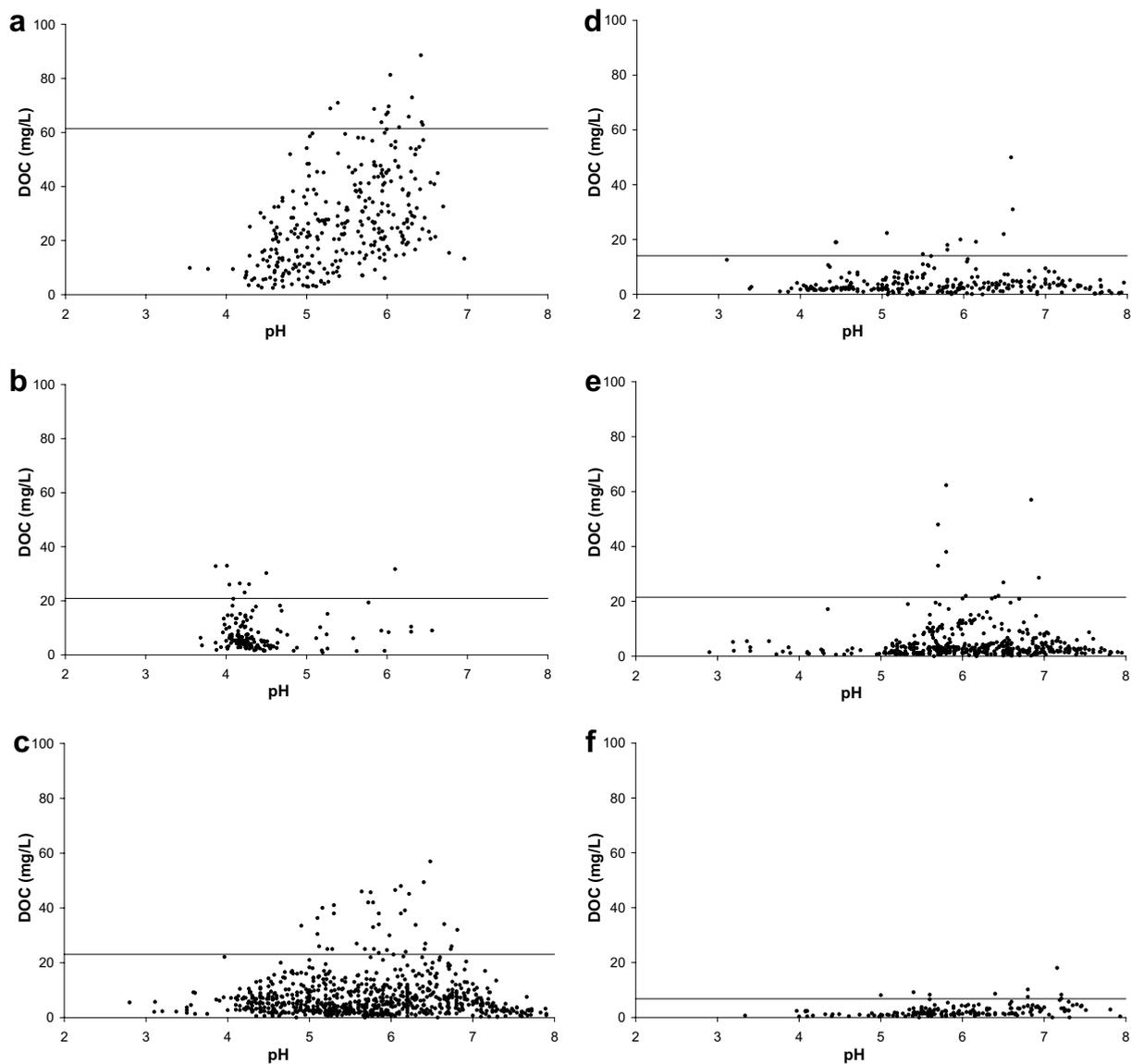


Fig. 3. DOC (mg/L) concentration versus pH shown for each groundwater group; — shows the 95% upper limit of the DOC concentration (mean + 2 × SD.); (a) agricultural-phreatic (61.4 mg C/L); (b) natural-phreatic (20.9 mg C/L); (c) agricultural-shallow (23.1 mg C/L); (d) natural-shallow (14.1 mg C/L); (e) agricultural-deep (21.5 mg C/L); and (f) natural-deep (6.8 mg C/L).

above pH 4.5 (Table 3b) showed very good correlation (R^2 0.926–0.977) for field data sets. Calculated slopes were close to 3 suggesting equilibrium with a mineral $\text{Al}(\text{OH})_3$ phase. Lowest slopes and log K values were found for the deepest groundwater. Land use type did not influence the log K and slope, except for the earlier mentioned natural-phreatic group. Derived log K values (fixed slope) were close to the theoretical equilibrium constant of gibbsite (9.40 at 281 K, Table 1) with satisfactory correlation coefficients.

In Fig. 5 the effect of DOC complexation on total Al concentration is shown for the agricultural-phreatic group (high DOC) and natural-deep group (low DOC). Equilibrium concentrations are shown for the situation with and without DOC complexation. These equilibrium Al concentrations were calculated with derived log K values from Table 3b (slope = 3) and plotted as a function of the pH (Weng et al., 2002b). The DOC concentration was set at the 95% upper limit that was shown in Fig. 3. The upper curve represents the model

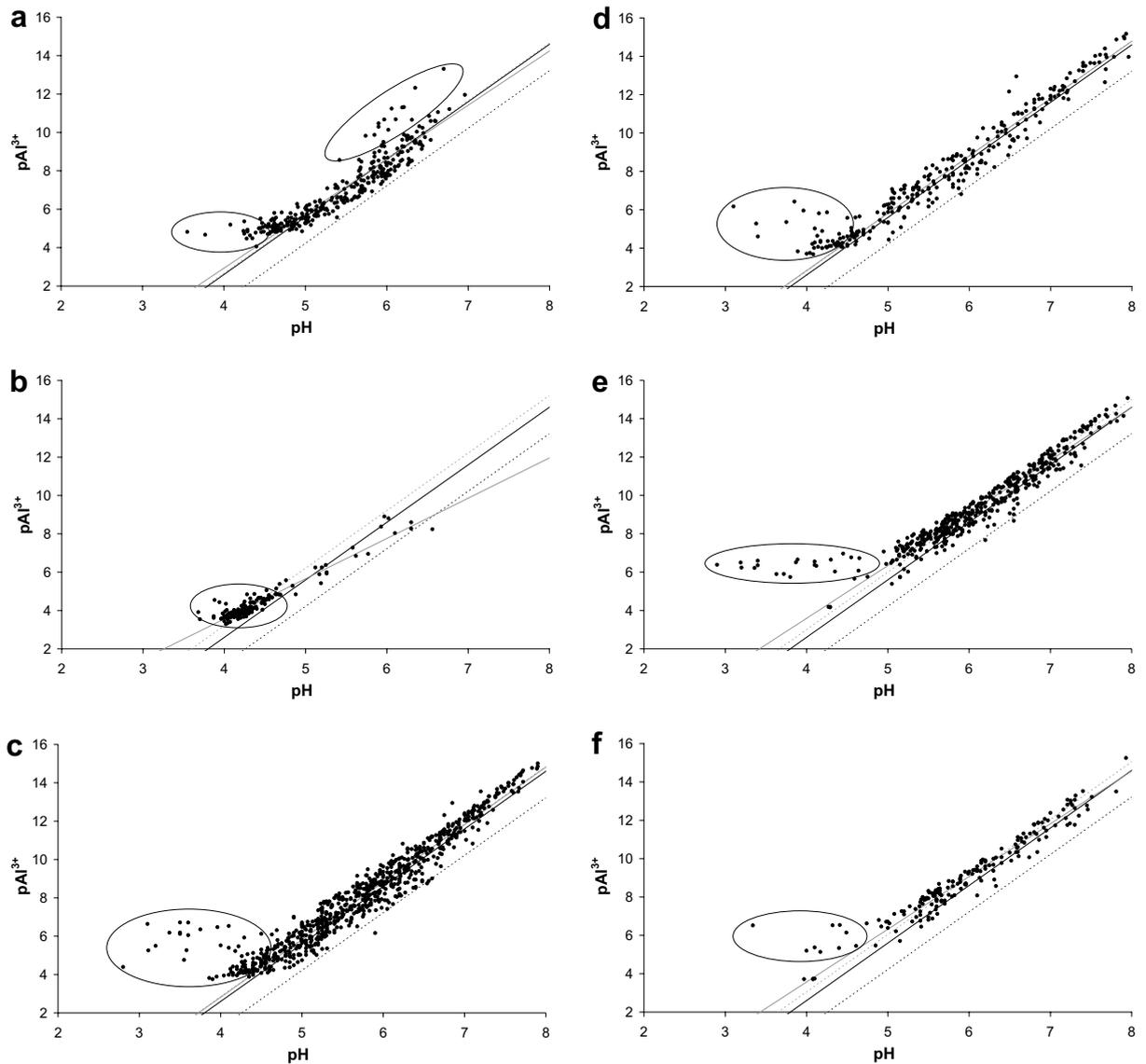


Fig. 4. Relationship between calculated $p(\text{Al}^{3+})$ and pH; data points are shown by circles •. Equilibrium lines are plotted for gibbsite 281 K (—), amorphous $\text{Al}(\text{OH})_3$ 281 K (---). Regression lines from Table 3b (except for natural-phreatic regression lines from Table 3a) are also shown (variable slope (—) and slope = 3 (---)); (a) agricultural-phreatic; (b) natural-phreatic; (c) agricultural-shallow; (d) natural-shallow; (e) agricultural-deep; and (f) natural-deep.

calculation for mineral equilibrium in the absence of DOC. At pH between 4.5 and 8 the DOC complexation did have a significant effect on the calculated Al concentration for the agricultural-phreatic groups, whereas this effect is much smaller for the natural-deep group with lower DOC concentrations. For the agricultural-phreatic group the difference between the Al concentration with and without DOC complexation is about a factor 10 on the Al concentration at pH 5.5.

4. Discussion

The largest differences for Al and DOC occur in the phreatic groups. In this most shallow groundwater, the effect of land use on the studied parameters is the largest. The land use effects disappeared during transport further down in the soil. The buffering capacity of the soil for pH and Al concentration seemed to be large enough and DOC mineralization also continued. However,

Table 3a
Results of regression between pH and pAl^{3+} for the different groundwater groups

	Linear regression			Regression slope = 3	
	log <i>K</i>	Slope	<i>R</i> ²	log <i>K</i>	<i>R</i> ²
Agricultural-phreatic	7.06 (0.35)	2.60 (0.06)	0.846	9.25 (0.04)	0.826
Natural-phreatic	4.84 (0.22)	2.10 (0.05)	0.921	8.79 (0.05)	0.754
Agricultural-shallow	7.21 (0.18)	2.69 (0.03)	0.904	9.01 (0.03)	0.892
Natural-shallow	7.24 (0.27)	2.69 (0.05)	0.924	9.01 (0.05)	0.912
Agricultural-deep	4.61 (0.25)	2.31 (0.04)	0.873	8.85 (0.04)	0.794
Natural-deep	6.06 (0.31)	2.54 (0.05)	0.930	8.84 (0.05)	0.898

Linear regression and regression with a fixed slope of 3; $\log(Al^{3+}) = \log K - \text{slope} \times \text{pH}$; standard deviation between parenthesis.

Table 3b
Results of regression between pH and pAl^{3+} for the different groundwater groups for samples with $\text{pH} \geq 4.5$

	Linear regression			Regression slope = 3	
	log <i>K</i>	Slope	<i>R</i> ²	log <i>K</i>	<i>R</i> ²
Agricultural-phreatic	8.39 (0.38)	2.83 (0.07)	0.926	9.34 (0.04)	0.855
Natural-phreatic	–	–	–	–	–
Agricultural-shallow	9.18 (0.16)	3.00 (0.03)	0.973	9.15 (0.02)	0.947
Natural-shallow	9.13 (0.26)	2.99 (0.04)	0.977	9.20 (0.04)	0.955
Agricultural-deep	7.41 (0.20)	2.75 (0.03)	0.970	9.00 (0.02)	0.934
Natural-deep	7.43 (0.30)	2.75 (0.05)	0.975	8.95 (0.04)	0.943

Linear regression and regression with a fixed slope of 3; $\log(Al^{3+}) = \log K - \text{slope} \times \text{pH}$; standard deviation between parenthesis.

the deep groundwater also showed low pH levels and related high Al concentrations. This indicated that acidification of groundwater does happen in Dutch sandy soils. Relating these high Al concentrations to the Dutch drinking water regulation (VROM, 2001) (0.2 mg Al L^{-1}), it was shown that this limit was exceeded in a several samples (Fig. 2). Phreatic groundwater showed Al concentrations that were for a large part above the drinking water limit. Although this effect diminished further downwards, the deepest groundwater also showed several measurements above or close to this limit. Serious attention should be paid to Al concentrations in groundwater from sandy soils, when this groundwater is to be used for drinking water.

The calculated 95% upper limit of DOC (Fig. 3) was remarkably high for the agricultural-phreatic group, which was already indicated by the median of the DOC concentration (Table 2). Agricultural land use affected the phreatic groundwater resulting in high DOC concentrations. These high DOC concentrations could be explained by the application of organic fertilizers and these high concentrations were pronounced closest to the soil surface. In contrast, the natural-deep groundwater

had the lowest DOC 95% upper limit of all groups. Increased residence time, shown here by the depth of the groundwater, resulted in decreased DOC concentration. During transport through the soil, DOC could have been mineralized or bound to mineral surfaces.

Calculated Al^{3+} showed a strong linear correlation with pH. The complexation of Al by DOC varied between 1% and 99% depending on pH and total DOC concentration of the measurements. Highest complexation of Al was found for the phreatic and shallow groundwater for both agricultural and natural land use. This variation in the amount of complexed Al emphasized the importance of taking complexation with DOC into account when studying Al chemistry of groundwater samples.

Below pH 4.5 some samples were undersaturated for the 3 Al-phases considered in Fig. 4. Previous research has also shown a deviation from the 1:3 relationship between pAl^{3+} and pH at low pH (<4.5). Adams (2000) explained this deviation in soil solutions as the result of equilibrium with an organic phase instead of a mineral phase. However, it might be expected that groundwater (deep) is not in equilibrium with an organic phase

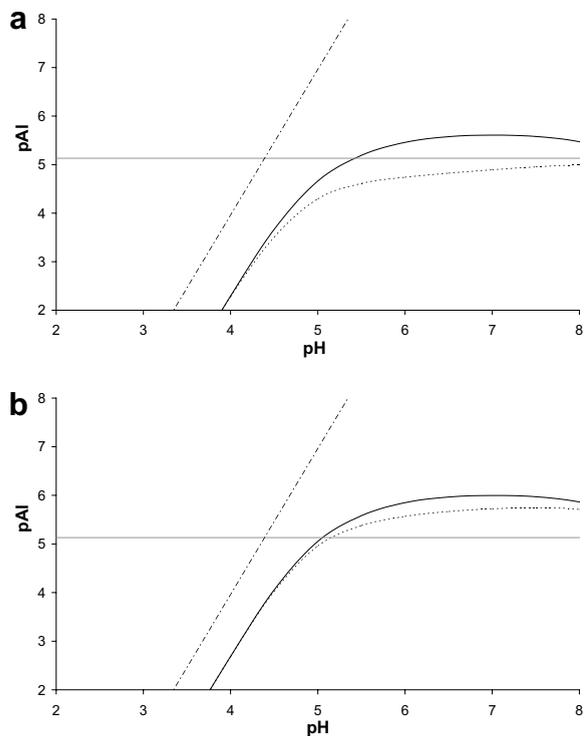


Fig. 5. Effect of DOC complexation on total dissolved Al in equilibrium with an $\text{Al}(\text{OH})_3$ mineral phase with a $\log K$ derived from regression of Table 3b (slope = 3). Results are shown for the two extremes, viz. (a) agricultural-phreatic and (b) natural-deep. Total Al in solution (pAl) plotted versus pH with (---) and without (—) of DOC complexation (used DOC concentrations see text and Fig. 3); the Dutch drinking water limit for Al (VROM, 2001) (—) is also plotted.

because sandy aquifer sediments were mainly low in organic matter and that organic matter is often less reactive (Hartog et al., 2002). Studies on natural waters (Neal, 1988; Haag et al., 2001) have shown that this deviation is the result of equilibrium with other mineral phases, e.g. AlSO_4OH , but minerals like imogolite (Farmer et al., 1980) or kaolinite (Zyseth et al., 1999) could also determine the Al concentration in podzols. Nevertheless, the authors could not find a mineral phase which explained the Al^{3+} activity at low pH. Therefore, the conclusion was reached that the deviating pAl^{3+} was the result of kinetic constraints of dissolution of Al containing minerals. The agricultural-phreatic group also showed the same disequilibrium with the studied mineral phases at a pH around 6.

The importance to take DOC complexation into account follows also from Fig. 5. Equilibrium Al concentration was calculated with $\log K$ values

derived in Table 3b (fixed slope). Using this $\log K$ value implies that equilibrium exists with an $\text{Al}(\text{hydr})\text{oxide}$ with a $\log K$ value derived for a specific groundwater group. At higher pH (5–8) the calculated Al concentration without DOC can be almost more than a factor of 10 lower than with DOC. The graphs also show that this calculated Al concentrations due to DOC were close to the drinking water limit. Since the DOC concentrations decrease with increasing groundwater depth, the influence of DOC complexation on total Al concentrations in groundwater is reduced with increasing groundwater depth.

5. Conclusions

Land use type and depth of the groundwater did affect the pH, Al concentration and DOC concentration in groundwater under Dutch sandy soils. The median pH increased gradually with the depth of the groundwater, because during transport the groundwater is buffered by the soil. The natural-phreatic groundwater showed a relatively low pH, which was also responsible for the very high Al concentrations in the groundwater. DOC concentrations showed increased Al levels for the agricultural-phreatic groundwater that resulted from the application of organic fertilizers on agricultural soils. The relationship between pAl^{3+} and pH showed that the majority of the groundwater samples under sandy soils were in equilibrium with a mineral $\text{Al}(\text{OH})_3$ phase at $\text{pH} > 4.5$. Below pH 4.5 the groundwater samples were mainly in disequilibrium with a mineral phase as a result of kinetic constraints or equilibrium with the organic phase. Equilibrium calculation of the total Al concentration with derived $\log K$ values in the presence and absence of DOC showed the importance of DOC complexation. This complexation is mainly important for the agricultural-phreatic groundwater. Agricultural-phreatic groundwater showed the highest DOC concentrations, whereas the lower DOC concentration in deeper layers resulted in smaller effects on total Al concentration.

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References

- Adams, M.L., 2000. The relationship between soil solution pH and Al^{3+} concentrations in a range of South Island (New Zealand) soils. *Aust. J. Soil Res.* 38, 141–153.
- Berggren, D., Mulder, J., 1995. The role of organic matter in controlling aluminium solubility in acidic mineral soil horizons. *Geochim. Cosmochim. Acta* 59, 4167–4180.
- Berggren, D., Mulder, J., Westerhof, R., 1998. Prolonged leaching of mineral forest soils with dilute HCl solutions: the solubility of Al and soil organic matter. *Eur. J. Soil Sci.* 49, 305–316.
- Bryan, S.E., Tipping, E., Hamilton-Taylor, J., 2002. Comparison of measured and modelled copper binding by natural organic matter in freshwaters. *Comput. Biochem. Phys. C* 133, 37–49.
- Christensen, J.B., Botma, J.J., Christensen, T.H., 1999. Complexation of Cu and Pb by DOC in polluted groundwater: a comparison of experimental data and predictions by computer speciation models (WHAM and MINTEQA2). *Water Res.* 33, 3231–3238.
- Cronan, C.S., Schofield, C.L., 1979. Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the Northeast. *Science* 204, 304–306.
- Cronan, C.S., Walker, W.J., Bloom, P.R., 1986. Predicting aqueous aluminium concentrations in natural waters. *Nature* 324, 140–143.
- Dahlgren, R.A., Driscoll, C.T., McAvoy, D.C., 1989. Aluminum precipitation and dissolution rates in spodosol Bs horizons in the northeastern USA. *Soil Sci. Soc. Am. J.* 53, 1045–1052.
- David, M.B., Driscoll, C.T., 1984. Aluminum speciation and equilibria in soil solutions of a haplorthod in the Adirondak Mountains (New York, USA). *Geoderma* 33, 297–318.
- Edmunds, W.M., Kinniburgh, D.G., 1986. The susceptibility of UK groundwater to acid deposition. *J. Geol. Soc. London* 143, 707–720.
- Farmer, V.C., 1999. The solubility characteristics of organic Al precipitates in allophanic Bs horizons could mimic those of Al-hydroxides and indicate the solubility of associated allophanes. *Eur. J. Soil Sci.* 50, 713–715.
- Farmer, V.C., Russell, J.D., Berrow, M.L., 1980. Imogolite and proto-imogolite allophane in spodic horizons: evidence for a mobile aluminium silicate complex in podzol formation. *J. Soil Sci.* 31, 673–684.
- Ge, Y., MacDonald, D., Sauvé, S., Hendershot, W., 2005. Modeling of Cd and Pb speciation in soil solutions by WinHumic V and NICA-Donnan model. *Environ. Modell. Softw.* 20, 353–359.
- Graf Pannatier, E., Walthert, L., Blaser, P., 2004. Solution chemistry in acid forest soils: are the BC:Al ratios as critical as expected in Switzerland? *J. Plant Nutr. Soil Sci.* 167, 160–168.
- Gustafsson, J.P., Berggren, D., Simonsson, M., Zysset, M., Mulder, J., 2001. Aluminium solubility mechanisms in moderately acid Bs horizons of podzolized soils. *Eur. J. Soil Sci.* 52, 655–665.
- Gustafsson, J.P., Lumsdon, D.G., Simonsson, M., 1998. Aluminium solubility characteristics of spodic B horizons containing imogolite-type minerals. *Clay Miner.* 33, 77–86.
- Guthrie, J.W., Hassan, N.M., Salam, M.S.A., Fafous, I.I., Murimboh, C.A., Murimboh, J., Chakrabarti, C.L., Grégoire, D.C., 2005. Complexation of Ni, Cu, Zn, and Cd by DOC in some metal-impacted freshwater lakes: a comparison of approaches using electrochemical determination of free-metal-ion and labile complexes and a computer speciation model, WHAM V and VI. *Anal. Chim. Acta* 528, 205–218.
- Haag, I., Moritz, K., Bittersohl, J., Lischeid, G., 2001. Factors controlling total concentration and aqueous speciation of aluminium in an acidic headwater stream of the Bavarian Forest National Park: a modelling approach. *Acta Hydrochim. Hydrobiol.* 29, 206–218.
- Hansen, B.K., Postma, D., 1995. Acidification, buffering, and salt effects in the unsaturated zone of a sandy aquifer sediment, Klosterhede, Denmark. *Water Resour. Res.* 31, 2795–2809.
- Hartog, N., Griffioen, J., Van der Weijden, C.H., 2002. Distribution and reactivity of O_2 -reducing components in sediments from a layered aquifer. *Environ. Sci. Technol.* 36, 2338–2344.
- Holmström, S.J.M., Van Hees, P.A.W., Lundström, U.S., 2005. Modelling aluminium chemistry in soil solution of untreated and dolomite treated podzolic soil. *Geoderma* 127, 280–292.
- Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E., McDowell, W.H., 1981. 'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. *Geochim. Cosmochim. Acta* 45, 1421–1437.
- Keizer, M.G., Van Riemsdijk, W.H., 1998. ECOSAT User Manual. Wageningen Agricultural University, Wageningen.
- Kinniburgh, D.G., Van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., Avena, M.J., 1999. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloid. Surface. A* 151, 147–166.
- Kjøller, C., Postma, D., Larsen, F., 2004. Groundwater acidification and the mobilization of trace metals in sandy aquifer. *Environ. Sci. Technol.* 38, 2829–2835.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley Interscience, New York.
- Lofts, S., Tipping, E., 2000. Solid-solution metal partitioning in the Humber rivers: application of WHAM and SCAMP. *Sci. Total Environ.* 251/252, 381–399.
- Lumsdon, D.G., Farmer, V.C., 1995. Solubility characteristics of proto-imogolite sols: how silic acid can de-toxicify aluminium solutions. *Eur. J. Soil Sci.* 46, 179–186.
- Mol, G., Vriend, S.P., Van Gaans, P.F.M., 2001. Environmental monitoring in the Netherlands: past developments and future challenges. *Environ. Monit. Assess.* 68, 313–335.
- Mol, G., Vriend, S.P., Van Gaans, P.F.M., 2003. Feldspar weathering as the key to understanding soil acidification monitoring data: a study of acid sandy soils in the Netherlands. *Chem. Geol.* 202, 417–441.
- Moss, P.D., Edmunds, W.M., 1992. Processes controlling acid attenuation in the unsaturated zone of a Triassic sandstone aquifer (UK), in the absence of carbonate minerals. *Appl. Geochem.* 7, 573–583.
- Mulder, J., Van Breemen, N., Eijck, H.C., 1989. Depletion of soil aluminium by acid deposition and implications for acid neutralization. *Nature* 337, 247–249.
- Neal, C., 1988. Aluminium solubility relationships in acid waters – a practical example of the need for a radical reappraisal. *J. Hydrol.* 104, 141–159.
- Nordstrom, D.K., Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. *Science* 232, 54–56.
- Oste, L.A., Temminghoff, E.J.M., Van Riemsdijk, W.H., 2002. Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration. *Environ. Sci. Technol.* 36, 208–214.

- Palmer, D.A., Wesolowski, D.J., 1992. Aluminum speciation and equilibria in aqueous solution: II the solubility of gibbsite in acidic sodium chloride solutions from 30 to 70 °C. *Geochim. Cosmochim. Acta* 56, 1093–1111.
- Pebesma, E.J., De Kwaadsteniet, J.W., 1997. Mapping groundwater quality in the Netherlands. *J. Hydrol.* 200, 364–386.
- Pinheiro, J.P., Mota, A.M., Benedetti, M.F., 2000. Effect of aluminum competition on lead and cadmium binding to humic acids at variable ionic strength. *Environ. Sci. Technol.* 34, 5137–5143.
- Skyllberg, U., 1999. pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. *Eur. J. Soil Sci.* 50, 95–106.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley, New York.
- Sullivan, T.J., Cosby, B.J., 1998. Modeling the concentration of aluminum in surface waters. *Water Air Soil Poll.* 105, 643–659.
- Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., De Haan, F.A.M., 1997. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol.* 31, 1109–1115.
- Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E., Thornton, I., 2003. The solid-solution partitioning of heavy metals (Cu, Zn, Cd and Pb) in upland soils of England and Wales. *Environ. Pollut.* 125, 213–225.
- Tye, A., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Zhao, F.-J., McGrath, S.P., 2004. Speciation and solubility of Cu, Ni and Pb in contaminated soils. *Eur. J. Soil Sci.* 55, 579–590.
- Ulrich, B., Mayer, R., Khanna, P.K., 1980. Chemical changes due to acid precipitation in a loess-derived soil in central Europe. *Soil Sci.* 130, 193–199.
- Unsworth, E.R., Zhang, H., Davison, W., 2005. Use of diffusive gradients in thin films to measure cadmium speciation in solutions with synthetic and natural ligands: comparison with model predictions. *Environ. Sci. Technol.* 39, 624–630.
- Van der Grift, B., Rozemeijer, J., Van Vliet, M., Broers, H.P., 2004. De kwaliteit van het grondwater in de provincie Noord-Brabant. Rapportage over de toestand van 2003 en de trends in de periode 1992 t/m 2003. NITG-TNO, Utrecht.
- Van Duijvenbooden, W., Gast, L.F.L., Taat, J., 1985. Landelijk meetnet grondwaterkwaliteit: eindrapport van de inrichtingsfase. Staatsuitgeverij, 's-Gravenhage.
- Van Hees, P.A.W., Lundström, U., Danielsson, R., Nyberg, L., 2001. Controlling mechanisms of aluminium in soil solution – an evaluation of 180 podzolic forest soils. *Chemosphere* 45, 1091–1101.
- VROM, 2001. Besluit van 9 januari 2001 tot wijziging van het Waterleidingbesluit in verband met de richtlijn betreffende de kwaliteit van voor menselijke consumptie bestemd water. Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, Den Haag.
- Walker, W.J., Cronan, C.S., Bloom, P.R., 1990. Aluminum solubility in organic soil horizons from northern and southern forested watersheds. *Soil Sci. Soc. Am. J.* 54, 369–374.
- Weng, L., Temminghoff, E.J.M., Lofts, S., Tipping, E., Van Riemsdijk, W.H., 2002a. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environ. Sci. Technol.* 36, 4804–4810.
- Weng, L., Temminghoff, E.J.M., Van Riemsdijk, W.H., 2002b. Aluminum speciation in natural waters: measurement using Donnan membrane technique and modeling using NICA-Donnan. *Water Res.* 36, 4215–4226.
- Wesselink, L.G., Mulder, J., 1995. Modelling Al-solubility controls in an acid forest soil, Solling, Germany. *Ecol. Model.* 83, 109–117.
- Wesselink, L.G., Van Breemen, N., Janssen, P.H., 1996. A simple model of soil organic matter complexation to predict the solubility of aluminium in acid forest soils. *Eur. J. Soil Sci.* 47, 373–384.
- Zysetz, M., Blaser, P., Luster, J., Gehring, A.U., 1999. Aluminum solubility control in different horizons of a podzol. *Soil Sci. Soc. Am. J.* 63, 1106–1115.