

Proton Binding by Groundwater Fulvic Acids of Different Age, Origins, and Structure Modeled with the Model V and NICA–Donnan Model

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The proton binding properties of four fulvic acids from pristine groundwater and leachate-polluted groundwater were measured at four different ionic strengths (0.005–0.12 M) and modeled by the Model V and the NICA–Donnan model in order to evaluate the necessity of detailed proton binding parameters for groundwater fulvic acids. The proton binding parameters derived from the various fulvic acids were very similar, and on the basis of these parameters, it was not possible to distinguish between pristine and polluted groundwater. Normalization of the proton charge density by the proton charge density at pH 7 for each fulvic acid made all four fulvic acids regress to the same curve. The effects of varying the proton binding parameters were evaluated by simulating cadmium complexation using sets of proton binding parameters for the four fulvic acids and default sets of proton binding parameters available in the models WHAM (based on Model V) and Ecosat (based on NICA–Donnan). The Model V was rather indifferent with respect to specific characteristics of fulvic acids proton binding, and for most practical uses, the default values available in the model can be used. The NICA–Donnan model resulted in larger deviations between simulations based on default values and specific parameters. However, the NICA–Donnan database is still rather limited, and specific proton binding parameters should be used until the database providing default values has been extended.

Introduction

The concentration of dissolved organic carbon (DOC) in groundwater varies from less than a few milligrams of C per

liter in most pristine groundwaters up to several hundred milligrams of C per liter in landfill leachate-polluted groundwaters. From the literature, it is known that DOC in groundwater is able to form dissolved complexes with heavy metals (1–4). This may increase the solubility and mobility of heavy metals in groundwater (5). It is therefore important to include the effect of DOC on the mobilization and transport of trace metals and in risk assessment of sites contaminated with heavy metals.

The DOC in groundwater consists primarily of fulvic and humic acids (2, 6, 7), and the ability of these humic substances to form metal complexes depends on the presence of acidic functional groups, such as carboxylic and phenolic groups (8). The metal binding by humic substances varies with the dissociation of the acidic groups, and hence modeling of metal binding by humic substances generally requires proton binding data for the humic substances studied in order to account for the pH effect (8–13). The different models available describing cation binding by humic substances (8, 14–16) employ their own proton binding model with unique combinations of physicochemical equations, assumptions, parametrizations, and data requirements. However, the strength of a model depends on its ability to deal with humic substances of different origin and structure (such as functional group and molecular weight distributions) and with varying solution chemistry (primarily ionic strength). At present, there have been few studies aimed at evaluating different model approaches. Some of the data available appear to conflict with model predictions with respect to the impact of molecular weight and polydispersity (width of the molecular weight distribution) of the humic substances on proton binding at different ionic strengths (11, 17).

The aim of this paper is to evaluate the proton binding properties of fulvic acids of different age and from different environments using two models, representing different modeling approaches; Model V (8) and NICA–Donnan (9, 16, 18). The consequences of the variations observed in proton binding properties of the various fulvic acids were evaluated by simulating cadmium binding using the full speciation models: WHAM for Model V and Ecosat for the NICA–Donnan model, respectively. The necessity of using site-specific proton binding parameters is discussed.

Models

Humic substances are highly heterogeneous at a structural (functional groups) level, and this is reflected by a marked heterogeneity in their ion binding behavior. Models describing ion binding by humic substances can be divided into two categories according to how this heterogeneity is treated. Models either assume a discrete distribution of binding affinities, as in Model V, or a continuous distribution of binding affinities, as in the NICA–Donnan model. These two models also account for the nonspecific binding of counterions but in slightly different ways. The differences in approach are reflected by different sets of preselected (fixed) and adjustable parameters. An overview of the two models and their parameters is given in Table 1.

Analysis of the proton binding curves of humic substances measured over a wide pH range usually shows evidence for a bimodal distribution in the site affinity distribution. A peak centered around $pK \approx 3$ is often thought to be associated with carboxylic sites while a more diffuse peak at pK 8–10 is often associated with phenolic sites. This is clearly an oversimplification and, for example, phenolic groups are generally believed to include also enolic and strongly acidic alcoholic groups.

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TABLE 1. Characteristic Features of the Applied Models [Based On Tipping and Hurley (8); Benedetti et al. (9); Kinniburgh et al. (16)]

	Model V	NICA–Donnan
basic approach	cation binding to chemically distinct discrete binding sites, taking nonspecific electrostatic interactions into account	specific binding of cations to humics (nonideal) and nonspecific electrostatic binding of cations to residual negative charge
description of binding sites	bimodal, discrete distribution, two types of sites resembling carboxylic and phenolic sites	bimodal, continuous distribution of proton affinities resembling carboxylic and phenolic sites
specific binding	monodentate and bidentate; corrected for electrostatic effect	monodentate; corrected for electrostatic effect
nonspecific binding	Boltzmann factor; accumulation of counterions in the diffuse double layer estimated with Donnan-type expression	Boltzmann factor related to the Donnan potential; accumulation of counterions in variable volume “gel” phase
adjustable, physical–chemical parameters	two median intrinsic proton binding constants for carboxylic and phenolic sites (K_A and K_B)	two median intrinsic proton binding constants for carboxylic (K_{H1}) and phenolic sites (K_{H2})
adjustable, model-related parameters	density of carboxylic sites (n_A) parameters determining the spread of the binding constants (ΔpK_A and ΔpK_B) parameter P determining the electrostatic interaction factor	density of each type of sites (Q_{max1} and Q_{max2}) parameters related to the apparent heterogeneity (width of the distribution), (m_{H1} and m_{H2}) Donnan volume, parameter b , related to the Donnan volume
fixed, model-related parameters	number of phenolic sites (n_B) relative to carboxylic sites ($n_B = n_A/2$) proportion of monodentate sites that form bidentate sites for metal binding molecular weight (1000–2000) and size of the humic molecules (spherical with radii from 0.65 to 0.82 nm)	relationship between solution ionic strength and Donnan volume (empirical relation)

Basic Concept of the Model V. Model V has been described in detail by Tipping and Hurley (8) and Tipping (19). The model is a discrete binding site model in which binding is modified by electrostatic interactions. There is an empirical relation between net humic charge and an electrostatic interaction factor. The model also takes into account the accumulation of counterions in the diffuse layer via a Donnan-type expression. The discrete binding sites are represented by two types of sites (types A and B), and within each type of site there are four different sites present in equal amounts. The two types of sites are described by intrinsic proton binding constants (pK_A and pK_B) and spreads of the values (ΔpK_A and ΔpK_B) within each type of sites. There are n_A (mequiv kg⁻¹) A-type sites (associated with carboxylic type groups) and $n_B = n_A/2$ (mequiv kg⁻¹) B-type of sites (often associated with phenolic type groups).

Metal binding occurs at single proton binding sites or by bidentate complexation between pairs of sites depending on a proximity factor that defines whether pairs of proton binding groups are close enough to form bidentate sites. The two types of sites (A and B) have separate intrinsic exchange constants (pK_{MHA} and pK_{MHB}). It is implicit in Model V that the variation in the binding affinities of the proton and metal ions on monodentate sites are perfectly correlated, i.e., a high proton affinity site also has a high affinity to all metal ions. However, the introduction of bidentate sites reduces the correlation between the proton affinity distribution and the metal ion affinity distribution.

Basic Concept of the NICA–Donnan Model. The Non-Ideal Competitive Adsorption (NICA) model is described in full by Benedetti et al. (9). The NICA model separates the intrinsic chemical heterogeneity of the humic material (which affects binding of all ions) from ion-specific effects of each particular ion. The NICA–Donnan model also considers the nonspecific binding of electrolyte ions by including a simple Donnan model in which the Donnan volume is the key parameter (16, 18). The Donnan potential is applied to both the specific binding and the nonspecific binding. Implicit in the NICA–Donnan model is a continuous distribution of

proton and metal ion binding affinities, but unlike in Model V, these affinities are no longer necessarily fully correlated. As with Model V, the overall proton affinity distribution is composed of contributions from both carboxylic and phenolic type groups.

The proton binding data give values of the modal proton binding constants (K_{H1} and K_{H2}) for the carboxylic and phenolic type sites, the total number of sites (Q_{max1} and Q_{max2}), and an apparent heterogeneity made up from the combined effect of nonideal behavior of the proton and chemical heterogeneity (m_{H1} and m_{H2}). The value of m_{Hi} is the product ($n_{Hi} \cdot p$) of the nonideal behavior of the proton ($0 < n_{Hi} \leq 1$) and the width of the distribution due to the intrinsic chemical heterogeneity of the dissolved organic matter ($0 < p \leq 1$). The values n_{Hi} and p can only be resolved from multicomponent (metal binding) data. Modeling metal binding requires four new parameters for each metal ion: two model binding constants for the metal ion (K_{i1} and K_{i2}) and two nonideality coefficients (n_{i1} and n_{i2}).

Experimental Section

Sites. Two leachate-polluted groundwater samples (L1 and L2) were obtained downgradient of Vejen Landfill, Vejen, Denmark. The two samples were taken 7 m downgradient of the landfill where leachate has entered the aquifer since the mid-1970s. The sampled zone was anoxic with methane and no sulfate. For a more detailed description of the sampling procedure, see Christensen et al. (5). Pristine groundwater was sampled from two Danish aquifers at Skagen and Tuse. The redox conditions at Skagen were anaerobic with methane and at Tuse were anoxic without nitrate but with sulfate. A detailed description of the sampling sites, sampling procedures, and site characterization is available elsewhere (6).

Isolation and Purification of the Humic Substances. The procedure used for isolation and purification of fulvic acids from the leachate-polluted samples (7) was based on the method described by Thurman and Malcolm (20) and was modified slightly for the pristine groundwater samples (21).

TABLE 2. Selected Structural Data for the Fulvic Acids Studied [Grøn et al. (6); Christensen et al. (7)]

	fraction of groundwater DOC (%)	E_4/E_6 ^c	age (years before present)	weight average molecular weight, M_w (Da)	polydispersity ^d	O/C atomic ratio	carboxylic group density ^e (equiv kg ⁻¹)	phenolic group density ^f (equiv kg ⁻¹)
Fulvic Acids								
Tuse ^a	58	18	4500 ^f	1904	1.3	0.66	6.2	2.7
Skagen ^a	67	18	2300 ^f	1670	1.6	0.54	6.2	2.1
L1 ^b	59	16	<30	1880	1.5	0.62	6.1	1.3
L2 ^b	67	18	<30	1770	1.4	0.60	5.9	0.8

^a Modified from Grøn et al. (6). ^b Christensen et al. (7). ^c E_4/E_6 refers to the absorbance ratio of light at 465 and 665 nm, respectively. ^d Polydispersity refers to the width of the molecular weight distribution. ^e Estimated from direct, aqueous titration with end points at pH values of 8 and 11. ^f ¹⁴C dating.

TABLE 3. Content of Inorganic Compounds in the Isolated and Purified Fulvic Acids

	Tuse		Skagen		L1		L2	
	mequiv kg ⁻¹	mM	mequiv kg ⁻¹	mM	mequiv kg ⁻¹	mM	mequiv kg ⁻¹	mM
Anions								
sulfate	32.6	0.0166	73.9	0.0379	20.9	0.0108	43.8	0.0221
chloride	19.14	0.0195	8.83	0.00906	11.0	0.0113	3.4	0.0034
Cations								
protons ^a	2255	2.313	1889	1.938	2171	2.257	2178	2.199
sodium	9.13	0.0093	91.3	0.0937	2.04	0.0021	3.80	0.00384
calcium	<25	<0.025	<25	<0.026	<25	<0.024	<25	<0.025
magnesium	<5	<0.005	<5	<0.005	<5	<0.005	<5	<0.005
potassium	6.9	0.0070	11.5	0.0118	2.36	0.0024	5.18	0.0052
ammonium	26.3	0.0268	39.0	0.0400	26.5	0.0027	12.9	0.0130
charge balance ^b	+2246		+1948		+2170		+2153	

^a The content of protons is determined from the initial pH in the acid/base titrations. ^b The substantial net positive charge is presumably balanced by negative sites on the fulvic acids.

The fulvic acids were preconcentrated using XAD-8 resin and further purified, proton saturated, and lyophilized before use.

Characteristics of the Fulvic Acids. The four fulvic acids studied (two from pristine groundwater and two from leachate-polluted groundwater) have all been characterized previously by Grøn et al. (6) and Christensen et al. (7). Selected structural characteristics are given in Table 2. The fulvic acids originated from very different environments with respect to age, redox conditions, microbial reactions, and substrates and represent a range of Danish groundwater fulvic acids.

The fulvic acids constituted approximately 60% of the DOC in all cases. Common features were a low degree of humification (high E_4/E_6 ratio), relative high polarity (high O/C ratio), and small molecules with a narrow molecular weight distribution (polydispersity ~1.5). The contents of carboxylic and phenolic groups were estimated by a simple titration performed previously by Christensen et al. (7). On the basis of these simple titrations, the number of phenolic groups is expected to be about 34–44% of the number of carboxylic groups for the fulvic acids from pristine groundwater and 14–20% for the fulvic acids from the leachate-polluted groundwaters.

Potentiometric Titrations. The potentiometric titrations were carried out using a fully automated titration system (22). The titration method is described in detail by Milne et al. (13). It was slightly modified in order to perform titrations at different ionic strengths on the same sample in series of continuous base and acid titrations. For potentiometric titrations, approximately 50 mg of humic substance was dissolved/suspended in 50 mL of Milli-Q water, giving a concentration of approximately 1 g L⁻¹. The titrations were carried out in a thermostated reaction vessel (25 °C) under a nitrogen atmosphere in order to exclude carbon dioxide. The pH was read using two pH electrodes (Russell pH Ltd)

calibrated with pH 4.005, 6.857, and 9.182 buffers before and after each titration. The calibration after the titration was used as a control of the electrode drift. The drift of the electrodes was in all titrations less than 3 mV. A single calomel reference electrode was connected to the vessel via an electrolyte bridge (0.1 M KNO₃). The pH values read by the duplicate pH electrodes were averaged; they usually agreed within ±0.002 pH (0.1 mV). After each addition of titrant, the rate of drift of each electrode was measured over a 1-min interval, and the readings were accepted when the rate of drift for both electrodes was less than 0.2 mV min⁻¹. For each data point, a maximum time for monitoring the pH drift was set to 20 min. If the drift criterion was not satisfied within this time, the titration was continued and the data point discarded. The titration of each sample of humic substance included four cycles at increasing ionic strengths. One cycle includes one base titration (~0.1 M KOH, standardized against the acid titrant) and one acid titration (0.1 M HNO₃). Before the start of the first titration cycle, the pH was read in the solution, and then KNO₃ was added in order to obtain the initial ionic strength. Data points were collected at approximately 5 mV intervals in the range of -200 to 200 mV (pH range 3.8–10.6). This range of pH was chosen to avoid errors in blank subtraction at very high and very low pH. After finishing the first acid titration, KNO₃ was added to obtain the ionic strength for the second cycle, and the titration was continued. Analysis of inorganic salt residuals in fulvic acid samples showed that a correction for the salt added with the fulvic acids was not necessary (Table 3). The contribution of the excess of cations and anions to the ionic strength was less than 5%.

Data Analysis. The ionic strengths were calculated for each data point taking into account both the background electrolyte ions and free H⁺ and OH⁻. From the calculated ionic strength, the activity coefficients were determined using the extended Debye–Hückel equation. Blank correction was

carried out by calculating, for each data point, the amount of titrant required to increase the pH of an equivalent volume of background electrolyte solution. This was subtracted from the volume of titrant used for the sample.

Modeling

The first modeling exercise fitted the experimental proton binding data to Model V and the NICA–Donnan model in order to obtain estimates of the characteristic proton binding parameters of the models for the four fulvic acids. However, the two models require different input files as shown below. Both models used seven parameters to describe the proton binding. One parameter was kept constant, and six were adjustable.

The second modeling exercise attempted to evaluate how important it is to have specific proton binding data for predicting the cadmium complexation by fulvic acids. Since the model parameters describing the proton binding in both models are partially correlated, it does not make much sense to vary them individually and from the goodness of the model simulations (rmsd in Model V or R^2 in the NICA–Donnan model; see later) to judge the sensitivity of the different parameters. In addition, the interest in proton binding of fulvic acids is primarily a basis for modeling complexation of heavy metals with fulvic acids. Therefore, it was chosen to evaluate the overall effect of the proton binding datasets of the four fulvic acids by simulating Cd binding using the specific proton data and the general Cd binding constant available as a default parameter in both models. For comparison also the default parameters for proton binding were used together with the default Cd binding parameter. The details are described below.

Model V. The input file for fitting proton binding data to Model V contained the net charge on the fulvic acids (Q) versus the pH at four different ionic strengths (0.005, 0.01, 0.03, and 0.12 M). Both acid and base titration data were used for modeling. The net charge on the fulvic acids (Q) was calculated from the initial charge on fulvic acids (Q_{ini}) and from changes in the charge on the fulvic acids during titration (ΔQ) derived from changes in pH ($Q = Q_{\text{ini}} + \Delta Q$). The initial charge on the fulvic acids (Q_{ini}) was estimated from the excess of cations (including H^+) over anions contained in the fulvic material (Table 3). The excess of H^+ is based on pH measurements after dissolution of the fulvic material and before adding salt (KNO_3).

NICA–Donnan Model. The input file for fitting proton binding data to the NICA–Donnan model consisted of the changes in charge on the fulvic acids (ΔQ), estimated from the blank corrected volume of acid/base added during the titration versus concentration of H^+ at three different ionic strengths (0.01, 0.03, and 0.12 M). Both acid and base titration data were used for fitting the model.

Metal Binding. Binding of cadmium to fulvic acids from pristine and leachate-polluted groundwater was modeled using WHAM (Model V; 23) and Ecosat (NICA–Donnan; 24). The calculations were made for pristine groundwater assuming a matrix of 10^{-3} M CaCl_2 (ionic strength 0.003 M), pH = 6.60, and a fulvic acid concentration varying from 0 to 50 mg of C L^{-1} . For leachate-polluted groundwater, the composition of the matrix was assumed to be as described by Christensen et al. (5); L1: pH = 6.60, 15.53 mM Na^+ , 13.43 mM NH_4^+ , 2.77 mM Ca^{2+} , 1.19 mM Mg^{2+} , 4.76 mM K^+ , 19.94 mM Cl^- (ionic strength 0.04 M). The fulvic acid concentration was varied from 0 to 300 mg of C L^{-1} . The total cadmium concentration was fixed at an environmentally realistic concentration (4.44×10^{-5} mM Cd equal to $5 \mu\text{g L}^{-1}$). The calculations were performed using the proton binding data obtained in this work and a default set of proton binding parameters provided with the models. To use the Ecosat model, it was necessary to assume that $n_{\text{H1}} = 1$ and that p

was identical for both type of sites. These assumptions were due to the fact that only m_{H1} is known from fitting proton binding parameters and the Ecosat model operates with n_{H1} and $p(m_{\text{H1}} = n_{\text{H1}}p)$. It should be noted that the default metal binding constants contained in the models were not evaluated in this paper but kept constant.

Results and Discussion

From the raw titration data, the net charge on the fulvic acids (Q , equiv kg^{-1}) was calculated and plotted versus pH as series of proton binding curves (Figures 1 and 2). The same figures show the model fitted proton binding curves for the Model V and the NICA–Donnan model, respectively.

Normalization. In general, the shapes of the curves were very similar for all fulvic acids, and the curves obtained at different ionic strength (0.005, 0.01, 0.03, and 0.12 M) were also similar in shape for all fulvic acids. The strong similarity in shape of the charging curves of the four fulvic acids can be demonstrated by normalizing the data. The proton charge density was normalized to the charge density at pH 7 and an ionic strength of 0.12 M (Figure 3). The normalized charge density, Q' , as a function of pH, is then given by

$$Q'(\text{pH}) = \frac{Q_{\text{H}}(\text{pH})}{Q_{\text{H}, \text{pH}=7, I=0.12}} \quad (1)$$

This normalization means that each of the curves is constrained to pass through the point (pH 7, $I = 1.0$). As can be seen from Figure 3, the four curves show remarkable concordance. This demonstrates that these fulvic acids show similar charging behavior subject to a single scaling factor that is related to the overall charge density. In practice, because the charge at pH 7 for the fulvic acids is mainly determined by the number of carboxylic type groups, this form of normalization can be expected to be particularly sensitive to the ratio of carboxylic to phenolic type sites.

Hysteresis Effects. Differences between the titration curves for the first titration with base and the first titration with acid were observed for all titrated fulvic acids and most pronounced between pH 6 and pH 9. This effect decreased as the fulvic acids underwent repeated titrations, and the ionic strength increased, but it did not disappear completely. Similar observations were made by Paxéus and Wedborg (25) and Milne et al. (13).

Effect of Ionic Strength. The effect of changing the ionic strength from about 0.005 to 0.12 M can be seen in Figures 1 and 2 for the four fulvic acids. The charge (Q , equiv kg^{-1}) on the fulvic material became more negative as the ionic strength increased. The dependence of the ionic strength was greatest at low pH as the titration curves for each ionic strength were nearly parallel until about pH 8, but above pH 8 the titration curves seemed to converge. In these experiments we found that by changing the ionic strength from about 0.005 to 0.12 M the charge on the fulvic acids became about 0.30 equiv kg^{-1} more negative at pH 4. The ionic strength effect was described from the acid curves in order to minimize the initial dispersion/aggregation problems, although the fulvic acids seemed to have been dissolved very well at all times. These findings were reasonable according to results reported in the literature. Almost parallel titration curves at different ionic strengths with greatest dependence of ionic strength at low pH were also observed by Milne et al. (13) and Bartschat et al. (14). The changes in charge on the humic material found by Milne et al. (13) and Bartschat et al. (14) were 0.4–0.45 equiv kg^{-1} on changing the ionic strength from 0.001 to 0.1 M. This was a slightly greater ionic strength effect than observed in these experiments.

Model V. Proton binding parameters for Model V are given in Table 4, and for comparison this table also contains

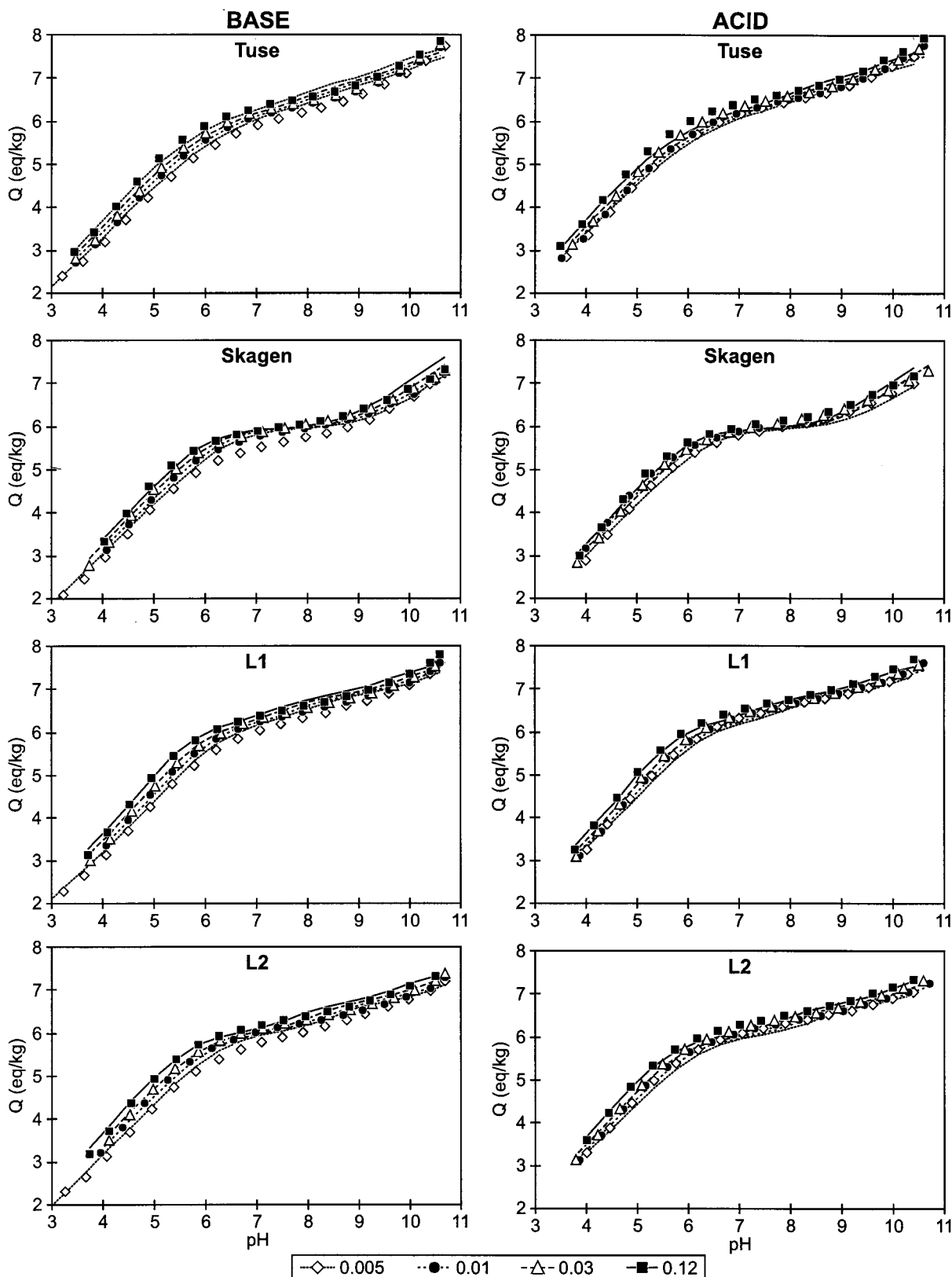


FIGURE 1. Proton binding curves. Plots of the observed and fitted charge (Q , equiv kg^{-1}) versus pH using Model V for fulvic acids from pristine (Tuse and Skagen) and leachate-polluted (L1 and L2) groundwater. The density of data of the experiments was $5\times$ greater than shown but was reduced for clarity.

some Model V parameters estimated previously from literature data (4, 8, 26). The proton binding parameters obtained for Model V in this work were average values of the acid and base titrations. Plots of the observed and fitted fulvic charges against pH are shown in Figure 1.

The content of carboxylic groups (n_A) estimated in Model V were in good agreement with the results of the simple titration (Table 2) showing a maximal deviation of 11%. The content of carboxylic groups found for fulvic acids from leachate-polluted and pristine groundwater was higher than

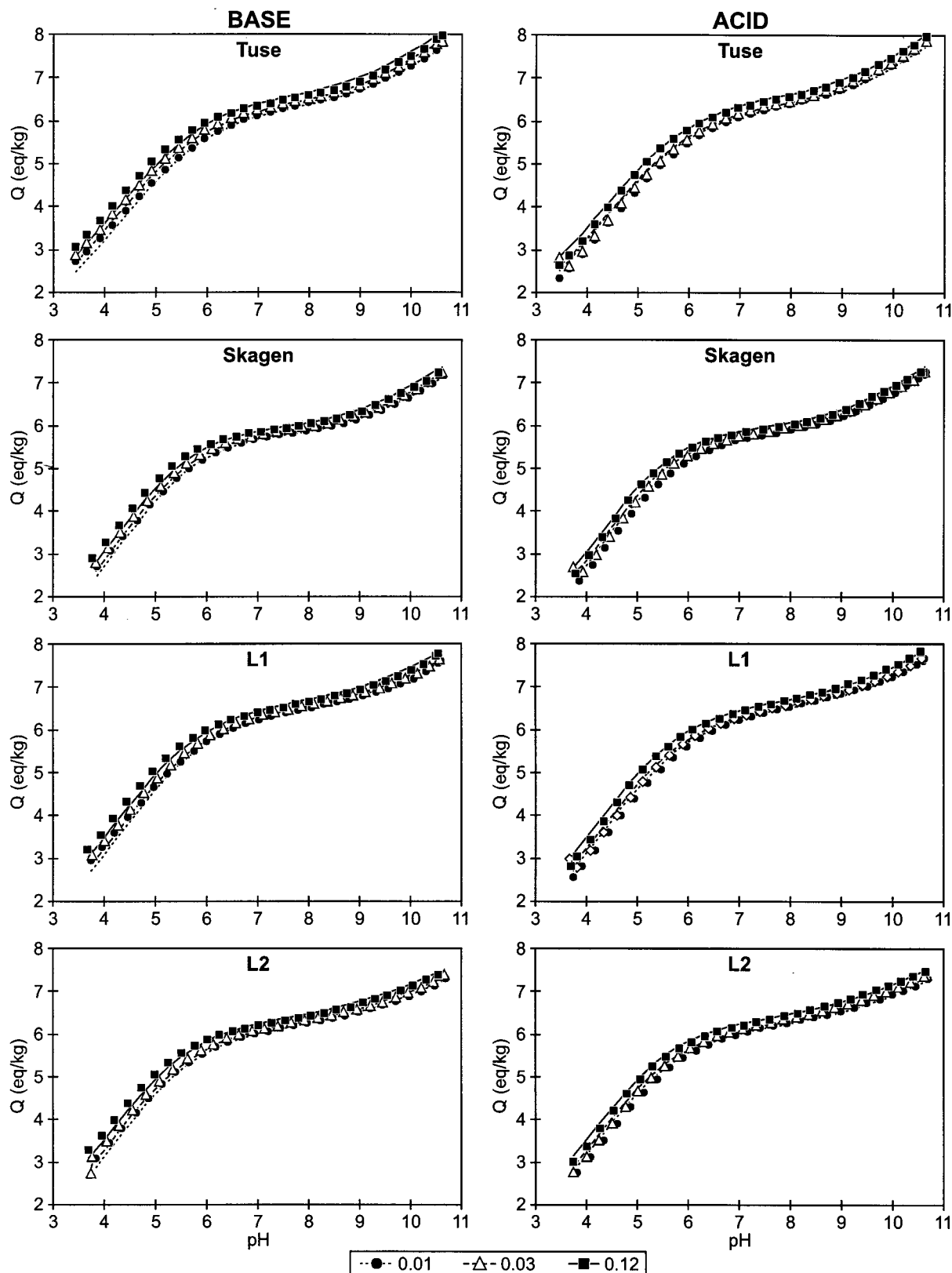


FIGURE 2. Proton binding curves. Plots of the observed and fitted charge (Q , equiv kg^{-1}) versus pH using the NICA–Donnan model for fulvic acids from pristine (Tuse and Skagen) and leachate-polluted (L1 and L2) groundwater. The changes in charge (ΔQ , equiv kg^{-1}) have been converted to Q using the initial charge (Q_{ini}) calculated from the titrations data. The density of data of the experiments was $3\times$ greater than shown but was reduced for clarity.

observed by Lead et al. (26) and Tipping and Hurley (8). Higgo et al. (4) also estimated the content of carboxylic groups in fulvic acids isolated from groundwater using Model V and found substantially greater values than found in this work.

The content of phenolic groups (n_B) in Model V is assumed to be 50% of the abundance of the carboxylic groups. This was based on published data for different humic substances (27). For fulvic acids from pristine and leachate-polluted

TABLE 4. Parameters Derived from Model V for Proton Binding to Fulvic Acids from Pristine (Tuse and Skagen) and Leachate-Polluted (L1 and L2) Groundwater^a

	$n_A \times 10^3$ (mequiv kg ⁻¹)	$n_B \times 10^3$ (mequiv kg ⁻¹)	pK _A	pK _B	ΔpK_A	ΔpK_B	-P	rmsd ^f (equiv kg ⁻¹)
Fulvic Acids								
Tuse	5.57	2.78 ^b	3.13	8.39	2.94	5.29	68.3	0.120
Skagen	5.96	2.98 ^b	3.62	10.10	3.19	2.49	63.4	0.110
L1	5.50	2.75 ^b	3.14	8.01	3.14	6.55	77.5	0.100
L2	6.01	3.01 ^b	3.28	10.60	2.95	6.49	87.0	0.100
Literature Values								
average FA ^c	4.73		3.26	9.64	3.34	5.52	103	
groundwater FA ^d	8.88		3.46	10.02	2.32	10.77	40.1	
groundwater FA ^d	7.57		3.20	10.20	2.37	5.04	71.4	
aquatic FA ^e	4.9		3.2	8.5	3.0	4.1	117	

^a Model V was fitted with six adjustable parameters (symbols used are defined in Table 1). ^b n_B has been fixed at a value equal to $n_A/2$. ^c Tipping and Hurley (8). The average parameters for fulvic acids are based on 5–8 fulvic acids from different origins. ^d Higgo et al. (4). ^e Lead et al. (26). The origin of the fulvic acid is not specified in the reference. ^f Root mean square deviation.

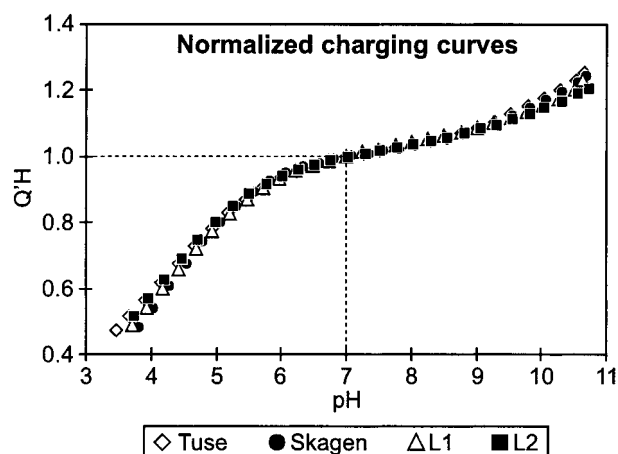


FIGURE 3. Normalized charging curves for fulvic acids from pristine (Tuse and Skagen) and leachate polluted groundwater fulvic acids (L1 and L2). The curves (ionic strength 0.12 M) are normalized with respect to the charge at pH 7.

groundwater, the agreement between this assumption ($n_B = 50\%$ of n_A) and the results of the simple titrations ($n_B = 15\text{--}30\%$ of n_A) seemed to be poor. However, this assumption was maintained in this work for the following reasons: First, in the simple titration, the content of phenolic groups was operationally defined (acidic groups between pH 8 and pH 11). Second, in the simple titration, the blank subtraction was done by titration of the electrolyte at high pH where the errors may have been large. The titration data presented in this work were corrected theoretically as described previously. Third, the phenolic groups are poorly defined in the curves given in Figure 1, and since many of the groups remain untitrated even at pH 10.5, estimation of the total number of such sites (titrated and nontitrated) is subject to errors. Thus, adjusting n_B would lead to poorer definition of the other parameters in the model.

The proton binding constants for the carboxylic groups (pK_A) and the phenolic groups (pK_B) were within the ranges of values observed by Tipping and Hurley (8), Higgo et al. (4), and Lead et al. (26). The pK_A values of the carboxylic acids correspond well with pK_A values found for simple aliphatic and aromatic mono- and polycarboxylic acids. The pK_B values found for the phenolic groups fell into two groups at about pH 8 and pH 10. The pK_B values were lower than found in simple phenols and are more consistent with phenols in which the aromatic ring system contains strongly electron-withdrawing substituents, such as keto groups (27, 28). A pK_B value of 10 for groundwater fulvic acids was also observed by Higgo et al. (4), whereas a pK_B of 8 was reported

by Lead et al. (26) for aquatic fulvic acids. The spread in the pK values (ΔpK_A and ΔpK_B) for the fulvic acids are within the ranges reported in the literature.

The electrostatic effect ($-P$) was similar for the fulvic acids and in good agreement with values reported for groundwater fulvic acids by Higgo et al. (4) but lower in magnitude than the values reported by Tipping and Hurley (8) and Lead et al. (26). A low electrostatic effect suggests low molecular weight material, and this was in agreement with the results of the characterization of the fulvic material showing small molecules with a narrow weight distribution (7).

It can be concluded that Model V was an adequate model for describing the proton binding properties of fulvic acids isolated from pristine and leachate-polluted groundwater. Generally, the proton binding parameters estimated by Model V for fulvic acids from leachate-polluted and pristine groundwater were very similar. In modeling proton binding properties of the dissolved fulvic acids, there is no need to distinguish between polluted and pristine groundwater.

NICA–Donnan Model. Modeling the proton titration data with the NICA–Donnan model, it was not possible to obtain a good fit between the observed and fitted fulvic charge when all four ionic strengths were considered. This was due to a pronounced hysteresis observed especially between the first and the second titration cycles. It was therefore necessary to exclude the first titration with base and acid (ionic strength 0.005 M). The estimated parameters for the NICA–Donnan model presented in Table 5 are therefore based on three ionic strengths (0.01, 0.03, and 0.12 M). Very few NICA–Donnan proton binding parameters exist in the literature for humic substances, and most of them have been derived from purified and extracted humic acid. Only one data set on groundwater fulvic acid (Broubster; 29) is available and is also included in Table 5 for comparison. Plots of observed and fitted charge versus pH are given in Figure 2.

The contents of carboxylic groups ($Q_{\max 1}$) were similar for all fulvic acids. A good agreement was obtained by comparing these estimates to values obtained by simple titration (Table 2). The contents of carboxylic groups in our fulvic acids were lower than for the Broubster groundwater fulvic acid (29) but were about twice as high as those reported in the literature for humic acids (9, 16, 30).

To be able to obtain a reasonable fit of the proton binding parameters for the fulvic acids, it was necessary to fix one parameter for the phenolic groups at a prefixed value. To do the modeling, by Model V and the NICA–Donnan model in as similar a way as possible, we chose to fix the content of phenolic groups ($Q_{\max 2}$) at 50% of carboxylic groups (done by iteration in the modeling procedure).

TABLE 5. Parameters Derived from the NICA–Donnan Model for Proton Binding to Fulvic Acids from Pristine (Tuse and Skagen) and Leachate-Polluted (L1 and L2) Groundwater^a

	<i>b</i>	$Q_{\max 1}$ (equiv kg ⁻¹)	$-\log K_{H1}$	m_{H1}	$Q_{\max 2}$ (equiv kg ⁻¹)	$-\log K_{H2}$	m_{H2}	<i>R</i> ²
Fulvic Acids								
Tuse	0.91	5.65	3.44	0.52	2.82 ^b	9.49	0.48	0.996
Skagen	0.90	5.61	3.39	0.62	2.80 ^b	9.51	0.47	0.996
L1	0.84	6.31	3.15	0.52	3.15 ^b	9.89	0.40	0.996
L2	0.87	5.74	3.19	0.56	2.87 ^b	9.93	0.34	0.996
Literature Values								
peat HA ^c	0.43	2.76	2.99	0.45	3.33	8.64	0.32	0.998
peat HA ^d (NICA)	— ^g	2.48	4.60	0.44	1.93	9.34	0.38	—
HA extracted wood ^e	—	2.18	5.12	0.46	1.54	9.78	0.48	—
groundwater FA ^f	0.72	7.68	2.19	0.29	2.29	8.30	0.25	0.996

^a The NICA–Donnan model was fitted with seven adjustable parameters (symbols used are defined in Table 1). ^b $Q_{\max 2}$ has been fixed at a value equal to $Q_{\max 1}/2$. ^c Kinniburgh et al. (16). ^d Benedetti et al. (9). ^e Temminghoff et al. (30). ^f Milne et al. (29). Groundwater from Broubster. The m_{H1} and m_{H2} values has been calculated from n_H and p values. The p value has been fixed based on results from peat HA (16). ^g —, not reported. b is a parameter related to the size of the variation of Donnan volume with ionic strength.

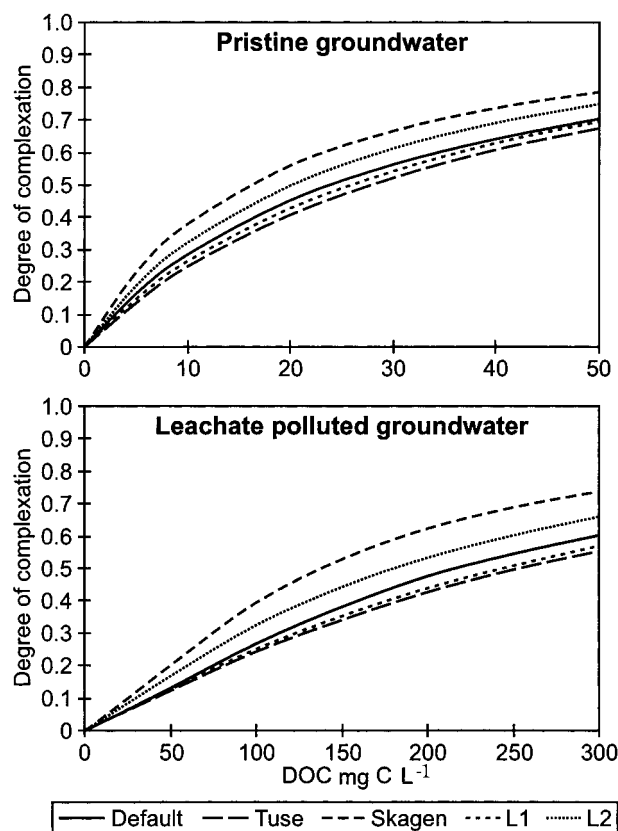


FIGURE 4. Model V calculations of cadmium complexation to fulvic acids using the specific proton binding parameters and default proton binding parameters, respectively. The calculations were performed for a pristine matrix (10^{-3} M CaCl₂) and a leachate-polluted groundwater matrix (5, 7). The total concentration of cadmium was 4.44×10^{-5} mM.

The proton affinity constants for both the carboxylic groups ($-\log K_{H1}$) and the phenolic groups ($-\log K_{H2}$) were very similar for all fulvic acids. Lower as well as higher affinity constants for carboxylic and phenolic groups have been reported (9, 16, 30). The proton affinity constants found for both carboxylic acids and phenolic groups corresponded well with the pK values of simple mono- and polycarboxylic acids and for phenols.

The apparent heterogeneity parameters m_{H1} for the carboxylic groups were similar for all fulvic acids but higher than those reported for humic acids, indicating a more ideal/less heterogeneous behavior for fulvic acids than for humic

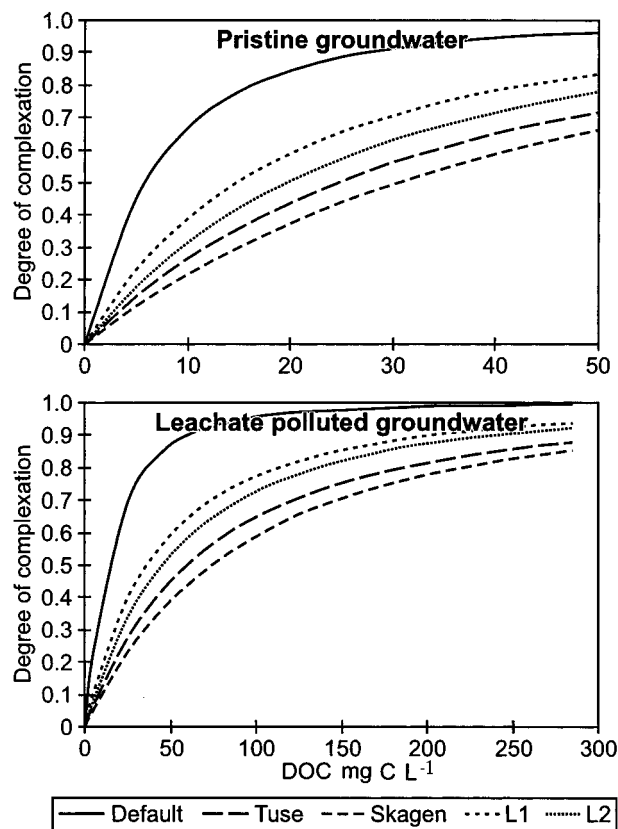


FIGURE 5. NICA–Donnan calculations of cadmium complexation to fulvic acids using the specific proton binding parameters and default proton binding parameters, respectively. The calculations were performed for a pristine matrix (10^{-3} M CaCl₂) and a leachate-polluted groundwater matrix (5, 7). The total concentration of cadmium was 4.44×10^{-5} mM.

acids. The m_{H2} parameters for the phenolic groups were lower than those observed for the carboxylic groups and showed some variation. The heterogeneity parameters for the Broubster fulvic acid depended on a partly fixed value (obtained from humic acids) and differed from the estimates obtained in this work.

The Donnan volume is determined from the parameter b , and for fulvic acids investigated in this work the b values varied between 0.84 and 0.91, which was greater than those observed for peat humic acids (16). The Donnan volume for fulvic acids therefore appears to be greater than those for humic acids.

Overall the NICA–Donnan model provided a good fit to the proton titration data obtained at different ionic strengths for fulvic acids from pristine and leachate-polluted groundwater. As with the Model V, the proton binding parameters fitted for the NICA–Donnan model were similar for pristine and leachate-polluted groundwater.

Comparison of NICA–Donnan and Model V Related Parameters. While the two models are mathematically quite different, their underlying physicochemical basis is very similar, especially for proton binding. Both models contain estimates for the density of carboxylic groups, the binding constant (pK) of the carboxylic groups, and the binding constant of the phenolic groups. They also both contain estimates of the spread of pK values as a measure of the heterogeneity. Good agreement was found for the densities and binding constants for the carboxylic groups between the two models. A considerable difference in the binding constants estimated of the phenolic groups by the two models was found. Model V estimated binding constants at about pK 8 and pK 10, whereas the NICA–Donnan model estimated binding constants between pK 9 and pK 10. As mentioned previously, the phenolic groups are poorly defined by the titration data, and therefore a large uncertainty in these estimates is to be expected. The binding constants obtained with the NICA–Donnan model were more in accordance with values expected from the pK values obtained for simple mono- and polycarboxylic acids and phenols.

Evaluation of the Necessity of Site-Specific Proton Binding Parameters in Model V. Similarities but also differences were found between Model V proton binding parameters described in the literature (4, 8, 26) and those found here. However, the differences did not greatly affect the estimated cadmium binding to fulvic acids. Using both the derived sets of proton binding parameters of the four fulvic acids and the default set of proton binding parameters, the degree of cadmium complexation (cadmium bound in fulvic acid complexes related to the total dissolved cadmium concentration) was calculated as a function of the fulvic acid content (Figure 4). The model calculations were performed (see earlier) for a pristine matrix and a leachate-polluted groundwater matrix. Comparing model results obtained for the specific proton binding parameters and the default proton binding parameters, it appears that the greatest difference in the degree of cadmium bound to fulvic acids was less than 0.1. The estimations by the default parameters fell in the middle of the range of the model runs based on the specific parameters. It appears that a default set of proton binding parameters would provide an estimate of the degree of cadmium complexation within a deviation of less than ± 0.1 from the estimates obtained by using specific proton parameters. Assuming that the free metal ion activity is the key species in an environmental context (controls solubility, sorption, and complexation), such a deviation in modeling of complexation by using default values is probably of little importance for practical purposes as long as the complexation is modest (a complexation degree less than 0.8, which means that less than 80% of dissolved Cd is complexed by fulvic acids). A variation of ± 0.1 in the degree of complexation will at a modest degree of complexation result in a variation of free metal ion concentration of less than a factor of 2. At a very high degree of complexation (higher than 0.8), a deviation of ± 0.1 may affect the free metal ion activity at an order of magnitude level and may become important.

Evaluation of the Necessity of Site-Specific Proton Binding Parameters in the NICA–Donnan Model. In terms of cadmium complexation predicted by the NICA–Donnan model (contained in the Ecosat model), Figure 5 shows a comparison of the predicted cadmium complexation based on the obtained proton binding parameters for fulvic acids and default parameters for humic acids contained in the

Ecosat model (currently no default data for fulvic acids are available in Ecosat). It appears from the figure that, using the default set of proton binding parameters, the predictions of cadmium binding were considerable higher than the predictions obtained by specific proton binding parameters (at least 0.3 degree of complexation). Predicting cadmium complexation using the four specific sets of proton binding parameters the maximal variation in the degree of complexation was observed between 0.5 and 0.7 corresponding to a maximal variation in the concentration of the free cadmium ion at a factor of 2.5. These model simulations showed that for the Ecosat model a set of proton binding parameters for groundwater fulvic acids is necessary in order to predict metal complexation by fulvic acids. Due to the similarities in proton binding parameters observed for the four fulvic acids presented in this paper, a set of proton binding parameters could be obtained from these data and considered as a default set of proton binding parameters for fulvic acids in the Ecosat model.

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Literature Cited

- (1) Saar, R. A.; Weber, J. H. *Can. J. Chem.* **1979**, *57*, 1263–1268.
- (2) Smith, B.; Higgo, J. J. W.; Moody, P.; Davis, J. R.; Williams, G. M.; Warwick, P. *Comparative study of humic substances in groundwater: 1. The extraction of humic material from Drigg groundwater and a study of its ability to form complexes with cobalt and nickel*; British Geological Survey: Nottingham, 1991; Technical Report WE/90/43.
- (3) Pempkowiak, J.; Zyczynska-Baloniak, I. Proceedings of the 3th National Humus Seminar. Humus-uutiset. *Finn. Humus News* **1991**, *3* (3).
- (4) Higgo, J. J.; Kinniburgh, D.; Smith, B.; Tipping, E. *Radiochim. Acta* **1993**, *61*, 91–103.
- (5) Christensen, J. B.; Jensen, D. L.; Christensen, T. H. *Water Res.* **1996**, *30*, 3037–3049.
- (6) Grøn, C.; Wassenaar, L.; Krog, M. *Environ. Int.* **1996**, *22*, 519–534.
- (7) Christensen, J. B.; Jensen, D. L.; Filip, Z.; Grøn, C.; Christensen, T. H. *Water Res.* **1998**, *32*, 125–135.
- (8) Tipping, E.; Hurley, M. A. *Geochim. Cosmochim. Acta* **1992**, *56*, 3627–3641.
- (9) Benedetti, M. F.; Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1995**, *29*, 446–457.
- (10) de Wit, J. C. M.; Nederlof, M. M.; Van Riemsdijk, W. H.; Koopal, L. K. *Water, Air Soil Pollut.* **1991**, *57–58*, 339–349.
- (11) de Wit, J. C. M.; Van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1993**, *27*, 2005–2014.
- (12) de Wit, J. C. M.; Van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1993**, *27*, 2015–2022.
- (13) Milne, C. J.; Kinniburgh, D. G.; de Wit, J. C. M.; Van Riemsdijk, W. H.; Koopal, L. K. *Geochim. Cosmochim. Acta* **1995**, *59*, 1101–1112.
- (14) Bartschat, B. M.; Cabaniss, S. E.; Morel, F. M. M. *Environ. Sci. Technol.* **1992**, *26*, 284–294.
- (15) Milne, C. J.; Kinniburgh, D. G.; de Wit, J. C. M.; Van Riemsdijk, W. H.; Koopal, L. K. *J. Colloid Interface Sci.* **1995**, *175*, 448–460.
- (16) Kinniburgh, D. G.; Milne, C. J.; Benedetti, M. F.; Pinheiro, J. P.; Filius, J.; Koopal, L. K.; van Riemsdijk, W. H. *Environ. Sci. Technol.* **1996**, *30*, 1687–1698.
- (17) Ephraim, J. H.; Pettersson, C.; Norden, M.; Allard, B. *Environ. Sci. Technol.* **1995**, *29*, 622–628.
- (18) Benedetti, M. F.; van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1996**, *30*, 1805–1813.
- (19) Tipping, E. *Colloid Surf.* **1993**, *73*, 117–131.
- (20) Thurman, E. M.; Malcolm, R. L. *Environ. Sci. Technol.* **1981**, *15*, 463–466.
- (21) Krog, M.; Grøn, C. *Sci. Total Environ.* **1995**, *172*, 159–162.
- (22) Kinniburgh, D. G.; Milne, C. J.; Venema, P. *Soil Sci. Soc. Am. J.* **1995**, *59*, 417–422.
- (23) Tipping, E. *Comput. Geosci.* **1994**, *20*, 973–1023.

- (24) Keizer, M. G.; van Riemsdijk W. H. *ECOSAT: A computer program for the calculation of speciation and transport in soil–water systems: Version 4.3 Users' Manual*; Department of Soil Science and Plant Nutrition, Wageningen Agricultural University: Wageningen, The Netherlands, 1994.
- (25) Paxéus, N.; Wedborg, M. *Anal. Chim. Acta* **1985**, *169*, 87–98.
- (26) Lead, J. R.; Hamilton-Taylor, J.; Tipping, E. *Anal. Chim. Acta* **1994**, *294*, 319–327.
- (27) Thurman, E. M. *Organic Geochemistry of Natural Waters*; Nijhoff/Junk Publishers: Dordrecht, The Netherlands, 1985.
- (28) Perdue, E. M. In *Humic Substances in Soil, Sediment, and Water*; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley and Sons: New York, 1985; pp 493–526.
- (29) Milne, C. J.; Crawford, M. B.; Kinniburgh, D. G.; Higgs, J. J. W. *Comparative evaluation of models for ion-binding by humic substances: PHREEQEV/Model V and NICA-Donnan*; Technical Report WD/96/2; British Geological Survey: Keyworth, 1996.
- (30) Temminghoff, E. J. M.; Van der Zee, S. E. A. T. M.; de Haan, F. A. M. *Environ. Sci. Technol.* **1997**, *31*, 1109–1115.

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