TECHNICAL REPORT

85-07

Complex forming properties of natural occuring fulvic acids
Part 1. Complexes with cadmium, copper and calcium

Jacob A. Marinsky,
A. Mathuthu,
M. Bicking and
J. Epharim

State University of New York at Buffalo
Buffalo, New York 14214,
July 1985

SVENSK KÄRNBRÄNSLEHANTERING AB
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 48 STOCKHOLM
TEL 08-67 95 40 TELEX 13108-SKB
TEL 08-665 28 00

COMPLEX FORMING PROPERTIES OF NATURAL OCCURRING FULVIC ACIDS

Part 1. Complexes with Cadmium, Copper and Calcium

Jacob A. Marinsky, A. Mathuthu, M. Bicking and J. Ephraim

State University of New York at Buffalo
Buffalo, New York 14214, July 1985

A list of other reports published in this series during 1985 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77) and 1984 (TR 85-01) is available through SKB.

COMPLEX FORMING PROPERTIES OF NATURAL OCCURRING FULVIC ACIDS

Part 1. Complexes with Cadmium, Copper and Calcium

Jacob A. Marinsky, A. Mathuthu, M. Bicking and J. Ephraim

Chemistry Department
State University of New York at Buffalo
Buffalo, New York 14214

July, 1985

CONTENTS

ABSTRACT

The experimental program developed in our earlier investigations of the protonation equilibria encountered with Armadale Horizons Bh and Suwannee River fulvic-acid has been employed in the present investigation of a Swedish fulvic acid source. Complications introduced by the polyelectrolyte nature and the degree of heterogeneity in the functional unit content of this natural organic acid molecule have been resolved as they were with the previous fulvic acid samples. The physical chemical properties of this fulvic acid have been compared with those resolved for the Armadale Horizons Bh and the Suwannee River fulvic acid as well.

The insight gained from these protonation studies and metal ion binding studies, also carried out in the course of this investigation, has led to the development of a model for interpretation of the binding of metal ions to fulvic acid at any pH, medium ionic strength, and metal ion and fulvic acid concentration level.

I. INTRODUCTION

The unified model developed earlier for the interpretation[1-6] of fulvic acid protonation and metal ion binding equilibria encountered in two different fulvic acid sources (Armadale Horizons Bh and Suwannee River)[7,8] has been used to reexamine more critically the binding data obtained in ion-exchange distribution experiments that had been conducted earlier to investigate the binding of trace level concentration of Eu(III)(Eu^{154}), Co(II)(Co^{60}), Zn(II)(Zn^{65}) and Cd(II)(Cd^{109}) to Armadale Horizons Bh fulvic acid at various experimental conditions of pH, FA concentration, and ionic strength.

Additional refinements that might be effected in the model through the above computational program were then to be tested in an experimental program facilitated by the accessibility of electrodes which could yield a direct and accurate assessment of the free metal ion under investigation. This requirement limited the investigation performed in this research period to the following metal ions: Cd(II), Cu(II), and Ca(II). However, it is the aim of the investigation to include also the metal ions UO_2^{+2}(VI), Fe(II) and Fe(III).

Because of the need to demonstrate the applicability of any refined model that might be developed for the consideration of metal ion speciation tendencies in the presence of fulvic acid to the equilibria encountered with organic substances dissolved in Swedish deep underground waters much of the research was carried out with a Swedish aquatic fulvic acid. However, a number of the experiments undertaken used Armadale Horizons Bh fulvic acid because of the limited supply of the Swedish fulvic acid source.

To facilitate the research carried out with the Swedish fulvic acid its protonation properties were investigated potentiometrically in aqueous and non aqueous media according to the methodology developed in our earlier investigations of other fulvic sources (Armadale Horizons Bh and Suwannee River).[9]

II. A REEXAMINATION OF EARLIER TRACE METAL ION BINDING STUDIES CARRIED OUT WITH ARMADALE HORIZONS Bh FULVIC ACID

The reasonably successful analysis of earlier potentiometric studies of Cu(II)-ion binding to the Armadale Horizons Bh and the Suwannee River fulvic acid sources have shown that the speciation tendencies of Cu(II)-ion in the presence of fulvic acid are rather well ancitipated with the model developed.[10] In this model the sequence of uni and bidentate sites, tentatively identified with the acidic molecules they most closely resembled, were presumed to interact with Cu(II)-ion as they would in the particular molecule they were identified with, i.e., salicylic, phthalic, aminocarboxylic, dihydroxyl acid. On this basis the Cu(II)-ion complexed species presumed to be formed with these sites were assigned formation constants identical with or closely resembling the literature values reported for them.[11]

In order to test whether the above model provided accurate estimates as well of the effect of fulvic acid on the speciation tendencies of di- and tri-valent metal ions, an objective of our program, the results of trace metal binding studies compiled in an ion-exchange distribution study carried out earlier[12] were examined with the model.

It was immediately discovered that there was no correlation between prediction and experiment when the model was employed exactly as it had been with the Cu(II), FA, Na(K)NO_3 systems. The binding of trace metal ion to the fulvic acid was severely underestimated. This failure of the model has now been attributed to an incomplete description of the function of the hydroxyl sites on the basis of the following analysis.

When the difference between the experimentally measured $(\frac{D_o-D}{D})$

and the model-based calculation of the ratio of bound to free trace metal ion ($\Sigma M_b/M_f$(calc)) is divided by the concentration of a hypothetical site, ΣC_s, and equated to an arbitrarily assigned stability constant, $\beta_{MA_s}{}^{(Z-1)+}$, as

$$\left(\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f^{2+}}\right)\frac{1}{(\exp-Z\varepsilon\Psi_{(a)}/kT)(\gamma_M^{Z+})}\left(\frac{1}{\alpha_x\Sigma C_s}\right) = \beta_{MS}^{(Z-1)+} \qquad (1)$$

shown the values of α_x, the degree of dissociation of the interacting site, S, can be related to each other by solution of the x simultaneous equations arrived at by equating the left-hand side of equation 1, which is invariant, in the sequence of the x experimental point so examined. By such an approach ΣC_s, the total concentration of site S, dissociated and undissociated, is cancelled in the computation. In equation 1, only α_x, ΣC_s and $\beta_{MS}{}^{(Z-1)+}$ are unaccessible; D_o is the measured distribution of trace metal ion between 1 g of resin and 1 g of solution in the FA-free but otherwise equivalent aqueous medium, D is the measured distribution in the FA-containing systems, $(\Sigma M_b/M_f)_{calc}$ is compiled from the model, the exponential term which corrects for deviation due to the charge on the FA molecule is accessible from the protonation studies, Z is the valence of the trace metal ion and γ_M is the single ion activity coefficient correction, proposed by Kielland, to compensate for the non-ideality introduced by long range Debyean interactions at the experimental ionic strength.

With the relative magnitudes of α_x made available in this way the Henderson-Hasselbalch equation,

$$\mathrm{pH} - \log \frac{\alpha_x \Sigma C_s}{(1-\alpha_x)\Sigma C_s} = \mathrm{p}K^{app}_{HS} \qquad (2)$$

given above, was used to identify site S. Different values of ΣC_s were employed in eq. 2 until a constant value of $\mathrm{p}K^{app}_{HS}$ was resolved. The $\mathrm{p}K^{app}_{HS}$ of 6.1 ± 0.2 so obtained unambiguously identified the HS site with the weakly acidic OH functional unit assigned earlier in the protonation studies.

The extra binding of Co(II), Zn(II), Cd(II), and Eu(III) obtained from the difference between D_o-D/D and $(\Sigma M_b/M_f)_{calc}$, computed by examining only their complexation by the several carboxylic acid moieties ascribed to the FA molecule, has been, on the basis of the above result, used in eq. 1, to evaluate the formation constant of the complexed species formed with the -OH site. These computations are summarized in Tables I-IV for experiments in which FA concentration, pH and medium ionic strength were varied.

From this reanalysis of the ion-exchange distribution data it is apparent that the previously undetected interaction of metal ion with the OH moiety dominates the complexation of the divalent and trivalent metal ions examined at trace-level concentrations. With the trivalent ion (Eu(III)) this domination is so extreme that the presence of the other complexed species is small enough to neglect.

One other factor that is noticeable is the scatter in the β values resolved. For example, in Table II, which summarizes the data obtained with Co^{60}, such scatter is especially noticeable. Much of this scatter, however, is attributable to the large experimental uncertainty encountered in some of the measurements. In those experiments where the value of D is not markedly different from D_o error in each measured value is introduced by statistical uncertainty in the observed measurement and the background correction, which when D_o and D are large, is not much smaller than the activity level of the sample itself. Such possibility of error was further enhanced by the fact that very small quantities of resin had to be used in these very same experiments to assure a measurable residual activity and the measurement of their weight had accuracy limits of ~3 to 4%. Since the computation of D_o and D were based on the dry resin weight additional uncertainty could arise from incorrect water content assessments introduced by nonuniformity in the water content of the resin. Such error in D_o and D is of course very much exaggerated in the value of D_o-D/D to explain much of the scatter in the data.

In those instances where D is quite small sizeable error is unavoidable because its value is based on the small difference between two large numbers, initial and final activity.

Another factor that may interfere with resolution of the parameter under investigation is contained in the potential for absorption of fulvic acid by the resin. At low pH fulvic acid is strongly absorbed by uncharged polystyrene based resin. If absorption of the fulvic acid by the highly charged polystyrene sulfonate resin had been encountered, however, its effect, a reduction in the value of the β parameter, would have been most noticeable at low pH, where the tendency for FA absorption, if any existed, would be largest. We note that the trend in the β parameter is toward higher values at low pH and low ionic strength to indicate that complication of the results by undetected absorption of the FA is unlikely. Instead, the possibility that the trace element may, at low pH and low ionic strength undergo ion-dipole interaction at the surface of the FA molecule may account for this trend. We note that at the higher ionic strength values there is a tendency for the β parameter to converge to a lower value than is obtained at the lower I values (see Tables III and IV).

III. STUDY OF THE PROTONATION PROPERTIES OF AN AQUATIC SWEDISH FULVIC ACID

The preceding analysis suggests that there is a need to modify the metal-ion binding model developed in our earlier examinations of Cu(II)-ion binding by two different fulvic acid sources. There is no doubt that in addition to being involved with the formation of both a uni- and bidentate complex the weakly acidic-OH is also involved in the formation of a third complex which, when exposed to trace level concentrations of di- and trivalent ions, dominates the complexation behavior of the metal ion in FA.

To facilitate examination of this aspect in the model refinement to be sought an aquatic fulvic acid source from Sweden was investigated potentiometrically in aqueous and non aqueous media according to the methodology developed in earlier studies of other fulvic acid sources (Armadale Horizons Bh and Suwannee River). The results of this research[9] provided a quantitative estimate of the non ideality introduced to the behavior of hydrogen and free metal ions by the polyelectrolyte nature of the fulvic acid molecule in solution at different simple salt concentration levels (0.0010, 0.010 and 0.10 M). After the appropriate corrections were made for variation of this deviation factor with both the degree of fulvic acid neutralization and the concentration level of the fulvic acid at each of these salt concentration levels it was possible to deduce the nature and the extent of functional heterogeneity in the fulvic acid molecule from the residual potentiometric pattern.

The insight gained with respect to the carboxylic and OH content of the Swedish fulvic acid molecule from (1) its potentiometric examination in non-aqueous medium during its neutralization with tetrabutyl ammonium hydroxide in the presence of the internal reference standard, parahydroxybenzoic acid and from (2) the protonation enhancement in aqueous medium, affected by the addition of both Eu(III) and Cu(II) to the fulvic acid sample facilitated the assignment of n functional sites, their abundance, A_n, and their acidity (pK_a^{int}).

It was possible, from a comparison of these data with similar data obtained with the Armadale Horizons Bh fulvic acid and the Suwannee River fulvic acid to show that the Swedish FA like the Armadale FA and unlike the Suwannee River FA contains both salicylic acid-like and dihydroxyl sites. The less effective removal of Cu^{+2} ion by the Swedish FA in comparison with the Armadale FA over the pH range studied was tentatively attributed (1) to a significantly smaller presence of amino acid site and (2) to the somewhat lower covalency of the Cu-O bonds originating in the more acidic sites associated with the Swedish FA sample.

The site assignments and their combination with each other ($pK_1^{int} = 1.7$; $A_1 = 26\%$ and $pK_3^{int} = 4.6$; $A_3 = 24\%$) and with the hydroxyl (phenolic) groups presumed to be ortho to them ($pK_2^{int} = 3.1$, $A_2 = 30\%$) and $pK_4^{int} = 5.6$; $A_4 = 20\%$) have permitted estimate of site combinations (phthalic, salicylic, dihydroxyl and amino acid in reduced quantity) accessible to multivalent metal ions.

IV. TEST OF REVISED BINDING MODEL

A. Analysis of Cd(II)-Ion Binding Data with Revised Model

To accommodate the results obtained in the analysis of the trace metal ion-binding studies in an acceptable revision of our earlier ion-binding model we have considered the dominant complex species observed to involve the weakly acidic-OH site together with a neighboring-C=O group which replaces the second ortho-positional-OH group in the FA molecule a certain percentage of the time. Indeed when a -C=O group is substituted for ~20% of the second-OH group and the chelate product is assigned a value of 10^6 there is excellent agreement between the experimentally observed and the model-based computation of Cd(II) removal from solution by FA. The β value of $\sim 2 \times 10^5$ resolved from the ion-exchange distribution measurements at the highest ionic strength is raised to 1 x 10^6 to accommodate the 80% smaller concentration value assigned to this site in the calculations.

The improvement in ion-binding predictive quality that the above change in the model provides can be seen in Table V where the experimental binding of Cd(II) in one experiment is compared with the model-predicted binding of Cd(II) before ($Cd_b(calc)_B$) and after ($Cd_b(calc)_A$) model modification.

Such improvement has convinced us that the revised binding model provides a better assessment of metal ion speciation in the presence of fulvic acid. The next sequence of tables presented are used to demonstrate fully the predictive quality of the newly revised model. All of the Cd(II)-ion binding data obtained with the Armadale Horizons Bh fulvic acid prior to this study and with the Armadale Horizons Bh and Swedish aquatic fulvic acid in this research period are summarized in these Tables. The model predicted binding of Cd(II) is compared with the experimentally observed binding of Cd(II) in the last two columns of these tables.

Once again the stability parameters employed in the model-based computations are literature-based. All four unidentate complexes were assigned the same value of 2.5 x 10^1. Unlike copper, the stability constant, β_{CdHA^+} of the unidentate complex formed by the cadmium with carboxylic acids is essentially insensitive to the varying acidic nature of the carboxylic acid. The β_{CdA} value of 7 x 10^2 selected for the phthalatelike chelate and the K_{Ex} values of 2.7 x 10^{-7}, 1.6 x 10^{-2}, and 1.2 x 10^{-3}, used respectively for the salicylic acid-like, the aminocarboxylic, and the dihydroxyl sites, are consistent with the appropriately larger literature-based values[11] of 2.882 x 10^3, 2.7 x 10^{-2}, 1.6 x 10^1, and 1.6 x 10^{-2} assigned to the corresponding Cu(II)-complexed species. The β value of 1 x 10^6 assigned to the third hydroxyl complexed species though somewhat larger than the formation constant of its analog, cadmium acetyl acetonate (log $\beta_{calc} > 5$) is considered reasonable.

On the whole agreement between experimentally-based estimates of bound Cd(II) and the newly revised model-based predictions are well within the uncertainty limits of the potentiometric measurements, calibration of the Cd(II)-ion selective electrode just prior to and immediately after completion of a number of these research periods experiments having shown that the E_o of the electrode could shift from 1 to 4 mV over the time interval of the measurement program. For example, the discrepancy between $Cd_b(calc)$ and $Cd_b(exp)$ at the beginning of the experiment summarized in Table V would, on this basis, indicate such a shift in E_o was in progress right from the start of the measurement program. The fact that the value of pCd appears to pass through a minimum with the early addition of base is contrary to mass-action based expectations and has to be a reflection of such bias in the initial potentiometric measurements of Cd(II).

A similar discrepancy between Cd_b(calc) and Cd_b(exp) at the beginning of both experiment A listed in Table VI and the only experiment listed in Table VIII is believed to arise from this same phenomenon. The irreproducible nature of this source of discrepancy is, however, apparent from inspection of the second and third set of data listed in sections B and C of Table VI and third set of data listed in section C of Table VII. In these experiments agreement between Cd_b(exp) and Cd_b(calc) is excellent at the start with divergence occurring later in the experiments. Drift in the E_o value apparently developed more slowly in these experiments. The agreement between Cd_b(exp) and Cd_b(calc) for the experiments listed in sections A and B of Table VII on the whole is excellent to indicate electrode stability throughout these experiments.

B. Analysis of Cu(II)-Ion Binding Data with Revised Model

In order to determine whether the revised model provides as good or better assessment of Cu(II)-ion speciation tendencies in the presence of fulvic acid than the earlier model representative Cu(II)-ion binding data obtained with the Swedish fulvic acid sample in the research period under review have been analyzed by both approaches (see Appendix I, II and IV for a detailed description of the unmodified model). In the only revision of the earlier model the stability constant of the carbonyl, hydroxyl chelated Cu(II), presumed to be formed with about 20% of the OH sites previously identified with the FA molecule, has been assigned a value of 10^9; the order of magnitude of this parameter is comparable to the published value for its acetyl acetonate analog[11] and justifies this assessment.

The results of these computations of bound Cu(II) by the two models employed are listed in columns 4 ($Ca_b(calc)_B$) and 5 ($Ca_b(calc)_A$) of Table X together with the experimentally based values (Ca_b(exp)) presented in column 6. The subscripts B and A identify the model employed in the computation, B referring to the model before revision and A, to the model after revision.

The improvement in predictive quality is less startling in this system than it was in the case of the Cd(II), FA, $NaNO_3$ system. Upon reflection this observation is not unexpected. Whereas the binding of Cd(II) ion by the proposed sites is dominated by the proposed site such is not the case with the Cu(II)-ion where the binding by the other sites is much more competitive. As a consequence the binding of Cu(II) is essentially more buffered.

Additional representative Cu(II)-ion binding data obtained at different experimental conditions from those presented in Table X are listed in Tables XI and XII to test further the predictive quality of the revised model. In Table XI the data reported were obtained as before with Cu(II) and FA present at a fixed molar ratio but in a lower ionic strength (0.010 M $NaNO_3$) medium. The experiment summarized in Table VII was carried out in 0.10 M $NaNO_3$ by adding $Cu(NO_3)$ stepwise to FA at a previously fixed degree of neutralization.

C. An Additional Test of the Revised Model in a Limited Analysis of Ca(II)-Ion Binding to Horizons Bh Fulvic Acid

Because of the restricted concentration and pH range in which the Ca(II)-ion selective (liquid membrane) electrode can be reliably employed study of the binding of Ca^{+2} ion to the fulvic acid molecule had to be limited to a relatively high concentration level of FA (0.288 millimoles in 50 ml) and an elevated pH range (6.4 to 7). The need for use of such sizeable quantities of FA in an experiment precluded the performance of any experiments with the limited supply of Swedish fulvic acid that was accessible to us.

In the only kind of experiment that was feasible 0.288 millimoles of FA contained in 50.0 ml of 0.10 M $NaNO_3$ were neutralized with standard base until a pH of 7 was reached. Calcium nitrate solution was then added stepwise. The pH and pCa of the equilibrated system were measured after each addition of $Ca(NO_3)_2$. To assure consistency in the measurement of free Ca^{+2} ion the electrode was calibrated, before and after an experiment by adding $Ca(NO_3)_2$ to the FA-free but otherwise equivalent $NaNO_3$ solution (pH ~6.8). Only the free Ca^{+2} ion concentration range in which the duplicate calibrations were reproduced to within 0.3 mV was used to compute the fulvic acid bound Ca (Ca_b(exp)). These Ca_b(exp) data are compared in Table XIII with the revised model-based computation of bound Cu (Cu_b(calc)). In the computation the four unidentate stability constants, β_{CaHA^+}, were assigned a common value of 1.7×10^1 to correspond to the formation constant that is characteristic of the unidentate carboxylate complexes formed with Ca^{+2} ion. Because there is little tendency for any special interaction of Ca^{+2} ion with the N atom of an aminocarboxylic moiety the possibility of the formation of such a chelate in the fulvic acid molecule was considered unlikely. The three other chelate possibilities and the additional one introduced in the revised model were considered in the computations. The formation constant of the Ca^{+2}-ion chelate with the phtalic acid-like site was assigned a value of 7.0×10^2 just as it had been before in the analysis of Cd^{+2}-ion binding to fulvic acid. The K_{Ex} values of 2.7×10^{-7} and 10^{-3} used to facilitate estimate of the quantities of Ca^{+2}-ion bound to the salicylic acid-like moiety and the dihydroxyl site were the same and slightly smaller than the parameters used to describe the binding of Cd^{+2} ion to these proposed sites. The assignment of parameters of this order of magnitude and similarity is consistent with their literature values in the several simple molecules they are considered to resemble in the heterogeneous array of sites that constitute the fulvic acid molecule. Finally, the carbonyl, hydroxyl chelate introduced into the revised form of the earlier computation model was reduced from the values of 10^6 and 10^9 assigned to the Cd(II) and Cu(II) chelates to a value of 1×10^4 to correspond with the much lower potential for interaction of Ca^{+2} ion with acetyl acetonate, the analog of this last chelating group presumed to exist in the fulvic acid molecule.

Representative data that were obtained as described above are summarized in Table XIII. Once again there is good correlation between the model-based predictions and experiment to attest to the sizeably broad scope of its applicability.

V. SUMMARY AND CONCLUSION

A. The Protonation Properties of a Swedish Fulvic Acid

Potentiometric studies of the neutralization of a Swedish (aquatic) fulvic acid with standard base in aqueous and non-aqueous media have been conducted. Analysis of the results have shown that the protonation behavior of this fulvic acid material is a reflection of (1) its polyelectrolyte nature and (2) its functional heterogeneity as it is with the other fulvic acids examined similarly. The several different functional units (carboxylic and -OH) that comprise this fulvic acid molecule are sufficiently different in acid strength to dominate the large change in apparent pK(pK_{FA}^{app}) with degree of neutralization (α) just as they did in the other sources. The polyelectrolyte contribution to the steadily increasing perturbation of the protonation equilibria with α has been estimated as it was with the Armadale source from the vertical displacement of the pK_{FA}^{app} versus α plots at the different ionic strength levels (0.0010, 0.010, 0.005 and 0.10) examined.

The relationship between pK_{FA}^{app} and pH at every ionic strength employed has been examined as well and the results obtained show that the Swedish fulvic acid molecule is impermeable to simple neutral salt just as the other fulvic acid molecules studies are. The divergence with increasing α of the curves obtained at different ionic strength levels shows that the Swedish fulvic acid molecule is a good deal more flexible than the Armadale and Suwannee River FA molecules.

Resolution of the functional site heterogeneity combined with assignment of their relative abundance and the intrinsic pK values associated with them has been facilitated as it was with the other fulvic acid sources by cancelling the calculated contribution to pK_{FA}^{app} of the increasing charge on the fulvic acid molecule surface in the course of its neutralization with standard base. The additional insight gained with respect to the carboxylic and OH content of the Swedish fulvic acid molecule from the potentiometric examination in non-aqueous medium of the neutralization of the fulvic acid in the presence of an internal reference standard, parahydroxybenzoic acid, and from the protonation enhancement in aqueous medium, affected by the addition of both Eu(III) and Cu(II) to the fulvic acid sample, has further facilitated the assignments of functional sites, their abundance and their acidity just as it did in the earlier examination of the Armadale Horizons Bh fulvic acid and the Suwannee River fulvic acid.

Study of the enhancement of proton release from the Swedish fulvic acid molecule by the presence of either an excess of Cu^{+2} or an excess of Eu^{+3} ion in the same way as before has provided additional insight with respect to the accessibility for chelation of heavy metal ions of bidentate sites in the Swedish fulvic acid molecule. Comparison of these data with similar data obtained with the Armadale Horizons Bh fulvic acid and the Suwannee River reference fulvic acid has shown that the Swedish FA like the Armadale FA and unlike the Suwannee River FA, contains both salicylic acid-like sites and dihydroxyl sites. The less effective removal of Cu^{+2} ion by the Swedish FA in comparison with the Armadale FA over the pH range studied has been attributed to (1) a significantly smaller presence of an amino site that is present in the Armadale FA and to (2) the lower covalency of the Cu-O bonds originating in the more acidic sites associated with the Swedish FA sample.

Finally the site assignments and their combination with each other (pK_1^{int} = 1.7, A = 26% and pK_3^{int} = 4.6, A = 24%) and with the hydroxyl (phenolic) groups presumed to be ortho to them (pK_2 = 3.1, A = 30% and pK_4 = 5.6, A = 20%) have permitted estimate of site combinations (phthalic, salicylic, dihydroxyl, and amino acid (in reduced quantity) accessible to multivalent metal ions.

B. Further Development of a Model for the Anticipation of Metal Ion Speciation in the Presence of Fulvic Acid

By using stability constants from the literature for Cu^{+2} ion complexed species most closely resembling the uni- and bidentate complexes presumed to be formed with the above sites and by correcting for non ideality introduced by the potential field emanating from the charged surface of the fulvic acid molecule it was possible to predict the Cu^{+2} ion binding characteristics of Armadale Horizons Bh and Suwannee River fulvic acid at different conditions. The computed complexation behavior compared favorably with the experimentally observed complexation behavior of the Cu^{+2} ion.

In this study the facility for estimating metal ion speciation tendencies in the presence of fulvic acid has been further enhanced. Reanalysis of cation-exchange distribution data obtained with trace concentration levels of several metal ions (Eu(III), Zn(II), Co(II) and Cd(II)) indicated that the model developed earlier to anticipate Cu(II)-ion binding was in need of some modification. It was deduced that about 20% of the OH sites of the FA molecule that were previously considered to be located next to another, more weakly acidic group in a bifunctional mode, were instead ortho to another potentially reactive functional unit tentatively identified as a carbonyl moiety. Substitution of this chelation unit for 20% of the dihydroxyl sites led to a capability, not available with the earlier model, for anticipating the complexation properties of Cd(II) to fulvic acids. The formation constant of 10^6 assigned to this proposed complex of Cd(II) on the basis of our analysis of the cation-exchange distribution measurements with trace-level concentrations of Cd(II) is in reasonable accord with the formation constant of $>10^5$ reported in the literature for the acetyl acetonate complex of Cd(II) that it is presumed to resemble.

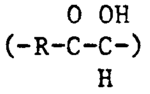
With the substitution of the above site for 20% of the dihydroxyl site employed in the computation of metal ion speciation with Armadale Horizons Bh and the Swedish aquatic fulvic acid the predictive quality of the computations was measurably improved. The neglect of this aspect in the earlier analysis procedure, while not noticeably affecting the predictive quality of the approach for speciation estimates in the Cu(II)-FA system, had been noticeably detrimental to such estimates for the Cd(II)-FA system.

Demonstration of the applicability of the modified approach for anticipating speciation of Ca(II) in the Ca(II)-FA system in the present research period is supportive of the very important claim that our revised model is generally applicable for anticipating speciation tendencies of various multivalent ions in the presence of fulvic acid.

C. Refinement of Earlier Estimates of the Effect of Fulvic Acid at the Low Concentration Levels Encountered in Deep Ground Waters on the Speciation of Trace Quantities of Eu(III)

On the basis of the reanalysis of our earlier cation-exchange distribution study of trace-level concentrations of Eu(III) in the presence of low concentration levels of Armadale Horizons Bh-fulvic at different degrees of neutralization and in the presence of different concentration levels of simple uni univalent electrolyte the following estimate of the speciation responses of the Europium to these experimental variables can be made:

a) At trace-level concentrations of Eu(III) the uniquely dominant species at any pH and ionic strength encountered in deep ground water will be the complex formed between the Eu(III) and the



$$(-R-\overset{O}{C}-\underset{H}{\overset{OH}{C}}-)$$

site presumed to be present as approximately 5% of the total acidity measurable in aqueous solutions of fulvic acid. Its formation constant is approximately 10^{10}. In most situations likely to be encountered essentially complete sequestering of the Eu(III) by this FA site must occur.

b) Only in those situations where the underground water source contains macro-levels of Cu(II) or Fe(III) can essentially complete complexation of trace levels of Eu(III) be successfully opposed.

VI. REFERENCES

1. Marinsky J.A., "An Interpretation of the Sensitivity of Weakly Acidic (Basic) Polyelectrolytes (Cross-Linked and Linear) Equilibria to Excess Neutral Salt, J. Phys. Chem., <u>89</u>, 0000 (1985).

2. Gamble D., Marinsky J.A. and Langford C., "Humic-Trace Metal Ion Equilibria in Natural Waters", in "Ion Exchange and Solvent Extraction, ed. by J.A. Marinsky and Y. Marcus, for Marcel Dekker, Inc., New York, New York, <u>9</u>, Ch. 7, 373-482 (1985).

3. J.A. Marinsky and M.M. Reddy, "Proton and Metal Ion Binding to Natural Organic Polyelectrolytes - I. Studies with Synthetic Model Compounds", Org. Geochem., <u>7</u>, 207-214 (1984).

4. J.A. Marinsky and M.M. Reddy, "Proton and Metal Ion Binding to Natural Organic Polyelectrolytes - II. Preliminary Investigation with a Peat and a Humic Acid", ibid., <u>7</u>, 215-221 (1984).

5. Marinsky J.A., Wolf A. and Bunzl K., "The Binding of Trace Amounts of Lead(II), Copper(II), Cadmium(II), Zinc(II) and Calcium(II) to Soil Organic Matter", Talanta, 27, 461-468 (1980).

6. Marinsky J.A., Gupta S. and Schindler P., "The Interaction of Cu(II) Ion with Humic Acid", J. Colloid Interface Sci., 89, 401-411 (1982).

7. Ephraim J., Alegret S., Mathuthu A. and Marinsky J.A., "The Influence of Polyelectrolyte Properties and Functionality Heterogeneity on the Protonation Equilibria of Armadale Horizons Bh Fulvic Acid", J. Env. Sci. and Tech., submitted 1985.

8. Ephraim J., Marinsky J.A. and Malcolm P.L., "The Influence of Polyelectrolyte Properties and Functionality Heterogeneity on the Protonation Equilibria of Suwannee River Fulvic Acid", J. Env. Sci. and Tech., submitted (1985).

9. Mathuthu A., Bicking M., Ephraim J. and Marinsky J.A., "The Influence of Polyelectrolyte Properties and Functional Heterogeneity on the Protonation Equilibria of a Swedish Aquatic Fulvic Acid", J. Env. Sci. and Technology, submitted 1985.

10. Ephraim J. and Marinsky J.A., "The Influence of Polyelectrolyte Properties and Functional Heterogeneity on the Copper-Ion Binding Equilibria in an Armadale Horizons Bh Fulvic Acid Sample", J. Env. Sci. and Technology, submitted 1985.

11. Sillén L.G. and Martell A.E., "Stability Constants of Metal-Ion Complexes", The Chemical Society, Burlington House, London (1964).

12. Marinsky J.A., Ephraim J., et al., Progress Reports to KBS (1982, 83).

Table I. The Binding of Trace Concentration Levels of $Zn^{+2}(Zn^{65})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o - D}{D}$	$\frac{D_o - D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
3.424	988.9	0.2937	0.2501	5.143
3.422	1033	0.2385	0.1951	4.029
3.682	1004	0.2747	0.2139	2.431
3.660	1003	0.2750	0.2160	2.581
3.945	867.3	0.4750	0.3875	2.408
3.961	987.4	0.2956	0.2062	1.235
4.133	757.8	0.6882	0.5746	2.321
4.084	762.9	0.6768	0.5706	2.579
4.398	482.5	1.651	1.490	3.288
4.447	466.0	1.745	1.573	3.107
4.945	267.8	3.778	3.476	2.245
4.810	333.3	2.839	2.577	2.246
4.787	295.9	3.323	3.067	2.814
5.632	91.61	12.96	12.30	1.901
5.827	69.01	17.54	16.66	1.807
5.709	90.13	13.19	12.46	1.667
4.414	491.0	1.605	1.440	3.066
6.202	42.33	29.22	27.54	1.695
6.492	37.37	33.23	30.23	1.357
5.571	90.73	13.10	12.49	2.170

$D_o = 1279$

$M_{FA} = 9.6992 \times 10^{-4}$

$\beta_{uni} = 5.0 \times 10^{1}$

$\beta_{phth\ chel} = 7.82 \times 10^{2}$

$K^{Ex}_{sal} = 7.08 \times 10^{-7}$

$K^{Ex}_{amino\ carb} = 0.016$

$K^{Ex}_{evol} = 2.0 \times 10^{-5}$

$I = 0.10$ M NaCl

Table IIA. The Binding of Trace Concentration Levels of $Co^{+2}(Co^{60})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
4.055	1250	0.1439	0.1254	3.334
3.940	1200	0.1917	0.1762	6.102
4.106	1242	0.1510	0.1309	3.097
3.967	1245	0.1489	0.1327	4.320
4.130	1242	0.1509	0.1301	2.912
3.987	1282	0.1153	0.09866	3.067
5.133	1058	0.3513	0.2702	0.6241
4.112	1066	0.3418	0.3215	7.503
4.702	1068	0.3395	0.2910	1.766
6.515	539.7	1.650	1.052	0.1967
5.253	1007	0.4198	0.3275	0.5812
4.149	1178	0.2136	0.1921	4.119
7.292	298.5	3.791	0.6280	0.06938
4.576	1160	0.2332	0.1923	1.554
4.661	1140	0.2543	0.2084	1.388
4.255	1158	0.2348	0.2094	3.521
6.810	477.0	1.998	0.8989	0.1274
5.009	1026	0.3940	0.3234	0.9835

$D_o = 1430$

$M_{FA} = 1.109 \times 10^{-4}$

$\beta_{uni} = 3.0 \times 10^{1}$

$\beta_{phth\ chel} = 7.82 \times 10^{2}$

$K^{Ex}_{sal} = 7.08 \times 10^{-7}$

$K^{Ex}_{amino\ carb} = 1.6 \times 10^{-2}$

$K^{Ex}_{evol} = 1.3 \times 10^{-5}$

$I = 0.10$ M NaCl

Table IIB. The Binding of Trace Concentration Levels of $Co^{+2}(Co^{60})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
3.410	1153	0.2404	0.2037	4.028
3.420	1218	0.1743	0.1371	2.649
3.617	1044	0.3702	0.3206	3.938
3.608	1066	0.3412	0.2923	3.665
3.695	1088	0.3139	0.2579	2.648
3.654	1051	0.3610	0.3085	3.480
3.892	891.3	0.6043	0.5281	3.450
3.857	880.6	0.6239	0.5518	3.905
4.137	726.5	0.9683	0.8565	3.191
4.025	819.0	0.7460	0.6521	3.139
4.317	644.2	1.220	1.073	2.650
4.206	692.2	1.066	0.9417	2.996
4.391	574.5	1.489	1.326	2.765
4.737	383.0	2.734	2.477	2.360
6.416	33.74	41.38	38.61	1.627
6.425	11.77	120.5	117.7	4.913
6.879	13.62	104.0	96.61	2.839
6.447	24.26	57.94	54.99	2.244
6.362	25.46	55.17	52.67	2.356
5.595	99.62	13.35	12.67	1.921
9.205	6.940	205.1	-1288	-29.25
8.945	6.480	219.7	- 601.1	-13.66
6.291	37.86	36.77	34.60	1.683
6.352	33.26	41.99	39.55	1.789
6.753	14.46	97.89	92.27	2.919

$M_{FA} = 9.283 \times 10^{-4}$

All other parameters the same as in Table IIA.

Table IIC. The Binding of Trace Concentration Levels of $Co^{+2}(Co^{60})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
4.239	847.8	0.6867	0.5602	2.557
4.253	811.1	0.7630	0.6338	2.801
4.423	888.7	0.6091	0.4404	1.317
4.403	798.7	0.7904	0.6269	1.963
4.648	663.4	1.156	0.9153	1.634
4.752	769.0	0.8596	0.5777	0.8131
4.962	473.1	2.023	1.639	1.429
5.163	406.2	2.520	2.018	1.115
5.350	352.0	3.063	2.431	0.8816
5.180	270.6	4.285	3.771	2.005
5.449	220.0	5.500	4.793	1.393
4.802	200.0	6.150	5.846	7.339
6.083	83.23	16.18	14.73	1.107
6.504	46.95	29.46	26.77	0.9283
6.519	66.34	20.56	17.80	0.6023
5.780	91.11	14.70	13.68	1.928
5.400	170.5	7.387	6.718	2.178
6.380	73.25	18.52	16.32	0.6993

D_o = 143,000
M_{FA} = 9.968×10^{-5}
I = 0.010 M NaCl

All other parameters the same as in Table IIA.

Table IID. The Binding of Trace Concentration Levels of $Co^{+2}(Co^{60})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
3.600	178.2	7.026	6.777	22.83
3.570	204.2	6.002	5.762	20.80
3.696	116.5	11.27	10.99	29.69
3.834	195.0	6.335	5.989	11.78
4.042	123.1	10.61	10.14	12.37
4.035	136.0	9.516	9.049	11.21
4.296	43.70	31.73	31.02	21.11
4.280	62.95	21.72	21.03	14.85
4.587	42.30	32.80	31.70	11.08
4.588	66.89	20.38	19.27	6.720
4.999	29.17	48.02	46.07	6.311
5.078	17.05	82.87	80.72	9.255
5.513	13.38	105.9	102.4	4.484
5.626	11.85	119.6	115.7	3.977
5.787	8.443	168.4	163.6	4.018
6.357	2.998	475.9	465.0	3.982
6.322	3.305	431.7	421.4	3.817
6.459	2.563	557.0	543.9	3.987
6.651	1.963	727.6	708.8	4.017
6.655	1.971	724.5	705.6	3.979
6.772	1.750	816.3	792.4	3.914
6.871	1.227	1164	1135	5.083
6.837	1.393	1026	998.7	4.618
7.288	0.7017	2037	1965	6.612
7.210	0.8051	1775	1715	6.003

D_o = 143,000

M_{FA} = 9.307×10^{-4}M

I = 0.010 M NaCl

All other parameters the same as in Table IIA.

Table IIIA. The Binding of Trace Concentration Levels of $Cd^{2+}(Cd^{109})$ to the R-OH Sites in Armadale Horizons Bh Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
4.875	803	179.0	174.7	13.21
4.895	698	206.0	201.6	14.56
5.178	397	363.0	356.5	13.54
5.110	505	285.0	279.1	12.36
5.480	220	654.0	644.6	12.45
5.469	227	635.0	625.7	12.38
5.925	741	1950	1934	14.28
5.939	708	2040	2024	14.51
6.178	38.3	3770	3748	16.62
6.136	43.8	3300	3279	15.79
6.345	36.1	5540	5512	17.89
6.158	25.1	5750	5729	26.42
6.465	6.80	21000	20970	55.19
6.488	12.8	11300	11260	28.53
6.504	11.4	12700	12660	31.24
6.556	11.4	12700	12660	28.72

$M_{FA} = 1.087 \times 10^{-3}$

$I = 0.001$ M $NaNO_3$

$\beta_{uni} = 2.5 \times 10^1$

$\beta_{phth} = 7.0 \times 10^2$

$K^{Ex}_{sal} = 2.7 \times 10^{-7}$

$K^{Ex}_{amino\ carb} = 1.6 \times 10^{-2}$

$K^{Ex}_{enol} = 1.3 \times 10^{-5}$

Table IIIB. The Binding of Trace Concentration Levels of $Cd^{2+}(Cd^{109})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
3.919	228	5.340	4.642	6.870
3.978	204	6.080	5.644	6.851
4.10	154	8.410	7.882	7.228
4.250	136	9.600	8.928	5.802
4.270	121	10.90	10.21	6.335
4.400	85.0	16.00	15.14	6.978
4.500	68.8	20.00	19.00	6.962
4.70	48.5	28.80	27.44	6.368
4.865	37.6	37.40	35.68	5.689
4.900	33.3	42.40	40.59	5.979
5.00	28.3	50.10	48.04	5.643
5.10	23.8	59.60	57.26	5.370
5.20	20.1	70.80	68.17	5.110
5.30	16.8	85.10	82.14	4.930
5.40	14.3	100	96.68	4.655
5.50	11.9	120.0	116.3	4.502
5.60	9.90	145.0	140.8	4.398
5.691	7.73	186.0	181.4	4.671
5.740	10.8	133.0	128.1	2.978
5.850	6.42	224.0	218.3	4.053
5.959	5.37	268.0	261.4	3.910
5.990	5.00	288.0	281.1	3.959
6.004	3.93	367.0	360.0	4.935
6.023	4.69	307.0	299.8	3.963
6.100	4.02	359.0	350.9	4.017
6.20	3.38	427.0	417.5	3.994
6.296	2.48	582.0	570.9	4.638
6.472	2.24	645.0	629.8	3.894
6.651	1.29	1120	1099	5.350
6.711	1.43	1010	985.8	4.474

M_{FA} = 1.087×10^{-3}

I = 0.010 M $NaNO_3$

All other parameters the same as in Table IIIA.

Table IIIC. The Binding of Trace Concentration Levels of $Cd^{2+}(Cd^{109})$ to the R-OH Sites in Armadale Horizons Bh Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
4.00	312	3.630	3.298	3.911
4.064	252	4.720	4.352	4.458
4.080	234	5.160	4.783	4.723
4.200	198	6.310	5.855	4.394
4.306	172	7.380	6.847	4.034
4.340	166	7.730	7.170	3.910
4.50	106	12.60	11.90	4.511
4.60	87.6	15.50	14.70	4.444
4.727	74.5	18.40	17.46	3.967
4.752	55.8	24.90	23.93	5.141
4.943	45.5	30.80	29.59	4.157
4.970	49.0	28.50	27.25	3.607
5.10	37.8	37.20	35.76	3.563
5.20	32.3	43.70	42.08	3.382
5.30	27.3	51.90	50.08	3.258
5.352	23.0	61.80	59.86	3.495
5.382	22.8	62.40	60.38	3.314
5.500	19.5	73.10	70.75	3.059
5.637	16.9	84.60	81.75	2.709
5.780	13.0	110.0	106.4	2.714
5.711	14.4	99.00	95.81	2.766

M_{FA} = 4.480×10^{-3}

I = 0.10 M $NaNO_3$

All other parameters the same as in Table IIIA.

Table IIID. The Binding of Trace Concentration Levels of $Cd^{2+}(Cd^{109})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	$\frac{D}{10^2}$	$\frac{D_o-D}{D}$	$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f}$	$\frac{\beta}{10^5}$
3.457	954.1	0.5150	0.4797	7.875
3.500	925.4	0.5620	0.5243	7.797
3.60	854.3	0.6920	0.6480	7.657
3.700	772.6	0.8710	0.8194	7.696
3.791	734.1	0.9690	0.9093	6.930
3.90	639.6	1.260	1.189	7.055
4.028	569.1	1.540	1.453	6.429
4.100	519.9	1.780	1.682	6.313
4.200	470	2.070	1.956	5.840
4.268	443	2.260	2.133	5.454
4.348	404	2.580	2.438	5.193
4.513	329	3.390	3.211	4.702
4.664	281	4.130	3.912	4.073
4.800	233	5.190	4.933	3.787
4.90	205	6.030	5.741	3.529
5.017	176	7.200	6.870	3.263
5.100	159	8.040	7.677	3.044
5.206	118	11.20	10.79	3.407
5.257	125	10.50	10.06	2.852
5.425	106	12.60	12.06	2.413
5.60	81.2	16.80	16.12	2.281
5.700	71.9	19.10	18.31	2.146
5.800	60.7	22.80	21.88	2.143
5.886	61.2	22.60	21.53	1.821
6.000	47.9	29.20	27.90	1.966
6.100	41.4	33.90	32.34	1.967
6.200	35.4	39.80	37.91	2.015
6.300	30.9	45.70	43.39	2.042
6.50	26.4	53.70	50.87	2.148
6.515	21.6	66.00	62.40	2.364

M_{FA} = 1.126×10^{-3}

I = 0.10 M $NaNO_3$

All other parameters the same as in Table IIIA.

Table IVA. The Binding of Trace Concentration Levels of $Eu^{+3}(Eu^{154})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o-D}{D \times 10^3}$	$\frac{\beta}{10^9}$
4.954	165	1333	25.32
4.969	176	1250	22.94
4.988	165	1333	23.43
5.043	106	2075	32.19
5.061	116	1897	28.23
5.081	103	2136	30.39
5.088	105	2095	29.34
5.118	104	2115	27.67
5.122	105	2095	27.16
5.143	110	2000	24.72
5.157	80.4	2736	32.77
5.183	139	1583	17.87
5.266	60.7	3624	33.94
5.310	70.0	3143	26.66

$D_o = 2.20 \times 10^8$

$M_{FA} = 9.0 \times 10^{-5}$

$I = 0.010$ M NaCl

$$\frac{\Sigma M_b}{M_f} <<< \frac{D_o-D}{D}$$

so that

$$\frac{D_o-D}{D} - \frac{\Sigma M_b}{M_f} = \frac{D_o-D}{D}$$

Table IVB. The Binding of Trace Concentration Levels of $Eu^{+3}(Eu^{154})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o-D}{D \times 10^3}$	$\frac{\beta}{10^9}$
4.705	3.54	621.5	10.42
4.758	3.37	652.8	9.693
4.908	1.60	1375	14.50
4.958	1.56	1410	13.27
4.992	1.58	1392	12.12
5.008	1.29	1705	14.32
5.269	49.3	4462	20.76
5.332	62.7	3509	14.17
5.625	49.0	4490	9.467
5.653	47.3	4651	9.226
5.821	35.3	6232	8.609
5.905	35.7	6162	7.131
6.390	8.10	27160	12.23
6.603	10.1	21780	6.903
6.909	12.0	18330	3.858
7.168	13.7	16060	2.628
7.249	10.3	21360	3.287
7.460	9.25	23780	3.224
7.526	9.13	24100	3.167
7.572	8.15	26990	3.480
7.652	8.35	26350	3.296
7.657	6.27	35090	4.382
7.665	8.51	25850	3.220
7.716	5.28	41670	5.106
7.725	9.33	23580	2.882
7.835	6.83	32210	3.822
7.869	6.52	33740	3.972
7.956	9.08	24230	2.802
7.960	9.67	22750	2.629
8.140	7.23	30430	3.421
8.426	6.76	32540	3.562
8.445	4.23	52010	5.686
8.816	4.13	53270	5.731
9.084	4.89	44990	4.814
9.128	7.41	29690	3.175
9.314	3.36	65480	6.987
9.400	2.90	75860	8.090
10.32	8.10	27160	2.888
9.611	3.59	61280	6.527
9.914	4.22	52130	5.547

D_o = 2.20×10^8
M_{FA} = 1.8×10^{-4}
I = 0.010 M NaCl

Table IVC. The Binding of Trace Concentration Levels of $Eu^{+3}(Eu^{154})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o - D}{D \times 10^3}$	$\frac{\beta}{10^9}$
4.347	247	7.286	1.772
4.385	379	4.748	1.059
4.470	285	6.315	1.159
4.476	327	5.504	0.9961
4.483	316	5.695	1.014
4.496	243	7.406	1.281
4.525	137	13.14	2.126
4.541	230	7.825	1.221
4.544	188	9.573	1.483
4.616	227	7.929	1.042
4.628	286	6.293	0.8046
4.739	202	8.910	0.8845
4.801	205	8.779	0.7568
4.854	150	12.00	0.9170
4.894	218	8.256	0.5762

D_o = 1.80×10^7

M_{FA} = 1.30×10^{-4}

I = 0.050 M NaCl

Table IVD. The Binding of Trace Concentration Levels of $Eu^{+3}(Eu^{154})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o - D}{D \times 10^3}$	$\frac{\beta}{10^9}$
3.890	48.8	4.507	3.813
3.917	42.4	5.188	4.126
3.964	43.7	5.033	3.594
4.064	35.8	6.144	3.489
4.104	34.4	6.394	3.313
4.243	22.4	9.820	3.704
4.282	36.0	6.110	2.108
4.453	16.0	13.75	3.215
4.469	14.7	14.96	3.374
4.662	9.44	23.30	3.397
4.795	9.50	23.16	2.505
4.999	3.15	69.84	4.809

$D_o = 2.20 \times 10^5$
$M_{FA} = 9.0 \times 10^{-4}$
$I = 0.10$ M NaCl

Table IVE. The Binding of Trace Concentration Levels of $Eu^{+3}(Eu^{154})$ to the R-OH Sites in Armadale Horizons Bh-Fulvic Acid.

pH	D	$\frac{D_o-D}{D \times 10^3}$	$\frac{\beta}{10^9}$
3.604	45.50	0.1781	3.072
3.678	32.50	0.2498	3.635
3.747	32.60	0.2490	3.093
3.820	34.90	0.2325	2.443
3.831	38.80	0.2091	2.142

$D_o = 8.15 \times 10^3$

$M_{FA} = 9.0 \times 10^{-5}$

$I = 0.30$ M NaCl

Table V. Cd(II)-Binding in Armadale Horizons Bh Fulvic Acid (Present study period).

Vol Base ml	pH	pCd	$Cd_b(calc)_B$ μmoles	$Cd_b(calc)_A$ μmoles	$Cd_b(exp)$ μmoles
0.040	3.382	3.781	0.23797	1.0747	0.46452
0.060	3.427	3.725	0.31284	1.3511	0.67955
0.030	3.449	3.781	0.20177	1.0237	0.46618
0.12	3.539	3.788	0.28356	1.3518	0.58397
0.16	3.616	3.800	0.31600	1.5149	0.80018
0.018	3.680	3.807	0.15058	0.99984	0.94943
0.22	3.770	3.822	0.38717	1.8542	1.1838
0.25	3.876	3.833	0.44902	2.1133	1.3686
0.29	3.994	3.852	0.49541	2.3297	1.6790
0.31	4.060	3.870	0.52790	2.4576	1.9634
0.27	3.866	3.885	0.40344	1.9612	2.1990
0.33	4.171	3.908	0.57823	2.6504	2.5295
0.35	4.239	3.926	0.61902	2.7863	2.7797
0.37	4.329	3.945	0.68466	2.9824	3.0330
0.39	4.421	3.971	0.74694	3.1597	3.3630
0.41	4.509	3.994	0.81366	3.3331	3.6389
0.43	4.619	4.024	0.89967	3.5406	3.9781
0.45	4.712	4.050	0.97432	3.7082	4.2536
0.47	4.837	4.087	1.0731	3.9165	4.6192
0.49	4.938	4.102	1.1926	4.1305	4.7579
0.50	5.011	4.128	1.2420	4.2254	4.9891
0.51	5.058	4.143	1.2785	4.2908	5.1161
0.52	5.123	4.166	1.3231	4.3706	5.3028
0.53	5.188	4.184	1.3828	4.4668	5.4421
0.54	5.269	4.210	1.4488	4.5711	5.6337
0.55	5.326	4.233	1.4823	4.6253	5.7939
0.56	5.418	4.259	1.5752	4.7555	5.9651
0.57	5.482	4.281	1.6313	4.8317	6.1022
0.58	5.581	4.319	1.7119	4.9369	6.3235
0.59	5.661	4.337	1.8308	5.0781	6.4216
0.60	5.767	4.371	1.9680	5.2340	6.5965
0.61	5.859	4.397	2.1177	5.3959	6.7212
0.62	5.980	4.434	2.3320	5.6175	6.8865
0.63	6.084	4.464	2.5531	5.8379	7.0106

Total millimoles FA = 0.070
Total millimoles Cd(II) = 0.00875

Table VIA. Cd(II)-Ion Binding to Armadale Horizons Bh Fulvic Acid (Data from Previous Period of Study; I = 0.100 M).

Vol of Base ml	pH	pCd	Cd_b(calc) μmoles	Cd_b(exp) μmoles
0.00	3.087	3.406	2.7080	0.28921
0.10	3.142	3.417	3.0054	0.74392
0.20	3.209	3.434	3.3259	1.4463
0.30	3.280	3.452	3.7121	2.1642
0.40	3.361	3.466	4.2506	2.6958
0.50	3.452	3.487	4.8526	3.4801
0.60	3.545	3.504	5.6191	4.0829
0.70	3.658	3.532	6.4827	5.0474
0.80	3.781	3.564	7.4856	6.0822
0.90	3.907	3.598	8.6006	7.1050
1.00	4.058	3.637	9.9669	8.1895
1.10	4.209	3.693	11.185	9.5980
1.20	4.377	3.756	12.185	10.985
1.30	4.551	3.822	13.098	12.241
1.45	4.828	3.944	14.200	14.124
1.50	4.926	3.990	14.502	14.710
1.60	5.143	4.094	15.051	15.828
1.70	5.389	4.206	15.653	16.770
1.80	5.653	4.332	16.239	17.579
1.90	5.975	4.472	17.378	18.243
2.00	6.386	4.646	19.620	18.821
2.10	6.886	4.828	24.179	19.223

Total millimoles FA = 0.2239
Total millimoles Cd(II) = 0.020

Table VIB. Cd(II)-Ion Binding in Armadale Horizons Bh Fulvic Acid (Data from Previous Period of Study; I = 0.100 M).

Vol of Base ml	pH	pCd	Cd_b(calc) µmoles	Cd_b(exp) µmoles
0.00	3.003	3.048		
0.10	3.062	3.055	5.1676	5.4189
0.20	3.119	3.062	5.6396	6.0450
0.30	3.168	3.065	6.2565	6.2615
0.40	3.263	3.079	6.8454	7.5656
0.50	3.351	3.093	7.5435	8.8310
0.60	3.441	3.110	8.2971	10.334
0.70	3.547	3.123	9.3663	11.428
0.80	3.660	3.151	10.245	13.766
0.90	3.784	3.171	11.547	15.329
0.95	3.846	3.185	12.148	16.396
1.00	3.912	3.119	15.340	10.843
1.05	3.981	3.216	13.486	18.651
1.10	4.053	3.229	14.337	19.546
1.15	4.141	3.246	15.306	20.686
1.20	4.196	3.263	15.951	21.784
1.25	4.277	3.280	16.959	22.841
1.30	3.346	3.301	7.4701	24.098
1.36	4.455	3.328	19.059	25.631
1.40	4.522	3.345	19.950	26.549
1.45	4.611	3.369	21.101	27.788
1.50	4.705	3.393	22.400	28.962
1.55	4.789	3.427	23.190	30.528
1.60	4.894	3.455	24.610	31.726
1.65	4.835	3.478	23.621	32.652
1.70	5.109	3.516	26.141	34.090
1.75	5.228	3.550	27.023	35.274
1.80	5.362	3.584	28.068	36.370
1.85	5.514	3.365	37.810	27.410
1.90	5.667	3.673	29.962	38.874
1.95	5.852	3.721	31.361	40.029
2.00	6.052	6.765	1.1203	49.991
2.05	6.236	3.806	35.736	41.786
2.10	6.497	3.871	39.821	42.921
2.15	6.771	3.936	45.292	43.899
2.20	7.053	4.001	51.390	44.742

Total millimoles FA = 0.2242

Total millimoles Cd(II) = 0.050

Table VIIA. Cd(II)-Ion Binding to Armadale Horizons Bh Fulvic Acid (Data from Previous Period of Study; I = 0.010 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) μmoles	Cd_b(exp) μmoles
0.00	3.692	4.086	0.94286	0.85722
0.50	3.904	4.118	1.2099	1.1134
1.00	4.172	4.176	1.6670	1.5659
1.50	4.524	4.255	2.5749	2.1093
2.00	5.002	4.413	3.0934	2.9716
2.50	5.677	4.665	3.5966	3.8538
2.75	6.212	4.874	3.8363	4.2883
3.00	6.926	5.130	4.5094	4.6034
3.25	7.938	5.486	6.2722	4.8245

Total millimoles FA = 0.0272
Total millimoles of Cd(II) = 0.0050

Table VIIB. Cd(II)-Ion Binding to Armadale Horizons Bh Fulvic Acid (Data from Previous Period of Study; I = 0.010 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) μmoles	Cd_b(exp) μmoles
0.00	3.546	4.094	0.94300	0.93283
0.10	3.566	4.094	1.0066	0.92478
0.20	3.588	4.098	1.0586	0.95417
0.30	3.611	4.101	1.1186	0.97409
0.40	3.633	4.105	1.1818	1.0031
0.60	3.688	4.116	1.3033	1.0878
0.80	3.749	4.127	1.4504	1.1707
1.00	3.806	4.142	1.6134	1.2863
1.20	3.878	4.167	1.7595	1.4804
1.40	3.955	4.182	1.9948	1.5868
1.60	4.043	4.211	2.2093	1.7949
1.80	4.137	4.248	2.4325	2.0454
2.00	4.239	4.288	2.6944	2.2951
2.10	4.293	4.303	2.8720	2.3819
2.20	4.350	4.339	2.9577	2.5856
2.30	4.402	4.361	3.1156	2.7005
2.40	4.474	4.405	3.2140	2.9181
2.50	4.546	4.445	3.3460	3.0977
2.70	4.687	4.518	3.6705	3.3860
2.90	4.833	4.603	3.9913	3.6679
3.10	4.996	4.701	4.3350	3.9330
3.30	5.174	4.815	4.8312	4.1763
3.50	5.374	4.950	4.8480	4.3941
3.70	5.577	5.089	4.8329	4.5584
4.00	5.927	5.305	4.8706	4.7300
4.20	6.198	5.481	4.8930	4.8193
4.40	6.492	5.667	4.9868	4.8818
4.60	6.855	5.861	5.3090	4.9241
4.70	6.999	5.942	5.4503	4.9369

Total millimoles FA = 0.05454
Total millimoles of Cd(II) = 0.0050

Table VIIC. Cd(II)-Ion Binding to Armadale Horizons Bh Fulvic Acid (Data from Previous Period of Study; I = 0.010 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) µmoles	Cd_b(exp) µmoles
0.00	3.581	4.581	0.34902	0.68064
0.25	3.628	4.581	0.42943	0.67408
0.50	3.689	4.584	0.52397	0.67668
0.75	3.766	4.599	0.62660	0.71524
1.00	3.846	4.627	0.74247	0.78944
1.25	3.944	4.663	0.88660	0.88015
1.50	4.060	4.710	1.0693	0.98993
1.75	4.180	4.767	1.2944	1.1096
2.00	4.320	4.835	1.5834	1.2347
2.25	4.494	4.950	1.8663	1.4095
2.50	4.671	5.072	2.2032	1.5515
2.75	4.876	5.223	2.6560	1.6811
3.00	5.094	5.405	2.6945	1.7886
3.25	5.325	5.599	2.7211	1.8634
3.50	5.571	5.818	2.7035	1.9163
3.75	5.860	6.065	2.6935	1.9515
4.00	6.159	6.302	2.6986	1.9710
4.25	6.514	6.542	2.7345	1.9824
4.50	6.927	6.803	2.6858	1.9894

Total millimoles FA = 0.0542
Total millimoles Cd(II) = 0.0020

Table VIII. Cd(II)-Ion Binding to Armadale Horizons Bh Fulvic Acid (Data from this Period of Study; I = 0.10 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) μmoles	Cd_b(exp) μmoles
0.02	3.520	3.647	1.1585	0.41429
0.01	3.510	3.647	1.1140	0.41655
0.03	3.560	3.647	1.1884	0.41204
0.04	3.567	3.643	1.2574	0.30541
0.05	3.593	3.643	1.3021	0.30314
0.06	3.607	3.640	1.2910	0.22191
0.07	3.640	3.643	1.3426	0.29858
0.08	3.652	3.640	1.3700	0.21733
0.09	3.707	3.643	1.4631	0.29403
0.10	3.749	3.643	1.5930	0.29176
0.11	3.764	3.643	1.5693	0.28948
0.12	3.797	3.647	1.6233	0.39175
0.13	3.821	3.651	1.6605	0.49310
0.14	3.873	3.651	1.7619	0.49087
0.15	3.892	3.654	1.7925	0.56574
0.16	3.944	3.658	1.8869	0.66554
0.17	3.970	3.661	1.9322	0.73924
0.18	4.027	3.665	2.0387	0.83748
0.19	4.063	3.672	2.0957	1.0089
0.20	4.117	3.676	2.1979	1.1047
0.21	4.150	3.679	2.2594	1.1755
0.22	4.219	3.686	2.3873	1.3415
0.23	4.259	3.694	2.4517	1.5284
0.24	4.321	3.701	2.5663	1.6889
0.25	4.368	3.708	2.6492	1.8468
0.26	4.441	3.710	2.8035	1.8901
0.27	4.489	3.720	2.8812	2.1112
0.28	4.565	3.730	3.0214	2.3274
0.29	4.626	3.744	3.1162	2.6226
0.30	4.707	3.755	3.2652	2.8476
0.31	4.771	3.765	3.3789	3.0472
0.32	4.859	3.776	3.5444	3.2617
0.33	4.928	3.791	3.6516	3.5462
0.34	5.027	3.798	3.8577	3.6748
0.35	5.101	3.819	3.9517	4.0517
0.36	5.110	3.831	3.9264	4.2583
0.37	5.303	3.855	4.2872	4.6565
0.38	5.414	3.870	4.4941	4.8939
0.39	5.523	3.887	4.6919	5.1535
0.40	5.670	3.909	4.9735	5.4751
0.41	5.803	3.931	5.2340	5.7810
0.42	5.973	3.945	5.6698	5.9673
0.43	6.172	3.977	6.1736	6.3727
0.44	6.354	4.002	6.7529	6.6692
0.45	6.613	4.031	7.8211	6.9926
0.46	6.836	4.067	8.8464	7.3654

Total millimoles FA = 0.04068
Total millimoles Cd(II) = 0.00117

Table IXA. Cd(II)-Ion Binding to Swedish Fulvic Acid (Data from this Period of Study; I = 0.10 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) μmoles	Cd_b(exp) μmoles
0.00	3.820	4.476	0.28972	0.57940
0.20	3.875	4.495	0.31997	0.65483
0.40	3.953	4.499	0.37194	0.66533
0.60	4.029	4.518	0.42239	0.73741
1.00	4.240	4.548	0.59190	0.84313
1.20	4.348	4.560	0.66302	0.88253
1.40	4.493	4.579	0.77199	0.94611
1.60	4.603	4.598	0.85067	1.0072
1.80	4.804	4.617	1.0045	1.0659
2.00	5.009	4.651	1.1321	1.1687
2.20	5.286	4.708	1.2645	1.3274
2.40	5.608	4.735	1.4124	1.3939
2.50	5.821	4.769	1.4868	1.4748
2.60	6.056	4.807	1.5738	1.5584
2.70	6.349	4.856	1.7088	1.6565
2.80	6.692	4.909	1.9380	1.7511

Total millimoles FA = 0.02759

Total millimoles Cd(II) = 0.002491

Table IXB. Cd(II)-Ion Binding to Swedish Fulvic Acid (Data from this Period of Study; I = 0.10 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) µmoles	Cd_b(exp) µmoles
0.00	3.723	4.459	0.55683	0.62070
0.20	3.892	4.473	0.52239	0.67283
0.40	3.980	4.912	0.19806	0.18175
0.60	4.096	4.503	0.73977	0.78064
0.80	4.208	4.525	0.89224	0.85842
1.00	4.355	4.547	1.0888	0.93266
1.20	4.517	4.576	1.3230	1.0271
1.40	4.717	4.621	1.5998	1.1649
1.60	4.930	4.680	1.8875	1.3273
1.80	5.180	4.757	2.0277	1.5105
2.00	5.465	4.867	2.1131	1.7238
2.20	5.465	4.867	2.1131	1.7211
2.40	6.366	5.170	2.3292	2.0990

Total millimoles FA = 0.02744
Total millimoles Cd(II) = 0.002476

Table IXC. Cd(II)-Ion Binding to Swedish Fulvic Acid (Data from this Period of Study; I = 0.10 M).

Vol Base Added ml	pH	pCd	Cd_b(calc) µmoles	Cd_b(exp) µmoles
0.00	3.749	4.745	0.18368	0.23344
0.20	3.788	4.751	0.18634	0.24383
0.40	3.865	4.758	0.21309	0.25643
0.60	3.912	4.765	0.22975	0.26887
0.80	3.988	4.772	0.26120	0.28118
1.00	4.053	4.782	0.28858	0.29992
1.40	4.218	4.806	0.36884	0.34474
1.60	4.456	4.813	0.53112	0.35613
1.80	4.604	4.824	0.64047	0.37548
2.00	4.808	4.841	0.79595	0.40616
2.20	5.014	4.861	0.94533	0.44138
2.40	5.320	4.892	1.1352	0.49451
2.60	5.631	4.937	1.2735	0.56654

Total millimoles FA = 0.02770
Total millimoles of Cd(II) = 0.001250

Table XA. The Binding of Cu(II) to Swedish (Aquatic) Fulvic Acid; A Comparison of the Predictive Quality of Two Models.

System: FA, $NaNO_3$; I = 0.10 M

Vol. NaOH ml	pH	pCu	$Cu_b(calc)_B$ µmoles	$Cu_b(calc)_A$ µmoles	$Cu_b(exp)$ µmoles
0.00	3.970	4.227	0.48167	1.1908	0.82443
0.10	4.013	4.248	0.49309	1.2023	0.95976
0.20	4.064	4.255	0.51981	1.2291	0.99979
0.30	4.124	4.262	0.55100	1.2604	1.0393
0.40	4.191	4.272	0.58542	1.2948	1.0970
0.50	4.267	4.276	0.63636	1.3458	1.1166
0.60	4.351	4.283	0.67551	1.3849	1.1545
0.70	4.443	4.293	0.72403	1.4332	1.2098
0.80	4.545	4.307	0.78039	1.4893	1.2874
0.90	4.671	4.317	0.86466	1.5729	1.3401
1.00	4.802	4.335	0.95550	1.6626	1.4357
1.10	4.970	4.359	1.0879	1.7923	1.5591
1.20	5.151	4.387	1.2543	1.9530	1.6956
1.30	5.386	4.427	1.5223	2.2052	1.8780
1.40	5.656	4.481	1.9340	2.5760	2.1007
1.50	5.985	4.554	2.6612	3.1993	2.3625
1.60	6.304	4.669	3.4326	3.8356	2.6973
1.70	6.596	4.829	3.9811	4.2839	3.0391
1.80	6.953	5.087	4.4018	4.6333	3.3840
1.90	7.262	5.470	4.1481	4.3992	3.6339

Total millimoles FA = 0.01421
Total millimoles Cu(II) = 0.003811
M_{NaOH} = 0.01007

Table XB. The Binding of Cu(II) to Swedish (Aquatic) Fulvic Acid; A Comparison of the Predictive Quality of Two Models.

System: FA, $NaNO_3$; I = 0.10 M

Vol. NaOH ml	pH	pCu	$Cu_b(calc)_B$ μmoles	$Cu_b(calc)_A$ μmoles	$Cu_b(exp)$ μmoles
0.00	3.926	3.948	0.53759	1.2469	1.9026
0.10	3.941	3.945	0.58324	1.2927	1.8516
0.20	3.987	3.945	0.62117	1.3307	1.8403
0.30	4.042	3.945	0.66524	1.3748	1.8289
0.40	4.104	3.952	0.70173	1.4112	1.9104
0.50	4.161	3.955	0.75959	1.4690	1.9386
0.60	4.230	3.962	0.81952	1.5288	2.0185
0.70	4.304	3.962	0.92257	1.6317	2.0076
0.80	4.391	3.973	1.0126	1.7214	2.1374
0.90	4.495	3.983	1.1002	1.8084	2.2519
1.00	4.607	3.987	1.2346	1.9417	2.2908
1.10	4.737	3.997	1.4021	2.1071	2.4021
1.20	4.867	4.011	1.5829	2.2846	2.5579
1.30	5.011	4.021	1.8238	2.5190	2.6636
1.40	5.222	4.037	2.2404	2.9167	2.8338
1.50	5.445	4.056	2.7840	3.4170	3.0300
1.60	5.730	4.081	3.6864	4.2045	3.2786
1.70	6.023	4.122	4.7552	5.0962	3.6623
1.80	6.277	4.168	5.6350	5.8343	4.0535
1.90	6.277	4.168	5.6351	5.8344	4.0467
2.00	6.654	4.303	6.4170	6.5071	4.9969
2.10	6.799	4.408	6.4838	6.5599	5.5568
2.20	6.920	4.516	6.4895	6.5598	6.0084
2.30	7.052	4.659	6.4450	6.5146	6.4589

Total millimoles FA = 0.01421
Total millimoles Cu(II) = 0.007622
M_{NaOH} = 0.01007

Table XI. An Examination of the Binding of Cu(II) Ion to a Swedish Fulvic Acid.

System: FA, $Cu(NO_3)_2$, $NaNO_3$; I = 0.010 M

Vol. NaOH ml	pH	pCu	Cu_b(calc) µmoles	Cu_b(exp) µmoles
0.00	3.894	4.226	1.4538	0.81755
0.10	3.923	4.234	1.5521	0.86635
0.20	3.959	4.248	1.6348	0.95411
0.30	4.011	4.263	1.6996	1.0456
0.40	4.129	4.299	1.5995	1.2606
0.50	4.209	4.299	1.7569	1.2556
0.60	4.297	4.314	1.9027	1.3375
0.70	4.393	4.336	2.0747	1.4551
0.80	4.518	4.373	2.2297	1.6432
0.90	4.638	4.416	2.2913	1.8437
1.00	4.781	4.482	2.4126	2.1178
1.10	4.959	4.533	2.6501	2.3025
1.20	5.123	4.606	2.8049	2.5334
1.30	5.365	4.716	3.0253	2.8173
1.40	5.584	4.833	3.1702	3.0505
1.50	5.930	5.074	3.2381	3.3736
1.60	6.218	5.359	3.0779	3.5836
1.70	6.556	5.775	2.7574	3.7236
1.80	6.873	6.432	1.9897	3.7917
1.90	7.262	7.404	1.3754	3.8089

Total millimoles FA = 0.01421
Total millimoles Cu(II) = 0.003811

Table XII. An Examination of the Binding of Cu(II) Ion to a Swedish Fulvic Acid.

System: FA, A^-, 0.10 M $NaNO_3$

Vol. $Cu(NO_3)_2$ ml	pH	pCu	Cu_b(calc) μmoles	Cu_b(exp) μmoles
0.10	5.972	6.688	2.0586	1.0191
0.12	5.943	6.484	2.1477	1.2186
0.16	5.861	6.074	2.3106	1.6033
0.20	5.810	5.790	2.4477	1.9740
0.24	5.742	5.548	2.5871	2.3218
0.28	5.700	5.345	2.7606	2.6442
0.32	5.634	5.198	2.8823	2.9593
0.36	5.603	5.068	3.0504	3.2534
0.40	5.566	4.938	3.2472	3.5064
0.44	5.531	4.808	3.4915	3.7036
0.48	5.490	4.717	3.6558	3.9217
0.52	5.471	4.658	3.7917	4.1841
0.56	5.458	4.588	3.9938	4.3901
0.60	5.446	4.549	4.1026	4.6715
0.64	5.419	4.493	4.2400	4.8746
0.68	5.407	4.447	4.3918	5.0933
0.72	5.380	4.391	4.5482	5.2407
0.76	5.378	4.423	4.4019	5.8057
0.80	5.372	4.384	4.5529	6.0261
0.84	5.362	4.300	4.9190	5.9636
0.88	5.346	4.268	5.0229	6.1679
0.92	5.339	4.219	5.2593	6.2316
0.96	5.326	4.191	5.3634	6.4249
1.00	5.316	4.163	5.4831	6.6036
1.04	5.267	4.139	5.4142	6.8026
1.08	5.296	4.100	5.7765	6.8442
1.12	5.280	4.076	5.8541	7.0096
1.16	5.275	4.069	5.8754	7.3447
1.20	5.267	4.051	5.9536	7.5583
1.24	5.265	4.037	6.0354	7.8093
1.28	5.263	4.026	6.0985	8.0903
1.32	5.275	4.023	6.1773	8.4632
1.36	5.252	4.009	6.1585	8.7031
1.40	5.255	3.988	6.3164	8.8481

Total millimoles FA = 0.02842

Total millimoles base = 0.0282

$M_{Cu(NO_3)_2}$ = 0.0103

Table XIIIA. Binding of Ca^{+2} to Armadale Horizons Bh Fulvic Acid Calculated Versus Experimental.

System: FA, A^-, $NaNO_3$; Ionic Strength = 0.10

Vol. $Ca(NO_3)_2$ ml	pH	pCa	Ca_b(calc) μmoles	Ca_b(exp) μmoles
0.10	6.947	4.737	8.7280	8.6140
0.12	6.848	4.462	12.787	9.6710
0.14	6.805	4.367	14.303	11.139
0.16	6.784	4.128	21.119	11.380
0.18	6.741	4.106	20.633	13.090
0.20	6.725	4.024	23.101	14.140
0.22	6.706	3.989	23.822	15.633
0.24	6.682	3.930	25.337	16.754
0.26	6.677	3.907	26.092	18.328
0.28	6.656	3.885	26.273	19.900
0.30	6.644	3.858	26.970	21.370
0.32	6.621	3.790	29.045	22.031
0.34	6.606	3.745	30.487	23.001
0.36	6.592	3.732	30.550	24.623
0.38	6.580	3.720	30.645	26.259
0.40	6.561	3.713	30.255	28.008
0.42	6.548	3.683	31.131	29.181
0.44	6.538	3.658	31.908	30.437
0.46	6.524	3.638	32.310	31.797
0.48	6.510	3.619	32.671	33.159
0.50	6.499	3.614	32.485	34.923
0.52	6.493	3.609	32.492	36.685
0.54	6.482	3.599	32.546	38.290
0.56	6.474	3.589	32.715	39.888
0.58	6.462	3.579	32.733	41.479
0.60	6.455	3.564	33.184	42.895
0.62	6.448	3.534	34.379	43.760
0.64	6.437	3.529	34.194	45.490
0.66	6.429	3.504	35.127	46.461
0.68	6.420	3.484	35.783	47.579
0.70	6.411	3.387	40.609	45.081
0.72	6.400	3.378	40.639	46.529
0.74	6.392	3.365	41.027	47.754

Total millimoles FA = 0.286
Total millimoles base = 0.28
$M_{Ca(NO_3)_2}$ = 0.09587

Table XIIIB. Binding of Ca^{+2} to Armadale Horizons Bh Fulvic Acid Calculated Versus Experimental.

System: FA, A^-, $NaNO_3$; Ionic Strength = 0.10

Vol. $Ca(NO_3)_2$ ml	pH	pCa	Ca_b(calc) μmoles	Ca_b(exp) μmoles
0.20	6.962	4.145	26.029	15.364
0.30	6.845	3.815	36.365	20.600
0.40	6.772	3.700	39.062	27.693
0.42	6.759	3.650	41.099	28.306
0.44	6.741	3.645	40.586	30.081
0.46	6.728	3.635	40.551	31.711
0.48	6.712	3.615	40.916	33.040
0.50	6.699	3.595	41.416	34.341
0.52	6.689	3.570	42.325	35.447
0.54	6.677	3.545	43.160	36.505
0.56	6.663	3.535	43.093	38.061
0.58	6.651	3.525	43.115	39.609
0.60	6.645	3.510	43.680	40.958
0.62	6.639	3.500	43.972	42.483
0.64	6.633	3.490	44.266	43.999
0.66	6.612	3.485	43.613	45.709
0.68	6.599	3.470	43.879	47.002
0.70	6.589	3.455	44.282	48.274
0.72	6.582	3.430	45.400	49.068
0.74	6.570	3.410	46.019	50.037
0.76	6.565	3.400	46.378	51.459
0.78	6.553	3.385	46.717	52.616
0.80	6.546	3.370	47.289	53.746
0.82	6.543	3.360	47.751	55.120
0.84	6.533	3.320	49.723	54.761
0.86	6.524	3.305	50.233	55.763
0.88	6.516	3.280	51.426	56.089
0.90	6.509	3.275	51.414	57.668
0.92	6.502	3.265	51.720	58.908
0.94	6.495	3.250	52.349	59.785
0.96	6.485	3.240	52.522	60.984
0.98	6.478	3.230	52.838	62.167
1.00	6.468	3.225	52.689	63.704

Total millimoles of FA = 0.288
Total millimoles of base = 0.28
$MCa(NO_3)$ = 0.09587

List of Technical Reports

1977–78
TR 121
KBS Technical Reports 1 – 120.
Summaries. Stockholm, May 1979.

1979
TR 79–28
The KBS Annual Report 1979.
KBS Technical Reports 79-01 – 79-27.
Summaries. Stockholm, March 1980.

1980
TR 80–26
The KBS Annual Report 1980.
KBS Technical Reports 80-01 – 80-25.
Summaries. Stockholm, March 1981.

1981
TR 81–17
The KBS Annual Report 1981.
KBS Technical Reports 81-01 – 81-16.
Summaries. Stockholm, April 1982.

1982
TR 82–28
The KBS Annual Report 1982.
KBS Technical Reports 82-01 – 82-27.
Summaries. Stockholm, July 1983.

1983
TR 83–77
The KBS Annual Report 1983.
KBS Technical Reports 83-01 – 83-76
Summaries. Stockholm, June 1984.

1984
TR 85–01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm June 1985.

1985
TR 85–01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984.
Stockholm June 1985.

TR 85–02
The Taavinunnanen gabbro massif. A compilation of results from geological, geophysical and hydrogeological investigations.
Bengt Gentzschein
Eva-Lena Tullborg
Swedish Geological Company
Uppsala, January 1985

TR 85–03
Porosities and diffusivities of some non-sorbing species in crystalline rocks.
Kristina Skagius
Ivars Neretnieks
The Royal Institute of Technology
Department of Chemical Engineering
Stockholm, 1985-02-07

TR 85–04
The chemical coherence of natural spent fuel at the Oklo nuclear reactors.
David B. Curtis
New Mexico, USA, March 1985

TR 85–05
Diffusivity measurements and electrical resistivity measurements in rock samples under mechanical stress.
Kristina Skagius
Ivars Neretnieks
The Royal Institute of Technology
Department of Chemical Engineering
Stockholm, 1985-04-15

TR 85-06
Mechanical properties of granitic rocks from Gideå, Sweden
Christer Ljunggren
Ove Stephansson
Ove Alm
Hossein Hakami
Ulf Mattila
Div of Rock Mechanics
University of Luleå
Luleå, Sweden, October 1985