ABSTRACT

YI-TAIH LUOR. A kinetic study of the dissociation of aluminum bound to an aquatic fulvic acid (Under the direction of MARK S. SHUMAN.)

The disssociation kinetics of aluminum-fulvic acid (Al-FA) as a function of the concentration of fulvic acid, pH, and ionic strength were studied with a fluorescence ligand exchange method using lumogallion. A graphical method and statistical non-linear regression were used for analyzing kinetic data. A two component, five parameters model appeared to fit the data best. For a fixed aluminum concentration, dissociation rates decreased as the concentration of fulvic acid increased and a greater fraction of the total aluminum appeared in the most slowly dissociating component. Increasing pH slightly decreased the dissociation rate. Ionic strength appeared to have no effect. The estimated pseudo-first-order dissociation rate constants for the two components were about 0.1 and 0.01 min^{-1} respectively.

Table of Contents

List of Tables

List of Figures

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I. Introduction

Aluminum in Natural Waters.

Aluminum is the most abundant metal within the earth crust (Garrels, et al., 1975), occuring mainly as aluminosilicate minerals (Buckman and Brady, 1961). These are mostly unstable in earth-surface weathering conditions and can be very mobile, forming both organic and inorganic metastable precipitates. These organic and inorganic metastable precipitates may release aluminum into streams, and lakes if the soil is acidified by acid deposition (Cronan, et al., 1979; Farmer, 1986). In northeastern North America, the additional acidification is possibly due to "acid rain" which contains sulfuric and nitric acids of industrial origin (Likens, et al., 1979; Hasselrot, et al., 1987), and the acid rain may cause low pH along with high aluminum concentration in both surface and soil waters (Driscoll, et al., 1980; Johnson, et al., 1981; Plankey and Patterson, 1987; Neal, et al., 1989).

In relation to human health, aluminum is a neurotoxin, and may also induce Alzheimer's disease, a common dementia in people over 65 years old (Perl, 1988).

The toxicity of aluminum is related to the form in which it is found, with inorganic aluminum the most toxic fraction to affect aquatic organisms such as fish. The survival of fish in acidic waters is related to the concentration of labile monomeric aluminum and pH. Complexation of aluminum with organic ligands seems to reduce aluminum toxicity to fish (Driscoll et al., 1980; Baker and Schofield, 1982). This toxicity appears to be associated with aluminum binding at the gill surface which induces suffocation (Neville and Campbell, 1988).

With respect to environmental samples, several methods have been utilized for the determination of monomeric aluminum species. For example, the Al complex with 8-hydroxyquinoline is extracted into butyl acetate or methyl isobutyl ketone and analyzed photometrically (Barnes, 1975; Driscoll, 1984; Campbell et al., 1986). Aluminum and pyrocatechol violet form a colored complex which is measured photometrically (Seip, et al., 1984; Tipping and Backes, 1988; Backes and Tipping, 1987a). An Al-lumogallion complex can be detected either photometrically or fluorimetrically (Hydes and Liss, 1976; Campbell, et al., 1983; Liator, 1987).

Analytical methods for environmental samples require identification of toxic forms of aluminum, such as the inorganic monomeric species. At the present time, there is no direct analytical technique in use that is capable of analyzing all Al^{+3} species in natural waters. All the methods rely on complicated operational procedures. Precise thermodynamic modeling is not possible because no reliable stability constants for Al-humic complexes are available.

The operational speciation of aluminum in natural waters is based on the procedure of Driscoll (1980). He classified aluminum into three soluble aluminum fractions in natural waters by using operational definitions based on acid solubility (acid soluble aluminum), and its interaction with a cation exchange column (labile monomeric aluminum is retained on the column, and non-labile monomeric aluminum is not retained). Labile monomeric aluminum species consist of Al^{+3} and its complexes with OH^-, F^-, and SO_4^{-2}. Non-labile monomeric aluminum species are those bound by organic ligands, the most important of which are presumed to be humic substances.

Objectives of This Research.

This work investigates the complexation of aluminum with Lake Drummond Fulvic Acid: 1) to evaluate proposed mechanisms of aluminum complexation by fulvic acid (FA), 2) to estimate the dissociation rate constants of Al-FA, 3) to appraise the effect of ionic strength and pH on Al-FA dissociation rates, 4) to evaluate the use of a kinetic method for non-operational speciation of aluminum in natural waters.

Ligand-exchange experiments were used to determine the dissociation rate constants of Al-FA complexes. The fluorimetric reagent lumogallion was chosen because it provides the basis of a method that is sensitive and relatively interference-free for determining aluminum in natural waters (Hydes and Liss, 1976). Ionic strength, pH, and Al:FA ratios were varied to observe the effect on dissociation rate constants of Al-FA.

II. Experimental Materials and Methods.

1). Materials.

An aluminum stock solution, Al(III), was prepared from Certified Atomic Absorption Standard Aluminum Reference Solution, 1.0 mL=1.0 mg Al in dilute HCl, from FISHER SCIENTIFIC COMPANY; 1.35 mL of this solution was diluted to 25.0 mL with 0.01 M of J.T. Baker Ultrex HCl to give a 2.0 mM stock solution. The solution was stored in a 25.0 mL HNO_3-cleaned volumetric flask. Aluminum working solutions of 2.0 and 4.0 µM Al and pH 5.0 or 5.5 were prepared by diluting 10.0 or 20.0 µL of the aluminum stock solution to 10.0 mL with working buffer solutions at the desired pH and ionic strength. Final pH adjustments were made by adding dilute HCl.

Stock 0.011 M NaAc/ 0.11 M NaCl buffer solution was prepared by diluting 2.2 mL of 0.5 M electrolytically-cleaned NaAc to 100.0 mL with distilled-deionized water, and adjusting to 0.11 ionic strength by adding 0.64284 g of Aldrich gold label reagent NaCl. Final pH was 5.61±0.01. This buffer solution was stored in a 100.0 mL HNO_3-cleaned volumetric flask. A stock 0.011 M NaAc/ 0.011 M NaCl buffer solution was also prepared. Working buffer solutions of pH 5.0 or 5.5 were prepared by adjusting the pH of the stock buffer with dilute HCl.

Lumogallion,[3-(2,4-dihydroxyphenylazo)-2-hydroxy-5-chlorobenzenesulphonic acid], was the fluorescence reagent (F.W. 344.0) used in these studies. A 2.5 mM stock lumogallion (Pfalz & Bauer) solution was prepared by dissolving 0.086 g in 100.0 mL of water. The solution was stored in a 100.0 mL, HNO_3-soaked volumetric flask. The final pH was 2.89. Lumogallion working solutions of pH 5.0 or 5.5 were prepared by diluting 200.0, 1000.0, and 2000.0 µL of the stock solution to 10.0 mL with the working buffer and resulting in 50.0, 250.0, and 500.0 µM lumogallion solution respectively. pH values were obtained by adding either dilute HCl or NaOH.

The FA used in this study was from Lake Drummond, near Suffolk, Virgina, and was isolated by using a XAD-8 resin procedure. This Lake Drummond Fulvic Acid (LDFA) is described by Thompson (1989). A stock solution was prepared by dissolving 0.205 g of solid LDFA in 100.0 mL of water, resulting in a 1000.0 mg DOC/L solution, which was refrigerated before use. LDFA working solutions were prepared by diluting 20.0, 100.0, 200.0, 400.0, and 1600.0 µL of the stock solution in 10.0 mL of working buffer, resulting in 2.0, 10.0, 20.0, 40.0, 160.0 mg DOC/L solutions respectively.

2). Instrumental.

The pH was measured with an Orion 701 digital pH meter and Orion combination electrode. Sample temperature was controlled with a Lauda RC-6 circulating temperature bath at $25.0\pm0.1^{o}C$.

Fluorescence and light scattering measurements were performed with a SLM-AMINCO Instruments Inc. model SPF 500-C spectrofluorometer. This instrument was controlled by an IBM-PC microcomputer and software which collected the intensity data and generated fluorescence spectra.

The following instrumental settings were used for measurements of fluorescence spectra: Ratio mode; Filter=1; Slit=5; Gain=1; Excitation wavelength 515.0 nm with a bandwidth of 5.0 nm; Emission wavelength 595.0 nm with a bandwidth of 5.0 nm; Integration=10. High voltage was usually set to about 355 V on the reference channel and about 775 V on the sample channel to maximize the signal to noise ratio. The 31 or 32 data points were collected for each run during two time regimes. The first 30 data points were collected at equal time spacings at 5.0 minutes intervals, and the final data points were collected at 24.0 and/or 48.0 hours.

3). Methods.

3.1) Experimental Procedures.

All experiments were conducted at $25^{o}C$. Most kinetic runs were carried out at a final aluminum concentration of 1.0 µM and a final fulvic acid concentration of 1.0, 5.0, 10.0, 20.0 and 80.0 mg DOC/L. The Al-FA solution and the lumogallion solution were allowed to stand about 12-18 hours in a covered beaker at room temperature. The lumogallion concentration used for most runs was 125.0 µM, a considerable excess over Al(III). The reaction was pseudo-first-order in lumogallion (Shuman, unpublished data). An example procedure is illustrated in Fig. II-1. The final pH values of the Al-FA and lumogallion solutions were rechecked before kinetic analysis and found to be within 0.04 pH units of the initial levels.

Kinetic runs were performed by mixing and following the fluorescence intensity of Al-Lum formation in 1.0 cm cuvettes. A pipette delivered 1.0 mL of lumogallion working solution into the cuvette, and the solution allowed to reach 25^{o}C, about 10-15 minutes. Data acquisition was initiated after another pipette transfered 1.0 mL of Al-FA working solution into this same cuvette. Data acquisition began at about two seconds after mixing. Final concentrations were 1/2 the working solution concentrations.

Two additional concurrent kinetic runs were carried out: i) no Al added, only FA and lumogallion working solutions were reacted, which was considered the blank. ii) 1.0 µM of aluminum and 125.0 µM of lumogallion, a solution which was used to correct for time-to-time variations in instrument performance.

100 µL of LDFA Stock

10 µL of Al Stock

<---------adding 5.0 mL of the stock buffer

adjusted to pH 5.5 ---------->

make up to 10.0 mL with the working buffer; (2 µM : 10.0 mg DOC/L)

stand over 12-18 hours

1.0 mL

CUVETTE mixing--->Al-FA(1 µM:5 mg DOC/L)
Lum.(125 µM)

1.0 mL

make up to 10.0 mL with the working buffer; (250 µM Lum)

adjusted to pH 5.5----------->

<------- adding 5.0 mL of the stock buffer

1 mL Stock Lumogallion

Figure II-1. The example procedure of (1 µM Al- 5 mg DOC/L FA)/125 µM Lum. preparation with 0.01 M NaAc/ 0.01 M NaCl buffer, at pH 5.5.

3.2) Kinetic Analysis.

The system examined was

$$\text{Al-FA} \rightleftharpoons \text{Al} + \text{FA}$$

$$\text{Al} + \text{Lum} \longrightarrow \text{Al-Lum}$$

Consider an aqueous mixture, Al-FA, consisting of n components in which each component, named AlL_i, is involved in the following reaction :

$$AlL_i + \text{Lum} \xrightarrow{k_i} \text{Al-Lum} + L_i$$

where L_i represents the i^{th} binding site on the organic macromolecule, and AlL_i reacts with a large excess of lumogallion to yield a common fluorescent product, Al-Lum. The overall reaction is monitored by the change in fluorescence intensity which is proportional to the concentration of Al-Lum. Each component, AlL_i,is assumed to undergo a pseudo-first-order reaction simultaneously with all other components. It is also assumed that no coagulation or precipitation occurs.

For any reactant, AlL_i, the first-order rate law is $d[AlL_i]/dt = -k_i*t$, or expressed by integral form, $[AlL_i]_t = [AlL_i]_0 * e^{(-ki*t)}$, where $[AlL_i]_t$ is the concentration of the aluminum complexed with L_i and unreacted with lumogallion at time t, $[AlL_i]_0$, is the original concentration of aluminum complexed with L_i and available for reacting with lumogallion, t is the reaction time, and k_i is the rate constant of the i^{th} component.

For a multi-component mixture such as the one considered here, the sum of the concentrations of all dissociating components at time t is

$$\sum_{i=1}^{n} C_{i(t)} = \sum_{i=1}^{n} (C_{i(0)} * e^{(-ki*t)}) \qquad (1)$$

where $C_{i(0)}$ is the initial concentration of AlL_i, the i^{th} component, and k_i is the pseudo-first-order rate constant.

Since the fluorescence intensity is related to the concentration of [Al-Lum], the time dependent concentration expression for Al-Lum can be written as,

$$I_t = a * [Al\text{-}Lum]_t = a * ([AlL_i]_0 - [AlL_i]_t) \qquad (2)$$

where "a" is a proportionality constant. Combining (1) and (2) gives

$$I_t = a * (\sum_{i=1}^{n} C_{i(0)} - \sum_{i=1}^{n} C_{i(0)} * e^{(-ki*t)})$$

$$= a * \sum_{i=1}^{n} C_{i(0)} * (1 - e^{(-ki*t)}) \qquad (3)$$

3.3) Data Treatment.

Several graphical methods were considered for determining the concentration of Al-FA complexes and dissociation rate constants. For example, the infinite-time method which utilizes an estimate of the asymptotic limit of fluorescence intensity (I_{max}) at long time was used to obtain rate constants and concentrations from the equation: $\ln(I_{max} - I_t)$ = constant-k*t where the constant of integration is the natural log of the original concentration of Al-FA complexes; $\ln(I_{max})$. The I_{max} is defined in the section of Infinite-Time Method. If the measured asymptotic limit is uncertain, the Guggenheim method (Guggenheim, 1926) can be used since it does not need the asymptotic limit. The Guggenheim method is based on plotting $\ln(I_{t+\Delta t} - I_t)$ versus time. A Time-lag method, which is closely related to the Guggenheim method, may be more convenient because it does not require the plotting of logarithms. In this study, the Infinite-Time method was selected for graphical analysis because the noise level of about 3.0 - 8.0% precluded use of the other two methods.

Graphical analysis is not reliable for systems in which the number of components is not known. Non-linear regression analysis is more suitable for such situations and was used for these studies. The infinite-time method was used for graphical display and for initial parameter estimates.

Infinite-Time Method.

If a maximum fluorescence intensity reading, Imax, is obtained at some long time, and it is assumed that $I_{max} = a * \sum_{i=1}^{n} [AlL_i]_0 = a * \sum_{i=1}^{n} C_{i(0)}$, and letting

$S = I_{max} - I_t$, then it can be shown that S/I_{max}

$$= \sum_{i=1}^{n} (C_{i(0)} * e^{(-ki*t)}) / \sum_{i=1}^{n} C_{i(0)}.$$

Note that S/I_{max} is the proportion of Al complexed with L_i which is unreacted with lumogallion at time t. Further, $\ln(S/I_{max}) = -k * t$. For a single component, $\ln(S/I_{max})$ vs. time, gives a single slope, but for mixtures, if components are kinetically well separated, linear segments with different slopes can be found with slopes reflecting the individual rate constants. For example, the equation for a two component mixture is $S/I_{max} = (C_{1(0)}/(C_{1(0)}+C_{2(0)}))* e^{(-k1*t)} + (C_{2(0)}/(C_{1(0)}+C_{2(0)}))* e^{(-k2*t)}$. This method of data analysis was used for obtaining first "guesses" for the parameter values in nonlinear analysis.

3.4) <u>Statistical Analysis</u>.

The statistics package, SYSTAT(Wilkinson, 1986), was used for statistical data analysis. The kinetic data fit best to a two component, five parameter model and was overdetermined by a three component model. The two component model,

$$I=I1*(1-EXP(-K1*T))+I2*(1-EXP(-k2*T))+X$$

where I is the measured fluorescence intensity, K1 and K2 are pseudo-first-order rate constants for the two reactions involving component 1 and 2, X is a time-independent term which includes a blank and fast reacting component, I1 and I2 are the initial fluorescence intensities for the two components, and T is the reaction time, the first data point recorded at 5 minutes after mixing. Note that this model does not need nor compute I_{max}. An initial estimate for K2 and for I2 was obtained graphically (see preceding section) from the slope (-slope*2.303) and intercept ($I_{max}*10^{-intercept}$) respectively of the long-time linear portion of the plot of log(S/I_{max}) vs. time and an estimate for K1 was calculated from the slope of the short-time linear portion of the same plot. Finally, an estimate for I1 was obtained by subtracting I2 from I_{max}.

III. Results & Discussion.

A linear standard curve of fluorescence intensity vs. Al-Lum concentration was obtained for aluminum concentrations from 0.2 to 2.0 µM at pH 5.5 (Fig. III-1). Aluminum contamination of buffer solutions was estimated to be about 90.0 nM.

Raw fluorescence intensity measurements are tabulated in Appendix I. Noise amounted to about 3.0 - 8.0 % of signal. Concentrations of aluminum and fulvic acid were below those that cause Al-FA coagulation (Hundt and O'Melia, 1988).

Preliminary kinetic runs in buffered solutions showed that Al-Lum formation was complete within 2 minutes at 1.0 µM of aluminum; thus, it was assumed that all inorganic aluminum species reacted with lumogallion before the first data point at 5 minutes.

Al-FA dissociation reactions were at least 70.0 % and most were 90.0 % complete within 150.0 minutes. The maximum fluorescence intensity was found at 24 hours after mixing and no significant changes were observed beyond that time in most cases. Plots of $\log(S/I_{max})$ vs. time are curved and show the existence of at least two Al-FA components simultaneously reacting (e.g., Fig. III-2).

Figure III-1. General appearence of maximum fluorescence intensity for varied concentrations of Al. Line is regression line.

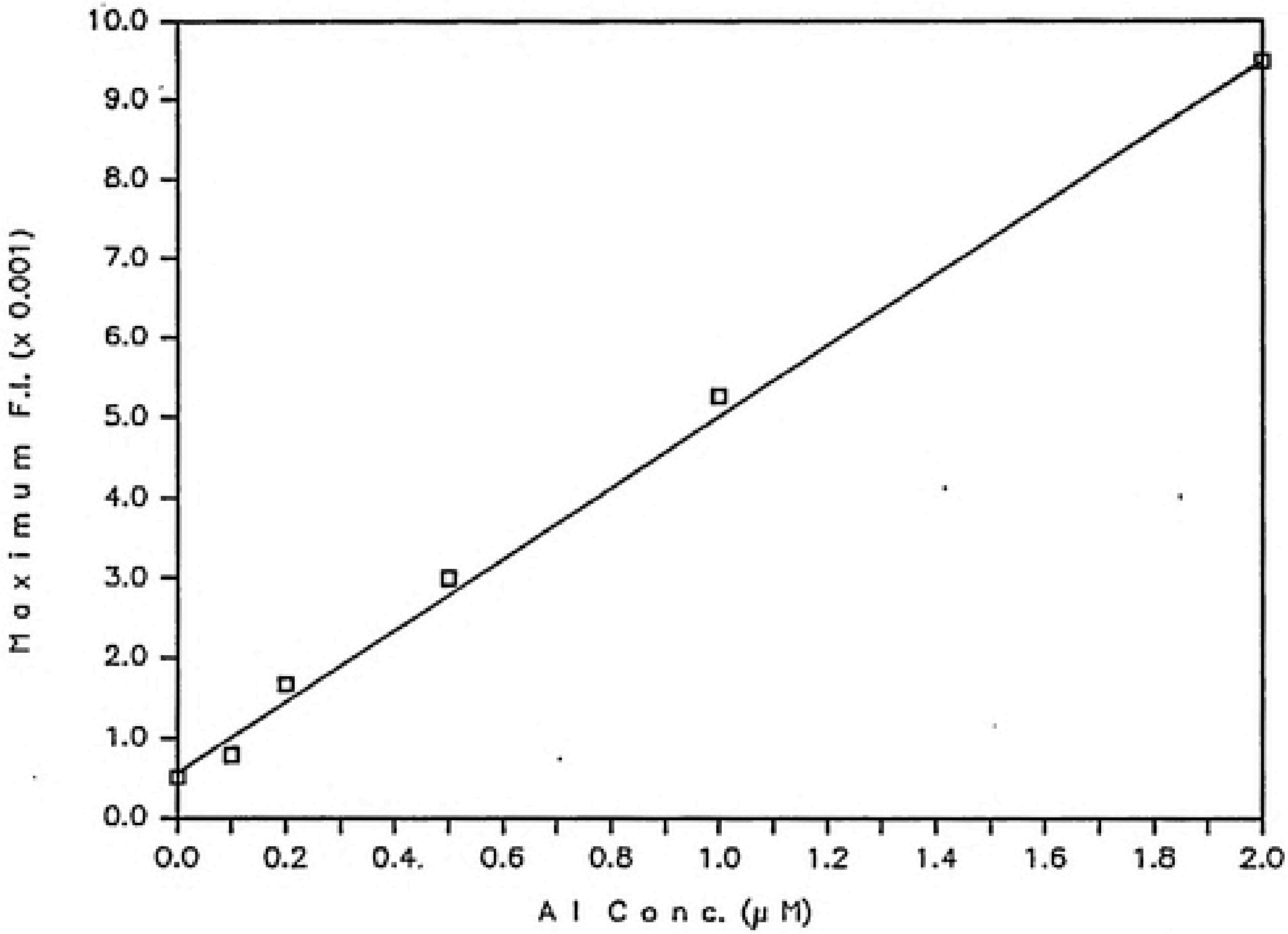
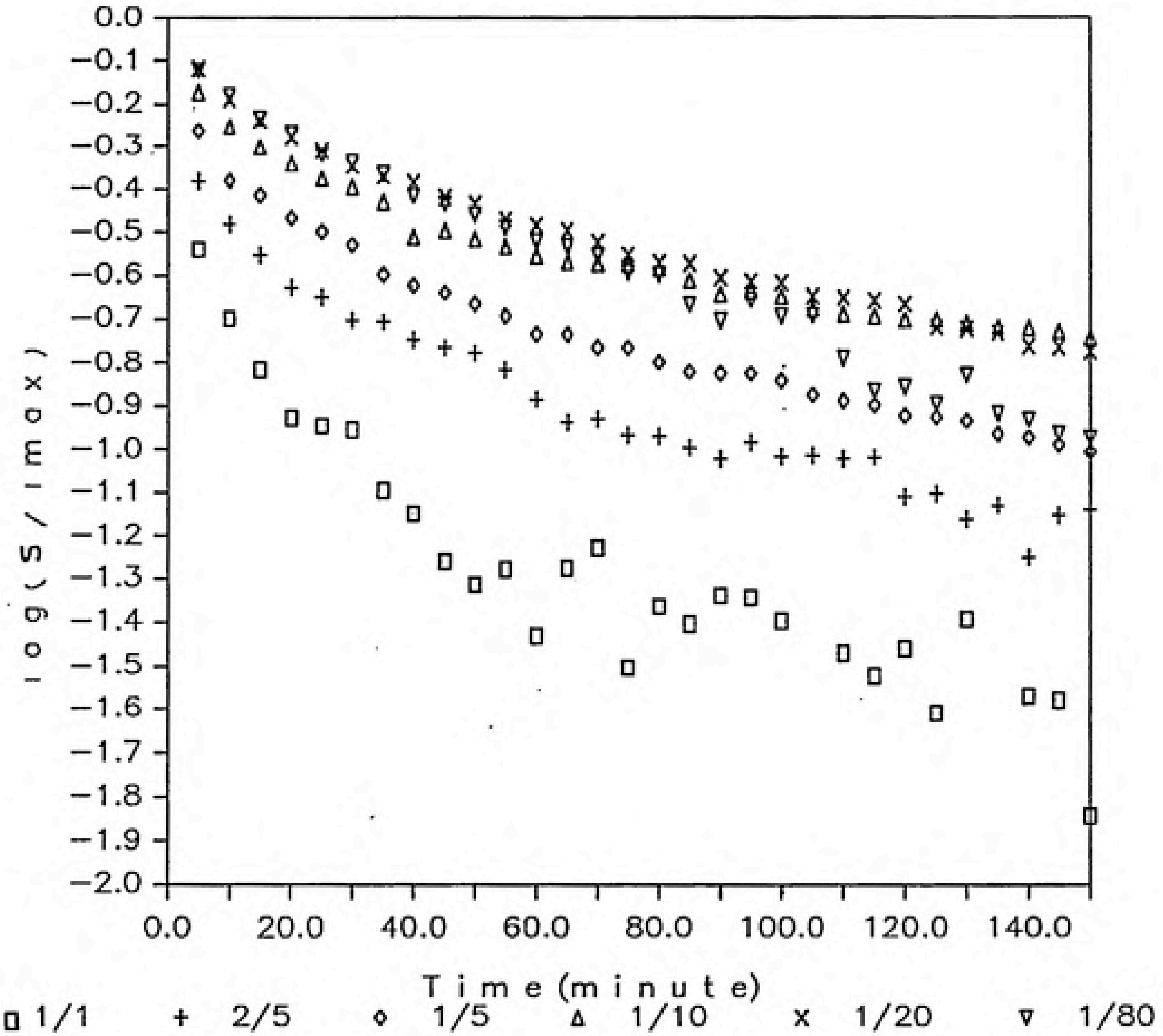


Figure III-2. Infinite-Time plot for various Al:FA ratios.



Non-linear regression analysis was used to estimate kinetic parameters for a two component/five parameter model. Results are tabulated in Table III-1. High cross-correlation among parameter estimates was observed and is typical of these estimates (Cabaniss & Shuman, 1988). High residuals at short time were observed in most cases indicating possible additional components. Results are tabulated in Appendix II.

The model actually estimated the concentration of three components, a fast dissociating component designated X in the model (see Table III-1) which includes the blank and kinetically unidentified components, mostly inorganic species, and two more slowly reacting components designated $AlFA_1$ and $AlFA_2$. The estimated rate constant for component $AlFA_1$ is about ten times greater than those of $AlFA_2$; thus, the order of dissociation rates is as follows: X > $AlFA_1$ > $AlFA_2$. Fit of the model to experimental intensity-time data is shown in Appendix IV, and is considered quite good.

1). <u>Effect of DOC</u>.

Effects of DOC, pH, and ionic strength were examined by comparing component distributions and rate constants.

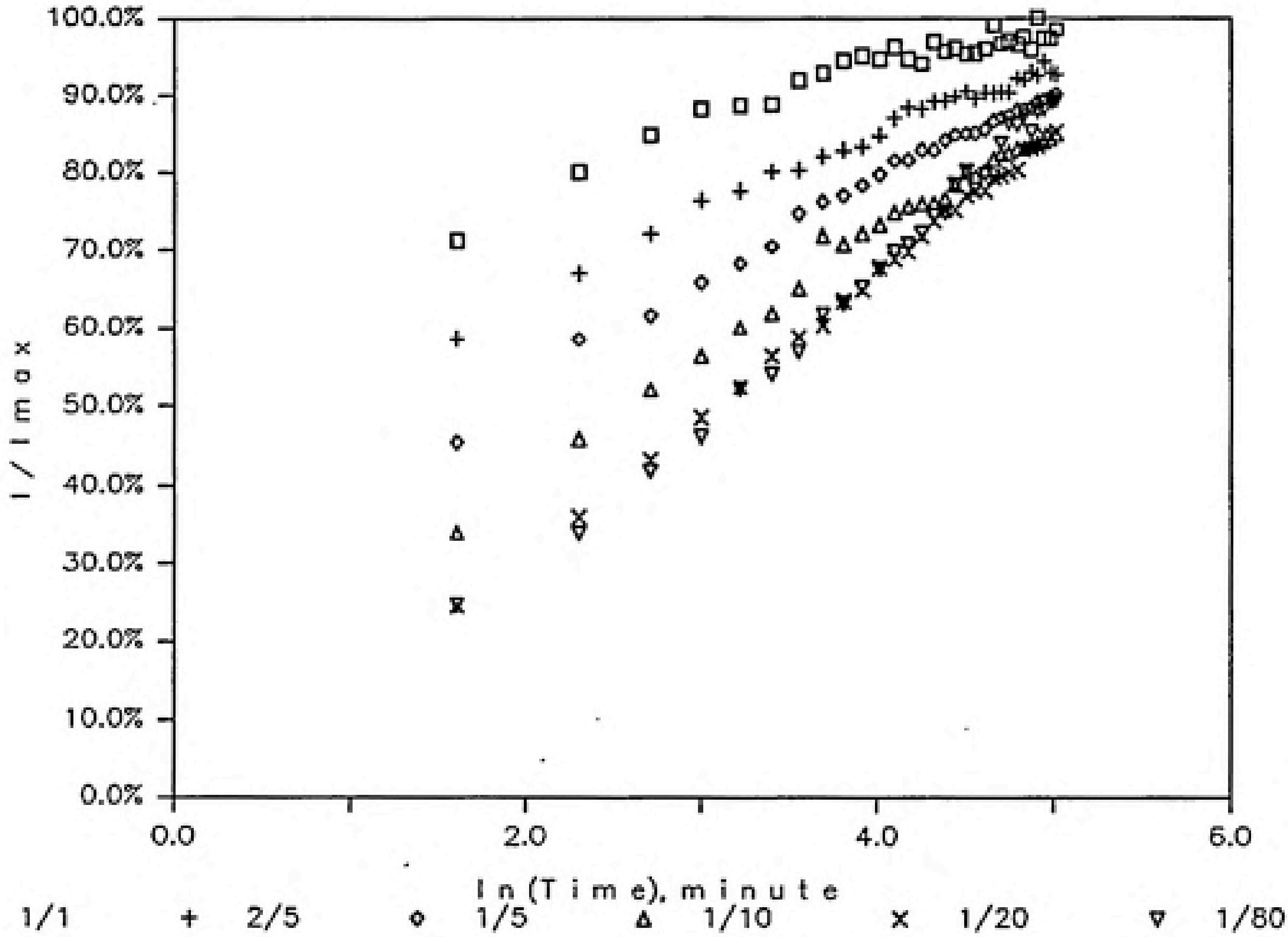
The dissociation of Al-FA is slower at higher DOC, the $t_{1/2}$ (time for 50% reaction) increases as the DOC increases (Fig. III-3). Also, the proportion of slower dissociating components, ($AlFA_1$+$AlFA_2$), increases from 45.9 to 89.5% as the concentration of fulvic acid increases from 1.0 to 80.0

Table III-1. Summary of kinetically distinguishable components.

[Al] (uM)	[LDFA] (mg DOC/L)	[Lum] (uM)	X %	AlFA$_1$ %	AlFA$_1$ K(min^{-1})	AlFA$_2$ %	AlFA$_2$ K(min^{-1})
				Parameter Estimates			
1.0	1.0	125.0	54.1	28.2	0.172155	17.7	0.030932
				SE	0.039089		0.006226
2.0	5.0	125.0	47.4	28.9	0.092401	23.8	0.009445
				SE	0.007611		0.001200
1.0	5.0	125.0	35.7	34.9	0.070334	29.4	0.007450
				SE	0.008756		0.000747
1.0	10.0	125.0	23.4	43.1	0.061402	33.5	0.006391
				SE	0.008092		0.000799
1.0	20.0	125.0	11.3	37.3	0.075396	51.4	0.008567
				SE	0.006914		0.000323
1.0	80.0	125.0	10.5	26.9	0.097311	62.6	0.011875
				SE	0.010984		0.000557
1.0	5.0	25.0	18.0	44.0	0.065878	38.0	0.006010
				SE	0.003129		0.000264
1.0	5.0	250.0	44.3	31.8	0.100952	23.8	0.019374
				SE	0.035961		0.010519
1.0[a]	5.0	125.0	33.6	35.7	0.086390	30.7	0.007573
				SE	0.013363		0.000577
1.0[b]	5.0	125.0	35.8	35.4	0.068224	28.8	0.007234
				SE	0.002576		0.000307

Kinetic data of the dissociation of Al-LDFA as determined by non-linear regression analysis with SYSTAT. The model is I=I1*(EXP(-K1*T))+I2*(EXP(-K2*T))+X, with the first data point at 5 minutes. SE is the standard error. Conditions are: 0.01 M NaAc/ 0.1 M NaCl, pH 5.5, 25^{o}C, except; a) average value of pH 5.0 for two data sets (08/25/89 & 10/08/89), b) 0.01 M NaAc/ 0.01 M NaCl.

Figure III-3. Percentage of Al which reacted with lumogallion at time t for various Al:FA ratios.



mg DOC/L. The fraction of $AlFA_1$ appears to have a maximum level of about 44 %, and varies within a fairly narrow range (28.0 - 44.0%). In contrast, $AlFA_2$ increases uniformly from 17.7 to 62.6% as the concentration of fulvic acid increases. As the Al:FA ratios decreases, where Al:FA ratio = μM Al/ mg DOC/L, more aluminum appears in $AlFA_1$+$AlFA_2$. Since $AlFA_1$ is more or less constant this may suggest a shift of aluminum binding to strongly bound, low concentration sites.

The dissociation rate constants (K) of $AlFA_1$ and $AlFA_2$ decrease as the FA concentration increase from 1.0 to 10.0 mg DOC/L, but then increase as [FA] increases from 10.0 to 80.0 mg DOC/L. The kinetic acceleration at lower Al:FA ratios is unexpected and there is no clear explanation. Observing Fig. III-4 and III-5, an inverse relationship between the proportion of total aluminum that is $AlFA_1$ and its dissociation rate constant is seen. On the other hand, increasing the proportion of $AlFA_2$ or X does not affect the dissociation rate of $AlFA_2$ consistently.

Another way of analyzing the data is to assume a fixed rate constant for the two components. Assuming the dissociation rate constant for $AlFA_1$ and $AlFA_2$ to be 0.1 and 0.01 min^{-1} respectively, the model , I=I1*(1-EXP(-0.1*T))+ I2*(1-EXP(-0.01*T))+X, was used for non-linear regression analysis. Results are tabulated in Table III-2 and plotted in Fig III-6. The proportion of $AlFA_1$+$AlFA_2$ increases from

Figure III-4. SYSTAT estimated portion of Al-FA components for varied Al:FA ratios.

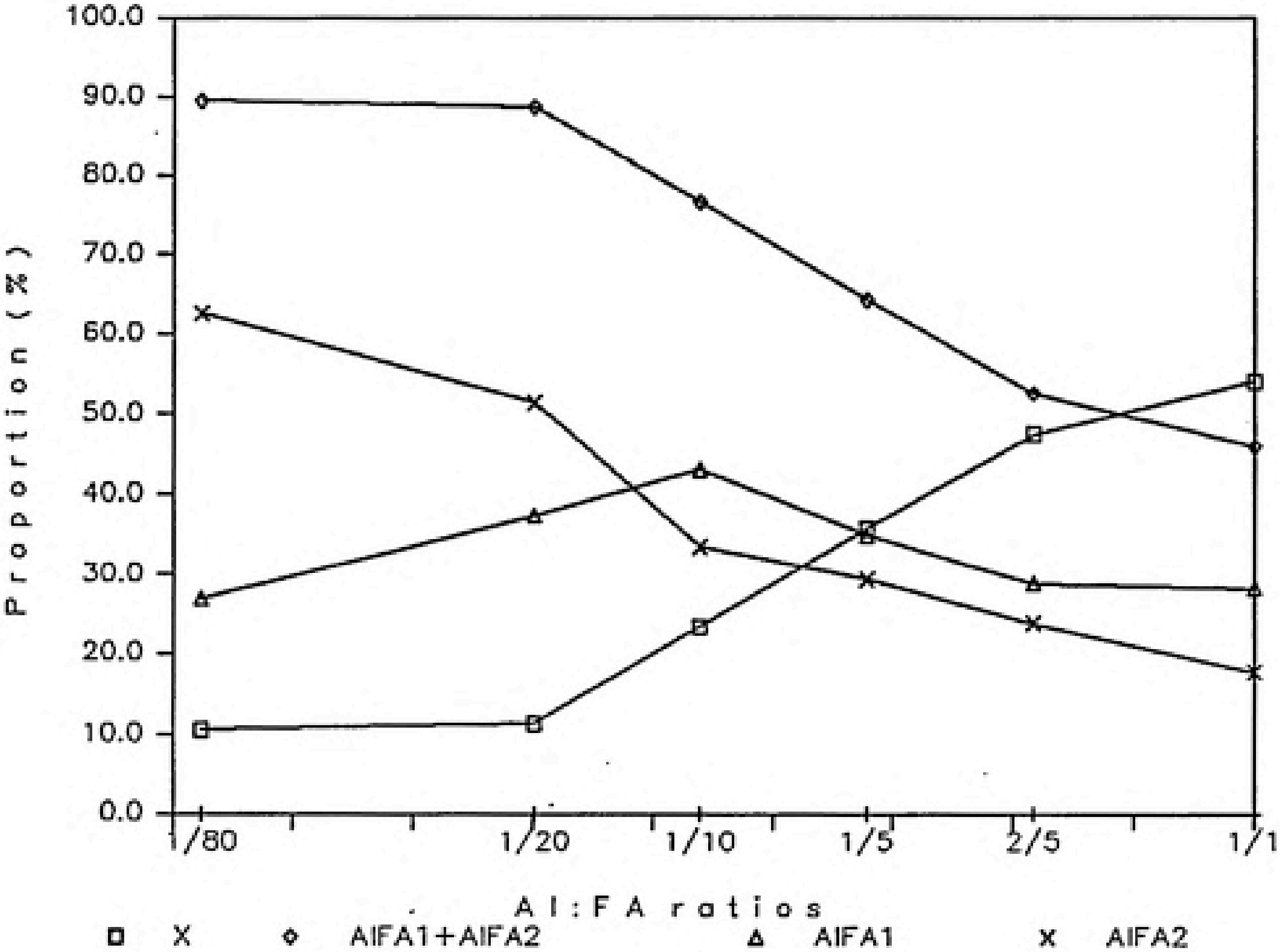


Figure III- 5 SYSTAT estimated dissociation rate constant of Al-FA components for varied Al:FA ratios.

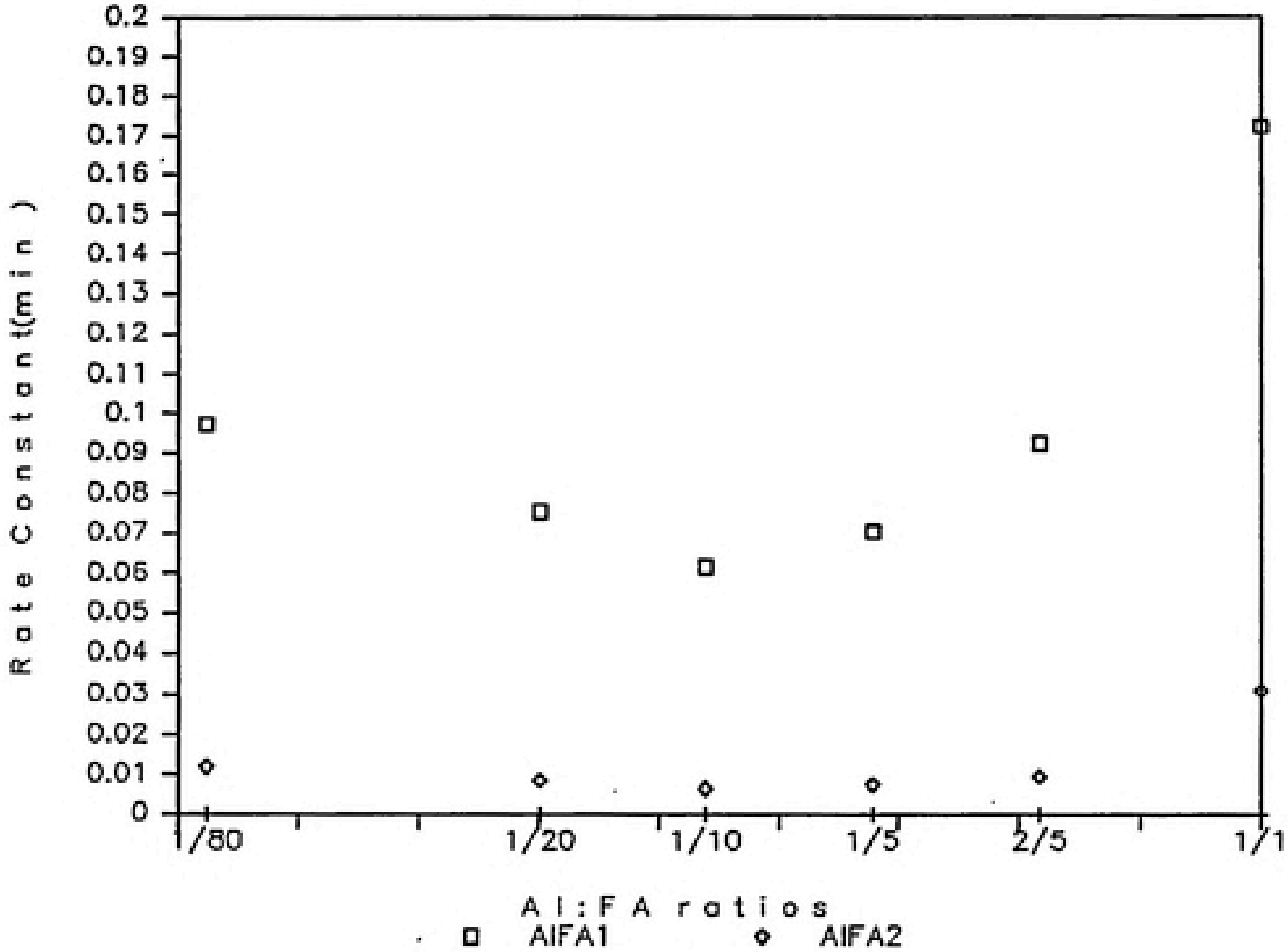
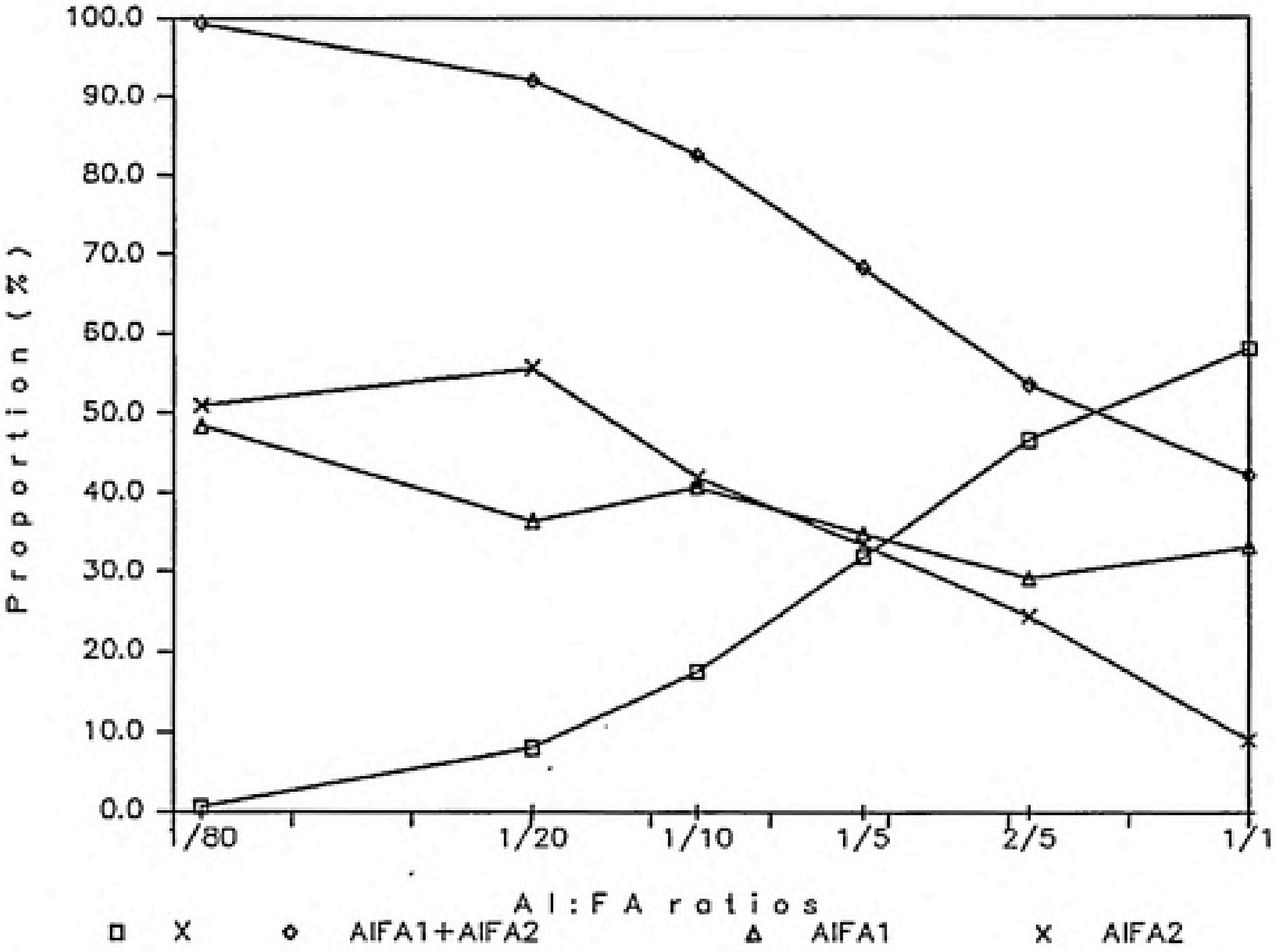


Table III-2. Proportion of kinetically distinguishable components for varied Al:FA ratios with fixed dissociation rate constants.

[Al] (µM)	[LDFA] (mg DOC/L)	[Lum] (µM)	X %	Parameter Estimates $AlFA_1$ %	$AlFA_2$ %
1.0	1.0	125.0	57.9	33.1	9.0
2.0	5.0	125.0	46.5	29.1	24.4
1.0	5.0	125.0	31.8	34.8	33.4
1.0	10.0	125.0	17.5	40.7	41.8
1.0	20.0	125.0	8.0	36.4	55.6
1.0	80.0	125.0	0.6	48.4	51.0

Kinetic data of the dissociation of Al-LDFA as determined by non-linear regression analysis with SYSTAT. The model is I=I1*(EXP(-0.1*T))+I2*(EXP(-0.01*T))+X, with the first data point at 5 minutes. Conditions are: 0.01 M NaAc/ 0.1 M NaCl, pH 5.5, 25°C.

Figure III-6. SYSTAT estimated portion of Al-FA components for varied Al:FA ratios. Dissociation rate constants were fixed to 0.1 min^{-1} for $AlFA_1$, 0.01 min^{-1} for $AlFA_2$.



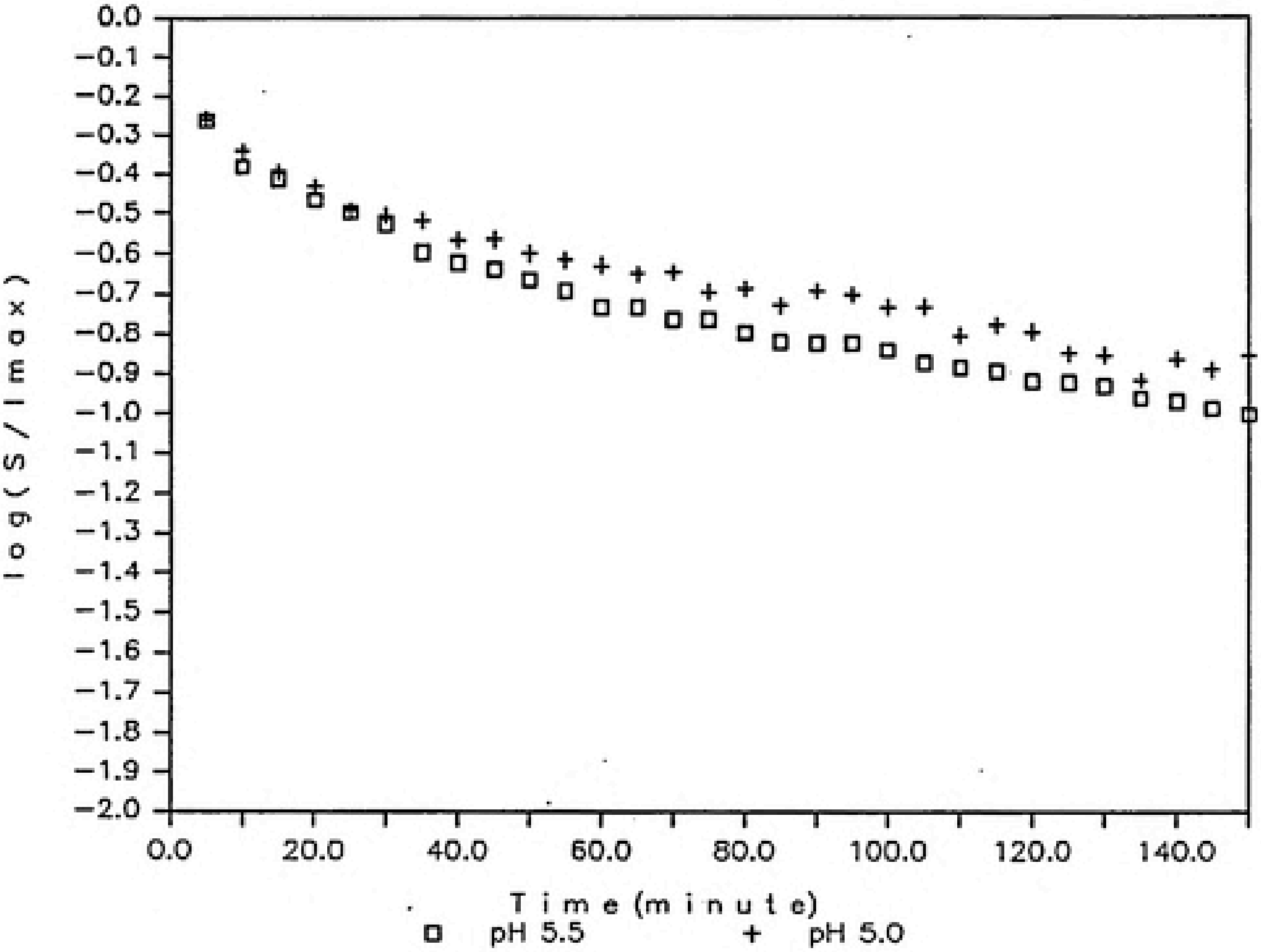
42.1 to 99.4 % as concentration of fulvic acid increases from 1.0 to 80.0 mg DOC/L. The fraction of $AlFA_2$ increases from 9.0 to 55.6% and appears to go through a maximum value at 20.0 mg DOC/L. The component $AlFA_1$ increases from 33.1 to 48.4 %. As above, the proportion of $AlFA_1$ increases less than $AlFA_2$. Residual plots for various Al:FA ratios show fairly good distributions except at 80.0 mg DOC/L. Results are shown in Appendix III.

2). Effect of pH.

An infinite-time plot, Fig. III-7 shows a small increase in Al-FA dissociation with increasing pH. However, Table III-1 shows that the estimated dissociation rate constant (K) of $AlFA_i$ is slightly higher at pH 5.0 than at pH 5.5, which is the expected trend. The difference here may be due to the graphical sensitivity to the choice of I_{max}.

All proportions of dissociating components seem to be more or less constant as pH increases, although theoretically, $AlFA_1$ and $AlFA_2$ might be expected to increase considering proton competition with aluminum for FA carboxylic or phenolic sites. The K of $AlFA_1$ does increase somewhat with proton concentration (from 0.0703 to 0.0864 min^{-1}, a 21.4% increase for about a three-fold proton concentration). Based on the variance ratio test, $F_{0.05}(1,1)=161.4$, there is no statistically significant difference between these two K values of $AlFA_1$(VR= 2.318,

Figure III-7. Infinite-Time plot at two pH values with Al:FA= 1 (µM)/ 5 (mg DOC/L).



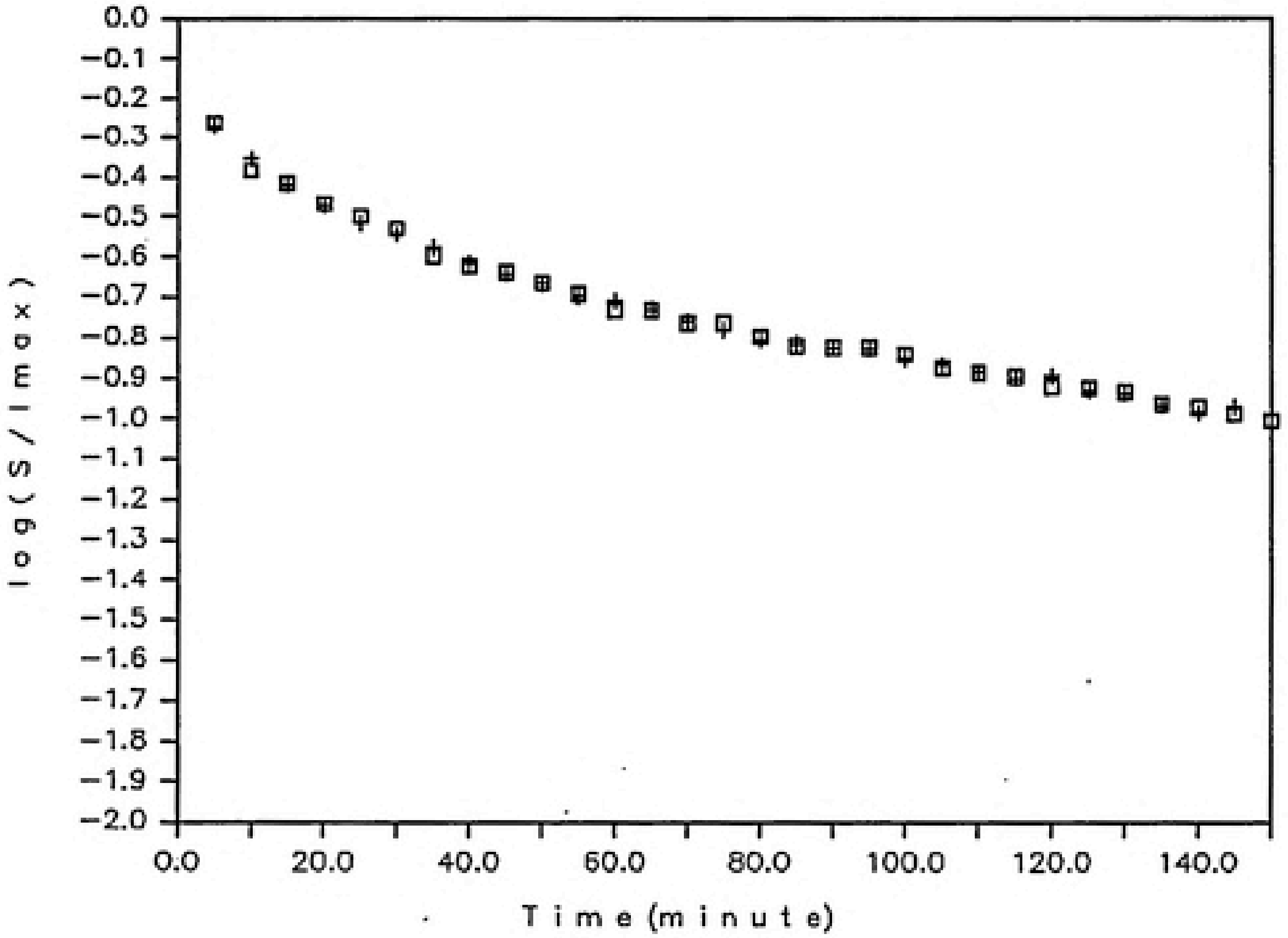
α= 0.05). The K of $AlFA_2$ remains nearly constant (from 0.00745 to 0.00757 min^{-1},a 1.7% increase) and there is no statistically significant difference between these two K values (VR= 1.654, α= 0.05). The small changes in K values for $AlFA_1$ and $AlFA_2$ suggests there is either slight or no H^+ competition for aluminum with these components at these pH values.

3). Effect of Ionic Strength.

Fig. III-8 displays the infinite-time plot for two values of ionic strength, which indicates no effect. On the basis of the estimation of SYSTAT, increasing ionic strength changes all parameters less than 3.0 %.

This result was not expected. Since fulvic acid is considered to be a negatively charged macromolecule, it should attract cationic aluminum and sodium simutaneously. Electrostatic repulsion between aluminum and sodium will decrease the attraction between aluminum and fulvic acid in the presence of Na^+. The ionic strength affects aluminum binding to fulvic acid by altering the charge density of the Al-FA complex. Therefore, the dissociation rates of $AlFA_i$ might be expected to increase as the ionic strength increases since the charge density on the macromolecule is expected to decrease. Cabaniss (unpublished data, 1989) observed a strong salt effect on dissociation rates of Ni-FA which is expected if the rate limiting step is separation of

Figure III-8. Infinite-Time plot for two values of ionic strength. (□) I = 0.11 M, (+) I= 0.02 M.



a 'territorially bound' cation from a negatively charged polyelectrolyte. No ionic strength effect here may suggest an alternate mechanism such as direct ligand (here, lumogallion) attachment.

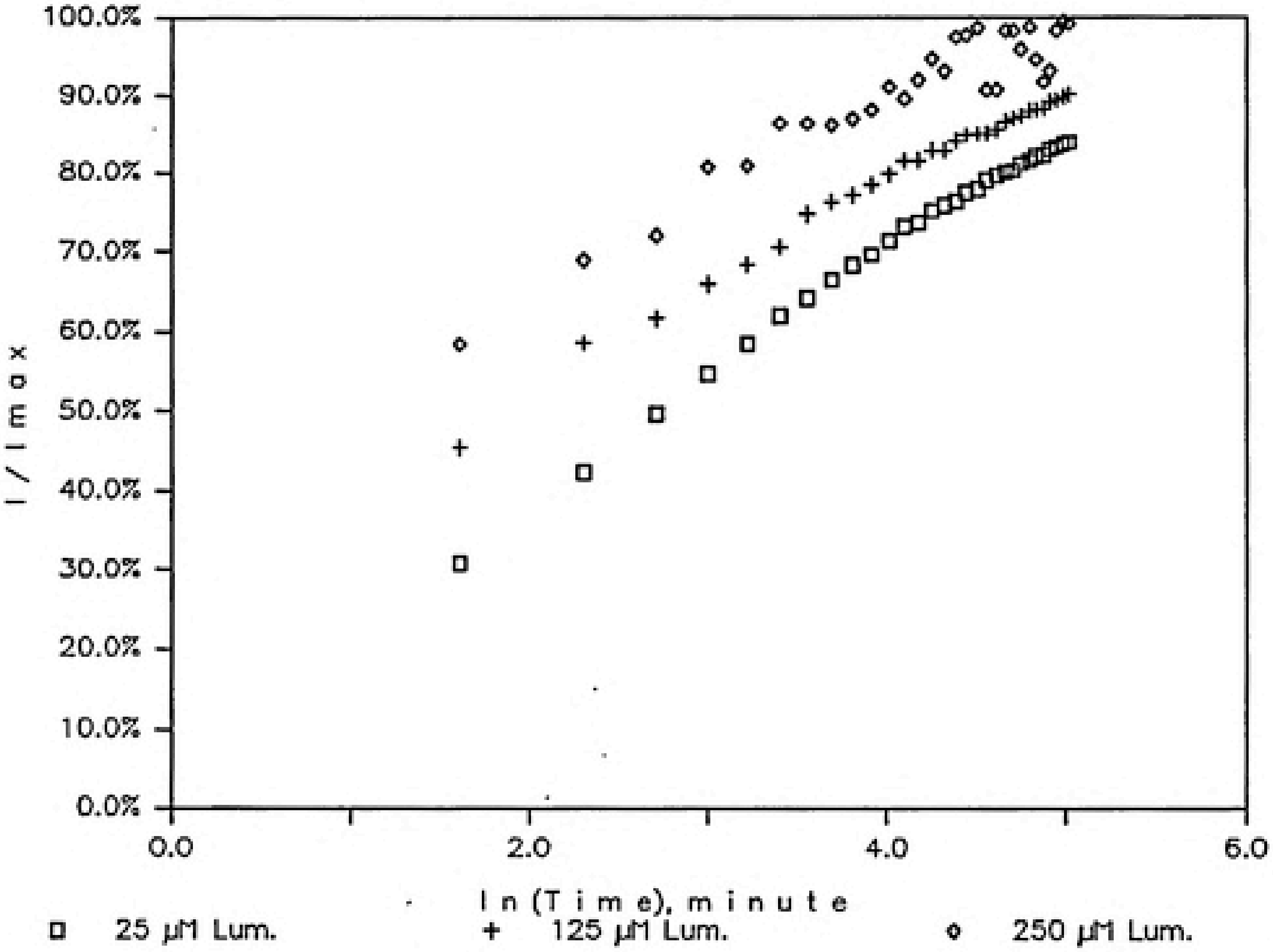
4). Effect of Lumogallion.

Inspection of Fig. III-9 shows that the half life approximately doubles when lumogallion concentration is halved from 250.0 to 125.0 µM indicating that the reaction rate is pseudo-first-order in lumogallion as has been noted previously (Shuman, unpublished data). This does not appear to hold when lumogallion concentration is reduced from 250.0 to 25.0 µM, possibly because the reagent is no longer in sufficient excess. The fitted rate constants roughly follow this same trend.

5). Comparison with Previous Work.

Mak and Langford (1982) used a fluorescence technique based on calcein blue to study the dissociation of Al-FA complexes via ligand exchange. Their well-characterized fulvic acid was extracted from the B_h horizon of a Prince Edward Podzol, Canada. They estimated the dissociation rate constants (k) for these complexes to be in the range of 0.0005 to 0.028 S^{-1} at pH 5.0-8.0 and 19.5^{o}C. In their data analysis, based on Guggenheim plots and non-linear regression, they designated two Al-FA complexes, Al-FA(I) the faster and Al-FA(II) the slower dissociating component.

Figure III-9. Percentage for three concentrations of lumogallion with Al:FA = 1 (μM)/ 5 (mg DOC/L), pH 5.5.



Mak and Langford's data covered the time span 0.0 - 7.0 minutes whereas the present study used data from 5.0 to 150.0 minutes. Thus it is only possible to compare $AlFA_1$ with Mak and Langford's Al-FA(II) for which there was some time overlap in the data. The average K_i's for $AlFA_1$ is about 0.0016 S^{-1} under conditions of 125.0 uM lumogallion, pH 5.5, 25^{o}C, and 0.01 M NaAc/0.1 M NaCl. Mak and Langford (1982) found Al-FA(II) to have a rate constant of about 0.0026 S^{-1}. Since this is a pseudo-first-order constant and Mak and Langford's reagent concentration was 200.0 uM, the rate constant must be reduced to 0.0026*(125/200)= 0.00163 S^{-1} for comparison. This compares with 0.00167 S^{-1} for the faster component ($AlFA_1$) in the present study. The comparison can only be approximate because of the limited time overlap between the data sets, but they are surprisingly close. Inspection of Fig. III-2 shows that $Al\text{-}FA_1$ has reacted nearly completely by about 20.0 minutes, as determined by the breakpoint, so perhaps the data overlap is sufficient. The aluminum recovery in the present study (close to 100.0 %) was much larger than 24 hours recoveries reported by Mak and Langford (around 35.0 %). This may be because the fluorescence reagent used in the present study, lumogallion, forms stronger complexes with aluminum than calcein blue. No stability constant are available to confirm this.

IV. Summary.

The kinetics of Al-FA dissociation was studied with a fluorescence ligand exchange method using lumogallion. The concentration of fulvic acid ranged from 1.0 to 80.0 mg DOC/L, aluminum concentrations were 1.0 and 2.0 µM, pH values were 5.0 and 5.5, and the ionic strength was either 0.11 M or 0.02 M.

A graphical method used for analyzing kinetic data indicated more than one component dissociated simultaneously. Non-linear regression analysis of the data (30 - 31 data points) was performed by using the SYSTAT statistical package. Of several models attempted, a two component, five parameters model, $I = I_1*(1-e^{(-K1*t)})+I_2*(1-e^{(-K2*t)})+X$, appeared to fit the data best.

The average dissociation rate constant (K) of $AlFA_1$, the faster reacting component, was almost ten times greater than that of a slower dissociating component, $AlFA_2$. The estimated pseudo-first-order rate constants for $AlFA_1$ and $AlFA_2$ were about 0.1 and 0.01 min^{-1} respectively and varied somewhat with Al:FA ratios. The portion of total aluminum as $AlFA_1$+$AlFA_2$ increased from 45.9 to 89.5 % as the concentration of fulvic acid increased from 1.0 to 80.0 mg

DOC/L. The proportion of $AlFA_1$ appeared to increase slightly whereas $AlFA_2$ increased about five-fold. The overall dissociation rates appeared to decrease as the concentration of fulvic acid increased from 1.0 to 80.0 mg DOC/L, but a reasonable fit to the data was obtained if these rate constants were assumed constant.

Increasing proton concentration increased the rate constant of $AlFA_1$ but not $AlFA_2$. The increase,however, was not statistically significant. Ionic strength appeared to have no effect. As the concentration of fulvic acid increased at constant aluminum concentration, an increasing fraction of aluminum was found to be associated with the most inert dissociating component, ($AlFA_2$).

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Neville, C. M. and Campbell, P. G. C. (1988) Possible mechanisms of aluminum toxicology in a dilute, acidic environment to fingerlings and older life stages of Salmonds. Water, Air, and Soil Pollution. 42: 311-327.

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Appendix I. Raw measurement of experiments.

1 µM Al, 125 µM Lum.,1 mg DOC/L, pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl
MODE:RATIO, FILTER:1, INTEG:1, SLIT:5, GAIN:1,
SAMPLE HV:850, REFERENCE HV:355, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	4801	-0.54028569	0.71178651	1.60943791
10	5397	-0.69929206	0.80014826	2.30258509
15	5715	-0.81614473	0.84729429	2.7080502
20	5948	-0.92752363	0.8818384	2.99573227
25	5982	-0.94645741	0.88687917	3.21887582
30	5995	-0.95392069	0.88880652	3.40119738
35	6204	-1.09578469	0.91979244	3.55534806
40	6266	-1.14864644	0.92898443	3.68887945
45	6375	-1.26078023	0.94514455	3.80666249
50	6418	-1.3144342	0.95151964	3.91202301
55	6390	-1.2787536	0.94736842	4.00733319
60	6496	-1.4327826	0.96308377	4.09434456
65	6387	-1.27509892	0.94692365	4.17438727
70	6347	-1.22909888	0.94099333	4.24849524
75	6534	-1.50469949	0.96871757	4.31748811
80	6453	-1.3635991	0.95670867	4.38202663
85	6479	-1.40410031	0.96056338	4.44265126
90	6436	-1.33902347	0.95418829	4.49980967
95	6439	-1.34326052	0.95463306	4.55387689
100	6475	-1.39761819	0.95997035	4.60517019
105	6684	-2.04365211	0.99095626	4.65396035
110	6517	-1.4710471	0.96619718	4.70048037
115	6543	-1.52363058	0.97005189	4.74493213
120	6512	-1.46162603	0.96545589	4.78749174
125	6579	-1.60887386	0.97538918	4.82831374
130	6472	-1.3928193	0.95952557	4.86753445
135	6745	0	1	4.90527478
140	6564	-1.57130337	0.97316531	4.94164242
145	6568	-1.58100868	0.97375834	4.97673374
150	6648	-1.84221021	0.98561898	5.01063529
1440	6573	-1.5934535	0.97449963	7.27239839

2 uM Al, 5 mg DOC mg/L, 125 uM Lum., pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:775, REFERENCE HV:355, EX:516 nm, EM: 596 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	5707	-0.38305697	0.58605463	1.60943791
10	6525	-0.48155904	0.67005545	2.30258509
15	7018	-0.55390086	0.72068186	2.7080502
20	7443	-0.62768708	0.76432532	2.99573227
25	7562	-0.65081088	0.77654549	3.21887582
30	7800	-0.701116	0.80098583	3.40119738
35	7821	-0.70584766	0.80314233	3.55534806
40	7990	-0.74592834	0.82049702	3.68887945
45	8064	-0.76471431	0.82809612	3.80666249
50	8111	-0.77708221	0.83292257	3.91202301
55	8248	-0.8152835	0.84699117	4.00733319
60	8468	-0.88466605	0.86958308	4.09434456
65	8611	-0.93654585	0.88426782	4.17438727
70	8595	-0.93042354	0.88262477	4.24849524
75	8689	-0.96769428	0.89227768	4.31748811
80	8695	-0.97018546	0.89289382	4.38202663
85	8754	-0.99547467	0.89895256	4.44265126
90	8811	-1.02139003	0.90480591	4.49980967
95	8729	-0.9845786	0.89638529	4.55387689
100	8800	-1.01626693	0.90367632	4.60517019
105	8794	-1.01349777	0.90306018	4.65396035
110	8810	-1.02092179	0.90470322	4.70048037
115	8803	-1.01765816	0.90398439	4.74493213
120	8982	-1.10994797	0.92236599	4.78749174
125	8969	-1.10254343	0.92103101	4.82831374
130	9067	-1.16174725	0.93109468	4.86753445
135	9015	-1.12933147	0.92575478	4.90527478
140	9191	-1.25048244	0.9438283	4.94164242
145	9052	-1.15214565	0.92955432	4.97673374
150	9034	-1.14089711	0.92770589	5.01063529
1440	9738	0	1	7.27239839

1 uM Al, 5 mg DOC/L, 125 uM Lum, pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:810, REFERENCE HV:355, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	2370	-0.26310269	0.45437117	1.60943791
10	3053	-0.38228106	0.58531442	2.30258509
15	3215	-0.41609049	0.6163727	2.7080502
20	3436	-0.46691758	0.65874233	2.99573227
25	3562	-0.49880208	0.68289877	3.21887582
30	3679	-0.53066371	0.70532975	3.40119738
35	3898	-0.59742217	0.74731595	3.55534806
40	3976	-0.6239159	0.76226994	3.68887945
45	4020	-0.6396064	0.77070552	3.80666249
50	4087	-0.66464364	0.78355061	3.91202301
55	4157	-0.69244162	0.79697086	4.00733319
60	4253	-0.73371129	0.81537577	4.09434456
65	4254	-0.73416251	0.81556748	4.17438727
70	4319	-0.76454514	0.82802914	4.24849524
75	4320	-0.76502957	0.82822086	4.31748811
80	4386	-0.79825949	0.84087423	4.38202663
85	4426	-0.81971049	0.84854294	4.44265126
90	4434	-0.82413083	0.85007669	4.49980967
95	4436	-0.82524298	0.85046012	4.55387689
100	4464	-0.84111974	0.85582822	4.60517019
105	4519	-0.8741048	0.8663727	4.65396035
110	4540	-0.88739088	0.87039877	4.70048037
115	4556	-0.89779364	0.87346626	4.74493213
120	4592	-0.92215299	0.8803681	4.78749174
125	4597	-0.92564693	0.88132669	4.82831374
130	4608	-0.933434	0.88343558	4.86753445
135	4650	-0.96452115	0.89148773	4.90527478
140	4661	-0.9730446	0.89359663	4.94164242
145	4682	-0.98979632	0.8976227	4.97673374
150	4701	-1.00553035	0.90126534	5.01063529
1440	5216	0	1	7.27239839

1 uM Al, 10 mg DOC/L, 125 uM Lum., pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:795, REFERENCE HV:355, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	(I/Imax)	ln(Time)
5	1713	-0.17261291	0.33988095	1.60943791
10	2313	-0.25402704	0.45892857	2.30258509
15	2624	-0.30311375	0.52063492	2.7080502
20	2844	-0.34152558	0.56428571	2.99573227
25	3031	-0.37707947	0.60138889	3.21887582
30	3124	-0.39590759	0.61984127	3.40119738
35	3283	-0.43011829	0.65138889	3.55534806
40	3619	-0.51271566	0.71805556	3.68887945
45	3564	-0.49807364	0.70714286	3.80666249
50	3636	-0.5173431	0.72142857	3.91202301
55	3693	-0.53322859	0.7327381	4.00733319
60	3771	-0.55595341	0.74821429	4.09434456
65	3815	-0.56931737	0.75694444	4.17438727
70	3827	-0.57303461	0.7593254	4.24849524
75	3832	-0.57459289	0.76031746	4.31748811
80	3862	-0.5840619	0.76626984	4.38202663
85	3949	-0.6127506	0.78353175	4.44265126
90	4033	-0.64237306	0.80019841	4.49980967
95	4012	-0.63477588	0.79603175	4.55387689
100	4045	-0.64677473	0.80257937	4.60517019
105	4120	-0.67534451	0.81746032	4.65396035
110	4150	-0.6873203	0.8234127	4.70048037
115	4163	-0.69261416	0.82599206	4.74493213
120	4184	-0.70130448	0.83015873	4.78749174
125	4184	-0.70130448	0.83015873	4.82831374
130	4205	-0.71017225	0.8343254	4.86753445
135	4222	-0.71748595	0.83769841	4.90527478
140	4228	-0.72009694	0.83888889	4.94164242
145	4244	-0.72713733	0.84206349	4.97673374
150	4276	-0.74157004	0.8484127	5.01063529
1440	4815	-1.10725986	0.95535714	7.27239839
2880	5040	-1.45546893	1	7.96554557

1 uM Al, 20 mg DOC/L, 125 uM Lum., pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:795 nm, REFERENCE HV:355 nm, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	1253	-0.11912952	0.24583088	1.60943791
10	1836	-0.18810483	0.36021189	2.30258509
15	2202	-0.2377693	0.43201883	2.7080502
20	2473	-0.27858733	0.48518737	2.99573227
25	2672	-0.31120957	0.52422994	3.21887582
30	2876	-0.34740694	0.56425348	3.40119738
35	3000	-0.37098056	0.58858152	3.55534806
40	3079	-0.38669524	0.60408083	3.68887945
45	3238	-0.42015951	0.63527565	3.80666249
50	3310	-0.43620505	0.64940161	3.91202301
55	3455	-0.47043776	0.67784972	4.00733319
60	3509	-0.48390921	0.68844418	4.09434456
65	3558	-0.49650579	0.69805768	4.17438727
70	3659	-0.52368328	0.71787326	4.24849524
75	3760	-0.5526757	0.73768884	4.31748811
80	3825	-0.57241285	0.75044144	4.38202663
85	3829	-0.57365725	0.75122621	4.44265126
90	3927	-0.60531502	0.77045321	4.49980967
95	3956	-0.61514341	0.77614283	4.55387689
100	3960	-0.61651667	0.7769276	4.60517019
105	4045	-0.64677473	0.79360408	4.65396035
110	4058	-0.6515941	0.7961546	4.70048037
115	4076	-0.65835661	0.79968609	4.74493213
120	4098	-0.6667675	0.80400235	4.78749174
125	4222	-0.71748595	0.82833039	4.82831374
130	4230	-0.72097078	0.82989994	4.86753445
135	4250	-0.72980718	0.83382382	4.90527478
140	4319	-0.76175159	0.84736119	4.94164242
145	4324	-0.76416033	0.84834216	4.97673374
150	4345	-0.77442551	0.85246223	5.01063529
1440	5094	-1.60733031	0.99941142	7.27239839
2880	5097	-1.61754948	1	7.96554557

1 uM Al, 80 mg DOC/L, 125 uM Lum., pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:750, REFERENCE HV:350, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	1329	-0.12258773	0.24592894	1.60943791
10	1835	-0.18016879	0.33956329	2.30258509
15	2261	-0.23537096	0.41839378	2.7080502
20	2496	-0.26912094	0.46188009	2.99573227
25	2819	-0.32025479	0.52165063	3.21887582
30	2925	-0.33843881	0.54126573	3.40119738
35	3079	-0.36629238	0.56976314	3.55534806
40	3336	-0.4171648	0.6173205	3.68887945
45	3411	-0.43320804	0.63119911	3.80666249
50	3530	-0.45994575	0.65321984	3.91202301
55	3653	-0.48942919	0.67598075	4.00733319
60	3775	-0.52079425	0.69855662	4.09434456
65	3824	-0.53405825	0.70762398	4.17438727
70	3898	-0.55489037	0.72131754	4.24849524
75	4027	-0.5937814	0.74518875	4.31748811
80	4041	-0.59821948	0.74777942	4.38202663
85	4239	-0.66638941	0.78441895	4.44265126
90	4331	-0.70211562	0.80144338	4.49980967
95	4211	-0.65607489	0.7792376	4.55387689
100	4307	-0.69250871	0.79700222	4.60517019
105	4303	-0.69092802	0.79626203	4.65396035
110	4525	-0.78872646	0.83734271	4.70048037
115	4664	-0.86348362	0.8630644	4.74493213
120	4650	-0.85534399	0.86047372	4.78749174
125	4716	-0.8951269	0.8726869	4.82831374
130	4603	-0.82908282	0.85177646	4.86753445
135	4752	-0.91846774	0.87934863	4.90527478
140	4771	-0.93131163	0.88286454	4.94164242
145	4818	-0.96481772	0.89156181	4.97673374
150	4831	-0.97456072	0.89396743	5.01063529
180	5006	-1.13283226	0.92635085	5.19295685
780	5404	0	1	6.65929392
840	5276	-1.62550537	0.97631384	6.73340189
900	5161	-1.34710906	0.95503331	6.80239476
960	5205	-1.43386226	0.96317543	6.86693328
1020	5263	-1.58349622	0.97390822	6.92755791
1080	5129	-1.29338264	0.94911177	6.98471632
1140	5085	-1.22892465	0.94096965	7.03878354
1200	4932	-1.05877334	0.91265729	7.09007684
1380	4691	-0.87962581	0.8680607	7.22983878
1440	4759	-0.92315562	0.88064397	7.27239839

1 uM Al, 5 mg DOC/L, 125 uM Lum., pH 5.0, 25^{o}C,082589,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:810, REFERENCE HV:355, EX:516 nm, EM:596 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	2647	-0.27016088	0.4631671	1.60943791
10	3248	-0.36484708	0.56832896	2.30258509
15	3575	-0.42660246	0.62554681	2.7080502
20	3815	-0.47826263	0.66754156	2.99573227
25	4003	-0.52351247	0.70043745	3.21887582
30	4149	-0.56222448	0.72598425	3.40119738
35	4268	-0.5965477	0.74680665	3.55534806
40	4346	-0.62061278	0.76045494	3.68887945
45	4433	-0.64912821	0.77567804	3.80666249
50	4493	-0.66994503	0.78617673	3.91202301
55	4561	-0.69481042	0.79807524	4.00733319
60	4611	-0.71404716	0.80682415	4.09434456
65	4684	-0.74375757	0.81959755	4.17438727
70	4698	-0.74969528	0.82204724	4.24849524
75	4760	-0.77701286	0.83289589	4.31748811
80	4783	-0.78760032	0.83692038	4.38202663
85	4804	-0.79749786	0.84059493	4.44265126
90	4820	-0.8051932	0.84339458	4.49980967
95	4843	-0.81649975	0.84741907	4.55387689
100	4889	-0.84003618	0.85546807	4.60517019
105	4909	-0.85068119	0.85896763	4.65396035
110	4919	-0.85610316	0.86071741	4.70048037
115	4950	-0.8733548	0.86614173	4.74493213
120	4981	-0.89132017	0.87156605	4.78749174
125	4975	-0.88778451	0.87051619	4.82831374
130	5029	-0.92069212	0.879965	4.86753445
135	5026	-0.91879701	0.87944007	4.90527478
140	5043	-0.92964696	0.8824147	4.94164242
145	5060	-0.94077493	0.88538933	4.97673374
150	5059	-0.94011239	0.88521435	5.01063529
1440	5715	0	1	7.27239839

1 uM Al, 5 mg DOC/L, 125 uM Lum., pH 5.0, 25°C, 100889,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:750, REFERENCE HV:350, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	3457	-0.25808458	0.44803007	1.60943791
10	4208	-0.34233263	0.54536029	2.30258509
15	4616	-0.39603052	0.59823743	2.7080502
20	4868	-0.43285223	0.63089684	2.99573227
25	5238	-0.49329092	0.67884914	3.21887582
30	5311	-0.50627714	0.68831001	3.40119738
35	5382	-0.51929137	0.69751166	3.55534806
40	5628	-0.56766172	0.72939347	3.68887945
45	5615	-0.56496616	0.72770866	3.80666249
50	5778	-0.60003844	0.74883359	3.91202301
55	5845	-0.61531843	0.75751685	4.00733319
60	5906	-0.62971364	0.7654225	4.09434456
65	5992	-0.65085496	0.77656817	4.17438727
70	5973	-0.64609483	0.77410575	4.24849524
75	6159	-0.6951036	0.79821151	4.31748811
80	6131	-0.68736295	0.79458269	4.38202663
85	6278	-0.72963333	0.81363401	4.44265126
90	6153	-0.69343324	0.7974339	4.49980967
95	6190	-0.70383768	0.80222913	4.55387689
100	6291	-0.73357735	0.81531882	4.60517019
105	6292	-0.73388223	0.81544842	4.65396035
110	6508	-0.80532528	0.8434422	4.70048037
115	6436	-0.78018225	0.83411094	4.74493213
120	6483	-0.79642914	0.84020218	4.78749174
125	6629	-0.85116267	0.8591239	4.82831374
130	6641	-0.85598375	0.86067911	4.86753445
135	6789	-0.92031248	0.87986003	4.90527478
140	6665	-0.8657895	0.86378953	4.94164242
145	6729	-0.89307506	0.87208398	4.97673374
150	6644	-0.85719743	0.86106791	5.01063529
180	6824	-0.93702736	0.88439606	5.19295685
780	7527	-1.61093041	0.97550544	6.65929392
840	7127	-1.11727692	0.92366511	6.73340189
900	7085	-1.08736286	0.91822188	6.80239476
960	7335	-1.30646724	0.95062208	6.86693328
1020	7381	-1.36234741	0.95658372	6.92755791
1080	7568	-1.7171305	0.98081908	6.98471632
1140	7716	0	1	7.03878354
1200	7347	-1.32036585	0.95217729	7.09007684
1380	7304	-1.272495	0.94660446	7.22983878
1440	7534	-1.62732083	0.97641265	7.27239839

1 µM Al, 5 mg DOC/L, 125 µM Lum., pH 5.5, 25°C,
0.01 M NaAc/0.01 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:840, REFERENCE HV:355, EX:516 nm, EM:596 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	2572	-0.27050352	0.46359048	1.60943791
10	3100	-0.35532504	0.55875991	2.30258509
15	3440	-0.42026584	0.62004326	2.7080502
20	3671	-0.47067218	0.66167988	2.99573227
25	3858	-0.51624975	0.69538572	3.21887582
30	3958	-0.54273933	0.71341024	3.40119738
35	4086	-0.57918908	0.73648161	3.55534806
40	4202	-0.61509139	0.75739005	3.68887945
45	4286	-0.6430771	0.77253064	3.80666249
50	4352	-0.66640527	0.78442682	3.91202301
55	4434	-0.69725126	0.79920692	4.00733319
60	4466	-0.70990919	0.80497477	4.09434456
65	4517	-0.73087778	0.81416727	4.17438727
70	4586	-0.76096138	0.82660418	4.24849524
75	4629	-0.78082094	0.83435472	4.31748811
80	4682	-0.80661856	0.84390771	4.38202663
85	4700	-0.8157406	0.84715213	4.44265126
90	4719	-0.82558192	0.85057678	4.49980967
95	4726	-0.82926463	0.8518385	4.55387689
100	4768	-0.85204185	0.8594088	4.60517019
105	4796	-0.86791861	0.86445566	4.65396035
110	4828	-0.88680395	0.8702235	4.70048037
115	4850	-0.90028103	0.8741889	4.74493213
120	4845	-0.89718112	0.87328767	4.78749174
125	4898	-0.93122309	0.88284066	4.82831374
130	4909	-0.93863559	0.88482336	4.86753445
135	4948	-0.9659852	0.89185292	4.90527478
140	4972	-0.98371397	0.8961788	4.94164242
145	4956	-0.97181474	0.89329488	4.97673374
150	4979	-0.98902418	0.89744052	5.01063529
1440	5548	0	1	7.27239839

1 uM Al, 5 mg DOC/L, 25 uM Lum., pH 5.5, 25°C.
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:840, REFERENCE HV:355, EX:515 nm, EM:595 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	1724	-0.15942573	0.30725361	1.60943791
10	2369	-0.23822726	0.42220638	2.30258509
15	2786	-0.29802182	0.49652468	2.7080502
20	3070	-0.3440356	0.54713955	2.99573227
25	3283	-0.38205729	0.5851007	3.21887582
30	3475	-0.41943902	0.61931919	3.40119738
35	3601	-0.44584421	0.64177508	3.55534806
40	3725	-0.47349858	0.66387453	3.68887945
45	3829	-0.49813257	0.68240955	3.80666249
50	3903	-0.5165524	0.69559793	3.91202301
55	4000	-0.54194473	0.7128854	4.00733319
60	4101	-0.57006332	0.73088576	4.09434456
65	4127	-0.57760637	0.73551952	4.17438727
70	4211	-0.60291223	0.75049011	4.24849524
75	4253	-0.6161405	0.75797541	4.31748811
80	4282	-0.62551529	0.76314382	4.38202663
85	4338	-0.64421186	0.77312422	4.44265126
90	4366	-0.65387092	0.77811442	4.49980967
95	4427	-0.67568856	0.78898592	4.55387689
100	4463	-0.68909838	0.79540189	4.60517019
105	4488	-0.69866051	0.79985742	4.65396035
110	4506	-0.70567799	0.80306541	4.70048037
115	4550	-0.72332488	0.81090715	4.74493213
120	4573	-0.73284291	0.81500624	4.78749174
125	4603	-0.74557973	0.82035288	4.82831374
130	4612	-0.74947478	0.82195687	4.86753445
135	4654	-0.76812833	0.82944217	4.90527478
140	4672	-0.77637467	0.83265015	4.94164242
145	4695	-0.78714479	0.83674924	4.97673374
150	4705	-0.79191207	0.83853146	5.01063529
1440	5611	0	1	7.27239839

1 uM Al, 5 mg DOC/L, 250 uM Lum., pH 5.5, 25^{o}C,
0.01 M NaAc/0.1 M NaCl,
MODE:RATIO, FILTER:1, INTEG:10, SLIT:5, GAIN:1,
SAMPLE HV:775, REFERENCE HV:355, EX:516 nm, EM:596 nm.

Time(minute)	I	log(S/Imax)	I/Imax	ln(Time)
5	1587	-0.38078685	0.58388521	1.60943791
10	1872	-0.50687909	0.68874172	2.30258509
15	1956	-0.55229448	0.7196468	2.7080502
20	2193	-0.71409015	0.80684327	2.99573227
25	2198	-0.71824611	0.80868286	3.21887582
30	2349	-0.86722308	0.86423841	3.40119738
35	2349	-0.86722308	0.86423841	3.55534806
40	2342	-0.8590616	0.86166299	3.68887945
45	2364	-0.88524619	0.86975717	3.80666249
50	2396	-0.92639358	0.88153054	3.91202301
55	2476	-1.05043408	0.91096394	4.00733319
60	2436	-0.98400034	0.89624724	4.09434456
65	2501	-1.09778972	0.92016188	4.17438727
70	2574	-1.27588696	0.94701987	4.24849524
75	2532	-1.1647365	0.93156733	4.31748811
80	2647	-1.5829911	0.97387785	4.38202663
85	2656	-1.64185776	0.97718911	4.44265126
90	2681	-1.86604772	0.98638705	4.49980967
95	2466	-1.03284891	0.90728477	4.55387689
100	2468	-1.03630944	0.9080206	4.60517019
105	2671	-1.76215159	0.98270787	4.65396035
110	2670	-1.75300821	0.98233996	4.70048037
115	2606	-1.38503143	0.95879323	4.74493213
120	2683	-1.8901814	0.98712288	4.78749174
125	2572	-1.26989659	0.94628403	4.82831374
130	2494	-1.08400143	0.91758646	4.86753445
135	2531	-1.16240784	0.93119941	4.90527478
140	2671	-1.76215159	0.98270787	4.94164242
145	2702	-2.23012946	0.99411332	4.97673374
150	2695	-2.07252161	0.9915379	5.01063529
1440	2718	0	1	7.27239839

Appendix II. Statistical outputs for regression on both $AlFA_i$ and K_i, and the model is
I=I1*(1-EXP(-K1*T))+I2*(1-EXP(-K2*T))+X.

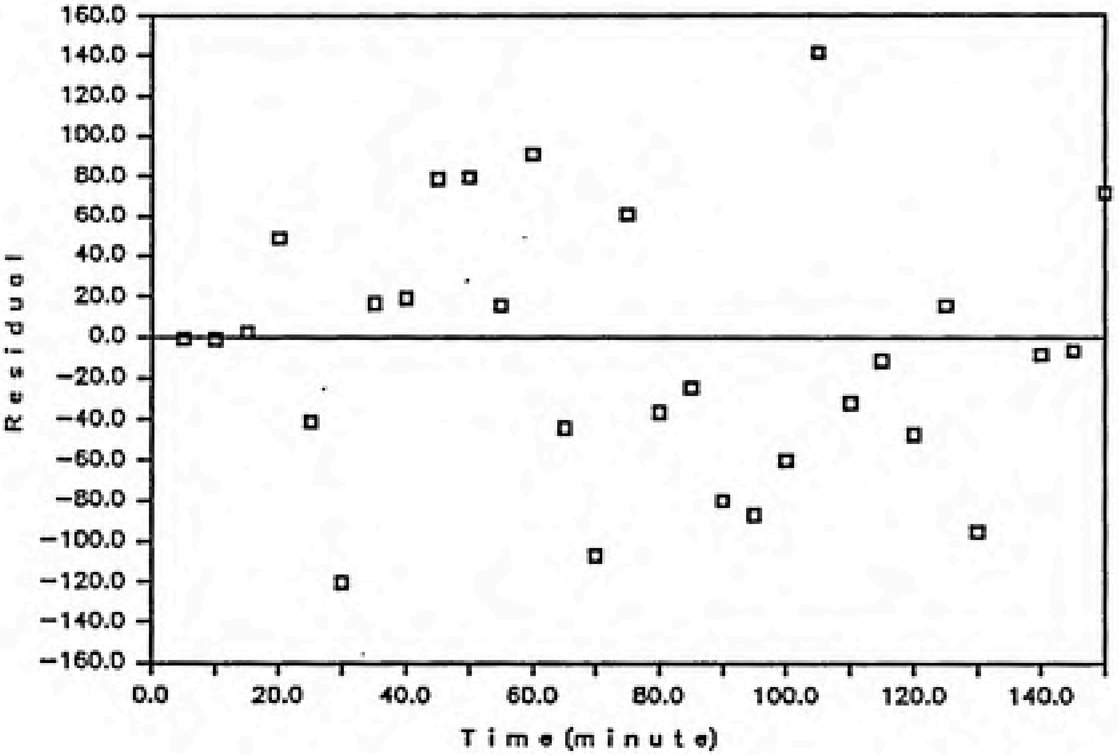
This result is under conditions such as: 1 μM Al, 1 mg DOC/L LDFA, 125 μM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1855.3670	428.9647
K1	0.172155	0.039089
I2	1168.8283	193.2934
K2	0.030932	0.006226
X	3563.6075	386.2067

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.526396	1.000000			
I2	0.190686	0.925880	1.000000		
K2	0.111323	0.862181	0.963248	1.000000	
X	-0.763106	-0.944935	-0.779061	-0.711637	1.000000



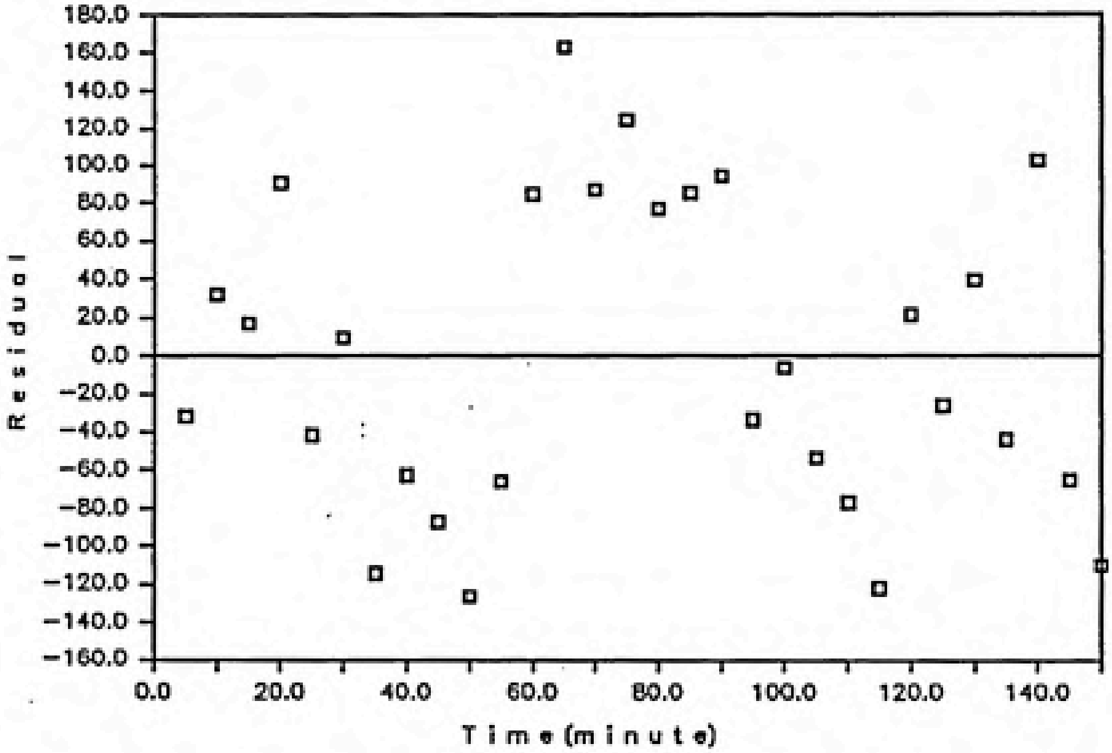
This result is under conditions such as: 2 µM Al, 5 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25^{o}C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2800.0883	202.0432
K1	0.092401	0.007611
I2	2307.0404	115.8811
K2	0.009445	0.001200
X	4596.1616	132.1407

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.359691	1.000000			
I2	0.066236	0.875642	1.000000		
K2	0.013655	0.820067	0.703339	1.000000	
X	-0.683258	-0.910920	-0.715896	-0.680548	1.000000



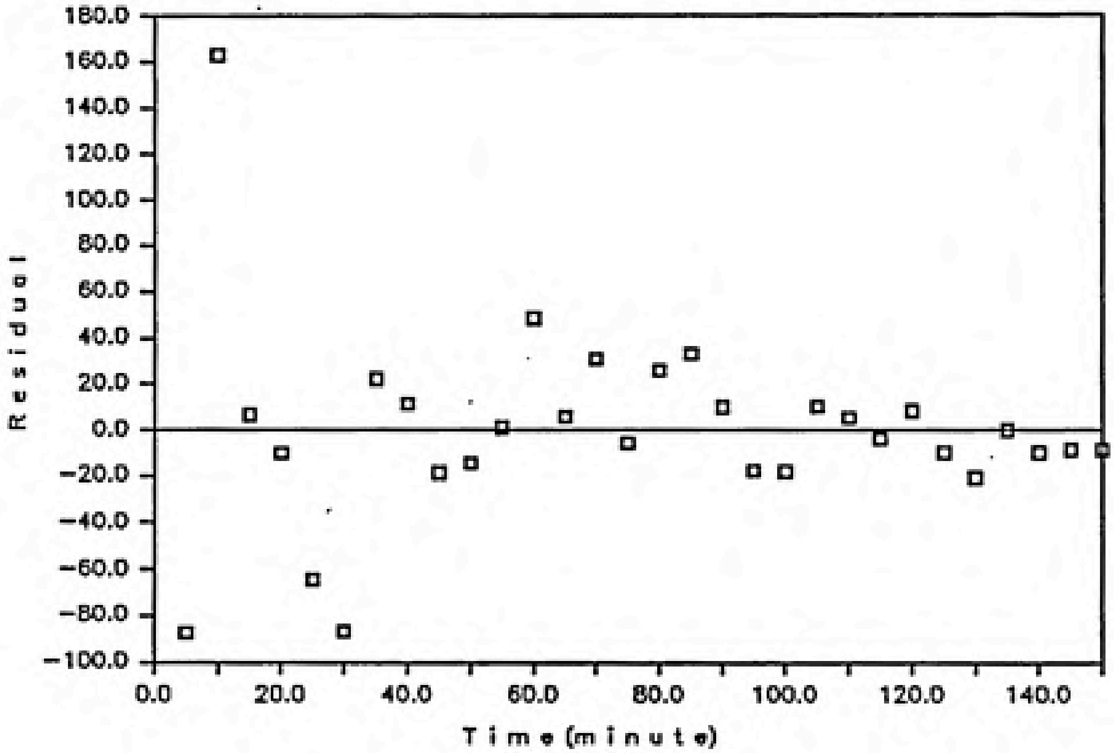
This result is nder conditions such as: 1 µM Al, 5 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1816.9730	79.2939
K1	0.070334	0.010262
I2	1531.1920	111.4798
K2	0.007450	0.000836
X	1862.3712	102.2015

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	-0.135731	1.000000			
I2	-0.379606	0.868486	1.000000		
K2	-0.470695	0.783584	0.671444	1.000000	
X	-0.333706	-0.862024	-0.658318	-0.575216	1.000000



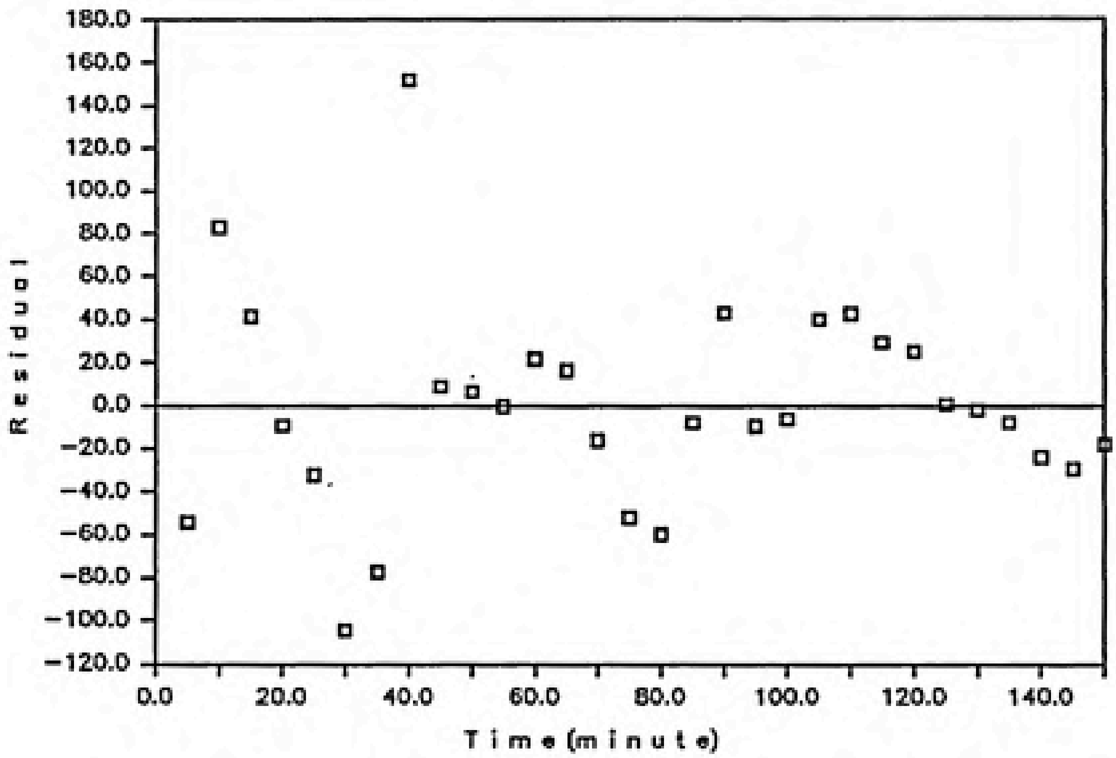
This result is under conditions such as: 1 µM Al, 10 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2123.4774	106.5910
K1	0.061402	0.008092
I2	1649.0210	131.4804
K2	0.006391	0.000799
X	1153.8123	116.2045

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	-0.201358	1.000000			
I2	-0.514923	0.864646	1.000000		
K2	-0.575630	0.791709	0.795217	1.000000	
X	-0.363995	-0.807626	-0.554982	-0.479669	1.000000



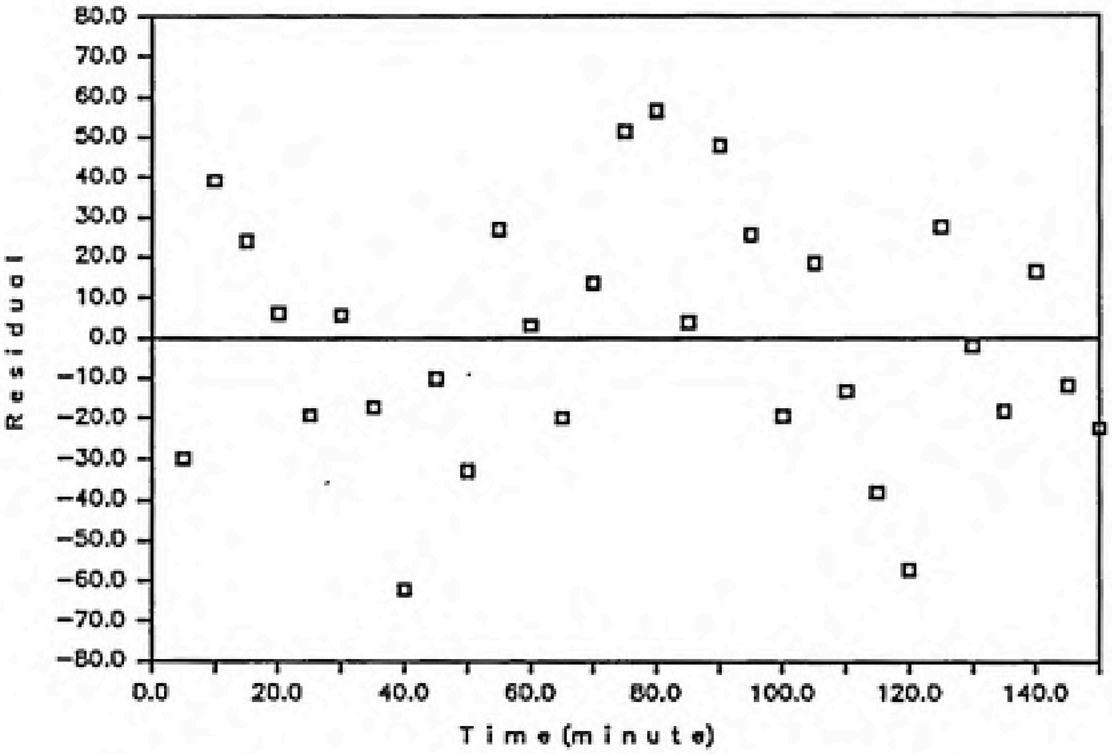
This result is under conditions such as: 1 µM Al, 20 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1898.2081	63.1602
K1	0.075396	0.006914
I2	2615.9768	69.8744
K2	0.008567	0.000323
X	577.0083	78.9461

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.489387	1.000000			
I2	0.274736	0.942761	1.000000		
K2	0.154443	0.867879	0.854794	1.000000	
X	-0.662494	-0.968530	-0.882243	-0.808136	1.000000



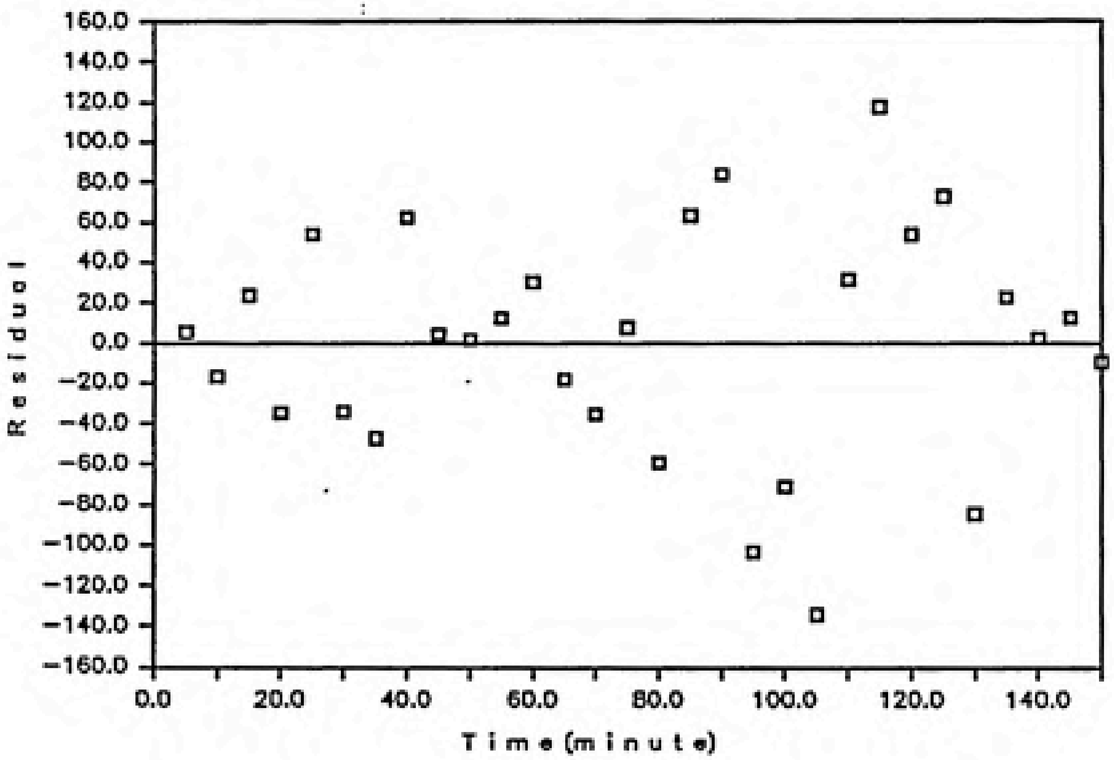
This result is under conditions such as: 1 µM Al, 80 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1453.0723	130.5830
K1	0.097311	0.010984
I2	3389.8322	73.0461
K2	0.011875	0.000557
X	568.6043	114.1094

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.245788	1.000000			
I2	-0.164699	0.811763	1.000000		
K2	-0.333549	0.622895	0.587411	1.000000	
X	-0.709246	-0.825796	-0.508455	-0.337712	1.000000



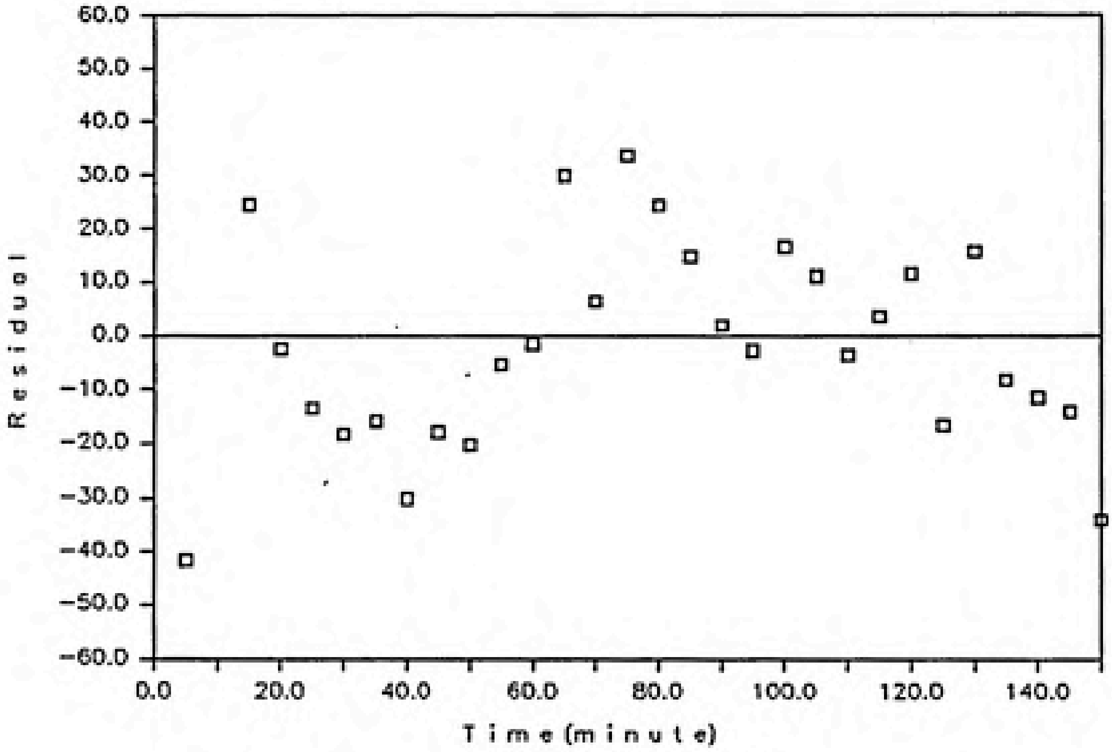
This result is under conditions such as: 1 uM Al, 5 mg DOC/L LDFA, 125 uM Lum, pH 5.0, 25^{o}C, 0.01 M NaAc/0.1 M NaCl, 08/25/89.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2180.0350	44.6321
K1	0.070265	0.003493
I2	1533.8393	43.5306
K2	0.006064	0.000320
X	1996.9971	53.1695

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.138391	1.000000			
I2	-0.189408	0.785311	1.000000		
K2	-0.324530	0.724488	0.557754	1.000000	
X	-0.621615	-0.832077	-0.535656	-0.455010	1.000000



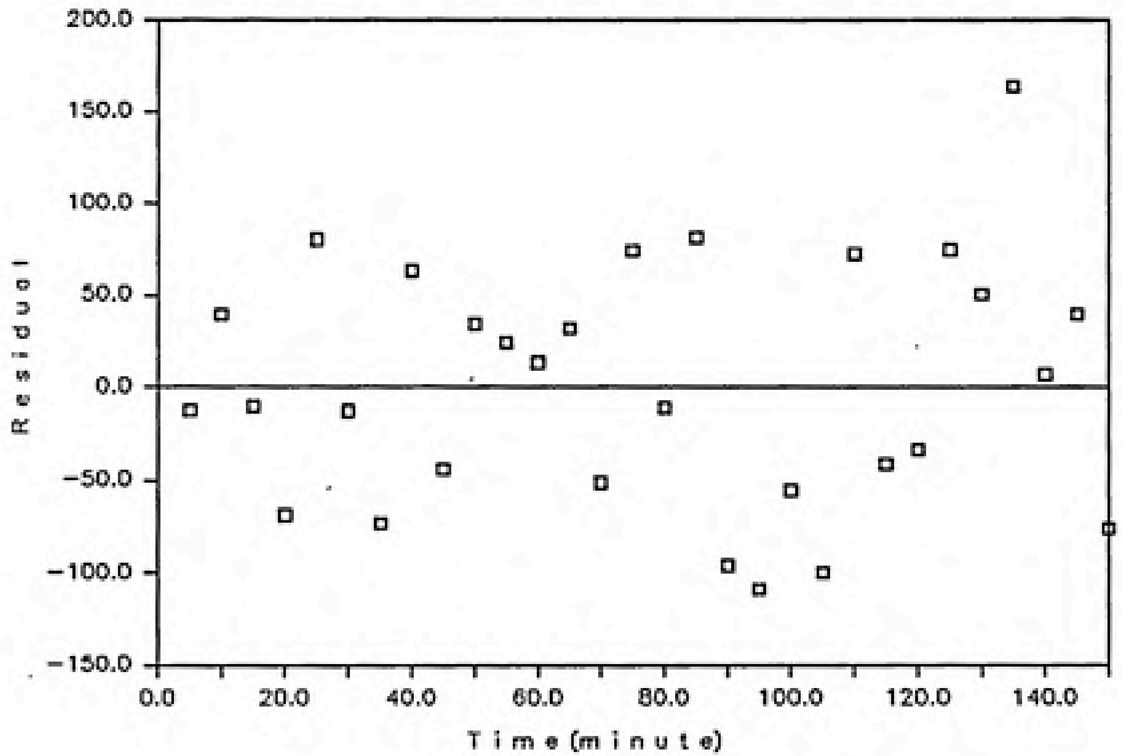
This result is under conditions such as: 1 uM Al, 5 mg DOC/L LDFA, 125 uM Lum, pH 5.0, 25^{o}C, 0.01 M NaAc/ 0.1 M NaCl, 10/08/89.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2462.9796	317.5335
K1	0.102514	0.023232
I2	2537.6408	159.2928
K2	0.009082	0.000834
X	2369.1795	366.4520

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	0.994130	1.000000			
I2	-0.561663	-0.503208	1.000000		
K2	-0.911538	-0.887915	0.602846	1.000000	
X	-0.999672	-0.995782	0.544381	0.903462	1.000000



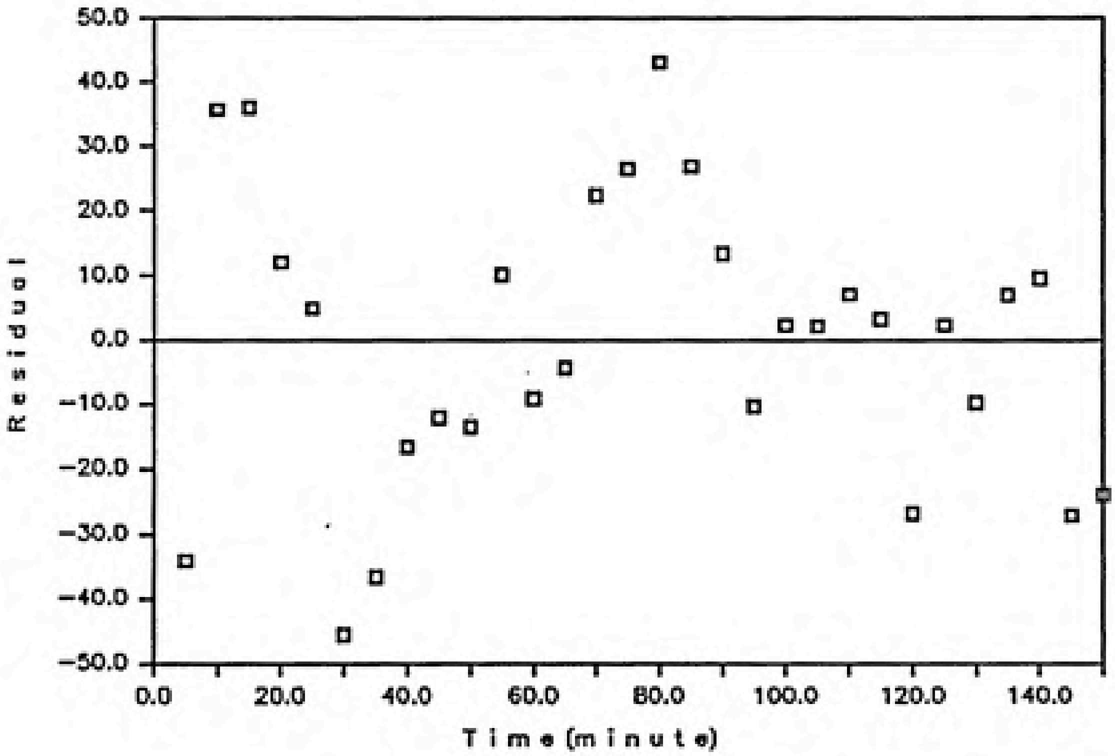
This result is under conditions such as: 1 µM Al, 5 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAC/0.01 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1963.8941	48.1083
K1	0.068224	0.002576
I2	1596.9891	38.0818
K2	0.007234	0.000307
X	1981.7413	41.1094

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	-0.070521	1.000000			
I2	-0.447337	0.680301	1.000000		
K2	-0.554129	0.570731	0.386927	1.000000	
X	-0.631185	-0.672487	-0.234433	-0.145523	1.000000



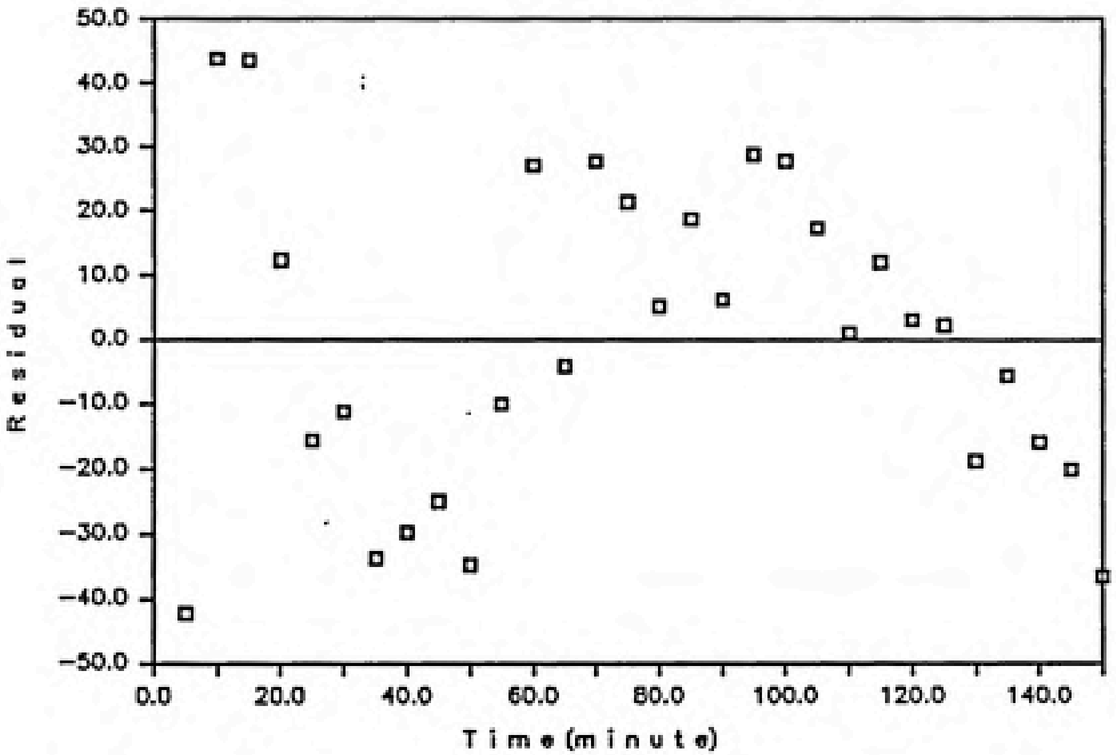
This result is under conditions such as: 1 µM Al, 5 mg DOC/L LDFA, 25 µM Lum, pH 5.5, 25^{o}C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2464.9384	49.1439
K1	0.065878	0.003129
I2	2129.7618	51.8530
K2	0.006010	0.000264
X	1011.4982	52.4105

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	-0.019364	1.000000			
I2	-0.325711	0.812196	1.000000		
K2	-0.430364	0.748502	0.606859	1.000000	
X	-0.506995	-0.822352	-0.538316	-0.468158	1.000000



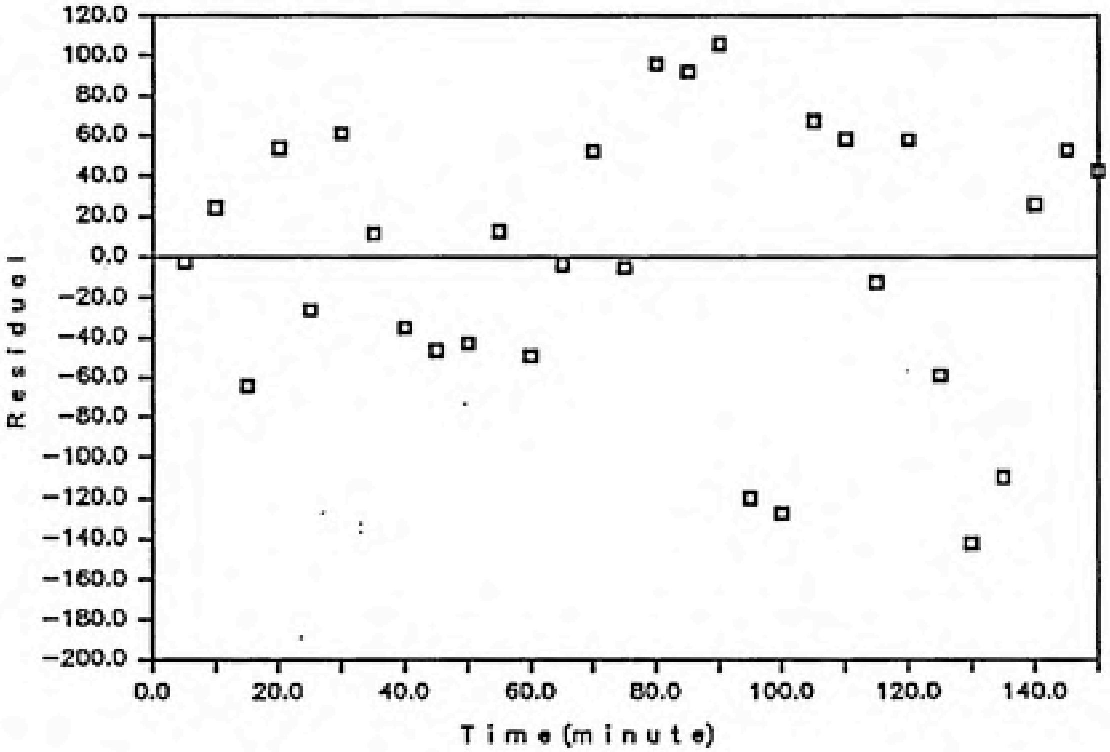
This result is under conditions such as: 1 µM Al, 5 mg DOC/L LDFA, 250 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	855.4664	301.9932
K1	0.100952	0.035961
I2	640.6047	221.5279
K2	0.019374	0.010519
X	1191.9971	152.6438

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	K1	I2	K2	X
I1	1.000000				
K1	-0.866653	1.000000			
I2	-0.925520	0.989835	1.000000		
K2	-0.932486	0.974441	0.989396	1.000000	
X	0.753212	-0.977987	-0.944705	-0.929929	1.000000



Appendix III. Statistical outputs for regression on $AlFA_i$, and the model is I=I1*(1-EXP(-0.1*T))+I2*(1-EXP(-0.01*T))+X

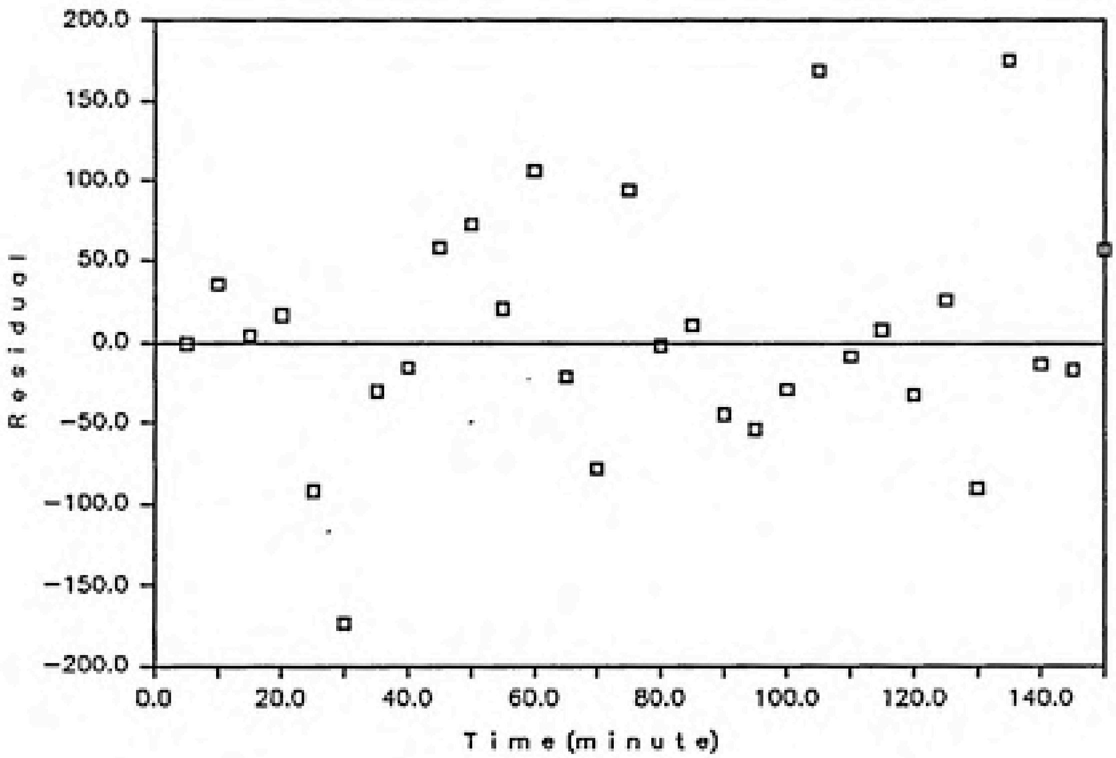
This result is under conditions such as: 1 uM Al, 1 mg DOC/L LDFA, 125 uM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2228.1634	151.4512
I2	601.9863	85.9100
X	3895.5960	119.6957

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.673833	1.000000	
X	-0.955033	0.443209	1.000000



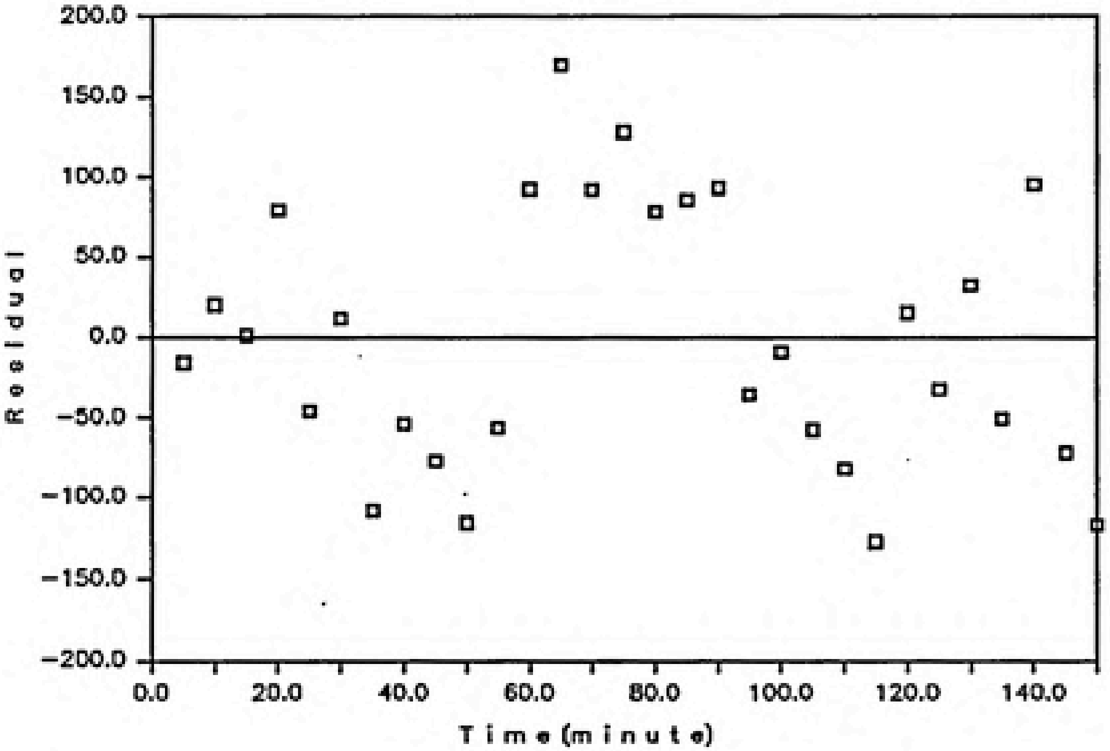
This result is under conditions such as: 2 μM Al, 5 mg DOC/L LDFA, 125 μM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2818.1561	160.2753
I2	2360.5648	88.4613
X	4498.9539	127.2832

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.676475	1.000000	
X	-0.958082	0.455597	1.000000



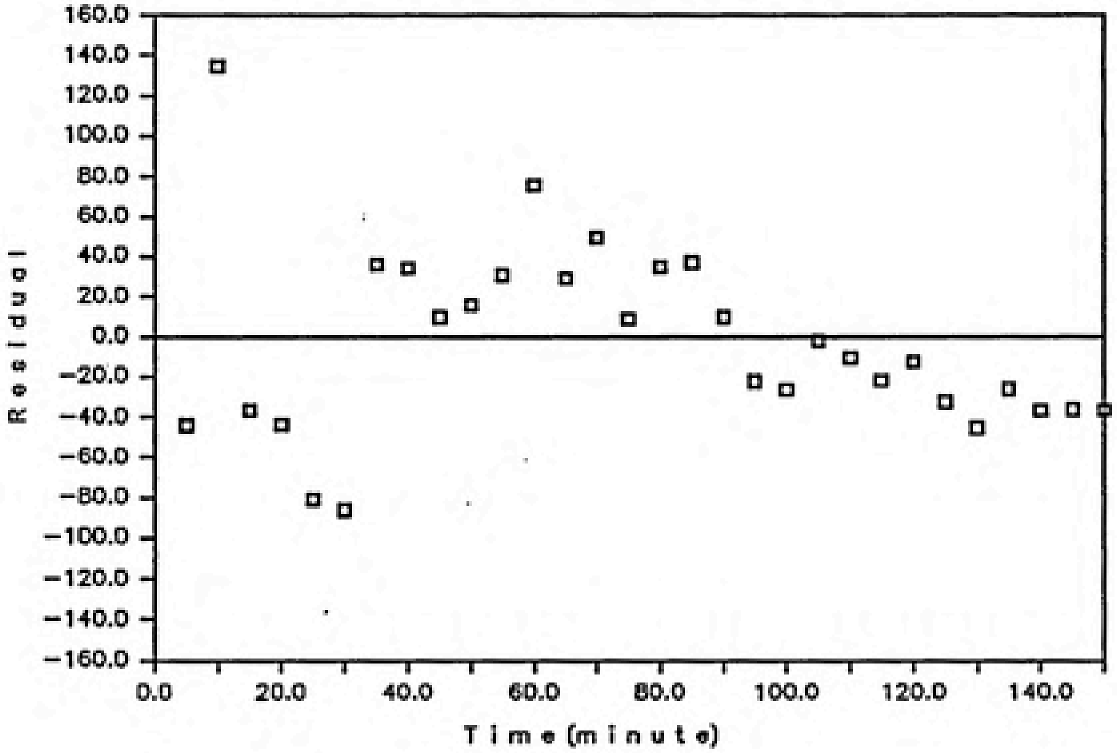
This result is under conditions such as: 1 μM Al, 5 mg DOC/L LDFA, 125 μM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1781.1743	83.7580
I2	1707.2956	61.3388
X	1629.7896	57.7196

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.812960	1.000000	
X	-0.938315	0.583775	1.000000



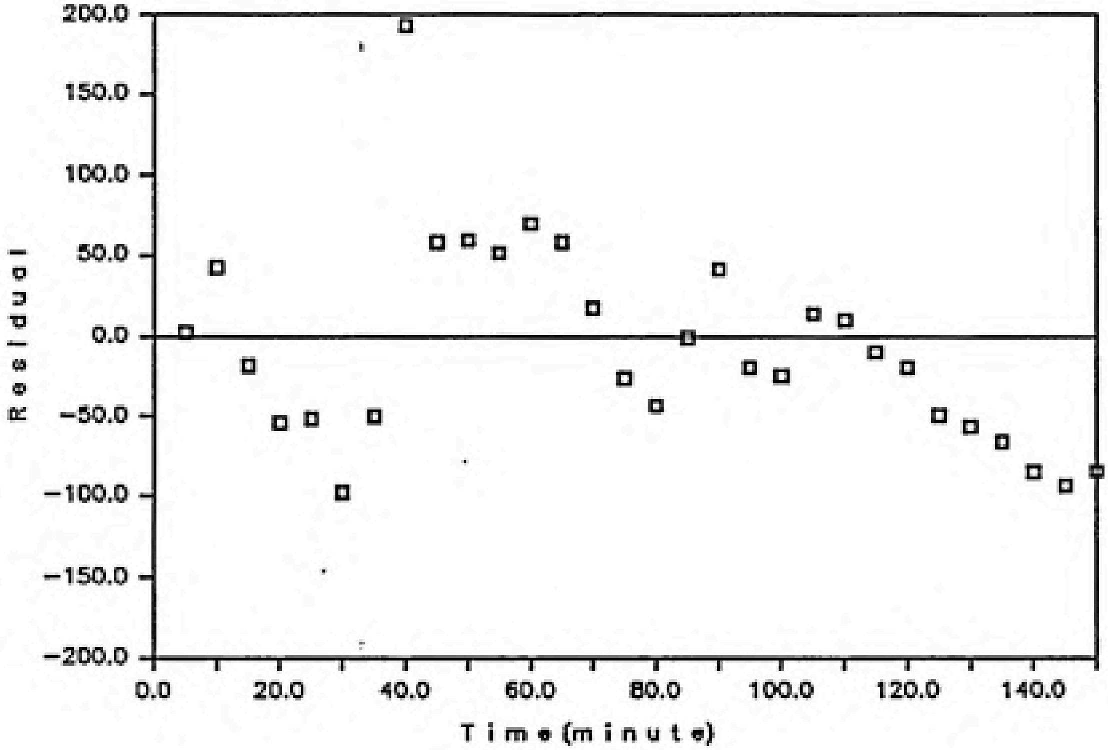
This result is under conditions such as: 1 µM Al, 10 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1955.3553	138.7135
I2	2011.1512	73.1577
X	843.1351	111.8516

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.647157	1.000000	
X	-0.957378	0.419452	1.000000



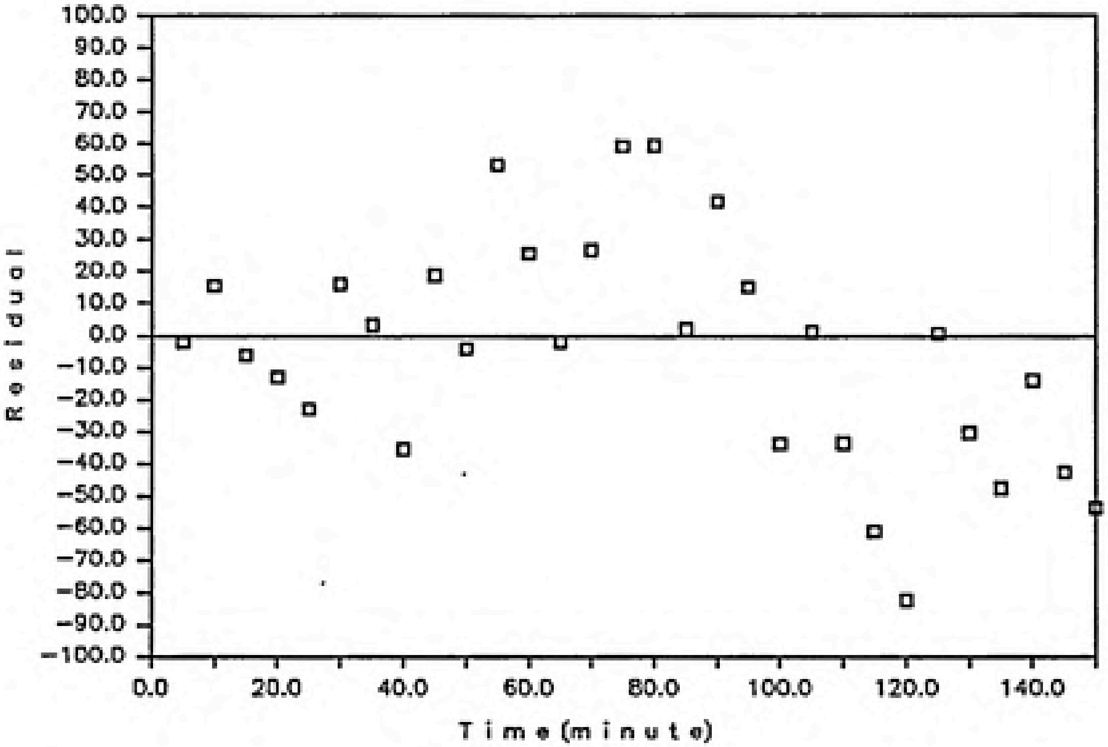
This result is under conditions such as: 1 µM Al, 20 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25°C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	1825.6918	75.0173
I2	2796.2431	39.2053
X	400.5190	60.4302

CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.652572	1.000000	
X	-0.958624	0.429462	1.000000



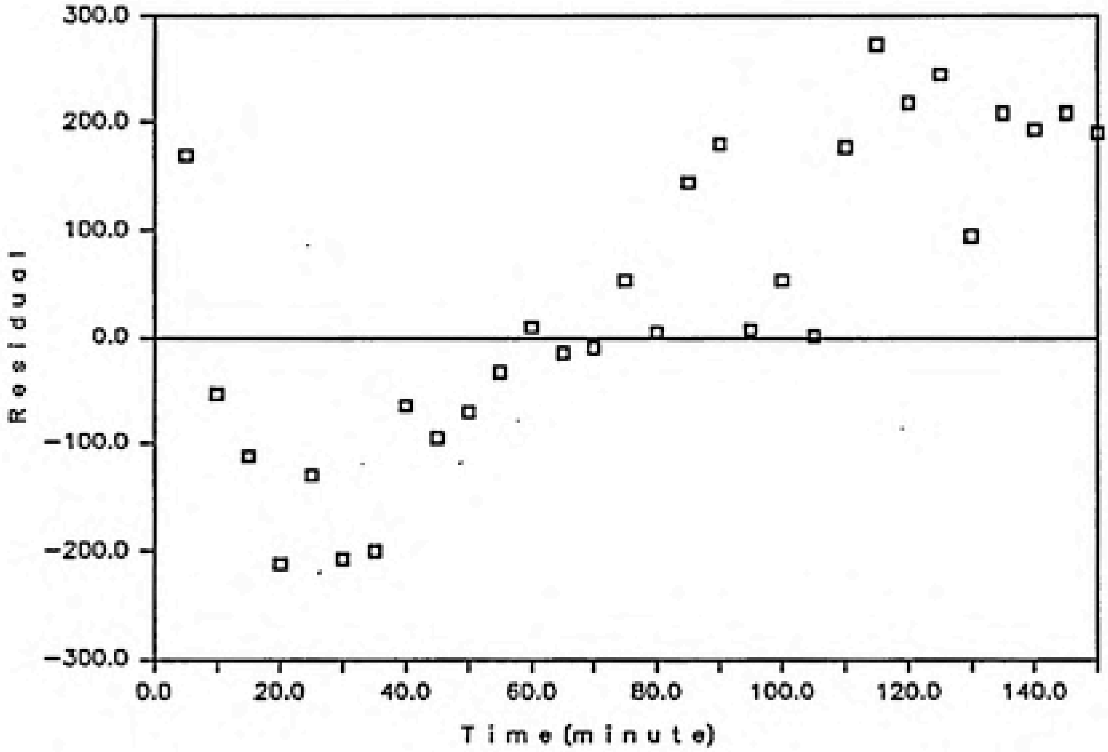
This result is under conditions such as: 1 µM Al, 80 mg DOC/L LDFA, 125 µM Lum, pH 5.5, 25^{o}C, 0.01 M NaAc/0.1 M NaCl.

PARAMETER ESTIMATES:

LABEL	ESTIMATE	STANDARD ERROR
I1	2534.1835	1541.8464
I2	2669.4534	270.9591
X	32.1968	1344.0954

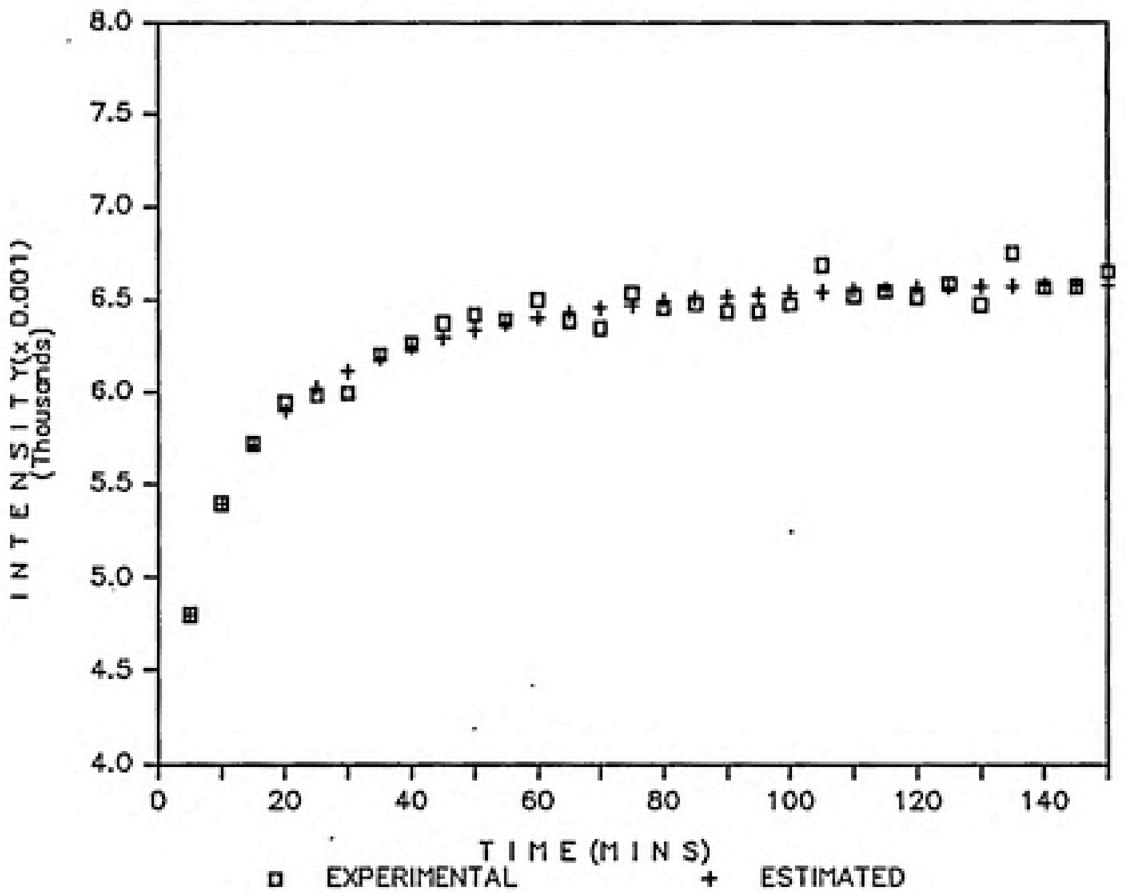
CORRELATION MATRIX OF PARAMETER ESTIMATES:

	I1	I2	X
I1	1.000000		
I2	-0.922419	1.000000	
X	-0.998537	0.902027	1.000000

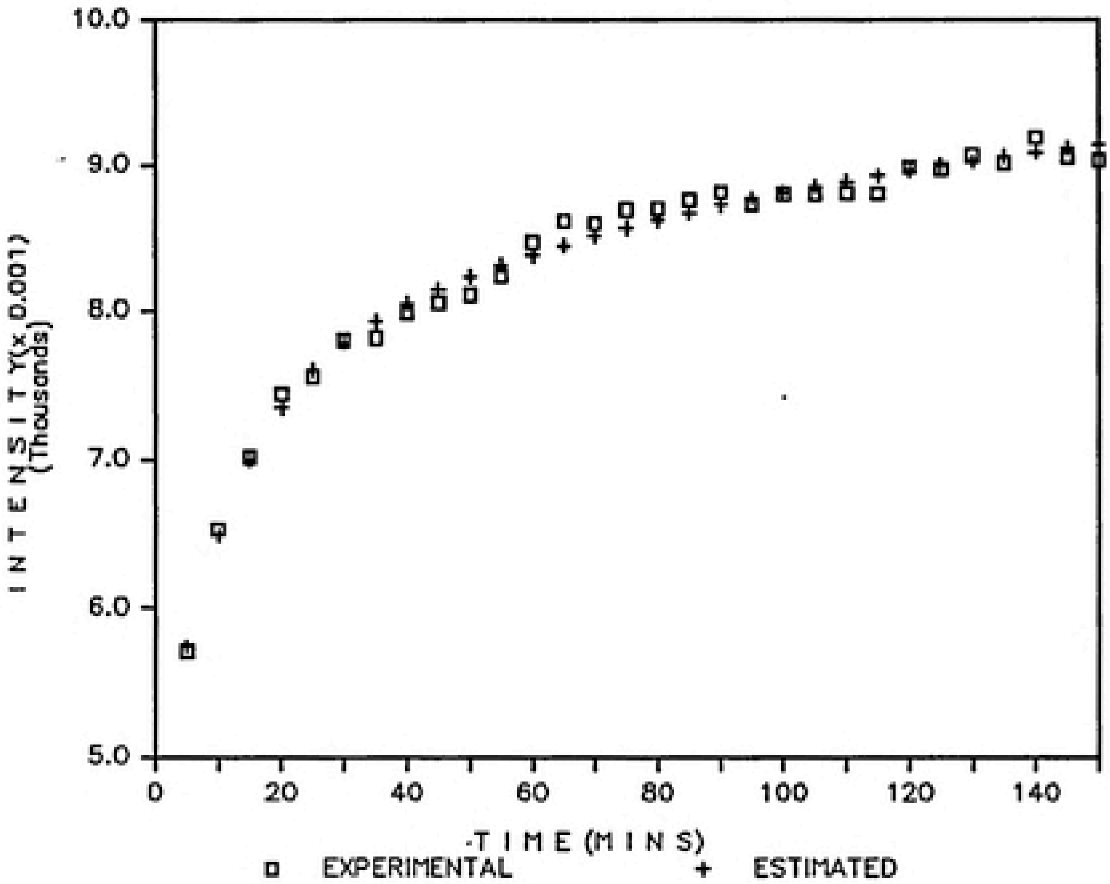


Appendx IV. The comparison of SYSTAT estimated and experimental fuorescence intensity for varied concentrations of Al.

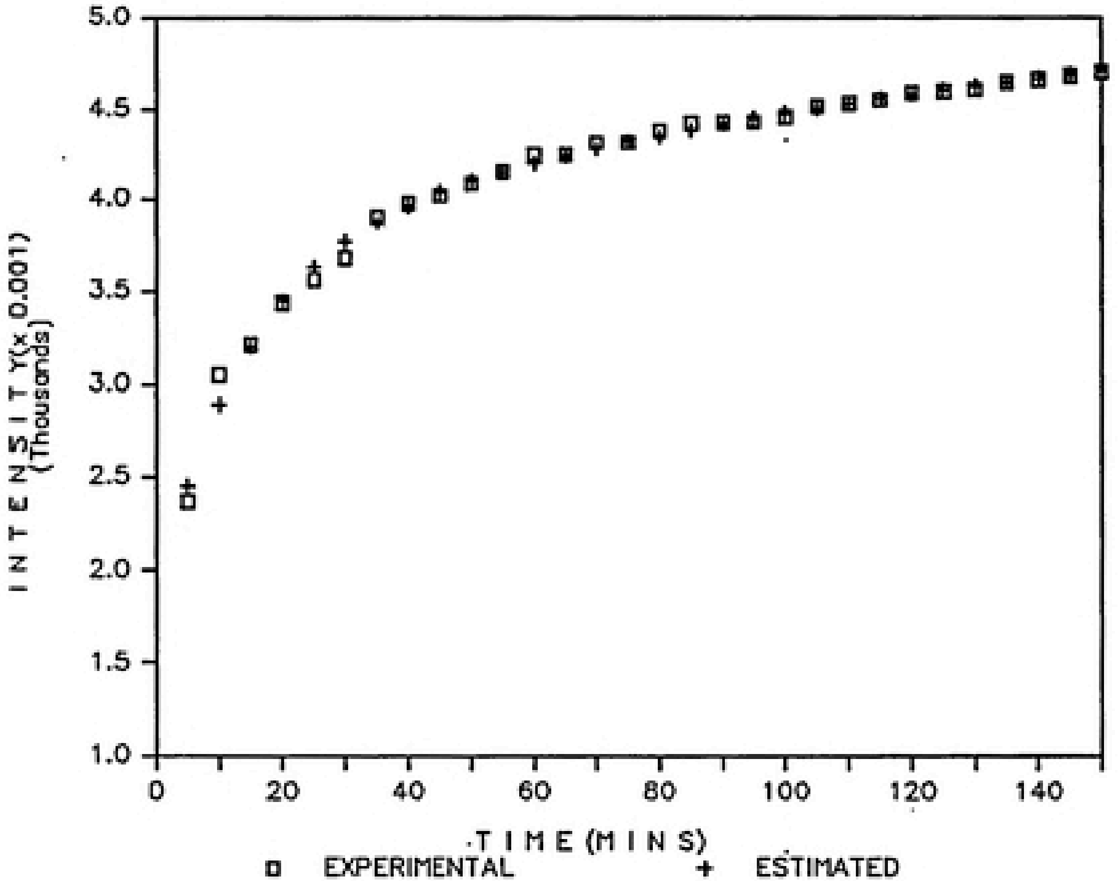
This plot is under conditions such as: 1.0 µM Al, 1.0 mg DOC/L LDFA, 125 µM Lum., pH 5.5, 25°C, 0.01 M NaAc/ 0.1 M NaCl.



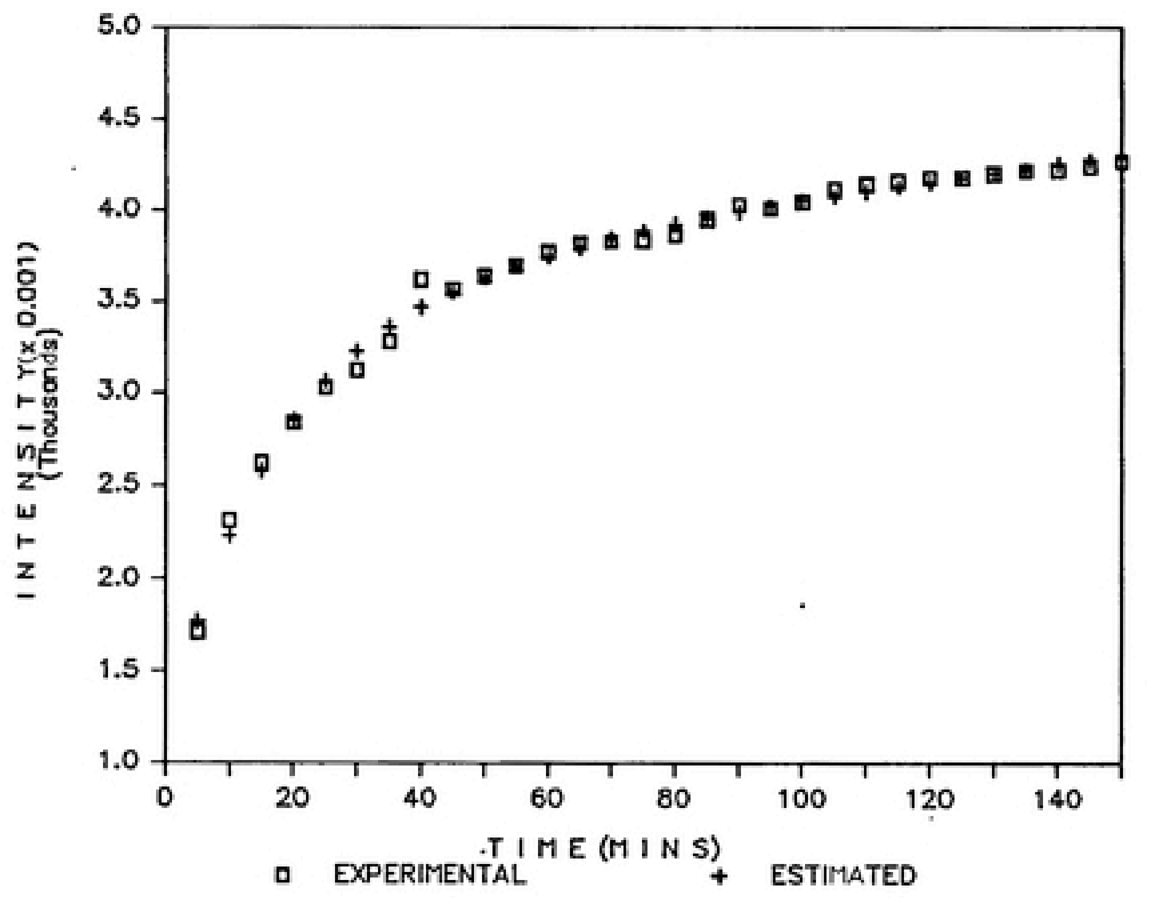
This plot is under conditions such as: 2.0 µM Al, 5.0 mg DOC/L LDFA, 125 µM Lum., pH 5.5, 25°C, 0.01 M NaAc/ 0.1 M NaCl.



This plot is under conditions such as: 1.0 µM Al, 5.0 mg DOC/L LDFA, 125 µM Lum., pH 5.5, 25°C, 0.01 M NaAc/ 0.1 M NaCl.



This plot is under conditions such as: 1.0 µM Al, 10.0 mg DOC/L LDFA, 125 µM Lum., pH 5.5, 25°C, 0.01 M NaAc/ 0.1 M NaCl.



This plot is under conditions such as: 1.0 µM Al, 20.0 mg DOC/L LDFA, 125 µM Lum., pH 5.5, 25°C, 0.01 M NaAc/ 0.1 M NaCl.