THE INFLUENCES OF TEMPERATURE ON AQUEOUS ALUMINIUM CHEMISTRY

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Abstract. Temperature affects the solubility of $Al(OH)_3(s)$, the solubility product formed, the hydrolysis and molecular weight distribution of aqueous Al species as well as the pH of the solutions. In the present work, identical solutions of inorganic Al (400, 600, and 800 μg Al L^{-1}) were stored for 1 mo at either 2 or 25 °C. In the solutions stored at 25 °C pH varied from 4.83 to 5.07, while in the corresponding solutions stored at 2 °C pH varied from 5.64 to 5.78. In spite of the relatively low pH at 25 °C, significant amounts of high molecular weight Al species were precipitated from the solution and the solubility product ($\log {}^*K_s$) of $Al(OH)_3$) (s) was low (9.0). Substantial amounts of high molecular weight Al species were also formed at 2 °C, but the majority was present as colloids in the solution. The solubility product (converted from 2 into 25 °C) was 10.2, reflecting a solubility product of an amorphous $Al(OH)_3$)(s) phase. The different physico-chemical forms of Al present at 2 and 25 °C should have relevance for water/soil chemistry modeling.

1. Introduction

Acidification of soil systems may cause a transfer of Al into aqueous solutions (Cronan and Schofield, 1979; Dickson, 1980, Seip *et al.*, 1989), where Al may be present in different physico-chemical forms, varying for instance in size and charge properties (Lydersen *et al.*, 1987a). Low molecular weight, inorganic forms of Al, often referred to as inorganic monomeric Al (Driscoll, 1984), are believed to be the most toxic species to aquatic biota, i.e., salmon and trout species (Driscoll *et al.*, 1980; Fivelstad and Leivestad, 1984). However, polynuclear hydroxy-Al species are observed to have phytotoxic effects (Parker *et al.*, 1989). Consequently low molecular weight inorganic Al species should be separated from high moleclar weight Al species (e.g. particles and colloids) when chemical and toxicological effects of Al are investigated.

In water/soil systems Al transformation processes, e.g. the mobilization of Al from slightly soluble sources into more reactive dissolved forms or *vice versa*, continuously occur. The detailed mechanisms are not well known as illustrated by the difficulties in modeling streamwater Al-concentrations (Stone and Seip, 1989). The effect of temperature on these processes is essential, but is most often ignored.

In the present work, synthetic inorganic Al solutions were used to investigate effects of temperature on the aqueous inorganic Al chemistry. Hollow-fiber ultrafiltration (Lydersen *et al.*, 1987b) combined with an extended Barnes/Driscoll method (Barnes, 1975; Driscoll, 1984) was used for the Al speciation purposes.

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2. Materials and Methods

2.1. SOLUTIONS

The experiments were based on synthetic, inorganic Al solutions. The solutions were prepared by dissolving $Al(NO_3)_3*6H_2O$ in acidified double distilled water (HCl, pH=1) at 2 °C. From this stock solution, 50 L solutions of 400, 600, and 800 $\mu g\ L^{-1}$ were prepared. The pH in the solutions varied from 3.7 to 4.0. Subsamples from these batch solutions were accurately weighed (4000 ± 1 mg) before addition of NaOH (Table I). The amount of NaOH added should theoretically increase the pH to 5.5 to 5.7 (estimated for 2 °C). The molar ratio of Al bound OH to total Al (OH:Al) varied from 1.9 to 2.4. After NaOH was added, the solutions were thoroughly mixed for 15 min on a shaking table before the solutions were split into two accurately weighed fractions of 2000 ± 1 mg. One fraction was kept at 25 °C, the other at 2 °C. After 1 mo of storage, the solutions were analyzed with respect to pH and different Al species.

2.2. FRACTIONATION

The analytical scheme is presented in Figure 1 and the Al fractions obtained are listed in Figure 2. Al was analyzed according to the Barnes/Driscoll method, a combined extraction/cation exchange technique (Barnes, 1975; Driscoll, 1984). Al was complexed with 8-hydroxyquinoline (HQ). Then pH was adjusted to 8.3 to minimize interferences (Barnes, 1975) before the complex immediately was extracted with methyl isobutyl ketone (MIBK) for 20 s prior to analysis. Using this method on untreated water samples, 2 fractions of dissolved Al are directly obtained:

Al_a: Total monomeric Al present in the solution, i.e., HQ/MIBK-extractable Al within 20 s; and

Al_0: Non-labile monomeric Al present in the solution, i.e., HQ/MIBK-extractable Al (within 20 s) present in the cation-exchange eluate.

To distinguish Al colloides from Al particles (precipitated), the upper 250 mL of

TABLE I

Amounts of NaOH added to different Al solutions

Al conc. $\mu g\ Al\ L^{-1}$	10^{-1} M NaOH mL	10^{-2} M NaOH mL	NaOH added μeq 4L	NaOH added $\mu eq\ L^{-1}$
400	4.8	2.0	500	125.0
400	5.1	2.0	530	132.5
600	7.5	2.0	770	192.5
600	7.8	2.0	800	200.0
800	10.1	2.0	1030	257.5
800	10.4	2.0	1060	265.0

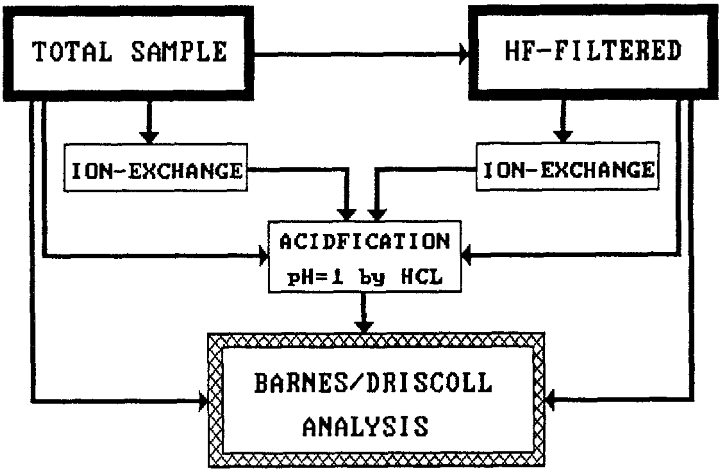

Fig. 1. A schematic presentation of the Al analytical work. HF: Hollow-fiber ultrafiltered.

each solution was carefully pumped into a polyethylene bottle using a peristaltic pump. 120 mL was used for cation exchange purposes. The remaining 130 mL and the cation exchange eluates were then acidified by HCl (pH=1) and stored for 48 hr prior to analysis. Thus, two more fractions are obtained:

Al_a*: Al_a measured in the acidified untreated samples; and
Al_0*: measured in the acidified cation exchanged eluates.

In the synthetic solutions the total amount of Al is known defined as Al_{tot}. Based on these 5 Al fractions (Al_{tot}, Al_a*, Al_a, Al_0* and Al_0), another 5 fractions can be calculated:

Al_i: Inorganic monomeric Al, i.e. HQ/MIBK-extractable Al retained on the cation exchange resin.
$Al_i = Al_a - Al_0$.
Ideally Al, should represent Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$.

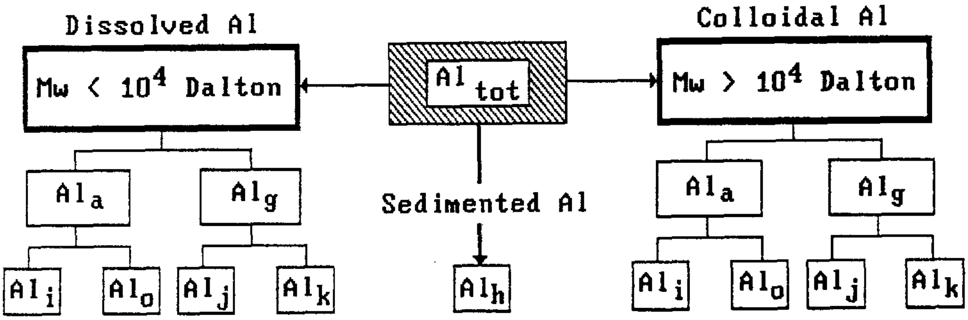

Fig. 2. The different Al-fractions obtained from the inorganic stock solutions. (Notation of subscripts, see text).

Al_g: Non HQ/MIBK-extractable Al within 20 s.
$Al_g = Al_a^* - Al_a$.
Ideally Al_g should represent the amount of colloids in solution.

Al_h: Precipitated Al complexes.
$Al_h = Al_{tot} - Al_a^*$.

Al_j: Non HQ/MIBK-extractable Al within 20 s, but retained on the cation-exchange resin.
$Al_j = Al_a^* - (Al_0^* + Al_j)$.
Ideally Al_j should represent net positively charged colloids, colloids with highly positive areas (probably at the corners and imperfection points of the structure) and strong dipolar complexes.

Al_k: Neither HQ/MIBK-extractable nor cation exchangeable Al.
$Al_k = Al_o^* - Al_o$.
Ideally Al_k should represent weak positively or negatively charged colloids as well as neutral and weak dipolar colloids.

Hollow-fiber ultrafiltration was performed on untreated water samples prior to the Al analysis (Lydersen *et al.*, 1987b). Thus each Al fraction can be divided into two molecular weight fractions (Al: Mw $> 10^4$ Dalton) and (Al: Mw $< 10^4$ Dalton) (Figure 2).

2.3. CATION EXCHANGE

Amberlite IR-120 was used as cation exchange resin. The length of the ion exchange column was 13 ± 0.5 cm, with a bed volume of 10 mL. As recommended by Driscoll (1984) the operational ion exchange flow rate was 3.8 mL min^{-1} (mL bed volume). Batches of resin were prepared by displacing some of the exchangeable H with Na ions on exchange sites. The amount of Na on the exchanger was adjusted such that when an eluant of comparable ionic strength to the solutions being analyzed was passed through the exchanger, the effluent pH was similar to the pH of the solutions being analyzed. A volume of 60 mL 10^{-4} M NaCl was always used for conditioning purposes. Then another 60 mL of eluate was collected for analysis.

2.4. HOLLOW-FIBER ULTRAFILTRATION

The hollow-fiber cartridge used was an Amicon H1P10-8 fiber with a nominal molecular weight cutoff level of 10^4 Dalton (D). The filtering flow rate was about 300 mL min^{-1} with a transmembrane pressure of about 10 psi (69 kPa). The pore size distribution of the membrane has been shown to be relatively narrow and sorption effects on the fibers (by mass balance calculations) are earlier shown to be minimal if the fibers are preconditioned with 250 mL of the sample water before the ultrafiltrate is collected for analysis (Lydersen *et al.*, 1987b).

2.5. ANALYSIS

The extraction and the cation exchange was performed at their respective storing temperatures, i.e., 2 or 25 °C. The equipment and reagents used (including the pH-buffers) were also kept at the corresponding temperatures.

After the extraction of the samples, the extracts were stored at 4 °C for at least 24 hr. The extracts were then stored at room temperature (20 °C) for 2 hr before the absorption measurements were conducted on a Shimadzu UV-120-02 spectrophotometer at 395 nm (Tikhonov, 1973; Bloom *et al.*, 1979).

pH was measured using a Radiometer PHM-80 with a combined glass-electrode, Radiometer GK 2401C.

2.6. THEORY

The Hydrolysis and Solubility Constants of $Al(OH)_3(s)$

In this paper solubility and hydrolysis constants are written in terms of H^+ and H_2O rather than OH^-. Thus, the equilibrium constants are written $*K$ instead of K. Subscript 's' refers to solubility product for a solid phase.

The first hydrolysis constant

$$\log{*K_1} = \log\left(\frac{[Al(OH)^{2+}]*[H^+]}{[Al^{3+}]} * \frac{\gamma\, Al(OH)^{2+}\ \gamma\, H^+}{\gamma\, Al^{3+}}\right) \tag{1}$$

γ = activity coeff.

is needed when calculating the solubility product, since $\log{*K_s} = [Al^{3+}]/[H^+]^3$. The $\log{*K_1}$ used in this paper (at 298.15 K = 25 °C) corresponds to the value recommended by Nordstrom *et al.* (1984).

$\log{*K_1}$ $= -4.987(0.08)$ (May *et al.*, 1979; Ball *et al.*, 1980)

The uncertainty is given in parentheses.

The average value from the literature is $\log{*K_1}$: $-$ 4.87 [$*K_1$= [(1.35 ± 1)×10^{-5}] (n=24)].

The solubility product, $\log{*K_s}$ of Al(OH)3(s), presented in the literature varies from 7.97 (Kittrick, 1966) to 11.40 (Dezelic *et al.*, 1971), i.e. from a highly crystalline to a highly amorphous Al(OH)3(s).

The hydrolysis and solubility constant ($\log{*K_1}$ and $\log{*K_s}$) were adjusted with respect to temperature by Van 't Hoff's relation:

$$\log{*K_1} = \log{*K_1}(Tr) - \frac{H^\circ_r(\mathrm{Tr})}{2.303*R} * [1/T - 1/Tr] \tag{2}$$

with Tr as the reference temperature (298.15 K = 25 °C). The H°_r value used for $\log{*K_1}$ is : 11.9(0.5) kcal mol^{-1} (Baes and Mesmer, 1976; Ball *et al.*, 1980), and for $\log{*K_s}$ is the value generally used for crystalline gibbsites (H°_r = -22.8 Kcal mol^{-1}, Nordstrom *et al.*, 1980). The H°_r for amorphous $Al(OH)_3(s)$ is not significantly higher and decreases toward the H°_r value of gibbsite by aging. Since the H°_r of amorphous $Al(OH)_3(s)$ is not constant, we are generally using the H°_r of crystalline gibbsites.

The temperature does not significantly affect the H°_{r} values within the temperature interval investigated (2 to 25 °C), i.e. approximately constant for both amorphous and crystalline phases.

The ionization constant of water ($-\log K_w = [OH^-][H^+]$) also affects pH ($-\log[H^+]$) and pOH ($-\log[OH^-]$). At 25 °C, $-\log K_w$ is 13.9965 (Weast and Astle, 1982), at 2 °C, $-\log K_w$ is 14.9015. At constant pH $[OH^-]$ is 8 times higher at 25 °C than at 2 °C. The change in the ionization of water with temperature is incorporated in the hydrolysis and solubility calculations of Al.

5. Analytical Considerations

The amount of Al^{3+} used for the solubility product calculations is estimated from the Al_i values according to the actual pH and temperature present. The $\log{}^*K_s$ values at 2 °C are converted into standard temperature (25 °C) by the Equation (2). Therefore, all $\log{}^*K_s$ values given in the text are directly comparable ($\log{}^*K_s$ at 25 °C).

The standard deviation of the Barnes/Driscoll method is shown to be approximately 1% of the mean (Sullivan *et al.*, 1986).

The pH was read when no pH drift (on the hundredth) was observed during one minute. The standard deviation of the pH measurements was ± 0.01 pH unit.

No organic compounds were present in the doubly distilled water used. All fraction analyzed should therefore only represent different inorganic fraction of Al. Since the major part of the $Al(OH)_3(s)$ formed has *not* physically precipitated from solution, it is more adequate to call it *formation* instead of *precipitation.* The adsorption of Al species onto the container walls was not a serious problem.

3. Results and Discussion

pH OF THE SOLUTIONS

In the solutions equilibrated at 2 °C, the pH values varied from 5.64 to 5.78, while at 25 °C pH varied between 4.83 and 5.07 (Table II). Change in the ionization constants for water due to temperature variations is one reason for the pH deviations. By converting the pH values measured at 2 °C into 25 °C pH should be 5.19 to 5.33 instead of that measured at 2 °C (5.64 to 5.78). The difference in measured pH at 2 and 25 °C may also indicate different Al/OH-arrangements present in the complexes (colloids and particles) formed at 2 °C compared with those formed at 25 °C. The hydrolysis, and the different polymerization processes are all deprotonation processes:

– *Hydrolysis*

$Al(OH_2)_6{}^{+3} = AlOH(OH_2)_5{}^{+2} + H^+$.

– *Chain structure*

$2Al_2(OH)_2(OH_2)_8{}^{+4} = Al_4(OH)_6(OH_2)_{12}{}^{+6} + 2H_2O + 2H^+$.

TABLE II

pH, log*K_s, molar ratio OH:Al, concentrations and molecular weight distribution of Al fractions present at 2 and 25 °C

°C		2 °C	25 °C[a]	molar	Al_{tot}	Al_a*			Al_a			Al_g			Al_j	Al_k	Al_h
temp.	pH	log*K_s	log*K_s	OH:Al	total	total	Mw>10^4D	Mw<10^4D	total	Mw>10^4D	Mw<10^4D	total	Mw>10^4D	Mw<10^4D	total	total	total
					µg Al L^{-1}												
2°	5.74	11.7	10.3	1.9	400	386	197	189	220	33	187	166	164	2	131	35	14
25°	5.02		9.0	1.9	400	179	99	80	69	2	67	110	97	13	75	35	221
2°	5.78	11.6	10.2	2.4	400	385	251	134	173	38	135	212	212	0	162	50	15
25°	5.07		9.0	2.4	400	162	111	51	60	16	44	102	95	7	56	46	238
2°	5.71	11.7	10.3	2.1	600	581	359	222	261	48	213	320	311	9	170	150	19
25°	4.95		9.1	2.1	600	287	152	135	102	4	98	185	148	37	100	85	313
2°	5.78	11.7	10.3	2.4	600	577	403	174	216	62	154	361	341	20	160	201	23
25°	5.07		9.0	2.4	600	227	150	77	53	2	51	174	148	26	93	81	373
2°	5.64	11.8	10.4	2.0	800	764	467	297	372	76	296	392	391	1	205	187	36
25°	4.83		9.1	2.0	800	473	219	254	201	20	181	272	199	73	119	153	327
2°	5.72	11.8	10.4	2.3	800	759	557	202	261	73	188	498	484	14	176	322	41
25°	4.95		9.0	2.3	800	408	272	136	106	14	92	302	258	44	150	152	392

[a] For sample studied at 2°C the values given in this column are obtained by using Equation (2).

– *From a chain structure to a ring structure*

$Al_6(OH)_{10}(OH_2)_{16}^{+8} = Al_6(OH)_{12}(OH_2)_{12}^{+6} + 2H_2O \pm \mathbf{2H^+}$.

The six-membered rings may coalesce in various ways, as a result of further dehydration and deprotonation.

Since more H^+ is released/produced in the Al complexing processes at 25 °C compared with at 2 °C, more of the polymerization processes have taken place at 25 °C compared with that at 2 °C.

log*K_s OF $Al(OH)_3(s)$

In the solutions stored at 2 °C average log*K_s was 10.3 [*$K_s = [(2.1 \pm 0.2) \times 10^{10}](n=6)]$ (Table II), indicating the presence of an amorphous $Al(OH)_3(s)$ phase. In the corresponding solutions kept at 25 °C average log*K_s was 9.0 [*$K_s = [(1.1 \pm 0.2) \times 10^9]$ $(n=6)]$ which is lower than that estimated for microcrystalline gibbsite (log*K_s = 9.35; Hem and Roberson, 1967).

The solubility product (*K_s) was approximately 20 times higher in solutions stored at 2 °C compared with those stored at 25 °C. Thus, temperature seems to be of major importance for the solubility product formed.

Al SPECIATION

Monomeric Species

In the synthetic inorganic Al solutions investigated, no organic monomeric Al (Al_0) should be present. Al_a should therefore be equal Al_i and represent the following monomeric species: $Al(OH_2)_6^{+3}$, $Al(OH)(OH_2)_5^{+2}$, $Al(OH)_2(OH_2)_4^{+}$. The distribution of these species is highly dependent on pH and temperature (Seip *et al.*, 1984; Schecher and Driscoll, 1987; Lydersen, 1989).

At 2 °C, 30 to 55% of Al_{tot} was present as Al_a, while in the corresponding solutions kept at 25 °C only 9 to 23% was present as Al_a. The amount of Al_a present in the solution was significantly influenced by temperature, even in solutions of equal Al:OH ratio. Smith and Hem (1972) observed no change in the concentration of inorganic monomeric Al during storage of solutions of identical OH:Al ratio. In contrast to the sited work (carried out at 25 °C) our experiments were carried out at two temperatures 2 and 25 °C. Consequently the OH:Al ratio would not be the same at both temperatures, even though the initial OH:Al ratio was identical in the solutions before the solutions were stored at 2 and 25 °C, respectively.

In spite of the H^+-concentrations being a factor 5 higher at 25 °C, the Al_a concentration was a factor 2.5 lower at 25 °C compared with the solutions stored at 2 °C. Taking the ionization of water into account, however, the calculated OH^- concentration should be about 30% lower at 2 °C compared with at 25 °C, even though pH was significantly higher at 2 °C.

Colloidal Species and Particles

At 2 °C, 180, 339 and 428 μg Al L^{-1} was present as colloids (Al_g) and particles

(Al_h) in solutions of 400, 600, and 800 μg Al L^{-1} respectively (Table II). The molar ratio OH:Al was 1.9 to 2.1. In the corresponding solutions kept at 25 °C, 331, 498 and 599 μg Al L^{-1} was present as Al_g and Al_h.

In the solutions where the molar ratio OH:Al was 2.3 to 2.4, 227, 384, and 539 μg Al L^{-1} was present as Al_g and Al_h at 2 °C, while 340, 547, and 694 μg Al L^{-1} was present as Al_g and Al_h in the corresponding solutions kept at 25 °C.

The concentration of Al present in solutions (Al_{tot}: 400, 600, and 800 μg Al L^{-1}) did not affect the percentage distribution of colloids and particles being formed, but the distribution was seriously influenced by temperature. At 2 °C, only 6 to 8% of the Al complexes (Al_g+Al_h) were sedimented out of the solution (Al_h) where pH varied from 5.64 to 5.78. At 25 °C, however, 40 to 60% was sedimented out (Al_h), even though pH was significantly lower (4.83 to 5.07). The remaining complexes were present as Al colloids (4.83 to 5.07). The remaining complexes were present as Al colloids (Al_g) (Table II). High temperature and high molar ratio OH:Al favors different polymerization steps. Polymerization or particle growth increases the area of neutralized structures involving Al ions held together by double OH bridges and increases the ratio of structural OH to Al which increases the probability of sedimentation (Hem and Roberson, 1967).

The viscosity at 2 °C is twice the viscosity at 25 °C (Weast and Astle, 1982). This may also contribute to the significantly higher amount of high molecular weight species kept in solution at 2 °C compared with at 25 °C.

The Al colloids present in the solution (Al_g) were divided in two groups: Al_j (colloids *retained* by the Amberlite IR–120 cation exchange column) and Al_k (colloids *not retained* by the cation exchange column).

More Al_j was present in the solutions stored at 2 °C than in the solutions stored at 25 °C. However, the percentage contribution of Al_j and Al_k was not significantly changed by temperature. At 2 °C, 35 to 79% of Al_g was present as Al_j and 21 to 65% as Al_k. In the corresponding solutions kept at 25 °C, 43 to 68% was present as Al_j and 32 to 57% as Al_k.

At both 2 and 25 °C, Al_j represented 40 to 50% of the total amount of Al retained by the cation exchange column (Al_j+Al_i), even if pH was 0.7 to 0.8 units lower at 25 than at 2 °C.

In spite of the low pH values measured at 25 °C (pH: 4.83 to 5.07), significant amounts of colloids and particles were formed. Smith and Hem (1972) found that microcrystalline gibbsite was ultimately formed even if the molar ratio OH:Al was as low as 0.94 and pH was about 4. Therefore, *$Al(OH)_3(s)$ does not have to be formed before the polymerization starts.*

Molecular weight distribution of Al species

At 2 °C, molar ratio OH:Al of 1.9 to 2.1, between 53 and 63% of Al_{tot} (Al_a + Al_g + Al_h) was present as high molecular weight species (MW $>$ 10^4 Dalton, while in the solutions having a molar OH:Al ratio of 2.3 to 2.4, between 66 and 76% of Al_{tot} was present on high molecular weight forms. However, only 6 ± 1% of the high molecular weight species were removed from solution by sedimentation (Figure 3).

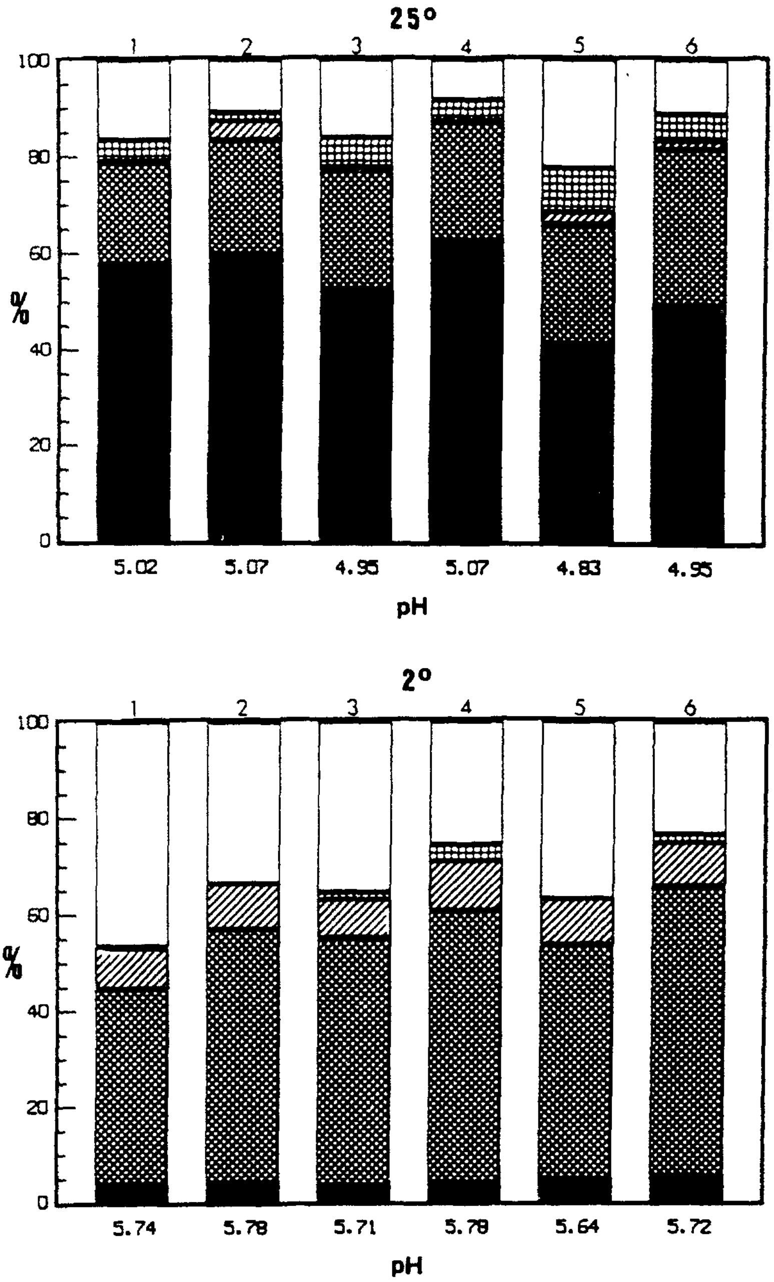

Fig. 3. pH and molecular weight disribution of different Al-fractions (%) present in corresponding solution stored for 1 mo at 2 and 25 °C, respectively. The initial OH:Al ratios are: (1) 1.9; (2) 2.4; (3) 2.1; (4) 2.4; (5) 2.0; (6) 2.3. (▭) Al_a (Mw < 10^4 Dalton) (▤) Al_g (Mw < 10^4 Dalton); (▨) Al_a (Mw > 10^4 Dalton) (▩) Al_g (Mw > 10^4 Dalton); (■) Al_h ($Al(OH)_3$ removed from solution due to sedimentation).

At 25 °C, molar ratio OH:Al of 1.9 to 2.1, 68 to 80% of Al_{tot} was present as high molecular weight species, while in the solutions where the molar OH:Al ratio was 2.3 to 2.4, 83 to 87% was present as high molecular weight species. In contrast to the solutions incubated at 2 °C, substantial amounts (60 to 70%) of high molecular weight species were removed from the solution due to sedimentation (Figure 3).

At 2 °C, never more then 5% of Al_g was present as low molecular weight species at 2 °C, while in the corresponding solutions kept at 25 °C, 7 to 27% of Al_g was low molecular weight species.

There is some literature suggesting that $Al(OH)_3(H_2O)_3$ (aq) may exist (May *et al.*, 1979). Based on this work, 0 to 10% of dissolved monomeric Al species (depending of pH) may be present as dissolved monomeric $Al(OH)_3(H_2O)_3$ (aq) at equilibrium with the solid phase, more at high temperature compared with low. If so, this specie may consequently be a contributor to the low molecular weight Al_g observed, assuming this specie to be non-HQ/MIBK-extractable.

According to the Barnes/Driscoll method, Al_a is defined as total monomeric Al. Al_a should therefore represent low molecular weight species only. However, between 15 and 29% of Al_a was present as high molecular weight species at 2 °C, while in general, less than 10% of Al_a was present as high molecular weight species at 25 °C.

4. Conclusions

Temperature affects the solubility, the hydrolysis and the molecular weight distributions of Al species as well as pH in the solutions. At 25 °C the degree of Al hydrolysis and the sedimentation of high molecular weight species are high compared to that observed at 2 °C and the $\log{}^*K_s$ of $Al(OH)_3(s)$ is significantly lower at 25 °C compared to that observed at 2 °C after 1 mo of storage.

Even though significant amounts of high molecular weight species also were formed at 2 °C, little sedimentation occurred even after 1 mo of storage, i.e. substantial amounts of high molecular weight inorganic Al species existed as colloids in the solution.

The polymerization processes seems more advanced at high temperatures (25 °C) than that observed at low temperature (2 °C), i.e. more of the combined deprotonation/condensation reactions are involved in the polymerization processes at 25 °C compared with at 2 °C. This may explain why pH in the solutions were significantly lower at 25 °C compared with at 2 °C.

In the solutions kept at 25 °C for 1 mo, $\log{}^*K_s$ was 9.0 which corresponds to a microcrystalline gibbsite, while at 2 °C $\log{}^*K_s$ was 10.3 (corrected to 25 °C) which reflects an amorphous $Al(OH)_3(s)$ structure. The solubility of an amorphous Al structure is very high compared to a microcrystalline gibbsite. In addition the majority of high molecular weight Al species existed as colloids in solution at 2 °C. The total surface of the al complexes on which water can react is therefore large, i.e. the dissolution conditions are very good. The dissolution condition of $Al(OH)_3(s)$

at low temperatures is essential for the interpretation of aqueous Al chemistry in natural fresh water systems in Scandinavia or in corresponding climatic regions of the world.

Obviously, not only the $Al(OH)_3(s)$ system is controlling the aqueous Al chemistry in natural water/soil systems. Other controlling mechanisms are also involved (Seip *et al.*, 1989). The presence of organic and inorganic ligands as humic substances, F^-, SiO_4^{-4}, and SO_4^{-2} may seriously change the solubility and distribution of Al-species. However, this work underline the importance of involving temperature in the Al chemistry when assessing the pathways of different Al species and their consequences to biota, as well as when Al species are to be identified.

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