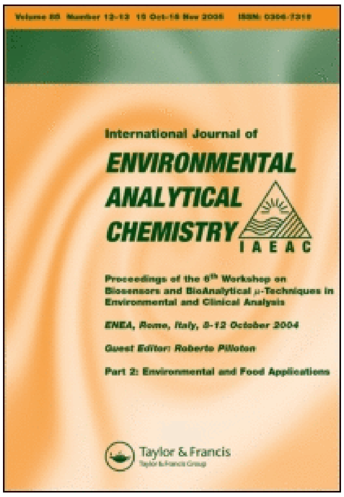

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A Comparison of Frequently Used Methods for the Determination of Aqueous Aluminum

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A Comparison of Frequently Used Methods for the Determination of Aqueous Aluminum

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In view of current international interest in the effects of acid deposition and consequent aluminum mobilization, a need has arisen to establish sound relationships between aluminum fractionation methodologies. We compare the results of two principal fractionation methods, the Barnes/Driscoll MIBK extraction method and the pyrocatechol violet method, for surface water samples from southern Norway. For samples analyzed immediately after collection with minimum pH and temperature changes, both methods are satisfactory, but the Barnes/Driscoll method was found to be more convenient for field analytical research. There are systematic differences, particularly for the organic monomeric aluminum fraction. Results for inorganic monomeric aluminum, which is most important biologically, are in very good agreement.

KEY WORDS: Aluminum transport, aluminium speciation, soil, surface waters, aluminum toxicity.

INTRODUCTION

Recent research in the northeastern U.S.,[1] southern Norway,[2,3] and Sweden[4] has established that increased mobilization and transport of aluminum from soils to surface waters is a major consequence of atmospheric deposition of mineral acids. The environmental consequences of increased concentrations of aqueous aluminum species include toxicity to fish and other aquatic organisms,[3,5,6] changes in surface water buffering systems,[7] alterations in the cycling of important nutrients,[8] and toxicity to terrestrial vegetation.[9] In view of the current international interest in the effects of acid deposition, it is critical to establish sound relationships between the various methodologies used for the fractionation and determination of aluminum species. Aluminum studies play a key role in several large national and international investigations of surface and soil water acidification currently in progress. The question of methodology is approached in different ways. For example, in the ALBIOS program (EPRI-sponsored Aluminum Bio-geochemistry Study), aluminum methods have been standardized for catchments in Norway, Sweden, West Germany, Canada, and throughout the U.S. This type of standardization is difficult to achieve, time-consuming and expensive. In contrast, the Surface Water Acidification Project (SWAP), a joint British–Scandinavian project[10], involves several research groups using different methods, though intercalibration is required. The two principal methods currently in use within SWAP and for aluminum speciation in general, are the Barnes/Driscoll extraction method[11,12] and the pyrocatechol violet method.[13,14]

The speciation of aqueous aluminum is controlled by environmental factors such as pH, temperature, and the concentration of aluminum-binding ligands (particularly organic matter and fluoride). Inorganic aluminum forms appear to be the primary toxic species.[6,15] The most toxic forms are apparently the simple hydroxides, $Al(OH)^{2+}$ and $Al(OH)_2^+$, while organically complexed and polymeric aluminum are much less toxic or essentially nontoxic. Therefore, any evaluation of the environmental impacts of aluminum must include speciation, rather than simply total aqueous concentration.

Seip *et al.*[14] compared Driscoll's earlier[16] aluminum fractionation and determination method (using ferron-orthophenanthroline) with the pyrocatechol violet method. Agreement between the two methods was reasonably good, but they found pyrocatechol violet to be superior, in general, due to its greater sensitivity and fewer interferences. In view of the rapid acceptance of Driscoll's latest[12] method, we found it appropriate to compare it with the frequently used pyrocatechol violet method (See e.g. Refs. 17–19).

MATERIALS AND METHODS

Water samples were collected in March and April, 1985, from 7 lakes, 2 rivers, and 6 streams (two of which were sampled twice) in the vicinity of Birkenes, Aust Agder County, southernmost Norway. Birkenes is located in the zone of maximum deposition of anthropogenic compounds in Norway, with an estimated annual input of 7 g $SO_4^{2-}\,m^{-2}\,yr^{-1}$.[20] Samples were transported immediately to a nearby mobile field laboratory and analyzed for pH, temperature, and conductivity, followed by fractionation and determination of aluminum by both the Barnes/Driscoll and pyrocatechol violet methods. Particular care was taken to minimize temperature changes prior to and during sample processing. Samples were later analyzed for total organic carbon (TOC) (analysis by the Norwegian Institute of Water Research using persulfate oxidation with an Astro Model 1850 Carbon Analyzer), major anions (by the Norwegian Institute of Air Research using a Dionex 10 ion chromatograph with Spectra Physics SP 4100 computing integrator), major cations (atomic absorption spectrophotometry), and total fluoride (Orion ion-selective electrode after complexation with TISAB buffer).[21] This enabled us to more fully describe the chemical composition of samples included in the comparison.

Both aluminum methods involve fractionation into labile (mainly inorganic) monomeric aluminum, non-labile (mainly organic) monomeric aluminum, and acid-soluble aluminum, as outlined by Driscoll.[16] Successive analyses are performed for total monomeric aluminum (Al_a) on a fresh, untreated water sample, for non-labile monomeric aluminum (Al_o) after passing an aliquot of the sample through a pH-adjusted acidic cation exchange resin (Amberlite IR-120), and for total acid-reactive aluminum (Al_r) after acidifying an aliquot of the sample to $pH = 1$. Labile monomeric aluminum (Al_i) is computed as the difference between Al_a and Al_o determinations.

Acid-soluble aluminum is computed as the difference between Al_r and Al_a, and includes aluminum forms which require acid digestion before analysis (polymeric, colloidal, highly stable organic and hydroxyorganic complexes).[15]

In the Barnes/Driscoll method, aluminum is complexed with 8-hydroxyquinoline, pH is adjusted to 8.3 to minimize interferences, and the aluminum hydroxyquinolate complex is then extracted into methyl isobutyl ketone (MIBK) prior to analysis by atomic absorption spectrophotometry[11] or spectrophotometry at 395 nm.[22–24] Iron may be present in sufficient quantities to interfere with the photometric determination of aluminum hydroxyquinolate in some surface waters (Schofield, personal communication), and occasionally in poorly drained soil soultions.[23,25] Absorbance measurement at 600 nm is therefore used to correct for iron interference. In addition to iron, numerous other inorganic ions form complexes with 8-hydroxyquinoline that absorb at 395 nm.[22] However, this method is not sensitive to interference at the levels of inorganic ions generally found in natural freshwaters.[23,25] In order to verify this lack of interference in samples from the Birkenes area, we selected 21 extracts from surface water samples collected in October and November, 1984, for ICP determination (inductively coupled argon plasma). Measured aliquots of MIBK extracts were evaporated to dryness under nitrogen, resuspended in dilute acid, and analyzed on a Jarrel–Ash model 975 Plasma Atomcomp ICP. Despite the potential analytical errors associated with changing solvents, there is good agreement between these two independent methods ($y = 1.02x + 2.25$, $R^2 = 0.98$, $n = 21$) (Figure 1).

In the pyrocatechol violet method, aluminum and pyrocatechol violet (3,3,'-trihydroxyfuchsone-2″-sulfonic acid) form a complex with an absorption maximum at 581 nm. Absorbance increases with pH to about pH = 6, and samples are therefore buffered at pH = 6.1 with hexamethylene tetramine during analysis. The color of PCV-Al complex develops slowly, but Seip *et al.*[14] recommended a four-minute interval before recording absorbance. $NH_2OH \cdot HCl$ and orthophenanthroline are added to reduce and complex iron, eliminating the need for absorbance correction. For the determination of acid-reactive aluminum (Al_r) in this comparison, samples were acidified to pH = 1 for one hour, followed by addition of the reducing reagents, PCV, and buffer. Absorbance was measured after 40 minutes.

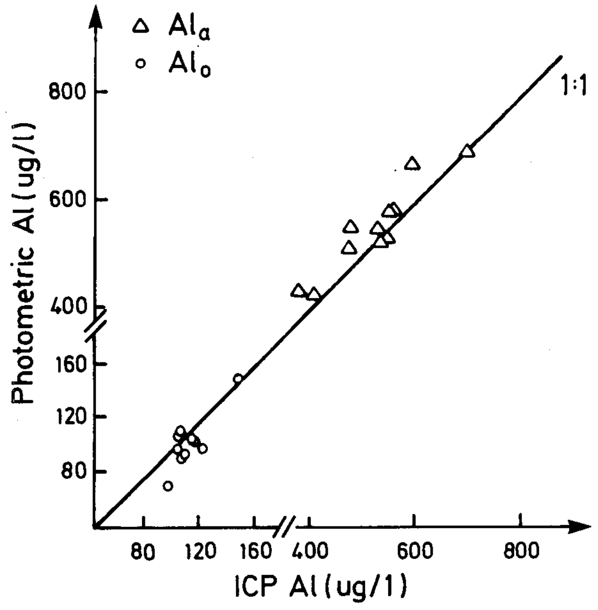

FIGURE 1 Measured concentrations of aluminum fractions using photometric versus ICP analysis of ketone extracts obtained in the Barnes/Driscoll method for 21 sample fractions collected at Birkenes in the autumn, 1984.

Aluminum speciation was calculated using a computer program MINEQL[26] for all samples included in the methods comparison by assuming equilibrium of dissolved species. Thermodynamic equilibrium constants were corrected for temperature. The thermodynamic data were as recommended by Nordstrom *et al.*,[27] giving the following $\log K$ values (at 4°C):

$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$	-5.65
$Al^{3+} + 2H_2O = Al(OH)_2{}^+ + 2H^+$	-11.35
$Al^{3+} + 3H_2O = Al(OH)_3{}^0 + 3H^+$	-18.59
$Al^{3+} + F^- = AlF^{2+}$	6.92

$Al^{3+} + 2F^- = AlF_2{}^+$	12.75
$Al^{3+} + SO_4^{2-} = AlSO_4{}^+$	3.20

RESULTS AND DISCUSSION

Results of all chemical analyses for the 17 samples included in the methods comparison are listed in Table I. The water chemistry was quite variable, with pH ranging from 4.0 to 6.3 and total acid reactive aluminum from 101 to 957 $\mu g\,l^{-1}$. In comparing the Barnes/Driscoll and PCV methods, we obtained very consistent results for all fractions (Figure 2). The PCV method yielded higher estimates of total monomeric (Al_a) and non-labile monomeric (Al_o) aluminum, while total acid-reactive (Al_r) estimates were slightly lower than for the Barnes/Driscoll method. The two methods gave nearly identical results for labile monomeric aluminum (Al_i). The following empirical relationships were obtained:

$$Al_{a(Extr)} = 0.96\,AL_{a(PCV)} - 27.32, \quad n = 17, \quad R^2 = 0.99$$

$$Al_{o(Extr)} = 0.93\,AL_{o(PCV)} - 23.98, \quad n = 17, \quad R^2 = 0.89$$

$$Al_{i(Extr)} = 0.94\,Al_{i(PCV)} + 3.33, \quad n = 17, \quad R^2 = 0.99$$

$$Al_{r(Extr)} = 1.02\,Al_{r(PCV)} + 32.38, \quad n = 17, \quad R^2 = 1.00$$

where Extr refers to Barnes/Driscoll extraction. The greatest variation was found between analyses of organic monomeric aluminum. The close agreement between methods for analysis of inorganic monomeric aluminum (Al_i) is particularly important, as this fraction is considered to include the toxic species.[15] The higher estimate of the PCV method relative to the Barnes/Driscoll method for Al_o is probably due to a higher affinity on the part of pyrocatechol violet as compared with 8-hydroxyquinoline for certain alumino-organic compounds. This results in the inclusion of these compounds in the monomeric category for PCV, but not Barnes/Driscoll determinations.

When separated into lake samples versus stream and river samples, a

TABLE I

Measured water chemistry data for samples used in the comparison of the Barnes/Driscoll and pyrocatechol violet methods.

Sample site	pH	TOC ($mg\,l^{-1}$)	Conductivity ($\mu S\,cm^{-1}$)	$\mu g\,l^{-1}$							$\mu eq\,l^{-1}$						
				F	Al_i[a]	Al_o[a]	Al_r[a]	Al^{3+}	AlF^{2+}	$AlF_2{}^+$	Ca^{2+}	Mg^{2+}	K^+	Na^+	$NO_3{}^-$	Cl^-	$SO_4{}^{2-}$
Valtjern	5.9	3.6	60	78	25	22	101	0	8	14	150	74	23	178	34	175	132
Hauglivatnet	5.4	3.8	60	173	149	65	331	7	71	64	134	75	14	148	31	170	162
Øygardtjern	5.4	3.0	63	83	65	34	166	4	33	25	130	81	30	173	43	183	155
Bersevatn	6.3	2.7	72	121	44	43	180	0	10	24	198	88	33	203	64	195	158
Sagetjern	4.7	5.5	57	60	205	86	396	106	74	4	69	46	13	120	27	128	131
Høgkleinvatn	4.4	6.3	64	50	207	81	394	126	63	3	34	38	6	116	27	116	122
Spjøtevatn	4.5	6.9	59	80	220	90	422	103	95	8	49	35	8	111	21	118	125
Tovdal River	4.9	2.6	33	69	195	40	322	87	81	6	42	24	4	63	14	68	85
Kiløyna River	5.9	1.8	71	90	96	38	238	5	41	28	154	91	26	200	61	199	175
BIE 01 (low flow)	4.9	3.1	52	141	428	96	673	192	170	13	69	41	7	123	21	122	152
BIE 01 (high flow)	4.4	4.3	55	92	443	128	748	276	120	4	45	37	8	131	23	85	175
BIE 03	4.5	3.9	52	102	627	137	957	416	136	0	40	31	4	139	10	91	185
BIE 04	5.0	3.2	49	131	298	87	515	102	145	18	67	39	5	124	17	121	147
BIE 05 (27/3)	4.9	2.7	55	135	506	77	719	261	170	10	76	44	10	124	36	124	154
BIE 05 (29/3)	4.9	2.6	55	134	482	92	719	242	168	10	75	43	11	123	46	121	162
BIE 10	5.3	2.4	47	110	394	79	617	157	133	10	83	41	12	116	21	115	147
BIE 11	6.0	1.9	84	75	83	59	268	4	30	22	221	95	29	223	84	243	183

[a] Reported aluminum values from Barnes/Driscoll method.

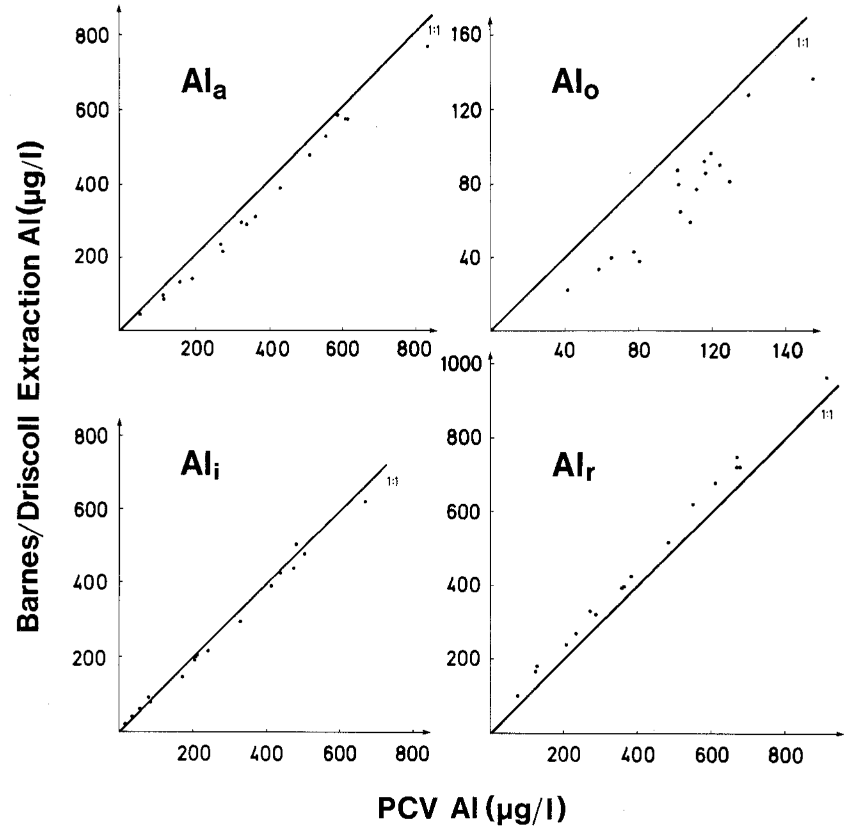

FIGURE 2 Measured concentrations of aluminum fractions by the Barnes/Driscoll extraction method versus the pyrocatechol violet method for A, total monomeric aluminum (Al_a); B, organic monomeric aluminum (Al_o); C, inorganic monomeric aluminum (Al_i); and D, total acid-reactive aluminum (Al_r).

positive correlation is observed between Al_0 and total organic carbon (TOC) (Figure 3) for both stationary and flowing waters. Flowing waters exhibited a higher Al_0 content for a given TOC level than did stationary waters. A strong correlation between Al_0 and TOC has been reported elsewhere.[15,28]

The predominant forms of monomeric aluminum determined in this study were alumino-fluoride complexes, AlF^{2+} and $AlF_2{}^+$ (together: 35%), organo-aluminum complexes (28%), and aqueous Al^{3+}

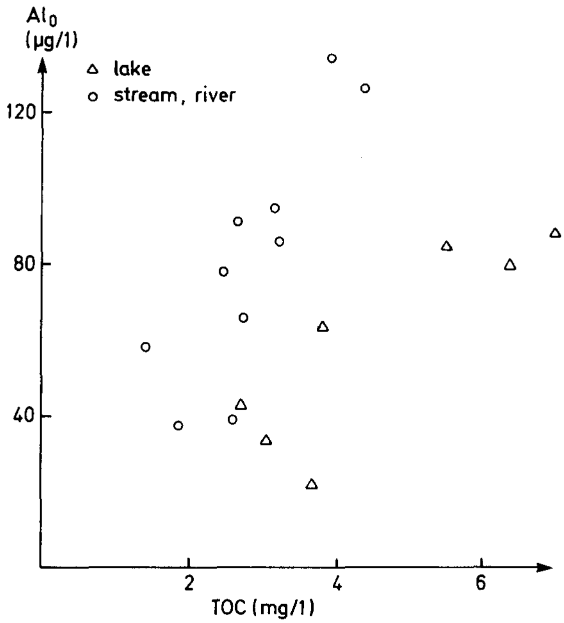

FIGURE 3 Organic monomeric aluminum (Al_0) in relation to total organic carbon (TOC) of water samples from lakes, rivers, and streams of southern Norway. Al_0 was determined using the Barnes/Driscoll method.

(27%) (Table I). The percentages are average values for all samples. Aluminum hydroxy and sulfate complexes were of lesser importance. Dominance of the inorganic monomeric fraction by fluoride-complexed and free aluminum is typical of very low pH surface waters,[28] as are found throughout much of southernmost Norway. High proportions of organo-aluminum have also been reported for acidic surface waters of upper New York State and New Hampshire[16,29] and southern Norway.[14]

Some form of the mineral gibbsite, $Al(OH)_3$, is often assumed to control the equilibrium concentration of Al^{3+} in freshwaters.[16,30] Under the assumption of gibbsite equilibrium, the relationship between pAl^{3+} and pH is linear with a slope equal to 3, which was found to be the case at Falls Brook in the Hubbard Brook Experimental Forest, New Hampshire.[30] In this study, we also found a roughly linear relationship ($R^2=0.80$) between pAl^{3+} and pH, but the slope was equal to 1.52 (±0.34, 95% C.I.) (Figure 4), significantly different from that required for gibbsite equilibrium. Hooper and Shoemaker[31] obtained similar results from 484 streamwater samples collected from Experimental Watershed 3, also at Hubbard Brook. They calculated a slope of the best-fit line equal to 1.3 (±0.04, 95% C.I.), also significantly different from 3. If aqueous Al^{3+} in surface waters of the Birkenes area is in equilibrium with an aluminum-containing mineral, it is apprently not gibbsite.

In order to assess the reproducibility of both analytical methods, we collected triplicate samples consecutively for each of the methods. Each of the three replicates was analyzed four times for total

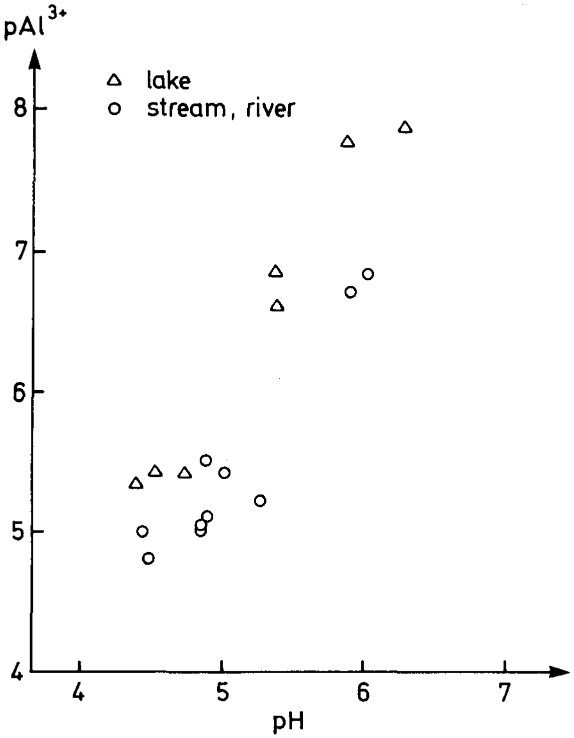

FIGURE 4 Relationship between pAl^{3+} and pH for water samples from lakes, rivers, and streams in southern Norway.

monomeric aluminum, yielding 12 analyses for each method, including both sampling and analytical errors. The sample analyzed in this way with the Barnes/Driscoll method yielded a mean and standard deviation of 544 and $6.4\,\mu g\,l^{-1}$ respectively, as compared with 615 and $6.5\,\mu g\,l^{-1}$ for a different sample analyzed with the PCV method. In both cases this 3×4 analysis resulted in a standard deviation of approximately 1% of the mean.

Both methods are sensitive to iron interference, which is corrected photometrically in the Barnes/Driscoll method, and by iron complexation in the PCV method. This interference was satisfactorily corrected by both methods in standards containing equivalent amounts of Al and Fe (Table II).

Aluminum fraction analytical data may not accurately reflect the actual aluminum concentrations in the monomeric form at the time of sampling unless the analyses are performed immediately after collection.[11,12] Sample pH and/or temperature may change during storage, leading to supersaturation and subsequent percipitation or shifts in speciation. Storage may also result in alterations from monomeric to polymeric forms.[11] To examine storage effects, we performed replicate analyses on samples that were collected from the Birkenes area in the fall of 1984 and spring of 1985 and from the Flekkefjord area, also in southernmost Norway, in the fall of 1984. Samples were stored at approximately 5°C in the dark. The data

TABLE II

Measurements of aluminum in standards containing equivalent concentrations of Al and Fe (as $FeSO_4 \cdot 7H_2O$) for the Barnes/Driscoll and pyrocatechol violet methods.

Al, Fe Standard concentration (μg/l)	Measured Al concentration (μg/l) after Fe-correction[a]	
	Barnes/Driscoll	PCV
40	35	40
100	100	108
200	199	201
400	401	388
600	597	580

[a] Fe-corrections were made photometrically in the Barnes/Driscoll method, and by sample reduction followed by o-phenanthroline complexation in the PCV method.

TABLE III

Changes during storage in measured concentrations of total monomeric (Al_a) and organic monomeric (Al_o) aluminum.[a]

Sample number	Location	Season	Al fraction	Initial conc. (μg/l)	Storage time (days)	Δ conc. (μg/l)
1	Birkenes	fall	Al_a	781	4	−29
2	Birkenes	fall	Al_a	638	4	−44
3	Birkenes	spring	Al_a	590	4	0
4	Birkenes	spring	Al_a	544	8	+9
5	Birkenes	spring	Al_a	657	8	−6
6	Flekkefjord	fall	Al_a	62	6	0
				62	35	0
7	Flekkefjord	fall	Al_a	264	1	−5
				264	35	+2
8	Flekkefjord	fall	Al_a	247	6	+17
				247	35	+22
9	Flekkefjord	fall	Al_a	73	1	+2
10	Flekkefjord	fall	Al_o	59	13	−9
11	Flekkefjord	fall	Al_o	91	14	+6
				91	21	+1
12	Flekkefjord	fall	Al_o	13	13	+20
13	Flekkefjord	fall	Al_o	34	13	+23
				34	21	+10

[a] Samples were analysed using the Barnes/Driscoll method after storage at approximately 5°C.

indicate changes in concentration which in some cases were considerably in excess of the reported 1% standard deviation for replicate analyses (Table III). Both spatial and temporal variations in storage effects were observed. We conclude that in some cases storage will lead to considerable errors in concentration estimation, while not in other cases. We suspect that TOC is important in this regard, with higher TOC samples having greater shifts from monomeric to polymeric forms with storage. We therefore recommend immediate sample processing unless storage has been demonstrated to be inconsequential for the samples in question.

CONCLUSION

The Barnes/Driscoll and pyrocatechol violet methods are both satisfactory for aluminum speciation. As to be expected, there are some systematic differences, particularly for the organic monomeric aluminum fraction. Results for inorganic monomeric aluminum, which is most important biologically, are in very good agreement. Immediate fractionation is easily done in the field with the Barnes/Driscoll method. MIBK extracts may be stored for several weeks if kept cool, in the dark, and if evaporation is minimized.[11] It is therefore possible to ion exchange and extract samples immediately after collection and later analyze MIBK extracts for aluminum in the laboratory. The PCV method, however, requires photometry on site if storage problems are to be completely eliminated. The PCV method is more tedious because it requires exact timing of the four minute interval between reagent addition and the recording of sample absorbance. Although this problem can be overcome with an automated system, such as flow injection analysis, this type of system is not easily transported to the field. For these reasons we have found the Barnes/Driscoll method to be more convenient for field analytical research. We emphasize that the demonstrated agreement between these two methods is likely dependent on the extreme caution taken to minimize changes in aluminum speciation in samples prior to and during processing (immediate analysis at field temperatures, and minimum pH change during column chromatography).

Additional aluminum fractionation methods are presently being developed. For example, LaZerte[32] has employed a slightly modified version of the Barnes[11] extraction technique coupled with equilibrium dialysis to discriminate between organic and inorganic monomers. A continued process of method development and intercomparison is needed to more accurately characterize the fractions of monomeric aluminum determined with these methods, and to assess the toxicity of the various aluminum ion species.

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