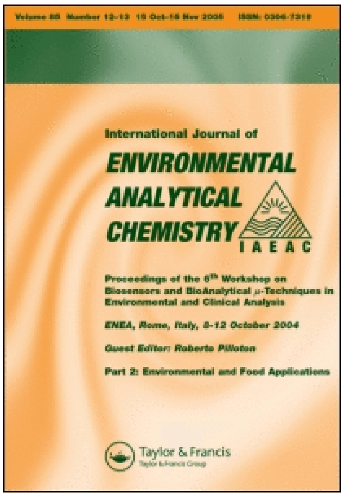

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Aluminium fractionation using cation exchange: comparison of results obtained after fractionation in the field and in the laboratory

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Aluminium fractionation using cation exchange: comparison of results obtained after fractionation in the field and in the laboratory

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Dissolved aluminium was fractionated in the field and the laboratory using a cation-exchange method. Although absolute differences between results obtained from field and laboratory fractionations were generally small, relative differences, expressed as the ratio between labile aluminium determined after laboratory fractionation (Al_{ll}) and that obtained after field fractionation (Al_{lf}) could be large. The differences found were not statistically significant, although this may simply reflect the spread in the results. Al_{ll}/Al_{lf} had no apparent relationship with the temperature difference between the field and the lab. Although some significant correlations were found between Al_{ll}/Al_{lf} and H^+, no significant correlations were found with the equivalent relative difference in $\{H^+\}$ between the lab and the field; nor was any significant correlation found with dissolved organic carbon.

Keywords: Aluminium; Fractionation; Cation exchange; Natural waters

1. Introduction

It is well known that certain fractions of dissolved aluminium (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and Al in other labile complexes) are toxic to many life forms, such as fish [1–3], some amphibians [4], some aquatic invertebrates [5, 6], and many plants [7–12]. It is important, therefore, to be able to estimate the concentrations of these fractions, and many methods have been developed for this purpose [13–19]. By far the most commonly used are cation-exchange methods based on the Driscoll [13] fractionation. In these, the labile fraction, assumed to represent the most toxic aluminium species, is found as the difference between total aluminium and the fraction of aluminium (non-labile aluminium) that passes through a cation-exchange column.

On-site measurements in the field will clearly produce more ecologically relevant data than measurements in the laboratory after transport and storage [20]. However, for practical reasons, most measurements are made in the laboratory, where some methods are used routinely within monitoring programmes. Thus, it is important that results

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obtained in the lab should as far as possible reflect the real situation in the field. It remains unclear to what extent this is the case. Preventing modification of sample composition during transportation and storage may be difficult [16, 21–23], especially if the sample is not at equilibrium to start with [19]. Factors such as changes in temperature [24–27], carbon dioxide degassing or microbial action with a resultant change in pH [28], and changes in organic matter could affect the speciation of aluminium.

Although aluminium fractionation using cation exchange has been carried out in the field [20], the results of field fractionation with this method have not to our knowledge been compared directly with the results of laboratory fractionation using the same method. The objective of this article was to compare results from aluminium fractionation carried out in the field and in the laboratory, using a cation-exchange method that is routinely used within the Norwegian Monitoring Programme for Forest Damage.

2. Experimental

Samples were taken from sites in southern Norway (table 1) mainly representing surface waters with pH ranging from weakly acid to weakly alkaline (table 2). Sampling of soil waters was attempted but proved problematic, as samples for field analysis needed to be fresh, and it was difficult to obtain sufficient soil water for analysis in the very short time period available. As a result, only a few soil water samples were obtained. Sampling was carried out at all times of the year when this was practical. During the winter, snow and ice cover generally prevented sampling, while the streams often dried up in the summer. Thus, most samples were taken in autumn and spring.

Al fractionation was carried out according to Method E of Wickstrøm *et al.* [29], which is the standard method used in the Norwegian Monitoring Programme for Forest Damage. In this method, the fractionation principle is cation exchange, following Driscoll [13]. Wickstrøm *et al.* [29] compared the measured labile aluminium fraction with that estimated using the program ALCHEMI [30], assuming that the labile aluminium fraction included hydroxide, fluoride, sulphate and silicate complexes, but not organic complexes. Good agreement was found ($r^2 = 0.99$). Wickstrøm *et al.* [29] also observed that some relatively labile organic complexes (e.g. with tartrate) might be

Table 1. Site data.

Site	Municipality	Latitude	Longitude	Water type	No. of samples
Årungen	Ås	59°41′	10°45′	Lake	12
Åsmosan	Ås	59°40′	10°47′	Mire	7
Nordskogen	Ås	59°40′	10°45′	Stream	19
Bjørnebekk	Ås	59°39′	10°49′	Stream	16
Askerødtjernet	Hobøl	59°32′	10°53′	Lake	4
	Hobøl	59°33′	10°53′	Stream	8
	Hobøl	59°32′	10°54′	Mineral soil water	3
	Birkenes	58°23′	08°15′	Stream	5
	Birkenes	58°23′	08°15′	Groundwater (peat)	1
	Birkenes	58°23′	08°15′	Mineral soil water	2

Table 2. Means (*M*), standard deviations (SD) and relative standard deviations (RSD, %) of total Al (Al_t), labile Al fractionated in the field (Al_{lf}) and the lab (Al_{ll}), $\{H^+\}$ determined in the field (H_f^+) and the lab (H_l^+), and DOC.[a]

			H_f^+			H_l^+			H_l^+/H_f^+	Al_t			Al_{lf}			Al_{ll}			Al_{ll}/Al_{lf}	DOC		
Site	Water type	*N*	*M*	SD	RSD	*M*	SD	RSD	(%)	*M*	SD	RSD	*M*	SD	RSD	*M*	SD	RSD	(%)	*M*	SD	RSD
Årungen	Lake	12	0.03	0.04	115	0.04	0.07	166	124	0.10	0.11	104	0.05	0.05	99	0.05	0.04	87	89	9.6	2.3	23
Åsmosan	Bog	7	1.0	1.2	119	0.36	0.26	72	36	0.19	0.13	66	0.06	0.04	63	0.08	0.05	58	125	18.7	5.6	30
Birkenes	SW	2	9.6	0.31	3.3	21	0.10	0.5	215	0.63	0.01	0.9	0.47	0.00	0.5	0.48	0.01	1.3	102	6.2	0.3	4.9
Birkenes	Stream	5	4.7	1.3	27	5.7	2.0	34	121	0.37	0.07	20	0.22	0.04	20	0.24	0.06	27	107	6.4	1.2	19
Bjørnebekk	Stream	16	18	10	58	19	8.5	45	106	0.88	0.20	22	0.38	0.11	30	0.42	0.11	27	111	25.2	4.8	19
Hobøl	Lake	4	5.9	7.5	127	4.6	5.1	112	78	0.33	0.02	5.5	0.11	0.03	30	0.09	0.06	65	86	10.5	0.6	5.8
Hobøl	SW	3	67	6.1	9.0	82	8.0	10	122	1.05	0.08	7.8	0.40	0.08	20	0.35	0.02	4.6	88	42.2	3.2	7.5
Hobøl	Stream	8	21	16	76	24	6.2	25	116	0.48	0.16	34	0.31	0.12	39	0.32	0.11	36	102	8.5	4.9	57
Nordskogen	Stream	19	0.60	0.61	101	0.49	0.28	56	82	0.32	0.15	47	0.08	0.09	105	0.11	0.10	92	141	13.6	3.9	29

[a] SW: soil water. Aluminium and DOC are in $mg\,L^{-1}$, H^+ in $\mu mol\,L^{-1}$.

included in the labile fraction: however, these are likely to be easily biodegradable and may not be very important in the field. We therefore assume here that the labile fraction includes the main inorganic aluminium species and excludes the organic species.

Water samples were taken from soil, lakes, streams, and a bog. Samples from lakes, streams, and the bog were obtained manually. The collection bottle used, intensively cleaned in the laboratory, was flushed three times using target sample water before starting sample collection. Soil water samples were obtained using suction lysimeters (Prenart Equipment Aps, Denmark or 655X1-B1M3, Soil Moisture Corp., Santa Barbara, CA). These lysimeters had been installed previously and could be assumed to be in equilibrium with soil water. As soon as the water samples were taken, fractionation was conducted as rapidly as possible in the field so that results should truly reflect the field situation. The sample was first filtered using a 0.45 µm membrane filter (Millipore Corporation, Bedford, MA), which is the filter pore size conventionally used to separate dissolved from particulate components. It was then divided into three sub-samples, for field fractionation, laboratory fractionation, and determination of total aluminium. Next, the pH (giving the hydrogen ion activity in the field, H_f^+) was determined in the sub-sample for field fractionation using a portable pH meter (PHM202). The effect of filtration on the sample was assumed to be slight [16], so that the pH determined after filtration was believed to reflect the true pH in the field. Simultaneously, the cation-exchange cartridge (Bond Elut Jr. SCX, Varian) was flushed using deionized water from a burette for 5 min through a fine tube with a length of 77 cm and 0.5 mm inner diameter. The flow rate passing through the cartridge was maintained at 3 mL min^{-1} for 10 min using a pump (Prenart Equipment Aps, Denmark) with the pressure maintained at around 400–600 mbar. After 5 min, the remainder of the water was discarded, and some of the sample was used to rinse the burette at least three times. The burette was then filled with filtered water from the sub-sample, which was passed through the tube for 1 min so that the tube system could be washed thoroughly. Subsequently, the fractionated water sample was collected for 10 min with the same flow rate and pressure as previously. After 10 min, fractionation was stopped using the tap on the burette. The fractionated sample was then stored in a clean polyethylene bottle until analysis. Polyethylene is a suitable material for water storage [31]. The second sub-sample, stored in a glass bottle with no air left in the bottle in order to minimize changes in the partial pressure of CO_2, was fractionated in the laboratory in the same way as in the field. Glass, although more easily broken than polyethylene, is more resistant to loss of carbon dioxide through container walls [32] and was used for sample storage where carbon dioxide loss could have affected the results obtained. The third sub-sample, also stored in a glass bottle in the same way, was used for determination of the total Al concentration. After transport to the lab, which took approximately 1 h for samples from Ås municipality, 2 h for samples from Hobøl municipality, and 5 h for samples from Birkenes municipality, the first and third sub-samples were stored immediately in a dark room at 4°C until analysis, while the second sub-sample was taken to the lab for fractionation when it reached room temperature, normally after about 4 h. The fractionation procedure was the same as in the field, and the pH was also determined, giving the hydrogen ion activity in the lab (H_l^+). Aluminium in the fractionated and total samples was analysed using ICP-AES. The total Al concentration (Al_t) and the non-labile Al concentration were determined from these samples, and the labile Al concentration (Al_{lf} for field-fractionated samples and Al_{ll} for lab-fractionated samples) was determined as the difference.

Bottles used for sub-samples for determination of total Al were completely filled with sample solution to make the bottle mouth air-tight in order to minimize loss of CO_2 to the atmosphere. A drop of concentrated HCl was added to these samples before storage, to minimize loss of Al to the container walls.

DOC was determined after oxidation using a Pt catalyst at 680°C in samples that had been filtered through a 0.45 μm membrane filter according to Ogner *et al.* [33] and stored in intensively cleaned bottles. All results were above the detection limit of $0.4\,\mathrm{mg\,L^{-1}}$.

In order to determine whether the field data and lab data were significantly different, Student's *t*-test was employed. Correlation analysis was used to test the significance of correlations of Al_{ll}/Al_{lf} with Al_t, DOC, H_l^+, H_f^+, and H_l^+/H_f^+. Statistical treatment was carried out using the Statistica software (StatSoft, Tulsa, OK).

3. Results and discussion

The means of labile Al fractionated in the field (Al_{lf}) and lab (Al_{ll}) differed only slightly (table 2). Mean values for $\{H^+\}$ determined in the field (H_f^+) and the lab (H_l^+) differed most in the Åsmosan, Birkenes soil water, and Hobøl soil water samples. However, even though the absolute differences between the values were often small, relative differences between field and laboratory values, expressed as Al_{ll}/Al_{lf} and H_l^+/H_f^+, could be large (table 2).

3.1 *Comparison of individual samples*

As the mean values do not fully capture the rather large variation, comparisons for individual samples are presented in figure 1. There was a general tendency for Al_{ll} to be higher than Al_{lf} (figure 1a) and for H_l^+ to be larger than H_f^+ (figure 1b). Linear regressions of Al_{ll} against Al_{lf} and H_l^+ against H_f^+ gave the following equations:

$$Al_{ll} = 1.02 \cdot Al_{lf} + 0.009\ (\mathrm{mg\,L^{-1}},\ r^2 = 0.96)$$

$$H_l^+ = 1.03 \cdot H_f^+ + 1.05\ (\mu\mathrm{M},\ r^2 = 0.85).$$

Despite the general tendency mentioned in the previous paragraph, there were no significant differences between field and laboratory results for labile aluminium or hydrogen at the level of $p < 0.05$ for any site, although the difference for hydrogen in soil water samples from Hobøl was nearly significant at $p = 0.06$ (table 3). Although this could be taken as indicating that results obtained in the laboratory reflect the field values adequately, it is more likely to be due to the variation in the results shown in figure 1. A larger-scale study would be necessary in order to draw firmer conclusions.

3.2 *Correlation of Al_{ll}/Al_{lf} with H^+ and DOC*

There were very few significant correlations of Al_{ll}/Al_{lf} with other variables (table 4), and several of those that were significant were for Hobøl lake and soil water samples,

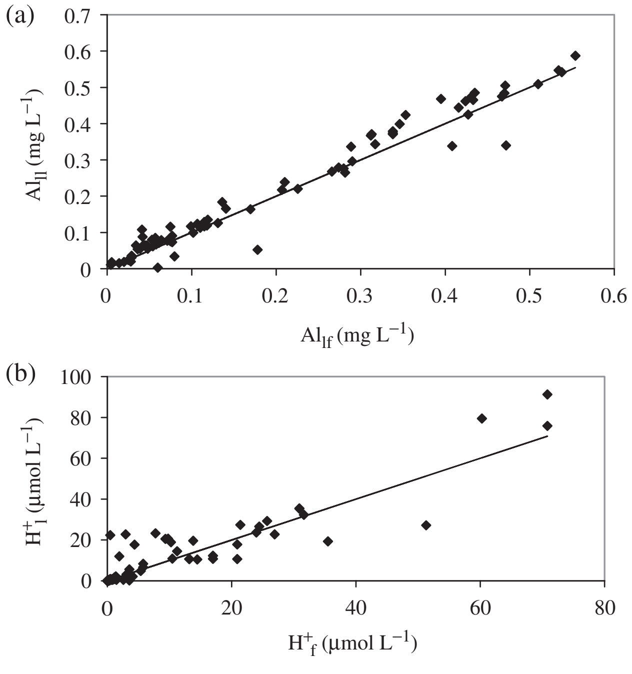

Figure 1. Comparison of individual values for (a) Al_{ll} and Al_{lf} and (b) H^+_l and H^+_f. Lines = 1 : 1.

Table 3. *p*-values obtained using two-tailed *t*-tests for the differences between Al_{lf} and Al_{ll} and between H^+_f and H^+_l.

Site	Water type	Al_{lf} and Al_{ll}	H^+_f and H^+_l
Årungen	Lake	0.96	0.76
Åsmosan	Bog	0.72	0.25
Nordskogen	Stream	0.65	0.37
Bjørnebekk	Stream	0.28	0.67
Hobøl	Stream	0.93	0.48
Hobøl	Lake	0.76	0.38
Hobøl	Soil	0.44	0.06
Birkenes	Stream	0.45	0.18
All sites		0.82	0.65

Table 4. Correlation coefficients (*r*) for the correlation of Al_{ll}/Al_{lf} with Al_t, DOC, H^+_l, H^+_f, and H^+_l/H^+_f.

	Årungen	Åsmosan	Nordskogen	Bjørnebekk	Hobøl lake	Hobøl stream	Hobøl soil water	Birkenes stream
Al_t	−0.26	−0.35	−0.40	−0.54	−0.90	0.20	**−1.00**	0.69
DOC	−0.05	−0.30	−0.30	−0.61	−0.69	0.66	0.09	−0.50
H^+_f	−0.13	−0.31	−0.16	−0.42	**−0.98**	0.21	0.68	0.51
H^+_l	−0.03	−0.23	**0.63**	−0.66	**−1.00**	**0.75**	0.90	0.06
H^+_l/H^+_f	0.18	0.06	0.35	0.16	0.43	−0.11	0.18	−0.34

[a] Significance ($p < 0.05$) is shown in bold.

which were very few in number. The majority of the significant correlations were with H_l^+ (Hobøl lake and stream, and Nordskogen stream). This could indicate that the pH sometimes had an effect on the fractionation obtained. There was no significant correlation with H_l^+/H_f^+. Neither was there any significant correlation with DOC. Although this could be taken as indicating that any changes in Al_l between the field and the laboratory were not due to the organic matter present, this is not certain, as changes in the composition of the organic matter could affect the speciation of aluminium regardless of the DOC concentration.

The variation found in the correlations of Al_{ll}/Al_{lf} with H^+ and DOC might reflect site-specific differences. The effect of factors such as the solid and quaternary geology, local land use, or differences in input of acidic precipitation (greater at Birkenes than at Ås or Hobøl) might make a general relationship between H^+, DOC, and Al fractions difficult to obtain.

3.3 *Effect of temperature*

In Norway, the temperature difference between the field and the laboratory varies greatly with the season. The lowest ambient winter temperature recorded in the field during sampling and fractionation was −0.2°C, while the highest summer temperature recorded was 20.2°C. The normal laboratory temperature under which fractionation was performed was 20–25°C. Equilibria between the various aluminium species are sensitive to temperature [24–27]. For example, modelling work has shown that the species distribution present in solution at around 0°C can be very different from that present at 25°C [26, 27]. Bi *et al.* [27] found that concentrations of the complexes $AlOH^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$ increased with temperature, while those of Al^{3+} and Al's fluoride, sulphate, and organic complexes decreased. In addition, when the temperature changes from 2°C to a stable 25°C, the sedimentation of Al complexes from solution could increase from 6–8% to 40–60% [25]. Dissolved organic matter, which can form complexes with aluminium and significantly influence the pH value by releasing acidity to water, is also sensitive to changes in temperature. It has been reported that a 3°C increase in water temperature resulted in a 20% reduction of particulate organic matter standing stock due to enhanced mineralization [34]. There could thus be changes in the aluminium species in solution as a result of changes in temperature. However, plotting the ratios Al_{ll}/Al_{lf} or H_l^+/H_f^+ against the temperature difference between the laboratory and the field showed no obvious general relationship (figure 2). For most samples, the temperature differences between field and laboratory did not appear to affect the fractionation of aluminium appreciably, although it is of course possible that the species distribution within the fractions could have changed.

3.4 *Effect of storage*

Although the effect of short-term storage (1–5 h) during transport to the lab and temperature equilibration there was included in our study, we did not study the effects of long-term sample storage, which may have an effect on measured concentrations of aluminium fractions. For example, Berdén *et al.* [35] found a reduction in concentrations of quickly reacting aluminium (Al_{qr}) with storage time. This reduction was greatest in the first few hours. A sample with a high DOC concentration

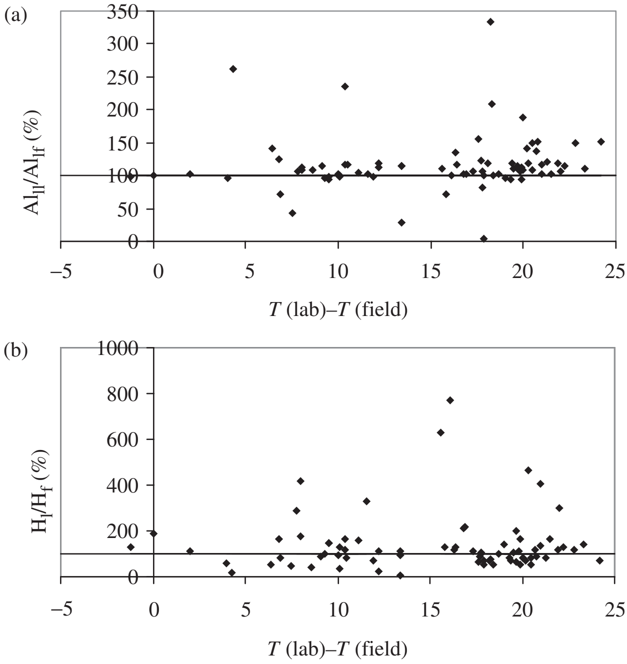

Figure 2. Dependence of the ratios (a) Al_{ll}/Al_{lf} and (b) H_l^+/H_f^+ on the temperature (°C) difference between laboratory and field.

(33.9 mg L^{-1}) and low Al_{qr} concentration (0.15 mg L^{-1}) was more sensitive to storage than one with a low DOC concentration (9.3 mg L^{-1}) and high Al_{qr} concentration (0.9 mg L^{-1}). Wickstrøm *et al.* [29] observed a reduction in the mean aluminium concentrations in all samples and fractions after storage for up to 30 days; however, these were not significant.

4. Conclusions

The absolute differences between results obtained from field and laboratory fractionations were generally small, but relative differences could be large. Although these differences were not statistically significant, this may simply be due to the spread in the results. Relative differences, expressed as Al_{ll}/Al_{lf}, had no apparent relationship with the temperature difference between the field and the lab. Although some significant correlations were found between Al_{ll}/Al_{lf} and H^+, no significant correlations were found with H_l^+/H_f^+; nor was any significant correlation found with DOC.

Our results do not show that laboratory determinations of labile Al do not correspond to the true values. Thus, laboratory determinations may truly reflect the situation in the field, at least if precautions are taken to avoid changes in the sample during transport and storage. However, because of small sample numbers and a large variation in the results, a larger-scale study would be necessary to show this with more certainty.

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