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# Water Chemistry Methods in Acid Deposition Research: A Comparative Study of Analyses from Canada, Norway, and the United States

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Identical aliquots (split samples) from lakes in the southeastern United States were analyzed in laboratories in the U.S. and Norway. A second set of split samples from lakes in the northeastern U.S. was analyzed in laboratories in the U.S. and Canada. Methods used by the laboratories were identical for most analytes. For 8 of 11 analytes, there was a statistically significant difference between the results from Norway and the U.S. For 15 of 17 analytes, there was a statistically significant difference between the results from Canada and the U.S. Linear equations describing the relationship between results from the U.S. and Norway (or Canada) explained over 90% of the variance for most analytes. Notable discrepancies occurred for labile inorganic aluminum and acid-neutralizing capacity, two analytes critical to acid deposition studies. A linear model explained about 35% of the variance for labile inorganic aluminum. Considerable laboratory bias was evident for acid-neutralizing capacity in both sets of split sample measurements. Difference in methodologies and holding times may account for these discrepancies. For any of the analytes, the practical significance of the differences is dependent on the objectives and constraints of each application. The effects of laboratory and methodology were statistically confounded. Standardizing analytical methods would assist the chemist in interpreting data from studies, notably those of lake acidification, in other nations.

**KEY WORDS:** Acid deposition, analytical methods, international laboratory bias.

## INTRODUCTION

Evidence of decreasing pH levels in freshwaters has been well documented in recent decades in southern Scandinavia<sup>1-3</sup> and Canada.<sup>4-7</sup> Extensive data bases for freshwater have been collected for the northeastern United States.<sup>8-10</sup> A systematic inventory<sup>11</sup> of the chemical status of representative surface water in the U.S. was conducted by the U.S. Environmental Protection Agency (EPA). The Eastern Lake Survey—Phase I (ELS), a survey of approximately 1600 lakes in the eastern United States, was conducted as part of the National Surface Water Survey (NSWS).<sup>11</sup> One objective of the ELS was to provide data of known quality. This was accomplished, in part, by using standardized techniques for measuring water quality analytes.<sup>12,13</sup> The large number of samples collected during the ELS required that several independent laboratories conduct analyses for many of the chemical analytes. A rigorous quality assurance program<sup>14</sup> was implemented to ensure that all of the variance for these analytes could be attributed to differences in the chemical composition of lake water rather than to sampling or analytical procedures.

There are no standard international methodologies for analysis of water samples.<sup>15</sup> Perceived differences in water chemistry may be attributed to acidification processes, differences in methodologies or both. The objective of this study was to compare the results from identical aliquots analyzed by ELS contract laboratories with those analyzed by Canadian and Norwegian laboratories. One set of identical aliquots (split samples) was analyzed by a second ELS laboratory and by two Norwegian laboratories, and another set of split samples were analyzed by ELS and Canadian laboratories. Each laboratory used its own techniques. Statistical analyses included linear regressions and tests of significant differences.

## METHODS

One hundred ten identical aliquots (split samples) from 97 lakes in the Southern Blue Ridge Mountains, North Carolina, were routed to the Norwegian Institute for Water Research (NIWA, Oslo, Norway) and Global Geochemical Corporation (Camoga Park, California) for analysis of 11 chemical analytes (Table 1). One hundred five split

**Table 1** Chemical analytes measured and methods used in the intercomparison study

Variable	Method of analysis		
	ELS	Canadian	Norwegian
ANC ( $\mu\text{eq L}^{-1}$ )	Gran analysis	Gran analysis	Fixed-endpoint
pH (pH units)	pH meter	pH meter	pH meter
Conductance ( $\mu\text{S cm}^{-1}$ )	Conductivity meter	Conductivity meter	Conductivity meter
DIC ( $\text{mg L}^{-1}$ )	Carbon analyzer	Carbon analyzer	Not compared
DOC ( $\text{mg L}^{-1}$ )	Carbon analyzer	Carbon analyzer	Not compared
Ca ( $\text{mg L}^{-1}$ )	AAS-flame	AAS-flame	AAS-flame
Fe ( $\text{mg L}^{-1}$ )	AAS-furnace	ICPES	Not compared
Na ( $\text{mg L}^{-1}$ )	AAS-flame	Flame photometry	AAS-flame
Mg ( $\text{mg L}^{-1}$ )	AAS-flame	AAS-flame	AAS-flame
Mn ( $\text{mg L}^{-1}$ )	AAS-flame	ICPES	Not compared
K ( $\text{mg L}^{-1}$ )	AAS-flame	Flame photometry	AAS-flame
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	IC	Not compared	AC
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	IC	IC	AC
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	IC	IC	AC
$\text{SiO}_2$ ( $\text{mg L}^{-1}$ )	AC	AC	Not compared
Total fluoride ( $\text{mg L}^{-1}$ )	ISE	ISE	Not compared
Total phosphorus ( $\text{mg L}^{-1}$ )	AC	AC	Not compared
Total Al ( $\text{mg L}^{-1}$ )	AAS-furnace	ICPES	Not compared
Labile inorganic (monomeric) Al ( $\text{Mg L}^{-1}$ ) (extractable)	AAS-furnace	Not compared	PCV (total reactive)

Abbreviations: ANC = Acid-neutralizing capacity, DICE =  $\text{CO}_2$ -equilibrated dissolved inorganic carbon, ICPES = Inductively-coupled plasma emission spectroscopy, AAS flame (furnace) = Flame (furnace) atomic absorption spectroscopy, AC = Automated colorimetry, PCV = Pyrocatechol violet, ISE = Ion sensitive electrode.

samples from 93 lakes in the Adirondack region of New York were routed to the Water Quality Laboratory of Environment Canada's Centre for Inland Waters (Burlington, Ontario), the Laboratory Services Branch of the Ontario Ministry of the Environment (Rexdale, Ontario) and Environmental Monitoring Services, Inc. (Thousand Oaks, California) for the analysis of 17 analytes (Table 1). The two Canadian laboratories tested for different analytes. Since both American laboratories were involved in the ELS, they shall be referred to as ELS laboratories in this paper. The collection, preservation, and preparation of the samples are described elsewhere<sup>16</sup> in greater detail.

Samples analyzed for acid-neutralizing capacity (ANC) and pH were held for less than one week after the time of sample preparation at the field laboratories. All other analytes were analyzed within two and four weeks of sample preparation. All of the chemical analytes except labile inorganic aluminum are reported to be stable beyond the maximum holding times specified for the present study.<sup>17</sup> Because of logistical constraints, ELS split samples for labile inorganic aluminum were held up to 16 hours prior to processing. Barnes<sup>18</sup> recommended that sample processing for labile inorganic aluminum analysis be conducted within several hours of collection. The processed samples can then be held for several weeks before they are analyzed. ELS samples for labile inorganic aluminum were held for a maximum of 7 days after they were processed.

References for all methods used in this study, and the raw data are given elsewhere.<sup>16</sup> For some analytes, the laboratories used the same analytical methods (Table 1). Norwegian ANC determinations were performed using a fixed endpoint titration. Canadian and ELS values for ANC were calculated using Gran analysis. The concentrations of Na and K were measured by flame atomic absorption spectroscopy in Norwegian and ELS laboratories, and by automated flame photometry in the Canadian laboratory. The Canadian and ELS laboratories used ion chromatography to determine concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  while the Norwegian laboratory used automated colorimetry. The Canadian laboratory used inductively-coupled plasma emission spectroscopy to determine the concentrations of Fe and Mn, while ELS laboratories used flame atomic absorption spectroscopy.

Total Al was measured by graphite furnace atomic absorption

spectroscopy in ELS aliquots and by inductively-coupled plasma emission spectroscopy (ICPES) at the Canadian laboratory. The determination of labile inorganic aluminum in ELS aliquots was by complexation with 8-hydroxyquinoline and extraction with methyl-isobutylketone (MIBK).<sup>18,19</sup> The Norwegian split samples were analyzed by an automated colorimetric technique involving the complexation of monomeric aluminum with pyrocatechol violet.<sup>20,21</sup>

Statistical analysis of the data included linear regressions and sign tests.<sup>22</sup> The objective of fitting a linear model to the data was to estimate the best linear equation representing the relationship between corresponding values from different laboratories. An assumption of linear regression is that one of the analytes (independent variable) has no associated measurement error. When comparing data from two laboratories, there is no reason to believe that one laboratory has measurement error and the other does not. Therefore, regression procedures were conducted with each laboratory designated as the standard (i.e., independent variable). Under ideal conditions, both laboratories will report identical values for an analyte in every sample. Under such circumstances, the  $y$ -intercept=0 and the slope=1, regardless of which laboratory is designated as the standard. A more reasonable expectation is that the two coefficients would closely approximate these ideal values. In practical terms, the  $y$ -intercept estimates the amount of uniform bias between pairs of reported values for each analyte. The slope estimates the unit change in values from one analytical laboratory per unit change in the corresponding value from the laboratory designated as the standard. If the slope is significantly different from unity, then laboratory bias is concentration-dependent.

For each regression procedure, the potential for influence by outlying observations was examined by successively fitting two linear models to each set of paired observations. The first model was based on all reported data. A second model was estimated using a subset of the reported data where outliers were discarded. The criterion for determining whether a pair was an outlier was defined<sup>23,24</sup> as a studentized residual  $>3.0$ .

The  $r^2$  statistic was used as a general assessment of the adequacy of the linear model. The magnitude of  $r^2$  represents the fraction of total variance in the data explained by a model. The value of  $r^2$  is generally increased by removing pairs of values which have student-

ized residuals  $>3.0$  However, lower values of  $r^2$  may result for the second analysis when (1) the  $r^2$  value exceeds about 0.99 and (2) the data removed lie at the extremes of a data set having considerable variance. With a simple linear model, it is difficult to explain more than 99% of the variance in data sets involving water chemistry analyses. When the  $r^2$  value approaches unity, the slope of the line with one laboratory's values as the standard approaches the reciprocal of the slope of the line with the other laboratory's values as the standard.

Standard sign tests<sup>22</sup> were also performed for each variable on both Norwegian-ELS pairs and Canadian-ELS pairs. The purpose of this analysis was to determine whether one laboratory had significantly different values overall for a given variable. For each variable, we tested the null hypothesis that the mean ELS value = the mean Norway value and the mean ELS value = the mean Canadian value. Unlike linear regression, the sign test tests for systematic differences without the assumption of any underlying functional relationships and with no attempt at characterizing a functional relationship.

## RESULTS

### ELS-Norwegian comparisons

The results of two regressions for each analyte are given in Table 2. In the first regression, ELS values are the standard (independent variable). In the second regression, values from the Norwegian Institute for Water Research (NIWR) are the standard. The slopes and intercepts reported represent the model yielding the higher  $r^2$  value when (1) all pairs of observations were used or (2) observations having studentized residuals  $>3.0$  were removed. A minimum of zero pairs and a maximum of 5 pairs were removed for any analysis (Table 2).

Linear models explained  $>90\%$  of the variance for 10 of the 11 analytes (Table 2). Nine analytes had values of  $r^2 > 0.95$ , regardless of which laboratory was used as the standard. For labile inorganic (extractable) aluminum, the linear model explained only 36.1 percent of the variance when ELS was the standard laboratory, and 29.1 percent of the variance when NIWR was the standard laboratory.

**Table 2** Results of sign tests and two linear regressions for each analyte in the Norway-ELS splits

Analyte	N <sup>a</sup>	Slope (SE) <sup>a</sup>	Y-intercept (SE) <sup>a</sup>	r <sup>2</sup>	Sign test
Ca	106	1.050 (0.007)**	0.098 (0.028)**	0.995	ELS < Norway**
	106	0.948 (0.007**)	-0.080 (0.027)**	0.995	
ALEX <sup>b</sup>	105	0.332 (0.044)**	0.001 (0.000)**	0.361	ELS > Norway**
	108	0.835 (0.127) NS	0.001 (0.000)*	0.291	
SO <sub>4</sub> <sup>2-</sup>	108	1.102 (0.009)**	-0.156 (0.029)**	0.992	ELS = Norway
	109	0.898 (0.005)**	0.161 (0.022)**	0.997	
Cl <sup>-</sup>	107	1.012 (0.017) NS	-0.201 (0.043)**	0.970	ELS > Norway**
	110	0.866 (0.004)**	0.439 (0.044)**	0.998	
ANC <sup>b</sup>	109	0.003 (0.003) NS	-9.39 (0.975)**	0.999	ELS > Norway**
	109	0.996 (0.003) NS	9.60 (0.950)**	0.999	
COND <sup>b</sup>	109	0.981 (0.002)**	1.616 (0.139)**	1.000	ELS < Norway**
	109	-1.627 (0.144)**	1.019 (0.002)**	0.999	
Na	106	1.091 (0.003)**	-0.130 (0.020)**	0.999	ELS = Norway
	106	0.915 (0.003)**	0.122 (0.018)**	0.999	
Mg	108	1.035 (0.008)**	0.005 (0.008) NS	0.994	ELS < Norway**
	108	0.961 (0.007)**	-0.000 (0.008) NS	0.994	
K	107	1.000 (0.11) NS	-0.041 (0.015)**	0.986	ELS > Norway**
	107	0.986 (0.11) NS	0.056 (0.015)**	0.986	
NO <sub>3</sub> <sup>-</sup>	110	1.008 (0.007) NS	-0.017 (0.008)*	0.994	ELS = Norway
	109	0.986 (0.005)*	0.015 (0.006)*	0.997	
pH	108	0.875 (0.023) NS	0.759 (0.158)**	0.933	ELS > Norway*
	108	1.067 (0.028)*	-0.347 (0.190) NS	0.933	

\*P &lt; 0.05.

\*\*P &lt; 0.01.

NS—Not significant.

<sup>a</sup>ELS was designated as the standard laboratory (i.e., independent variable) in the first region and the Norwegian Institute for Water Research was designated as the standard laboratory in the second. For each analyte the slope and intercept reported represent the models yielding the higher values of r<sup>2</sup> with or without observations having studentized residuals > 3.0 removed.

<sup>b</sup>Abbreviations: ANC=acid neutralizing capacity, ALEX=monomeric (labile inorganic) extractable aluminum, COND=conductance.



The estimated slope was significantly different from the ideal value of one for Ca,  $\text{SO}_4^{2-}$ , conductance, Na, and Mg regardless of which laboratory was the standard. Therefore, laboratory bias was concentration-dependent for these analytes. The estimated slope was significantly different from one for extractable aluminum when ELS was the standard laboratory, and for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and pH when NIWR was the standard laboratory. Only acid-neutralizing capacity and K had slopes equal to one regardless of which laboratory was the standard.

The estimated y-intercept was significantly different from the ideal value of zero for all analytes, regardless of which laboratory was the standard, except for Mg, and pH. For Mg, the y-intercept was not significantly different from zero. For pH, the y-intercept was significantly different from zero when NIWR was the standard laboratory.

In general, linear models explained a high percentage of total variance. However, none of the models had both the slope and y-intercept that were not significantly different from their ideal values. A uniform bias (slope not significantly different from 1, y-intercept=0) was observed for acid-neutralizing capacity and K, regardless of which laboratory was designated as the standard. For the remaining analytes, the bias was concentration-dependent or uniform, (Y-intercept=0, slope was not significantly different from one) depending upon which laboratory was designated as the standard.

Overall, values from ELS were higher than from NIWR for extractable aluminum,  $\text{Cl}^-$ , acid-neutralizing capacity, K, and pH (sign test Table 2). Values from NIWR were higher than those from ELS for Ca, conductance, and Mg. The values from the two laboratories were not significantly different for  $\text{SO}_4^{2-}$ , Na, and  $\text{NO}_3^-$ .

### ELS-Canadian comparisons

The results of two regressions for each analyte are given in Table 3. The ELS laboratory was designated as the standard in the first regression, and the Canadian laboratory was the standard in the second regression. Like the ELS-NIWR comparisons, the slopes and intercepts in Table 3 represent the models yielding the higher  $r^2$  when (1) all pairs of observations were used or (2) observations having studentized residuals  $>3.0$  were removed. A minimum of zero and a maximum of four pairs were removed for any analysis.

Linear models explained >90% of the variance for 11 of the 17 analytes regardless of which laboratory was designated the standard. Ten analytes had values of  $r^2 > 0.95$  regardless of which laboratory was the standard. The values of  $r^2$  for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and pH were either slightly less than 0.90 for both analyses, or slightly greater than 0.90 for one analysis and slightly less than 0.90 for the other. The value of  $r^2$  changed slightly for  $\text{Cl}^-$ , Fe, Mn, and pH depending on which laboratory was designated the standard (Table 3). Linear models explained only 41.7 percent of the variance for total phosphorus, less than 66 percent of the variance for Fe and less than 85 percent for Mn (Table 3).

The estimated slope was significantly different from unity for total aluminum, dissolved organic carbon, total fluoride, Na, Mg, K,  $\text{SiO}_2$ , Fe, Mn, and pH regardless of which laboratory was designated as the standard. Therefore, laboratory bias was concentration-dependent for these analytes. When a Canadian laboratory was designated as the standard, the estimated slope was significantly different from unity for  $\text{SO}_4^{2-}$  and total phosphorus. When the ELS laboratory was designated as the standard, the estimated slope was significantly different from unity for  $\text{Cl}^-$ . The estimated slopes were not significantly different from unity, regardless of which laboratory was the standard, for Ca,  $\text{CO}_2$ -equilibrated dissolved inorganic carbon (DICE), acid-neutralizing capacity and conductance.

The estimated  $y$ -intercept was significantly different from the ideal value of zero for Ca, total aluminum, DICE, total fluoride, acid-neutralizing capacity, Na, Mg, K, and  $\text{SiO}_2$  regardless of which laboratory was designated as the standard. The estimated  $y$ -intercept was not significantly different from zero, regardless of which laboratory was designated as the standard, for dissolved organic carbon, conductance and Mn. When the ELS laboratory was designated as the standard, the estimated  $y$ -intercept was significantly different from zero for  $\text{Cl}^-$ , Fe, and Mn. When the Canadian laboratory was designated as the standard, the estimated  $y$ -intercept was significantly different from zero for  $\text{SO}_4^{2-}$  and total phosphorus.

Because neither the slope nor the  $y$ -intercept was significantly different from the ideal, there was no bias for conductance regardless of which laboratory was designated as the standard. For the remaining analytes, there was either a uniform bias or a bias that was concentration-dependent, depending upon which laboratory was designated as the standard.

Table 3 Results of sign tests and two linear regressions for each analyte in the Canada-ELS splits

Analyte	N <sup>a</sup>	Slope (SE) <sup>a</sup>	Y-intercept (SE) <sup>a</sup>	r <sup>2</sup>	Sign test
ANC <sup>b</sup>	102	0.999 (0.002) NS	-14.311 (1.088)**	0.999	ELS > Canada**
	102	1.001 (0.002) NS	14.440 (1.073)**	0.999	
COND <sup>b</sup>	104	1.000 (0.000) NS	0.000 (0.000) NS	1.000	ELS = Canada
	104	1.000 (0.000) NS	0.000 (0.000) NS	1.000	
Na	103	0.971 (0.002)**	-0.008 (0.003)*	0.999	ELS > Canada*
	103	1.029 (0.002)**	0.008 (0.003)**	0.999	
Mg	102	0.939 (0.003)**	0.023 (0.003)**	0.999	ELS > Canada*
	102	1.063 (0.003)**	-0.024 (0.005)**	0.999	
K	104	0.916 (0.004)**	-0.006 (0.0028)**	0.998	ELS > Canada*
	104	1.089 (0.005)**	0.007 (0.002)**	0.998	
SiO <sub>2</sub>	103	0.926 (0.006)**	0.052 (0.015)**	0.996	ELS > Canada**
	102	1.067 (0.007)**	-0.039 (0.015)*	0.996	
Fe	103	1.260 (0.091)**	0.042 (0.008)**	0.654	ELS < Canada**
	102	0.453 (0.035)**	0.002 (0.005) NS	0.631	
Mn	105	1.143 (0.057)**	0.002 (0.002) NS	0.797	ELS < Canada**
	104	1.759 (0.032)**	0.002 (0.001) NS	0.849	
pH	102	0.794 (0.025)**	-1.16 (0.154)**	0.911	ELS > Canada**
	104	1.093 (0.036)**	-0.429 (0.221) NS	0.898	

Ca	103	0.988 (0.004) NS	0.212 (0.030)**	0.998	ELS < Canada**
	103	1.010 (0.031) NS	-0.227 (0.036)**	0.998	
ALTL <sup>b</sup>	104	0.731 (0.024)**	-0.015 (0.005)**	0.901	ELS > Canada**
	104	1.232 (0.040)**	0.034 (0.006)**	0.901	
SO <sub>4</sub> <sup>2-</sup>	102	0.934 (0.032)*	0.176 (0.180) NS	0.895	ELS > Canada*
	102	0.958 (0.033) NS	0.387 (0.179)*	0.958	
DICE <sup>b</sup>	101	1.008 (0.007) NS	0.312 (0.031)**	0.996	ELS < Canada**
	101	0.992 (0.007) NS	0.081 (0.034)*	0.996	
DOC <sup>b</sup>	102	0.871 (0.014)**	0.013 (0.059) NS	0.976	ELS > Canada**
	102	1.121 (0.018)**	0.077 (0.066) NS	0.976	
Cl <sup>-</sup>	101	0.718 (0.024)**	0.137 (0.035)**	0.897	ELS > Canada*
	103	1.068 (0.035) NS	0.023 (0.054) NS	0.902	
FTL <sup>b</sup>	102	1.052 (0.016)**	-0.002 (0.001)*	0.977	ELS = Canada
	102	0.929 (0.014)**	0.003 (0.001)*	0.977	
PTL <sup>b</sup>	102	0.910 (0.108) NS	-0.001 (0.001) NS	0.417	ELS > Canada**
	102	0.458 (0.054)**	0.004 (0.000)**	0.417	

\* $P < 0.05$ .\*\* $P < 0.01$ .

NS—Not significant.

\*ELS was designated as the standard laboratory (i.e., independent variable) in the first regression, the corresponding Canadian laboratory was designated as the standard laboratory in the second. The slope and intercept reported represent the models yielding the higher values of  $r^2$  with or without observations having studentized residuals  $> 3.0$  removed.

<sup>b</sup>Abbreviations: ALTL = total aluminum, DOC = dissolved organic carbon, DICE = CO<sub>2</sub>-equilibrated dissolved inorganic carbon, FTL = total fluoride, PTL = total phosphorus, ANC = acid-neutralizing capacity, COND = conductance.

Overall, values from ELS were higher than from the Canadian laboratories for total aluminum,  $\text{SO}_4^{2-}$ , dissolved organic carbon,  $\text{Cl}^-$ , total phosphorus, acid-neutralizing capacity, Na, Mg, K,  $\text{SiO}_2$ , and pH (sign tests Table 3). Values from the Canadian laboratories were greater than those from the ELS laboratory for Ca, DICE, Fe, and Mn. The values for the ELS and Canadian laboratories were not significantly different for total fluoride and conductance.

## DISCUSSION

Based on strict interpretation of the statistical analyses, there were significant differences between the ELS and Norwegian results and between the ELS and Canadian results. Laboratory bias was either uniform or concentration-dependent for nearly all analytes. However, data were highly comparable for most analytes, since  $r^2$  exceeded 0.95 for 19 out of 28 comparisons. The sign test evaluates whether there is or is not a significant difference between corresponding observations in two sets of samples. As such, the question addressed is "are they the same overall?" There is no quantification of underlying relationships. In contrast, the evaluation of linear models tests the equivalence of the results from each laboratory and estimates the linear model that characterizes the relationship between laboratories.

In this study, the effects of laboratory and method are statistically confounded. In the ELS-NIWR comparisons different analytical methods were used for ANC,  $\text{NO}_3^-$ , and labile inorganic aluminum. In the ELS-Canadian comparisons, different analytical methods were used for Fe, Na, Mn, K, and total aluminum. Although differences between the laboratories occurred for all of these analytes, it is impossible to eliminate differences in analytical methodology as the source of the difference. We suggest detailed studies of differences resulting from these methods. Standardizing analytical methods would assist the chemist in interpreting data from acid deposition studies in other nations.

While it is clear that there were statistically significant differences between split sample data for most analytes, interpretation of the results for application must consider practical significance. As an

example, for Na in the ELS-NIWA data, the slope estimate when the ELS laboratory was designated as the standard was 1.091, and the  $y$ -intercept was  $-0.130$ . While these estimates were significantly different statistically from the ideal values of 1.0 and 0.0, respectively, there is some doubt about the practical significance of the differences. The mean observed ELS value for Na was  $3.03 \text{ mg L}^{-1}$  which corresponds to a Norwegian value of  $3.13 \text{ mg L}^{-1}$ . The practical significance of such a difference will be largely dependent upon the objectives and constraints of each particular application. Thus, the results of this investigation can only serve as a guide to general comparability and the magnitude of expected differences.

Two of the most critical analytes<sup>25-27</sup> used in assessing the acidification of natural waters are ANC and Al. A brief discussion of these analytes is therefore in order.

Two chemical mechanisms could conceivably decrease ANC in Norwegian and Canadian split samples, and this would result in a negative  $y$ -intercept. One mechanism is the addition of strong acid to the sample, and the other is the precipitation of  $\text{CaCO}_3$ . Samples were not preserved with acid prior to shipment. Therefore, the introduction of a strong acid can be ruled out. A lack of  $\text{CO}_2$ -fixation, due to a cessation of photosynthetic activity, could cause the precipitation of  $\text{CaCO}_3$ . ANC was determined by a different method in the ELS laboratory than in the Norwegian laboratory. This difference may also account for the observed negative  $y$ -intercept for ANC in Table 2. For samples with low ANC, the fixed-endpoint titration has been reported to consistently underestimate this variable when compared to Gran analysis.<sup>28,29</sup>

Comparability of total Al concentrations between ELS and Canadian values was quite good. This can be expected since both aliquots were pretreated in similar manner and were analyzed on comparable instruments. The slightly negative intercept is probably due to the inability of ICP emission spectroscopy to detect extremely low levels of Al ( $20\text{--}50 \mu\text{g L}^{-1}$ ).

The comparison between the 8-hydroxyquinoline extractable Al (ELS) and the pyrocatechol violet reactive Al (Norwegian) is most interesting. Both methods are reported to estimate the monomeric fraction of the total Al in water samples with comparable precision.<sup>15</sup> However, the fraction of the variance explained by a linear equation between ELS extractable and Norwegian reactive Al

is demonstrably poor (Table 2). The slope is also significantly less than one. Holding time undoubtedly plays a major role with respect to Al speciation. Norwegian splits were held for up to two weeks prior to pyrocatechol violet analysis. During this time, the formation of  $\text{Al}(\text{OH})_3$  may have occurred. This removes Al monomers and dimers from the reaction scheme and yields lower values for these species. If  $\text{CO}_2$  had been lost, the pH would have increased, and Al would have precipitated<sup>30</sup> as  $\text{Al}(\text{OH})_3$ . A shift from inorganic monomeric Al to strongly bound organic complexes may also have occurred in samples with elevated dissolved organic carbon levels.<sup>21</sup>

## CONCLUSIONS

For most analytes there were statistically significant differences between ELS and Norway or Canada split sample data. The practical significance of these differences will depend upon both the nature of the variable and the application in question. Consideration of all possible applications is beyond the scope of this investigation. For ANC and Al, two analytes critical to acidic deposition studies, methodologies, holding times, and concentrations may account for the observed differences. The effects of laboratory and analytical method were statistically confounded in this study. We suggest detailed intralaboratory studies of different methods. Standardizing analytical methods would assist the chemist in interpreting data from acid deposition studies in other nations.

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