



Modelling of aluminium speciation as a complement to laboratory-based analysis

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1. INTRODUCTION

The toxic effects of Aluminium (Al) on fauna and flora are central to the acidification issue. Aluminium is a very strong buffer (Driscoll and Postek 1996; Skyllberg 1999; Simonsson 2000), therefore if water in a catchment falls from circum-neutral to lower pH due to acidification many of these excess hydrogen ions will displace Aluminium from the soil. The adverse effects of elevated Al in freshwaters have been shown in many studies, however the level of toxicity posed by Al is heavily dependant on the form it takes. Therefore when monitoring Al in freshwaters it is important to be able to differentiate between potentially toxic forms of Al and more benign forms. Speciating Al in the laboratory for each sample taken is obviously the most effective method of quantifying the toxic and non-toxic forms of Al, however due to complexity and cost this is not a standard analysis in routine environmental monitoring. This report presents the results from a project evaluating computer software which can be used to speciate Al, and how well they can model Al speciation undertaken in the laboratory.

1.1 BASIC ALUMINIUM CHEMISTRY AND SPECIATION

A basic understanding of Al chemistry is required to help interpret the results presented in this report. The table below shows a simple schematic breakdown of common Al-complexes in freshwaters.

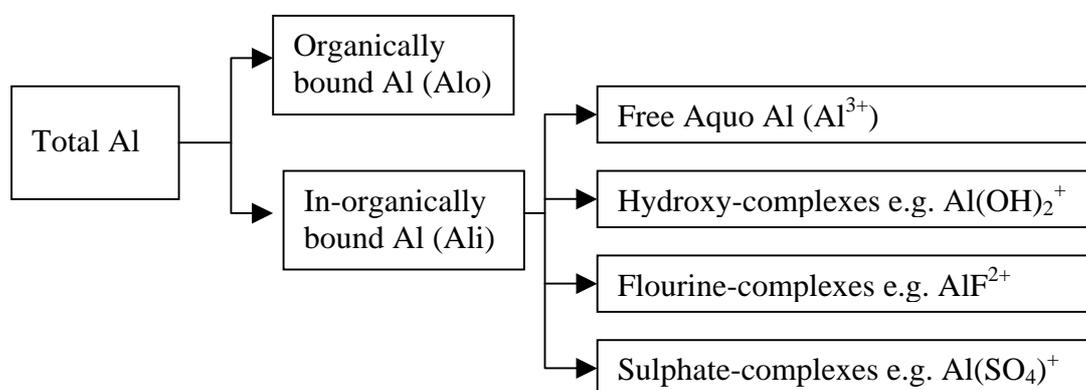


Figure 1. Schematic diagram of Aluminium speciation

It is commonly held that the cationic, inorganic forms of Al are the most toxic, due to example to their interaction with the negatively charged surfaces of fish gills. Therefore the aspects of Al speciation of most interest here are the division of Al_{tot} into A_{lo} and A_{li}, followed by a breakdown of A_{li} in to cationic, neutral and anionic forms. This second stage is based thermodynamic and kinetic data (van Hees et al. 2001), and can therefore can be calculated with a reasonable degree of accuracy. The more difficult speciation is between A_{lo} and A_{li}. There are many laboratory methods proposed for this division, however the one of the most dominant are based on the

method propose by Driscoll (1984), where the sample is passed through a cation exchange column and the cationic inorganic Al is retained in the column and the neutrally charged and anionic ions (mainly Al_o) Al passes freely through. It is this stage which has proved so difficult to model, mainly due to the large variability in the binding properties of organic matter (Tipping et al. 1991). As Al_o can account for 30 to 75% of Al in Swedish freshwaters (van Hees et al. 2001), it is critical that any speciation method can reliably differentiate between organic and inorganic Al.

2. PROJECT METHODS

Known Al speciation data from 3 data sources have been used to calibrate and assess the effectiveness of two mechanistic models in determining Al.

2.1 COMPUTER MODELS

Two mechanistic, equilibrium computer modelling programs have been used in this study, The Windermere Humic Aqueous Model (WHAM) 6,0¹ and Visual MINTEQ² 2.22. WHAM is the result of research by Tipping and co-workers to describe specific and non-specific binding of cations by humic substances. Visual MINTEQ is based on the US Environmental Protection Agency's MINTEQA2 4,0³ software. Further development of the program and the addition of the Stockholm Humic Model (SHM) allow for organic and inorganic speciation.

Both models work by calculating the amount of Al bound to each available ligand. The binding of Al to inorganic ligands is more clearly understood, and it is the Al binding to organic ligands which is the more difficult and critical part of the model. The problem arises due to the extreme heterogeneous nature of organic molecules making it hard to present a generalised binding capacity for a "typical organic molecule".

Pervious work with WHAM has shown success in replicating laboratory batch titrations involving Aluminium in organic soil (Tipping et al. 1995; de Wit et al. 1999), however in a study by De Wit et al. (de Wit et al. 2001) where WHAM was used to simulate field data the results were poor. It seems the application of models is heavily dependant on both the quality and quantity of calibration data. As the scope of this study is to apply these models to large data sets the issue of calibration will be central.

Both models assume that Humic Substances (HS) consist of humic acids (HA) and fulvic acids (FA). By definition, HA are not soluble, therefore in this experiment HS are assumed to consist solely of FA. The samples were measured for Total Organic

¹ WHAM website - http://www.windermere.ceh.ac.uk/Aquatic_Processes/index.html

² Visual MINTEQ website - <http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm>

³ EPAs MINTEQA2 4.0 website - <http://epa.gov/ceampubl/mmedia/minteq/index.htm>

Carbon (TOC), and in water samples this is assumed to be present as Dissolved Organic Carbon (DOC). HS are commonly assumed to be 50% carbon by weight; therefore HS are equal to twice the TOC values. The model can then be calibrated by adjusting the fraction of these HS which are “active” in binding cations e.g. Al.

Calibration was undertaken by systematically varying the percentage of FA assumed “active” and recording the subsequent Al speciation. Optimised values were obtained by minimising the root of mean squared deviation (RMSD) between the measured and calculated inorganic cationic Al (Al^{3+}), according to:

$$RMSD - Al^{3+} = \left(\sum_{i=1}^n \frac{(Al^{3+}_{calc,i} - Al^{3+}_{meas,i})^2}{n} \right)^{0,5} \quad [1]$$

2,2 DATA SETS

Two main data sets have been used to calibrate and test the models; the results from Riksinventering national survey of lakes in both 1995 and 2000 and smaller scale but intensive sampling of Krycklan catchment in Northern Sweden.

The national survey (Riksinventering abv. RI) undertaken in 1995 sampled ca. 4100 lakes and in 2000 sampled ca. 3400 lakes. The Institution for Environmental Assessment, SLU undertook analysis except for Aluminium speciation which was run by the Institute of Applied Environmental Research (ITM). Aluminium fractionation used a cation exchange column coupled to an auto-analyser. For full information on analytical methods and techniques refer to Riksinventering 1995 and 2000 reports (Wilander et al. 1998; Wilander et al. 2003)

The Krycklan catchment is located ~60km inland from the Baltic Sea in Northern Sweden (64°14'N, 10°46'E). Streamwater samples were taken during the springflood 2003 using the grab-sample method at 16 sites located throughout the catchment. The sampling was intensive during the spring flood period and the sites were selected at the more easily available access points. The sites represent both low and high order streams and varied land type. Sampling was intensive during the peak flow of the spring flood with larger spacing as the flow receded. In total 160 samples from 14 sites and 14 dates were used in this study.

Table 1. Analysis techniques employed during Krycklan survey, spring 2003.

Parameter	Sampling instrument & laboratory
Flow	On-site stage height measured and the flow (l/s) calculated from the height using a rating curve
TOC	Shimadzu TOC-V Total Organic Carbon Analyzer - Örebro universitet
PH	Measured same day as sampling using Orion pH meter
Anions /	Anions (Stockholm Univ, Geosciences) : Ion Chrom
Cations	Cations (Stockholm Univ, Geosciences): ICP-OES
Fluorine	Orion F-selective electrode after treatment with TISAB buffer – IMA, Uppsala
Aluminium	Cation-exchange column direct coupled to ICP-OES – IMA Uppsala

2.3 SUMMARY OF PROJECT

The models have been calibrated and tested in a systematic order to examine their accuracy in predicting Al speciation from basic water chemistry parameters. Below is a schematic layout showing the various stages of testing along with a short description. A full description of methods is presented alongside the results for each stage.

1. Sensitivity Analysis Aim – to determine which chemical parameters are important in determining Al speciation
2. Influence of site type Aim - how the vegetation cover of a site influences the Al speciation
3. Up-scaling to national level Aim –validating if the models can accommodate variations in lake chemistry from RI lakes.
4. Al categorisation Aim – If modelled Al speciation is to be used in environmental assessment (e.g. assessment of liming needs) then the most important is how well the models can place each target in Al categories.
5. Calibration sample size Aim – to assess how stable the models are when the calibration data sets are increased and decreased.

3. PROJECT RESULTS

The results of this project have been subdivided into five separate fields, these each cover separate topics and therefore will be discussed in turn. To facilitate this, both the presentation of results and subsequent discussion, have been grouped together for each field.

3.1 SENSITIVITY ANALYSIS

The sensitivity analysis was undertaken to identify the chemical parameters important in controlling Al speciation and in particular Ali. It is critical to understand which chemical parameters are required to effectively model Ali from both a scientific and a practical viewpoint. Scientifically identifying these parameters help to identify dominant ligands in Al binding, and practically it is important to know the minimum chemical analysis required to perform a modelled Al speciation.

The sensitivity analysis was run individually on each data set by compiling the data to form a mean sample. This sample was then modelled with each chemical parameter systematically varied to represent the highest and lowest observed values. The resulting modelled Ali was then compared to the laboratory observed values of Ali. Parameters showing the largest changes in Ali are those which are most critical in modelling Al speciation.

All the data sets showed consistent results, with the most important parameters controlling Ali being Al_{tot}, pH, TOC and F. Fe and to a lesser extent Ca also showed some importance.

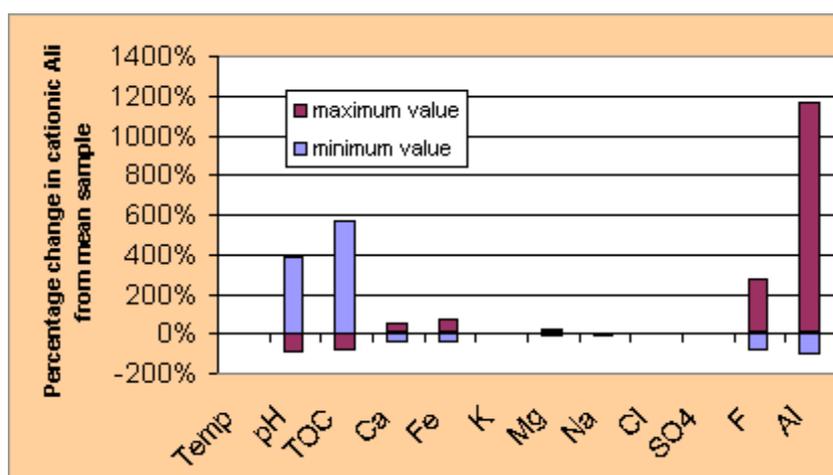


Figure 2. Mean sensitivity analysis from all the data sets shown as a deviation in Ali from observed values. A mean is presented as all the data sets showed consistent results.

3,2 DIVISION OF THE DATA SET BY SITE TYPE

Using the closely sampled Kryklan data it was possible to calibrate the models to assess the influence of different site types upon Al speciation. This will help in deciding if the data needs to be divided in to groups and separate calibrations run, or if an average calibration can successfully model all site types. In the Kryklan data set the sample sites were divided into one of four categories: Forested Headwaters, Mire Headwaters, Mixed Headwaters and Mixed Downstream. The models were calibrated to each individual site and then to each category. The figure below shows the results of this investigation, the X-axis is the percentage of FA which is assumed active, this is the calibration variable within the models and therefore variation in this will give differing modelled Ali.

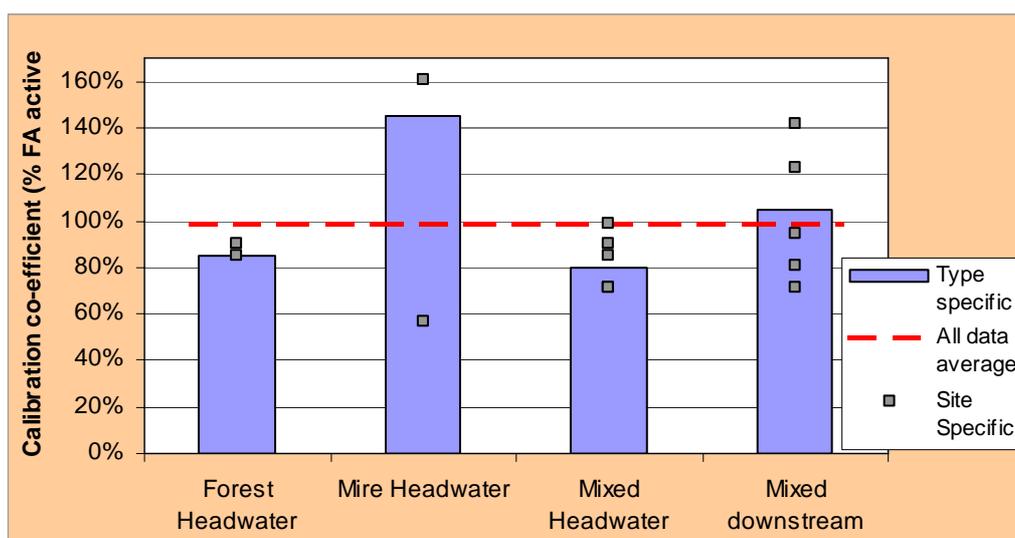


Figure 3. Results of individual and site categorised sample from the Kryklan survey

The most extreme values are for mire headwater streams; all others showed both reasonable intra- and inter-fit. Forest sites show the tightest intra-grouping and it can be assumed that the introduction of water from wetland and open sites contributes to the variation seen in the mixed up and down stream sites. As the intended target groups for this model are lakes and possibly larger streams, the mire values can be removed. With these two extreme values removed the average value for all the samples provides a reasonable fit the samples. Therefore, it can be concluded that on a large-scale, individual calibration to site type is not needed in order to obtain a reasonable modelled Ali result. However these results to indicate that further investigation of small headwater streams would be beneficial, this is especially true when considering that it is often these small streams which can have the highest Ali concentrations.

3.3 UP-SCALING TO NATIONAL LEVEL

The detailed study of Kryklan catchment showed that a single calibration can generalise the major landuse types, the next stage was to up-scale from a catchment size survey to a national scale. The 1995 survey was based on a random selection of lakes, and the 2000 survey had a closer focus on the more acid lakes. Both surveys had Al speciation undertaken by ITM in Stockholm. The WHAM model has been applied to both data sets and the Visual MINTEQ to the 2000 data. As the results

from the WHAM model were better than with Visual MINTEQ and in view of the high time demands of Visual MINTEQ only WHAM was applied to the 1995 data.

The data fell into clear pH categories, which is not unexpected due to the strong relationship between pH and Al solubility. Therefore the models were first divided into pH classes which then received individual calibrations for each class.

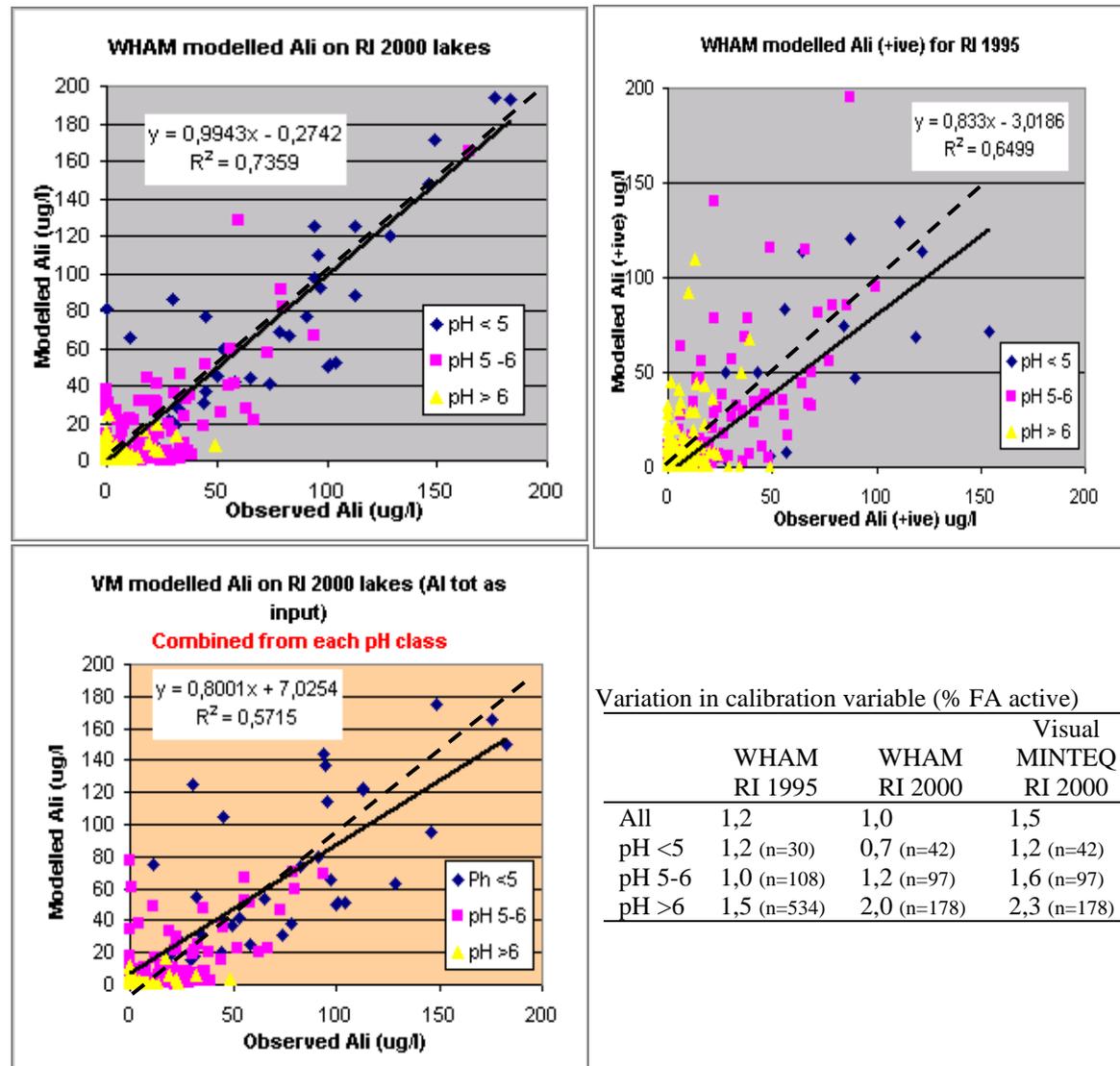


Figure 4. Comparison of observed and modelled Ali from RI 2000 and 1995 using WHAM and Visual MINTEQ. Dashed lines represent a 1:1 fit.

The results for RI 2000 show a fit falling very close to a 1:1 line and with an R^2 of 0,74. This is a very good fit, especially considering that both the lab and modelled results are subject to possible theoretical and analytical errors. The results of the RI 1995 data show again a close relationship to a 1:1 line but a poorer r^2 value. This is expected as the 1995 data is dominated by low Ali samples and therefore there are few points over $150\mu\text{g/l}$ which gives an “unstable” trend line that is strongly controlled by just a few samples. When comparing the results of the WHAM modelling and Visual MINTEQ the clearest observation is that they show similar results. This is a positive result which re-enforces the validity of both models as the

WHAM model bases its Alo/Ali speciation on literature values and Visual MINTEQ bases its Alo/Ali speciation on an empirical relationship taken from a restricted number of samples of Swedish sites. However, overall the results from the WHAM modelling indicate a better fit, and when also considering the ease of application the WHAM model would be selected in preference to Visual MINTEQ

3.4 AL CATEGORIZATION

The basis for wanting to speciate Al is the adverse effects of certain fractions of Al on aquatic fauna. Therefore, examining the data above may give an un-necessarily negative result as this compares the absolute difference between the observed and modelled Ali. Of more interest from a toxicological viewpoint is to assign categories of Ali based on biological observations and to measure the models effectiveness in placing a sample in the correct category. Naturvårdsverket liming handbook from 2002 (Naturvårdsverket 2002) assigns three categories, primarily based on pH, but with Ali limits.

Category	pH lower limit	Alk lower limit (meq/l)	Ali upper limit ($\mu\text{g/l}$)	Key fauna
1	6,3	0,15	30	Salmon
2	6,0	0,10	50	Roach, Minnow, Trout, Crayfish, River mussels, gastropods, mayfly
3	5,6	0,07	--	Absence of the above

Table 2. Classification of Ali into categories, after Naturvårdsverket liming handbook, 2002.

A more robust measure of the modelled Ali can be achieved by seeing how often the observed and modelled Ali falls in the same category. There will of course still be an edge effect associated with each category boundary (e.g. Observed at $30\mu\text{g/l}$ and modelled at $29\mu\text{g/l}$ would be deemed an error). However, as the majority of the lakes in the national surveys have very low Ali concentrations the results will better communicate the effectiveness of the models.

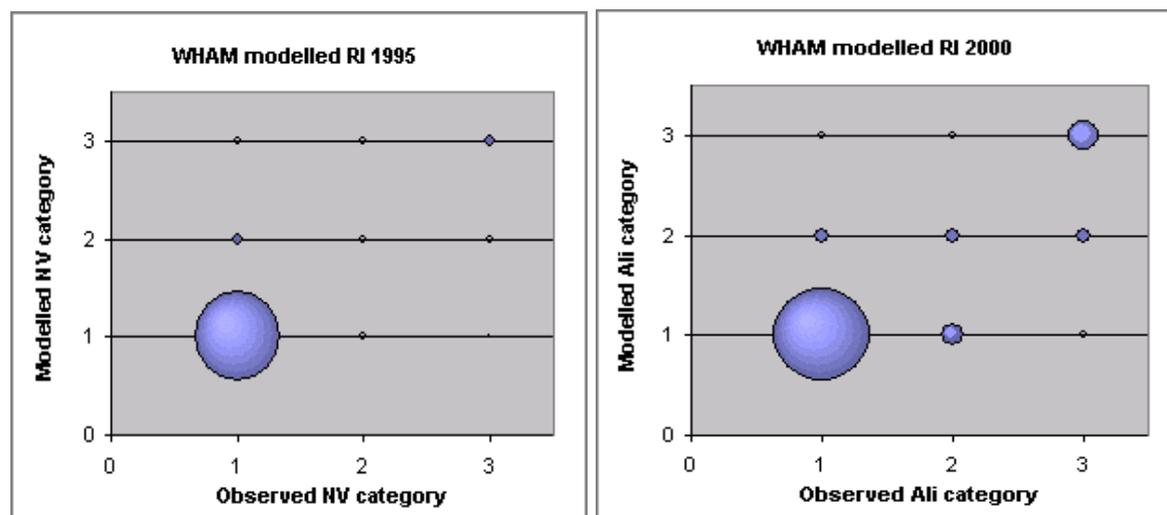


Figure 5. Observed and modelled Ali categories for RI 2000 and 1995 using WHAM

The above figures show firstly the dominance of lakes with less than 30µg/l (category 1). The level of samples which are placed in the correct category by the model is 93% and 88% for RI 1995 and 2000 respectively. The other critical statistic is the number of samples placed in the wrong category, obviously this is 7% and 12%, but the critical areas are a category 3 and 1 miss-calibrations, and these total just 1,5% and 1,6% for RI 1995 and 2000.

These results show that although the r^2 values for the modelled data lie at 0,74 and 0,64 when the results are examined from a biological impact point of view the models are able to predict Ali well.

3.5 CALIBRATION SAMPLE SIZE

The results shown so far above have been for Ali modelled using the whole dataset as a calibration set. However, criticism of models such as WHAM has been due to their poor applicability outside of calibration (de Wit et al. 2001). The long-term goal is to be able to apply the model to “blind data” using the calibration based on the results presented in this paper. If a calibrated model is to be applied to new data sets without further calibration then it is vital that the model continues to give reliable Aluminum speciation results. To test this, the WHAM model was calibrated with increasing smaller fractions of the RI2000 lakes data set and run on the remaining samples.

Table 3 – Effect of reduced calibration set size. Calibrations used randomly selected samples and were run in triplicate. Values in brackets show standard deviations.

Calibrated with	X-Y plot: Observed vs. Modelled Ali		NV Ali categories	
	r^2	Slope	Correct category	Major error category (1:3 or 3:1)
All samples 100%	0,80	0,93	88%	1,6%
158 samples 50%	0,84 ($\pm 0,04$)	0,91 ($\pm 0,01$)	90% ($\pm 2,1\%$)	1,3% ($\pm 0,6\%$)
79 samples 25%	0,81 ($\pm 0,05$)	0,97 ($\pm 0,20$)	89% ($\pm 1,2\%$)	0,9% ($\pm 0,01\%$)
16 samples 5%	0,84 ($\pm 0,01$)	1,25 ($\pm 0,06$)	87% ($\pm 2,1\%$)	0,4% ($\pm 0,4\%$)

As can be seen from the table above, both the absolute results from the X-Y plot and the results of Ali categorization show little variation even when the calibration set is equivalent to only 5% of the data set. This would suggest a relatively stable calibration of the model and therefore its application outside the calibration data is assumed to be feasible.

4. CONCLUSIONS & RECOMMENDATIONS

The results presented in this paper have shown that mechanistic models, and specifically WHAM can provide Al speciation results with reasonable accuracy and consistency. The results of the model cannot provide an exact figure of Ali but can give us a reliable tool for placing water samples into toxicological categories. As the background to this project is the assessment of water quality with regards to quality criteria assessment then the categorisation of Ali into toxic and non-toxic is more relevant than an exact prediction of Ali concentration to the nearest $\mu\text{g/l}$.

Providing the necessary input variables are available then WHAM is a tool which can quickly, easily and in-expensively provide a reasonable estimate of Ali concentration and a reliable estimate of Ali toxicology.

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