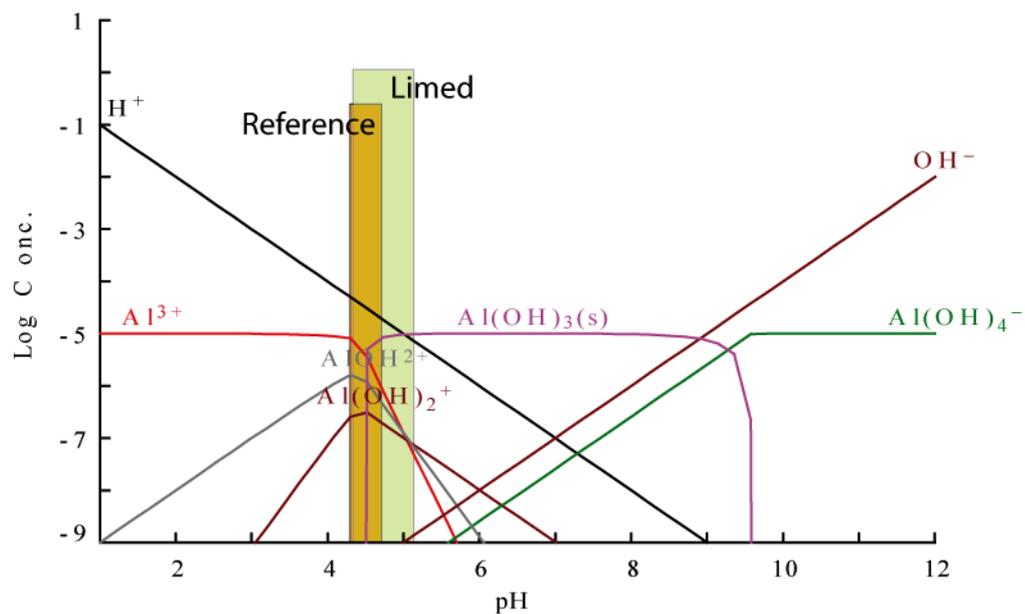# Modelling inorganic Aluminium in the SKOKAL streams

I. Calibration
II. Scenario Testing

Neil Cory[1], Stefan Löfgren[2] and Kevin Bishop[2]

[1] Forest Resource Management
Swedish University of Agricultural Sciences
90183 Umeå

[2] Department Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050   SE 750 07 Uppsala

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I. Calibration

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Summary

Due to the issue of acidification of surface waters, Aluminium (Al) concentration and speciation has come under scrutiny because of the toxic effect of elevated concentrations of certain Al forms. The complexity, costs and analytical uncertainty associated with Al fractionation analysis mean that Al fractionation is routine part of many environmental assessment programmes. However, recent advances in the modelling of chemical speciation in surface water, and principally in the modelling of organic/inorganic interaction, make it possible to retroactively model Al speciation from standard monitoring samples. Presented here are the results of the calibration of the Windermere Humic Aqueous Model (WHAM) to five of the SKOKAL sites made up of five streams with limed catchments and five streams with non-treated catchments. This paired catchment set up makes it possible to see the effects that the experimental liming programme has had upon surface water concentrations inorganic Aluminium (Ali). Individual calibrations were applied to each stream using 229 samples where Ali concentrations were analytically determined. This model was then applied to the full data set (1204 samples) to give a 16 year time series of Ali concentrations.

In calibration the model gave a fit between observed and modelled Ali with an r^2 of 0.888. Modelling of the full data set showed little difference between the Ali concentrations for the limed and reference streams for 3 of the sites. Site G showed consistently lower Ali in the limed stream than the reference stream. Site L showed Ali concentrations that were higher in the limed stream than the reference stream. Overall, all but one site showed Ali concentrations in excess of limits for acid sensitive species. At all sites the peak episodic values (90th percentile) showed exceedence by between ~3-20 times the limit for acid tolerant species.

Background

The issue of surface water acidification has been one of the central environmental problems in Sweden, with remediation through liming costing over 2 billion crowns (~200 million USD) during the period 1976-2002 (Lydersen, Löfgren et al. 2002). This remediation has been undertaken to buffer the excess acidity from the deposition of anthropogenic sulphate. Aluminium (Al) is critical to the issue of acidification because it is often the combination of depressed pH along with elevated concentrations of Al, and specifically inorganic Aluminium (Al_i), that are attributed to declines or disappearance of aquatic organisms, principally fish (Poleo, Ostbye et al. 1997; Brodeur, Okland et al. 2001; Ytrestoyl, Finstad et al. 2001) but also invertebrates (Herrmann 2001).

The concentration and speciation of Al are strongly connected to the acidity of a system. In the pH range 4.5 – 5.5 Al is a 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 these excess hydrogen ions may displace Al from the soil to surface waters. However, the toxicity of Al is due to a combination of concentration and speciation. Both Al solubility and toxicity are dependant on the presence of binding ligands. In organic rich boreal waters, the dominant ligand is DOC. The organic acids in DOC are another, largely natural, source of acidity in surface waters (Kortelainen and Saukkonen 1995). By decreasing pH, DOC increases Al solubility and influences the speciation of Al towards more toxic forms. At the same time though, DOC is a ligand that binds a portion of the Al in organic forms that are less toxic (Laitinen and Valtonen 1995; Gensemer and Playle 1999). The double-edged nature of organic acidity complicates the issue of distinguishing natural from anthropogenic pH decline and Al toxicity. A further hindrance to the monitoring of Al is the considerable cost and often high analytical uncertainty involved in the analysis of individual Al fractions.

SKOKAL data

The data from the SKOKAL streams provides an excellent basis for assessing the effect of forest liming on stream water quality. Used in this study are five SKOKAL sites with paired streams in the close vicinity of each other draining limed catchments (G24, O24, P24, R24 and L24, Figure 1), as well as non-treated reference streams (G24R, O24R, P24R, R24R and L24R. Detailed information regarding the catchment characteristics, water sampling and analytical techniques are found in Larsson & Westling (1997) and Zetterberg & Westling (2005).
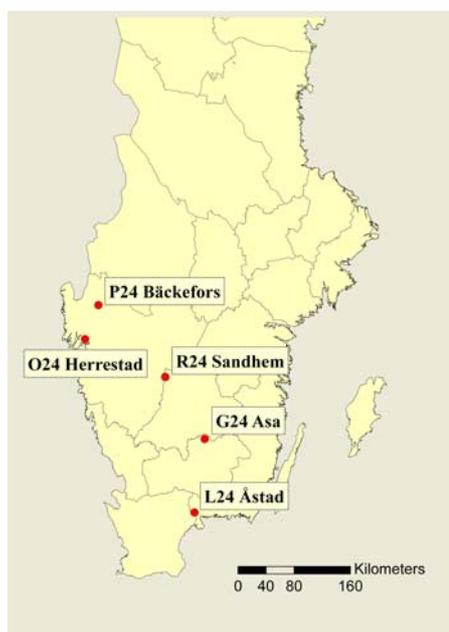
However, Al fractionation data is only available for a subset of the data and in order to assess the toxicological impact of Al in both the reference and limed rivers modelling of Al speciation plays an important role.

Figure 1 – Overview map of study sites. Names refer to the limed sites.

Modelling of Inorganic Aluminium

The heterogeneous nature of DOC has complicated attempts at modelling Al speciation (Tipping, Woof et al. 1991). However advances in modelling of cation binding to organic matter (Tipping 1994) have allowed the successful modelling of Al speciation in organic rich freshwater environments (Cory, Andren et al. in press). This modelling was based on a calibration of the Windermere Humic Aqueous

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Model, WHAM (Tipping 1994). WHAM assumes that humic substances consist of humic acids and fulvic acids (FA). As FA are more mobile they are assumed to make up the majority of dissolved organic matter (Tipping 2002). WHAM regards FA as hypothetical spherical molecules carrying proton dissociating groups capable of binding metals by specific binding. These binding sites include strong and weak acids with different median pKa values. The non-specific binding occurs through accumulation in the diffuse double layer around the charged surface of the FA.

The calibration process used systematic adjustment of the amount of fulvic acid active in binding cations to reduce the root mean square error between observed and modelled Al_i. Previous applications of the WHAM model in this manor have been successful in modelling Al speciation for both Swedish National Survey data for rivers and lakes (Cory, Andren et al. in press), and with in depth studies of springflood stream chemistry in Northern Sweden (Cory 2006).

Data Processing
As discussed above, binding of Al by DOC is an important factor and direct DOC measurements were only available for 46% of the samples. However, colour was measured on 94% of the samples, and the strong empirical relationship between water colour and DOC concentration was used to model DOC in the samples where it was not measured directly. Empirical relationships for colour to DOC were established for each stream, all had r^2 values >0.80.

Proposed Toxicological Limits for inorganic Aluminium
Although Al toxicity varies widely with fish species (Poleo, Ostbye et al. 1997) boundaries have been proposed for the commonly studied Atlantic salmon (*Salmo salar)* (Ytrestoyl, Finstad et al. 2001) and these are in close agreement with guidelines published by the Swedish EPA (SEPA 2002).The Swedish Environmental Protection Agency has defined three toxicological classes for Al_i: no toxicological effect (<30_g/l), effects on sensitive species (30-50_g/l) and effects on tolerant species (>50_g/l) (SEPA 2002). Ytrestoyl et al (2001), proposed similar categories, but also included an exposure time, no effect (<30ug/l), chronic effects, after 7 days exposure (30-50ug/l) and acute effects, after 24 hours exposure (>50ug/l).

Calibration of WHAM to SKOKAL rivers
WHAM was calibrated for each stream individually using the available observed Al_i samples (total n=229). The resulting fit (Figure 1) of modelled to observed Al_i had an r^2 of 0.888 (observed negative values and 2 outliers have been removed).

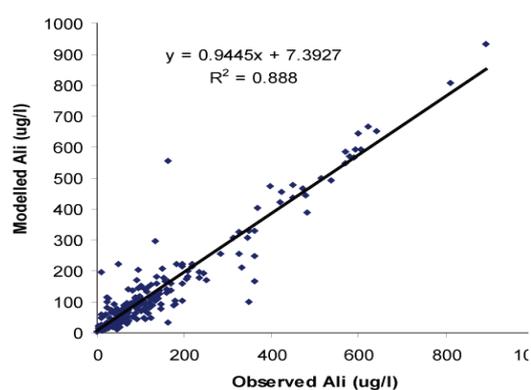| Stream	% active Fulvic Acid	Calibration factor
Overall	45%	0.9
G24	40%	0.8
G24 R	35%	0.7
O24	60%	1.2
O24 R	50%	1.0
P24	45%	0.9
P24 R	40%	0.8
R24	35%	0.7
R24 R	25%	0.5
L24	55%	1.1
L24 R	40%	0.8

Figure 1 – Calibration results for WHAM from the SKOKAL streams

The calibrated results showed a small, but consistent trend with reference stream requiring less of the fulvic acid to be active in binding Al. This implied that in the un-limed reference streams there is more Al in inorganic forms and therefore optimal calibration is achieved with a lower active FA %.

Results of modelling

The calibration, based on 229 observationswas then used to model Ali for all the samples with available data, 1204 samples. The values for both the limed and reference streams show regular peaks in Ali during spring and autumn (Figure 2). This is consistent with an increase in Ali during high flow episodes, snow melt in the spring and rainfall episodes in the autumn. Episodic increases in Ali are caused by three main factors:

1. The rapid superficial runoff dilutes the buffering capacity of the system, lowering pH and thereby making Al more soluble.
2. More superficial flow pathway generally pass through more organic rich horizons giving more organic acids, these organic rich layers help lower the pH and are also a store of Al.

Points 1&2 give elevated levels of total Al in run off, and the lower pH means that inorganic cationic forms of Al are more common. However, organic matter has a double-edges property as it also binds inorganic Al increasing the faction of neutrally changed Alo. However even an increase in Alo can give an apparent increase in Ali due to the in-direct measurement of Ali as discussed in point 3.

3. Ali is measured indirectly as the difference in Altot and Alo, a large increase in Alo means that both Alo and Altot are large in comparison to Ali. As there is a considerable analytical error associated with the determination of Alo and Altot the "observed" Ali concentrations can be observed to be an order of magnitude from what the actually are.
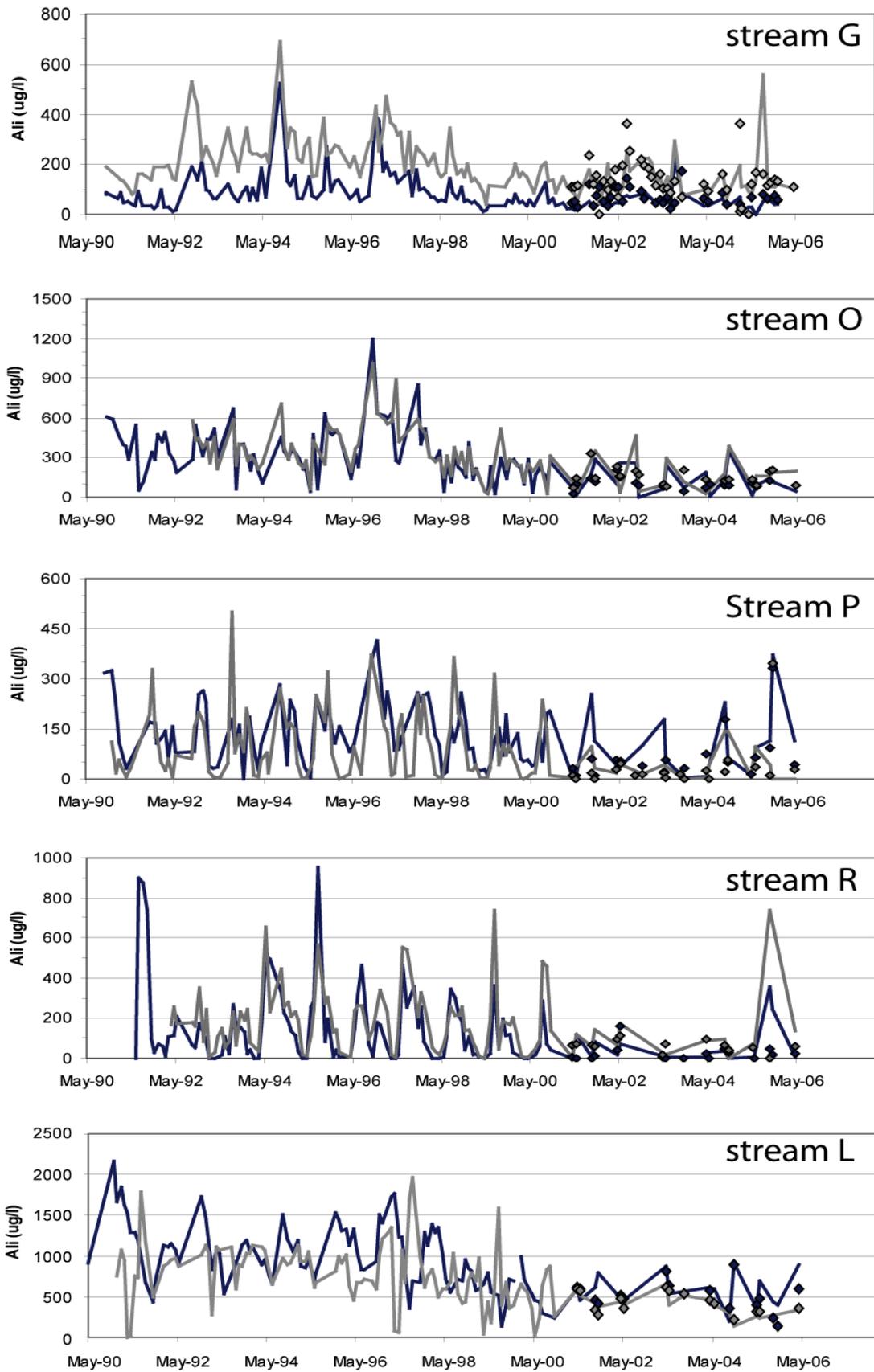
Figure 2 – Modelling of Ali from the SKOKAL data (1204 points) using WHAM calibrated with the available observed Ali data (204 points). Reference streams shown with a grey line (observed points with grey markers), limed streams shown with dark line (observed points with dark markers).

The modelled Ali did not show clear differences between the limed and reference streams. Site G was the only area where the reference stream (G24R) had consistently higher Ali concentrations. At site R the reference stream (R24R) shows higher concentrations of Ali during episodes. At site O the reference and limed streams had similar values throughout the study period. Site L showed higher concentrations of Ali in the limed (L24) rather than reference stream (L24R), the same was true for many of the observations at site P. These high concentrations of Ali even in the limed streams are not unexpected as the pH of the systems observed are still extremely low (reference median pH 4.48, limed median pH 4.68). In this pH range the Al forms are strongly cationic (Figure 3).
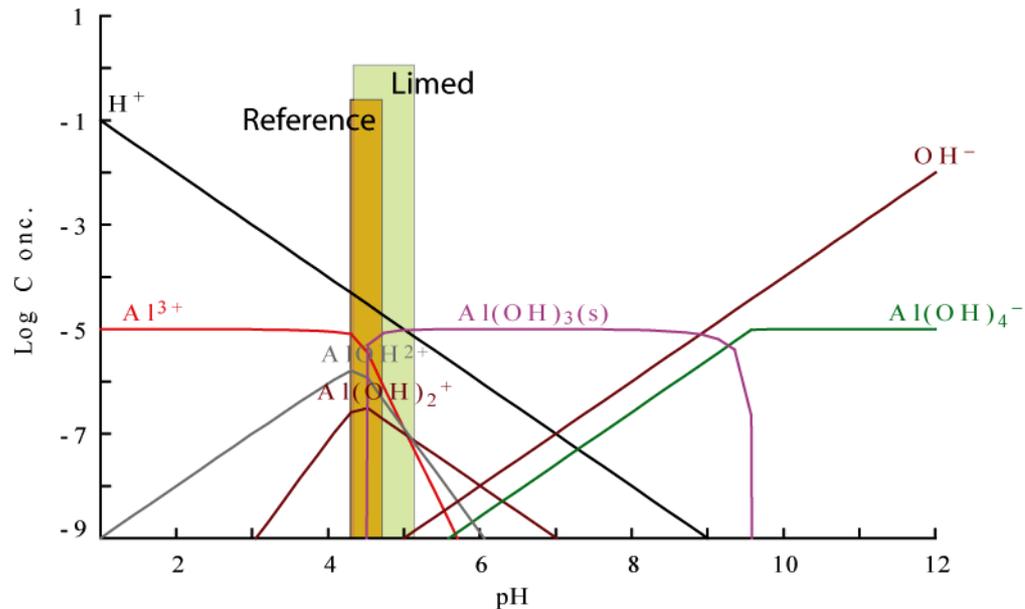

Figure 3 - Theoretical Al speciation in the absence of DOC (created with MEDUSA v.18). The pH ranges (25th-75th percentiles) are shown for the limed and reference streams.

In order for a larger change in the speciation of Al to be seen, especially during episodic conditions then a larger increase in pH would be required.

From a toxicological viewpoint none of the streams, limed or reference, maintained low enough concentration of Ali to be deemed suitable for acid sensitive fish (table 1). This is based upon both the median conditions and episodic events (90th percentile). The reference site P24R is the only stream to show a median value within the Ali range tolerable for acid tolerant species, however during episodic conditions the concentration of Ali exceeded this limit by four fold.

Table 1 – Modelled Ali for the SKOKAL streams given as median and 90th percentile.

		Ali (µg/l)	
		Median	90th
G24	Limed	64	167
	Reference	171	344
O24	Limed	283	530
	Reference	277	539
P24	Limed	112	249
	Reference	46	232
R24	Limed	64	313
	Reference	146	420
L24	Limed	875	1464
	Reference	684	1111

An interesting observation from stream G24 and O24, and to a lesser extent L24 is a drop in Ali concentrations at the end of 1998. Prior to this point the observations showed both higher concentrations and more temporal variations with larger peak values. This may reflect and underlying

environmental change as indicated by the inconsistent patterns between the sites. However, it may also be due to a change in sampling or analysis method or personnel. Al samples are not stable in storage and even a change in the time between sampling and analysis can affect the analytical results. Based on the results from the same laboratory, a similar drop in Ali was documented in the end of the 1990's at the integrated monitoring stream at Gårdsjön (Löfgren 2006).

Proposed further work

This report presents the results of calibrations of WHAM to model Ali in the SKOKAL rivers. In the second report scenario testing is undertaken to see the increase in pH required in order to reduce Ali levels below toxicity limits.

Brodeur, J. C., F. Okland, B. Finstad, D. G. Dixon and R. S. McKinley (2001). Effects of subchronic exposure to aluminium in acidic water on bioenergetics of Atlantic salmon (Salmo salar). Ecotoxicology and Environmental Safety **49**(3): 226-234.

Cory, N. (2006). Natural and Anthropogenic Influences on Aluminium in the Humic Rich Waters of Northern Sweden. Dept. of Environmental Assessment. Uppsala, Swedish University of Agricultural Sciences.

Cory, N., C. Andren and K. Bishop (in press). Modelling inorganic Aluminium with WHAM in environmental monitoring. Applied Geochemistry.

Driscoll, C. T. and K. M. Postek (1996). The chemistry of aluminium in surface waters. The environmental chemistry of Aluminium. G. Sposito, Lewis Publishers**:** 363-418.

Gensemer, R. W. and R. C. Playle (1999). The bioavailability and toxicity of aluminum in aquatic environments. Critical Reviews in Environmental Science and Technology **29**: 315-450.

Herrmann, J. (2001). Aluminium is harmful to benthic invertebrates in acidified waters, but at what threshold(s)? Water Air and Soil Pollution **130**(1-4): 837-842.

Kortelainen, P. and S. Saukkonen (1995). Organic vs minerogenic acidity in headwater streams in Finland. Water Air and Soil Pollution **85**(2): 559-564.

Laitinen, M. and T. Valtonen (1995). Cardiovascular, Ventilatory and Hematological Responses of Brown Trout (Salmo-Trutta L), to the Combined Effects of Acidity and Aluminum in Humic Water at Winter Temperatures. Aquatic Toxicology **31**(2): 99-112.

Larsson, P.-E. and O. Westling (1997). Ytvatten i kalkade avrinningsområden - årsrapport 1996. Effektuppföljning av Skogsstyrelsens program för kalkning och vitaliseringsgödsling av skogsmark. IVL rapport B1297**:** 65pp (In Swedish).

Lydersen, E., S. Löfgren and R. T. Arnesen (2002). Metals in Scandinavian surface waters: Effects of acidification, liming, and potential reacidification. Crtitical reviews in environmental science and technology **23**(2&3): 73-295.

Löfgren, S. (2006). Integrerad övervakning ac miljötillståndet i svensk skogsmark - IM., Department of Environmental Assessment, SLU, report 2006:12**:** 48pp (In Swedish with English summary).

Poleo, A. B. S., K. Ostbye, S. A. Oxnevad, R. A. Andersen, E. Heibo and L. A. Vollestad (1997). Toxicity of acid aluminium-rich water to seven freshwater fish species: A comparative laboratory study. Environmental Pollution **96**(2): 129-139.

SEPA (2002). Kalkning av sjöar och vattendrag (in swedish, English transl. "Liming of lakes and rivers"). Stockholm, Swedish Environmental Protection Agency.

Simonsson, M. (2000). Interactions of aluminium and fulvic acid in moderately acid solutions: stoichiometry of the H+/Al3+ exchange. European Journal of Soil Science **51**(4): 655-666.

Skyllberg, U. (1999). pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. European Journal of Soil Science **50**(1): 95-106.

Tipping, E. (1994). WHAM - A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Computers & Geosciences **20**(6): 973-1023.

Tipping, E. (2002). Cation binding by humic substances, Cambridge University Press.

Tipping, E., C. Woof and M. A. Harley (1991). Humic substances in acid surface waters; modelling Aluminium binding, contribution to ionic charge-blanace and control of pH. Water Research **25**(4): 425-435.

Ytrestoyl, T., B. Finstad and R. S. McKinley (2001). Swimming performance and blood chemistry in Atlantic salmon spawners exposed to acid river water with elevated aluminium concentrations. Journal of Fish Biology **58**(4): 1025-1038.

Zetterberg, T. and O. Westling (2005). Utlakning från kalkade avrinningsområden. Effektuppföljning ac Skogsstyrelsens program för kalkning och vitaliseringsgödsling ac skogsmark., IVL rapport B1642**:** 21pp (In Swedish).
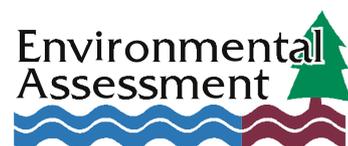
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II. Scenario Testing

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  Swedish University of Agricultural Sciences
  90183 Umeå

[2] Department Environmental Assessment
  Swedish University of Agricultural Sciences
  Box 7050   SE 750 07 Uppsala

Summary

A site specific calibration of the mechanistic equilibrium model WHAM is used here to test scenarios involving a systematic increase in surface water pH in five of the SKOKAL rivers. The effects of this pH increase on the concentration of inorganic Aluminium (Ali) are assessed from a toxicological view point. The modelling showed that increasing pH resulted in a reduction in the concentration of Ali in all the studied watercourses. With a pH increase of +0.5 and +1.0 pH units the fraction of Al bound to organic matter increased, with a larger pH increase (+2pH units) Ali moved into the anionic phase.

From a toxicological viewpoint, low initial pH and DOC (an active ligand in binding Al) meant that even with an increase of 1 pH units 4 of the 10 streams achieved conditions suitable for acid tolerant species, and only 3 of these were suitable for acid sensitive species. With a pH increase of 2 units, 8 of the streams had conditions suitable for acid sensitive species.

This calibration and modelling could act as a firm base from which modelling of Ali in the remaining SKOKAL sites could be possible.

Background

In the first part of this report (I. Calibration), we demonstrated that the mechanistic equilibrium model WHAM could be successfully calibrated to model inorganic Aluminium (Ali) in five of the SKOKAL watercourses. Both the modelled results and the analytically determined Ali concentrations showed only small differences in the Ali concentrations from the limed and reference streams. The speciation of Al is heavily dependant on two main factors; pH, and the present binding ligands, predominantly DOC. In these watercourses there is a relatively low concentration of DOC (median 11 mg/l), resulting in a large inorganic phase for Al. This is coupled with low pH conditions in both the limed and reference streams (median 4.68 and 4.48 respectively), means that cationic forms of inorganic Al dominate. It is elevated concentrations of these cationic forms of Ali which have been linked with toxic effects on aquatic organisms (Poleo, Ostbye et al. 1997; Brodeur, Okland et al. 2001; Ytrestoyl, Finstad et al. 2001).

Assuming that we can not change the DOC dynamics of the system, the remaining intervention that can be undertaking is to increase pH through liming. The current results of the SKOKAL liming project have shown only limited effects on Ali concentrations (see first report). This report presents results from the use of WHAM to assess the impact on Ali concentrations from different increases in pH. This will help in assessing the required level of intervention required to bring the streams back to conditions where acid sensitive species can survive. An important issue that is not discussed in this report is that under the Environmental Quality Objectives remediation projects for acidification should aim to return water systems to their pre-industrial condition, this may however be a naturally acidic system.

Modelling basis

The modelling of Ali in the five SKOKAL watercourses in this study follows the calibration work undertaken in the first report. For a more detailed description of the WHAM model we refer to the previous report.

The "scenario testing" presented is based on the assumption that the observed Altot and DOC time series are at relevant levels and a simplified modelling approach where pH can be changed and balanced by a change in Ca^{2+} and HCO_3^+ concentration to hold the charge balance neutral. pH was systematically increased by 0.5, 1.0 and 2.0 pH units and the resulting impact on the speciation of Al recorded. Presented here are the concentrations of Al^{3+} in µg/l. Although previous work has used the total concentration of cationic Ali so that publish toxicological limits can be used, the increasing of pH applied here exposes a limitation of the modelling software. The current WHAM software addresses the dissolved phases and does not allow for precipitation of Al at neutral charge ($Al(OH)_3$). This means that as pH increases we would have an over estimate of Ali^{n+} until pH was high enough for anionic forms to be present. In this application of the model the most toxicologically relevant speices is Al^{3+} and therefore results are shown for this species throughout this report.

As the exposure time for toxicological effects is relatively short, results are presented here for both peak values (90th percentile), as well as median values.

Results of modelling

Full results for each stream pair are given in Appendix 1. A summary of the results is presented below.

The modelling showed a consistent reduction in Al^{3+} concentration in all streams, both limed and reference (table 1). Reductions were seen in both the median concentration and the peak episodic concentrations. From a toxicological viewpoint, the episodic values are of more interest, and here reductions to levels below 50 µg/l (Ali limit for acid tolerant species) occurred only after a more significant increase in pH (>+1pH unit). After a 2pH unit increase low concentrations of Al^{3+} were seen in all but streams L24 and L24R. It should be noted that these are an optimistic estimate of the toxicology as Ali concentrations will be higher than the Al^{3+} results reported here.

Table 1 – Summary of modelling results. Background colouring defines different toxicological boundaries, green < 30 µg/l, orange 30-50 µg/l and red >50 µg/l.

Median		Current	+ 0.5 pH	+ 1.0 pH	+ 2.0 pH
G24	Limed	54	18	5	0
	Reference	154	88	34	1
O24	Limed	253	167	78	3
	Reference	253	177	93	5
P24	Limed	87	37	8	0
	Reference	12	3	0	0
R24	Limed	27	8	1	0
	Reference	128	79	28	1
L24	Limed	751	685	496	47
	Reference	684	665	649	372

Episodic (90th percentile)		Current	+ 0.5 pH	+ 1.0 pH	+ 2.0 pH
G24	Limed	134	74	22	1
	Reference	303	232	138	6
O24	Limed	479	382	257	17
	Reference	491	394	271	25
P24	Limed	199	106	31	0
	Reference	108	59	14	0
R24	Limed	161	90	20	0
	Reference	334	279	180	13
L24	Limed	1198	1070	847	261
	Reference	1111	1099	1088	766

(Both tables header: Al^{3+} (ug/l))

The reductions seen were due to an increase in the fraction binding to organic matter, a move to cationic forms of lower valency, and, in the higher pH ranges a move from cationic to anionic forms of Ali. Figure 1 shows the results for sites G24 and G24R as an illustration of the change in Al speciation. Both these sites show a decrease in Ali^{n+} with an increase in pH, this is compensated by an increase in the organic fraction for increases of 0.5 and 1 pH units. When the pH increase is sufficient to move in to the stable zone for anionc Al forms then $Al(OH)_4^-$ plays an important role.
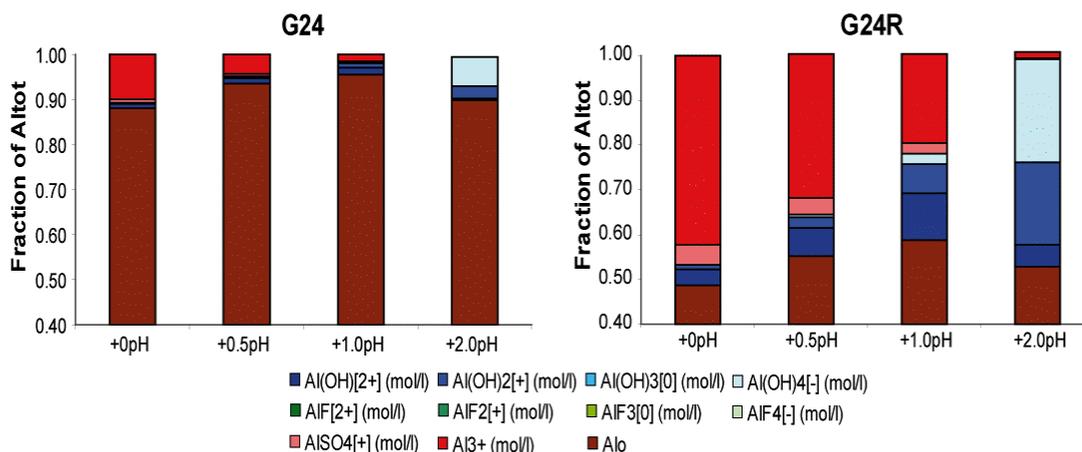
Figure 1 – Modelled Al fractionation for sites G24 and G24R, note scale on the y-axis and that Alo is still the dominant fraction.

Discussion

With current conditions none of the streams showed tolerable Al^{3+} concentrations during episodic conditions. A pH increase of >1pH unit was required to lower Al^{3+} concentrations in any of the streams to levels deemed toxicologically tolerable. In all but stream P24 the limed stream showed lower Al^{3+} concentration than the reference streams indicating a small but far from necessary positive effect of the forest liming program. In the limed streams, a higher binding capacity of Ali to fulvic acids have been shown (report I), which probably is the explanation for this.

There are two important areas of the modelling which should be given attention. Firstly the results presented here must be seen as optimistic because Al^{3+} data is presented instead of Ali^{n+} data. Although Al^{3+} has the highest valency, the other cationic fractions will also play a role in determining the total toxicological impact. However, limitations of the model prohibit us at this time from predicting the complicated solid / dissolved phase interactions including mineral precipitation which occur as the pH moves through the zone where Al is neutrally charged.

The second area which must be considered is the flux of Altot from soil to stream. Al solubility as well as ion exchange is strongly pH related and therefore an increase in pH should theoretically lead to a fall in the flux of Al moving into the stream. This has been seen in MAGIC modelling of the recovery for heavily acidified in the Czech Republic where a 38% reduction in Altot was predicted (Hruska, Moldan et al. 2002). Except for a more stepwise drop in Altot in 1998/99 in stream G24, O24 and to some extent L24 (report I), similar results have not been seen in observed data in Sweden. Data from the Aneboda and Gårdsjön catchments show no significant changes in Altot despite increases in pH (Löfgren 2006) . In this study, Altot has been held constant with increasing pH, and based upon the practical observation from Gårdsjön and Aneboda this is justified assuming pH increases of 0,2-0,3 pH-units. However, at such large pH increases as assumed in this report it is most probable that the Altot leakage from the soils would be reduced and our results might therefore give a too conservative estimate of possible Ali reductions.

Other factors which are not assessed here could be the impact of different forestry practices affecting pH and DOC in runoff. Any measure reducing DOC or pH would enhance the Ali fraction as long as the leakage of Altot is constant.

Further work

The calibration of WHAM to modelling of Ali in these ten SKOKAL streams and the subsequent scenario testing has given us an insight into the Al dynamics of the water courses. With an established calibration, the obvious extension of this work would be to model Ali concentrations in the other five SKOKAL streams and other environmental monitoring sites such as the PMK5 streams where Altot but not Ali is available. Similar scenario testing would give us a much broader view of the impacts of

current liming intervention, and the extent of liming required to reduce Ali concentrations below toxic limits.

The effects of a speculative reduction in Altot with increasing pH could also be assessed through systematic variations in the concentrations of Altot.

References

Brodeur, J. C., F. Okland, B. Finstad, D. G. Dixon and R. S. McKinley (2001). Effects of subchronic exposure to aluminium in acidic water on bioenergetics of Atlantic salmon (Salmo salar). Ecotoxicology and Environmental Safety **49**(3): 226-234.

Hruska, J., F. Moldan and P. Kram (2002). Recovery from acidification in central Europe - observed and predicted changes of soil and streamwater chemistry in the Lysina. catchment, Czech Republic. Environmental Pollution **120**(2): 261-274.

Löfgren, S. (2006). Integrerad övervakning ac miljötillståndet i svensk skogsmark - IM., Department of Environmental Assessment, SLU, report 2006:12**:** 48pp (In Swedish with English summary).

Poleo, A. B. S., K. Ostbye, S. A. Oxnevad, R. A. Andersen, E. Heibo and L. A. Vollestad (1997). Toxicity of acid aluminium-rich water to seven freshwater fish species: A comparative laboratory study. Environmental Pollution **96**(2): 129-139.

Ytrestoyl, T., B. Finstad and R. S. McKinley (2001). Swimming performance and blood chemistry in Atlantic salmon spawners exposed to acid river water with elevated aluminium concentrations. Journal of Fish Biology **58**(4): 1025-1038.

G24

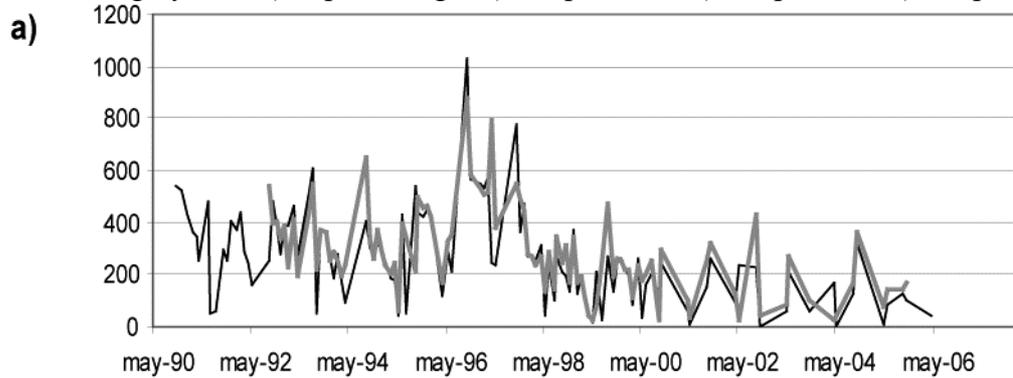Modelled Al^{3+} concentrations in µg/l.G24 shown with a single black line, G24R with a thicker grey line. a)no pH change, b)+0.5pH units, c)+1.0pH unit, d)+2.0pH units.
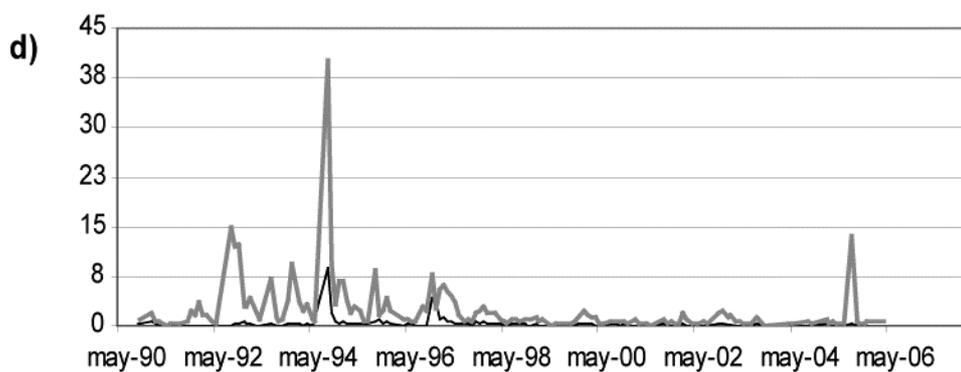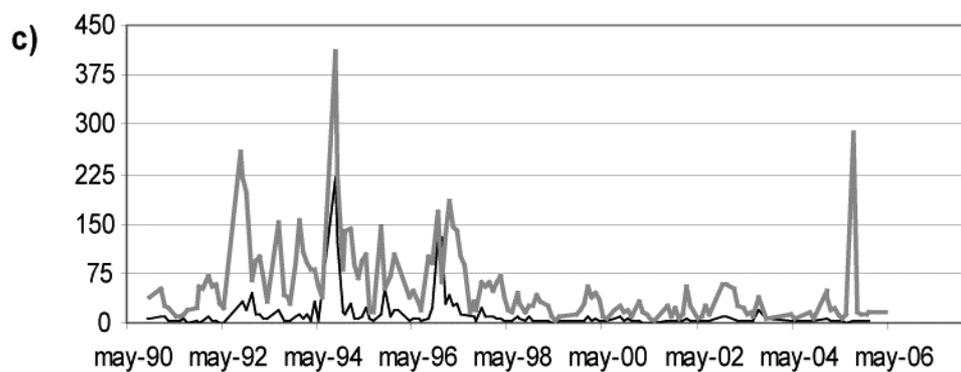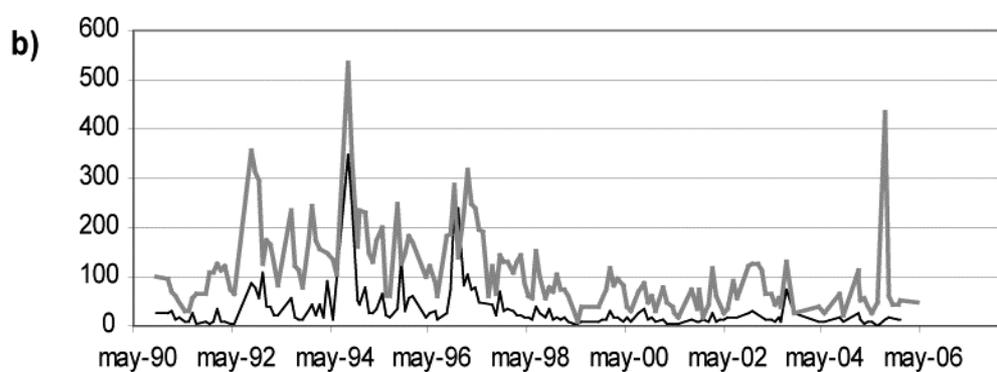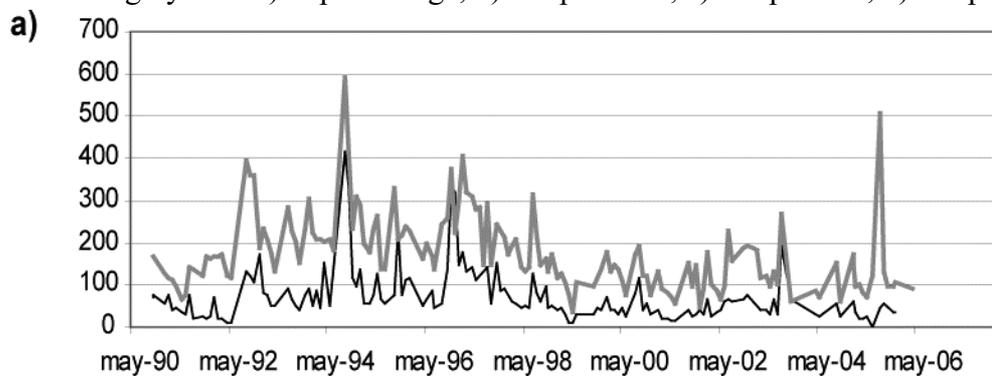
O24

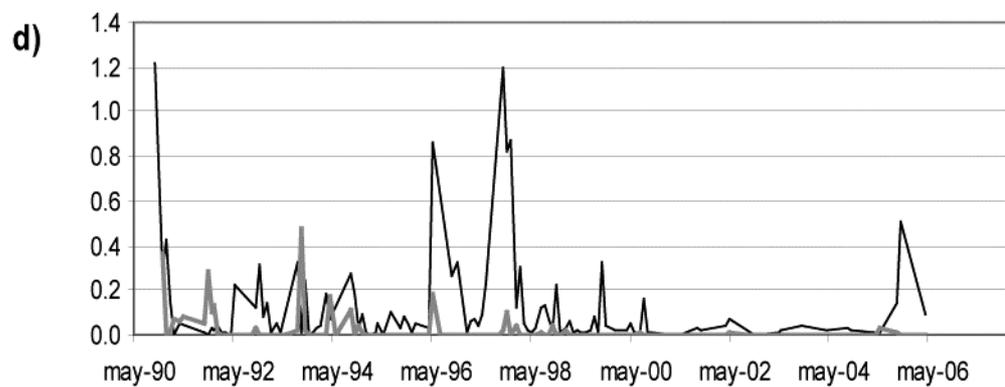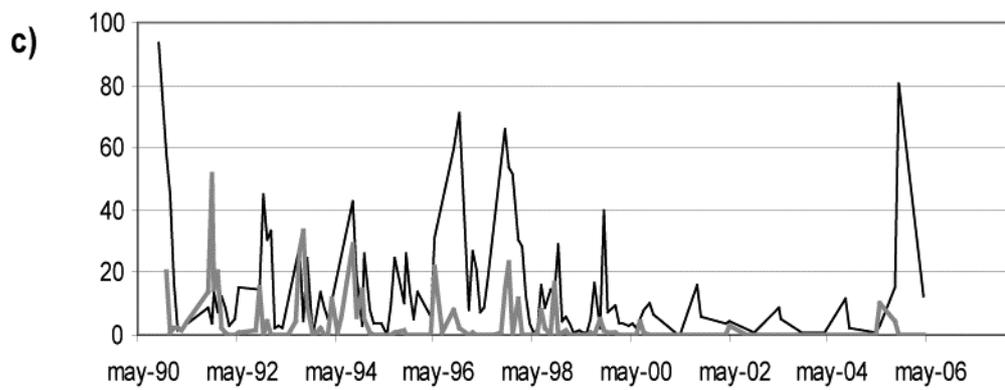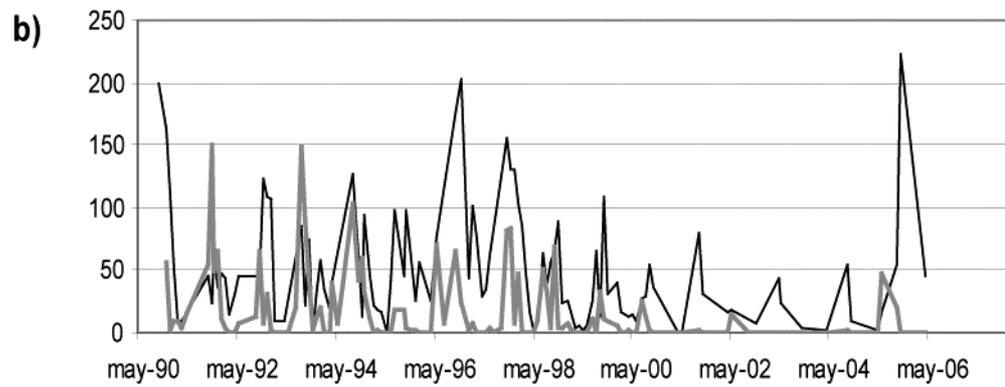Modelled Al^{3+} concentrations in µg/l.O24 shown with a single black line, O24R with a thicker grey line. a)no pH change, b)+0.5pH units, c)+1.0pH unit, d)+2.0pH units.
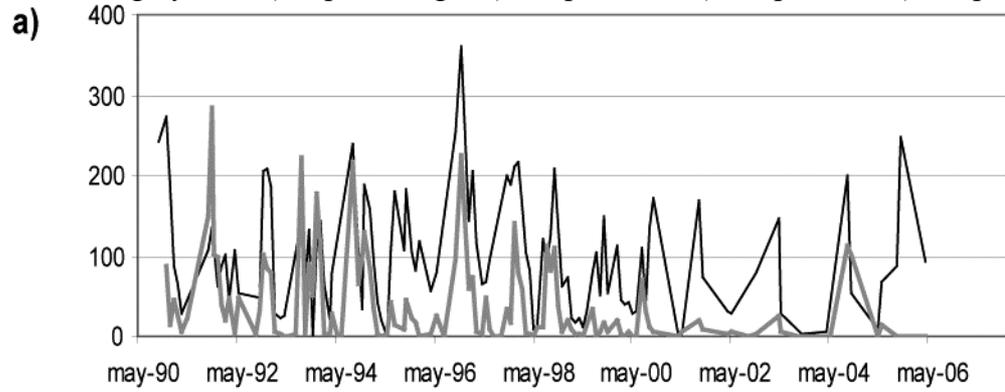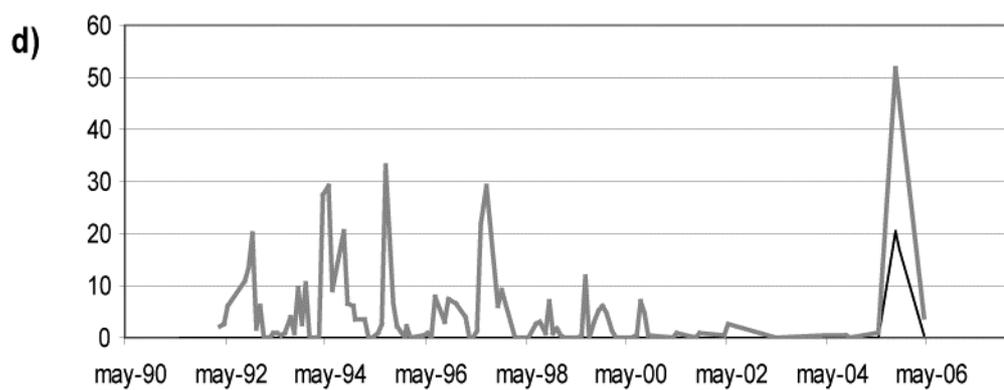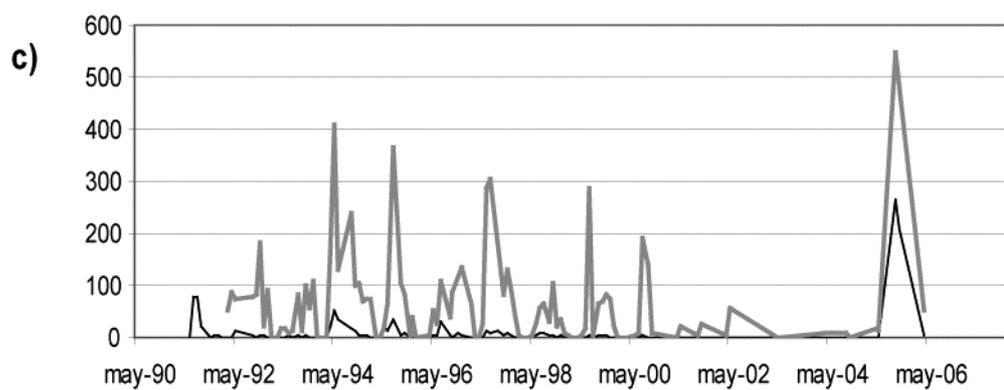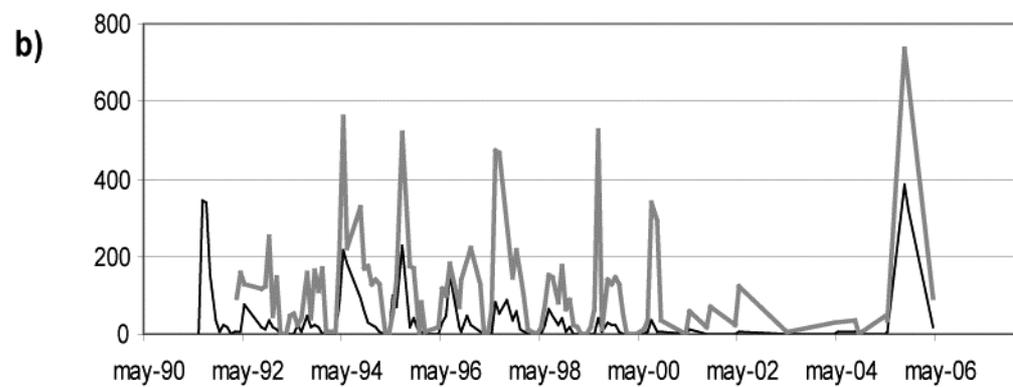

7
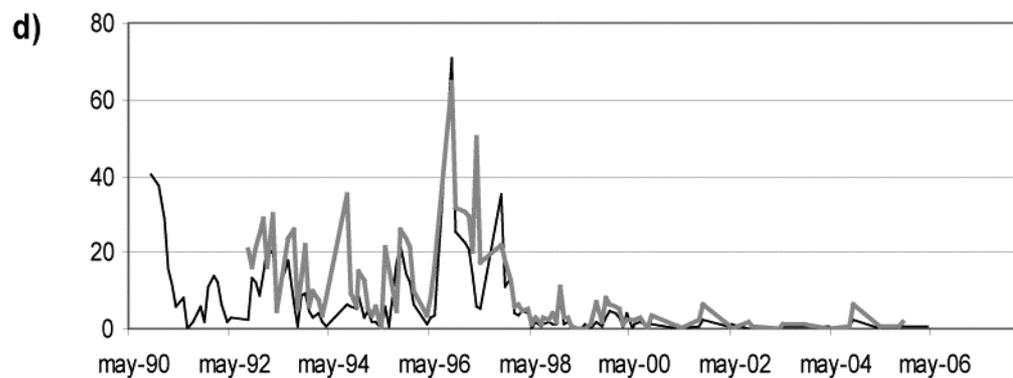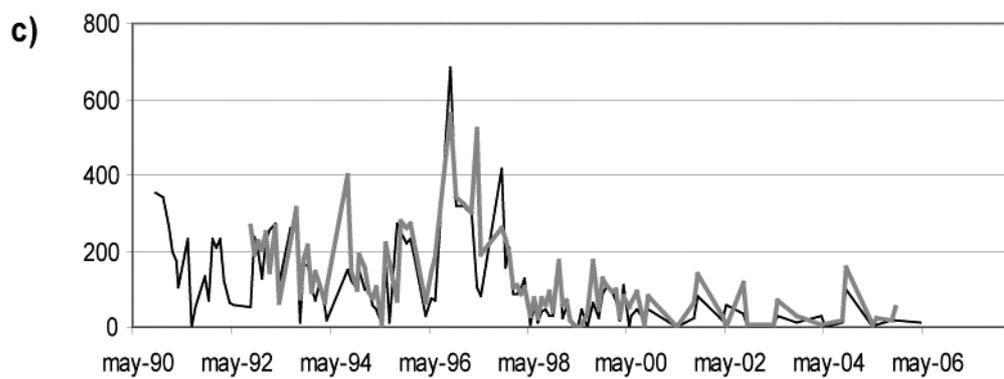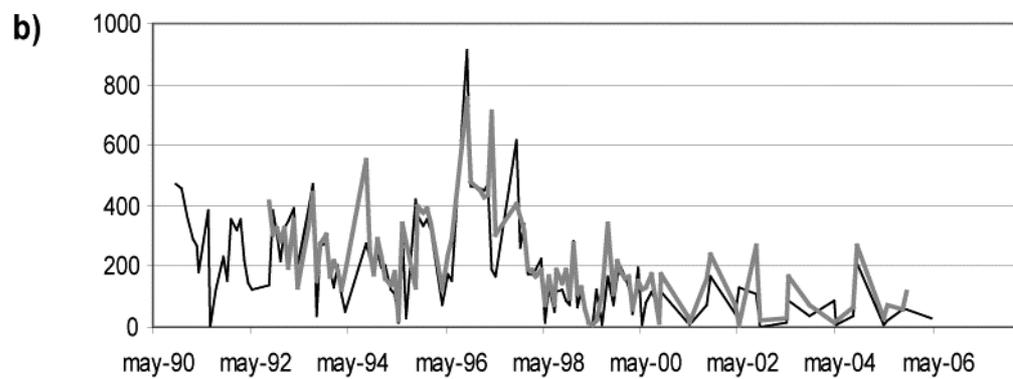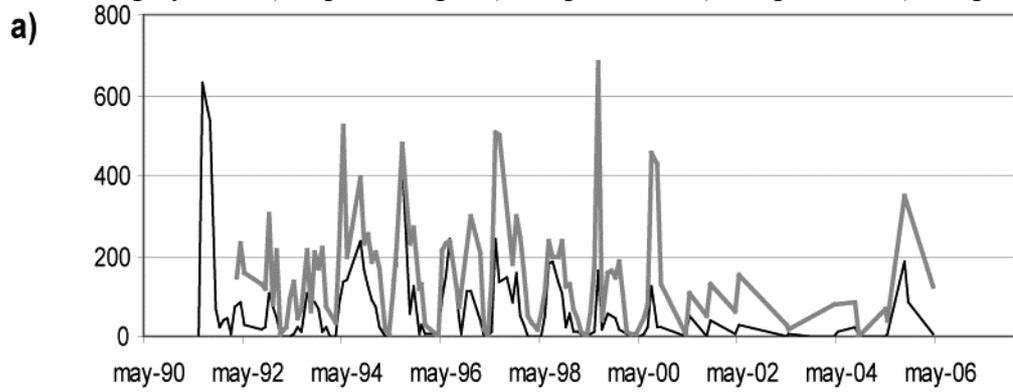
P24

Modelled Al^{3+} concentrations in µg/l. P24 shown with a single black line, P24R with a thicker grey line. a)no pH change, b)+0.5pH units, c)+1.0pH unit, d)+2.0pH units.

a)

b)

c)

d)

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R24

Modelled Al^{3+} concentrations in μg/l. R24 shown with a single black line, R24R with a thicker grey line. a)no pH change, b)+0.5pH units, c)+1.0pH unit, d)+2.0pH units.

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L24

Modelled Al^{3+} concentrations in µg/l. L24 shown with a single black line, L24R with a thicker grey line. a)no pH change, b)+0.5pH units, c)+1.0pH unit, d)+2.0pH units.