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Trace metal concentrations in acidic, headwater streams in Sweden explained by chemical, climatic, and land use variations

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Abstract

Long term data series (1996–2009) for eleven acidic, headwater streams (<10 km²) in Sweden were analyzed to determine factors controlling concentrations of trace metals. In-stream chemical data as well climatic, flow, and deposition chemistry data were used to develop models predicting concentrations of chromium (Cr), lead (Pb), and zinc (Zn). Data were initially analyzed using partial least squares to determine a set of variables that could predict metal concentrations across all sites. Organic matter (as absorbance) and iron related positively to Pb and Cr while pH related negatively to Pb and Zn. Other variables such as conductivity, manganese, and temperature were important as well. Multiple linear regression was then used to determine minimally adequate prediction models which explained an average of 35 % (Cr), 52 % (Zn), and 72 % (Pb) of metal variation across all sites. While models explained at least 50 % of variation in the majority of sites for Pb (10) and Zn (8), only three sites met this criterion for Cr. Investigation of variation between site models for each metal revealed geographical (altitude), chemical (sulfate), and land use (silviculture) influences on predictive power of the models. Residual analysis revealed seasonal differences in the ability of the models to predict metal concentrations as well. Expected future changes in model variables were applied and results showed the potential for long term increases (Pb) or decreases (Zn) for trace metal concentrations at these sites.

1 Introduction

Trace metals are naturally present in atmospheric, terrestrial and aquatic environments; however, anthropogenic impacts have affected availability and cycling greatly. Efforts in understanding processes controlling mobility of trace metals in running waters are increasing with implementation of the European Water Framework Directive, especially given that such understanding is critical to assessing potential impacts from metals on the hydrosphere and in separation of natural and anthropogenic impacts on availability

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and variability. While rivers with large, generally urban catchments or polluted streams have been well studied, headwater streams have received less attention, especially with respect to metals chemistry.

Headwaters are an important resource for biodiversity and human welfare (Lowe and Likens, 2005; Bishop et al., 2008) mainly because they cover a substantial portion of the watercourse length, providing a large proportion of water and solutes to downstream sites (Alexander et al., 2007). This is especially true in Sweden where streams with catchment sizes less than 10 km² make up approximately 90 % of the total length of all perennial watercourses in Sweden (Bishop et al., 2008). It is widely known that variability in water quality is related to catchment size with small catchment watercourses typically showing the highest variability in both space (Wolock et al., 1997; Temnerud and Bishop, 2005) and time (Nagorski et al., 2003; Buffam et al., 2007). Significant efforts have been made to quantify the variability of headwaters (Rawlins et al., 1999; Likens and Buso, 2006) but few studies discussing trace metals in Scandinavian headwaters have been published even though the boreal Northern Hemisphere is rich in these types of systems.

Cycling of trace metals is complex because many factors influence metal behavior including biotic and abiotic chemical processes, hydrology, climate, land use and the properties of the metals themselves. A general regulator of mobility, pH affects the solubility of many metal ions. However, other factors can affect the mobility and transport of metals to and within surface water systems. Organic matter (OM) mineralization and chemical processes (e.g. changes in ionic strength) can alter metal solubility and mobility (Landre et al., 2009; Porcal et al., 2009). The form of metal (e.g. dissolved, colloidal, or particulate) may also be an important factor when describing temporal variation of metal concentrations (e.g. lead “Pb” and zinc “Zn”) in surface waters (Sherrell and Ross, 1999; Ross and Sherrell, 1999). The different factors affecting trace metal mobility may explain confounding evidence of increasing metals (e.g. Pb) in some streams in Sweden (Huser et al., 2011) even as deposition of metals has been decreasing since the 1970s (Ruhling and Tyler, 2004).

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The aim of this study is to determine factors that can predict trace metal variability in small, acidic headwater streams in Sweden. In-stream chemical, climatic, and land-use characteristics likely affect trace metal concentrations together or in part, depending on the metal and its specific reactivity. Although metal mobility may relate to numerous factors, we attempt to explain variability using a few dominant variables. A unique long-term chemical data series (1996–2009) for the streams is available and was used to develop predictive models describing changes in chromium (Cr), Pb, and Zn concentrations in these streams. Site specific models are then compared to large scale chemical, land use, climatic and geographic variables to determine if differences in explanatory power of the models can be explained. Predicted future changes in metal concentrations, based on recent trends in model variables, are discussed as well.

2 Methods

2.1 Study area

The streams included in this study are situated across Sweden (Fig. 1) and the data time series ranged from 1996 through 2009. Only monitoring sites that were not directly influenced by point sources (e.g. wastewater treatment plants, mining facilities, industrial plants, etc.) were included in the analysis. This initial group of monitoring sites totaled 139 streams that were included in a study to determine long-term trends for metals in streams and rivers in Sweden (Huser et al., 2011). From these sites, streams that had maximum catchment size of 10 km² and a median pH value less than 6.0 were selected (11 sites) because metals generally tend to be mostly in the dissolved form under these conditions (Köhler, 2010; Sjöstedt et al., 2009).

To further analyze data spatially, the country was divided into two regions based on the “*limes norrlandicus*” ecotone which divides Sweden into a southern nemoral and boreo-nemoral zone and a northern boreal and alpine zone (Fig. 1). Climate also

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varies between the regions with the major difference, outside of ecosystem type, being the southern region is warmer than the north. Thus, the *limes norrlandicus* represents the approximate boundary separating areas where flow is low during winter with pronounced snowmelt in spring (the north) and flow is more or less continuous during the year with little to no accumulation of snow during winter (south).

2.2 Data collection and chemical analysis

All in-stream data were collected as part of the national monitoring program and downloaded from the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences (<http://www.slu.se/vatten-miljo>). All metals were analyzed at the same laboratory using ICP-MS and the same analytical methods, all accredited by the Swedish Board for Accreditation and Conformity Assessment (SWEDAC), were used during the time period of the study (1996–2009). Details on methods, detection limits, quality control and other information for the study metals and other parameters can be found at the website referenced above. Data analyzed include total concentrations of trace metals Cr, Pb, and Zn along with potential drivers including in-stream chemical, climatic, flow, deposition chemistry, and land-use data. Deposition chemistry data were downloaded from the Swedish Environmental Research Institute (http://www3.ivl.se/miljo/db/IVL_luft_registersida.htm) where information on quality assurance and control and methods are available. Most data were log transformed due to negative skew affecting normality, however, some variables (percent land use and absorbance and flow ratios) were arcsine, square root transformed due to their binomial nature.

Flow values were determined on a daily basis using the hydrological catchment HYPE (Hydrological Predictions for the Environment) model for Sweden (SHYPE) and data were downloaded directly from the Swedish Meteorological and Hydrological Institute (SMHI, <http://homer.smhi.se/>). The SHYPE model simulates water and substances from precipitation through soil, river, and lakes to the catchment outlet (Lindstrom et al., 2010). Catchments are divided into sub-basins (median = 18 km²) which grouped into

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classes depending on land use, soil type and elevation. If the monitoring location for metal and chemistry data was not located at the outlet, a ratio of catchment areas between the catchment outlet and monitoring point was used to adjust modeled flow.

In order to separate base flow from total flow for each stream, a FORTRAN program called Base Flow Index (USGS, Colorado) was used for base flow separation. The program implements a deterministic procedure that combines a local minimums approach with a recession slope test (Hydrology, 1980). The method may not yield the true base flow but the index has been found to be consistent and indicative of base flow, and can be useful for analysis of long term trends. The Institute of Hydrology separation method was used along with a partition length (N , number of days over which a minimum flow is detected) and turning point test factor (F , no units) of 3 and 0.9, respectively (Wahl and Wahl, 1995). As N is increased from a low value (e.g. 1), peak flows are eliminated from the pool of potential turning points. Once a critical N -value is reached, all peak flows are theoretically eliminated. Thus, the drop in estimated base flow becomes less pronounced and any further increase in N will result in an underestimate of actual base flow. The point of slope change indicates an appropriate value for N in most cases. For example, if watershed related runoff from a storm event takes two to three days to pass through the system, the point of slope change would be approximately $N = 3$.

Temperature and precipitation were collected from the PTHBV database where observations from SMHI meteorological stations were used to interpolate values for a 4×4 km grid using a geostatistical method developed by Johansson (2002). Runoff was modeled using HBVSweden, which is a rainfall-runoff model that has been in use since the 1970s and includes conceptual numerical description of hydrologic processes at the catchment scale. It has been successful applied to small scale plots (Lindstrom and Rodhe, 1992) as well as entire drainage basins (Baltic Sea, Bergstrom and Carlsson, 1994).

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2.3 Statistical analysis

Monthly data were available for all sites. Outliers were considered in the analysis (on an individual stream basis) and data were excluded if the measurement was at least two times higher than other measurements in the data set and the filtered (Abs_f) versus unfiltered absorbance (Abs_{uf} , at 420 nm) for the sample did not indicate elevated particulates (i.e. ratio greater than 0.9), meaning there was some sort of analytical error, sample contamination, or unusual natural conditions. These outliers were later entered back into the data set to determine if they could be predicted using the models developed herein. Between 0 and 2 % of samples at each site (1 % overall average) were considered outliers using this definition. Less than detection limit values were treated by dividing the detection limit by two. The number of values that were lower than the detection limit in the chemistry data set was low (between 0 % and 2.3 %) for all parameters included in this study.

Most data were log10 transformed except for factors with a binomial distribution. 45 independent variables were initially included in the dataset for each metal; however, ten variables with high bivariate correlations (>0.8) were excluded from analysis to reduce instability in the matrix inversion due to multicollinearity (Table 1). Seven variables only varied between sites (land use, altitude and latitude) and were not used in individual site analysis. Abs_f was used as a proxy for total organic carbon ($TOC \text{ mg l}^{-1} = 4.3 + 32.4 \times Abs_f$, $r^2 = 0.88$, RMS error = 2.6) which eliminated correlations between TOC and Abs_f , Abs_{uf} , and iron (Fe). The remaining 28 independent variables were used in partial least squares (PLS) modeling using SIMCA+ (Umetrics V. 12.0.1.0). PLS creates a linear model by projecting predicted and observed variables in a new space using a latent variable approach to model the covariance structure between two matrices (\mathbf{X} and \mathbf{Y}) and maximize the correlation between \mathbf{X} and \mathbf{Y} variables. PLS was used as an initial step to reduce the number of parameters used in multiple linear regression (MLR) modeling based on the variable importance for the projection (VIP). VIP values are calculated for each independent variable by summing the squares of the PLS

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weights, which are weighted by the amount of the dependent variable explained in the model. A set of common variables was determined by including terms that had strong prediction effects ($VIP \geq 0.9$) in more than 50 % of the individual PLS site models. This group of terms was then used in MLR analysis.

After reducing the number of independent variables via PLS, MLR analysis was performed and a single, minimally adequate model (common model) with greater generality was developed for all sites. Dominant variables were substituted into the model until the average of individual site variances explained increased by less than two percent (all values as adjusted r^2). After common models were developed for each metal, residual analysis was conducted to detect potential outliers, extreme values or other factors that could bias the results of model fitting. The common model for each metal was then applied to the entire data set and expected future changes in model variables were applied to predict future concentrations of each metal.

3 Results

The sites included in this study (Fig. 1) were generally comparable in terms of water chemistry and land use (Table 2). Median trace metal concentrations (Table 3) varied between streams but were less variable than other in-stream parameters with minimum to maximum ratios of 2.8, 5.2, and 4.5 for median Cr, Pb, and Zn, respectively. In total, 28 independent variables were used in the modeling process with results described below.

3.1 PLS analysis

PLS analysis was conducted to determine which of the independent variables were most strongly related to each metal. Variables at this level of analysis included in-stream chemical, deposition, flow, and climatic data (Table 1). To determine if factors such as suspended particles or flow conditions might influence the results strongly,

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PLS analysis was conducted on the entire dataset for each metal using two conditions which set limitations on the data included in the analysis including: only low suspended particulate matter ($Abs_f/Abs_{uf} > 0.9$, 66 % of total data) and only low runoff or base flow dominated periods (base flow/total flow > 0.9 , 64 % of total data). In some cases, PLS models with limited data decreased in predictive power when compared to models using all data. If a model did improve, however, explained variation generally increased by less than 5 % (data not shown). Thus, the entire data set was used for modeling purposes for each metal.

PLS modeling by individual site for Cr, Pb, and Zn showed varying importance for the 28 variables used in the study. Of the most dominant variables with VIP scores ≥ 0.9 (Table 4), Abs_f and aluminum (Al), related positively to all metals while sulfate (SO_4) related negatively. Temperature (Temp) was also a dominant variable that related positively to Cr concentrations but was mixed (positively and negatively related) for Pb and Zn. Pb and Zn were negatively related to pH while Cr and Pb were positively related to Fe. Cr was negatively related to nitrate-nitrite (NO_2/NO_3) and Zn was positively related to conductivity (Cond). These variables and others listed in Table 4 were used in MLR analysis detailed below.

3.2 Multivariate linear regression analysis

MLR analysis for Pb included 8 terms (dominant variables with $VIP \geq 0.9$) from the initial PLS analysis. Site specific MLR resulted in a common model including Abs_f , Fe, and pH (Fig. 2) with ten of the eleven sites having greater than 50 % of variance explained (Table 5). Two examples of model fit for monitoring data are provided in Fig. 4. Ringsmobäcken ($r^2 = 0.40$) was the only site that did not follow the general pattern detected at the other sites. No combination of independent variables (all 28 were tested) could explain more than 50 % of the variation for Pb at Ringsmobäcken. Investigation of residuals of model fit for the common model revealed a distinct break in the dataset beginning in 2007 where residuals skewed to the negative and residual

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variance decreased substantially. While variance explained in the data improved somewhat when the common model was applied only to data before 2007 ($r^2 = 0.44$), it improved substantially when applied to data from 2007–2009 ($r^2 = 0.66$). It is unknown why there is such a substantial difference between these two periods but the potential exists for a change in sampling personnel, equipment, or monitoring location within the stream reach.

The initial MLR model for Zn included 11 terms with VIP scores >0.9 in the PLS analysis (Table 4). Development of the common model (Fig. 2) from site specific MLR analysis resulted in three dominant terms (pH, Cond, Mn) and provided generally good explanation ($>50\%$) of variability in Zn for eight of the eleven sites (Table 5). Similar to Pb, analysis of model fit for Ringsmobäcken revealed a distinct change beginning in 2007 when overall model variance decreased and residuals were no longer centered but negatively skewed. Common model application to the split time series revealed no improvement to model fit from 1996–2005 ($r^2 = 0.24$) but substantial improvement when the model was applied to more recent data from 2007–2009 ($r^2 = 0.59$). Aneboda IM, a site just downstream from a wetland that was also poorly described by the common model ($r^2 = 0.01$), did not show any obvious long-term temporal changes throughout the time series but appeared to be affected by seasonal changes in flow. Analysis of the common model residuals by month (data not shown) revealed better model fit during March and April, months typically with higher flow due to spring melt. Additional residual analysis confirmed this with higher flows generally resulting in lower model residuals.

MLR analysis for Cr included 11 terms ($VIP \geq 0.9$) from initial PLS modeling. Although there were 11 variables that were present in at least 50% of the PLS site models, the standard errors for VIP factors was generally much higher than for Zn or Pb (Table 4), indicating higher variability in the ability of the variables to predict Cr concentrations. In contrast to Pb and Zn, site specific MLR models were generally poor at explaining variations in Cr concentrations in the 11 streams. The common model (Table 5) explained greater than 50% of variance at only three of the eleven sites (35%

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average). Due to the low predictive power of the common model, all 28 variables were included in a second attempt using MLR to find an adequate model but no increase in variance explained was found and the original variables used above remained the best possible factors for the common model.

5 3.3 Variation in model predictive power by site and season

Investigation of the differences in variability explained between site models revealed chemical, climatic, geographical, and land use effects on site model predictive power. Medians of the values used in the initial PLS models (excluding the variables making up the common models) along with land use and geographical data were used in MLR regression to determine if any relationships could be found within variance explained (r^2) between the sites. Relationships between variance explained and SO_4 and harvested area (both positively correlated) for Pb ($r^2 = 0.87$) and Si and altitude (positively and negatively correlated, respectively) for Cr ($r^2 = 0.81$) were detected (Fig. 4). No pattern for model predictive power between sites was detected for Zn.

To determine seasonal variability in predictive power of the common models, means of the model residuals were compared by month (Fig. 5). Residuals for Pb generally skewed negatively during the fall and winter seasons (September through December) while Zn model residuals skewed negatively from November through February. Both Zn and Pb model residuals were positively skewed from late spring into the summer months. Residuals for Cr showed no trend by season.

4 Discussion

PLS was used to screen 28 chemical, flow, deposition chemistry, and climatic variables to develop a set of dominant variables for use in MLR analysis to develop common models describing variation in Cr, Pb and Zn in small catchment, acidic streams in Sweden.

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Common models were developed for the three metals by analyzing site specific data and then applied to the data set as a whole.

4.1 Parameters controlling metal concentrations

Mobility and form of all metals in this study are affected by stream chemistry (to varying degrees). The strongest chemical predictors were organic matter (Abs_f) and pH and it is well known that that these two parameters are related to trace metal mobility in surface waters. Cr, Pb, and Zn have been shown to interact strongly with dissolved organic carbon (DOC) or TOC in streams (Landre et al., 2009; Gundersen and Steinnes, 2003), generally increasing overall mobility. Abs_f appears to control much of the within site variation for Pb (and to a lesser extent Cr) correlating positively to metal concentration. Both pH (negatively correlated) and Fe (positively correlated) were also important components in the common model for Pb. The strong relationship between Pb and Fe and Abs_f is not unexpected as others have shown similar results (Pokrovsky and Schott, 2002) and organo-metallic complexation is a well known phenomenon (e.g. Weng et al., 2002). However, Tipping et al. (2002) suggested that Fe (as well as Al) can act as a competitor with metals for common binding sites on OM. Wällstedt et al. (2010) instead postulated that increasing Fe-colloid formation was responsible, at least in part, for increasing trace metal concentrations (i.e. V and As) in streams across Southern Sweden. While Fe was a dominant factor among site models, it explained only 8% additional variation (average across site models) in Pb concentration after pH and Abs_f were added to the model (64% of variation explained). However, the importance of Fe varied across sites and was positively correlated to the Fe/TOC (or Abs_f) ratio in the streams. Thus, while Fe was of lesser importance when predicting Pb variation across sites on average compared to Abs_f , it became more important as the Fe/TOC ratio increased above 0.04.

The weaker relationship (relative to Abs_f) between Pb and pH supports other studies showing that effects of acidification are relatively minor in comparison to changes in DOC with respect to Pb transport (Neal et al., 1997; Tipping et al., 2003). This was

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not the case for all sites in this study. For example, if pH and Abs_f at Pipbäcken Nedre (median pH 4.7) increased by 10 % and 20 % respectively, Pb concentrations would be expected to decrease by approximately 4.1 %. If we take a look at a less acidic site (Svartberget, median pH 5.1), however, the same increase in pH and Abs_f results in an increase (12 %) in average Pb concentration. Although this is a hypothetical scenario, it appears that in very acidic streams, pH exerts more influence on Pb concentrations while at higher pH (but still acidic), organic matter exerts more control. In support of this, data for filtered and unfiltered metal concentrations at 24 stream sites in Sweden (including five of the sites included herein) showed 85 to 100 % of Pb detected was in dissolved form at pH values less than 4.8 (Köhler, 2010). From pH 4.8 to pH 6.0, dissolved Pb was as low as 39 % of the total concentration, indicating organic or colloid bound Pb fractions were more dominant.

The most common variables determined for Zn with PLS analysis were pH (10 sites), Mn (10 sites) and Cond (9 sites). pH was negatively related to Zn while Cond and Mn were positively related. Other factors not included in the final common model included Fe and Al (significant factor at 9 sites). While Zn has been shown to bind with OM in freshwaters, the affinity of Zn for binding sites is lower than that found for other metals (Bergkvist et al., 1989). In addition, Zn is generally found in mostly dissolved form under a wide range of pH values (Gundersen and Steinnes, 2003), including streams in Sweden (Köhler, 2010). Thus, the fact that pH explains a large amount of Zn variation in these streams is not surprising. The strong positive relationship between Cond and Zn concentrations is also not surprising given that metal solubility is positively related to ionic strength of a solution (Helz et al., 1975). Mn, nearly as important for the common model as Cond, is more difficult to explain but may relate to Zn concentrations in a number of ways. Zn tends to solubilize under both low pH and redox conditions (Sims and Patrick, 1978). Mn, being redox sensitive, may be an indicator of low redox conditions and is generally first to become reduced compared to a number of other potential electron acceptors ($Mn > NO_3^- > Fe > SO_4^{2-}$). In support of this is the inverse relationship between Mn concentrations and both flow and runoff at eight of eleven

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5 sites indicating greater chance for low redox conditions and Mn reduction under low flow conditions. However, the positive relationship between Mn and Zn could also be a dilution of groundwater inputs containing Mn and Zn (Carpenter and Hayes, 1978) under high flow conditions but it is difficult to discern the true nature of the relationship between these two elements without additional data (i.e. redox or groundwater input). MnO₂ dissolution and release of adsorbed Zn could be expected with decreasing pH but Mn and pH appear to operate independently, at least in these streams, because there was no general relationship detected between the two variables.

10 Only three of the eleven sites were adequately described by the common model for Cr. The chemistry of Cr is complex due to multiple oxidation states, the potential effects of stream chemistry, and interactions with both organic and inorganic constituents. Another factor that may limit the understanding of Cr in these streams is the prevalence of relatively low Cr concentrations. The median values for Cr at the study sites are considered either low or very low for Sweden (Swedish EPA, 1999) and it can be difficult to generalize overall processes driving Cr concentrations at these levels. Analytical variability may overwhelm natural in-stream variation at low concentrations making determination of controlling processes difficult. Nonetheless, at the three sites where greater than 50% of variance was explained, either Abs_f and/or Fe were significant, positively correlated factors in the common model. These three sites also had the smallest catchments in the study (between 0.19 and 0.52 km²). With larger catchments including a high percentage of surface water (e.g. lakes) the controlling mechanisms for Cr may be more complex. Reduction of Cr (VI) to the less mobile Cr (III) is generally favored in systems with higher organic matter (Bartlett, 1991) and Cr (III) tends to be more stable at low pH (Richard and Bourg, 1991). Organic matter (e.g. DOC), however, has been shown to increase the pH range of solubility for Cr (III) in laboratory tests (Remoundaki et al., 2007). Increasing temperature, the final term in the common model, has been shown to lead to increases in DOC (Dalva and Moore, 1991), potentially increasing solubility of Cr. However, given the poor explanatory power of the model, it is difficult to generalize about factors that control Cr concentrations in these streams.

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4.2 Common model applied to all data

The common model developed by assessing dominant factors across individual site models was applied to the entire dataset for each metal. Results were similar when comparing the average r^2 of the individual site common models for Zn and Cr to the common model applied to all data (Table 3). The comparison for Pb, however, was substantially different with the common model underperforming when applied to the dataset as a whole. Variability in predictive power between Pb site models was explained well ($r^2 = 0.86$, $p = 0.001$) by median sulfate concentration and Silva (Fig. 4) with no other parameters significantly ($p < 0.05$) contributing to variability explained. The relationship between sulfate and predictive power of the models likely represents an acidification signal, with variability explained increasing as median sulfate increases. Erlandsson et al. (2008) showed TOC concentrations in some Swedish streams were driven partly by SO_4^{2-} , which may indicate that Pb concentrations in areas affected by anthropogenic acidification would be better predicted using a model including organic matter. Three sites with some of the lowest r^2 values (excluding Ringsmobäcken) were all located north of the limes norrlandicus divide (Fig. 1) and receive less sulfate deposition than stations located further south (Ruhling and Tyler, 2004), supporting the importance of SO_4 on model performance. Silva was also positively correlated with model variance explained and may indicate changes in degradation and mobility (or type) of organic matter and associated Pb (Vuori et al., 2003).

Variability in predictive power for Zn models could not be explained between sites (with or without Aneboda IM being included), likely meaning that the relationship of the common model variables to Zn between sites is less affected by large scale differences (e.g. land use, climate, etc.). The similarity between average variability explained by site and variability explained in the entire dataset using the common model seems to support this. Variability in Cr site model predictive power was explained well ($r^2 = 0.81$, $p = 0.0031$) by differences in median Si (positively correlated, 55%) and altitude (negatively correlated, 26%). Further interpretation is not presented, however due to the overall poor performance of the common model.

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4.3 Seasonal variability

Median model residuals by month for Pb and Zn were generally close to zero but some seasonal patterns were detected (Fig. 5). Model residuals for Pb skewed negatively in the fall to early winter period (September–December), meaning the model over predicts the actual Pb concentration in the streams. This time of year is generally wetter, especially in Southern Sweden, with decreasing temperatures. While wetter conditions can increase the transport of carbon to streams (Erlandsson et al., 2008) the data for study sites herein show the opposite with higher flow and runoff correlating to lower Abs_f (or TOC). The type of OM exported to the streams during this period may affect Pb transport and mobility, but no information exists in the dataset to assess this hypothesis. Residuals skewed to the positive and variability increased during summer months which are typically drier and base flow tends to be a larger portion of the total flow. Both median Abs_f and Fe increase (by almost a factor of two) during summer at these sites while pH increases to a lesser extent (0.2 units). Reduced transport of watershed sources of Pb along with varying types of OM present (e.g. greater autochthonous production) would likely lead to over prediction by the model (negative residuals) which is not the case here. Because Pb and Zn residuals were generally similar, especially during the summer, low flow period, we theorize that some process or processes not included in the models may be responsible. One possible explanation for positive residuals for both Pb and Zn during summer may be resuspension of sediments under low flow conditions. Median Abs_f/Abs_{uf} values were lowest (i.e. higher particulates) during summer under low flow conditions and wind or sampling activity may have disturbed bottom sediments during sample collection. An alternative explanation may be that the higher percentage of groundwater in the streams (base flow/total flow was highest during summer) led to a relatively higher amount of solutes in the streams. Without additional data on metal partitioning, however, it is difficult to speculate further on the reasons behind the similar seasonal trends for Pb and Zn residuals.

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4.4 Model applicability to peak values and outliers

Model variance was equally distributed compared to dependent variable concentrations and thus models were able to predict values close to the mean as well as peak or extreme values for Pb and Zn. In cases where a number of peak values (but not by definition outliers, as indicated in the methods) for any of the metals were present at a site, these values were excluded (whether model fit was good for these points or not) and MLR analysis was conducted again to determine if these values unproportionally influenced amount of variability explained in the model. For example, three elevated values for Pb (between 1.14 and 1.76 $\mu\text{g l}^{-1}$) at Kindlahöjden (median Pb = 0.38 $\mu\text{g l}^{-1}$) were excluded and the amount of variation explained decreased somewhat but remained high (r^2 of 0.83 versus 0.93). Of the others sites for Pb where extreme values were removed (Aneboda IM, Pibäcken Nedre) decrease in variation explained was low (less than 5 %) or a slight increase was detected (Sågebäcken). When MLR analysis was conducted after peak removal for Zn at three sites where elevated peaks were detected (Aneboda IM, Ringsmobäcken, Sågebäcken), variation explained improved although only marginally (<5 %) at each site. The analysis of the common models for Pb and Zn shows that the variables are able to predict not only values near the median but peak or extreme values near an order of magnitude higher than the median for both metals.

The models were also applied to outliers that were removed from the dataset before analysis began. One data point for Pb was removed as an outlier from the original dataset for Kindlahöjden IM before analysis. When this value was entered back into dataset (Fig. 6), the common model under predicted the actual value by 38 % and the value had a z-score (number of standard deviations from the mean) higher than 3, indicating it is likely an outlier as originally suspected. One Zn data point was removed from the dataset for Svartberget (Fig. 6) and when it was included, the common model prediction was within 8.6 % of the actual value. Even though the Zn concentration had a z-score ($z = 4.6$) greater than 3, this value is probably not an outlier, at least based on the common model developed for Zn.

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4.5 Past trends and future changes in metal concentrations

Many of the variables included in the common models developed for Pb and Zn have shown long-term, consistent changes in the past and are likely to continue to change in the future. According to Moldan et al. (2004), pH values have increased (from the 1970s) and are expected to increase further in many acidified systems in Sweden over the next 20 yr due to reduced deposition of acidifying compounds. Although the study by Moldan et al. (2004) focuses on lakes, similar trends were also found for streams in Sweden (Fölster and Wilander, 2002). Based on these data, at least seven of the eleven streams included in our study appear to be acidified relative to 1860 (Table 2) and pH is expected to increase over the next 20 yr. DOC levels have generally increased in Sweden from 1990–2004 (Monteith et al., 2007) and may continue to do so in the future. In a large scale study (139 streams across Sweden), Huser et al. (2011) showed long-term (1996–2009) increasing trends for pH, Fe, TOC and decreasing trends for conductivity in streams and rivers in Sweden. Because the study by Huser et al. (2011) included streams in our study, the long term trends were used to estimate future changes in common model variables to predict potential changes in Pb and Zn (Table 6) in 10 sites included in this study (excluding Ringsmobäcken). Trends for all Pb and Zn model variables (except Mn) were available. Using Theil slopes (% change yr^{-1}) from the Huser et al. (2011) trend data, all sites showed decreasing Zn concentrations caused by increasing pH and/or decreasing conductivity. Three of these sites (Kindlahöjden IM, Lill-Fämtan, and Pipbäcken Nedre) were previously shown to have decreasing trends in Zn concentration from 1996–2009 (Huser et al., 2011). These three sites also had the greatest 20 yr predicted future changes in Zn (greater than $1.5\% \text{yr}^{-1}$) based on the common model developed in this study.

Pb concentrations are expected to increase over the next 20 yr (1.3 to 57.3 %) based on trend data for pH, Fe, and TOC (used as a proxy for Abs_f , $r^2 = 0.88$); however, the model results showed decreasing concentrations for three of the sites. These sites either had significant trends only for pH (Gammtratten IM, Pipbäcken Nedre) or had

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5 a relatively low median pH (Aneboda IM) compared to the other sites. As discussed previously, it appears that in very acidic streams (i.e. median pH < 5), pH likely exerts a greater effect on Pb concentration compared with other parameters due to the high amounts of non-colloidal, dissolved Pb. Sites previously shown to have long term decreasing (Pipbäcken Nedre) or increasing (Svartberget) trends (Huser et al., 2011) showed similar trends for expected future changes in Pb concentrations based on the common model developed herein. Although we show expected future trends for Zn and Pb, care should be taken when interpreting the results because the extrapolation of future changes in model variables is based on recent trends (1996–2009) that may or may not continue into the future.

5 Summary

15 Long term data series (1996–2009) for eleven acidic, small catchment streams in Sweden were analyzed to develop predictive models able to explain variability for trace metal concentrations. Models developed for Pb (pH, Abs_f, Fe) and Zn (pH, Cond, Mn) explained more than 50 % of metal variation for most sites while the model developed for Cr was poor and further explanation into potential drivers was not possible. The dependence of Pb on the model variables was not surprising, given that others have shown similar results for other types of water courses. On the other hand, OM has previously been shown to control Zn mobility, but described little to no variation in Zn concentrations and was not included in the common model. This is probably due, at least in part, to the acidic nature of the study streams. Model variance was equally distributed compared to the dependent variable concentrations and thus models were able to predict values close to the mean as well as peak or extreme values for Pb and Zn. In some cases, when suspected outliers were added back in to the dataset, it appeared they were naturally high values and model fit was good while in other cases they were likely outliers probably caused by contamination, laboratory error, or some other problem. Model variance did vary by season, indicating changes in factors such as

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flow regime, sediment resuspension, or DOC mobility and type may alter the prediction level of the models and further research into the mechanisms behind these seasonal differences is warranted. When model parameters were adjusted to reflect potential future scenarios for variables such as Ab_{sp} , pH, and Cond both increases (Pb) and decreases (Zn) were generally seen for the streams included in this study. The results are able to explain the sometimes confounding evidence between decreasing metals deposition over the past 30 yr and increasing concentrations for metals like Pb in some streams in Sweden and may be useful for predicting future problems relating to issues such as toxicity and water quality standards for metals in this region.

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Table 1. Variable information and % missing values (from a total of 1689). All data log transformed except pH and where indicated (*).

Variable	Description	Unit	% missing
Abs _{uf} *	Filtered/unfiltered Abs		0.0
Abs _f	Filtered absorbance	420 nm 5 cm ⁻¹	0.0
Abs _{uf} **	Unfiltered absorbance	420 nm 5 cm ⁻¹	0.0
Al	Total aluminum	µg l ⁻¹	0.8
Alk**	Alkalinity	mekv l ⁻¹	0.1
Alt	Altitude	m.a.s.l.	0.0
BF*	Baseflow	m ³ s ⁻¹	0.0
BF/F*	Baseflow/total flow		0.0
Ca**	Calcium	mekv l ⁻¹	0.0
Cl**	Chloride	mekv l ⁻¹	0.3
Cond	Conductivity	mS/m25	0.0
Cr	Chromium	µg l ⁻¹	28.6
F	Fluoride	mg l ⁻¹	0.3
Fe	Iron	µg l ⁻¹	2.0
Flow	Total flow	m ³ s ⁻¹	0.7
Forest*	Forest	% total area	0.0
K	Potassium	mekv l ⁻¹	0.3
Mg	Magnesium	mekv l ⁻¹	0.0
Mn	Manganese	µg l ⁻¹	2.8
Na**	Sodium	mekv l ⁻¹	0.0
NH ₄	Ammonia	µg l ⁻¹	0.0
NO ₂ NO ₃	Nitrate-nitrite	µg l ⁻¹	0.0
Pb	Lead	µg l ⁻¹	13.9
pH	pH		0.0

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Table 1. Continued.

Variable	Description	Unit	% missing
Precip	Precipitation	mm	0.7
Runoff	Runoff	mm	0.4
Si	Silica	mg l ⁻¹	0.0
Silva*	Harvested area	% total area	0.0
SO ₄	Sulfate	mekv l ⁻¹	0.4
Temp	Temperature	K	0.0
TN	Total nitrogen	µg l ⁻¹	0.0
TOC**	Total organic carbon	mg l ⁻¹	20.4
Total Area	Watershed area	km ²	0.0
TP	Total phosphorus	µg l ⁻¹	0.1
Water*	Surface water area	% total area	0.0
Wetland*	Wetland area	% total area	0.0
Y	Latitude		0.0
Zn	Zinc	µg l ⁻¹	14.5
Parameters measured in direct precipitation			
H+	Hydrogen	µekv m ⁻²	16.9
Cl**	Chloride	mg m ⁻²	16.0
NO ₃ **	Nitrate	mg m ⁻²	16.4
SO ₄	Sulfate	mg m ⁻²	16.0
NH ₄	Ammonia	mg m ⁻²	16.1
Ca	Calcium	mg m ⁻²	16.2
Mg	Magnesium	mg m ⁻²	16.5
Na**	Sodium	mg m ⁻²	16.2
K	Potassium	mg m ⁻²	16.2
Cond**	Conductivity	mS m ⁻¹	16.1

* Square root, arcsine transformed.

** Removed due to multicollinearity (correlation factor >0.8).

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Table 2. Selected site parameters (medians), land use (% area), estimated anthropogenic acidification (ΔpH) since 1860, and future expected recovery (ΔpH future) for each stream by 2030 except where no data (ND) is indicated.

Name	Area (km ²)	pH	ΔpH	ΔpH future	Cond (mS cm ⁻¹)	SO ₄ ²⁻ (meq l ⁻¹)	TOC (mg l ⁻¹)	Fe ($\mu\text{g l}^{-1}$)	Wetland	Open Water	Forest	Harvested	Other
Aneboda IM	0.19	4.51	-1.22	+0.11	5.8	0.147	18.7	910	15	14	54	5	11
Bråtångsbäcken	5.75	4.73	-1.55	-0.07	3.4	0.068	16.8	600	7	2	85	7	0
Gammtratten IM	0.52	5.64	-0.23	+0.03	1.7	0.042	7.5	357	1	0	99	0	0
Kindlahöjden IM	0.24	4.58	-1.46	+0.14	3.1	0.107	7.4	292	0	0	100	0	0
Kvarnebäcken	6.98	5.18	-1.26	+0.12	3.6	0.066	9.9	410	12	6	78	4	0
Lill-Fämtan	5.95	4.79	-0.36	+0.03	1.7	0.034	9.6	355	5	3	91	0	1
Lommabäcken Nedre	1.06	4.43	ND	ND	3.7	0.070	16.1	455	3	4	92	0	0
Pipbäcken Nedre	1.35	4.78	-1.25	-0.02	5.2	0.100	7.9	989	37	3	51	9	0
Ringsmobäcken	1.82	4.40	ND	ND	4.4	0.055	12.6	315	15	5	77	3	0
Sågebäcken	4.40	4.87	-1.17	+0.03	4.6	0.073	15.5	960	13	4	72	9	1
Svartberget	1.94	5.13	-0.64	+0.01	2.9	0.091	19.8	1200	20	2	74	4	0

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Table 4. Dominant independent variables (present in more than 50% of PLS site models) with VIP factors ≥ 0.9 . *N* = number of sites where model variable was included and SE = VIP standard error.

	Cr			Pb			Zn		
	<i>N</i>	VIP	SE	<i>N</i>	VIP	SE	<i>N</i>	VIP	SE
Abs _f	9	1.8	0.53	11	2.0	0.24	7	1.4	0.28
Al	9	1.6	0.76	11	1.6	0.30	9	1.6	0.38
Cond	7	1.2	0.77				9	1.6	0.38
Fe	11	1.9	0.43	11	1.9	0.33			
Flow							6	1.1	0.25
K	8	1.3	0.49				6	1.2	0.31
Mg	6	1.3	0.88				7	1.4	0.27
Mn				7	1.2	0.44	10	1.5	0.42
NO ₂ NO ₃	7	1.1	0.70						
pH				7	1.2	0.37	10	1.5	0.35
Runoff							6	1.0	0.26
SO ₄	10	1.4	0.52	8	1.4	0.24	9	1.3	0.32
Temp	9	1.2	0.48	8	1.1	0.29	7	1.2	0.25
TN	6	1.2	0.81						
TP	6	1.5	0.45	7	1.3	0.36			

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Table 5. Step-wise multiple linear regression models and variance explained (r^2) by site and using all data. Statistically significant variables are shown in order of importance (absolute value of the t -ratio).

Name	Pb ¹		Zn ²		Cr ³	
	r^2	Terms	r^2	Terms	r^2	Terms
Aneboda IM	0.93	Abs _f , pH	0.01		0.75	Fe
Bråtångsbäcken	0.85	Abs _f , Fe, pH	0.59	Mn, C, pH	0.26	Fe
Gammtratten IM	0.54	Fe, pH	0.56	pH, Mn, C	0.74	Fe, T
Kindlahöjden IM	0.84	Abs _f , pH, Fe	0.75	C, pH	0.70	Abs _f
Kvarnebäcken	0.70	Fe, pH	0.54	C, Mn	0.13	Fe, Abs _f
Lill-Fämtan	0.59	Abs _f , pH, Fe	0.45	Mn, C, pH	0.15	Fe, T
Lommabäcken Nedre	0.62	Abs _f , pH	0.56	Mn, C, pH	0.16	Fe
Pipbäcken Nedre	0.88	Abs _f , pH, Fe	0.59	C, pH	0.33	
Ringsmobäcken	0.40	pH, Abs _f , Fe	0.24	Mn, pH	0.07	Fe
Sågebäcken	0.79	Fe, Abs _f	0.74	C, Mn, pH	0.24	Fe
Svartberget	0.77	Abs _f , pH, Fe	0.66	pH, Mn, C	0.31	Fe, T , Abs _f
Average	0.72		0.52		0.35	
All data ⁴	0.52		0.55		0.35	

¹ Pb model terms Fe, Abs_f, pH.

² Zn model terms pH, Cond (C), Mn.

³ Cr model terms Fe, Abs_f, Temp (T).

⁴ Model applied to all data available for each metal instead of by individual site.

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Table 6. Predicted changes (Δ % Total) in Pb and Zn during the next 20 yr based on previous long-term trends (1996–2009, Huser et al., 2011) for common model variables (pH, TOC, Fe, and Cond) shown as % change per year (Δ % yr⁻¹). TOC was used as a proxy for Abs_f. Aneboda IM was excluded from Zn analysis (NA) due to low model power. NT = no significant trend detected.

Stream	Δ % yr ⁻¹				Δ % Total	
	pH	TOC	Fe	Cond	Pb	Zn
Aneboda IM	0.28	NT	1.9	-2.0	-5.1	NA
Bråtängsbäcken	0.34	2.3	3.5	-2.1	31.7	-21.4
Gammtratten IM	0.27	NT	NT	NT	-9.1	-21.9
Kindlahöjden IM†	0.36	2.0	2.6	-3.4	1.3	-78.7
Kvarnebäcken	NT	NT	2.0	NT	10.0	0.0
Lill-Fämtan†	0.34	3.1	4.1	-2.7	30.5	-43.3
Lommabäcken Nedre	0.30	3.1	3.3	-2.3	28.0	-20.9
Pipbäcken Nedre*†	0.58	NT	NT	-2.3	-4.1	-30.1
Sågebäcken	NT	NT	1.8	NT	18.8	0.0
Svartberget*	NT	3.5	NT	-2.3	57.3	-16.7

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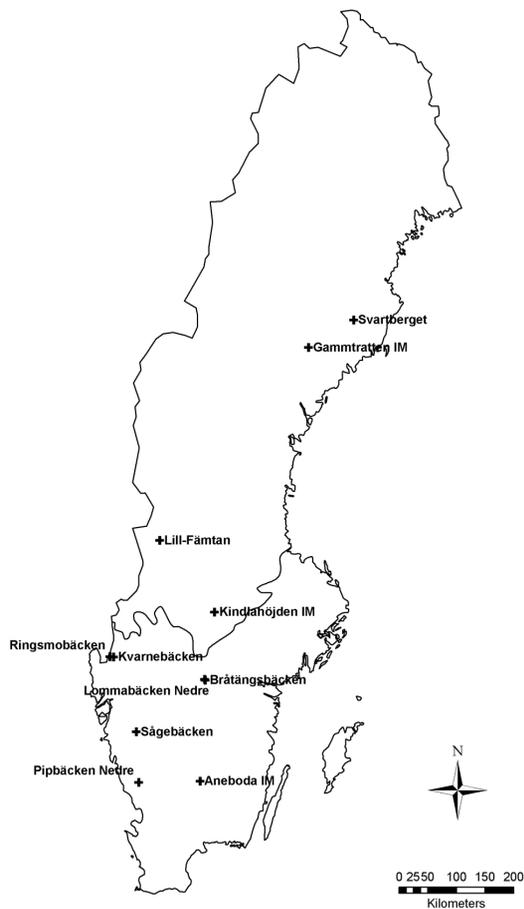


Fig. 1. Stream sites and the *limes norrlandicus* boundary separating Sweden into northern and southern climactic region.

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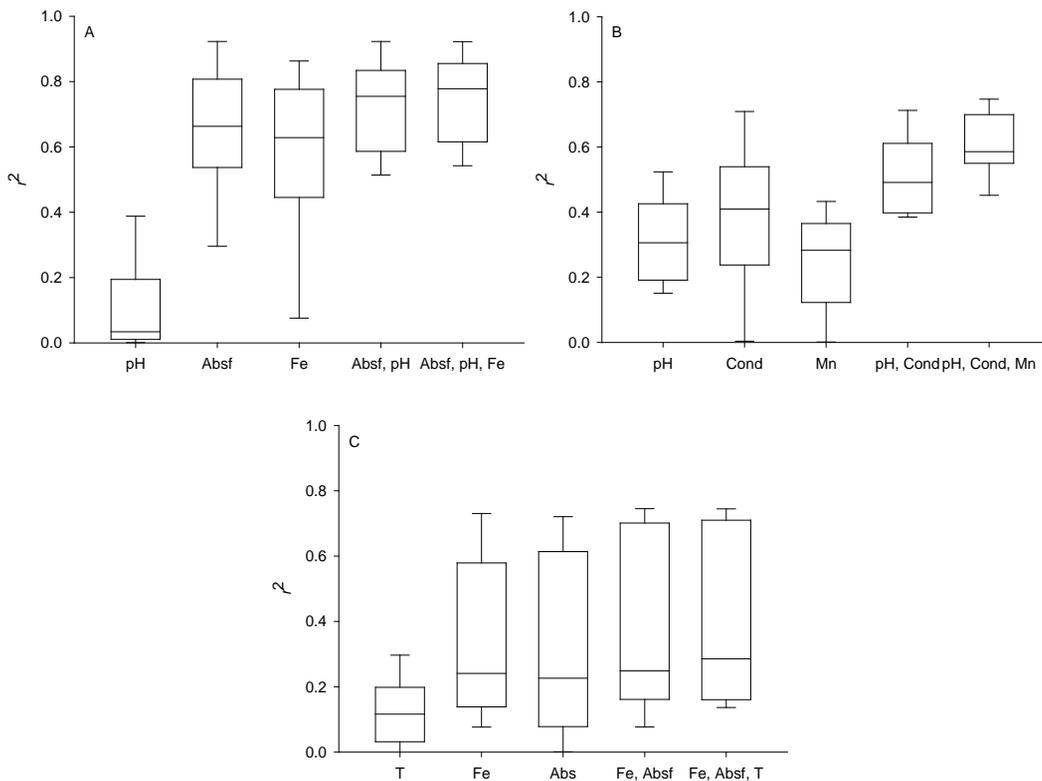


Fig. 2. Variables included in each common model for Pb (A), Zn (B, Aneboda removed), and Cr (C). Box plots are shown with medians, 25 and 75th quantiles and 10 and 90% quantiles (whiskers).

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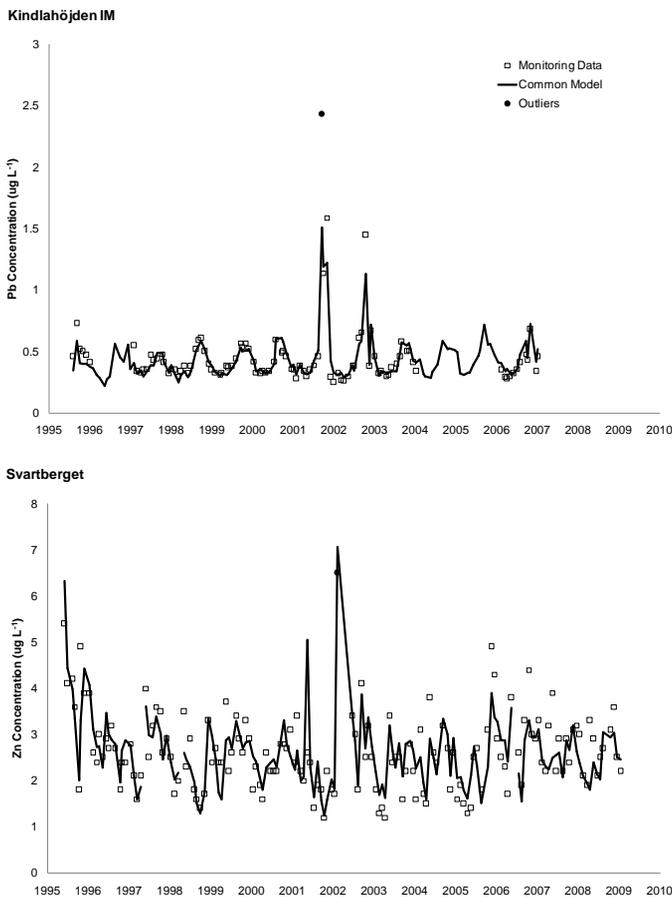
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Fig. 3. Monitored and modeled data for Zn and Pb from selected sites. Data originally excluded from analysis as outliers are shown as well.

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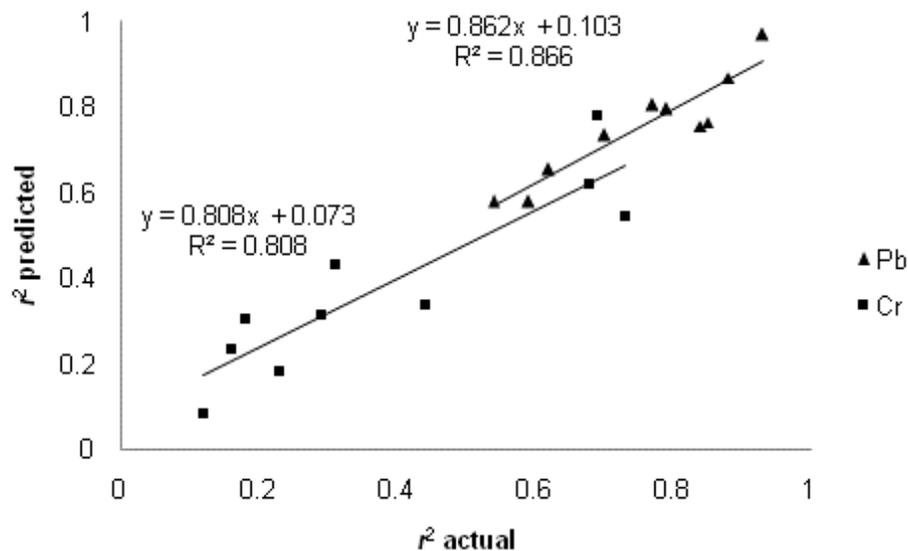


Fig. 4. Actual variance explained by the common model for each site versus predicted variance based on SO_4 and Silva (Pb) or Si and Alt (Cr). Ringsmobäcken was excluded from the analysis.

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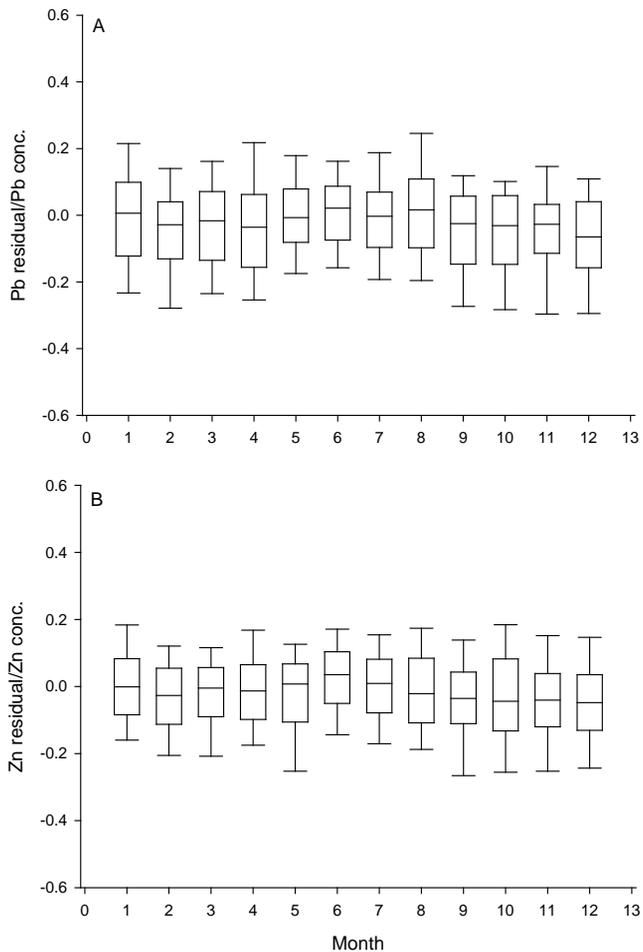


Fig. 5. Model residuals (untransformed, excluding Aneboda for Zn) by month for Pb **(A)** and Zn **(B)**.