

Can the distribution of headwater stream chemistry be predicted from downstream observations?

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Abstract:

Small streams with catchment areas <2 km² make up the majority of all stream length and are of great ecological importance. Surveys of first and second order streams reveal great spatial and temporal variability in the water chemistry of these headwaters, but their assessment presents a serious challenge since systematic, representative data are usually only collected in larger streams and rivers. Using low flow synoptic survey data from seven mesoscale Swedish catchments, this study tests the hypothesis that downstream monitoring data can be used to predict key features of the distribution of chemistry in headwater streams [median and interquartile range (IQR)]. Three ecologically relevant analytes were tested: pH, acid neutralizing capacity (ANC) and total organic carbon (TOC). For all seven catchments, the outlets (36–127 km²) were considerably less acid with lower TOC than the median of the headwaters (<2 km², $N = 19$ –45). Among catchments, headwater median and IQR were positively correlated with the value at the outlet, for all three analytes. A univariate general linear model (GLM) was used to predict the headwater chemistry distribution for each catchment from its outlet chemistry, using the relationship established with the other six catchments. Headwater median pH and IQR of ANC were well predicted by a single downstream sample [median adj. $R^2 \sim 0.7$, normalized root mean squared error (NRMSE) <0.7]. Other response variables were not as well predicted, with median adj. R^2 ranging from 0.08 to 0.48, and NRMSE up to 1.1. A minority of models were significant at $\alpha = 0.05$, in part due to the limited availability of catchments with such extensive survey data. However, the clear trends observed suggest that with additional model development, downstream chemistry could ultimately provide a valuable tool for characterizing the range of chemistry in the contributing headwaters. Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

The importance of headwaters as a resource for biodiversity and human welfare is increasingly recognized (Lowe and Likens, 2005; Bishop *et al.*, 2008). One of the reasons is that headwaters make up most of the watercourse length and hence provide a large proportion of water and solutes to downstream locations (Person *et al.*, 1936; Leopold *et al.*, 1964). In Sweden, for example, streams with catchment size <2 km² make up approximately 80% of the total length of all perennial watercourses (Nisell *et al.*, 2007). Studies of the biota in headwaters have also found them to be important for biodiversity, in part because of species endemic to headwaters (Meyer *et al.*, 2007).

It is widely known that variability in water quality changes with catchment size, typically with small watercourses showing the highest variability in space (Wolock *et al.*, 1997; Temnerud and Bishop, 2005) and time (Nagorski *et al.*, 2003; Buffam *et al.*, 2007). Significant efforts (e.g. Hutchins *et al.*, 1999; Smart *et al.*,

2001; Likens and Buso, 2006) have been made to quantify the variability of headwaters. One of the most notable recent studies is the US EPA's 'Wadeable Stream Assessment' (WSA) (US European Protection Agency, 2006). The WSA was a statistically valid survey of the biological condition of small perennial streams at the continent scale based on 1 : 100 000 scale maps. But since many first and second order streams are not found on maps of this scale, headwaters are likely to be considerably underrepresented even in that survey.

In spite of these recent efforts, headwater stream ecosystems are not systematically documented, and it is rare to find either the current status or degree of human influence satisfactorily quantified in the multitude of headwaters (Gergel *et al.*, 1999; McGlynn *et al.*, 2004). This observation led Bishop *et al.* (2008) to describe headwaters as 'Aqua Incognita'. The absence of systematic coverage of headwaters results in part not only from a bias in environmental monitoring towards larger watercourses, but also from the sheer magnitude and complexity of the problem. These challenges do not make the need to better characterize headwaters any less urgent. For instance, the European Union Water Framework Directive clearly states that all waterbodies should be considered in evaluating the status of the environment.

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A pertinent question, however, is whether there are any practical methods for making such a characterization.

Readily derived GIS data from maps and satellite images have been used to model some chemical constituents in larger rivers (Alexander *et al.*, 2007), but are seldom effective at modelling headwater chemistry (Strayer *et al.*, 2003a,b; Temnerud, 2005). This is presumably in large part due to the greater importance of small-scale heterogeneity in headwater catchment characteristics, as compared to riverine catchments where much of the variability averages out at larger spatial scales. One example of a difficult-to-estimate catchment variable whose heterogeneity contributes to variability in water chemistry is the thickness of the soil. In addition, recent studies have indicated that downstream chemistry is frequently not just the average of headwater chemistry (Wolock *et al.*, 1997; Temnerud *et al.*, 2007; Buffam *et al.*, 2008), suggesting that map-based models built using large streams/catchments may not be directly transferable to small streams.

An alternative way to characterize the situation in headwaters is to model the distribution of headwater chemistry based on available monitoring data from further downstream (e.g. Bishop *et al.*, 2008). This study tests the hypothesis that the chemistry measured at a single outlet location in a mesoscale catchment is correlated with the distribution [median and interquartile range (IQR)] of key water chemistry parameters in the headwaters of the same catchment. To do this, we have used a dataset of synoptic surveys of acid neutralizing capacity (ANC), total organic carbon (TOC) and pH from seven mesoscale catchments ranging from 36 to 127 km² in size. We present correlation analyses and predictions for headwater distributions.

METHODS

Sampling approach

The synoptic surveys used in this study were designed to provide a snapshot of the water chemistry in the stream networks during low flow conditions (Table I and Figure 1). In total, there are data from seven synoptic surveys conducted between 2000 and 2007 distributed

across Sweden (Figure 2). These sites span a north–south gradient of 800 km through the north-temperate and boreal zones. All sampling during a given survey was carried out during a 1–3 day period when weather and flow conditions were relatively stable in June or October.

All of the catchments have at least one upstream headwater site that has been monitored for runoff and chemistry regularly for a decade or more (Edström and Rystam, 1994; IM, 2008; Köhler *et al.*, 2008; Löfgren, 2008; Temnerud *et al.*, 2009), except for R. Ottervattsbäcken and R. Sörbäcken which have been sampled twice and once, respectively (Temnerud and Bishop, 2005; Temnerud *et al.*, 2007). For the sites with monitoring sites, stream flow was at <25th percentile relative to the long-term record. For two sites without stream flow measurements, stream flow was judged to be <25th percentile based on regional flow conditions.

Study sites

Headwaters are defined as first order streams smaller than 2 km² in each of the seven drainage networks sampled (Table I). All catchments consisted mainly of forest (>80%) with a dominance of Norway spruce (*Picea abies*). Mires and small humic lakes made up most of the remaining parts of the catchments, while the proportion of agricultural and developed areas was minimal (<1%). The mean annual air temperature in the catchments ranged from 7 °C in the southernmost catchment, R. Anråse å, to 1.7 °C in the northernmost, Krycklan. Mean annual rainfall and runoff ranged from 1050 and 550 mm, respectively at R. Anråse å, to 612 and 323 mm at R. Krycklan. For R. Anråse å, median altitude with maximum and minimum in brackets is 89 m (11–147), R. Lugnån 206 (166–247), R. Danshytteån 206 (122–311), R. Getryggsån 279 (182–338) and R. Krycklan 243 (126–369).

Chemical analyses

After collecting, all water samples were kept dark and cool until they were analysed. pH was measured shortly after returning to the laboratory using a Ross 8102 low-conductivity combination electrode (ThermoOrion) and diluted buffers. TOC was measured by combustion and

Table I. Datasets used in the analysis, including year and month of sampling (all at low flow). *N* is the number of headwaters

Dataset	River	Year	M	Outlet latitude and longitude	N	HW size ^a	Outlet size
A7	Anråse å ^b	2007	10	58°01'; 11°51'	45	0.48	86
D7	Danshytteån ^b	2007	10	59°42'; 15°05'	34	0.48	80
G7	Getryggsån ^b	2007	10	59°48'; 15°17'	21	0.45	36
K5	Krycklan ^c	2005	6	64°14'; 19°46'	24	0.62	70
L7	Lugnån ^b	2007	10	57°06'; 14°48'	27	0.69	127
O0	Ottervattsbäcken ^d	2000	6	64°02'; 19°06'	31	0.70	78
S0	Sörbäcken ^d	2000	6	64°19'; 18°38'	19	0.72	63

HW, headwaters.

^a It is median of all sub-catchments with an area <2 km².

^b Temnerud *et al.* (2009).

^c Buffam *et al.* (2008).

^d Temnerud and Bishop (2005).

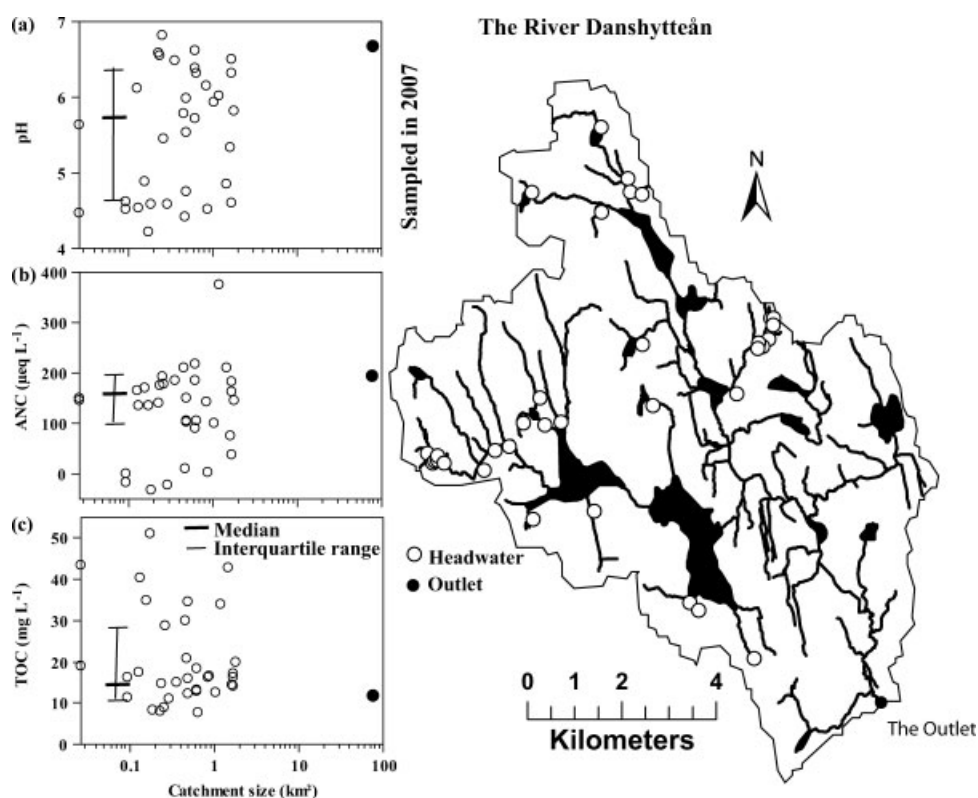


Figure 1. One example of a sampled stream network, R. Danshytteån (dataset D7), where the circles indicate samples with sub-catchment size $<2 \text{ km}^2$ and their chemistry is compared to the outlet (the black dot). Black filled areas are surface waters. Plots based on the dataset D7, sampled in 2007, are shown on the left; (a) pH, (b) ANC (in eq L^{-1}), (c) TOC (in mg L^{-1}). In the plots, headwaters are circles and the outlet is a black dot. Thick black lines are the median value and thin horizontal lines are the IQR

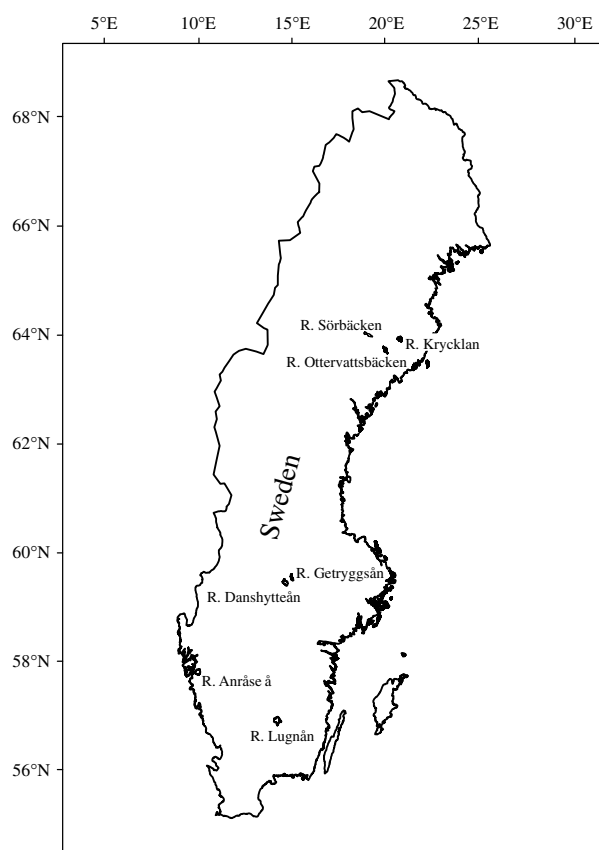


Figure 2. Map of Sweden with the seven investigated catchments (Table I for coordinates)

analysis as CO_2 using a Shimadzu TOC-VPCH analyser after acidification and sparging to remove inorganic carbon. Samples for major cation analyses (K, Mg, Na, Ca) were preserved with ultrapure HNO_3 (1% v/v) and stored cool until elemental analysis by inductively coupled plasma optical emission spectroscopy. Samples for strong acid anions (SO_4^{2-} and Cl^-) were stored frozen until analysis on a Dionex ion chromatograph system, whereas NO_3^- was analysed by flow injection analysis. The typical precision in anion and cation analyses based on measurements of certified standards was better than 2%. ANC was calculated as the difference between strong base cations and strong inorganic acid anions (Köhler *et al.*, 2001).

Statistical analysis

All statistics and modelling were done using SPSS (v16.02) and the significance (α) level was set to 0.05. Variability in the chemistry of headwaters was expressed as $\text{IQR} = 75\text{th percentile} - 25\text{th percentile}$. The normality of distributions was tested using the Shapiro–Wilk test. Correlations between the outlets and their headwaters were evaluated for both the median chemistry and the IQR using Kendall's tau rank correlation coefficient.

A univariate general linear model (GLM) was used to model the chemistry in headwaters from the outlet chemistry. The covariate was the outlet chemistry, with only one outlet chemistry variable in each model. An intercept was included in all models. Most variables were

normally distributed, except ANC headwater IQR which was natural log-transformed to improve the distribution before use in the GLM. Leave-one-out cross-validation was used for each GLM model, $n = 6$ in each model, for a total of seven models for each response variable. The null hypothesis (H_0) of this analysis was that there is no correlation between the outlet chemistry and the median or IQR of the headwaters, and H_1 was that there is a correlation. The statistical power ($1 - \beta$) gives the probability that the hypothesis is correctly rejected. Statistical power above 80% indicates that the H_0 was correctly rejected.

RESULTS

Headwater chemistry ranged widely within each catchment at the time of sampling. The median headwater IQR was 1.1 pH units, 94 $\mu\text{eq l}^{-1}$ ANC and 11 mg l^{-1} TOC (Table II), while the total range of headwater values was much greater (Figure 1). Headwater medians were more acidic than the outlets, with a median headwater pH of 5.8 and ANC of 147 $\mu\text{eq l}^{-1}$ compared to the outlet median pH of 6.7 and ANC of 227 $\mu\text{eq l}^{-1}$. The headwater TOC was also higher than the outlet TOC, median of 16 and 12 mg l^{-1} , respectively.

For pH, there was a significant positive correlation between outlet and headwater median values, but not with the headwater IQR (Table III). For ANC, there was a

significant correlation between outlet and headwater IQR. Headwater median and IQR of TOC were co-correlated. Interestingly, headwater median TOC was well correlated with outlet pH, but was not significantly correlated with outlet TOC (Table III).

All models relating outlet chemistry to headwater medians and IQR had positive slopes, that is, higher values at the outlet indicated higher median and variability of the respective analytes in the headwaters (Figure 3). In predicting median headwater pH from the outlet value, five of seven GLM models were significant with statistical power $>80\%$, and a median adj. R^2 of 0.68 (Table IV). Six of seven GLM models predicting headwater IQR from outlet ANC were significant, with a median adj. R^2 of 0.72. The other four parameters gave rise to few models which were significant at the $\alpha = 0.05$ level (Table IV), though median adj. R^2 ranged up 0.48 (for median ANC). Only one GLM model was significant for TOC, however, the NRMSEs were relatively low when comparing TOC with the six significant pH models (Table IV). In Figure 4, box plots of headwater chemistry and the predicted median and IQR are included in the same plot.

DISCUSSION

The question of how aquatic ecosystems interact at different scales across the landscape is a fundamental concern for many issues in water management. There would be great practical and theoretical benefits of being able to translate processes and understanding from one scale to predict patterns and results at another scale. One approach for dealing with these scale issues is the transformation of mechanistic understanding and/or empirical observation at a certain scale for use at another scale of interest. Upscaling involves information transformation from smaller scales to understand patterns and predict effects at a larger spatial scale. In stream biogeochemistry, this can be exemplified by attempting to use detailed process knowledge from plot and transect studies to predict catchment scale properties (Cory *et al.*, 2007; Petrone

Table II. Median values with IQR in brackets. ANC in $\mu\text{eq l}^{-1}$ and TOC in mg l^{-1} (Table I and Methods for abbreviations)

Dataset	pH HW	pH Out	ANC HW	ANC Out	TOC HW	TOC Out
A7	6.6 (2.1)	7.0	113 (326)	237	8.6 (6.4)	6.7
D7	5.7 (1.7)	6.7	143 (94)	192	16 (16)	12
G7	4.9 (0.6)	6.4	88 (30)	138	27 (18)	12
K5	6.0 (1.1)	6.9	144 (76)	271	15 (6.1)	10
L7	6.1 (1.4)	6.6	198 (142)	266	20 (17)	15
O0	5.6 (0.9)	6.5	130 (56)	175	20 (11)	15
S0	6.4 (0.8)	6.9	152 (102)	227	12 (5.2)	10

HW is headwaters with sub-catchment size $<2 \text{ km}^2$ and 'out' is the outlet.

Table III. Kendall's tau correlation between outlet chemistry (out), median for headwaters (med) and the IQR in headwaters, $n = 7$

		pH Out	pH Med	pH IQR	ANC Out	ANC Med	ANC IQR	TOC Out	TOC Med	TOC IQR
pH	Out									
pH	Med	0.81 ^a								
pH	IQR	0.43	0.43							
ANC	Out	0.43	0.62	0.43						
ANC	Med	0.24	0.43	0.05	0.62					
ANC	IQR	0.71 ^a	0.71 ^a	0.52	0.71 ^a	0.33				
TOC	Out	-0.62	-0.43	-0.24	-0.24	0.14	-0.52			
TOC	Med	-0.91 ^b	-0.71 ^a	-0.33	-0.33	-0.14	-0.62	0.52		
TOC	IQR	-0.62	-0.43	-0.05	-0.24	-0.24	-0.33	0.24	0.71 ^a	

ANC, acid neutralizing capacity; IQR, interquartile range; TOC, total organic carbon

^a Significant at the <0.05 level.

^b Significant at the <0.01 level.

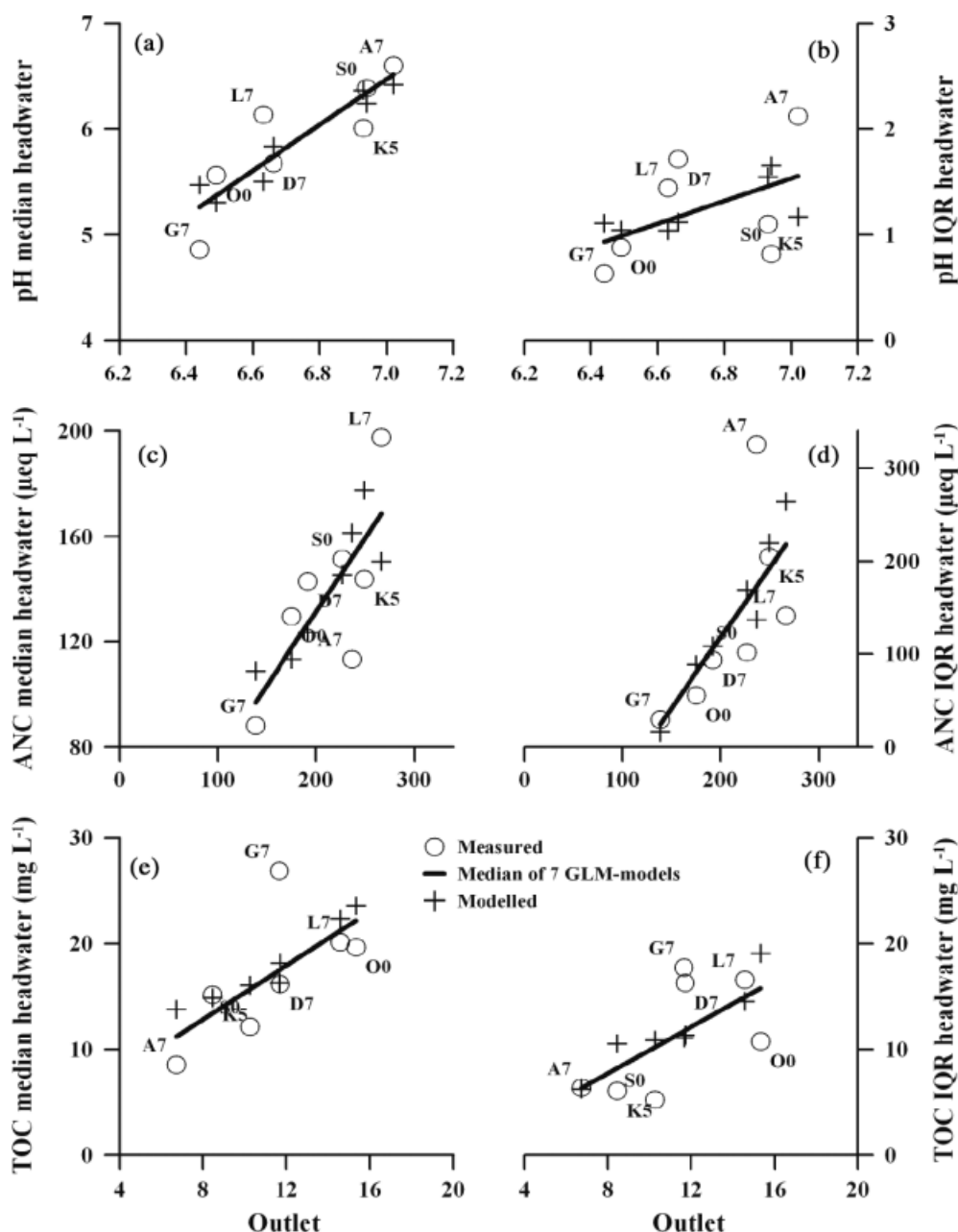


Figure 3. Headwaters versus outlet chemistry; (a and b) pH, (c and d) ANC, (e and f) TOC. In the left panels, the y axis is the median of headwaters while in the right panels the y axis is the headwater variability (expressed as IQR). The x axis is the outlet value. The black line is the median of seven GLM models (Table IV), the cross represents predicted values. The GLM model for ANC IQR is based on data transformed by natural logarithm (\ln). See section Methods for details

et al., 2007). Conversely, downscaling deals with disaggregating of information from a larger scale to understand processes and variability at smaller scales. One example of this is the challenge of assessing the multitude of headwaters when systematic monitoring has focussed on larger downstream systems. This paper deals with the latter question, how to push back the frontiers of *Aqua Incognita*.

In this study, we found that downstream chemical data correlated to varying degrees with the distribution of upstream chemistry across a widely dispersed set of north-temperate and boreal catchments sampled at low flow (Figure 3, Table III). This illustrates that a single chemistry sample from the outlet of a catchment

has useful information about the catchment's headwater chemistry distribution. These results suggest that by characterizing downstream chemistry, one can estimate two key parameters of the population distribution (median and IQR) of chemistry in headwaters, which make up the bulk of any stream network. Even with our relatively small number of sample catchments, some key parameters of the headwater chemistry distribution were successfully predicted from a single sample of downstream chemistry (Table IV). The strongest correlation and most robust GLM models between headwaters and outlets were found for ANC and median pH. The TOC was not predicted as well (Figure 4). The fact that we could successfully model median headwater pH is particularly encouraging

Table IV. GLM results predicting the median and the IQR of headwater chemistry from the outlet chemistry value

Var	Res	<i>n</i>	Intercept	<i>B</i>	<i>r</i> ² _{adj}	<i>p</i>	Power	NRMSE
pH	Median	5/7	−8.5 (1.9)	2.1 (0.27)	0.68 (0.18)	0.03 (0.02)	0.72 (0.18)	0.58
	IQR	0/7	−6.8 (3.4)	1.2 (0.50)	0.08 (0.25)	0.30 (0.28)	0.15 (0.10)	1.1
ANC	Median	1/7	9.8 (26)	0.60 (0.12)	0.48 (0.16)	0.08 (0.07)	0.44 (0.17)	0.75
	IQR ^a	6/7	−11 (1.0)	3.0 (0.18)	0.72 (0.11)	0.02 (0.02)	0.79 (0.17)	0.69
TOC	Median	1/7	1.9 (2.0)	1.3 (0.18)	0.31 (0.04)	0.15 (0.02)	0.28 (0.03)	0.73
	IQR	0/7	−1.2 (2.0)	1.1 (0.10)	0.25 (0.20)	0.18 (0.13)	0.24 (0.12)	1.1

The models take the form headwater value = intercept + *B* × (outlet value), where the headwater value is either the median or IQR of the headwater stream chemistry. Models: the number of significant models with statistical power >80% (before slash) out of seven total models (after slash); for the remaining categories, numbers outside the parentheses are the median value of all significant models and inside the parentheses are the IQR of the values of all the significant models. NRMSE, normalized root mean squared error.

^aThe model was based on natural log-transformed data.

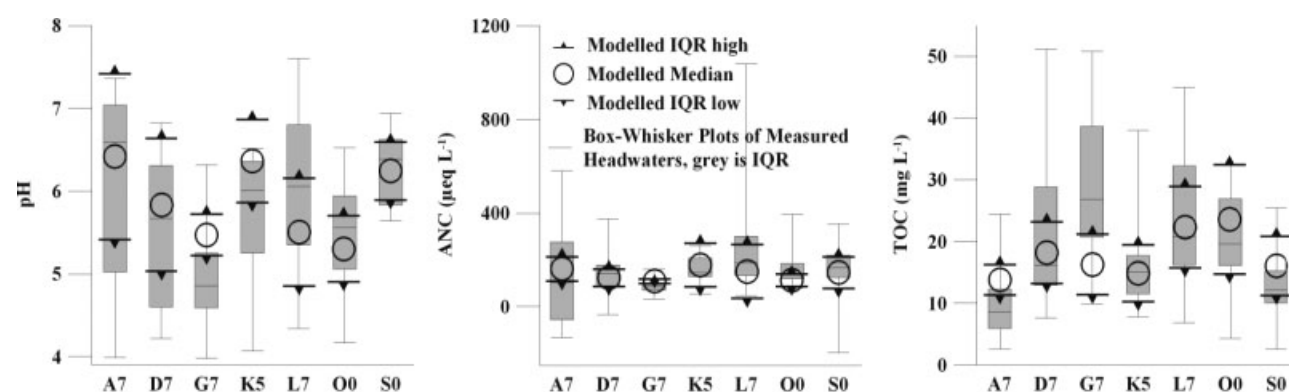


Figure 4. Box plot based on headwater chemistry, grey area is the measured IQR, with the predicted chemistry added as a circle for median and line with bump as the predicted IQR (assuming equal variability around the median value)

for further studies of this kind, since variation in pH is correlated to variation in aquatic biodiversity in Swedish streams (Fölster *et al.*, 2007).

The chemistry of the outlet is not simply an average of the headwaters. For all seven catchments, outlet ANC, TOC and pH were offset from headwater median values, with higher ANC, higher pH and lower TOC at the outlets. One possible explanation of this recurring set of patterns between headwaters and downstream is that older groundwater flowing along deeper catchment pathways with higher ANC and pH as well as lower TOC concentrations becomes a larger component of runoff further downstream (Buffam *et al.*, 2007; Laudon *et al.*, 2007). Another possibility is that in-stream processing reduces the TOC concentrations and makes water less acid as it moves downstream. But in these shaded, nutrient-poor streams with a low mean transit time (Temnerud *et al.*, 2007), the potential for in-stream transformation is small (Köhler *et al.*, 2002; Berggren *et al.*, 2007). Lakes in the stream network could increase transit times between headwaters and outlet, but these were rare in the current study. Therefore, we believe it is more likely that the offset of the headwater median relative to the outlet chemistry values is related to inputs of groundwater between the headwaters and the outlet. These downstream inputs, and lakes, with their many processes (e.g. McKnight and Bencala, 1990; Pers *et al.*, 2001; Fisher *et al.*, 2002; Köhler *et al.*, 2002), are part of the landscape mosaic that has been used to explain the patterns of differing

chemistry as one moves downstream in a stream network (Pringle *et al.*, 1988; Hunsaker and Levine, 1995; Strayer *et al.*, 2003b; Ågren *et al.*, 2007; Temnerud *et al.*, 2007; Asano *et al.*, 2009).

The correlation between headwaters chemistry and their outlet could change depending on season or flow situation. The present dataset is focused on the summer/autumn season at low flow, but efforts are ongoing to perform similar surveys across a broad range of flow regimes and seasons (e.g. Buffam *et al.*, 2008). The prevailing flow pathways for ground and soil water in combination with the riparian soil type (Aitkenhead *et al.*, 1999; Laudon *et al.*, 2004; Burt and Pinay, 2005) are among the most important factors regulating the amount of TOC and ANC entering small streams (Bishop *et al.*, 2004). Thus, changes in ground water table are important as well as the timing of when those changes occur. It will be important in future studies to examine the role of seasonality and different flow situations.

GIS data easily derived from maps or satellite images (land use, soil, vegetation and altitude, etc.) are seldom sufficient to model small stream water chemistry (Temnerud, 2005), but if the approach proposed in this study would be combined with map data, it might be possible to move beyond analysing the distribution of headwater chemistry to predicting the likelihood that a specific stream is in a particular category with regard to status and degree of human influence. This would be a valuable tool to estimate the past and present status of all

running waters based on existing long-term monitoring data.

CONCLUSION

In this study, we demonstrate the feasibility of modelling the distribution of headwater chemistry from measurements made at a single mesoscale catchment outlet site. Due to the relative scarcity of synoptic survey data in headwaters, more data are needed to adequately validate models such as those presented here and to advance the modelling effort. However, based on these initial results the approach shows promise. Coupled to GIS-derived watershed data, it may open a way to improve quantification of the chemical status of small streams using existing data.

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