Biogeosciences

Open Access

Spatial patterns of some trace elements in four Swedish stream networks

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Abstract. Four river basins in southern Sweden, with catchment sizes from 0.3 to 127 km^2 (median 1.9), were sampled in October 2007. The 243 samples were analysed for 26 trace elements (Ag, As, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, Ga, Ge, In, La, Li, Mo, Ni, Pb, Sb, Se, Sn, Tl, Ti, U, V and Zn) to identify spatial patterns within drainage networks. The range and median of each element were defined for different stream orders, and relationships to catchment characteristics, including deposition history, were explored. The sampling design made it possible to compare the differences along 40 stream reaches, above and below 53 stream junctions with 107 tributaries and between the 77 inlets and outlets of 36 lakes. The largest concentration differences (at reaches, junctions and lakes) were observed for lakes, with outlets usually having lower concentration compared to the inlets for As, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Ni, Pb, Sn, Ti, Tl, U, V and Zn. Significantly lower concentrations were observed for Cd and Co when comparing headwaters with downstream sites in each catchment. Common factor analysis (FA) revealed that As, Bi, Cr, Ga, Ge, Tl and V co-vary positively with Al, Fe and total organic carbon (TOC) and negatively with La, Li and pH. The strong removal of a large number of trace elements when passing through lakes is evident though in the FA, where lake surface coverage plots opposite to many of those elements. Forest volume does not respond in a similar systematic fashion and, surprisingly, the amount of wetland does not relate strongly to either Fe or TOC at any of the rivers. A better understanding of the quantitative removal of organic carbon and iron will aid in understanding trace element fluxes from landscapes rich in organic matter and iron.

1 Introduction

The importance of headwaters as a resource for biodiversity and human welfare is increasingly recognised (Lowe and Likens, 2005; Bishop et al., 2008). One reason is that headwaters make up most of the watercourse length and hence provide a large proportion of water and solutes to downstream sites (Alexander et al., 2007). For example, streams with catchment size < 2 km^2 make up approximately 80 % of the total length of all perennial watercourses in Sweden (Nisell et al., 2007). Headwaters also provide the most direct indication of what the terrestrial landscape is contributing to surface waters before in-stream and in-lake processes begin to alter the chemistry of runoff water.

It is widely known that the variability in water quality changes with catchment size. Typically small watercourses show 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 (e.g. Hutchins et al., 1999; Smart et al., 2001; Likens and Buso, 2006).

The distribution and concentration of a large number of trace elements in the landscape is useful in a variety of ways. Since increasing trace element use in the technosphere is increasing their spread in the environment, it is important to define current levels and patterns against which future changes can be judged (Grahn et al., 2006; Karlsson et al., 2006; Reimann et al., 2009). Documentation of trace elements can also help in defining controls on the heterogeneity of terrestrial exports to surface waters (Lofts and Tipping, 2000),
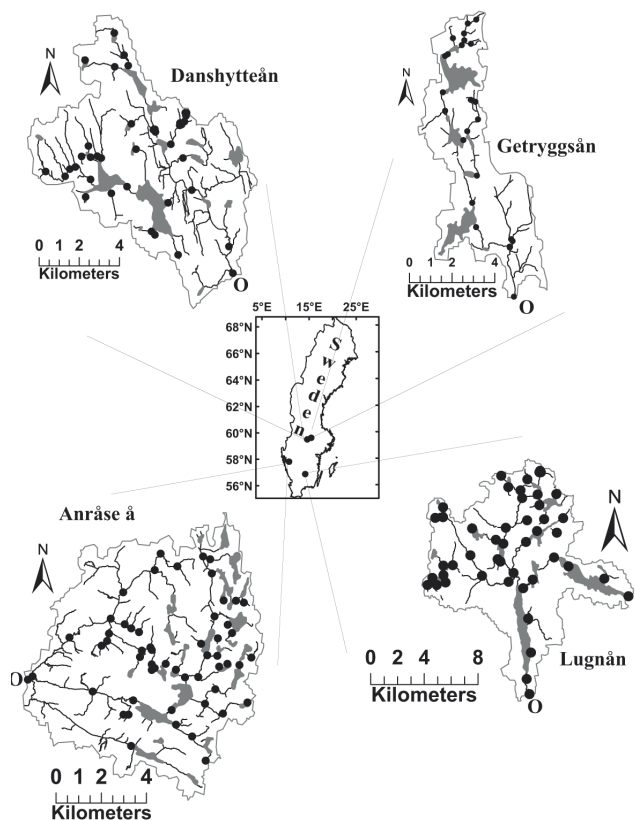
Fig. 1. Map of Sweden with the four rivers included: Danshytteån (R. D.), Getryggsån (R. G.), Anråse å (R. A.) and Lugnån (R. L.). The black dots are sampled sites. For stream junctions one dot could indicate that samples were taken upstream and downstream of the junction. O indicates the outlets of the rivers.

lake processes (Johansson et al., 2001; Taillefert and Gaillard, 2002) and downstream transformations that can be of value in managing land use for water quality (Reimann et al., 2009). Quantifying landscape variation and potential drivers of water quality is relevant for management of forestry practices and nutrient leaching.

Some studies estimating the spatial variability of trace elements in Scandinavia, at spatial scales from $10\text{–}100\,\text{km}^2$, have been published (Tarvainen et al., 1997; Edén et al., 1999; Andersson et al., 2006; Dahlqvist et al., 2007; Reimann et al., 2009; Lidman et al., 2012). The novel focus in this study is on headwaters, $< 2\,\text{km}^2$, in combination with larger streams in the channel network of complete rivers, including the lakes embedded in those networks.

The boreal Northern Hemisphere is rich in lakes, and they need to be accounted for when spatial patterns of stream networks are evaluated. Lakes can significantly change the concentration of total organic carbon (TOC), Al, Fe and trace elements in streams, as the water velocity decreases and water depth increases which allows biological, chemical and physical processes to proceed further than they can in run-

ning waters (Drever, 1997). Examples of such processes are; flocculation (von Wachenfeldt and Tranvik, 2008) and sedimentation of particles, changes in pH and redox potential, all of which have been described chemically (Honeyman and Santschi, 1988; Lofts and Tipping, 2000). Lakes in the Swedish boreal landscape usually have higher buffering capacity and pH at the outlet than at the inlets (Meili, 1992).

The aim of this study is to characterize the spatial variability of a range of trace elements (Ag, As, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, Ga, Ge, In, La, Li, Mo, Ni, Pb, Sb, Se, Sn, Tl, Ti, U, V and Zn) entering the drainage network in the headwaters of four river networks varying in land use, landscape type, geographical location and impact by acid rain. The downstream changes in concentrations are also quantified at the river outlet for an accumulated area of between 0.3 and $127\,\text{km}^2$. In each of these rivers, Swedish long-term monitoring sites exist. This makes it possible to locate the sampling occasions in the long-term variation of other water chemistry parameters of importance for trace elements including pH, Fe, Al and TOC. The main hypothesis (1) is that trace elements and TOC (as well as Al and Fe) show the same general pattern of catchment outputs and downstream changes. Trace element concentration changes in downstream areas would then be mainly due to TOC sources and sinks, with the position and volume of lakes being a major factor since TOC (in combination with Al and Fe) is the main carrier of trace elements (Lyvén et al., 2003). Furthermore, we expect (2) that a number of elements show significant co-variation due to their geochemical resemblance. In addition, we test (3) if the history of the acid deposition or sea salt inputs may impact trace element mobilisation at the landscape level.

2 Methods

2.1 Sampling approach

The synoptic surveys used in this study were designed to provide a snapshot of the water chemistry in the stream networks (Fig. 1 and Table 1). All sampling was carried out in October 2007 over a one to three day period per catchment when the weather was stable. A total of 243 grab samples were taken, and the majority of the samples were taken at headwaters (Fig. 2 and Table 1), which in this study are defined as sites with a catchment size of $< 2\,\text{km}^2$.

2.2 Study area

The four studied rivers, Anråse å (R. A.), Danshytteån (R. D.), Getryggsån (R. G.), and Lugnån (R. L.), are located in southern Sweden (Fig. 1 and Table 1). The rivers include four existing Swedish long-term monitoring sites; Asa Experimental Forest and Research Station in R. L., Buskbäcken in R. G., Gårdsjön in R. A. and Kindla in R. D. The dominant vegetation type is coniferous forest ($> 80\,\%$), mainly *Picea abies*, Norway spruce, on till soils (Table 1). Mires

Table 1. Map material for each catchment, median with 5th and 95th percentiles in parentheses. Outlet runoff is the daily HYPE modelled runoff during sampling compared to percentiles (perc) for October 1990–2010. For more details, see the Methods section.

	Anråse å (R. A.)	Lugnån (R. L.)	Danshytteån (R. D.)	Getryggsån (R. G.)
Outlet latitude (N) and longitude (E)	58°01', 11°51'	57°06', 14°48'	59°42', 15°05'	59°48', 15°17'
Sampling dates in October 2007	16–18	23–25	9–10	10
Total sites, n	90	64	55	34
Altitude (m a.s.l.)	89 (14/138)	206 (167/236)	206 (148/293)	279 (201/336)
Catchment size (km^2)	2.0 (0.13/35)	3.4 (0.31/78)	1.2 (0.08/62)	1.1 (0.08/33)
Outlet size (km^2)	86	127	80	36
Outlet altitude (m a.s.l.)	12	166	122	182
Outlet runoff ($m^3 s^{-1}$)	0.33 [20–30perc]	0.81 [70–80perc]	0.25 [30–40perc]	0.13 [50–40perc]
Headwaters (HW), n	45	26	34	21
Stream reaches, n	13	10	9	8
Distance between reaches sites (km)	1.6 (0.6/7)	2.4 (0.4/3.7)	1.1 (0.1/2.0)	0.4 (0.1/2.8)
Stream junctions, n	25	9	11	8
Distance between junctions sites (m)	270 (63/1390)	227 (97/1886)	192 (45/1253)	128 (39/2818)
Lakes, n	12	15	4	5
Distance to lake outlet (km)	11 (6/16)	14 (2/20)	11 (9/17)	10 (3/14)
Lake outlet compared to the end of the stream branch (%)	80 (33/92)	88 (7/96)	65 (51/97)	61 (21/83)
Stream length to sites (km)	10 (4/16)	16 (6/21)	14 (10/17)	14 (3/16)
Stream density ($km^2 km^{-1}$)	0.43 (0.2/1.6)	1.3 (0.5/5.3)	0.61 (0.2/1.8)	0.47 (0.2/1.2)
Land use map (%)				
Lake surface coverage	4.7 (0.0/20)	3.9 (0.0/19)	0.2 (0.0/10)	0.3 (0.0/20)
Urban	0.0 (0.0/0.3)	0	0	0.0 (0.0/0.9)
Forest	80 (65/95)	80 (69/94)	91 (83/100)	89 (66/99)
Wetland	7.3 (0.0/17)	4.7 (0.0/24	4.2 (0.0/12)	5.1 (0.0/26)
Open land	1.3 (0.0/5.4)	3.1 (0.0/7.6)	0.8 (0.0/5.3)	1.3 (0.0/4.3)
Pasture	0.6 (0.0/6.4)	2.4 (0.0/6.9)	0.0 (0.0/1.0)	0.0 (0.0/0.5)
Arable fields	0.0 (0.0/16)	2.8 (0.0/17)	0.0 (0.0/1.4)	0.0 (0.0/1.1)
CORINE (%)				
Solitary houses	0 (0/0.3)	0	0	0
Industrial	0 (0/0.3)	0	0	0
Camping	0	0	0	0 (0/0.4)
Arable land	0 (0/20)	5.2 (0/17)	0 (0/7.6)	0 (0/1.0)
Pastures	1.2 (0/9.1)	3.3 (0.0/8.6)	0 (0/0.5)	0 (0/1.2)
Broad-leaved forest not on mires	0.8 (0/18)	3.8 (0.0/14)	1.7 (0/8.4)	0 (0/2.0)
Broad-leaved forest on mires	0	0 (0/0.2)	0 (0/1.2)	0 (0/0.4)
Coniferous forest on lichen-dominated areas	0 (0/0.4)	0 (0/0.1)	0.8 (0/7.6)	6.9 (0.6/16)
Coniferous forest 5–15 m	18 (6.5/41)	9.1 (1.8/22)	16 (0/31)	19 (8.7/46)
Coniferous forest > 15m	42 (16/68)	47 (23/71)	45 (9.1/91)	27 (15/57)
Coniferous forest on mires	2.0 (0/8.6)	3.6 (0/15)	1.5 (0/7.6)	0.9 (0/8.9)
Coniferous forest on open bedrock	0.1 (0/5.5)	0	0 (0/0.3)	0
Mixed forest not on mires	8.7 (0/21)	5.3 (0/11)	8.9 (0/23)	4.3 (0/16)
Mixed forest on mires	0 (0/0.1)	0 (0/0.8)	0 (0/0.2)	0 (0/0.2)
Clear-felled areas	5.6 (0/15)	8.5 (0.5/21)	13 (0/31)	22 (0.5/47)
Younger forest	0 (0/1.5)	2.8 (0/7.4)	3.0 (0/12)	2.2 (0.0/9.7)
Inland marshes	0	0 (0/0.2)	0 (0/0.5)	0 (0/0.1)
Wet mires	0	0 (0/0.1)	0	0
Other mires	3.0 (0/11)	0 (0/2.2)	0 (0/5.4)	3.6 (0/17)
Lakes and ponds, open surface	4.4 (0/20)	4.1 (0/20)	0 (0/11)	0 (0/20)
Lakes and ponds, surface being grown over	0 (0/0.2)	0	0 (0/0.1)	0

Table 1. Continued.

	Anråse å (R. A.)	Lugnån (R. L.)	Danshytteån (R. D.)	Getryggsån (R. G.)
kNN database				
The age of the forest stand (yr)	55 (45/74)	54 (43/65)	56 (39/77)	50 (32/79)
Average height of the forest (m)	16 (12/19)	16 (13/19)	14 (10/19)	12 (7.0/16)
Birch[B] ($m^3\,ha^{-1}$)	17 (12/22)	13.6 (10.4/19	11.9 (4.2/20)	7.5 (2.5/16)
Spruce[S] ($m^3\,ha^{-1}$)	99 (49/167)	119.8 (71.5/163	73.8 (40.1/130)	41.3 (20.9/63)
Pine[P] ($m^3\,ha^{-1}$)	61 (48/75)	55.4 (34.1/72)	74.5 (45.4/109)	73.6 (48.0/114)
Oak[O] ($m^3\,ha^{-1}$)	1.3 (0.1/6.5)	3.8 (1.6/6.8)	0.1 (0/0.7)	0 (0/0.2)
Other forest ($m^3\,ha^{-1}$)	4.7 (1.4/13)	5.3 (3.1/10)	3.3 (0.8/8.1)	2.0 (0.3/5.8)
Forest volume, total ($m^3\,ha^{-1}$)	188 (127/256)	199 (151/248)	166 (120/241)	129 (79/181)
Soil type (%)				
Organic	16 (0/29)	2.1 (0/24)	4.4 (0/24)	22 (2.6/77)
Clay	2.9 (0/23)	0 (0/0.1)	0.0 (0/0.2)	0 (0/0.1)
Silt	0 (0/5.3)	0	0	0
Sand	1.2 (0/14	0	0 (0/1.8)	0
Glacifluvial	0 (0/5.1)	0 (0/0.9)	0	0 (0/0.1)
Till	2.7 (0/7.1)	70 (54/93)	77 (42/100)	63 (0/81)
Thin soil cover	0	0	0	0 (0/97)
Bare rock	64 (47/79)	15 (2.6/36)	7.1 (0/46)	2.2 (0/5.5)
Lake surface coverage	5.7 (0/19)	3.7 (0/21)	0.3 (0/13)	0 (0/22)

For CORINE classes a short-name was given; for details see http://www.eea.europa.eu/publications/COR0-landcover. [B] is *Betula* spp., [S] is Norway spruce (*Picea abies*), [P] is Scots pine (*Pinus silvestris*) and [O] is English oak (*Quercus robur*).

and small humic lakes made up most of the remaining parts of the catchments, while the proportions of agricultural and developed areas were minimal ($< 1\%$). The mean annual air temperature (1961–1990) in the catchments ranged from $7\,°C$ in the southernmost catchment, R. A., to $4\,°C$ in the northernmost catchment, R. G. Mean annual rainfall and runoff ranged from 1050 and 550 mm at R. A. to 750 and 250 mm at R. L., respectively. Daily runoff for 1990–2010 at each river outlet was modelled based on HYPE (Lindström et al., 2010) data downloaded 25 January 2012 from http://vattenweb.smhi.se (HYPE version 3.5.3 using catchment typology SVAR 2010:2). The runoff were normalised according to (daily Q in 2007 – median Q for the whole period 1990–2010)/ interquartile range of Q for the whole period 1990–2010 (Fig. 2). Runoff at the time of sampling in October 2007 was compared to percentiles based on October 1990–2010 (Table 1). Marine impacts, such as chloride deposition, were largest at R. A. and in decreasing order R. L., R. D. and R. G. Medians for bulk deposition of chloride [$mEq\,L^{-1}$] during 2007 were 0.053 (Gårdsjön), 0.020 (Aneboda) and 0.012 (Kindla) (Löfgren et al., 2011) (in the cited work Gårdsjön is a site inside R. A., Aneboda is approximately 50 km south-west of R. L. and Kindla is inside R. D.). Liming activities have historically taken place in all rivers, to the largest extent in R. A. and then in decreasing order R. L., R. D. and R. G. (Temnerud et al., 2009; Fölster et al., 2011). For R. G. no liming occurred in 2005–2007, and in the other three rivers we know that liming took place

during 2005–2007 (Table 2 in Temnerud et al., 2009), which also could affect downstream sites. The percentage of estimated sites affected by liming in R. A. was 69 %, in R. D. was 17 % and in R. L. 56 %. When estimating the degree of acidification in 2007, using metaMAGIC (Erlandsson et al., 2008), no sites in R. G. were considered to be acidified, 4 % of the sites in R. D., 28 % of the sites in R. L. and 38 % of the sites in R. A. This estimation is in accordance with the pattern of sulphur deposition over the country that is highest in the south-west and decreasing in both the north and the east (Moldan et al., 2004).

The R. A. catchment has larger median coverage of lake surface coverage and wetlands than the other three river catchments (Table 1), and a more heterogeneous soil mostly consisting of bare rock, while the other catchments were dominated by till. The arable land areas were small, with the largest portion in R. L., which also had the largest volume of forest. The R. D. catchment has the smallest percentage of lake surface coverage, and the forest has equal volumes of pine and spruce. The smallest catchment, R. G., has the highest percentage of wetlands and the forest is dominated by pine. For other details, see Temnerud et al. (2009).

2.3 Chemical analyses

After collection, all water samples were kept dark and cool until they were analysed. Total organic carbon (TOC) was measured as CO_2 after combustion using a Shimadzu TOC-VPCH analyser, after acidification and sparging to remove

inorganic carbon. It has previously been shown that dissolved organic carbon (DOC) and TOC differ on average by less than 5 % (Ivarsson and Jansson, 1994; Köhler, 1999), so TOC is essentially identical to DOC in these waters (see also Gadmar et al., 2002). Total nitrogen (N) is the sum of Kjeldahl nitrogen and of nitrite and nitrate analysed according to the standard SS-EN ISO 13395. Total phosphorous (P) was analysed according to SS-EN ISO 6878.

Unfiltered samples for ICP-OES analysis (aluminium (Al), barium (Ba), calcium (Ca), iron (Fe), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), sodium (Na), sulphur (S), silicon (Si), strontium (Sr) and titanium (Ti)) were preserved with concentrated nitric acid (redistilled from reagent grade acid) to a final concentration of 0.15 M. These samples were analysed for silver (Ag), arsenic (As), gold (Au), beryllium (Be), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), gallium (Ga), germanium (Ge), indium (In), lithium (Li), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), tin (Sn), thallium (Tl), uranium (U), vanadium (V) and zinc (Zn) with an ICP-MS (Agilent 4500) equipped with an ultrasonic nebulizer (U-6000AT+, CETAC). Samples for anion (sulphate (SO_4) and chloride (Cl)) analysis were stored frozen until analysed on a Dionex ion chromatograph system. The typical precision in anion and cation analyses based on measurements of certified standards was better than 2 %. For limit of detection (LOD), 3 times the standard deviation of the blank was used for the trace elements, see Table 2. Acid neutralizing capacity (ANC) was calculated as the difference between strong base cations and strong inorganic acid anions (Köhler et al., 2001). ICP-OES and anion analysis were performed at the Department of Geological Sciences, Stockholm University, ICP-MS and TOC at Örebro University, and N, P and pH at Vattenlaboratoriet, Uppsala Municipality, respectively.

2.4 Map material

To relate trace elements to catchment character, we used land use maps on the scale 1 : 100 000 (SNLS, 2002) and soil maps, along with the kNN database of vegetation that contains forestry variables estimated from Landsat 2000 satellite photos (Reese et al., 2003) (Table 1). The variable "organic soil type" is referred to as "peat" in this study. A land use data set called CORINE, provided by the European Environment Agency, was also used (EEA, 2002). Digital soil data were available for R. A. (SGU, 2001). For the other catchments, photographs of these soil maps, with GIS coordinates, were digitalised manually: R. L. year 1876 and scale 1 : 200 000, R. D. year 1879 and scale 1 : 50 000, and R. G. year 1930 and scale 1 : 50 000 and for a small part (~ 10 %) map from year 1872 and scale 1 : 50 000. The percentages of each variable on each catchment from the land use and soil maps were used in the modelling. In addition to the data read directly from each map, three variables were calculated from the map in-

formation: stream length (m), drainage density (km^{-1}), and altitude (m). Drainage density is the ratio of the total length of streams within a catchment to the total area of the catchment. In Swedish glacial till catchments, the Quaternary soils usually have larger impact on stream water chemistry than the bed rock geology (Lax et al., 1995; Lax, 2005).

2.5 Statistical analysis

In order to estimate the variability of water chemistry between catchments, robust coefficient of variation (CV) was used. Robust CV = $100 \times$ normalised IQR/median, where IQR is the interquartile range (75–25 percentile) and normalised IQR is IQR multiplied by 0.7413 (PTA, 2006). The factor 0.7413 makes IQR comparable to standard deviation; if the distribution is normal, normalised IQR values would equal standard deviation. Since the data are not normally distributed (tested using one-sample Kolmogorov–Smirnov test) and there are generally few samples, normalised IQR was used. A Piper diagram was used to evaluate the differences in major cations and anions (Piper, 1944); the diagram was made using the software GW_Chart version 1.23.3.0 for MS Windows (Winston, 2000).

Common factor analysis (FA), also called principal axis factoring, was performed to check for latent structures in trace elements, major chemistry and physical parameters using the oblique (non-orthogonal) rotation method Oblimin ($\delta = 0$) and Kaiser normalisation (SPSS for Windows v19.0). The Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy tests whether the partial correlations among variables are small. KMO should be greater than 0.6 in order to make FA valid to perform. Another indicator of the strength of the relationship among variables is Bartlett's test of sphericity, which is used to test the null hypothesis that the variables in the correlation matrix are uncorrelated. When the significance level is small enough to reject the hypothesis ($p < 0.0001$), the relationship among variables is strong, and FA can be conducted. In FA the variance of a single variable is decomposed into common variance that is shared by other variables included in the model and unique variance that is specific to a particular variable (Gauch, 1982). Principal component analysis (PCA), a similar multivariate procedure, considers the total variance and makes no distinction between common and unique variance (Gauch, 1982). Oblique rotation allows the factors to correlate, and if the factors are truly uncorrelated, orthogonal and oblique rotation produce similar results (Costello and Osborne, 2005).

Chloride was omitted from all FA analyses since it made the matrix indefinite, i.e. the eigenvalues were not positive. Of all variables in Table 1, the following were used: altitude, forest volume, lake surface, drainage density, forest, wetland, open fields (arable, pasture and open field), because the other variables made the matrix indefinite or gave KMO < 0.6. Likewise, F, N, Na and P were omitted for R. D., and Ca, F, K, Mg, Mn, N, Na, P, and SO_4 for R. G., respectively.

Table 2. Chemistry results for each catchment. Median with 5th and 95th percentiles in parentheses. U is units, where n is $ng\,L^{-1}$, μ is $\mu g\,L^{-1}$, m is $mg\,L^{-1}$ and eq is $\mu eq\,L^{-1}$. LOD is limit of detection for trace elements. All is the average of all catchments, median and robust coefficient of variation (CV). Bold numbers are significant ($\alpha < 0.05$ and $1-\beta > 0.80$) difference between headwaters and downstream, where "+" indicate higher concentration in watercourses $> 2\,km^2$, bold without sign denotes a decrease.

C	U	LOD	R. A.	R. L.	R. D.	R. G.	All	Europe median*
pH			**+6.9**	6.5	5.9	**+5.3**	6.4;	7.7
			(4.3/7.2)	(5.1/7.0)	(4.5/6.7)	**(4.0/6.7)**	17	
ANC	eq		189	260	141	**+99**	165;	n.a.
			(−92/457)	(89/397)	(−19/211)	**(40/188)**	76	
TOC	m		8.2	19	15	**16**	13;	4.99
			(4.1/17)	(6.5/40)	(8.2/43)	**(6.6/50)**	69	
Cl			13	6.3	2.5	2.2	6.3;	8.81
			(11/21)	(5.1/7.6)	(2.0/12)	(1.5/3.8)	113	
F			0.046	0.14	0.086	0.14	0.10;	0.10
			(0.031/0.10)	(0.097/0.24)	(0.055/0.14)	(0.092/0.20)	60	
SO$_4$			3.8	4.2	2.5	**+1.8**	3.4;	16.1
			(2.2/7.1)	(2.2/6.4)	(1.2/4.2)	**(0.7/2.8)**	41	
Al			0.22	0.29	**0.43**	**0.36**	0.31;	0.018
			(0.087/0.59)	(0.064/0.61)	**(0.12/1.1)**	**(0.085/0.68)**	65	
Ca			5.4	4.7	2.1	**+1.4**	3.2;	40.2
			(0.66/9.8)	(1.9/7.5)	(0.49/3.2)	**(0.75/3.2)**	82	
Fe			0.29	0.99	0.85	**1.1**	0.67;	0.067
			(0.058/1.0)	(0.15/2.9)	(0.28/3.2)	**(0.095/3.3)**	107	
K			0.50	0.72	0.30	**+0.22**	0.42;	1.60
			(0.23/1.9)	(0.28/1.2)	(0.070/0.57)	**(0.086/0.42)**	73	
Mg			1.0	1.2	0.60	0.46	0.95;	6.0
			(0.72/2.8)	(0.80/1.9)	(0.27/1.1)	(0.26/0.60)	52	
Na			6.0	4.0	2.1	1.8	4.0;	6.58
			(4.9/10)	(3.2/4.7)	(1.7/6.7)	(1.4/2.2)	64	
Si		0.0005	1.8	4.2	**4.1**	**4.7**	3.6;	8.03
			(0.52/4.5)	(1.2/7.0)	**(2.1/7.4)**	**(1.7/5.9)**	55	
Ba	μ	0.47	8.6	15	**8.4**	**7.5**	9.2;	24.9
			(5.8/13)	(11/24)	**(6.1/13)**	**(4.7/10)**	45	
La		1.0	4.3	4.9	3.0	2.5	3.8;	0.034
			(1.1/7.7)	(1.7/7.3)	(1.6/5.1)	(1.1/4.2)	44	
Mn			19	48	45	29	37;	15.9
			(5/112)	(11/179)	(17/245)	(7/124)	79	
N			354	572	320	**326**	383;	n.a.
			(206/767)	(289/806)	(214/586)	**(173/449)**	47	
P			8.0	15	8.0	**12**	11;	n.a.
			(0.0/50)	(7.3/43)	(0.0/21)	**(0.0/23)**	61	
Sr		0.01	14	26	8.8	7.5	12;	110
			(6.4/37)	(16/33)	(3.9/12)	(5.2/9.7)	95	
Ti		0.1	**+1.5**	2.3	**2.2**	**2.8**	2.1;	0.9
			(0.3/17)	(0.5/5.8)	**(0.7/6.8)**	**(0.3/7.3)**	96	
Zn		0.0005	**2.7**	1.7	3.9	**3.6**	6.8;	2.68
			(1.3/9.0)	(0.84/3.2)	(1.2/6.3)	**(2.0/11)**	90	
As	n	15	234	306	328	**335**	270;	630
			(155/390)	(136/547)	(152/660)	**(163/785)**	40	
Be		2	23	41	**106**	58	44;	9
			(9.0/60)	(19/83)	**(46/208)**	**(25/116)**	74	
Bi		0.2	2.0	5.1	8.4	**12**	4.8;	2
			(0.7/8.6)	(1.1/11)	(3.4/36)	**(2.4/44)**	106	
Cd		0.3	**14**	**10**	**18**	**18**	13;	10
			(6.5/53)	**(2.7/23)**	**(4.3/41)**	**(7.2/48)**	80	
Co		0.1	**306**	**375**	**461**	**211**	331;	160
			(69/1762)	**(51/1503)**	**(56/2265)**	**(23/798)**	96	

Table 2. Continued.

C	U	LOD	R. A.	R. L.	R. D.	R. G.	All	Europe median*
Cr	n	7	239	538	**299**	**328**	306;	380
			(107/598)	(143/1106)	**(97/999)**	**(102/1016)**	85	
Cu		3	564	713	346	409	541;	880
			(273/1566)	(410/1262)	(203/2183)	(188/708)	55	
Ga		0.2	19	26	**37**	**48**	26;	11
			(4/131)	(5/72)	**(10/130)**	**(7/135)**	103	
Ge		1	10	11	**19**	**17**	12;	9
			(5/21)	(5/17)	**(8/34)**	**(7/23)**	49	
Li		3	+**784**	616	520	**372**	626;	2100
			(447/2562)	(372/1049)	(338/972)	**(263/722)**	35	
Mo		0.4	+**34**	31	48	58	38;	220
			(11/138)	(14/69)	(16/140)	(31/112)	58	
Ni		0.3	673	681	334	**310**	516;	1910
			(318/1644)	(205/1053)	(128/707)	**(111/613)**	58	
Pb		0.2	240	407	547	**869**	380;	93
			(81/1729)	(74/1182)	(169/2108)	**(133/3513)**	91	
Sb		0.1	53	51	56	46	52;	70
			(32/79)	(30/63)	(29/85)	(32/94)	21	
Sn		0.4	6.3	12	18	**22**	11;	n.a.
			(2.0/31)	(1.8/35)	(5.5/127)	**(7.4/65)**	94	
Tl		0.2	9.0	10	**11**	**14**	11;	5
			(5.0/22)	(3/20)	**(5.0/20)**	**(5.3/21)**	49	
U		0.1	47	81	154	388	89;	320
			(14/144)	(24/220)	(56/798)	(183/1066)	116	
V		0.5	359	552	889	**1367**	541;	460
			(112/1489)	(95/1575)	(219/2753)	**(121/2792)**	108	

* Median water data from Salminen et al. (2005), and n.a. indicates elements not analysed.

Statistical power analysis was performed using SPSS for Windows (v19.0). The post hoc analysis of the difference in means between headwaters and downstream using two-tailed Student's t test. H0 was that there is no difference between headwater and downstream sites. H1 was that there is one. The statistical power $(1 - \beta)$ gives the probability that the hypothesis is correctly rejected, a value above 0.80 indicates that H0 was correctly rejected.

Median and robust coefficient of variation (CV) of the difference in stream water chemistry between 40 stream reaches (all four rivers put together), 53 stream junctions with 107 tributaries vs. downstream comparisons, and 36 lakes with 77 inlets vs. outlet comparisons (Table 1). To test if the difference was significant, both Wilcoxon and paired Student's t test were used.

3 Results

In Sweden groundwater tables are usually low in September and October. During 2007 the groundwater tables were lower than usual for this time of the year for the four rivers (SGU, 2012). The weather in September 2007 was normal (compared to 30 yr averages), while it was $1\,°C$ colder and precipitation was $50\,\%$ lower than usual in October (SMHI,

2012). During the sampling the HYPE modelled runoff was low and stable in R. A. and in R. G., while for R. L. and R. D. the sampling took place during the descending limb of a minor runoff episode (Fig. 2).

3.1 Variability of chemical variables

The Piper diagram shows that the majority of the samples were dominated by the cations Na and K and by the anions Cl, and to a lesser degree SO_4 (Fig. 3). R. A. and R. L., which are located closer to the sea and which are more heavily impacted by acid rain, had on average twice as high average concentrations of the marine derived ions Cl, Mg, Na and SO_4. This was also the case for the elements Cu, K, Li, Ni and Sr. R. D. and R. G. had higher concentrations of Be, Bi, U and V. The following elements were under the LOD: Ag and Au < 0.1, In < 0.5 and Se < 500 (all in $ng\,L^{-1}$).

The rivers are discussed in the following order: R. A., R. L., R. D., and R. G. This is in accordance with the natural gradient from the Swedish south-west coast (R. A.) up northeast to R. G. (Fig. 1). The median value decreased monotonically for Cl, Li, Na and pH (Table 2), from R. A. to R. G., while the opposite trend was observed for As, Bi, Ga, Pb, Sn, Tl, U and V. The elements with the highest robust CVs (> 100), using all 243 sites, were in decreasing order U, Cl,
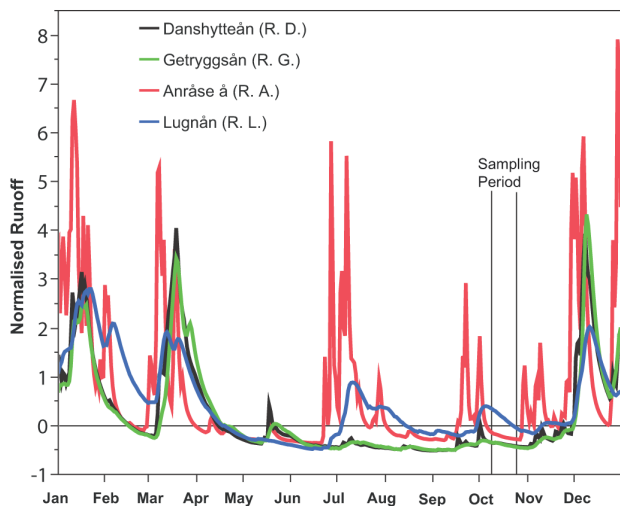
Fig. 2. Normalised daily HYPE modelled runoff (Q; see Methods section for details) for 2007, where River Anråse å is represented by the red line, River Lugnån by the blue line, River Danshytteån by the black line and River Getryggsån by the green line. The vertical solid lines indicate the sampling period for all rivers in October 2007. The sampling took a maximum of three days per river; see Table 1 for exact dates and to get modelled runoff in $m^3\,s^{-1}$.

Fig. 3. Piper diagram, where River Anråse å is represented by triangles, River Lugnån by open squares, River Danshytteån by open circles and River Getryggsån by crosses.

V, Fe, Bi, and Ga (the column denoted "All" in Table 2). At the other end of the scale, the chemical variables with the lowest robust CVs (< 41) were in increasing order pH, Sb, Li, As and SO_4 (Table 2). Robust CVs for Al and TOC were 65 and 69, respectively, meaning they are essentially "median" robust CVs of all chemical variables. Five chemical variables were chosen to exemplify trace element variation with catchment size and pH: Li, V, Ga, Sb and La. Higher variability with lower catchment size was generally seen for those chemical variables (Fig. 4). Higher pH was associated with lower V and Sb concentrations (Fig. 4d and h), while La and Li concentrations increased with pH (Fig. 4b and j). Both Pb and Zn follow the pattern of Sb and V (results not shown), while no clear pH dependence was observed for Co, Cu or Ni.

3.2 Clusters of chemical variables

All common factor analyses (FA) pass Bartlett's test of sphericity and KMO values were usually over 0.7, except for R. G. which was 0.6. These tests indicate that all shown FA analyses shown were valid to perform, although the values were borderline for R. G.

In the factor analysis three groupings were identified (Fig. 5a):

– Near the far end of the first factor, opposite to pH, was a cluster of Al, As, Bi, Cr, Fe, Ga, Ge, Pb, Si, Tl, TOC and V, mainly substances associated with low pH conditions. This cluster is hereafter termed $FA1_{Chem}1+$.

– Another cluster, $FA1_{Chem}2+$, includes Be, Cd, Sb, U and Zn, close to $FA1_{Chem}1+$ but with slightly smaller eigenvalues.

– A third cluster, $FA2_{Chem}1+$, includes ANC, Ca, K, La, Mg, Na, SO_4 and Sr, located at the positive end of the second factor.

Along the first factor lake surface coverage was the map information with the highest negative eigenvalue (Fig. 5a), opposite of $FA1_{Chem}1+$. Positive values along the first axis were forest and altitude (Fig. 5a). Cluster $FA2_{Chem}1+$ co-varies positively with open fields (such as arable, pasture and open fields), while forest coverage and altitude were opposite to $FA2_{Chem}1+$ (Fig. 5a). The patterns observed in Fig. 5a could, to some degree, be observed in Fig. 5c–f, although the pattern for R. A. (Fig. 5e) was roughly a mirror image of the FA analysis for the other three rivers. Perhaps the most notable FA result was that Cu did not co-vary with TOC and Zn (Fig. 5a, c–f). Based on the score plot, some sites in R. A. and R. D. showed differences between the four rivers, but most sites overlapped based on scores, indicating that they have a rather similar spatial pattern (Fig. 5b). The Piper plot confirms the rather good similarity between the rivers, except one site at R. L. that behaved differently (Fig. 3).

3.3 Headwaters compared to downstream

The variability was generally higher in the headwaters ($< 2\,km^2$) compared to sites further downstream. The median concentration values decreased with increasing catchment size, with some exceptions. The catchment with the fewest significant chemical differences between headwaters

and downstream sites was R. L. The biggest differences were observed for R. G., with both increasing (ANC, Ca, K, pH and SO_4) and decreasing (Al, As, Ba, Be, Cd, Co, Cr, Fe, Ga, Ge, Li, N, Ni, P, Pb, Si, Sn, Ti, Tl, TOC, V and Zn) concentrations with increasing catchment size (Table 2). All significant changes in R. D. showed lower downstream concentrations (Al, Ba, Be, Cd, Co, Cr, Ga, Ge, Si, Ti and Tl). In R. A., both significant increases (Li, Mo, pH and Ti) and decreases (Cd, Co and Zn) were detected (Table 2).

3.4 Comparison of stream reaches, stream junctions and lakes

When comparing concentrations within the same stream channel ($n = 40$) the following showed significant differences: Cl, K, Mg, Mo, Na, Ni, Sb, Sr, Ti and V (Table 3), which all increased in concentration except Sb, which decreased. The 53 stream junctions had in total 107 tributaries and the following elements changed significantly when comparing inlets with the site downstream the junction: Cd, Co, Ge, pH and Tl increased while the others decreased in concentration (Table 3). For 36 lakes, comparisons of 77 pairs of inlet vs. outlet concentrations gave significant differences for: Al, As, Ba, Bi, Ca, Cd, Cl, Co, Cr, Fe, Ga, Ge, K, N, Na, Ni, P, Pb, pH, Si, Sn, SO_4, Ti, Tl, TOC, U, V and Zn (Table 3); all with decreasing concentrations except for Ca, K, pH and SO_4, which showed an increase.

3.5 Comparison with long-term time series and analysis of sampling technique

We used data, covering the period October 1996–2009, from 132 reference sites at the Swedish national environmental monitoring programme for watercourses in southern Sweden for comparison with observed concentrations in the present study (same sites as in Huser et al., 2011). Concentrations of Co, Fe and TOC from this study were usually higher than the median of the national programme, while this study's values were lower for Cu, Mo and Zn. In general, the observed concentrations of Al, Fe, Pb and TOC were higher in our study compared to the median of water samples in the Geochemical Atlas of Europe (the column denoted "Europe median" in Table 2) (Salminen et al., 2005). While Ca, K, Mo, pH and SO_4 were lower in our study compared to the median in the Geochemical Atlas of Europe.

This study was based on unfiltered samples because the filtering process in these humic and iron rich systems may create artefacts (Sholkovitz, 1992; Köhler, 2010). There were few sites that had enough inorganic particles in our study to change that. However, in the lower parts of R. A. there were silty soils and livestock, potentially influencing the amount of inorganic particles suspended in the samples. Acidifying (using HNO_3) the unfiltered samples at R. A. could be the reason why some rather similar trace elements had the highest or the lowest robust CV. Thus, the lack of filtering could
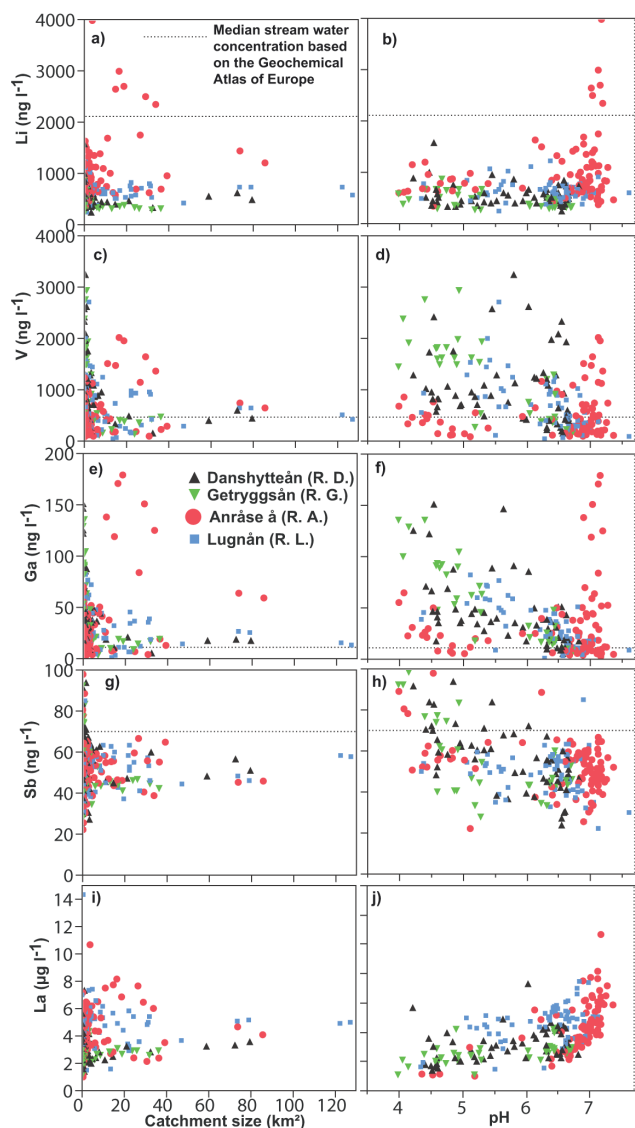

Fig. 4. Chemistry variation with catchment size (left panel) and pH (right panel) for several trace elements; **(a–b)** Li, **(c–d)** V, **(e–f)** Ga, **(g–h)** Sb and **(i–j)** La. River Anråse å is represented by red dots, River Lugnån by blue squares, River Danshytteån by black triangles (pointed up) and River Getryggsån by green triangles (pointed down). Dashed lines are median stream water concentrations and pH according to the Geochemical Atlas of Europe (Salminen et al., 2005). For La the European value, $0.034\,\mu g\,L^{-1}$, is too low to be seen on the graph.

be the cause of the apparent increases in Li and Mo in downstream sites. This was the only river where we found significant differences between filtered (at $0.45\,\mu m$) and unfiltered absorbance at $420\,nm$ (absDIFF) (Fig. 6). At all other rivers absDIFF was smaller than 7 % on average.
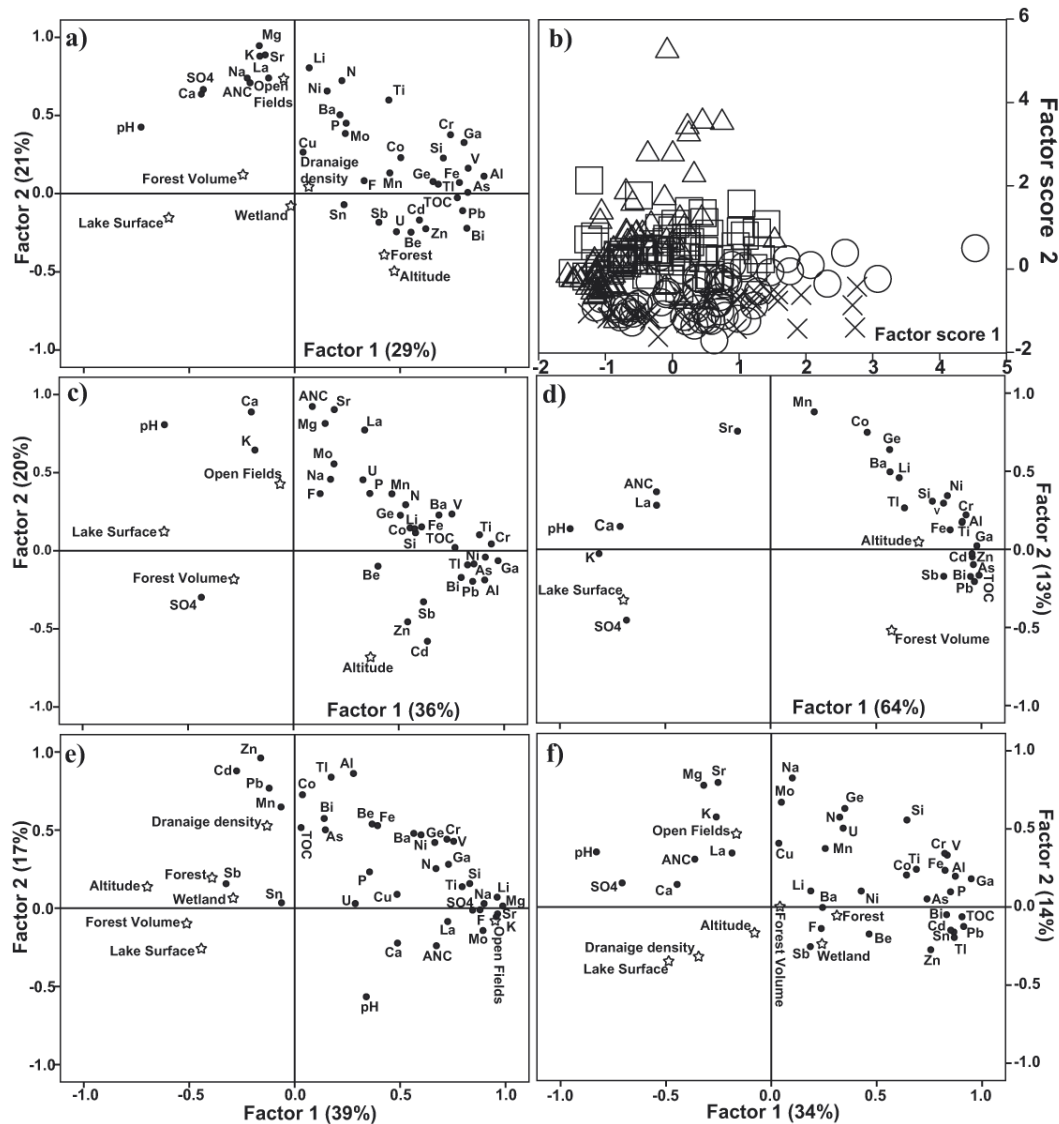
Fig. 5. Common factor analysis of water chemistry and map material (Table 1): **(a–b)** data from all four rivers, where **(a)** is the loading plot, **(b)** is the score plot. Loading plots for **(c)** Danshytteån (R. D.), **(d)** Getryggsån (R. G.), **(e)** Anråse å (R. A.) and **(f)** Lugnån (R. L.). In **(b)** R. A. is represented by triangles, R. L. by open squares, R. D. by open circles and R. G. by crosses. For **(a)** and **(c–f)** black dots are water chemistry and open stars are physical parameters (map information).

4   Discussion

Trace elements may originate from anthropogenic point or diffuse sources or from the bedrock and soil. They are mobilised under favourable geochemical conditions (typically acidic pH) in the presence of colloidal carrier phases such as organic carbon or sesquioxide particles (Al, Fe and Mn oxyhydroxides) and in the form of other inorganic complexes such as chlorides, fluorides, hydroxides, carbonates or sulphates. Organic carbon is a major controlling factor on both trace elements mobility and pH in most of the running waters and lakes in this study. The main hypothesis in this study was that trace elements follow the same spatial pattern as TOC,

and that concentration decreases from upstream to downstream sites, mainly due to the position and volume of lakes. We can not reject the hypothesis for As, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Ni, Pb, Sn, Ti, Tl, U, V and Zn (Fig. 5a), as they follow a similar spatial pattern as TOC (as well as Al and Fe) when comparing lake inlets and outlets (Table 3). The largest absolute changes in sites downstream of lakes were observed for sites in R. D. and R. G. that have a lower lake surface coverage and also lower specific average runoff. The trace elements that did not show a significant decrease in concentration when comparing inlets with outlets at lakes were Cu, La, Li, Mo, Sb and Sr (but also Mg and Mn) (Table 3), most of which are discussed below. Significant increases in lakes

Table 3. Median and robust coefficient of variation (CV) of the difference between (1) stream reaches ($n = 40$), (2) stream junctions (53 junctions with 107 tributaries vs. downstream comparisons) and (3) lakes (36 lakes with 77 inlets vs. outlets comparisons). Significant differences using both Wilcoxon and paired Student's t test are marked with * for $p < 0.05$ and ** for $p < 0.01$. For units, see Table 2.

C	(1) Reaches	(2) Junctions	(3) Lakes
Al	5.1 (10)	−0.08 (−1116)	−127** (−1.6)
ANC	5.9 (5.0)	3.5 (12)	32 (2.9)
As	−1.9 (−23)	−6.4 (−9.6)	−17* (−7.6)
Ba	0.23 (4.4)	−0.08 (−12)	−0.60* (−4.0)
Be	3.2 (2.9)	−0.06 (−162)	−8.1** (−2.6)
Bi	0.35 (3.3)	−0.14 (−15)	−1.3** (−3.3)
Ca	48 (6.3)	39 (14)	802** (2.0)
Cd	−0.10 (−27)	−0.90* (−5.8)	−4.9** (−1.9)
Cl	0.13** (2.4)	0.07 (11)	−0.33** (−2.0)
Co	41 (2.9)	−12* (−16)	−174** (−2.0)
Cr	32 (2.6)	−8.2 (−12)	−72** (−3.0)
Cu	45 (3.5)	50 (2.8)	−1.8 (−114)
F	0.0010 (7.0)	0.0010 (15)	0.00 (27)
Fe	70 (2.6)	0.49 (524)	−138** (−3.8)
Ga	2.4 (4.1)	−0.67 (−18)	−9.8** (−2.7)
Ge	0.95 (3.2)	−0.69* (−4.8)	−0.76* (−6.2)
K	34** (2.2)	7.8 (16)	55* (2.9)
La	0.22 (1.9)	−0.08 (−9.3)	0.12 (10)
Li	50 (2.8)	−6.8 (−28)	−29 (−6.8)
Mg	62** (1.4)	2.5 (54)	−0.42 (−409)
Mn	0.98 (14)	−0.08 (−197)	−3.8 (−6.9)
Mo	4.0** (2.6)	0.29 (50)	−2.4 (−7.6)
N	9.0 (7.7)	−3.0 (−27)	−37* (−3.8)
Na	123* (2.2)	24 (17)	−182* (−2.3)
Ni	41* (2.3)	−13 (−8.9)	−90** (−2.1)
P	0 (4.3^{IQR})	−1.0 (−5.2)	−1.0* (−6.7)
Pb	40 (3.3)	−3.5 (−42)	−149** (−3.0)
pH	0.03 (5.7)	0.04* (5.1)	0.31** (3.1)
Sb	−2.1* (−2.3)	0.32 (24)	3.1 (2.9)
Si	223 (2.9)	24 (34)	−1103** (−1.6)
Sn	0.07 (48)	−0.49 (−9.6)	−2.1** (−5.3)
SO$_4$	0.02 (12)	0.04 (14)	0.40** (2.2)
Sr	0.50** (2.0)	−0.03 (−49)	0.01 (243)
Ti	0.26* (3.4)	0.07 (14)	−0.68** (−2.3)
Tl	0.80 (3.3)	−0.38* (−5.8)	−2.8** (−1.8)
TOC	0.03 (27)	−0.14 (−17)	−2.0** (−4.8)
U	15 (2.6)	−4.0 (−9.4)	−11* (−4.1)
V	53* (3.8)	−26 (−9.0)	−182** (−2.7)
Zn	87 (4.9)	−163 (−5.2)	−691** (−2.0)

Index IQR = normalised interquartile range (since median is null).

were detected for Ca, K, pH and SO$_4$. These results suggest that there could be a connection between the levels of Cu, La, Li, Mo, Sb and Sr and those of Ca, K, pH and SO$_4$. In R. G. there was a significant decrease in TOC between headwater and downstream sites, along with Al, Ba, Be, Bi, Cd, Co, Cr, Fe, Ga, Ge, Li, Ni, Pb, Si, Sn, Ti, Tl, U, V and Zn, while ANC, Ca, K, pH and SO$_4$ increased. In the other rivers
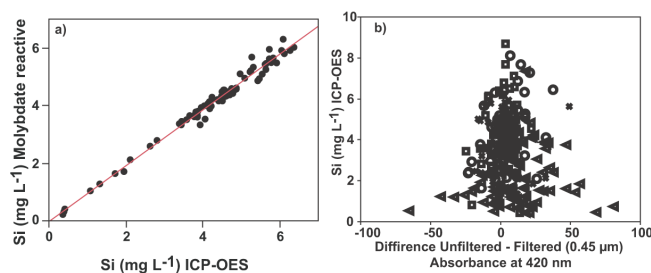

Fig. 6. (a) Concentration of molybdate reactive silica (mg L^{-1}) against total silica measured by ICP-OES measured at the monitoring sites (Aneboda, Gårdsjön and Kindla) that were within the samples catchments, and **(b)** comparison of absorbance at 420 nm, unfiltered – filtered (0.45 μm), against total silica (mg L^{-1}) ICP-OES in the presented data set. R. A. is represented by triangles, R. L. by open squares, R. D. by open circles and R. G. by crosses.

there were significant downstream decreases in Cd and Co. At R. D. the concentrations of Al, Ba, Be, Cr, Ga, Ge, Si, Ti and Tl decreased downstream, and for R. A. there was an increase in concentration of Li, Mo, pH and Ti (Table 2).

Elements for which significant downstream losses were observed at all rivers include Al, Be, Fe, Ga, Ge, Si, Ti and Tl. All of these elements have in common that they bind comparatively strong to hydroxide ions (Stumm and Morgan, 1996). They may form neutral species in water when pH increases, such as may be observed during the passage of a lake with internal alkalinity production. Elements that mainly form cationic species, such as La and Sr, or predominantly exist in the anionic form, such as As, Mo, Sb or V, are not removed during a lake passage or are removed only when iron is removed simultaneously.

For R. A., R. L. and R. D., no significant changes in TOC were detected between headwater and downstream sites. The same holds for pH in R. L. and R. D. It is unclear how much the differences/ similarities in the spatial patterns of chemistry between the four rivers could be due to differences/ similarities in the runoff rates during sampling (Fig. 2). Classic heavy metals such as Cd, Co, Cu, Pb or Zn do not show any strong geographical or sea salt controlled pattern contrary to what we expected. Only Pb and Zn seem to be mobilised preferentially under acidic conditions, while Co, Cu and Ni display varying concentrations irrespective of pH. This behaviour could indicate that the latter elements were mobilised depending on geological variations of trace minerals, while Pb and Zn were present but immobilised under higher pH.

The overall FA analysis indicates that there were roughly three clusters of elements, major elements to the upper left, Fe and TOC related trace elements to the right and a number of elements in between those two groups. This indicates various drivers, and element behaviour also varies in between rivers. Al, Fe and TOC have a strong negative correlation to pH in many Swedish surface waters, indicating TOC as a major driver for pH, Fe and Al mobility (Köhler et al., 2000;
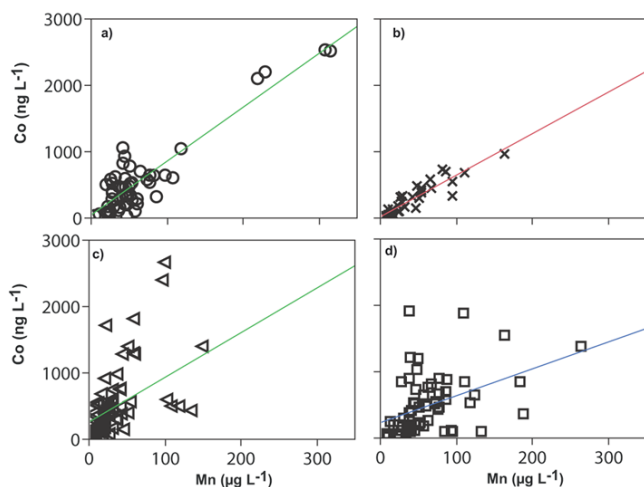
Fig. 7. Concentration of total cobalt ($ng\,L^{-1}$) against total manganese ($\mu g\,L^{-1}$) at the four rivers **(a)** Danshytteån, **(b)** Getryggsån, **(c)** Anråse å and **(d)** Lugnån.

Buffam et al., 2007; Sjöstedt et al., 2010), which is why these two factors are confounded. A detailed analysis of this behaviour is outside the scope of this article and will thus not be presented here. Instead we want to focus here on some specific observations only. The trace elements described here may be divided in many different ways according to their physical and chemical properties.

4.1 Major soluble cations (Ca, K, Mg and Na)

The major cation concentrations in the streams are controlled by deposition, weathering, biomass uptake and ion-exchange. Detailed descriptions of these processes and fitted models to cation fluxes of three sites inside the catchments R. A., R. L. and R. D. may be found in Köhler et al. (2011). Higher deposition fluxes of both anthropogenically derived acids and marine derived sea salt both lead to increasing salt loads in R. A. and R. L. as compared to R. D. and R. G. sites. If the Piper plot (Fig. 3) where to be presented separately for each river, it would be easier to note that some sites, in each river, differ in their composition (as the Piper plots in Fölster et al., 2011, with the same sites but sampling in spring 2008). For R. G. no liming occurred in 2005–2007, but 27 % of the sites differed anyway in their Ca / Mg ratio. A few other sites (one in each river) seem to have a different composition due to unknown liming activity or due to Quaternary soils with a different chemical signature. In R. A. elevated Ca concentrations were due to liming activity. After excluding limed sites almost constant Ca / Mg ratios were observed at almost all other sites, indicating somewhat homogeneous net cation mobilisation at most sites.

4.2 Major soluble components in anionic form (C, Cl, F, N, P, S and Si)

At the rivers R. A. and R. L., which are close to the sea, marine derived S and Cl are much higher than at the other rivers, while this was not the case for F, N and P. The two latter are heavily influenced by agricultural practice and plant uptake, while the concentration variations in F probably reflect variations in F bearing minerals such as apatite or muscovite, etc. Si was mainly in soluble form. Comparisons of molybdate reactive Si and Si determined with ICP-OES at R. A. and R. L. (slope $= 1.00 \pm 0.05$, $n = 44$, $R^2 = 0.92$) do not indicate any differences (Fig. 6a). We thus assume that the possible contribution from Si by clay particles (< 0.2 ppm) is negligible. Initially Si was derived from weathering and does not show any geographical pattern. Recently the importance of Si recycling from biologically derived material was documented in boreal areas (Engström et al., 2010). Our finding of Si clustering together with TOC and Fe may be a hint that significant amounts of Si have been recycled and were mobilised together with TOC from organic rich riparian soils.

4.3 Trace cations in stable oxidation states (Al, Ba, Be, Bi, Cd, Co, Cs, Cu, Ga, Ge, La, Li, Ni, Sn, Sr, Pb, Ti, U and Zn)

Our overall and site specific FA analyses confirm many of the known drivers for trace element mobility, such as the effect of pH on trace elements concentration in general (Figs. 4–5), and the strong binding of Co to MnO_2, Cr to Al, and Pb to $Fe(OH)_3$. Many of those latter elements relate in a very linear fashion at all sites (for Co vs. Mn and Al vs. Cr, see Figs. 7–8, respectively). The liming activity (both Ca and pH) could have an impact on the spatial patterns at other sites (Egeberg and Håkedal, 1998; Lydersen et al., 2002), but it is considered to be low in our case, since none of the trace elements were related to dose of liming in R. A. and R. L. (data not shown). However, Fe concentrations decrease with increasing lime dose at both rivers. For Pb and Zn we used the equations published by Ejhed et al. (2012) to estimate the fraction of those elements that would not pass a 0.45 μm filter. The equations were based on a large data set of samples ($n = 800$) from Swedish watercourses and lakes that were sampled for both total and filtered metals. As those empirical equations were mainly driven by pH and water colour, we chose to plot the calculated fraction as a function of pH for each site (Fig. 9). The calculated fraction of metals in particulate form rises with pH and was generally much higher for Pb than for Zn.

In R. A., the river that is most affected by marine sea salt spray, we observed strong correlations of Cl to a large number of trace elements. At this river a significant correlation between SO_4 and Cu was also observed. This may indicate an effect of soil solution ionic strength from marine sea salt
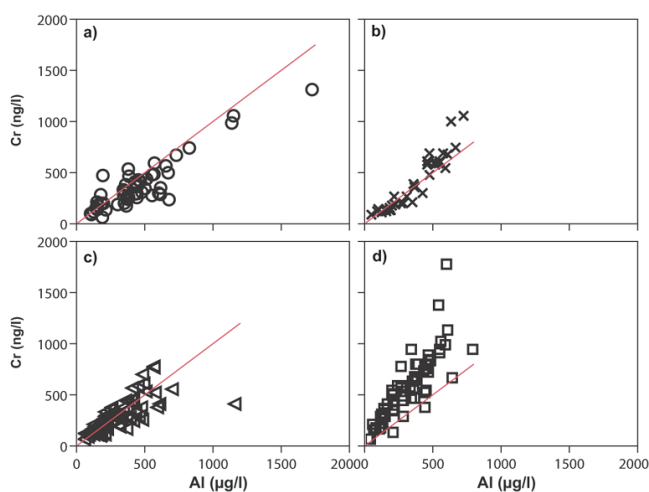
Fig. 8. Concentration of total chromium ($\mathrm{ng\,L^{-1}}$) against total aluminium ($\mathrm{\mu g\,L^{-1}}$) at the four rivers **(a)** Danshytteån, **(b)** Getryggsån, **(c)** Anråse å and **(d)** Lugnån.
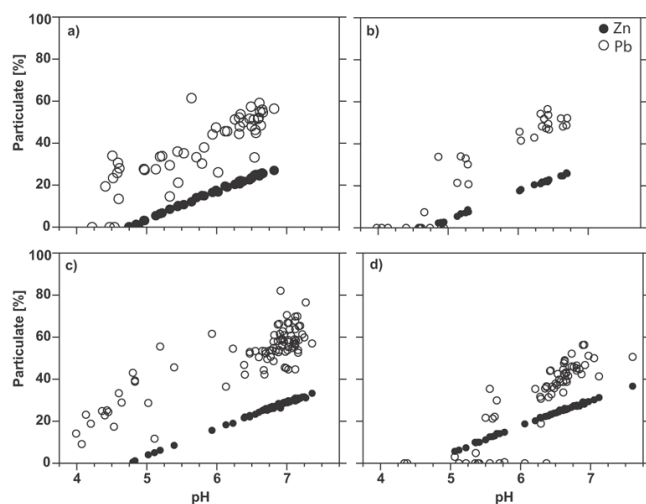

Fig. 9. Particulate fraction of Pb and Zn based on equations by Ejhed et al. (2012), estimating the fraction (%) that would not pass a 0.45 μm filter at the four rivers **(a)** Danshytteån, **(b)** Getryggsån, **(c)** Anråse å and **(d)** Lugnån. The equations were based on a large data set of samples ($n = 800$) from Swedish watercourses and lakes that were sampled for both total and filtered metals. As those empirical equations were mainly driven by pH and water colour, we chose to plot the calculated fraction as a function of pH for each site.

sources on the mobilisation of elements at that river and/or mobilisation of Cu due to the impact of acid rain.

According to our FA analysis (Fig. 5), Cu does not co-vary strongly with Al, Fe, TOC or Zn, despite that organic ligands are known to strongly bind Cu (Bresnahan et al., 1978; Hart, 1981). Cu and Zn behaved differently during the passage from the inlet to the outlet of lakes (Table 3), possibly due to differences in sedimentation (see Table 11.5 in Stumm, 1992). Similar findings for Cu were observed in a Swedish

national survey of 1200 lakes (see PCA plots on page 196 and 202 in SEPA, 1999). Cu behaved differently compared to Zn (Table 2), and had no significant correlation with TOC, when evaluating Swedish time series of trace elements in 139 streams (Huser et al., 2011). Other articles have dealt with this difference in behaviour between Cu and Zn (e.g. Ross and Sherrell, 1999; Lawlor and Tipping, 2003; Tipping et al., 2010).

The non-hydrolysed cations La and Sr were not removed during river or lake passage. Elements potentially binding strongly to colloidal phases of Al, Fe, Mn and/or organic matter such as Co, Cr, Pb and maybe even Ba and Ga are removed when alkalinity, pH or TOC changes occur. Surprisingly this is not the case for Cu and U, which both are known to bind strongly to these colloidal phases. Potentially La, Cu and U bind very strong to fractions of organic matter that are not easily removed during lake passage. Alternatively in the case of La, the strong relationship of La to ANC may be due to the co-variation of La with alkalinity ($R^2 = 0.76$) at R. A., potentially indicating La mobilisation from carbonates in solution (Johannesson et al., 2004).

4.4 Trace cationic elements in varying (I-IV) oxidation states (Cr, Fe, Mn and Tl)

We have no analytical data on the oxidation state of these elements despite this being a strong driver for their mobility and binding. Fe and Mn are known to partly exist as Fe(II) and Mn(II) in the presence of organic matter, preventing hydrolysis. We assume though that the majority of both of those elements were mostly present in their oxidized form Fe(III) and Mn(IV+) in these well-oxygenated surface waters. The strong correlation of Co with Mn may be an indicator that Mn was present as $\mathrm{MnO_2}$ colloid, to which Co is known to bind strongly (Pokrovsky et al., 2011). In a similar way we may argue for Cr being in the anionic form as Cr(V) bound to aluminium or organic aluminium colloids (cf. strong correlation between Al and Cr in the Fig. 8).

4.5 Trace anionic elements (As, Mo, Sb and V)

The anionic elements As, Mo, Sb and V did not seem to behave in a similar manner (Fig. 5). While As and V were removed at R. G., potentially together with Fe in accordance with the predicted speciation calculations by Wällstedt et al. (2010), Mo did not showed any removal (Tables 2–3). Very little information was available for Mo in boreal surface waters.

4.6 Land use

In our analysis we did not find any of our available landscape variables adding significant additional explained variance to the FA analysis (Fig. 5). The information contained in our landscape data is probably too unspecific for exploring geochemical variations quantitatively and instead represents

only chemical, physical and biological processes. The strong removal of a large number of trace elements when passing through lakes is evident though in the FA analysis where lake surface coverage plots opposite to many of those elements (Fig. 5). Forest volume does not respond in a similar systematic fashion, and, surprisingly, the amount of wetland does not relate strongly to either TOC or Fe at any of the rivers. More detailed spatial analysis including extent and thickness of the riparian strips might help to understand this better.

Our analysis is a first step in better understanding processes that drive trace elements concentrations and trace elements retention in the Swedish landscape. Many of the trace elements studied here are co-transported with organic matter, and a better understanding of quantitative organic carbon, Al and Fe removal in stream reaches and lakes will aid in the understanding of the fate of many trace elements, e.g. the systematic study of the transformation conditions of dissolved to particulate forms of Al and Fe such as described in Sjöstedt et al. (2010). Both systematic studies of temporal and spatial variation of filtered and unfiltered trace element concentrations (Huser et al., 2012) and speciation modelling of trace elements are under way to better elucidate trace element removal processes. Reasonable data for natural background concentrations of a large number of elements is required by the EU Water Framework Directive. Defining reliable background concentrations based on geographical information only seems a very challenging task. Our analysis implies that lake position, morphology and volume are the most important drivers for trace elements concentration as compared to many other natural landscape features in the investigated catchments.

5   Conclusions

The main hypothesis in this study was that trace elements and TOC (as well as Al and Fe) show the same general pattern of catchment outputs and downstream changes. Common factor analysis revealed that this seems to hold true for As, Be, Bi, Cd, Cr, Ga, Ge, Pb, Tl, U, V and Zn, as they usually co-vary positively with Al, Fe and TOC, and negatively with La, Li, pH and Sr. Hypothesis (1) did not seem to hold true for Ba, Cu, Mo and Sn. The other trace elements did not show the same clear pattern. As we speculated in the Introduction, hypothesis (2), many trace elements behaved similarly in those spatial patterns. The largest differences, both in number and magnitude, were observed when comparing the lake inlets with their outlets, with lower concentrations of As, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Ni, Pb, Sn, Ti, Tl, U, V and Zn at the lake outlets. The strong removal of a large number of trace elements when passing through lakes is evident in the FA analysis where lake surface coverage plots opposite to many of those elements. Forest coverage/volume did usually not correspond in a similar systematic fashion, and, surprisingly, the amount of wetland did not relate strongly to Al, Fe, TOC or most trace elements at any of the rivers. With regards to

hypothesis (3), the elements Cu, Pb and Zn appear prone to mobilisation in acidified environments rich in SO_4 or under acidic conditions, while this does not seem to be the case for Co and Ni.

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