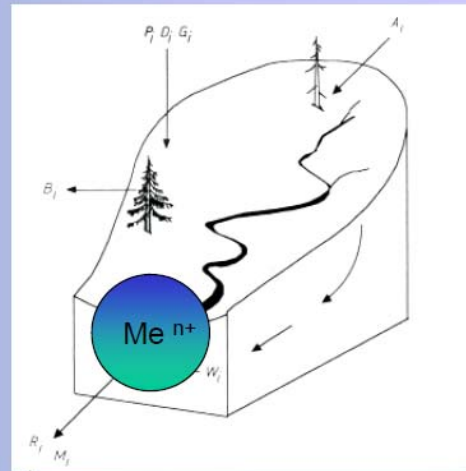
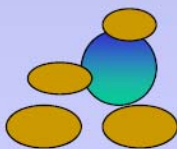


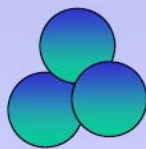
Simple classification of binding forms of metals in surface waters



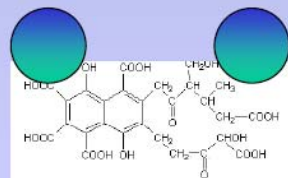
inorganic colloids



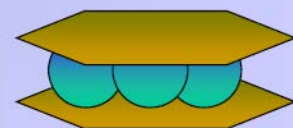
ionic form



organic colloids



mineralbound



COMPARING FILTERED AND UNFILTERED METAL CONCENTRATIONS IN SOME SWEDISH SURFACE WATERS

Stephan J. Köhler

Institutionen för vatten och miljö, SLU
Box 7050
750 07 Uppsala
Tel. 018 – 67 31 10

<http://www.ma.slu.se>

Illustration: Simple view of how metals bind to carriers in surface waters

Tryck: Institutionen för vatten och miljö, SLU
Uppsala, 2010-05-06

Table of Contents

Background.....	5
Material and methods.....	7
Definitions	7
Results from other studies	7
Metal sampling technique used in the Swedish environmental monitoring program	8
Alternate proposed methods for sampling.....	9
Blank tests and potential error sources	9
Experimental setup	10
Results.....	12
Results from the 2009 autumn sampling (Set 1)	12
Analysis of lab filtered fractions for all metals	13
Analysis of streams and rivers	16
Analysis of lakes	16
Trends in space:.....	17
Trends in time.....	20
Relationships between filtered metal concentrations and iron.....	22
Comparison between field and lab filtration	24
Potential effect of filtration on the classification of surface waters	25
Relating these findings to the long-term monitoring time series dataset	26
Sampling campaign in the Krycklan catchment (Set 2)	27
Seasonal sampling campaign in the Dalarna region (Set 3)	29
Effects of sample storage time and effect of sedimentation technique (Set 4).....	31
Discussion.....	34
Comparison between lab and field filtered samples.....	34
Effects of applying the Swedish sample setup	34
Temporal and spatial variation	35
Carrier substances and metal geochemistry.....	35

Is it possible to estimate filtered metal concentrations for lead?.....	37
Summary and suggestions for future studies.....	38
Acknowledgements.....	39
References.....	39
Attachments	40

BACKGROUND

Metals in surface waters may have a large impact on biota in lakes, streams and rivers. There is still a large ongoing discussion in the literature about whether measuring total metals or the so-called dissolved fraction is more relevant for quantifying how harmful metals are for biota. Historically, only the filtered part of the metals, i.e. the quantity of metal that will pass through a filter with 0.45µm nominal size, is quantified in many surface water environmental monitoring programs that are concerned with the environmental effects of toxic substances. The reason for this is many-fold. Almost all trivalent and many of the divalent heavy metals such as lead (Pb), cadmium (Cd), zinc (Zn) and nickel (Ni) tend to bind to charged surfaces on particulates in the water at higher pH. These particles may be of inorganic, organic or mixed organic/inorganic origin, some of which would settle during a longer sedimentation process while others remain in the aqueous phase as dispersed colloids. The weight fraction of metals bound to these particles ($\text{Me}_{\text{weight\%/particle weight\%}}$) may be many orders or magnitude higher than the respective weight fraction per water ($\text{Me}_{\text{weight\%/water weight\%}}$). Accordingly, small changes in the overall particulate concentration will have large effects on the overall weight fraction per water which is generally what is measured. Particle concentrations change with flow and as such, may affect temporal trends in metal concentrations in surface waters under varying hydrologic conditions and climate extremes. In order to eliminate these flow driven fluctuations and in an attempt to distinguish metal reactivity, a filtration step has been agreed upon in the large majority of sampling protocols. This is the case in the European sampling methodology. According to the proposed document COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE Technical Report - 2009 – 025 metals that are measured with the purpose of establishing environmental quality standards “As the establishment of environmental quality standards (EQS) has been limited for the majority of priority substances to water only, the principle matrix for assessing compliance with respect to EQS is whole water, ***or for metals, the liquid fraction obtained by filtration of the whole water sample.***” need to be filtered prior to their determination. Later it is mentioned in § 9.1 that: “If experience has shown that no significant amounts of particles occur, the filtration may be omitted.”

In the Swedish environmental monitoring program, the flux of metals from land to ocean is of central interest, which is why the type of sampling protocol mentioned above was not followed. This is due to the possibility of particulate bound metals being potentially available under conditions where changes in the chemical regime occur.

In order to comply with European sampling programs, it is of interest to analyze and study the differences in metal concentrations in Swedish surface waters under the different sampling protocols.

In detail the following questions were of interest:

- Is there a bias in metal concentration between samples that are acidified, left for sedimentation, and then decanted compared to those that are first filtered and then acidified as described in the guidance document No 19?
- Is there a bias in metal concentration if the samples are filtered in the field or in the lab but are otherwise treated similarly?
- Is there a bias in metal concentration if the samples are acidified, left for sedimentation, and then decanted between those that are acidified and then filtered?
- Is there a bias in metal concentration if the time the samples are left acidified during the sedimentation step is varied?

MATERIAL AND METHODS

Definitions

Total metal [TM] content in this study refers to the part of the metal that may be recovered in the supernatant aqueous phase of an acidified, non-filtered water sample. It includes truly dissolved metal, colloidal metal and metal desorbed from mineral and organic particles present in the water sample. The majority of the metals bound into the mineral lattice of geogenic origin are probably not recovered with this method.

Adsorbed metal [AM] content in this study refers to the part of the metal that may be desorbed from mineral or organic particles present in the water sample that would not pass through a 0.45 micrometer filter.

Filtered metal [FM] in this study refers to the part of the metal present in the water sample that will pass through a previously acid rinsed and washed filter of 0.45 micrometer filter size.

Colloidal metal [CM] in this study refers to the part of the metal present in the water sample that will pass through a 0.45 micrometer filter, will not sediment by gravity over long time periods but is not truly dissolved. This metal is instead bound to a colloidal carrier material such as ferric hydroxides, aluminium hydroxides, manganese oxy-hydroxides and organic compounds or associations of any of the latter with the former.

Dissolved metal [DM] in this study refers to the part of the metal present in the water sample that is either in hydrated form or present as an ion association of hydrated metal and inorganic anions such as hydroxide, sulphate, chloride or fluoride.

$$[\text{TM}] = [\text{AM}] + [\text{FM}] = [\text{AM}] + [\text{CM}] + [\text{DM}]$$

$$[\text{FM}] = [\text{CM}] + [\text{DM}]$$

Results from other studies

The analysis of filtered and unfiltered metals has been studied in a large number of projects in other countries. Because this report specifically focuses on metals monitoring in Sweden, the results from studies conducted in other countries will not be reported here in detail. Results from other metal filtration studies were kindly made available by Daniel Larsson from the County Administrative Board of Dalarna (D. Larsson pers. comm.), by

Hjalmar Laudon, SLU Dept. Forest Ecology and Management Umeå (H. Laudon pers. comm.) and by Christian Demandt from IVM (C. Demandt, pers. comm.). These three data sets encompass more than 1000 individual water samples.

Metal sampling technique used in the Swedish environmental monitoring program

Water samples are taken at specified sampling points using acid washed 60ml polyethylene bottles of whole water samples and then sent immediately to the Department of Aquatic Sciences and Assessment (IVM) laboratory. On arrival of the sample, usually occurring within one to two days after sampling for the large majority of samples, the bottle is opened and preserved with Suprapur© nitric acid at a ratio of 0.5ml concentrated acid per 100ml sample. The sample is then stored for a time period that may vary between several weeks and a few months to allow for a complete sedimentation of particles present. An aliquot of the supernatant is then carefully poured off in a clean sample vial and analyzed without dilution using an Elan DRC-e ICP-MS with a Scott spray chamber, quartz nebulizer and platinum cones according to SS-EN 17294-2:2005. If the sample falls outside the calibration range it is diluted and reanalyzed. This sampling technique is labeled *Type A* in the following sections.

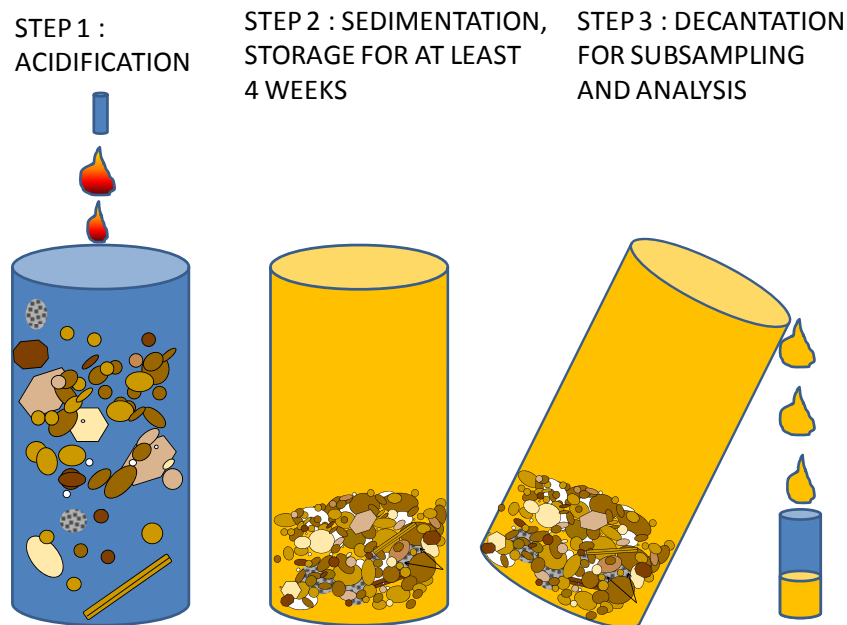


Figure 1: Sketch of steps involved in the sampling technique labeled Type A.

Alternate proposed methods for sampling

According to EN ISO 17294-2:2004 I § 8 the sample is filtered through a filter with 0.45 micrometer nominal pore size prior to the acid conservation with supra pure nitric acid. The filtration can either occur directly in the field or directly after arrival in the laboratory. *Type B* implies that the sample is filtered on arrival in the laboratory while *Type C* implies that the filtration is done directly in the field. For the filtration step, acid and ultra-pure water washed 20mL polyethylene syringes were used. The filters that were employed are acid and ultrapure water washed Filtropur S polyethersulfon (PES) supplied by Sarstedts (Ref 83.1826) with a filter diameter of 25 mm and a nominal pore size of 0.45 μm . For the field filtration, the pre-rinsed and filter equipped syringes were sent in closed plastic bags together with prefixed filters. The samplers wore single-use plastic gloves during the sampling and filtration process. The filtration setup is shown in a photo below:



Figure 2: Sampling setup used for the filtration (*Type B* and *Type C*). Pouring the sample into a syringe that is connected to a filter (to the left) and then adding the plunger for preparation of filtration (to the right). The first 5ml of the filtered sample are discarded.

Blank tests and potential error sources

The risk for contaminating the sample by using an incorrect sampling protocol, from external sources or due to improper sample storage is large, especially if trace concentrations are to be determined. However, not all metals are contaminated as easily as others. Zinc is an example of a metal that may function as a good indicator for sample contamination during sampling or sample filtration due to its presence in air, dust

particles, technical liquids, etc. This kind of error may be detected by filtration of pure water in the field.

Elevated concentrations of metals may also arise due to cross contamination from reused sampling bottles or from metals present in the pure acid used for sample acidification. This kind of error may be quantified using external standards.

During the analytical determination, metal concentration may be affected by errors in calibration or sample carry over. This kind of error may be quantified using internal standards.

Experimental setup

To test the effect of the different sampling and preservation techniques, the following experimental design was employed.

Table 1: Initial layout for the study displaying the amount of samples in each sample group and their respective treatment (n= 615).

month	October	November	December
20 lakes	Type A Type B	-	-
25 rivers and streams	Type A Type B	Type A Type B Type C	Type A Type B Type C
75 rivers and streams	Type A Type B	Type A Type B Type C	-

This setup allows for the testing of potential effects of differing metal filtration techniques in both lakes and streams as well as any effects that chemical composition and geographical location may have on the analytical results. For some 60 streams and rivers, three repeated samplings, over time, were conducted to detect potential temporal trends. Metals analyzed in this study include copper, zinc, cadmium, lead, chromium, nickel, arsenic, vanadium and molybdenum for all samples. Iron, manganese and aluminum were analyzed using a Varian Vista AX ICP-AES with a quartz nebulizer and cyclone spray chamber for a smaller subset.

Due to practical problems with sampling at some of the sites, the actual setup differed slightly from the one displayed above. The figures in Table 2 designate the total number of samples that were treated according to the various methods.

Table 2: Actual layout for the study displaying the amount of samples in each sample group and their respective treatment (n= 557).

month		October	November	December
lakes	Type A	34	15	0
	Type B	34	15	0
	Type C	0	0	0
coastal rivers and streams	Type A	38	38	26
	Type B	38	41	29
	Type C	0	0	29
inland rivers and streams	Type A	26	31	24
	Type B	26	39	37
	Type C	0	0	37

To compensate for the slightly smaller number of samples (557 instead of 615), total concentrations for both aluminium and iron were determined in almost all samples even if that was not part of the regular monitoring program.

RESULTS

Results from the 2009 autumn sampling (Set 1)

During the three months October, November and December 2009, a large number of smaller inland streams, larger inland rivers and rivers flowing into the Baltic and North Sea, and a number of lakes from Southern Sweden were sampled and treated according to the protocol described in Table 7. The running waters that were sampled were selected from a larger set of monitoring stations with respect to their geographic distribution and a number of water chemical parameters with the aim of subsampling a representative group of sites. The geographical distribution of the inland and the sites along or close to the coast, along with the lake sites, is displayed in Figure 3.

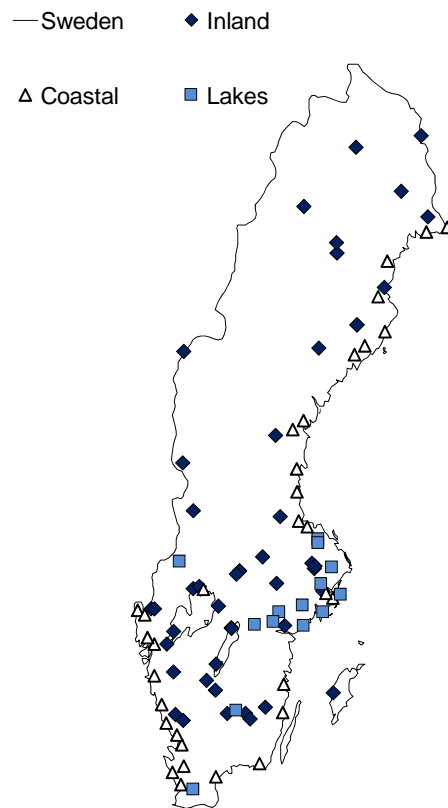


Figure 3: Map of the sampled lakes (light blue squares), inland streams and rivers (dark blue diamonds) and the streams and rivers close to or on the coast (white triangles).

Analysis of lab filtered fractions for all metals

All lab filtered samples may be classified according to their [FM]/[TM] ratio. This analysis allows for distinction between metals occurring mostly in the filtered fraction and those where either (a) a significant fraction is removed during the filtration process or (b) a significant amount of metal is leached from mineral particles or smaller particles with significant metal content influenced the metal content (particle contamination).

In order to identify which quantitative effects were observed the results were classified according to a number of percentiles and then colored according to the observed [FM]/[TM] ratio. Yellow and red fields require **special attention** while both green and white fields are regarded as acceptable.

Table 3: Analysis of frequency of [FM]/[TM] in the whole data set for various metals #.

	Cu	Zn	Cd	Pb	Cr	Ni
lower 5%	0.64	0.41	0.61	0.22	0.31	0.66
lower 25%	0.84	0.64	0.80	0.45	0.72	0.85
median	0.92	0.82	0.90	0.61	0.86	0.91
upper 75%	1.03	0.94	1.00	0.79	0.93	0.96
upper 95%	1.61	1.32	1.20	0.94	1.00	1.15
	Co	As	V	Mo	Fe	Mn
lower 5%	0.31	0.76	0.43	0.92	0.19	0.18
lower 25%	0.56	0.85	0.67	0.95	0.47	0.41
median	0.72	0.91	0.75	1.00	0.62	0.66
upper 75%	0.91	0.95	0.86	1.03	0.75	0.91
upper 95%	0.99	1.00	0.95	1.10	0.94	1.00

White fields indicate fractions [FM]/[TM] above 1 representative of samples where leaching or particle contamination occurred, green fields indicate fractions [FM]/[TM] between 0.5 and 1, yellow fields indicate fractions [FM]/[TM] between 0.25 and 0.5 and red fields indicate fractions [FM]/[TM] below 0.25. For this dataset samples with metal concentrations below 3*limit of quantification have been removed. This limit has been chosen arbitrarily.

None of the median fractions of [FM]/[TM] is above unity indicating significant fractions of the metals in particulate form. According to Table 3, the metals may be divided into two classes using the lower 25% of the samples as separation criteria; those with [FM]/[TM] fractions near unity (close to 0.7 or above) in more than 75% of the sampling occasions and those where the fraction in 25% of the samples is close to 0.5 or below.

The metals arsenic (As), molybdenum (Mo), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni) and zinc (Zn) belong to the first class. As an example, the fraction [FM]/[TM] is plotted as a function of pH in Figure 4.

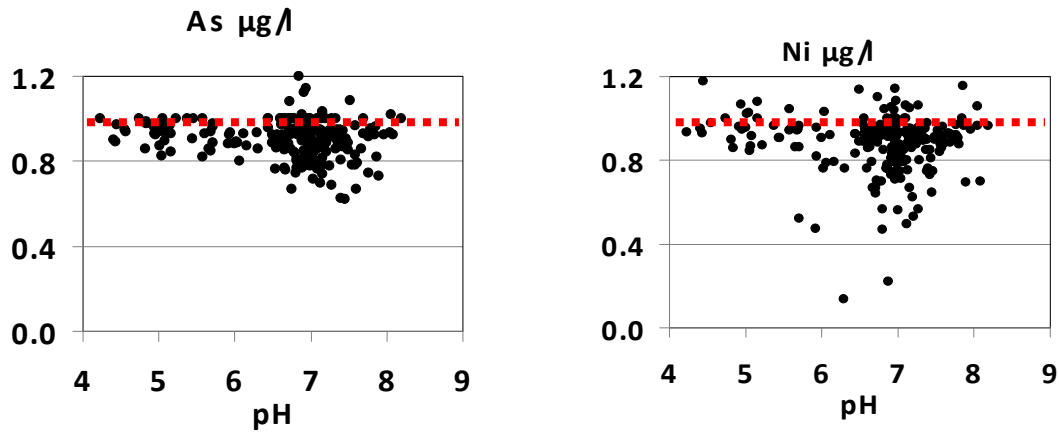


Figure 4: [FM]/[TM] as a function of pH for the metals arsenic (As) and nickel (Ni) as a function of sample pH in the whole dataset.

The other metals, lead (Pb), cobalt (Co), vanadium (V), iron (Fe) and manganese (Mn), belong to the second class. Due to the high toxicity of Cr(VI) and Cd, **caution should be taken at higher pH** levels where a trend to lower fractions in the dissolved form may be observed.

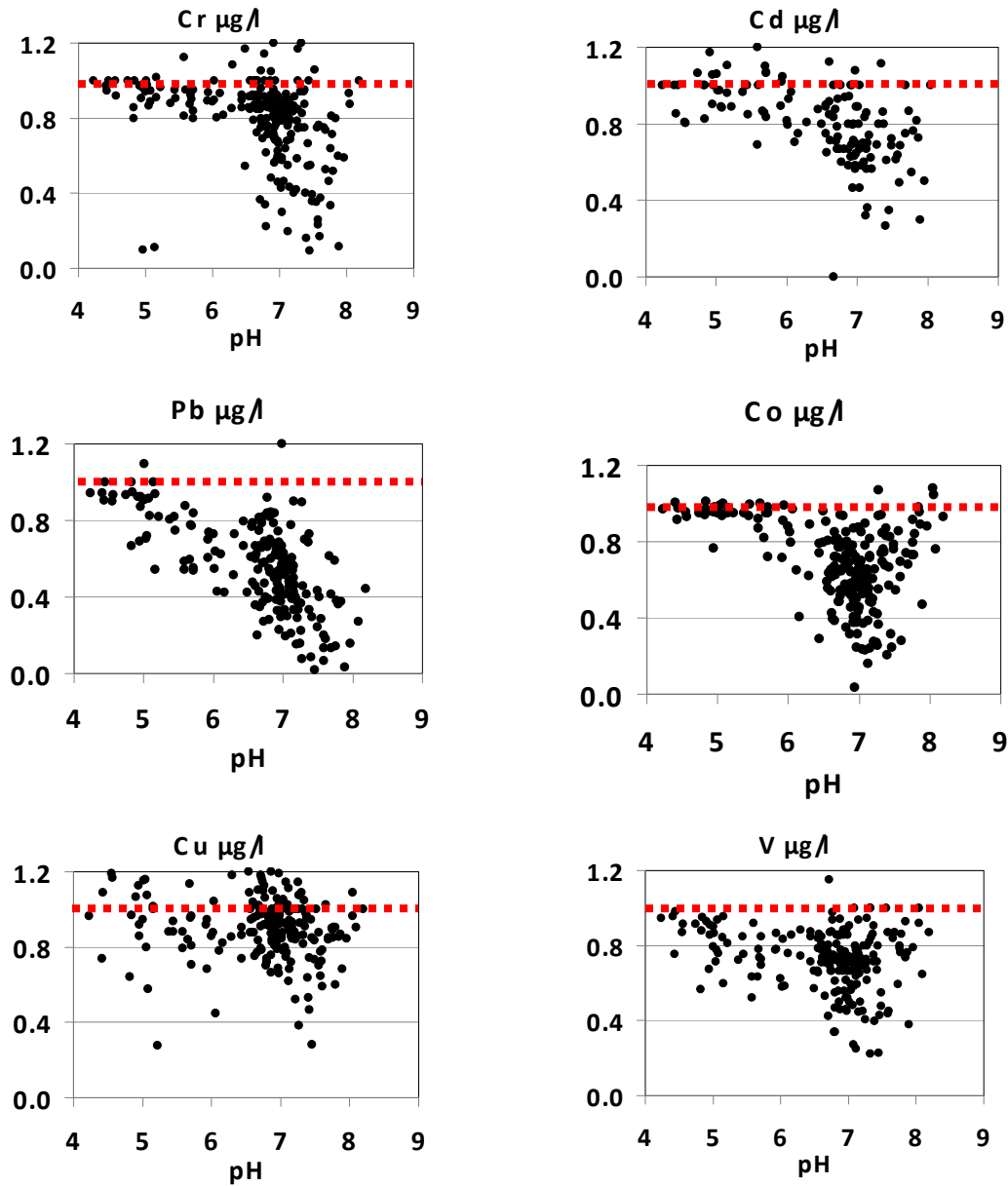


Figure 5: [FM]/[TM] as a function of pH for the six metals chromium (Cr), cadmium (Cd), lead (Pb), cobalt (Co), copper (Cu) and vanadium (V) as a function of pH in the whole dataset.

Within the complete data set Cr, Cd, Pb, Co, Cu and V have a significant amount of samples that indicate decreasing amounts of metals are in the dissolved form when pH is above 6.

Instead of dividing the sample set into ecoregions (Herbert, 2009), the sampled sites were classified into five different classes: small inland streams (Area < 50 km²), larger inland streams (Area > 50 km²), large coastal river mouths (Area > 1000 km²), smaller coastal streams (Area < 1000 km²) and lakes.

Analysis of streams and rivers

The results from the smaller streams with catchment areas below 50 km² are displayed in the attachment (see Figure 22 and Figure 23) and cover the pH range 4 to 8. Patterns emerge for lead, cobalt, iron and aluminum and indicate that the [FM]/[TM] ratio decreases with increasing pH and increases with increasing TOC. Arsenate, zinc and vanadium are mostly in the filtered fraction. The role of iron is most probably of minor importance.

The larger inland streams are fewer in number and cover a different pH range (6.5-8). The trends that were visible for cobalt and lead also apply in these streams while both aluminum and iron show a large amount of scattering (Figure 24 and Figure 25). The ratio of [FM]/[TM] is lower for cobalt in this set than for any other metal.

The large river mouths also cover a narrow pH range (6.5 to 8). Patterns seen for the smaller streams also seem to apply to this data set (Figure 26 and Figure 27). Additionally, it is possible that iron affects the [FM]/[TM] ratio for lead which is discussed further down.

The smaller coastal streams (Figure 28 and Figure 29) show surprisingly clear trends but the small number of samples (n= 16) available at this stage does not yet allow for definitive conclusions. The [FM]/[TM] ratio for lead, iron and aluminum decreases with pH while that for cobalt increases.

Analysis of lakes

Figure 30 and Figure 31 show clear trends of decreasing [FM]/[TM] ratios for lead, iron and aluminum with increasing pH. Cobalt shows minimum ratios around pH 6.5 which might be connected to the binding of Co to carbonate ions but awaits further study. Both cobalt and lead show an increasing [FM]/[TM] ratio with increasing iron concentration. None of the other metals have a clear trend with any of the driving variables and seem to occur mostly as [FM]. Interestingly, nickel occurs almost exclusively in the dissolved form.

Trends in space:

Trends in filtered metal concentrations in space may also be detected. This was studied further for the four metals arsenic (As), cobalt (Co), lead (Pb) and vanadium (V). For this analysis, all samples were plotted i.e. also the acidic streams and rivers. Most metal concentrations in Swedish running surface waters follow a clear geographical trend with increasing metal concentration towards the southern part of the country. The lines in the diagrams below are the reference values for regional background concentrations that were chosen in 1999 by the Swedish EPA (Wiederholm, 1999) for both lakes and streams. In this study, no distinction is made between larger and smaller rivers but instead inland and coastal running waters have been separated (observe the varying scales on the y-axis).

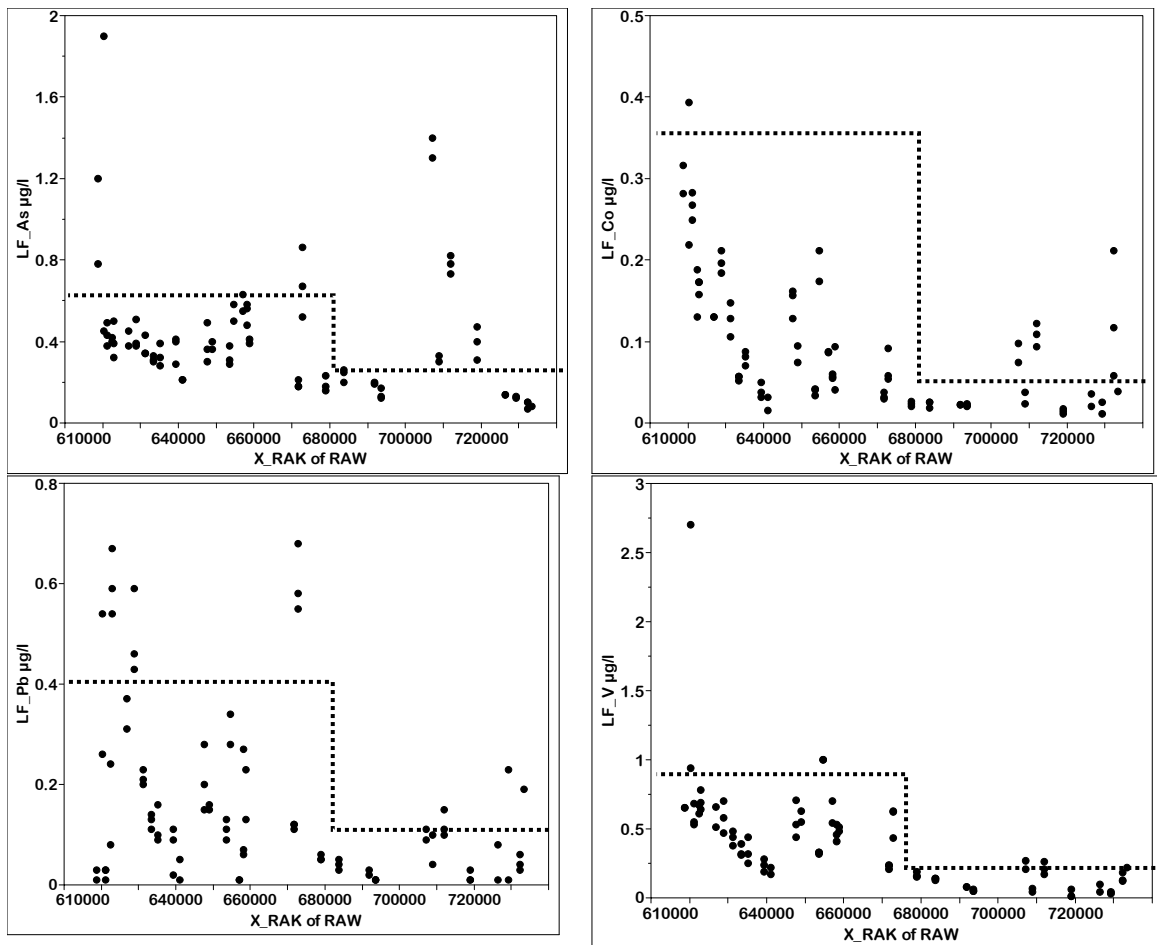


Figure 6: Coastal: Filtered metal concentration in $\mu\text{g L}^{-1}$ of some selected metals arsenic (As), cobalt (Co), lead (Pb) and vanadium (V) from upper left to lower right) as a function of increasing northbound coordinate X.

Most of the samples within the coastal streams and rivers are just outside a factor of two (or less) of the background values that were defined in 1999. Some significant deviation occurs for arsenic where concentrations of up to four times the background were determined. For lead it appears that natural background concentrations might actually be lower both in the Northern and the Southern part of the country than what was defined earlier. This might be due to decreasing levels of lead in surface waters as deposition of lead decreased drastically in recent years.

With the exception of arsenic, many inland streams and rivers have metal concentrations higher than what was defined as natural background levels in 1999. The largest deviations occur for the metals cobalt and vanadium but some points show large deviations for lead as well.

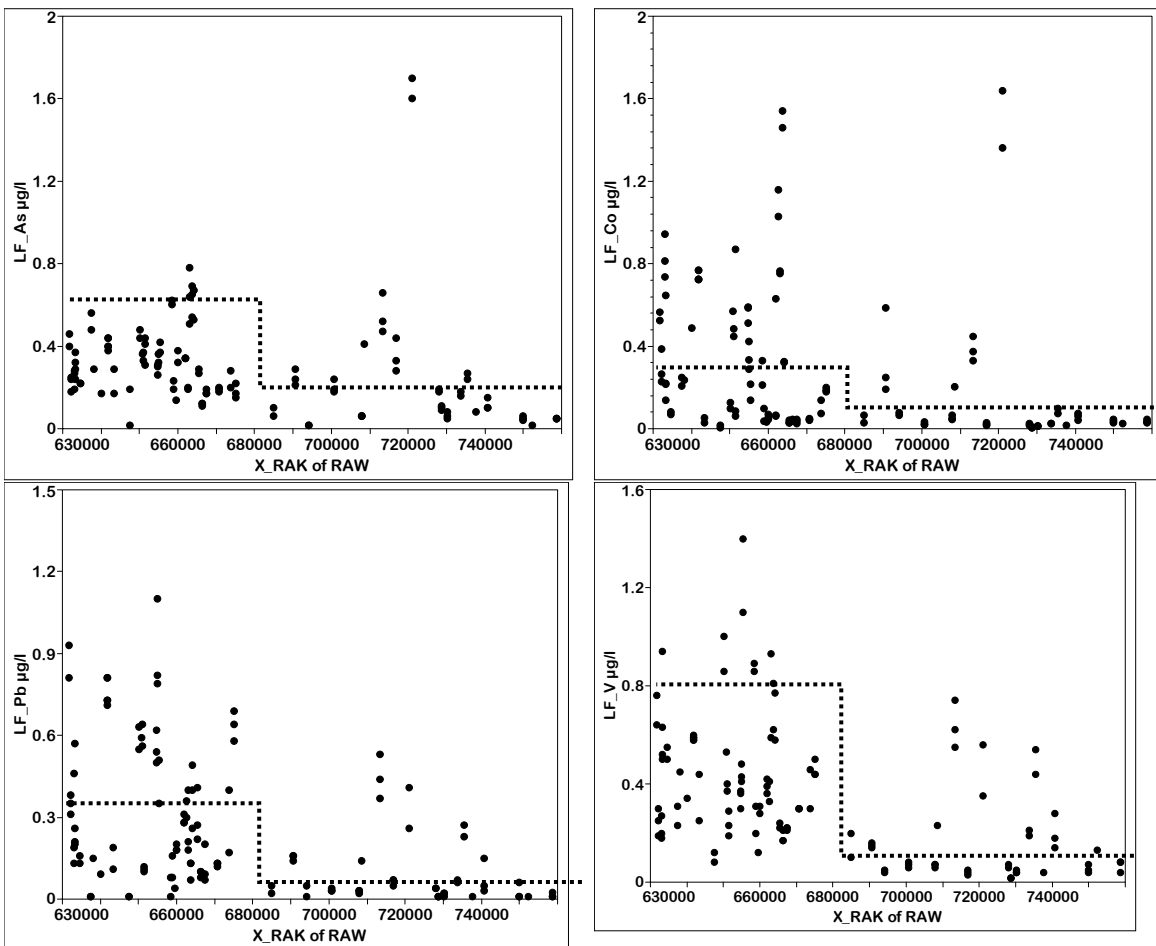


Figure 7: Inland streams and rivers: Filtered metal concentration in $\mu\text{g L}^{-1}$ of some selected metals arsenic (As) , cobalt (Co) , lead (Pb) and vanadium (V) from upper left to lower right) as a function of increasing northbound coordinate X.

The lake survey portion of this study only encompassed lakes from southern Sweden due to the freezing conditions during winter in the northern part of the country. A large number of lakes have filtered metal concentrations that are above natural background levels. Because this dataset does not contain any lakes from northern Sweden, only trends within the southern part of the country may be analyzed. For the southern lakes, no obvious spatial trends for filtered metal concentrations, as a function of geographical North, were observed. Instead, large variations of more than a factor of five may occur regionally that might be connected to internal lake processes. Especially large regional variations occur for lead.

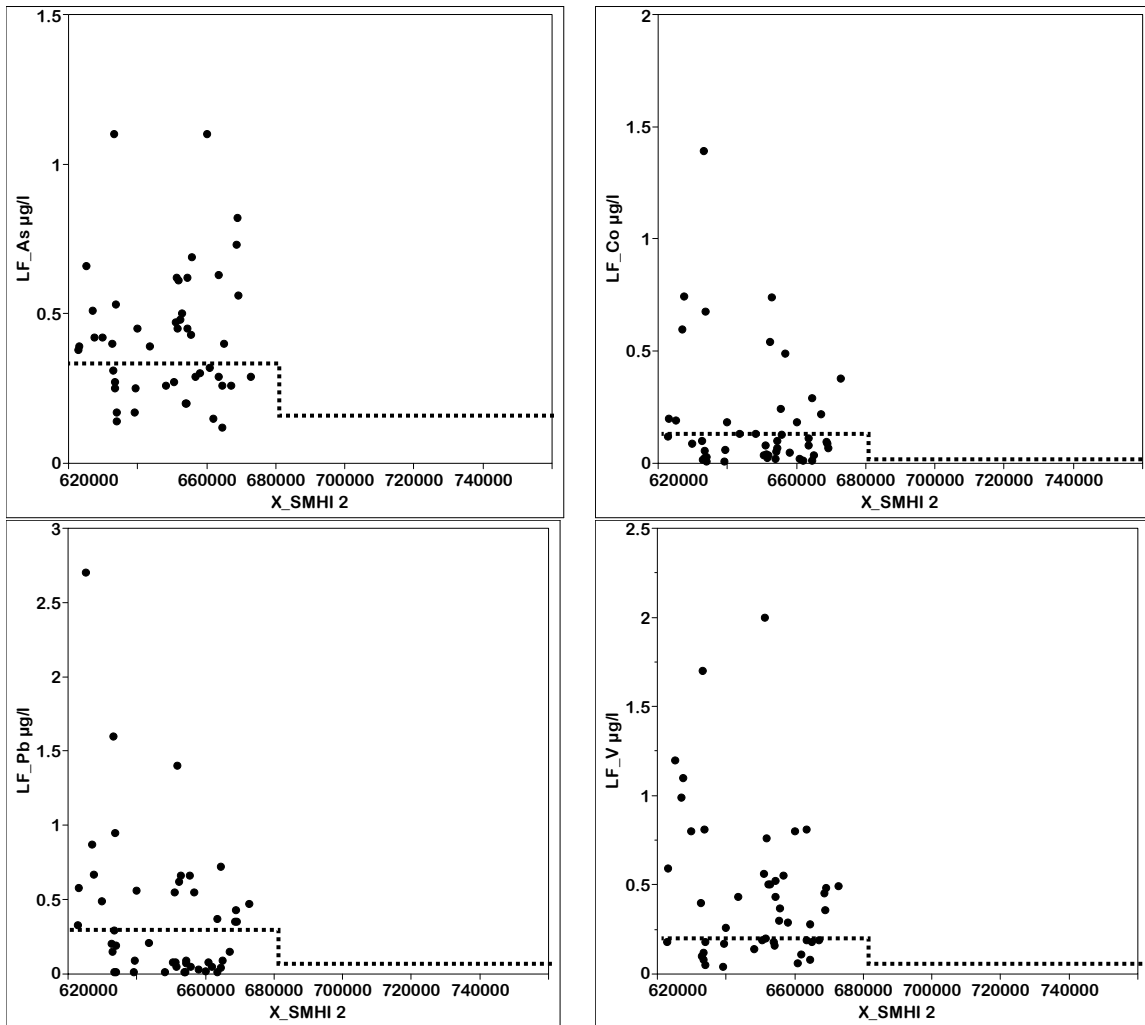


Figure 8: Lakes: Filtered metal [FM] concentration in $\mu\text{g L}^{-1}$ of some selected metals arsenic (As) , cobalt (Co) , lead (Pb) and vanadium (V) from upper left to lower right) as a function of increasing northbound coordinate X.

Trends in time

The dataset is too small to allow for a thorough analysis of temporal effects on the analysis technique of metals. One should also bear in mind that samples from spring flood and part of the autumn rain periods, where most of the water and most of the particulate material is transported in the streams and rivers, are not part of this study. Nevertheless, the inland streams and rivers dataset contains three consecutive samples which were taken at 19 stations during the period of October to December.

Due to the high scatter in the data, using a simple, overall correction factor when converting total metal concentrations into dissolved forms is not recommended. Instead, site specific studies at places with observed concentrations above those of the natural background concentrations must be conducted. This may be illustrated with the available short time series of $[FM]/[TM]$ fractions at different sites (Figure 9 and Figure 10).

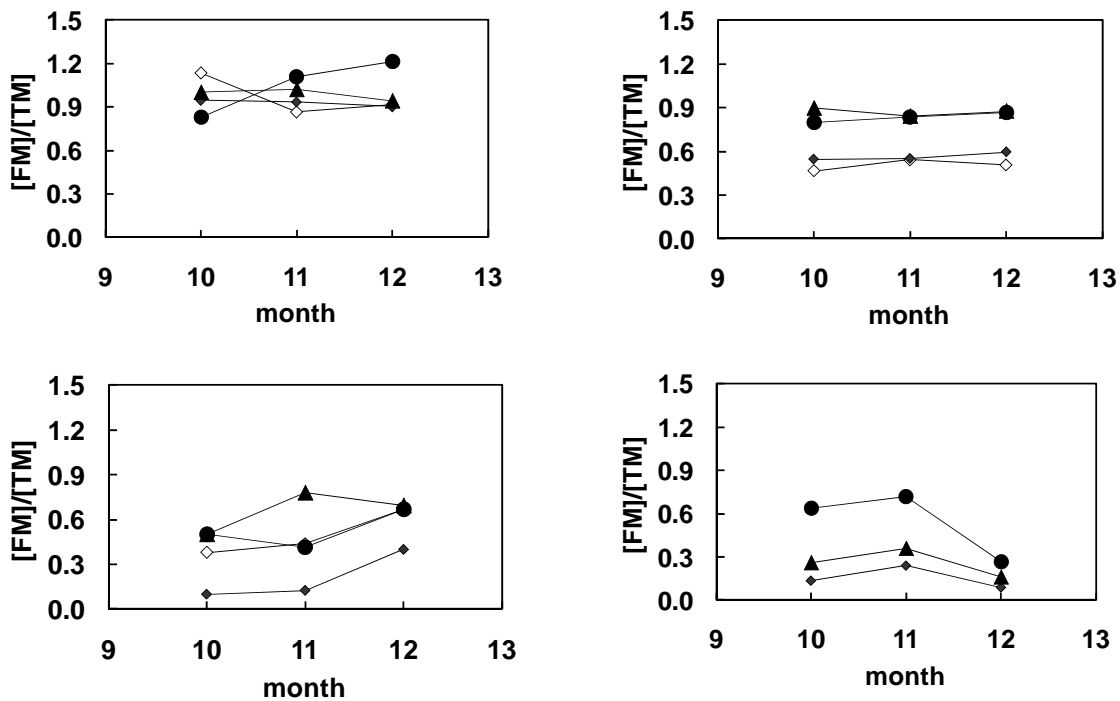


Figure 9: $[FM]/[TM]$ ratios at the sites Svartberget, Dammån, Killingi and Sävjaån Kuggebro from upper left to lower right, for metals cadmium (●), lead (◆), chromium (▲) and iron (◇).

Correction functions for both *Svartberget* (at this site all metals are mostly in the dissolved form) and *Dammån* (all metals behave differently but are almost constant over time) could be generated. However, the sites *Killingi* and *Sävjaån Kuggebro* show a

significant temporal pattern, making it difficult to determine correction factors. A similar analysis was conducted for the coastal streams and rivers.

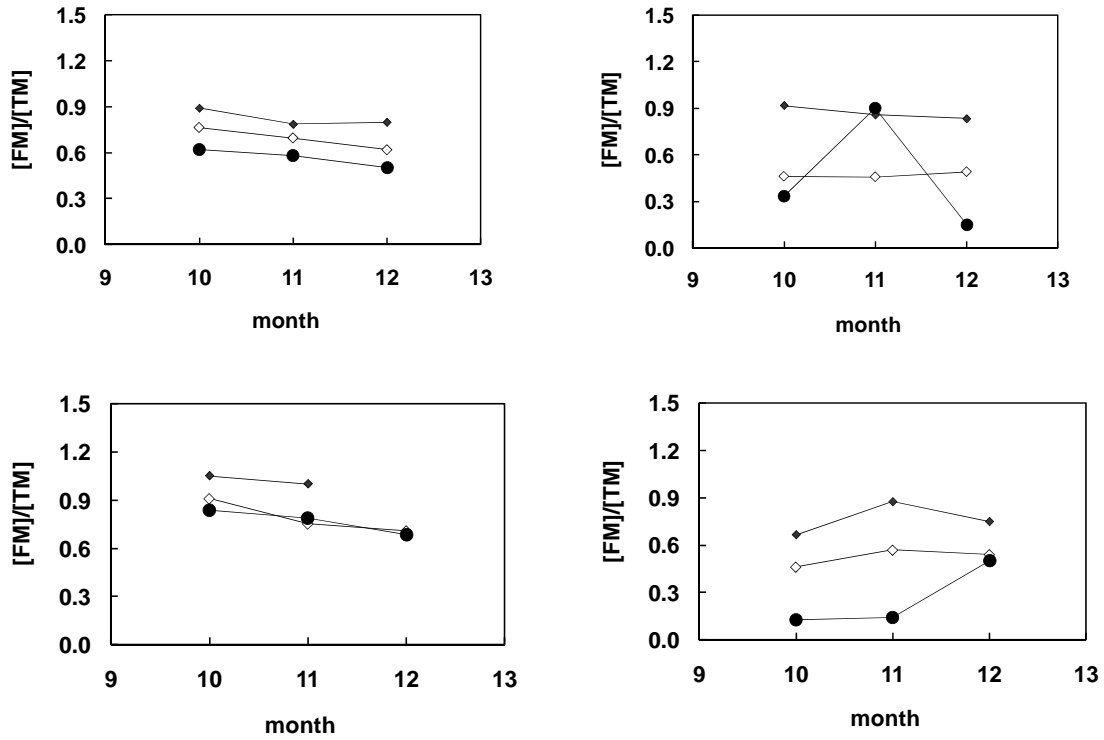


Figure 10.: $[FM]/[TM]$ ratios at the sites Gavleån Gävle, Botorpström Brunnsö, Lyckebyån Lyckeby and Indalsälven Bergforsen from upper left to lower right for metals cadmium (●), lead (◆), chromium (▲) and iron (◇).

Relationships between filtered metal concentrations and iron

From earlier studies (Andersson et al., 2006; Benedetti et al., 2002; Herbert, 2009; Pokrovsky and Schott, 2002) it is known that many metals may be bound to colloidal iron present in many surface waters. This colloidal iron is so small that it can pass through a 0.45 micrometer filter. To determine if the same holds true for this study, the fraction of dissolved nickel (Ni), dissolved cobalt (Co), dissolved arsenic (As) and dissolved lead (Pb) were compared to the fraction of dissolved iron (Fe) for the those samples where both high lead (> 0.5ppb) and high iron (> 200ppb) concentrations occurred for running waters and lakes separately.

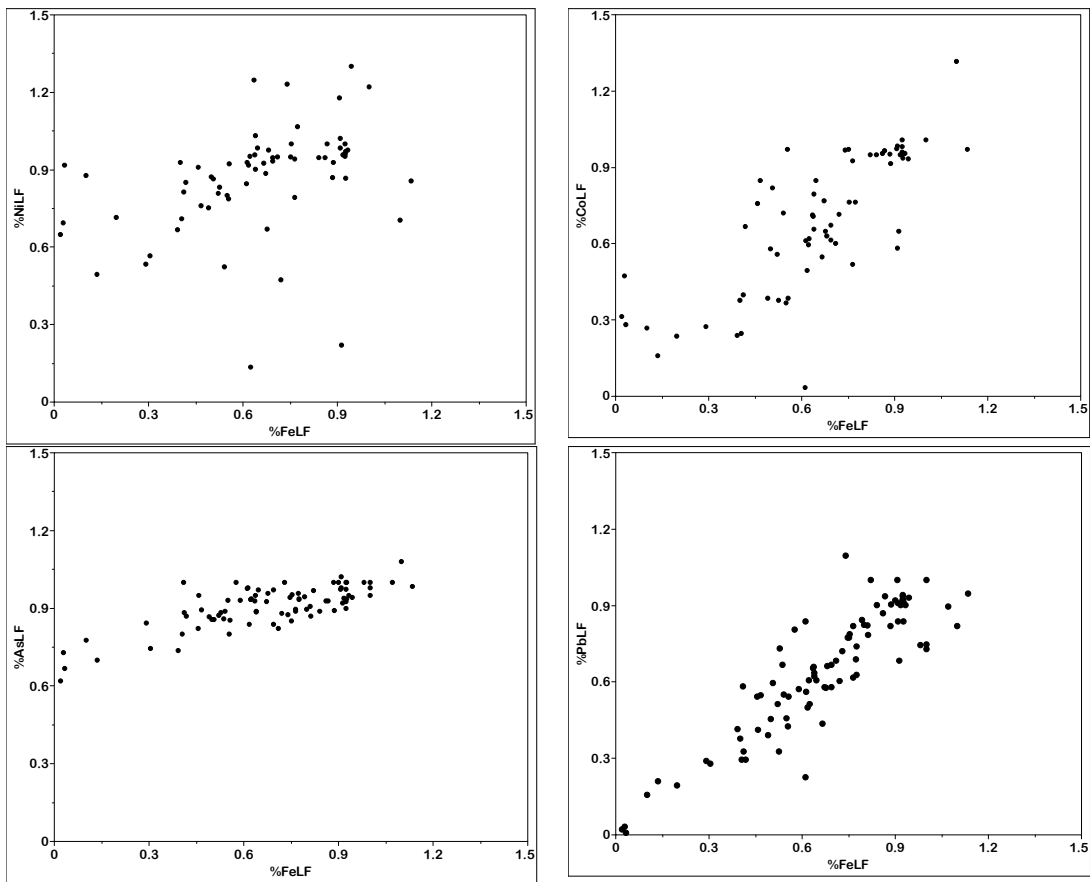


Figure 11: Plot of percentage of filtered metal fraction [FM]/[TM] for various metals as a function of fraction of filtered iron for samples with high lead (> 0.5 ppb) and elevated iron (> 200ppb) concentrations but excluding the lake sample population.

In these samples, iron and/or organic rich iron colloids are most probably affecting both cobalt and lead, and to some extent nickel and arsenic.

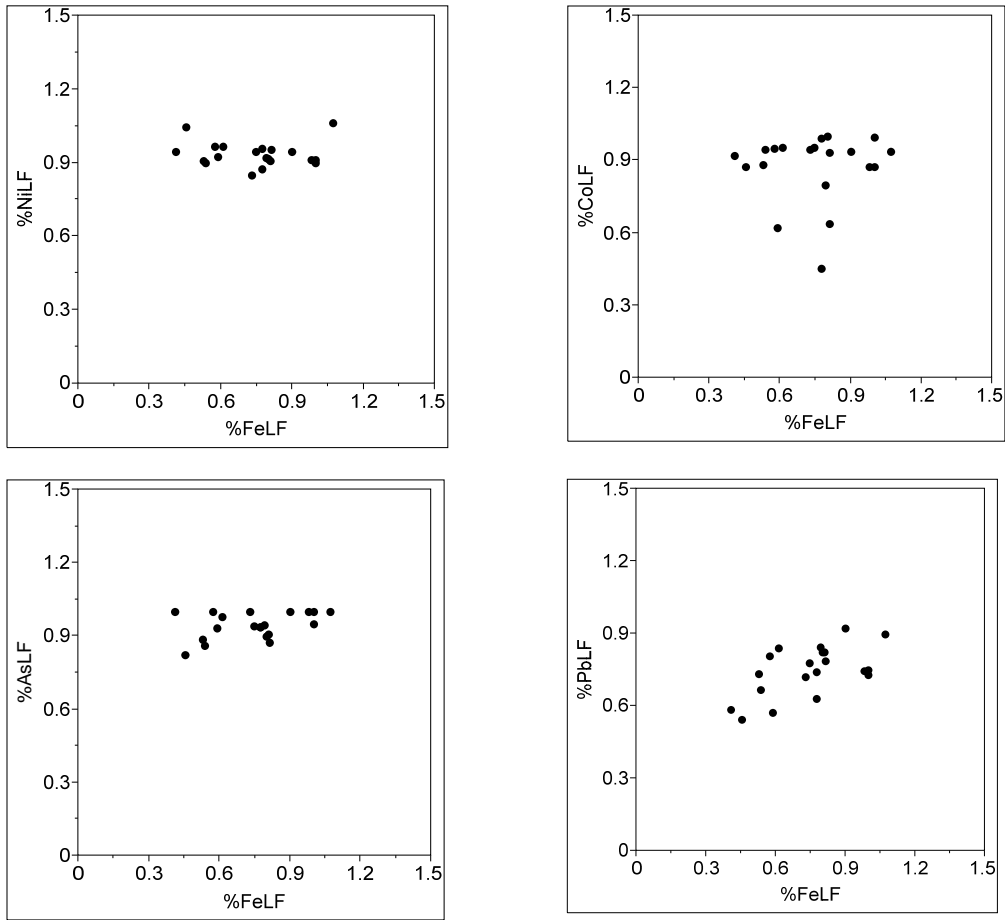


Figure 12: Plot of percentage of filtered metal fraction [FM]/[TM] for various metals as a function of fraction of filtered iron for samples with high lead (> 0.5 ppb) and elevated iron (> 200ppb) concentrations for the lake sample population.

It is evident that dissolved metal fractions in the lakes are almost independent of the fraction of dissolved iron. A weak relationship is observed for lead. This indicates that the colloidal carrier substances for different metals differ in the lake and stream and river sample populations.

Comparison between field and lab filtration

During the December campaign, around 50 samples were filtered both in the field and the laboratory. This small set may be used to compare the potential effect of contamination, precipitation and associated artifacts.

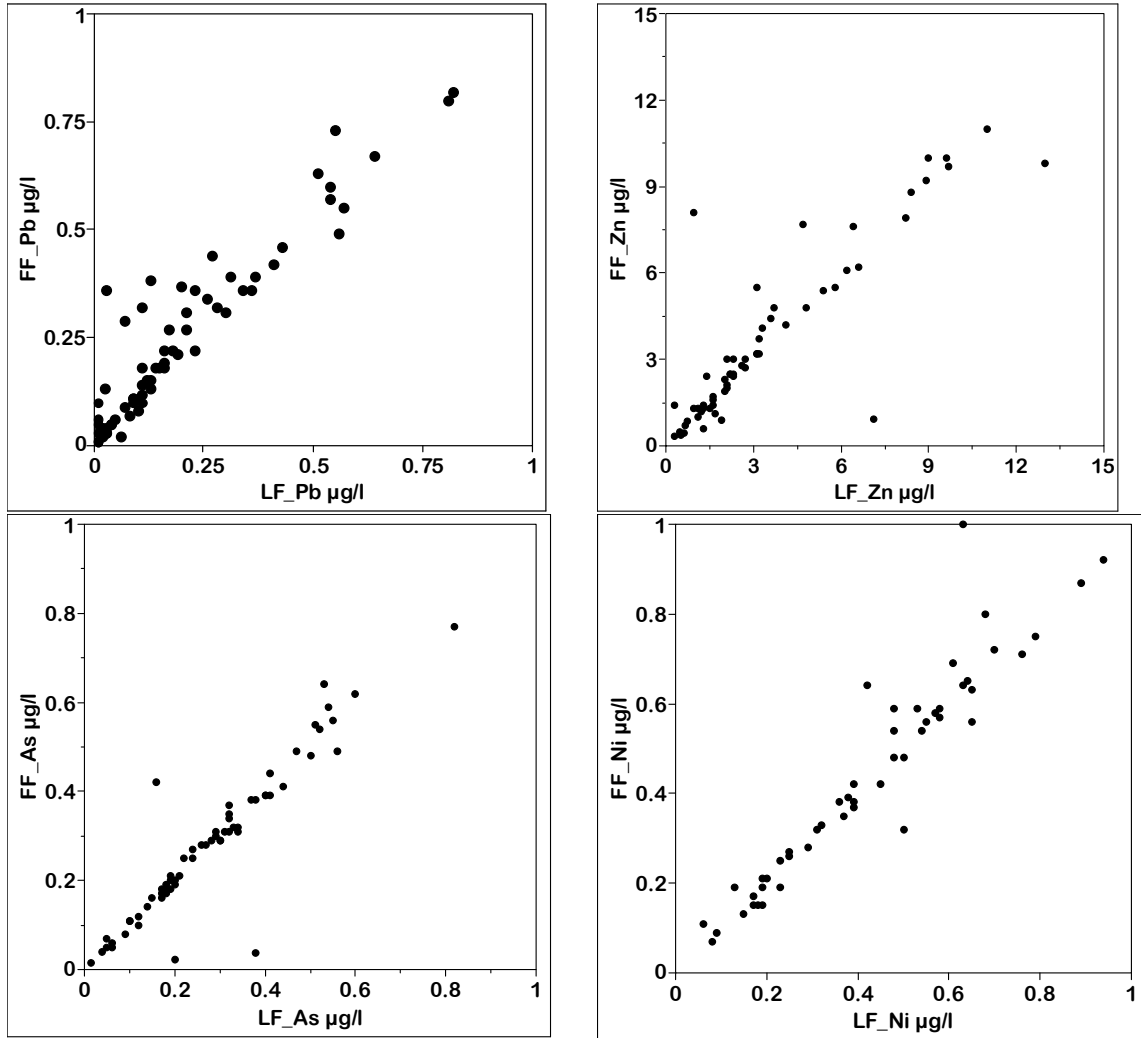


Figure 13: Comparison between measured filtered metal concentrations for lead, zinc, arsenic and nickel from upper left to lower right in $\mu\text{g L}^{-1}$.

These data indicate that contamination cannot be excluded but is probably of minor importance. Higher field filtered samples indicate a contamination problem while working in an uncontrolled environment. This probably occurred for some samples with regards to zinc, lead and to a lesser extent for nickel (one sample for arsenic). Lower values from laboratory-filtered samples may indicate either contamination (in the field) or precipitation of formerly dissolved colloids. This occurred twice for arsenic and once for zinc.

Potential effect of filtration on the classification of surface waters

The data for the filtered and unfiltered metal concentrations may also be used to test whether the filtration procedure would have any impact on the decision of whether metal concentrations are above the background concentrations defined in 1999 at any site. For this purpose, samples with any metal concentration above three times the background for large rivers (as defined in table 10 of the Swedish EPA document *bedömningsgrunder*, Wiederholm, 1999, page 153) and having a pH above 6 were identified.

Table 4: Yellow samples are those that are above “3BG” of 6 ppb for Cu, 18 ppb for Zn, 0.05 for Cd, 1.2 ppb for Pb, 2.5 ppb for Cr, 8 ppb for Ni, 1.0 ppb for Co, 1.8 ppb for As and 2.4 ppb for V. Sample sites that are underlined in the lower part of the table mark those that would not be classified as abnormal if filtered metal concentrations were to be used. “3BG” is defined as a metal concentration higher than 3 times the natural background concentration (Wiederholm, 1999).

Name	TYPE	[km ²] SIZE	unfiltered [(g L ⁻¹)]										[] pH	[mM] ALK	[mg L ⁻¹] TOC
			Cu	Zn	Cd	Pb	Cr	Ni	Co	As	V				
Bällstaån	inland	7	12	68	0.083	3.9	2.8	3.7	1.05	1	3.9	7.45	2.218	13.5	
Bällstaån	inland	7	5.6	37	0.12	1.3	0.94	3.6	0.754	0.9	1.9	7.6	3.604	11.6	
Norrhultsbäcken	inland	21	0.88	4.5	0.252	0.39	0.54	4.4	0.221	0.31	0.7	6.29	0.107	12	
Norrhultsbäcken	inland	21	0.92	3.9	1.1	0.33	0.44	0.61	0.273	0.36	0.6	6.03	0.05	13.2	
Dammån	inland	34	0.33	10	0.049	0.64	0.19	0.25	0.457	0.28	0.43	6.02	0.04	11.1	
Ostvik	inland	150	3.8	24	0.059	0.61	0.76	4.7	1.4	2	0.6	6.06	0.11	14.6	
Dalbergsån Dalbergså	inland	832	5	10	0.016	1.9	0.95	1.2	0.35	0.57	1.9	7.21	0.586	15.3	
Dalbergsån Dalbergså	inland	832	4.2	15	0.028	3	2.2	1.9	0.78	0.63	4	7.12	0.729	14.1	
Kolbäcksån Semla	inland	2205	1.4	18	0.03	0.97	0.47	0.65	1.15	n.d.	n.d.	6.94	0.232	11.7	
Kolbäcksån Semla	inland	2205	1.3	20	0.016	0.62	0.27	0.41	0.053	n.d.	n.d.	6.91	0.175	10.5	
Killingi	inland	2347	0.94	28	0.009	0.15	0.13	0.64	0.044	0.06	0.08	6.75	0.285	2.7	
Sävjaån Kuggebro	inland	3441	3.1	9.3	0.047	0.52	1.2	11	0	0.83	0	7.58	2.685	20.7	
Sävjaån Kuggebro	inland	3441	3.4	10	0.05	0.54	1.4	11	2.03	0.81	1.7	7.49	2.555	24.1	
Sävjaån Kuggebro	inland	3441	4.7	21	0.136	1.5	2.7	10	0	0.86	0	7.4	2.271	22.1	
Gavleån Gävle	coast	2453	6.2	12	0.044	1.1	0.5	1.2	0.109	0.62	0.63	6.93	0.254	16.7	
Helgeån Hammarsjön	coast	4144	2.1	6	0.026	0.63	0.51	1.1	0.518	2	3.2	7.34	0.808	13.5	
Helgeån Hammarsjön	coast	4144	1.8	10	0.039	1.3	0.74	1.5	0.919	0.61	2.1	7.15	0.418	19.7	
Emån Emsfors	coast	4441	1.1	1.7	0.05	0.2	0.17	0.82	0.077	0.34	0.39	7.31	0.487	9.2	
Stockholm,jvb	coast	22650	9.1	6.8	0.005	0.9	0.17	2.5	0.079	0.6	0.53	7.59	0.993	10.4	
Svarta Sjö	lake	0	0.68	3.1	0.01	3.2	0.28	0.37	0.238	0.7	1.4	6.83	0.163	19	
Name	TYPE	[km ²] SIZE	filtered [(g L ⁻¹)]										[] pH	[mM] ALK	[ppm] TOC
Cu	Zn	Cd	Pb	Cr	Ni	Co	As	V							
Bällstaån	inland	7	3.4	31	0.029	0.08	0.26	2.4	0.33	0.62	0.89	7.45	2.218	13.5	
Bällstaån	inland	7	3.3	18	0.059	<0.02	0.16	3.3	0.212	0.6	0.86	7.6	3.604	11.6	
Norrhultsbäcken	inland	21	0.75	2.6	0.203	0.2	0.46	0.6	0.137	0.29	0.52	6.29	0.107	12	
Norrhultsbäcken	inland	21	0.96	4.1	1.02	0.21	0.44	0.63	0.217	0.32	0.5	6.03	0.05	13.2	
<u>Dammån</u>	inland	34	0.29	9.5	0.039	0.35	0.17	0.19	0.388	0.25	0.25	6.02	0.04	11.1	
Ostvik	inland	150	1.7	15	0.057	0.26	0.61	3.7	1.36	1.6	0.35	6.06	0.11	14.6	
<u>Dalbergsån Dalbergså</u>	inland	832	2.6	3.9	0.009	0.55	0.38	0.64	0.096	0.48	0.86	7.21	0.586	15.3	
<u>Dalbergsån Dalbergså</u>	inland	832	2.6	3.6	0.009	0.63	0.43	0.94	0.124	0.44	1	7.12	0.729	14.1	
<u>Kolbäcksån Semla</u>	inland	2205	1.2	13	0.014	0.22	0.32	0.55	0.041	n.d.	n.d.	6.94	0.232	11.7	
<u>Kolbäcksån Semla</u>	inland	2205	1.2	16	0.01	0.27	0.22	0.38	0.029	0.27	0.22	6.91	0.175	10.5	
Killingi	inland	2347	0.94	26	0.006	0.06	0.09	0.58	0.035	0.04	0.07	6.75	0.285	2.7	
Sävjaån Kuggebro	inland	3441	2.4	4.1	0.03	0.07	0.31	10	0	0.65	n.d.	7.58	2.685	20.7	
Sävjaån Kuggebro	inland	3441	2.5	5.3	0.036	0.13	0.5	9.9	1.54	0.69	0.81	7.49	2.555	24.1	
Sävjaån Kuggebro	inland	3441	2.5	4.7	0.036	0.13	0.43	7.6	1.46	0.54	0.62	7.4	2.271	22.1	
Gavleån Gävle	coast	2453	5.5	9.6	0.035	0.55	0.4	1.1	0.054	0.52	0.43	6.93	0.254	16.7	
<u>Helgeån Hammarsjön</u>	coast	4144	2.2	4.2	0.029	0.26	0.42	1	0.393	1.9	2.7	7.34	0.808	13.5	
<u>Helgeån Hammarsjön</u>	coast	4144	1.3	3	0.014	0.54	0.32	1	0.219	0.45	0.94	7.15	0.418	19.7	
<u>Emån Emsfors</u>	coast	4441	1.2	1.5	0.04	0.14	0.16	0.75	0.057	0.31	0.32	7.31	0.487	9.2	
Stockholm,jvb	coast	22650	6.6	3.8	0.008	0.06	0.13	2.4	0.055	0.58	0.46	7.59	0.993	10.4	
Svarta Sjö	<u>lake</u>	0	0.62	2.6	<0.005	2.7	0.2	0.34	0.19	0.66	1.2	6.83	0.163	19	

From the above table, it is obvious that the filtered metal concentrations will tend to decrease the amount of sites and number of metals that are identified as exceeding the background. This is evident for the sites where lead (Pb), vanadium (V) or chromium (Cr) is a problem because those metals tend to be in the particulate fraction at pH above 6.

Relating these findings to the long-term monitoring time series dataset

The range of observed values for pH, TOC and total metal concentration from the autumn sampling campaign can be compared with data from the long-term environmental monitoring programs in lakes, streams and rivers during the same period (October to December). For this purpose, existing data (from regular monitoring programs available at the department) were selected that contained samples from the same autumn period during autumn. Initially, pH, conductivity, absorbance, total organic carbon and most of the metals were classified in the three sample classes (inland, costal and lakes). Then the respective distribution parameters were divided to test whether the sampled dataset would span the range of the existing long-term monitoring dataset. These data are displayed in Table 7, Table 8 and Table 9 in the Annex. From Table 9 it may be concluded that most parameters within dataset 1 are representative for the whole monitoring program, i.e. all ratios are within the range 0.5 and 1.5, indicating less than 50% deviation from the average. Some exceptions occur notably for absorbance, TOC and cobalt in the lake dataset where higher values occurred in the sub-sampled set. This could be due to the fact that only lakes in the southern part were sampled, which tend to be affected to a higher degree by human impact. For the inland streams, a tendency towards higher iron, lead, cadmium and cobalt concentrations, when compared to the long-term data, was observed. This could be due to the subjective selection process of the sites.

Sampling campaign in the Krycklan catchment (Set 2)

This dataset consists of around 400 samples that were sampled in the Krycklan research project during 2006 and is similar to that described by Björkvald et al. (2008) and analyzed in Stockholm. Results are available for zinc, copper, aluminum and iron, and a smaller number of chromium analyses. The waters sampled are from a mixed catchment encompassing forested areas, wetlands, arable land and lower lying sediment dominated streams. The geographical analysis of this dataset is outside the scope of this report so only [FM]/[TM] ratios for the whole dataset will be reported.

In this dataset, the three metals that are of primary interest, i.e. copper, zinc and chromium, show high [FM]/[TM] ratios that are on average 1.17, 1.47 and 1.01 respectively. Only around 15-20% of all samples have [FM]/[TM] ratios that are below 0.4.

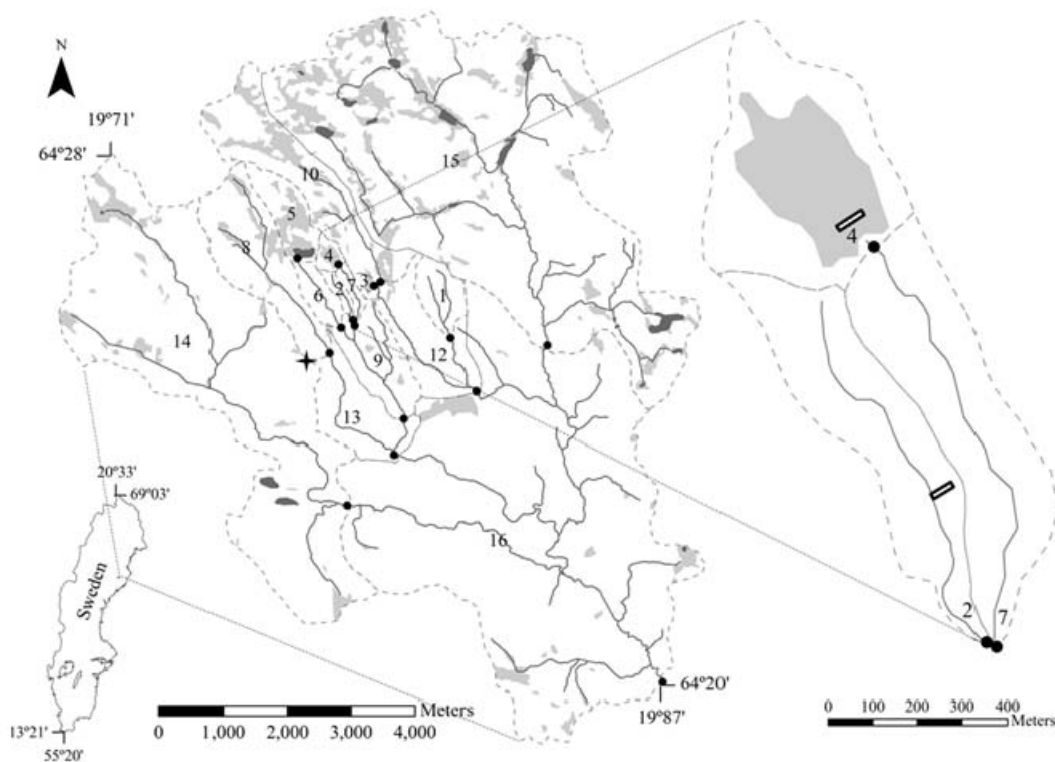
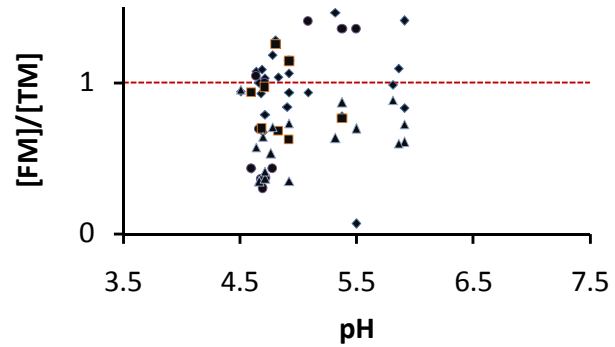


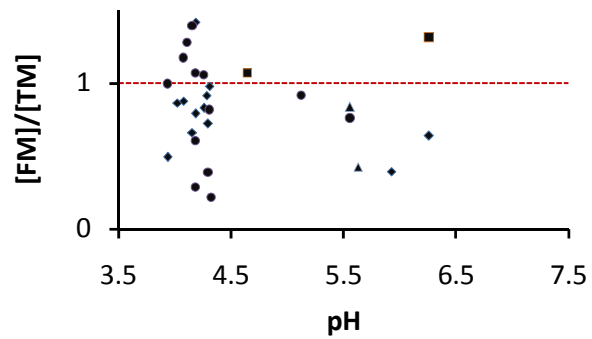
Figure 14: Location and sampling sites of the Krycklan study.

No clear patterns emerge as can be seen in the figure below where the [FM]/[TM] ratio is plotted as a function of pH at three selected sites within the Krycklan area. The three sites are one stream originating from a mostly forested area, one from a wetland and a third location that is downstream of the previous two after the two streams have combined.

Results from the forested site



Results from the wetland site



Results from the mixed site downstreams of both the wetland and forested site.

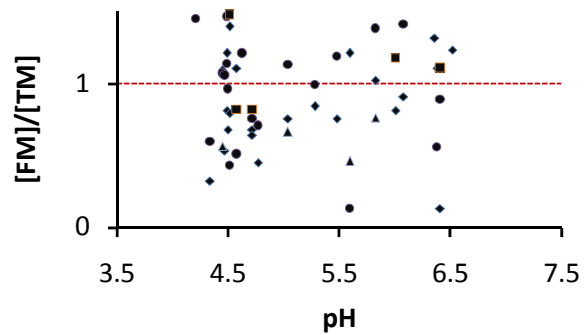


Figure 15: [FM]/[TM] ratio plotted against field pH for the metals copper (♦) , zinc (●) and chromium (■) at different sites within the Krycklan area revealing no clear pattern to either pH or landuse type. Mire site (red dots), forested site (blue dots), mixed site (violet dots) and remaining sites (black dots) during the sampling campaign 2006.

In this dataset the risk for contaminating the sample while performing the filtration operation in the field is obvious for both zinc and chromium as a significant portion of the samples have ratios of [FM]/[TM] above unity.

Seasonal sampling campaign in the Dalarna region (Set 3)

This dataset was collected in the Dalarna region during 2008 and is thus only applicable for a particular region but is very valuable as it covers the potential annual variation of [FM]/[TM] ratios. The same streams were sampled during spring, summer and autumn for nickel, copper, lead, zinc, chromium and cadmium.

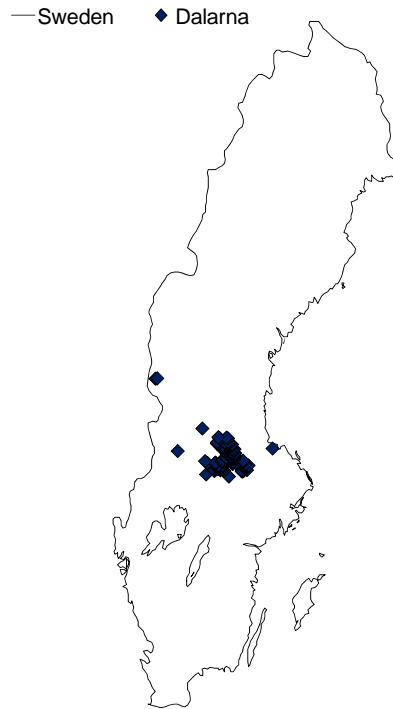


Figure 16: map of Sweden with the location of the sampled sites in the region of Dalarna.

An analysis of the temporal effects of the [FM]/[TM] ratio does not indicate any significant change in pattern. In all three seasons the ratio is mostly related to pH.

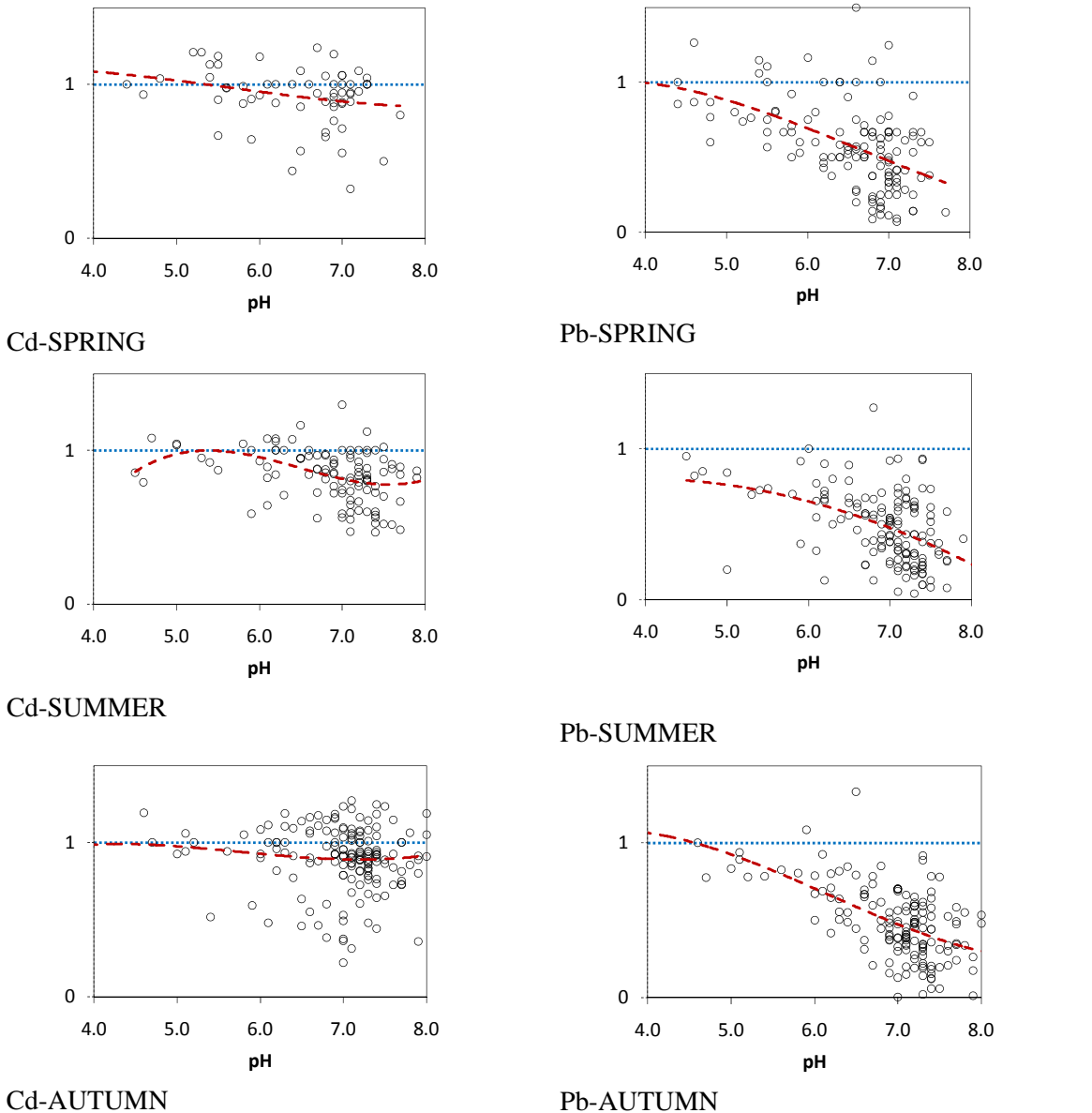


Figure 17: Spring, summer and autumn data for cadmium (left) and lead (right). Blue line is a reference line referring to $[FM]/[TM]$ equal to unity and the red line is a fit of a 3rd order polynomial on the untreated data that describes the variation of $[FM]/[TM]$ as a function of pH.

Contamination seems to have occurred within this dataset for cadmium for some samples, ($[FM]/[TM]$ is larger than unity in some of the graphs but to a much smaller degree than in dataset 2 from the previous section. Lead contamination does not seem to be an issue for the very large majority of the samples.

Effects of sample storage time and effect of sedimentation technique (Set 4)

This dataset contains laboratory tests involving a sedimentation-decantation or a filtration technique for sample separation, effects of storage time as well as blank tests using external calibration references. During autumn 2008, the laboratory at the department completed a study on the effect of filtration, time of storage and contamination risk when using filters on a series of samples (Wallman and Andersson 2009).

Twenty samples from a number of sites across the country were collected and sampled according to (a) technique Type A and (b) technique Type B (see Figure 1 and Figure 2) but also having acidified the sample before filtration. Yellow and red fields require **special attention** while both green and white fields are regarded as acceptable.

Table 5 Analysis of frequency of [FM]/[TM] in data set 4 (n= 20) for various metals for the second experiment (a) #.

	Cu	Zn	Cd	Pb	Cr	Ni
lower 5%	0.81	0.74	0.69	0.76	0.77	0.73
lower 25%	0.85	0.82	0.84	0.89	0.88	0.84
median	0.91	0.87	0.94	0.95	0.90	0.96
upper 75%	0.96	0.96	1.02	0.97	0.94	0.99
upper 95%	0.98	0.98	1.08	0.98	0.97	1.11
	Co	As	V	Mo	Fe	Mn
lower 5%	0.73	0.83	0.90	n.a.	0.87	0.92
lower 25%	0.85	0.88	0.91	n.a.	0.93	0.95
median	0.88	0.94	0.95	n.a.	0.95	0.98
upper 75%	0.93	0.97	0.99	n.a.	0.98	0.99
upper 95%	0.97	1.05	1.11	n.a.	1.01	1.01

White fields indicate fractions [FM]/[TM] above 1 and are representative of samples where leaching or particle contamination occurred; green fields indicate fractions [FM]/[TM] between 0.5 and 1; yellow fields indicate fractions [FM]/[TM] between 0.25 and 0.5 and red fields indicate fractions [FM]/[TM] below 0.25. Samples with metal concentrations below 3*limit of quantification have been removed. Molybdenum was not part of this study (n.a. = not analyzed).

The comparison (Table 5 and Table 6) indicates that experiments (a) and (b) have a similar outcome within an error margin of less than 30% on average. Results of a filtered acidified sample are thus comparable to those obtained from a sample that is acidified, left for sedimentation and then decanted.

Table 6 Analysis of frequency of [FM]/[TM in data set 4 (n= 20) for various metals for the second experiment (b) #.

	Cu	Zn	Cd	Pb	Cr	Ni
lower 5%	0.76	0.55	0.48	0.22	0.53	0.59
lower 25%	0.81	0.64	0.68	0.34	0.71	0.74
Median	0.88	0.70	0.85	0.43	0.88	0.84
upper 75%	1.03	0.85	0.93	0.70	0.95	0.89
upper 95%	1.24	0.93	1.10	1.03	0.98	1.02
	Co	As	V	Mo	Fe	Mn
lower 5%	0.25	0.75	0.27	n.a.	0.26	0.06
lower 25%	0.39	0.89	0.59	n.a.	0.44	0.14
Median	0.54	0.92	0.73	n.a.	0.59	0.44
upper 75%	0.86	0.99	0.86	n.a.	0.76	0.95
upper 95%	0.88	1.05	1.00	n.a.	0.92	1.02
# White fields indicate fractions [FM]/[TM] above 1 representative of samples were leaching or particle contamination occurred, green fields fractions [FM]/[TM] between 0.5 and 1, yellow fields fractions [FM]/[TM] between 0.25 and 0.5 and red fields indicate fractions [FM]/[TM] below 0.25. For this dataset samples with metal concentrations below 3*limit of quantification have been removed. Molybdenum was not part of this study (n.a. = not analyzed).						

The comparison of the present report and the data from the autumn 2008 study done at the department in Table 3 and Table 6 reveal that both have similar findings as similar metals reveal similar [FM]/[TM] ratios as tables have comparable colour patterns.

The main conclusion of that internal study is thus fourfold:

- No significant difference can be observed between samples that were handled according to *Type A* (see Figure 1 and Table 5) and those handled according to *Type B* but also filtered prior to analysis. This implies that contamination risks from filtering samples in the lab are small and metal contamination through particles not settled but transferred to the analysis vessel may be neglected.
- There is a significant difference between *Type A* and *Type B* handling for all metals (Table 6). For most of the metals, notably Al, As, Cd, Cu, Cr, Ni, V and Zn this difference is minor in comparison to interannual changes in concentrations and noise in the analytical procedure when working close to the detection limits. However, for Co, Pb, Fe and Mn, there is a significant difference even when taking into account the temporal variation.
- The time of storage between collection and analysis (i.e. the time between step 1 and step 3 in Figure 1) has a noticeable effect in some samples. For most samples this effect is masked by the temporal variability in metal concentration at the sampling site. The resultant effect of increasing concentration as a function of storage time was largest for lead, chromium, aluminum and iron.

From the archived data, a subsample of around 80 samples was used to test the effect of increased sample storage time. These samples were reanalyzed at different points in time from 10 to 50 days after their initial analysis due to discrepancies discovered in the quality assurance protocol with one of the metals at the first analysis date. In general, no trend was detected for metal concentration (either increasing or decreasing) over time when averaging the whole dataset; with all metals having mean differences below 10%. Chromium is the only metal where higher concentrations (i.e up to 40%), over time, were measured in almost all cases. Total concentrations of chromium are very low however and the quantitative effects of this are thus very small.

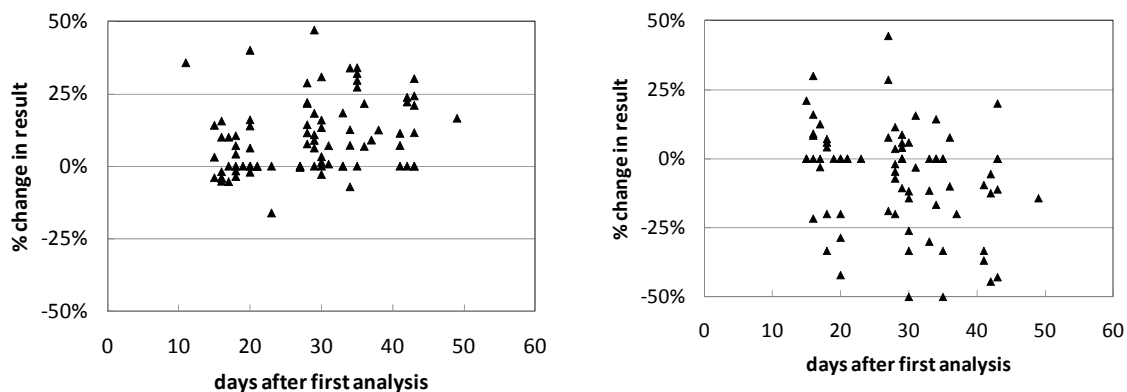


Figure 18: Relative changes in metal concentrations as a function between first and second analysis date for chromium (left) and cadmium (right).

DISCUSSION

Comparison between lab and field filtered samples

The high [FM]/[TM] ratios observed for both zinc and copper in data set 2 in the Krycklan area that were sampled by a number of different researchers are indicative of sample contamination in a large amount of samples and give rise to concern about collecting and filtering samples in the field. This is especially true under harsher conditions such as those typically encountered during spring flood or high flow events, which are represented by a large number of samples in this data set.

The number of samples with similar problems in data set 1 (data from the SLU laboratory) and data set 3 (data from the dalarna area) are much smaller. In both these cases, the samples were taken by experienced personnel. With a few exceptions at distinct sites, **sample contamination does not seem to be a major issue when experienced personnel collect and filter samples in the field.**

The comparison between the lab and field filtered samples suggest that changes in sample character during the time course of 1 day between the sampling and the arrival in the laboratory may be neglected. In future studies the **filtering of samples in the lab directly** on sample arrival is sufficient and will not introduce artificial effects that can change the composition of the sample.

Effects of applying the Swedish sample setup

According to Figure 1, several potential sources of systematic errors may occur when determining metal concentrations. During high flow periods amorphous, biogenic and minerogenic matter may be sampled that may release a significant amount of metals when brought in contact with concentrated nitric acid. Amorphous material may dissolve completely within hours, organic matter may precipitate and minerals may be partly attacked during holding times of days to weeks, releasing metals that are part of the mineral structure. In the future much shorter holding times ideally below one week will be followed. In addition, colloidal matter may enter the sample vial during the decantation step.

When comparing metal concentrations in lab filtered and unfiltered samples, all these factors may have affected the original constitution of the sample. Precipitation of organic matter due to the high ionic strength and low solubility of organic matter at pH below 2

could be a general concern in both methods and might lead to lower concentrations of dissolved metal concentrations.

Increased storage time of the sample will lead to increased metal concentrations of both lead and chromium. One way to reduce this variation is to decide to **fix the amount of time** the sample is allowed to settle to 1 week or 4 weeks in the future. Currently the holding time is below two weeks in general.

Sites that are of concern due to their large fluctuations in particulate matter and high metal loads **should be filtered** in the lab during part of the year under high flow conditions.

Temporal and spatial variation

Different sites behave differently with regard to both temporal variation in the fraction of dissolved metals and the absolute differences. For most metals the controlling factor for the [FM]/[TM] ratio seems to be pH, iron and TOC. In a future study a **statistical analysis of covariation** with other chemical parameters, size and flow could help to estimate ratios at various sites. From the various patterns shown in Figure 9 and Figure 10 it seems obvious that site specific ratios are most appropriate when trying to transform metal concentrations from total metal [TM] to filtered metal [FM].

The inland samples of this study indicate that they were biased to higher metal concentrations for almost all metals when compared to the long time monitoring data which is indicative of a subjective sample selection. For the lake sample population only cobalt and TOC differ significantly. As Co is not especially well correlated to TOC (see Figure 30) **this should be followed up**.

The coastal streams represent a sample population with lower metal concentrations. This is most probably due to the above average size of rivers that were included in this study.

Carrier substances and metal geochemistry

Many metals are mainly transported in the form of purely inorganic (i.e. iron- and or aluminum hydroxides) and mixed organic-inorganic colloids (i.e. iron-humic colloids). Some general observations can be made, using the data in this study, which may help to understand the transfer of metals from the land to the ocean. For this purpose, median values of all observed data within each class of samples (lakes, and coastal and inland

streams) were plotted as a function of pH. Clear patterns appear for most systems. Increasing metal to carbon ratios with increasing pH and decreasing metal to iron ratios with increasing pH that all are in accordance with what is known from the literature and what is expected when using equilibrium models. This is promising for further study of mobility of metals across the Swedish landscape.

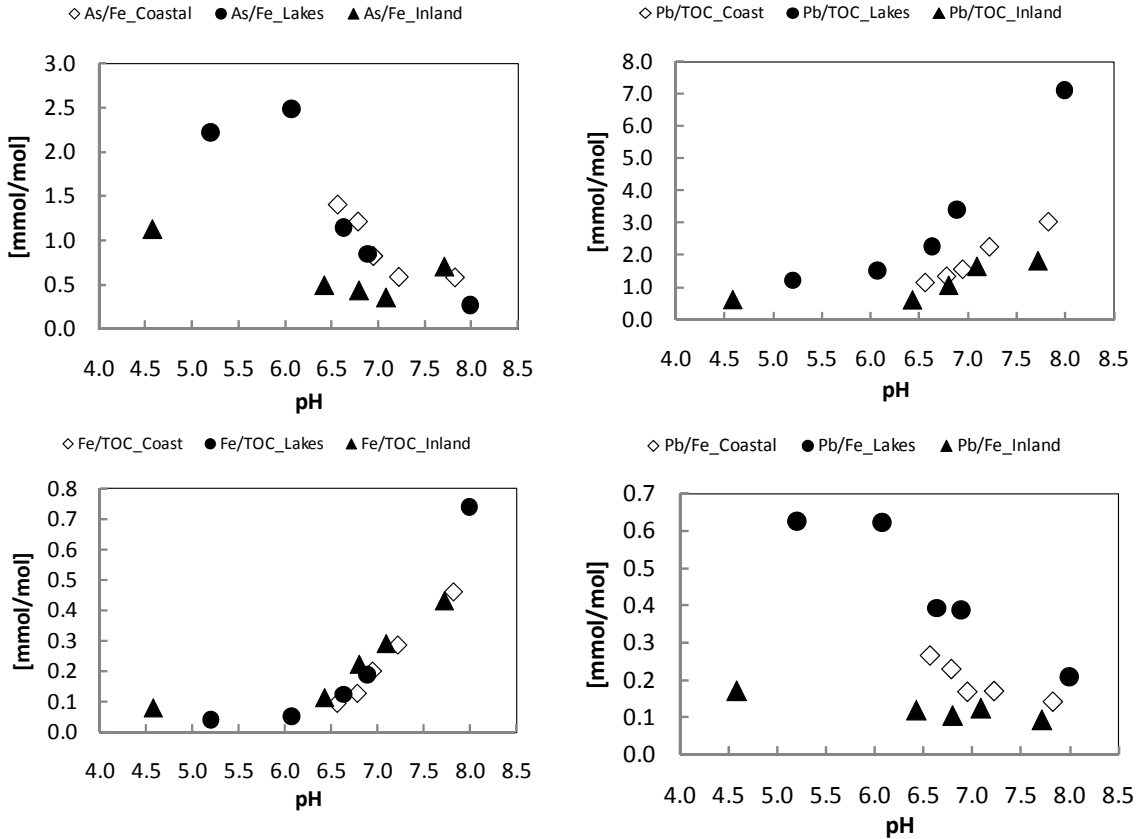


Figure 19: Relationships between median pH and median ratios of metal to metal or metal to carbon ratios for the various sample groups lakes, and inland and costal streams.

For the coastal streams and rivers, significant correlations were detected between unfiltered absorbance (abs_OF) and particulate iron ([TM]-[FM]). Also the amount of particulate vanadium seems to be related to the amount of particulate iron.

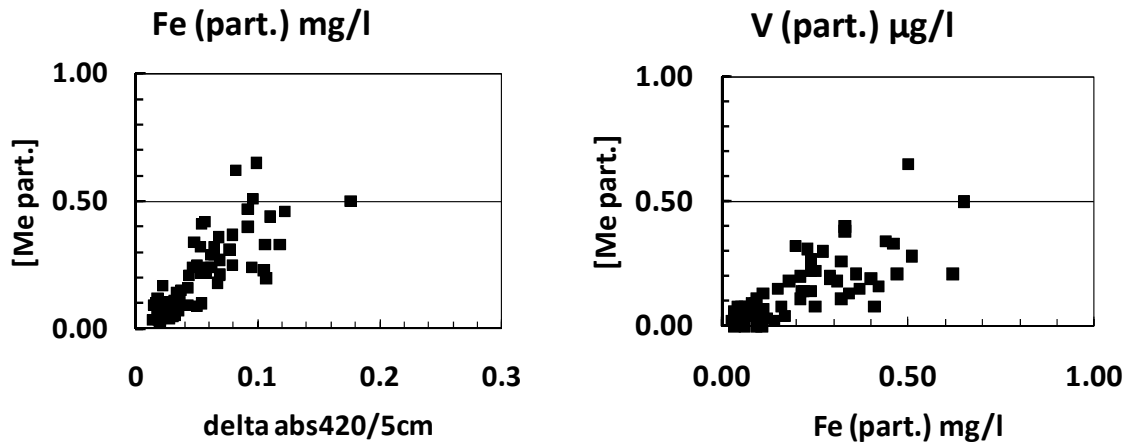


Figure 20: Relationships between particulate amounts of iron and unfiltered absorbance (abs_OF) and particulate amount of iron and particulate amount of vanadium in the coastal streams and rivers.

The above relationships are poorer for both the inland streams and lakes. This is probably due to different processes in those environments. Potential differences include flocculation processes induced when both pH and salt concentration increases closer to the sea.

The relationships above indicate that it is **worth pursuing the statistical and chemical analysis of both filtered and total metal analysis further** with the aim of better understanding the biogeochemical importance of carrier substances (e.g., Fe and organic carbon) and estimating the fraction of total metal that might be taken up actively or passively by stream and lake biota that is discussed in a report by the SEPA (NATURVÅRDSVERKET, 2008).

Is it possible to estimate filtered metal concentrations for lead?

Due to its toxicity, lead is one of the metals that is still of concern in some environments. This metal merits thus to be studied in more detail. A statistical approach was used in an attempt to estimate filtered metal concentration using only data available from the ordinary sampling program (i.e. no metal data). Principal components Analysis (PCA) is a very powerful tool for quantifying multiple relationships between variables and to what extent these relationships may be used to predict other parameters. In this case the filtered lead concentration of the inland streams and rivers may be modeled from existing data of the long term monitoring program with a precision that is close to the analytical error (Figure 21). This approach is very promising and should be pursued for other metals as well.

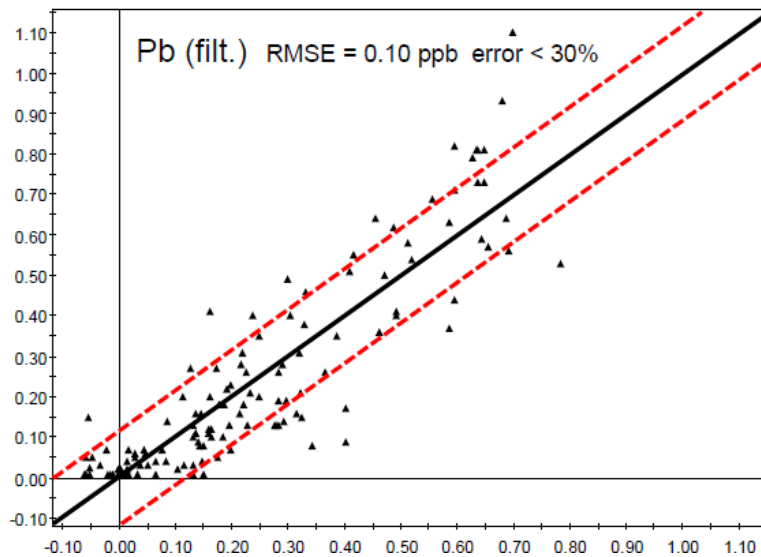


Figure 21: Comparison between measured and modeled filtered lead concentration using the predictive variables pH, abs_F, TOC, abs_OF, Al, Pb, Fe, Alkalinity, Ca and spec. conductivity.

Summary and suggestions for future studies

A number of metals (vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, molybdenum, cadmium and lead) were analyzed in a large number of Swedish surface waters in both filtered and unfiltered samples. Concentrations of most metals are not significantly affected by the method of sampling, sample separation and preservation technique commonly used within the Swedish National Environmental Monitoring program. Copper, zinc, cadmium, chromium, nickel, arsenic and vanadium are in a majority of the samples in the so called dissolved form ($94 \pm 154\%$ ¹) and the fraction of filtered to total metal indicates no trend with potential driving variables such as iron, pH or total organic carbon for these metals. Lead, vanadium and cobalt have concentrations that **are much lower** (up to a factor of four) in filtered as compared to unfiltered samples ($70 \pm 48\%$). For all three metals the relative fraction is related to the aforementioned driving variables with both TOC and iron leading to increased fraction of filtered metal. The effect with pH is the opposite. In 10% of all samples lead and cobalt are more than 60% in the particulate form. As the dissolved part is of interest only, correction factors of around 4 would need to be applied when defining the availability of lead and cobalt in the studied Swedish surface waters. Filtered metal concentrations were lower at around 40% of the sites that had elevated unfiltered metal concentrations. This indicates that it **might be worthwhile starting site specific sampling campaigns** at individual sites with the

¹ This high standard deviation is mainly due to a large number of samples with ratios of [FM]/[TM] for copper above unity.

aim of identifying sites with elevated filtered concentrations **before taking legal action**. The following answers to the posed questions may be formulated:

- There is **no significant bias** in metal concentration if the samples are treated according to the Swedish procedure or acidified and then filtered.
- There is **no significant bias** in metal concentration if the samples are filtered in the field or in the lab but are otherwise treated similarly. The few differences that occurred may all be traced down to 2-3 sampling sites that were known to have temporary problems with metal contamination.
- Except for chromium, were slight changes in concentration occurred; there is **no significant bias in concentration** if the time the samples are left acidified during the sedimentation step is varied.
- **A large bias in metal concentration** (up to a factor of four) between samples that are acidified left for sedimentation and then decanted between those that are first filtered and then acidified as described in the guidance document No 19 occurs for the metals **lead, vanadium and cobalt**.
- For all other metals, and considering the lower 25% of the sample population, the difference is on average below 35%. This is within the range of temporal variation observed at all sites and **thus needs no further study**.

Prolonged sampling at selected sites at least **during another 6 months encompassing both spring flood and part of the summer is still necessary** for a more thorough analysis of the controlling factors of the ratio of filtered to total metal concentration, especially at situation with more extreme flow conditions. Also, given the good results for transferring unfiltered to filtered concentrations in the case of lead, we recommend **to study potential methods** for estimating filtered metal concentrations for other metals including filtered and unfiltered absorbance, filtered organic carbon (DOC) absorbance spectra and other parameters if possible.

ACKNOWLEDGEMENTS

I want to thank the following people for contributions to fruitful discussions during this study: Kjell Johansson, Christan Demandt, Anna-Lena From, Johanna Andersson, Lars Sonesten, Brian Huser and Anders Düker.

REFERENCES

- Andersson, K., Dahlgvist, R., Turner, D., Stolpe, B., Larsson, T., Ingri, J. and Andersson, P., 2006. Colloidal rare earth elements in a boreal river: Changing sources and distributions during the spring flood. *Geochimica et Cosmochimica Acta*, 70(13): 3261-3274.
- Benedetti, M., Ranville, J.F., Ponthieu, M. and Pinheiro, J.P., 2002. Field-flow fractionation characterization and binding properties of particulate and colloidal organic matter from the Rio Amazon and Rio Negro. *Organic Geochemistry*, 33(3): 269-279.
- Björkvald, L., Buffam, I., Laudon, H. and Morth, C.M., 2008. Hydrogeochemistry of Fe and Mn in small boreal streams: The role of seasonality, landscape type and scale. *Geochimica Et Cosmochimica Acta*, 72(12): 2789-2804.
- Herbert, R., Björkvald, L., Wällstedt, T och Johansson K., 2009. Bakgrundshalter av metaller i Svenska inlands- och kustvatten, Department of Aquatic Sciences and Assessment, SLU, Uppsala.
- NATURVÅRDSVERKET (The Swedish Environmental Protection Agency), 2008. Förslag till gränsvärden för särskilda förorenande ämnen, Stockholm.
- Pokrovsky, O.S. and Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology*, 190: 141-179.
- Wallmann, C. and Andersson J. 2009. Internal report on analysis techniques for heavy metals "Tungmetallanalys – Jämförelse av ICP-MS-resultat från ofiltrerade, konserverade prov och filtrerade prov".
- Wiederholm, T., 1999. Bedömningsgrunder för miljö kvalitet. Sjöar och vattendrag, Bakgrundsrapport 1 - Naturvårdsverket Rapport 4920, Naturvårdsverket, Stockholm.

ATTACHMENTS

Figures and Tables.

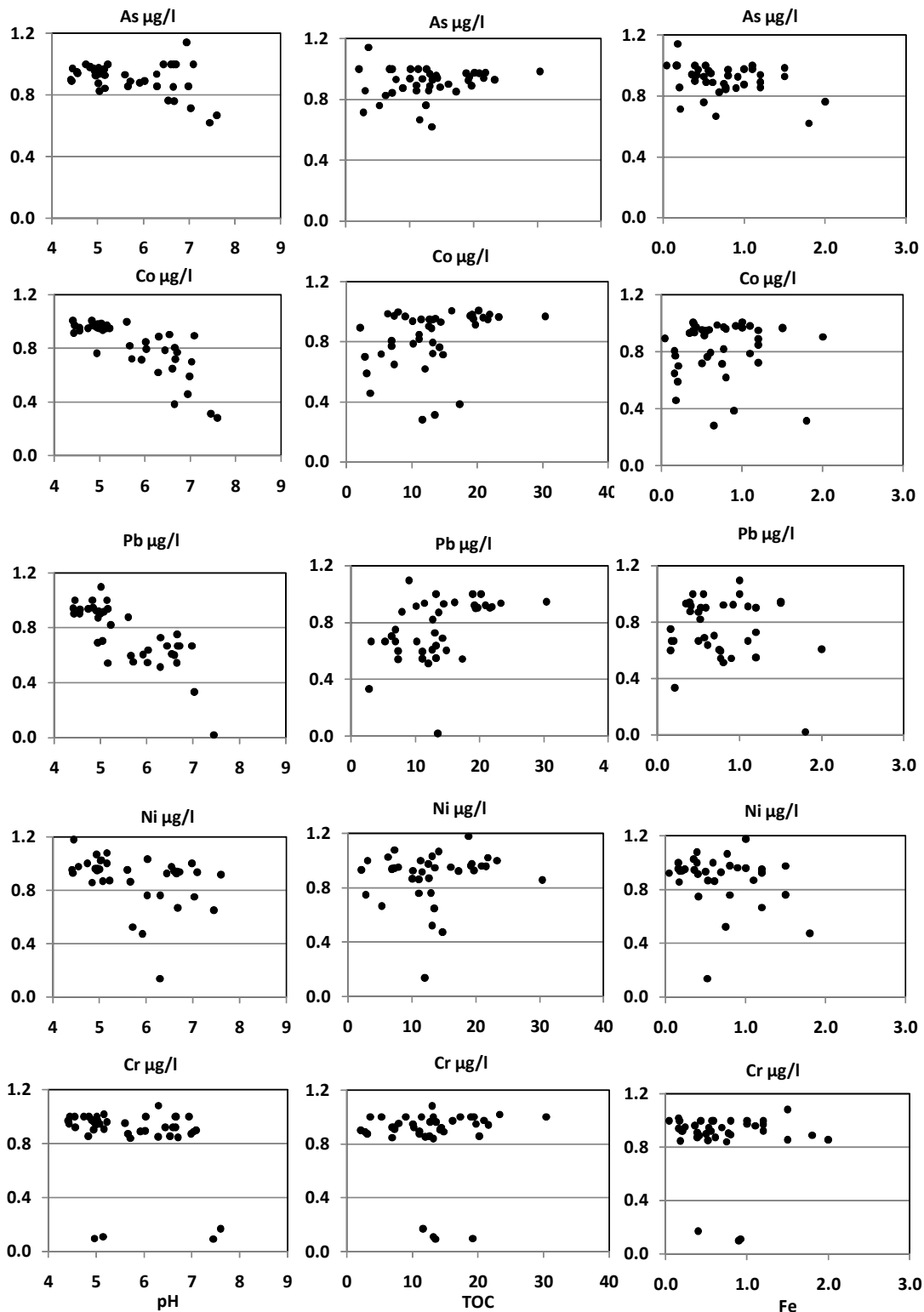


Figure 22: [FM]/[TM] for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron [TM] for sampled streams with a catchment size below 50 km² (Part A).

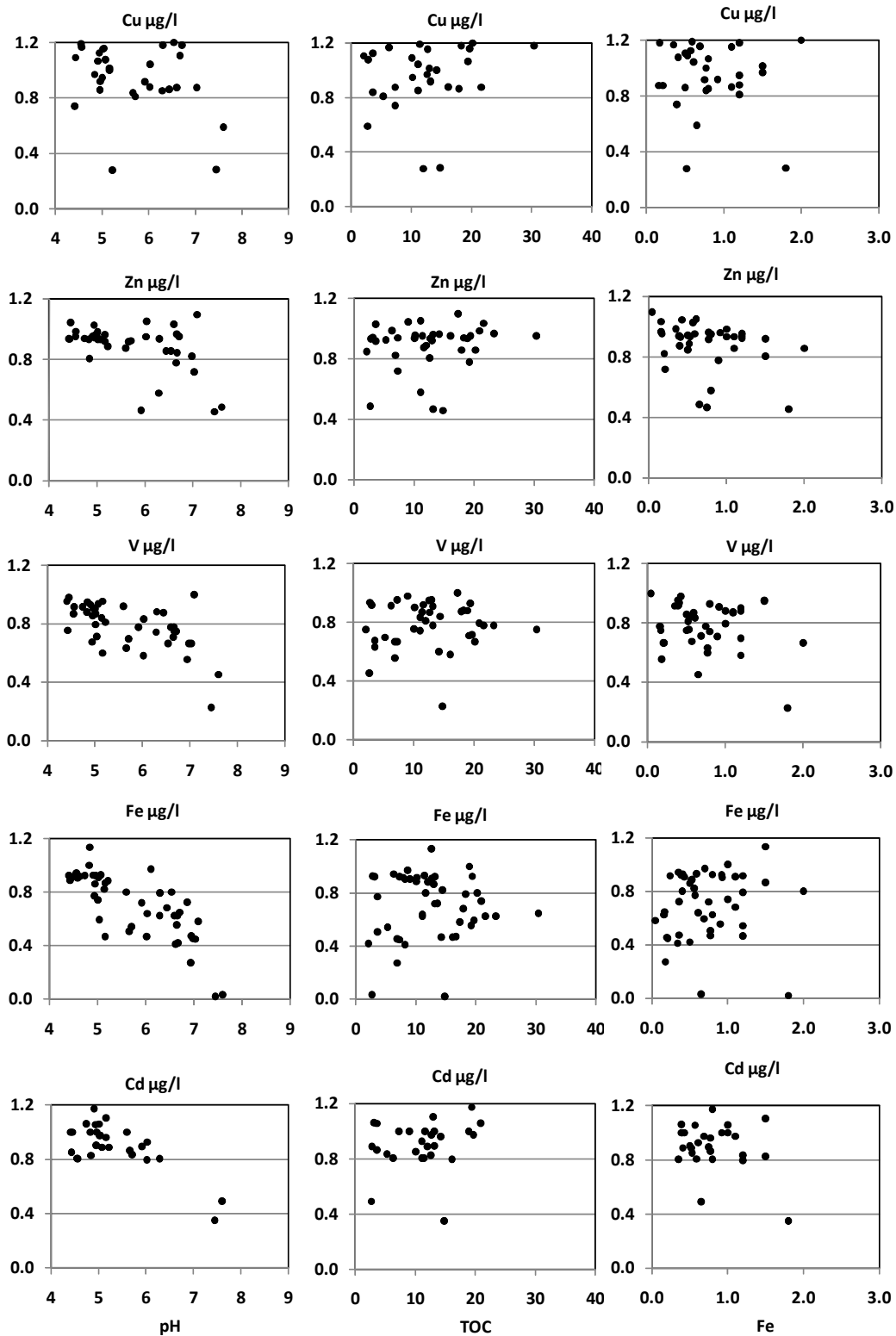


Figure 23: [FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for sampled streams with a catchment size below 50 km² (Part B).

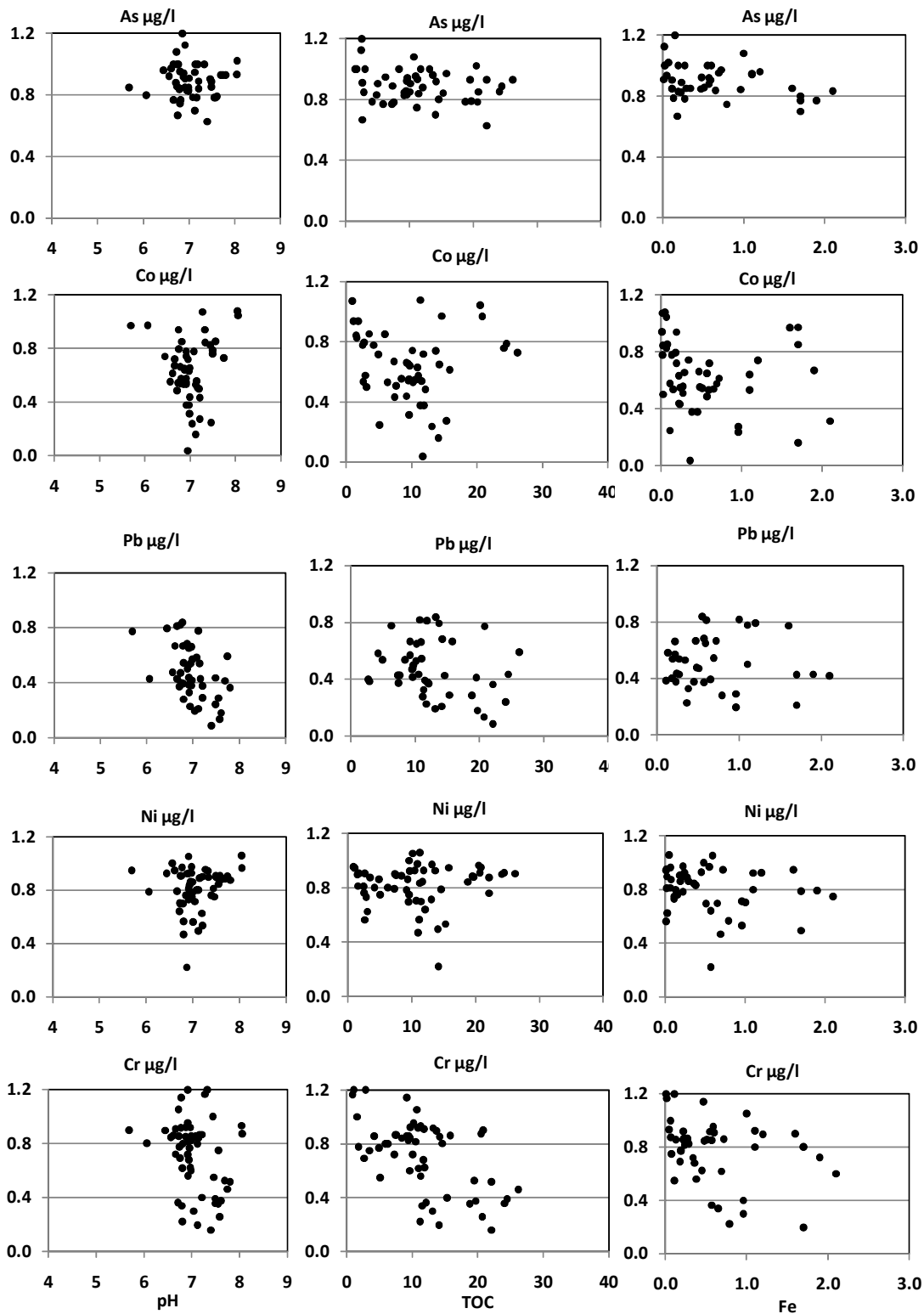


Figure 24: $[FM]/[TM]$ for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron $[TM]$ for sampled streams with a catchment size above 50 km^2 (Part A).

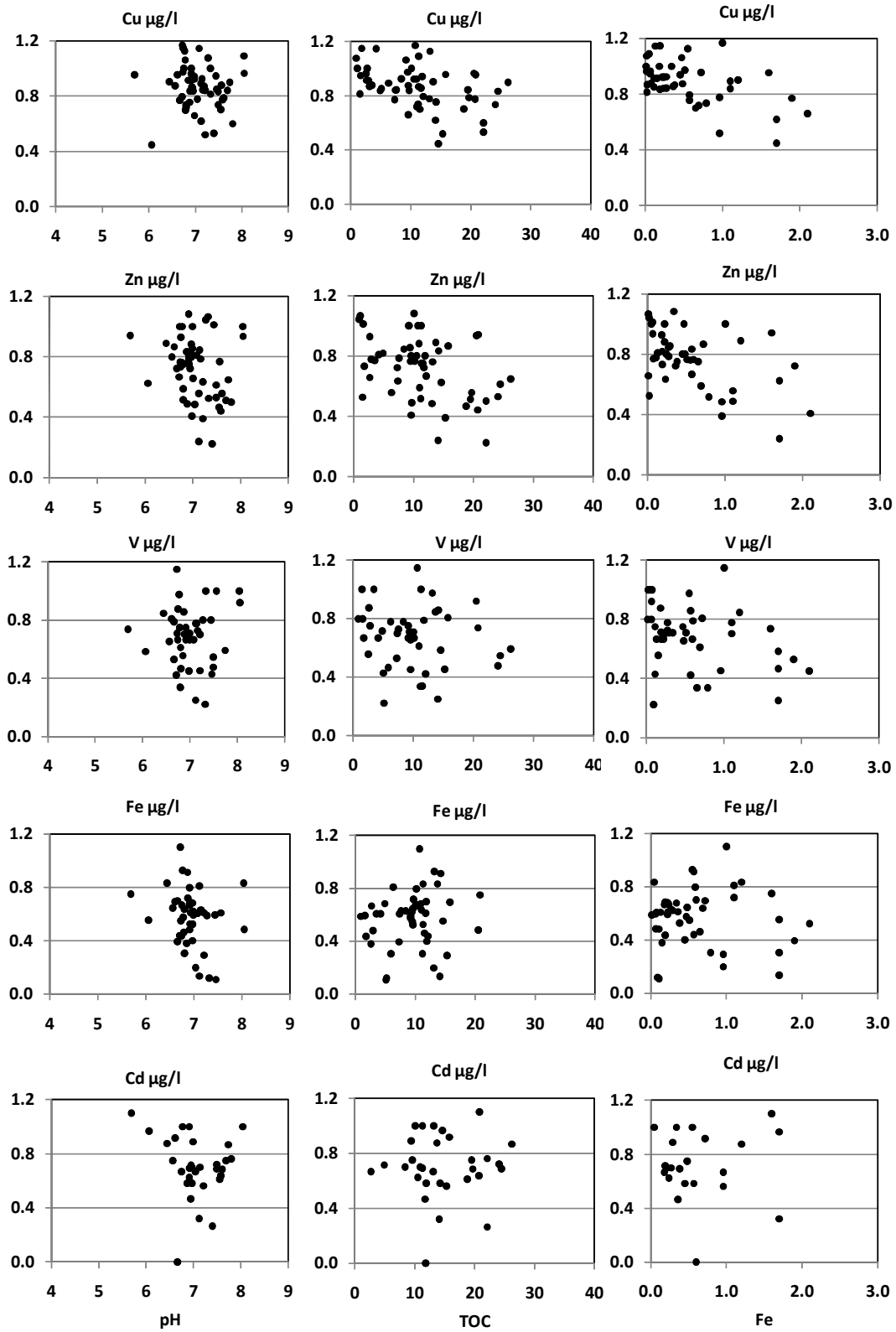


Figure 25: FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for sampled streams with a catchment size above 50 km² (Part B).

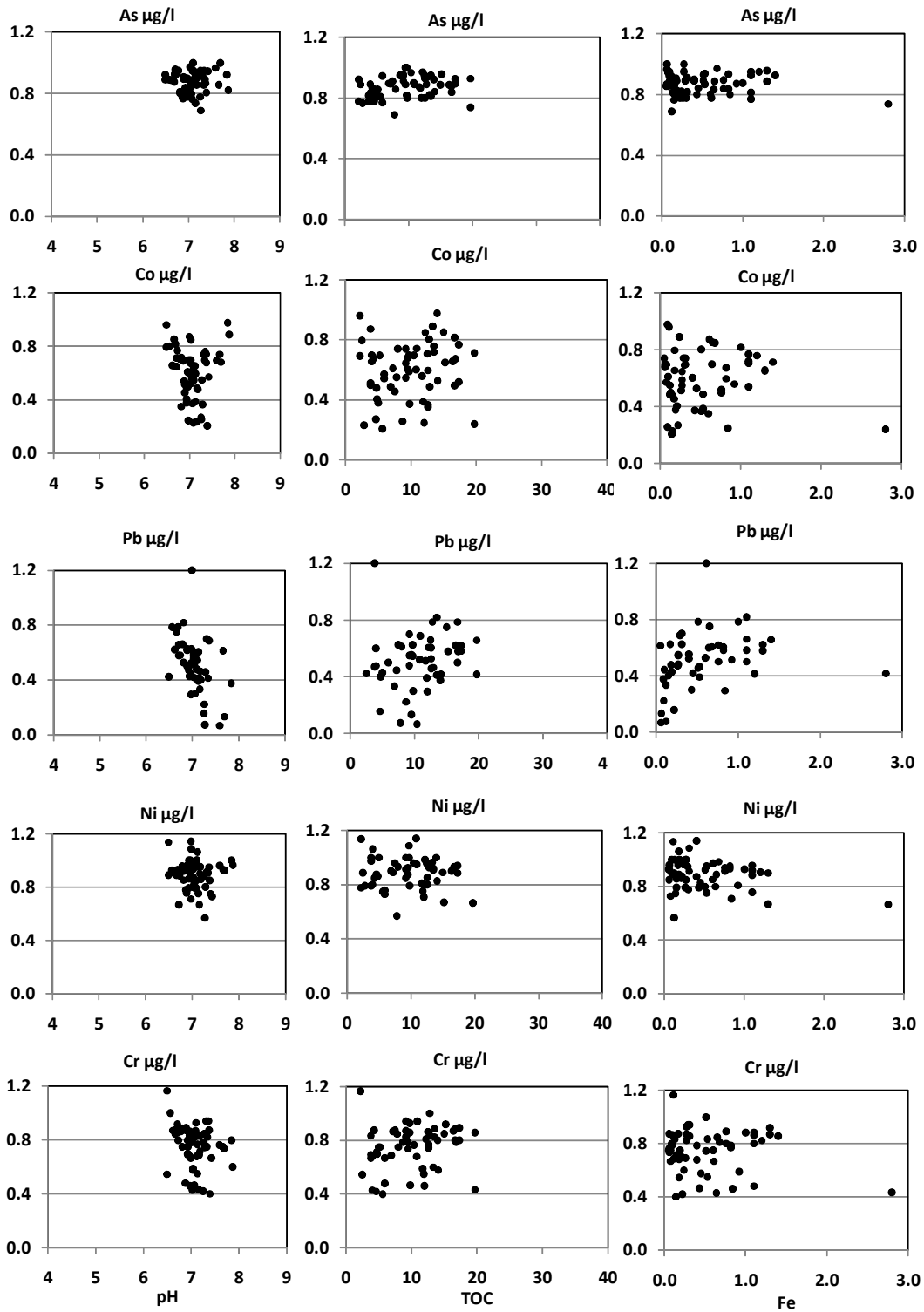


Figure 26: [FM]/[TM] for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron [TM] for sampled coastal streams with a catchment size above 1000 km² (Part A).

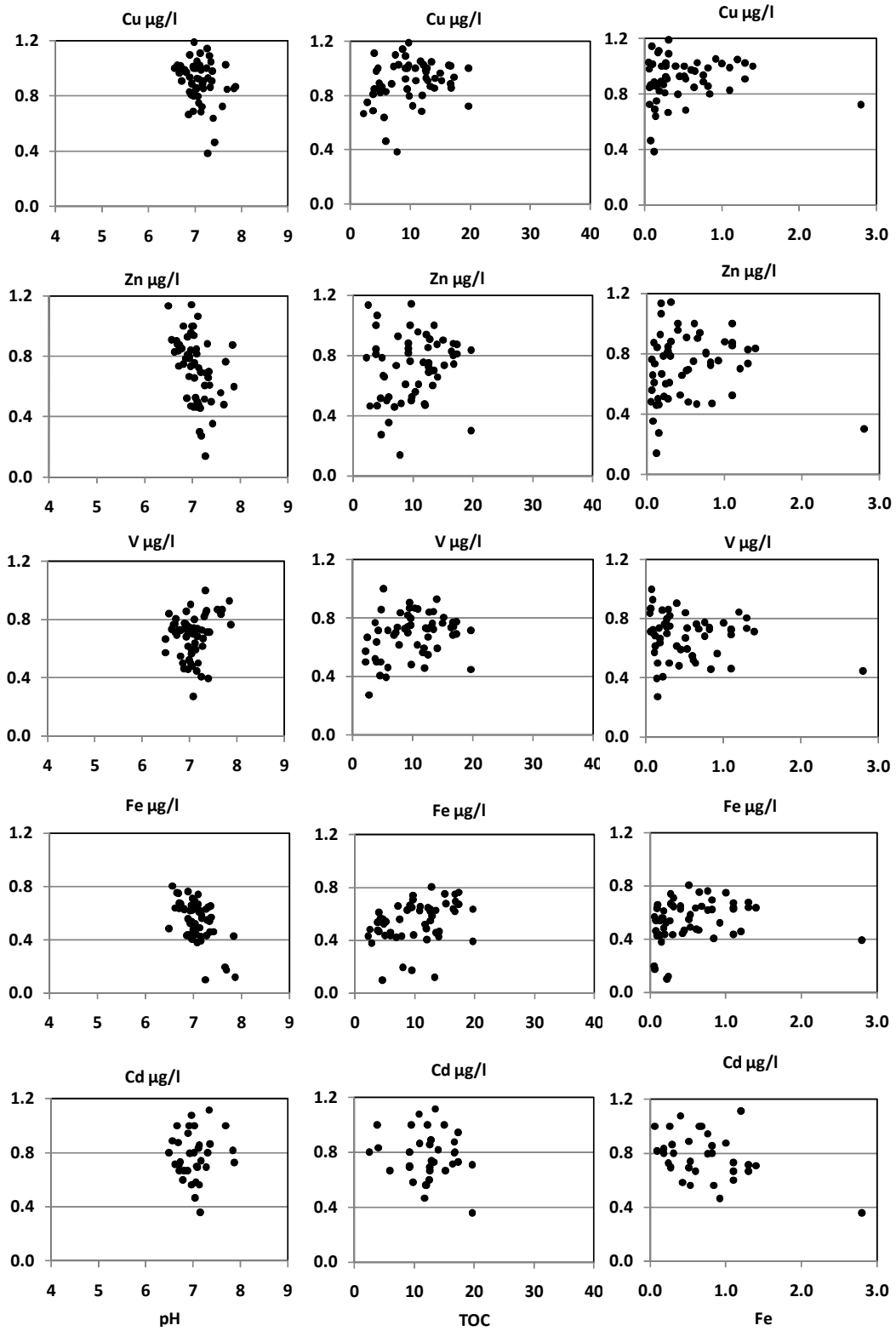


Figure 27: [FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for sampled coastal streams with a catchment size above 1000 km² (Part B).

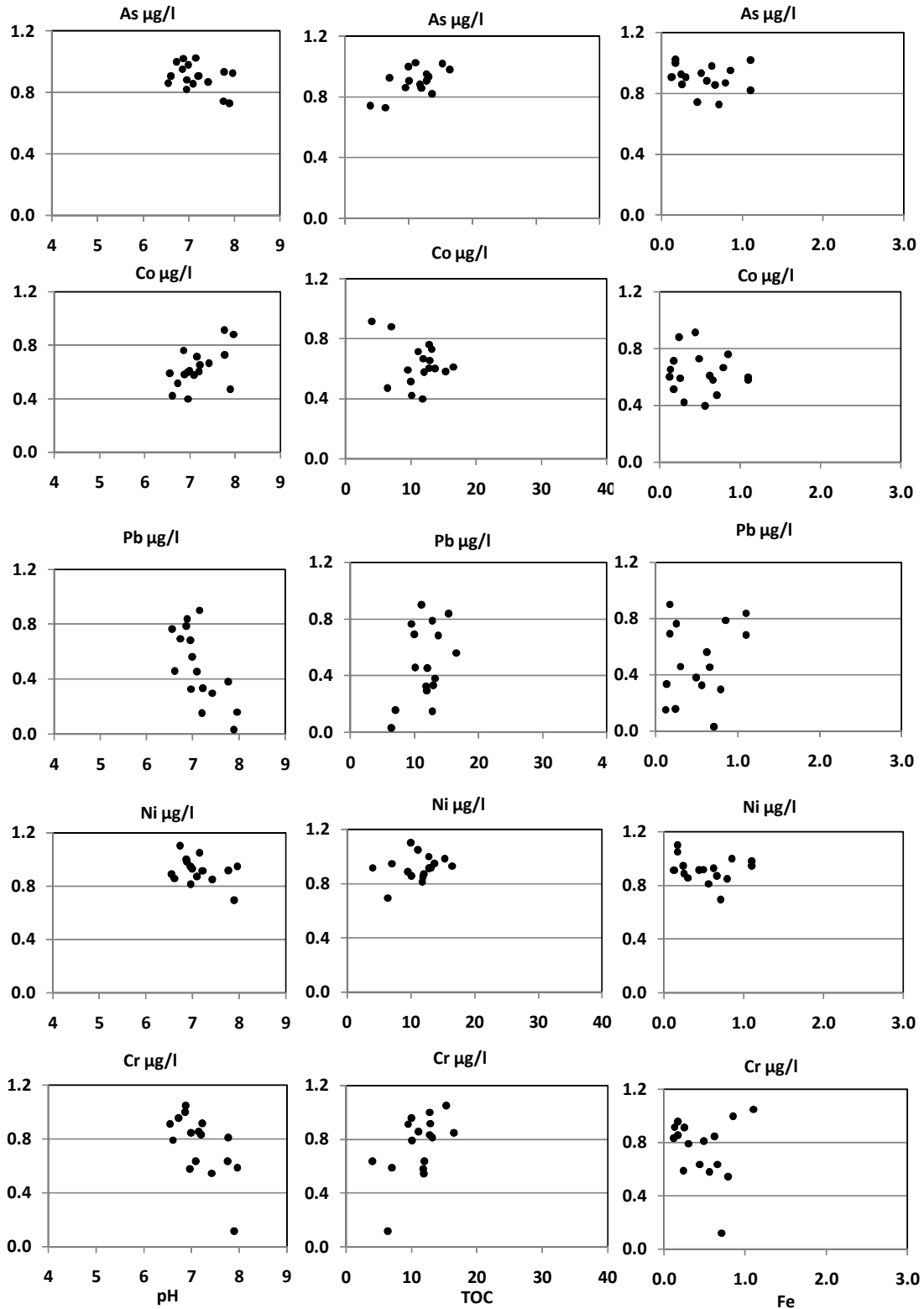


Figure 28: [FM]/[TM] for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron [TM] for sampled coastal streams with a catchment size below 1000 km² (Part A).

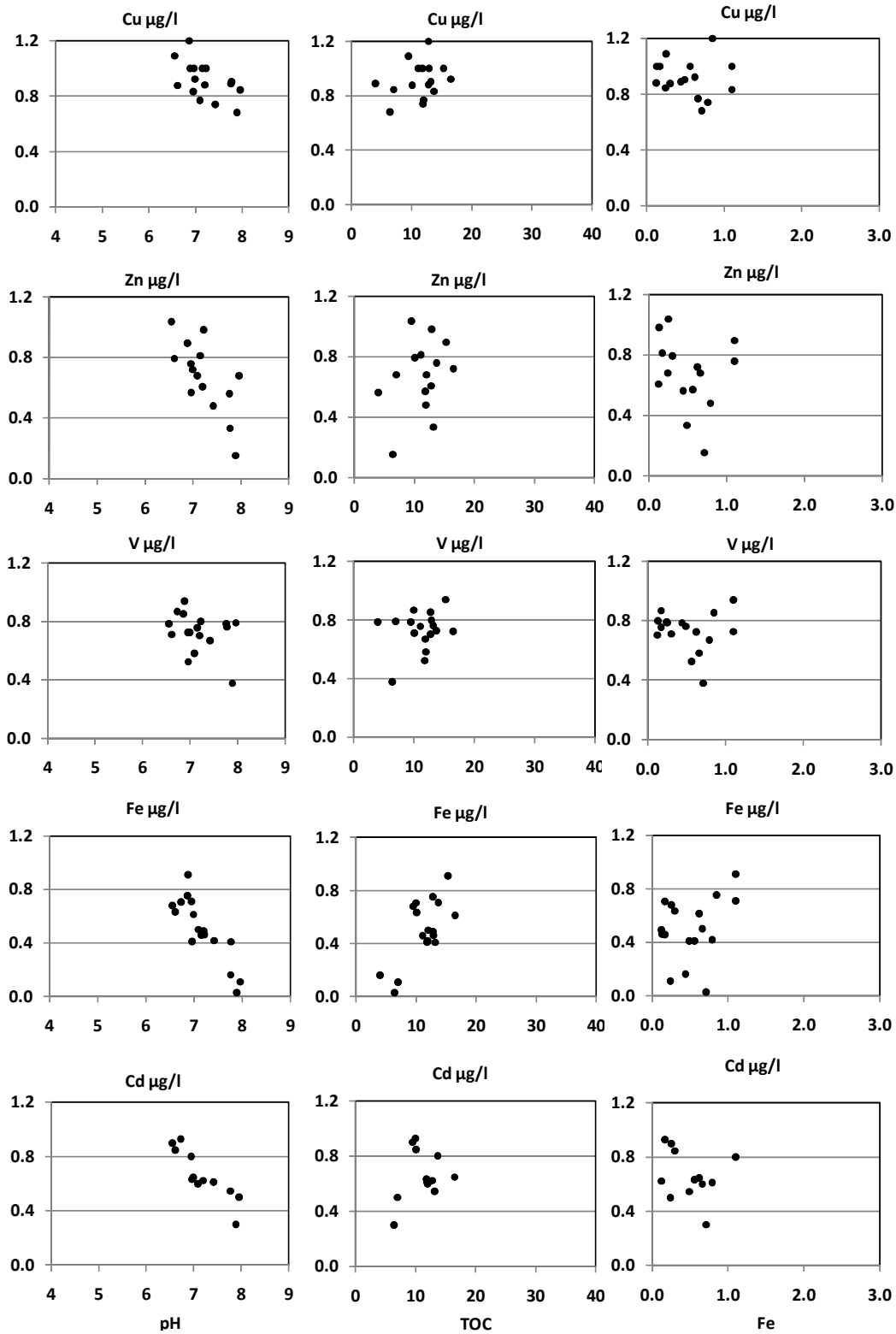


Figure 29: [FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for sampled coastal streams with a catchment size below 1000 km² (Part B).

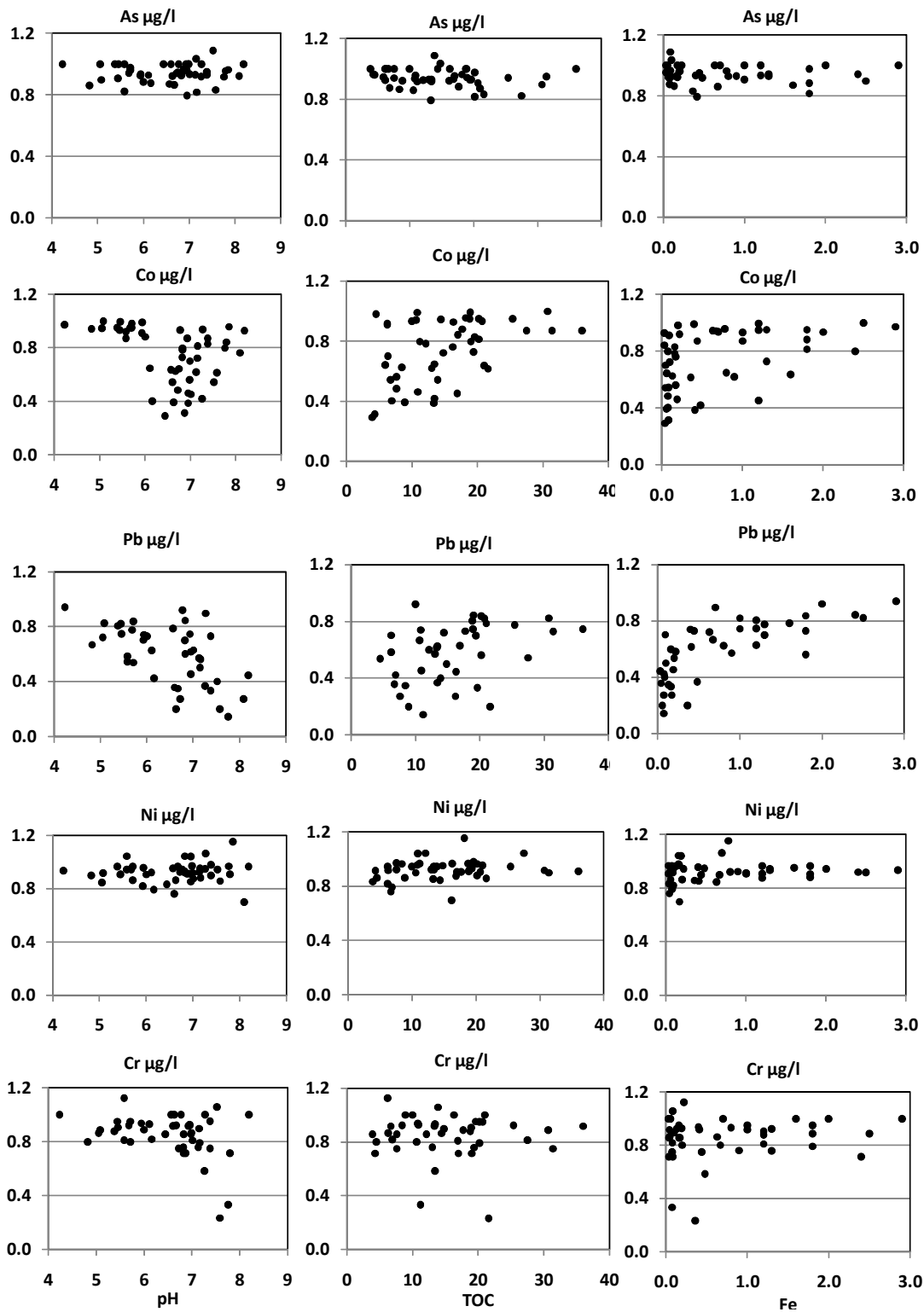


Figure 30: [FM]/[TM] for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron [TM] for sampled lakes (Part A).

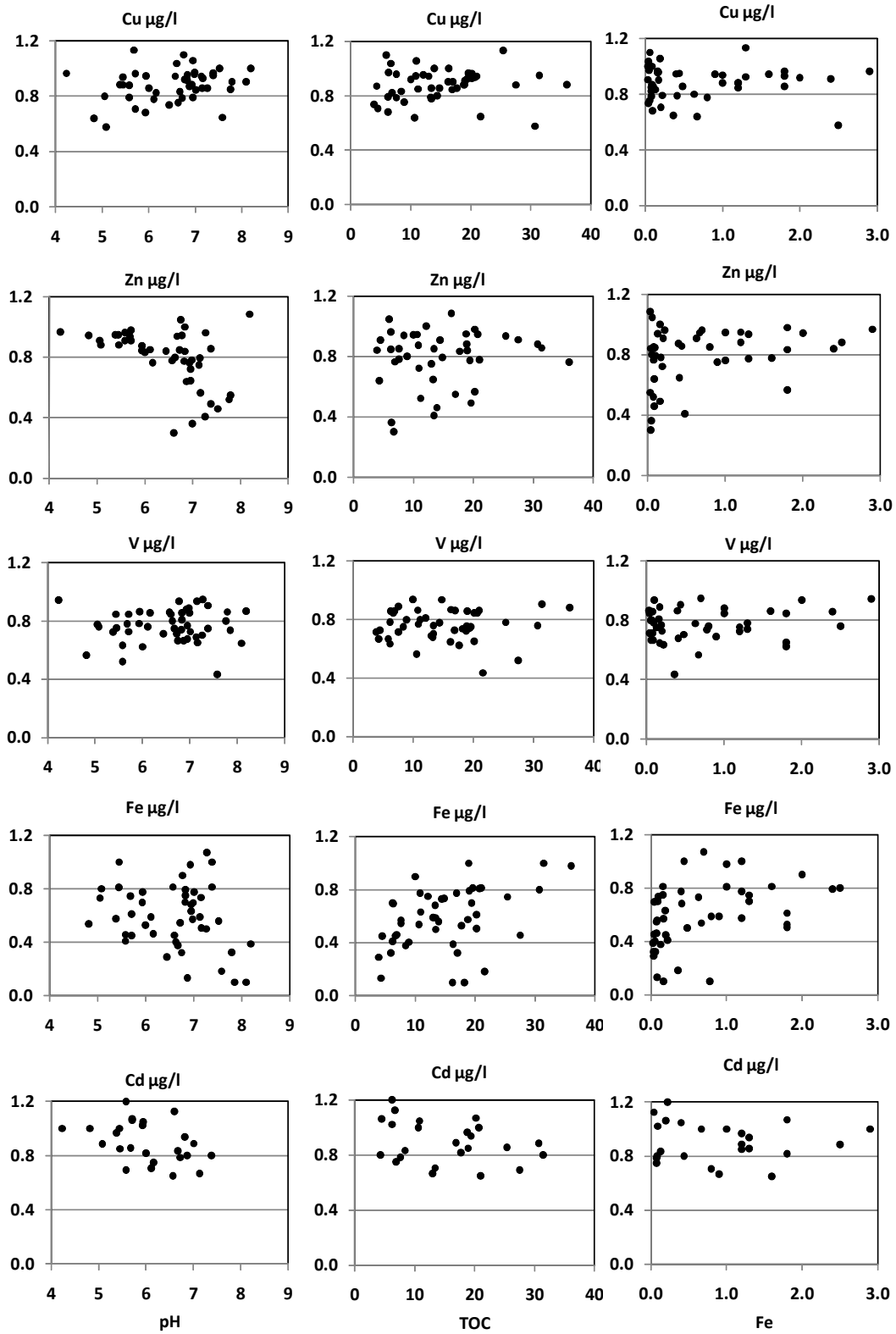


Figure 31: [FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for sampled lakes (Part B).

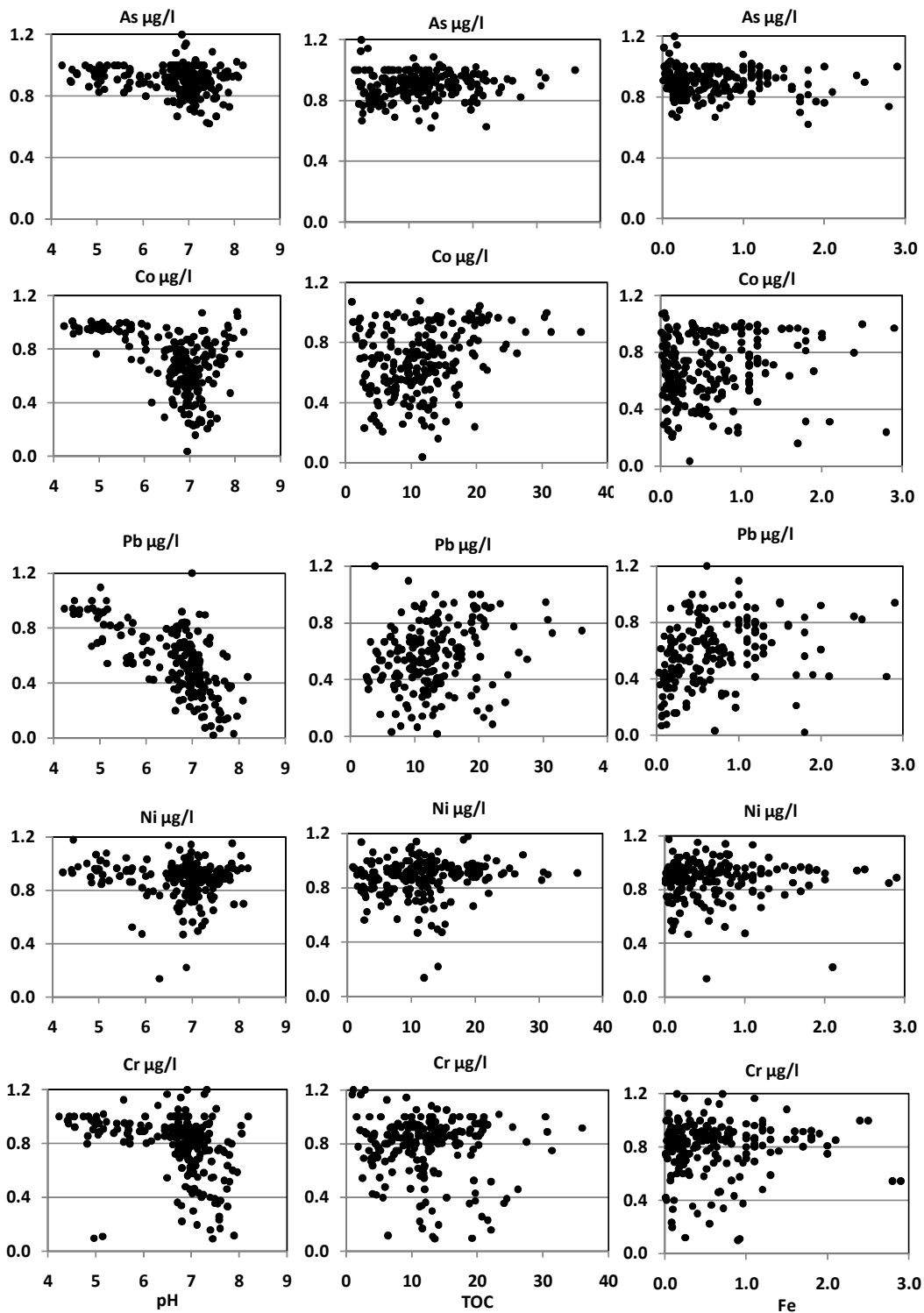


Figure 32: [FM]/[TM] for selected metals (As, Co, Pb, Ni and Cr) as a function of pH, TOC and total iron [TM] for all samples (Part A).

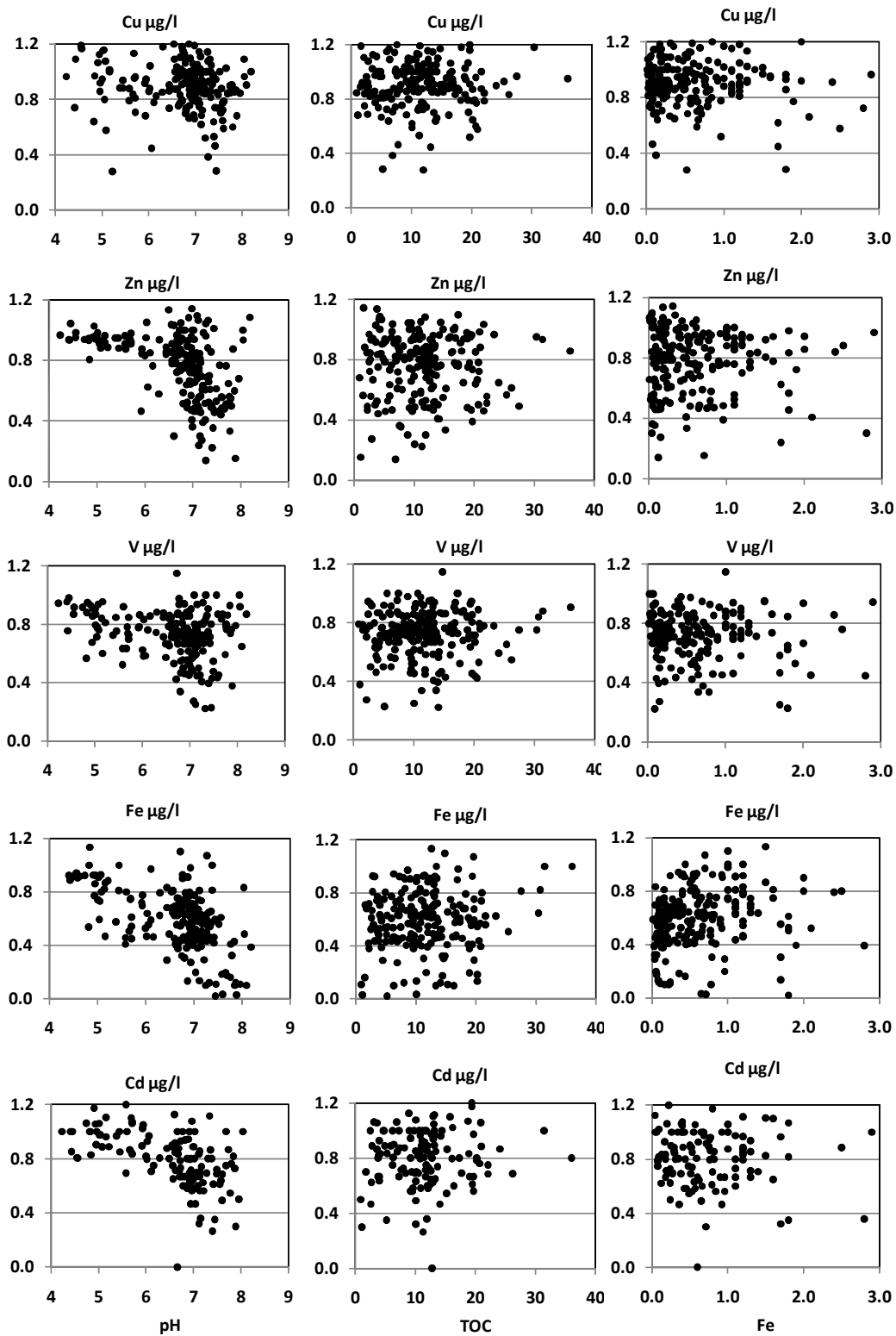
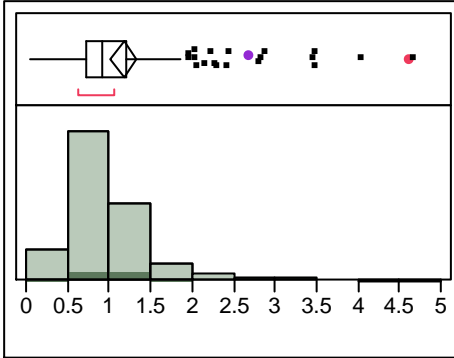


Figure 33: [FM]/[TM] for selected metals (Cu, Zn, V, Fe and Cd) as a function of pH, TOC and total iron [TM] for all samples (Part B).

Figure 34: Distribution of [FM]/[TM] ratios for copper, zinc and chromium in waters sampled during 2006 in the Krycklan area.

Distributions

Cu frac



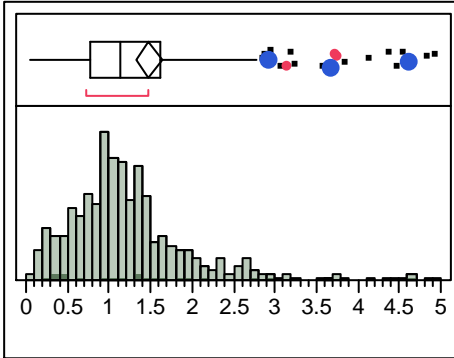
Quantiles

100.0%	maximum	14.750
99.5%		14.646
97.5%		3.486
90.0%		1.680
75.0%	quartile	1.208
50.0%	median	0.923
25.0%	quartile	0.719
10.0%		0.460
2.5%		0.286
0.5%		0.059
0.0%	minimum	0.048

Moments

Mean	1.1722198
Std Dev	1.4158106
Std Err Mean	0.0747236
upper 95% Mean	1.3191722
low er 95% Mean	1.0252674
N	359

Zn frac



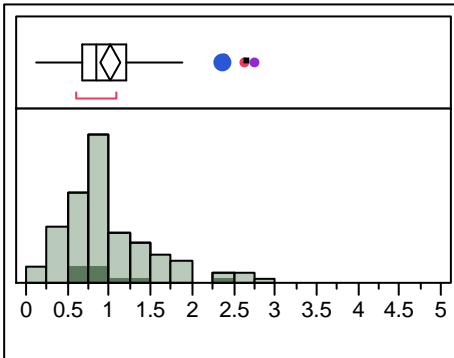
Quantiles

100.0%	maximum	21.690
99.5%		10.563
97.5%		5.171
90.0%		2.612
75.0%	quartile	1.608
50.0%	median	1.134
25.0%	quartile	0.784
10.0%		0.434
2.5%		0.204
0.5%		0.092
0.0%	minimum	0.055

Moments

Mean	1.4773825
Std Dev	1.6119845
Std Err Mean	0.079034
upper 95% Mean	1.6327395
low er 95% Mean	1.3220256
N	416

Cr frac



Quantiles

100.0%	maximum	2.7548
99.5%		2.7548
97.5%		2.6470
90.0%		1.7837
75.0%	quartile	1.2119
50.0%	median	0.8560
25.0%	quartile	0.6706
10.0%		0.4009
2.5%		0.2133
0.5%		0.1189
0.0%	minimum	0.1189

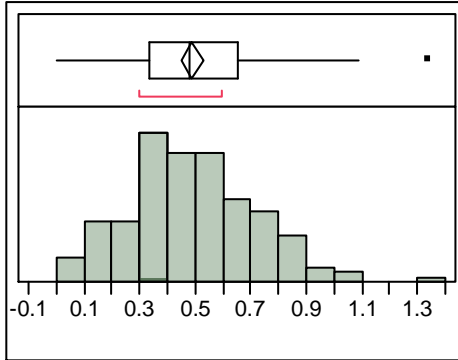
Moments

Mean	1.005102
Std Dev	0.5680381
Std Err Mean	0.0616124
upper 95% Mean	1.127625
low er 95% Mean	0.882579
N	85

Figure 35 C1a: Distribution of [FM]/[TM] ratios for lead, cadmium and copper in waters sampled during 2006 in the Dalarna region.

Distributions

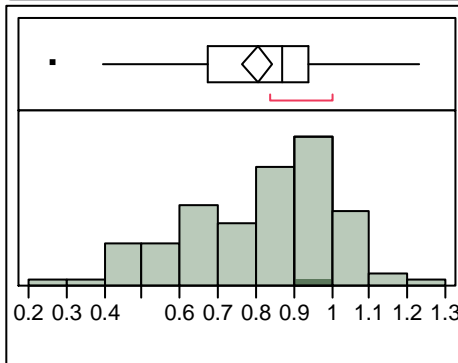
Pb frac höst 2009



Quantiles		
100.0%	maximum	1.3333
99.5%		1.3333
97.5%		0.9469
90.0%		0.7976
75.0%	quartile	0.6511
50.0%	median	0.4824
25.0%	quartile	0.3328
10.0%		0.1913
2.5%		0.0522
0.5%		0.0025
0.0%	minimum	0.0025

Moments	
Mean	0.4901481
Std Dev	0.2351612
Std Err Mean	0.0190117
upper 95% Mean	0.5277093
low er 95% Mean	0.4525869
N	153

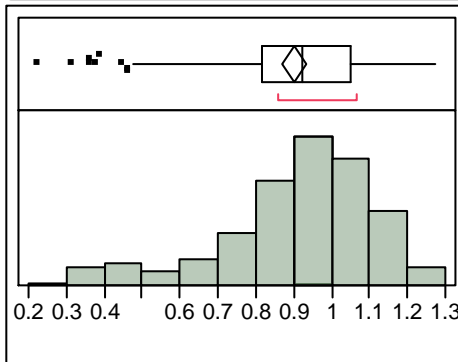
Cd frac höst 2009



Quantiles		
100.0%	maximum	1.2308
99.5%		1.2308
97.5%		1.1885
90.0%		1.0000
75.0%	quartile	0.9393
50.0%	median	0.8710
25.0%	quartile	0.6716
10.0%		0.5142
2.5%		0.3979
0.5%		0.2619
0.0%	minimum	0.2619

Moments	
Mean	0.8055094
Std Dev	0.1970502
Std Err Mean	0.0200074
upper 95% Mean	0.8452238
low er 95% Mean	0.7657949
N	97

Cu frac höst 2009



Quantiles		
100.0%	maximum	1.2727
99.5%		1.2727
97.5%		1.2324
90.0%		1.1496
75.0%	quartile	1.0490
50.0%	median	0.9231
25.0%	quartile	0.8170
10.0%		0.5963
2.5%		0.3636
0.5%		0.2222
0.0%	minimum	0.2222

Moments	
Mean	0.9015995
Std Dev	0.2073691
Std Err Mean	0.0161928
upper 95% Mean	0.9335742
low er 95% Mean	0.8696248
N	164

Figure 36 C1a: Distribution of [FM]/[TM] ratios for zink, chromium and nickel in waters sampled during 2006 in the Dalarna region.

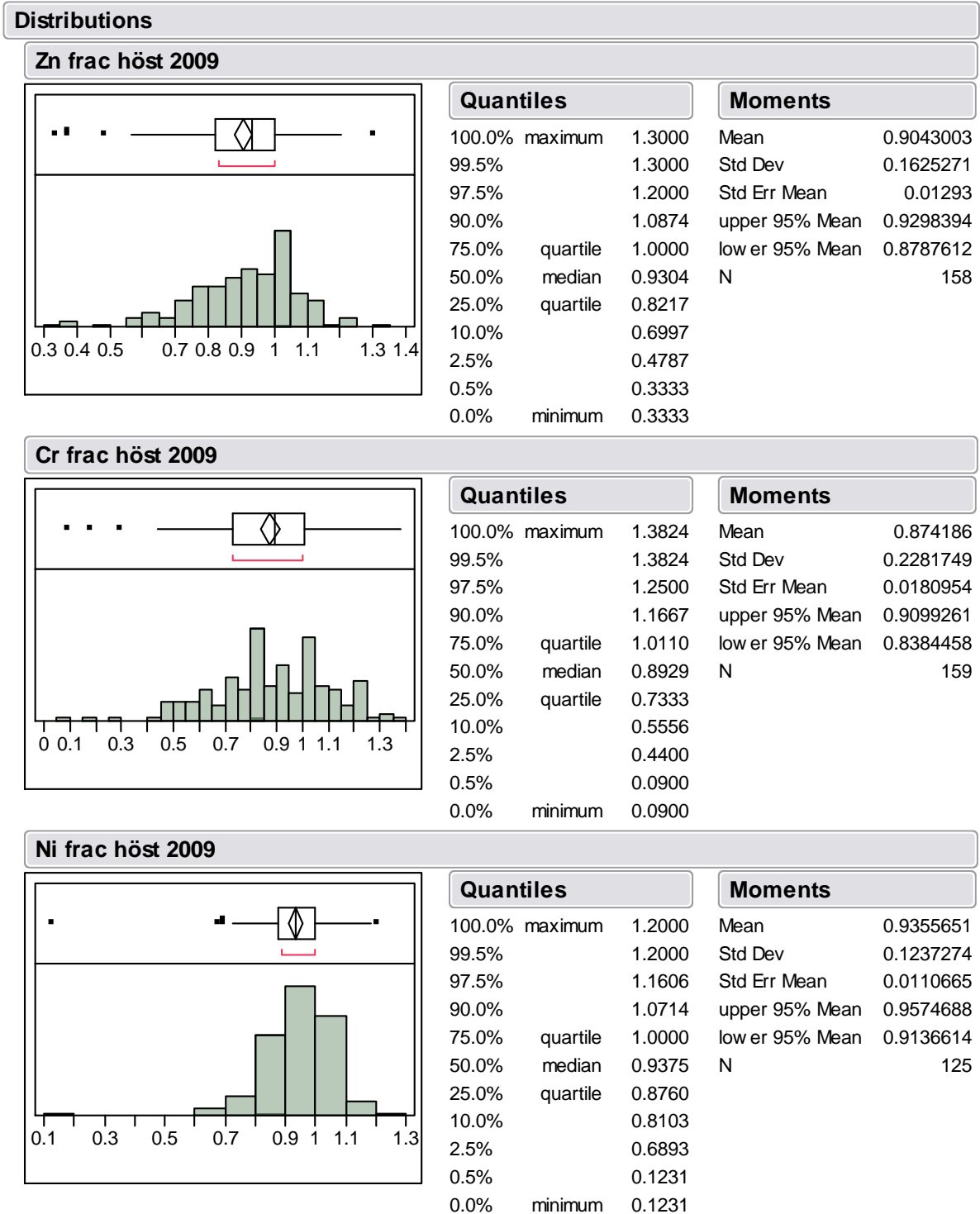


Table 7: Analysis of selected percentiles (0.95; 0.75; 0.5, 0.25 and 0.05) of selected water chemical parameters in the 2009 autumn samples.

	pH	[mS m ⁻¹] Kond_25	[5cm ⁻¹] Abs._OF	[5cm ⁻¹] Abs._F	[ppm] TOC	[ppb] Fe	[ppb] Al	[ppb] As	[ppb] Cu	[ppb] Pb	[ppb] Cd	[ppb] Cr	[ppb] Zn	[ppb] Co	[ppb] Ni
Coastal															
0.95	7.83	64.36	0.341	0.225	14.42	1430	382	1.12	3.20	0.75	0.03	0.82	11.27	0.49	2.72
0.75	7.22	16.35	0.232	0.174	11.30	696	197	0.55	1.51	0.44	0.02	0.56	5.35	0.25	1.15
0.5	6.95	9.12	0.147	0.102	8.80	380	103	0.42	1.20	0.24	0.01	0.38	3.70	0.12	0.86
0.25	6.78	4.34	0.100	0.052	5.90	162	45	0.26	0.98	0.14	0.01	0.27	2.60	0.07	0.62
0.05	6.56	2.93	0.058	0.038	3.68	75	27	0.14	0.62	0.07	0.01	0.12	1.51	0.03	0.28
lakes															
0.95	7.99	23.90	0.520	0.379	16.90	2687	299	0.97	2.53	2.07	0.04	0.60	9.27	0.54	1.02
0.75	6.89	6.54	0.206	0.156	11.45	468	163	0.53	0.95	0.67	0.02	0.34	5.55	0.16	0.59
0.5	6.63	4.89	0.111	0.075	8.40	225	88	0.35	0.58	0.33	0.01	0.21	2.65	0.06	0.40
0.25	6.07	3.04	0.067	0.044	6.10	69	45	0.23	0.36	0.16	0.01	0.12	1.15	0.03	0.26
0.05	5.20	1.79	0.026	0.015	2.30	21	16	0.06	0.15	0.05	0.00	0.05	0.66	0.01	0.12
Inland															
0.95	7.72	28.80	0.526	0.389	19.67	1825	435	1.71	1.56	0.62	0.06	0.65	13.00	0.67	1.56
0.75	7.09	7.16	0.296	0.232	13.33	834	210	0.39	0.90	0.38	0.03	0.42	3.10	0.26	0.62
0.5	6.80	4.33	0.187	0.146	9.80	470	89	0.27	0.50	0.18	0.01	0.22	2.20	0.11	0.40
0.25	6.43	2.76	0.103	0.075	5.65	138	33	0.09	0.30	0.06	0.01	0.11	1.50	0.04	0.22
0.05	4.58	2.08	0.027	0.019	1.86	32	9	0.05	0.20	0.02	0.00	0.08	0.78	0.02	0.11

Table 8: Analysis of selected percentiles (0.95; 0.75; 0.5, 0.25 and 0.05) of selected water chemical parameters in the extracted long-term dataset from the same sites and during the same autumn period.

	pH	[mS m ⁻¹] Kond_25	[5cm ⁻¹] Abs._OF	[5cm ⁻¹] Abs._F	[ppm] TOC	[ppb] Fe	[ppb] Al	[ppb] As	[ppb] Cu	[ppb] Pb	[ppb] Cd	[ppb] Cr	[ppb] Zn	[ppb] Co	[ppb] Ni
Coastal															
0.95	7.74	44.97	0.415	0.315	17.23	1100	319	0.95	3.05	0.90	0.04	0.59	9.70	0.32	2.47
0.75	7.25	9.85	0.269	0.199	12.65	658	160	0.46	1.20	0.41	0.01	0.28	4.45	0.18	0.88
0.5	7.02	5.79	0.162	0.122	9.65	300	79	0.34	0.85	0.17	0.01	0.18	2.50	0.08	0.63
0.25	6.88	3.37	0.076	0.047	5.50	143	34	0.19	0.49	0.09	0.01	0.13	1.40	0.05	0.31
0.05	6.61	2.40	0.023	0.013	2.31	27	11	0.08	0.31	0.03	0.01	0.06	0.61	0.03	0.17
lakes															
0.95	7.83	30.42	0.855	0.777	31.16	2465	447	1.07	2.03	1.67	0.04	0.64	11.00	0.77	1.70
0.75	7.14	9.23	0.451	0.382	19.45	1200	185	0.59	1.00	0.72	0.02	0.34	6.90	0.23	0.70
0.5	6.76	6.05	0.226	0.142	14.15	405	110	0.43	0.61	0.34	0.01	0.23	2.80	0.12	0.44
0.25	5.88	3.98	0.109	0.070	8.78	91	54	0.28	0.43	0.16	0.01	0.12	1.10	0.07	0.33
0.05	5.06	2.23	0.042	0.020	4.99	39	10	0.16	0.23	0.03	0.01	0.05	0.48	0.03	0.19
Inland															
0.95	7.62	50.14	0.577	0.436	22.22	1725	600	0.87	4.73	1.32	0.12	1.40	21.30	1.00	5.15
0.75	6.97	6.84	0.407	0.278	18.85	1000	310	0.50	1.35	0.75	0.04	0.63	7.95	0.59	1.55
0.5	6.67	4.48	0.276	0.207	13.10	600	210	0.36	0.62	0.52	0.02	0.36	4.50	0.27	0.61
0.25	5.16	3.07	0.164	0.121	8.80	358	59	0.23	0.30	0.23	0.01	0.19	1.80	0.09	0.39
0.05	4.59	2.00	0.052	0.029	2.79	106	15	0.06	0.15	0.03	0.01	0.08	0.60	0.03	0.14

Table 9: Ratios of respective values from Table 7 divided by those from Table 8. Values deviating strongly from unity are indicative of an overrepresentation of certain parameters such as in the case of cadmium and lead in the lake data set.

	pH	Kond_25	Abs._OF	Abs._F	TOC	Fe	Al	As	Cu	Pb	Cd	Cr	Zn	Co	Ni
Coastal															
0.95	1.0	0.7	1.2	1.4	1.2	0.8	0.8	0.8	1.0	1.2	1.3	0.7	0.9	0.7	0.9
0.75	1.0	0.6	1.2	1.1	1.1	0.9	0.8	0.8	0.8	0.9	0.8	0.5	0.8	0.7	0.8
0.5	1.0	0.6	1.1	1.2	1.1	0.8	0.8	0.8	0.7	0.7	0.7	0.5	0.7	0.6	0.7
0.25	1.0	0.8	0.8	0.9	0.9	0.9	0.7	0.7	0.5	0.7	0.8	0.5	0.5	0.6	0.5
0.05	1.0	0.8	0.4	0.3	0.6	0.4	0.4	0.6	0.5	0.4	1.0	0.5	0.4	0.8	0.6
Lakes															
0.95	1.0	1.3	1.6	2.1	1.8	0.9	1.5	1.1	0.8	0.8	0.9	1.1	1.2	1.4	1.7
0.75	1.0	1.4	2.2	2.5	1.7	2.6	1.1	1.1	1.1	1.1	1.2	1.0	1.2	1.5	1.2
0.5	1.0	1.2	2.0	1.9	1.7	1.8	1.3	1.2	1.1	1.0	1.1	1.1	1.1	1.9	1.1
0.25	1.0	1.3	1.6	1.6	1.4	1.3	1.2	1.2	1.2	1.0	1.0	1.0	1.0	2.3	1.3
0.05	1.0	1.2	1.6	1.4	2.2	1.9	0.6	2.6	1.5	0.7	2.0	1.0	0.7	1.8	1.7
Inland															
0.95	1.0	1.7	1.1	1.1	1.1	0.9	1.4	0.5	3.0	2.1	1.9	2.2	1.6	1.5	3.3
0.75	1.0	1.0	1.4	1.2	1.4	1.2	1.5	1.3	1.5	2.0	1.5	1.5	2.6	2.2	2.5
0.5	1.0	1.0	1.5	1.4	1.3	1.3	2.4	1.3	1.2	2.9	2.7	1.6	2.0	2.4	1.5
0.25	0.8	1.1	1.6	1.6	1.6	2.6	1.8	2.6	1.0	3.8	1.2	1.7	1.2	2.6	1.8
0.05	1.0	1.0	1.9	1.5	1.5	3.3	1.6	1.3	0.8	1.5	1.1	1.0	0.8	1.3	1.2