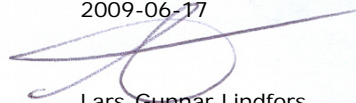


Testing the Biotic Ligand Model for Swedish surface water conditions

- a pilot study to investigate the applicability of BLM in Sweden

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Summary <p>Biotic Ligand Models (BLMs) have been developed for a number of metals (e.g. Cu, Zn, Ni), in order to account for bioavailability in metal risk assessment. The BLMs predict the bioavailable fraction of a metal in the water, based on water chemistry, and calculate site-specific PNEC-values, to which measured dissolved concentrations can be compared. Concerns have been raised that these models may not apply in the Swedish environment, due to the large difference in Swedish water chemistry compared to those European waters, for which the models have mainly been validated. IVL has, in close collaboration with industrial partners undertaken a pilot study, with the aim of testing the applicability of Biotic Ligand Models for assessing metal toxicity in Swedish waters. The study concerned the metals copper (Cu), zinc (Zn) and nickel (Ni), cadmium (Cd) and chromium (Cr).</p> <p>The overall conclusions of the project are that a) BLM-models can and should be applied as a natural element when assessing metal risks in Swedish waters, preferably as a sub-step in a tiered approach; b) The chemical conditions of Swedish water bodies are generally in agreement with the BLM requirements concerning the two key parameters pH and DOC, when it concerns the metals Cu, Zn, and Ni; c) Swedish national monitoring programmes should focus on routine measurements of dissolved metal concentrations, and also on measurements of DOC. If the currently used method is regarded as equivalent to filtration through a 0.45 µm filter, this should be clearly stated in the national monitoring databases; d) Models are available for Cu, Zn, and will soon be available for Ni. The BLMs are regularly improved and updated; e) Concerning chromium, BLMs are currently not available. It is therefore considered that all soluble chromium (III) is bioavailable and thus contributes to toxicity ; f) Cadmium is assessed using a hardness correction and the proposed Cd-EQs are to be compared with dissolved monitoring data.</p> <p>In order to assess the model results, a validation exercise should be performed for soft waters regarding Zn, in particular for soft waters with a high pH-value.</p>	
Keyword Biotic Ligand Model, BLM, metal, toxicity, bioavailability, water chemistry	
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Foreword

Within the recent development in scientific and regulatory guidance documents on environmental risk assessment methods for metals and the setting of Environmental Quality Standards, the use of Biotic Ligand Models (BLM) in estimating bioavailability of metals in water types has proven to be a useful tool. At the European level, BLMs are increasingly applied in this context. It is of utmost importance that the models are validated in representative European waters so as to enable regulators to use the tools with confidence in the results it produces. There has been some uncertainty as to what extent Swedish/Scandinavian water types fall within the validated ranges of application for the models. Therefore Naturvårdsverket (Swedish EPA) and MITF (Metal Information Task Force, including the Swedish Steel Producers' Federation, SveMin, Scandinavian Copper Development Association and Nordic Galvanizers) initiated this pilot project with IVL Swedish Environmental Research Institute entitled "Testing the Biotic Ligand Model for Swedish surface waters conditions" with the aim of assessing the applicability of BLM in Swedish waters. A key component of the project has been to characterize Swedish waters and estimate the extent of water bodies for which the critical parameters are within or without the model validation ranges. The project has also identified data gaps and addressed the implications of using BLMs in Sweden, as well as highlighted needs for further development, validation, and improvements.

A large proportion of the research at IVL Swedish Environmental Research Institute is known as co-financed research, that is, research jointly financed by the state and the business community. The present pilot project is an excellent example of a co-financed research project, where the aim of the research is to pursue issues of great interest to industry that has relevance for society in general.

We believe that the involvement of both regulators and industrial stake holders in this work has resulted in a report that will be recognized and useful for all parties. We would also like to stress the unique cooperation that took place between national and international counterparts, public as well as private, which gave the project access to the latest science and model developments. In particular we would like to acknowledge the active collaboration of:

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Summary

In line with recent EU legislation on water quality, it is recommended that bioavailability and preferably also natural background concentrations be taken into account when assessing metal toxicity in aquatic systems. As a result, so called Biotic Ligand Models (BLMs) have been developed for a number of metals (e.g. Cu, Zn, Ni), which predict the bioavailable fraction of a metal in the water, based on water chemistry, and calculate site-specific PNEC-values, to which measured dissolved concentrations can be compared. The models have been used in the EU risk assessment procedures, and are reaching a high level of acceptance in most of Europe. Concerns have been raised that these models may not apply in the Swedish environment, due to the large difference in Swedish water chemistry compared to those European waters, for which the models have mainly been validated.

IVL has, in close collaboration with industrial partners in Sweden and Europe undertaken a pilot study, with the aim of testing the applicability of Biotic Ligand Models for assessing metal toxicity in Swedish waters. The study was mainly focused on the metals copper (Cu), zinc (Zn) and nickel (Ni), for which BLMs have been developed, but also cadmium (Cd) and chromium (Cr) were investigated in the context of bioavailability and risk assessment.

The study was performed in two parts. First, a survey of representative Swedish waters was performed based on the underlying factors ultimately determining the water chemistry in order to investigate to what extent the water chemistry parameters may fall outside the BLM boundaries. Eleven reference sites were selected to represent the majority of Swedish geological and climatological conditions, which in turn influence the water chemistry parameters crucial for BLM application.

The second part of the study, included test-running of two available BLM tools in order to check their applicability, such as data requirements, user-friendliness and outcome. These were the full Cu-BLM, and a simplified version of the Zn-BLM. The outcome from BLM-runs was also compared to results using the currently recommended methods for metal risk assessment. For Zn, the exercise was extended to a full Species Sensitivity Distribution (SSD) Normalization Approach, which allows a broader set of conditions to be run as it turned out that some sampling stations were falling outside of the Zn-BLM validation range.

The results from the survey show that the key parameters pH and DOC are more or less always within the validation ranges for all the existing BLMs and for all the selected reference sites. The third key parameter, which is hardness, is perfectly within the validation ranges in 5 of 11 of the reference sites, represented mainly by areas in the south and central part of Sweden. When it concerns copper, the hardness parameter is mostly within the validation range for the remaining sites as well, except for three; Stensjön, Gråda in Östra Dalälven, and Fiolen, which all have lower CaCO₃-levels than model boundaries. For the other sites,, the water samples were often softer than waters used in the validation exercises during the BLM development.

Test-running of the Cu-BLM, shows that the number of potential risk sites is dramatically reduced when compared to the single-PNEC method suggested by the Swedish EPA. However, it does also show that the latter can actually miss out on some potential risks compared to the BLM-method.

The Zn-BLM tool is user-friendly, but turned out not to be applicable for some Swedish waters. Thus a full SSD normalization was performed, which is equivalent to using the full Cu-BLM. The BLM-method again substantially reduces the number of potential risk sites when compared to using total concentrations and a single PNEC-value. It was, however, pointed out that for some Swedish waters, especially where Ca-levels <3 mg/L, results should be interpreted with caution, as the models have not been validated in this range (See 3.2 beginning).

An equivalent model for nickel is on its way, but at the time of this study, the user-friendly version had not yet been released.

There is a lot to gain from applying the BLM-methodology when assessing risks of metals in Sweden, preferably as a step in a tiered process, where monitoring data could first be compared to a generic PNEC, and potential risk sites then proceed to the BLM evaluation step. In doing this, the number of potential risk sites is reduced and remediation efforts or other measures can be focused on areas where they are really needed. This would make the risk assessment more time and cost efficient.

The overall conclusions of the project are:

- BLM-models can and should be applied as a natural element when assessing metal risks in Swedish waters, preferably as a sub-step in a tiered approach.
- The chemical conditions of Swedish water bodies are generally in agreement with the BLM requirements concerning the two key parameters pH and DOC, when it concerns the metals Cu, Zn, and Ni.
- Swedish national monitoring programmes should focus on routine measurements of dissolved metal concentrations, and also on measurements of DOC. If the currently used method is regarded as equivalent to filtration through a 0.45 µm filter, this should be clearly stated in the national monitoring databases
- Models are available for Cu, Zn, and will soon be available for Ni. The BLMs are regularly improved and updated.
- Concerning chromium, BLMs are currently not available. It is therefore considered that all soluble chromium (III) is bioavailable and thus contributes to toxicity.
- Cadmium is assessed using a hardness correction and the proposed Cd-EQs are to be compared with dissolved monitoring data.

Future steps for improvements:

- In order to assess the model results, a validation exercise should be performed for soft waters regarding Zn, in particular for soft waters with a high pH-value.

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1 Introduction

In implementing the EU Water Framework Directive (WFD), member states are encouraged to take into account bioavailability and natural background concentrations when assessing the risk of metals in aquatic systems. In doing so, site-specific no-effect concentrations (NOECs) or predicted no effect concentrations (PNECs) should ultimately be determined, to which measured concentrations can be compared. The metals currently on the priority list of the EU Water Framework Directive (WFD; Directive 2000/60/EC) are lead (Pb), cadmium (Cd), mercury (Hg) and nickel (Ni) (COM(2006) 397 final). Other metals such as copper (Cu), zinc (Zn) and chromium (Cr), have also been addressed as potentially problematic in some European countries (e.g. Sweden) and Swedish guidelines have been established on how to assess risks associated with these as well (Naturvårdsverket, 2008). EU-wide risk assessments have been performed for several of the metals above, either by the Commission or as voluntary initiatives by industry (e.g. ECB, 2005; ECB, 2008; ECB, 2007; ECI, 2008). In the establishment of environmental quality standards for metals under the EU water framework directive, considerable efforts have been devoted to elaborating methods for taking bioavailability into account, mainly through the development of so-called biotic ligand models (BLMs). Substantial progress has been made for copper, zinc and nickel, and user-friendly versions of BLMs are available for Cu, Zn and in a near future also for Ni. The BLMs are reaching wide acceptance on the European level and are being used for implementation of the WFD in an increasing number of European countries. From the Swedish point of view, concerns have been raised that the BLMs may not be applicable in this area, due to a difference in water chemistry when compared to the European waters, for which the BLMs have mainly been validated.

1.1 Aim of study

The objectives of the current study are to assess the applicability of BLM in Swedish waters by studying a sample of representative Swedish waters and assess the potential of using BLM in Sweden with regard to the critical parameters and their respective model validation ranges. The aim is also to identify and highlight data gaps and to address the implications of using the BLM in Sweden, and identify needs for further development, validation and improvement. In particular, its applicability for the metals Cu, Zn, Ni, Cd and Cr will be discussed.

1.2 Structure of report

This report is divided into several sections and sub-chapters, where section 2, background, sets the conditions for BLM application in Sweden, thus it describes the general water chemistry in Swedish waters, as well as the main factors governing the key parameters (2.1), it gives brief descriptions of the existing BLMs, which have been developed so far, as well as approaches for considering bioavailability of metals where BLMs are currently not available (2.2) and it summarizes the current status of European risk assessment of metals (2.3). Chapter 3 describes the general methodology for the current project and in chapter 4 the results are presented. Finally, the results are discussed in chapter 5 and in chapter 6 the conclusions are drawn and some recommendations given.

2 Background

Many metals are essential substances for natural organisms, including humans. This is true for elements such as copper, zinc, nickel, chromium and iron. The essentiality means that lack of such metals will lead to deficiency symptoms, and ultimately, death. On the other hand, too high concentration will lead to toxic responses, and ultimately, death. Therefore, there is an optimal concentration range, which is illustrated by Figure 1.

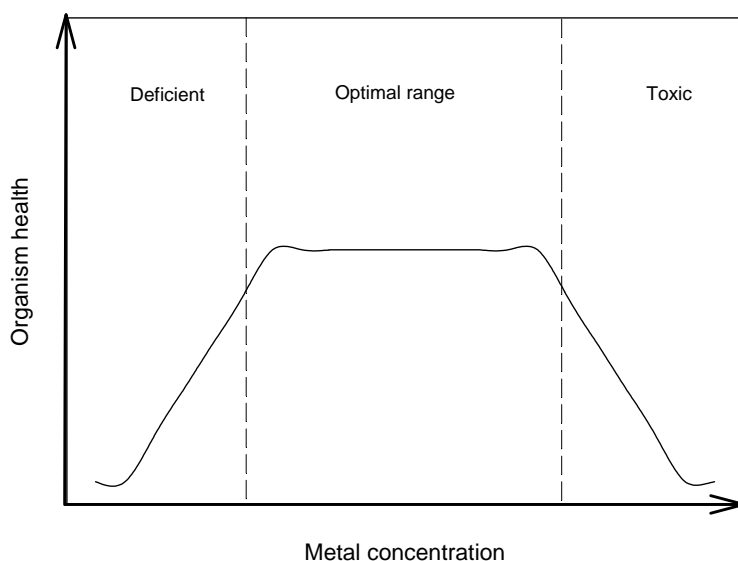


Figure 1. Qualitative illustration of organism response to varying concentrations of a metal in the aquatic environment

Metals such as the ones mentioned above occur naturally in the earth's crust, to various extents in different geographical regions. Therefore, the natural concentration of metals in aquatic systems is highly variable. For Cu, natural concentrations globally vary between about 0.2 – 30 µg/L in freshwater systems and from 0.03 to 0.4 µg/L in open ocean saltwater (Bowen, 1985, OSPAR 2000¹). As a result, organisms living in the various ecosystems are used to, and thus adapted to varying concentrations of metals, the so-called background concentrations. Very slow changes in metal concentrations, will up to a certain extent lead to slow re-adaptation of the organisms living there, whereas sudden changes may lead to deficiency/toxic responses and possibly organism death.

In order to tell the status of a water body with regards to metal concentration and its potential to cause damage to the aquatic organisms, it is thus necessary to determine the natural background concentration of the same water body (ICMM, 2007). As many metals have diffuse sources, pristine conditions are rare in the world. For this reason, it may be more realistic to use long-term equilibrated ambient concentrations rather than true background concentrations. It has become increasingly accepted that also other conditions, such as hardness, content of organic matter and pH may influence metal toxicity. For example, a high presence of competing cations (e.g. Ca²⁺, Mg²⁺) will reduce metal binding to the target organism (biotic ligand). Similarly, a high content of dissolved organic matter (i.e. organic matter other than the target organisms) will form metal complexes with the metal ion and reduce binding. In addition, certain other metal species, e.g.

¹ OSPAR, 2000. OSPAR quality status report 2000. Chapter 4- Chemistry.

MeOH, are not able to bind or bind to a lesser extent, and thus metal speciation is an important factor that may influence the binding potential. As a consequence, the water chemistry of the surface water ultimately governs the bioavailability of metals. In the case of Sweden, concerns have been raised that since Swedish conditions are different from typical European surface waters, the proposed methods for metal risk assessment may therefore not apply.

In the following, the general conditions of Swedish waters are described, and their impact on crucial bioavailability parameters such as pH, DOC, hardness and alkalinity. This was then used as a basis for selecting appropriate reference sites as described later in this report. Because of the profound influence that the bedrock geology and climate have on weathering and thus water chemistry it is important to cover as many types of waters as possible when assessing the bioavailability of metals as a function of water quality parameters such as pH, hardness, TOC, etc.

2.1 Water chemistry of Swedish surface waters

Weathering of the bedrock is the ultimate supplier of cations and anions to the watershed. Hence weathering ultimately determines the water chemistry of a watershed. The impact of weathering on water chemistry is mainly relevant for assessing metal bioavailability when it concerns its influence on hardness and pH. Weathering of bedrock is principally governed by two factors: climate and the geology of the bedrock.

Bedrock weathering (together with hydrology) determines which and at what rate cations are supplied to the water. This has an impact on hardness and buffering capacity and hence on the pH of the water. As a result, the bedrock composition in the watershed (e.g. presence/absence of carbonates) is crucial since this is a determining factor for the weathering rate (Stallard, 1998).

The other important factor determining the weathering rate is the climate, either by itself or through its influence on vegetation (Stallard, 1998). From a local perspective, the supply of water is the most important factor for determining the weathering rate. The organic material of the soils, and thus ultimately the vegetation, is very important as the supplier of proton donors and complexing agents in the form of organic acids for weathering reactions and as a mediator for the moisture budget of the soil and controlling soil structure (Stallard, 1998; Ugolini and Spaltenstein, 1998).

In the following sections the weathering processes and their influence on the water chemistry of Swedish surface waters, and hence ultimately on the applicability of the BLM model in Sweden, will be described in more detail. The information on geology comes from Lundqvist (1994) and Fredén (1994). The information on vegetation and climate, comes from Lundmark (1990), Eriksson and Odin (1990) and Sohlberg (1990), unless otherwise stated. The information regarding the area distribution of watersheds is from Raab and Vedin (1995).

2.1.1 Influence of bedrock weathering on water chemistry

In general, the weathering rates in Sweden are low, for several reasons. The low weathering rates make Swedish waters generally much softer than the rest of EU waters with the exception of Finland where conditions are similar.

Firstly, the bedrock mainly consists of old igneous and metamorphic aluminosilicates rocks, rich in Si, which are very resistant to weathering (Stallard, 1998). Examples of this type of rocks are granites and gneisses. All reference sites chosen have this bedrock in their entire or in parts of their watershed. There are two major exceptions to this general rule. The bedrock of the southern and northwestern part of Skåne as well as the islands of Gotland and Öland are partly or completely composed of sedimentary rocks such as limestone, sandstone and claystone. Sedimentary rocks are more easily eroded. Hence, the weathering rate is much higher and carbonates will be supplied to the watershed, which make waters in these areas significantly harder than in other areas. The reference sites Kävlingeån and Rönneån (see Figure 2 - description given in section 3.2) have sedimentary rocks in parts of their watershed.

Secondly, the Swedish bedrock is part of the Baltic shield, a tectonic unit that has already been extensively eroded and therefore have very small variations in topography, which further reduces the weathering rate (Stallard, 1998). One important exception to this is the mountain range between Sweden and Norway, the Scandes. These mountains are geologically fairly young, and the summits reach 2200 m a s l. The Scandes are composed to different degrees of metamorphosed sedimentary rocks (e.g. sandstones and limestone), as well as igneous rocks. The igneous rocks are both rich in Si (e.g. granites, gneiss) and poor in Si (e.g. basalt). The sites Abiskojaure and Ume älv (Stornorrfor) have all and parts of their watersheds in the Scandes, respectively.

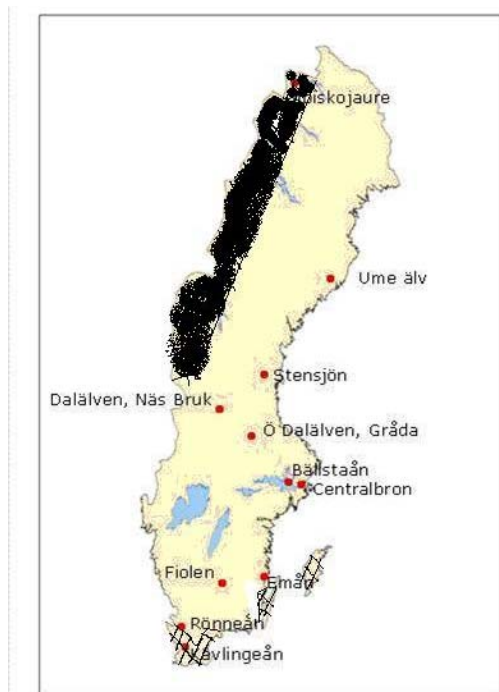


Figure 2. The three main geological regions in Sweden: sedimentary rocks (hatched), the Scandes mountain range (black) and granitoid bedrock (the rest). The map also shows the reference sites used in the current study, which are described in detail later in the report (section 3.2).

2.1.2 Influence of climate on water chemistry

The third explanation for the low weathering rates in Sweden is that the generally low temperature further reduces the weathering rate, either by itself or indirectly, through decreased biological activity (biomass of vegetation) and turn-over of organic matter (Stallard, 1998).

The majority of Sweden, 70%, is covered by the subarctic and northern Boreal climate zones (Algesten, 2003). In the northern boreal and subarctic regions the vegetation increases the weathering rate (Humborg et al, 2004). The hydrology is also very important. In the subarctic and northern boreal climate zones the residence time for soil water rock interactions is the most important factor for the weathering rate, followed by lithology, i.e. rock type (Brink et al, 2007). The importance of hydrology and vegetation is probably also relevant for the southern boreal zones and the northern temperate zones covering the rest of Sweden (c.f. Stallard, 1998). There can of course be local exceptions to this, e.g. in the case of softer sedimentary rocks.

For a given set of conditions (lithology, climate, slope) there is presumably an optimum soil depth for weathering (Stallard, 1998). The dominating soil types of Sweden in the northern boreal zones are till, and where the drainage is poor, peat. There are also extensive glaciofluvial deposits. In the southern boreal and northern temperate zones of Sweden the dominating soil types is till, followed by clay and clay till. Where the drainage is poor, peat is prevalent. There are also extensive glaciofluvial deposits and there are regions where only very little or no soil exist on higher ground.

Vegetation and turn over of organic matter, which are influenced by climate also determines the concentrations of total organic carbon (TOC) in the water. However, the water residence time may be more important than the temperature for the flux of organic carbon in Boreal climate zones (Tranvik and Jansson, 2002). The areal coverage of lakes in a watershed is the most important regulator for the export of TOC from the watershed to the coast in the boreal climate zones (Algesten et al, 2003; Mattsson et al 2005). The TOC is lost through mineralization and subsequent emission to the atmosphere. There is a positive correlation between the percentage of peatlands in the watershed and TOC in the rivers (Mattsson et al, 2005; Mattsson et al, 2007). There is a negative correlation between TOC concentration and pH in boreal climate zones, since organic acids are the main source of acids (Mattsson et al, 2007). The combination of the supply of TOC and hence organic acids in the Boreal climate zones and the low buffering capacity of the waters, is the main reason for the low pH in Swedish waters compared to the rest of Europe.

2.1.2.1 Climate zones

Sweden can be divided into 8 climate zones (Figure 3). The climate zones are mainly categorized based on temperature, precipitation and vegetation, which together with geology influence water chemistry.

One parameter that is used to describe the climate is the T-sum. T-sum is a measure of the heat during the growth season and is derived by adding, during a period of one year, the mean air temperature over +5 °C for each day when the mean temperature of the air is >+5 °C. As an example, days with +18 °C as mean air temperature contribute with 13 day degrees. In the following, the 8 climate zones are described in brief. In selecting reference sites, as many climate zones as possible were sought to be covered, but also other aspects were considered (see section 3.2).

- Climate zone 1, subarctic. T-sum<750 day degrees. The climate is extremely cold with continuous frosts from mid-October to May (Ångström, 1974). The precipitation is

between 1000 and 2000 mm per year to the headwater areas (Carlsson and Sanner, 1994). On the high altitudes (summits above 2200 masl) the soil cover is non-existent except for weathered rocks and the vegetation is barren. The tree line is around 800 to 650 masl. Here the vegetation is composed of alpine pastures and deciduous brushwood and short deciduous forests. On lower levels coniferous forests and peat bogs dominate.

- Climate zone 2, northern boreal. T-sum between 750 and 900 day degrees. Coniferous forests dominate and where drainage is poor, peat bogs dominate. Some agricultural areas on clay soils in river valleys and along lakes.
- Climate zone 3 northern Boreal. T-sum has between 900 and 1300 day degrees. Coniferous forests dominate and where drainage is poor, peat bogs dominate. Some agricultural areas on clay soils in river valleys and along lakes.
- Climate zone 4, northern Boreal. T-sum more than 900 day degrees, dry summer and mildly humid climate. Coniferous forests dominate and where drainage is poor, peat bogs dominate. Some agricultural areas on clay soils in river valleys and along lakes and the Baltic Sea coast.
- Climate zone 5, southern Boreal T-sum > 1300 day degrees, dry summers and less mildly humid climate. Coniferous forests dominate and where drainage is poor, peat bogs dominate. Extensive agricultural areas in some regions.
- Climate zone 6 northern temperate. T-sum>1300, mildly humid and less dry summers. Coniferous forests and open areas dominate. Extensive agricultural areas in some regions.
- Climate zone 7, southern Boreal. T-sum 1150 – 1500 day degrees, mildly to medium humid. Coniferous forests dominate and where drainage is poor, peat bogs dominate. Some agricultural areas on clay soils in river valleys and along lakes.
- Climate zone 8, northern temperate. T-sum>1300 day degrees, strongly to very strongly humid climate. Deciduous forests and open areas dominate. Extensive agricultural areas.

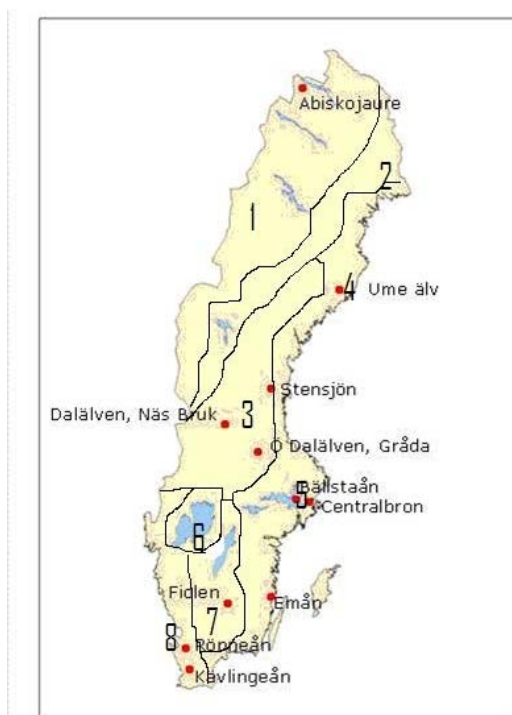


Figure 3. The 8 climate zones in Sweden. The map also shows the reference sites used in the current study, which are described in detail later in the report (section 3.2).

2.2 Biotic ligand models and other risk assessment methods for metals

The main tools used in the current assessment are the biotic ligand models. Thus, this section is devoted solely to describing the principles and various types of models available, and in case no such models are available it describes other currently used risk assessment methods for metals and their status within the EU RA procedure.

As mentioned above, the EU Water Framework Directive opens up for the possibility to consider natural background concentration and bioavailability when setting environmental quality standards, thus generating site-specific predicted no effect concentrations (PNEC-values) for the particular water body of interest. As a result of this, so-called biotic ligand models (BLMs) have been developed for a number of metals. BLMs have been developed for acute toxicity of metals, primarily Cu, Zn, Ag, Ni and Cd (Di Toro et al., 2001; Hydroqual., 2007) and for chronic toxicity for Cu (ECI, 2008; De Schamphelaere et al, 2006a; De Schamphelaere K.A.C, 2003; De Schamphelaere K.A.C. and Janssen C.R., 2004a.; De Schamphelaere et al., 2004; Bossuyt, et al., 2004; De Schamphelaere et al, 2006b; De Schamphelaere et al., 2003. De Schamphelaere and Janssen, 2005), Zn (De Schamphelaere et al., 2005, van Assche, 2008, UK Environment Agency, 2008) and Ni (Mattelet et al., 2008, Van Laer et al., 2006; Deleebeek et al., 2007; Deleebeek et al., 2008; Deleebeek et al. 2008; Deleebeek et al., 2007). A summary document on the application of BLMs to setting water quality standards was developed by Van Sprang et al. (2008). The generation of user friendly BLMs for chronic effects of metals is an on-going process with the most advanced progress reported for Cu, but Zn and Ni are not far behind. In the current study, only BLMs for

chronic effects were used, as the main interest in the risk identification process is in long-term effects as a result of chemical load on the water body.

The general principles behind the BLM are well established, in that they predict metal toxicity using a combination of existing biological and chemical models; the biological part is based on the gill site interaction model (Pagenkopf, 1983) and the chemical part involves chemical speciation calculations performed using the principles in the WHAM model (Tipping, 1994). A schematic presentation of the BLM mechanisms is shown in Figure 4.

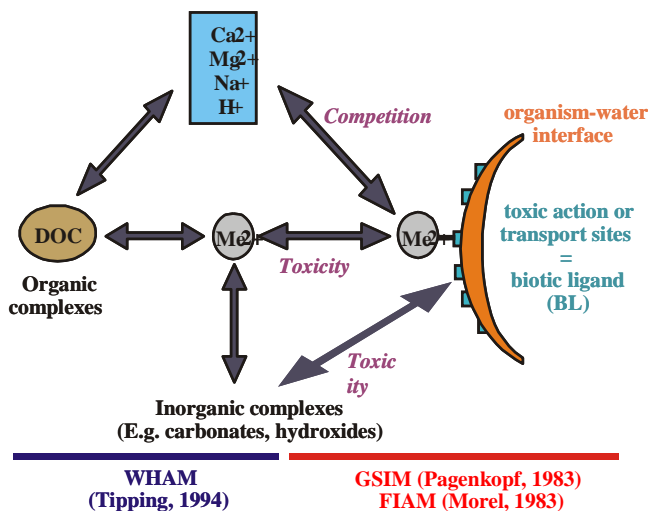


Figure 4. Mechanisms generally considered in the BLM when predicting the bioavailable fraction (re-constructed from ICM, 2007).

The application of the BLM performs two functions. First, it provides a geochemical normalization which removes the influence of abiotic factors in the comparison of individual toxicity tests, which may have been performed using different water chemistries. This is accomplished by the chemical speciation software within the BLM, and ensures that all data within a given Species Sensitivity Distribution (SSD) are evaluated on an equivalent basis. Second, the BLM takes into account the competitive effects of positively-charged constituents of freshwater, such as Ca²⁺, Mg²⁺, and H⁺, on the uptake of metal ions at the site of action on the organisms.

The use of site-specific water chemistry input data in the BLM results in model calculations of the metal bioavailable fraction, which can be applied to the reference toxicity database to generate site-specific NOEC values, which are used in a Species Sensitivity Distribution (SSD) to calculate HC5-values (Hazardous Concentration, protecting 95 % of the population) and PNECs. By dividing measured dissolved environmental concentrations (MECs) for the same sites with the PNECs obtained, risk ratios are generated (MEC/PNEC). A ratio >1 implies that effects cannot be ruled out and risk-reducing measures should be taken.

2.2.1 The Copper BLM

The Cu-BLM has been thoroughly tested and validated in natural waters and its performance is generally considered to be of high quality (ECI, 2008; De Schamphelaere et al, 2006 a,b; De Schamphelaere K.A.C, 2003; De Schamphelaere K.A.C. and Janssen C.R., 2004a.; De Schamphelaere et al., 2004; Bossuyt, et al., 2004; De Schamphelaere et al., 2003. De Schamphelaere and Janssen, 2005). The Cu-BLM functions as described above, site-specific water chemistry input data are used to calculate NOECs, based on the bioavailable fraction and the reference toxicity database, from which HC5-values are derived using SSD analysis and site-specific PNEC-values determined. In order to run the Cu-BLM, 13 input parameters are currently required:

- Temperature (°C)
- pH
- Cu (µg/L)
- Dissolved organic carbon (DOC; mg/L),
- Humic acid content (HA, %)
- Ca²⁺ (mg/L)
- Mg²⁺ (mg/L)
- Na⁺(mg/L)
- K⁺(mg/L)
- SO₄²⁻ (mg/L)
- Cl⁻ (mg/L)
- S⁻ (mg/L)
- Alkalinity (mg/L CaCO₃)

Out of these 13 parameters, the critical parameters are pH, DOC and CaCO₃. These need to be carefully measured and quality checked, whereas the remaining parameters have relatively small impact and in some cases even default values are satisfactory for the model run. Still, they are needed as input to the model. The current Cu-BLM is straightforward and easy to use, but fairly time-consuming when numerous samples are to be assessed, mainly because of the extensive input data requirements. The International Copper Association recently developed a further simplification and an even more user-friendly version was released early in the year 2009 (EURAS, 2009).

2.2.2 The Zinc BLM

The approach behind the development of BLMs for zinc is slightly different than for copper. Models were derived for chronic toxicity to species from three trophic levels (algae, daphnia, fish) and combined into one predictive user friendly Excel tool (van Assche, 2008), which was described in detail by Schamphelaere et al. (2005). The Zn-BLM tool only requires three input parameters; pH, DOC (mg/L) and Ca²⁺ (mg/L) or CaCO₃ (mg/L) as an alternative. Using these input parameters, bioavailability factors (BioF) are determined for each species and sample, and these are calculated according to:

$$\text{BioF} = 1/\text{WER}$$

where WER = Water Effect Ratio is calculated as

$$\text{WER} = \text{NOEC}_{\text{local,A}} / \text{NOEC}_{\text{ref,A}}$$

where $NOEC_{local,A}$ is a site-specific no-observed-effect-value for species A and $NOEC_{ref,A}$ is a no-observed-effect-concentration value for that species under water conditions which represent “realistic worst case” conditions of high bioavailability. These “realistic worst case” conditions were set as defined in the EU risk assessment. The highest BioF value derived among the three organisms is then applied to the measured dissolved concentration of Zn to generate the maximum bioavailable concentration of Zn, the C_{BioZn} , which in turn is compared to a generic PNEC-value.

However, the BioF approach based on “realistic worst case” conditions has the disadvantage that reference conditions have to be set. In the EU RA, these conditions were defined as the 10th percentile values of the parameters driving bioavailability. The definition of these conditions can be subject of debate: they may indeed vary from one country to another. As the set of reference conditions is based on statistical evaluation of large EU-wide datasets, there is still a possibility that for a certain site, actual water chemistry parameters may result in even higher bioavailability than the EU reference conditions., which is indeed often the case in Swedish waters. The implication for the BLM is that it predicts a BioF-value > 100%, i.e. the bioavailable Zn is higher than the dissolved metal concentration, which is of course not possible.. In these cases, it may be assumed that all dissolved Zn is bioavailable. The limitation following from setting a reference set of conditions can be avoided by using a full SSD normalization approach. The International Zinc Association is currently in the process of developing such approach. There is already evidence for zinc to apply a cross-species extrapolation for the three trophic levels, based on the available information from the open literature. This is specifically true for the algae and fish. Further testing is currently ongoing to confirm the applicability of the Daphnia BLM to dissimilar species across the invertebrates. This should be completed within a 1 year time frame. No user-friendly tool is available yet, but scientists can already calculate site-specific PNECs or EQSs based on this approach (D. Haesaerts, pers.comm.). So, the full SSD approach was applied to the current assessment.

The exercise was carried out by Dr de Schamphelaere at the University of Gent in Belgium, and is described in detail in Appendix 2.

2.2.3 The Nickel BLM

The Biotic Ligand Model for chronic effects of Nickel used in the EU risk assessment (the NiRA BLM) was developed and validated within the framework of the Existing Substances Regulation (793/93/EEC). Again, the NiRA BLM utilizes site-specific water chemistry and abiotic factors to normalize ecotoxicity data, and the integration of the normalized data (i.e., the HC5/AF, where the HC5 = the outcome of the SSD analysis and the AF is the assessment factor) is the site specific EQS. This site specific EQS is compared with measured site specific dissolved Ni concentrations to determine compliance. As for Cu and Zn, the critical factors which affect Ni toxicity include pH, hardness and DOC.

Biotic Ligand Models for chronic effects of Ni have been developed for four species across three trophic levels for bioavailability correction covering the algae *Pseudokirchneriella subcapitata*, two invertebrates (*Daphnia magna* and *Ceriodaphnia dubia*), and the fish *Oncorhynchus mykiss*. These BLMs have been applied to the Ni toxicity database to normalize toxicity values to a set of standard water quality parameters and to reduce intra-species variability in the data set. The cross-species normalization approach was confirmed by conducting a spot-check study for invertebrates and vascular plants. The spot check study was performed on three non-crustacean invertebrates (the midge larvae *Chironomus tentans*, the rotifer *Brachionus calyciflorus*, and the snail *Lymnaea stagnalis*) and one higher plant (duck weed, *Lemna minor*). The results indicated that the four available BLMs were

capable of predicting toxicity to the test species used in the spot testing exercise within a factor of 2, which confirmed the cross-species extrapolation approach.

The Ni BLM for chronic effects that was used in the risk assessment process (NiRA) is currently (January 2009) being converted into a more user friendly software interface (HydroQual (HQ) BLM model). The development of a user-friendly Ni BLM software interface greatly facilitates the calculation of chronic Ni toxicity for specific sites or river basins. The HQ Ni BLM is currently in the final stages of validation, which will ensure that a sufficient number of water chemistry combinations are considered in the calibration of the HQ BLM with the NiRA BLMs. At present, the three components of the model (speciation, normalization, HC5 modeling) are consistent with the Ni BLM model used in the NiRA; however, quality assurance/quality control (QA/QC) confirmation is required prior to the finalization of the HQ BLM model. Thus it has not been possible to apply the Ni BLM in the current project.

2.3 Use of BLMs in EU regulatory frameworks

The BLMs and their use as described above have been accepted under the EU RAs of Zn, Ni and Cu. The importance of incorporating bioavailability in the assessment of metal exposures and toxicity and exposure in EU surface waters is also recognized under the EU Water Framework Directive. The EU Directive 2008/105/EC on environmental quality standards in the field of water policy, states :

“ In the case of metals the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment. Member States may, when assessing the monitoring results against the EQS, take into account:

(a) natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and

(b) hardness, pH or other water quality parameters that affect the bioavailability of metals. “

The focus on dissolved concentrations is because of the common understanding that only this fraction can contribute to bioavailability and thus toxicity. Historically, Swedish monitoring activities have focussed on total metal concentrations, and guidance values have been set up for these. As the awareness of the importance of bioavailability has increased, it is now nationally accepted that the new established guidance or limit values set up for Cu, Zn and Cr in order to help water authorities in determining the chemical status of water bodies, should be compared to measured dissolved concentrations (Naturvårdsverket, 2008). Currently, there are on-going discussions concerning whether the existing methods for chemical analysis of metals are actually “equivalent” to filtration through a 0.45 µm filter, and thus count as dissolved concentrations. This has, however, not yet been clarified in the national databases (http://info1.ma.slu.se/IMA/dv_program.html, January 2009), thus they appear to the user as total concentrations, and have been treated as such in the current project. The new Swedish guidance document also states that, but not how, bioavailability and natural background levels should be taken into account. A very brief description of the BLM is included but no clear methodology on how, if and when to use them. On the EU-level, a short guidance document for EQS-setting including BLM-application has been developed (Van Sprang et al., 2008). Additionally, the EU Commission’s working group on environmental quality standards (WG-EQS) is developing an in-depth guidance document for setting environmental quality standards (for water, sediment and biota) under the Water Framework Directive. The draft guidance

document (December 2008) includes a tiered approach for metals' EQS whereby bioavailability can be accounted for through the use of BLMs (Figure 5). The approach described in the EC guidance document is in line with the approach followed in the risk assessment for copper, zinc and nickel. When it concerns cadmium and chromium, other approaches have been applied in the risk assessment process, outlined below.

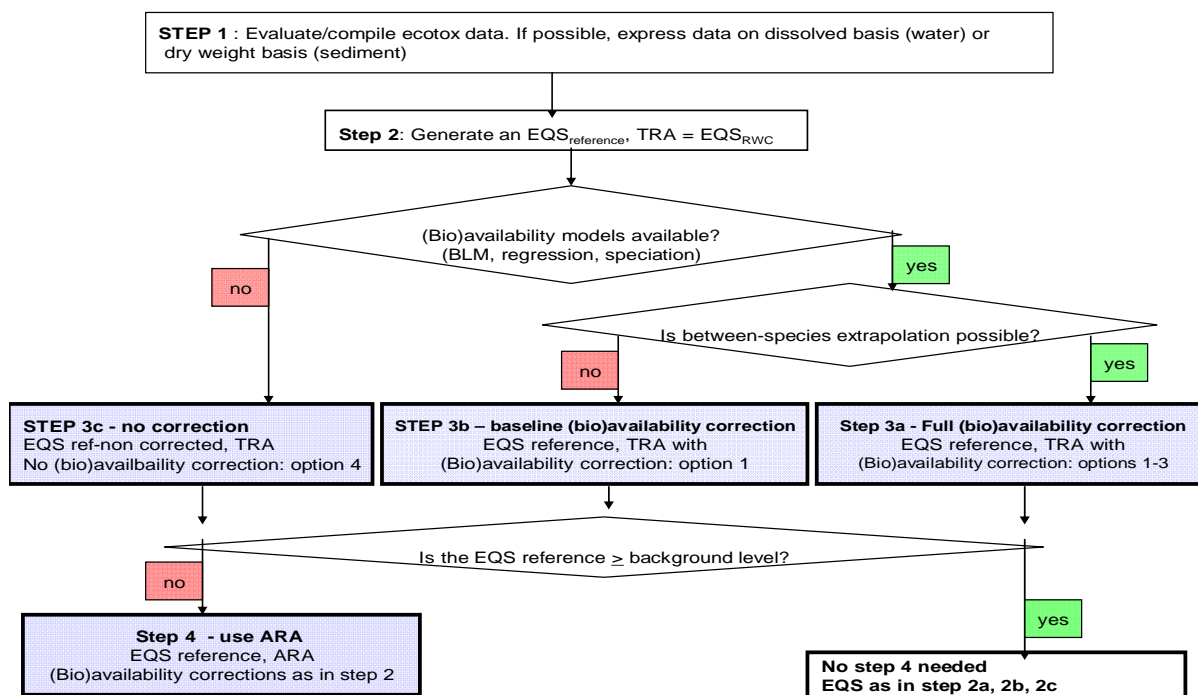


Figure 5. Scheme of guidance on EQS-setting. Draft (December 2008)

2.3.1 The Cadmium Approach: Hardness correction

The approach followed in the cadmium Risk Assessment is similar to the one used in the EQS Directive (2008/105/EC). It takes water characteristics into account by considering one mitigating parameter, i.e. water hardness which plays an important role in cadmium toxicity. An equation based on the regressions of the natural log of the toxicity chronic values for algae, Daphnia and fish against the natural log of the water hardness was used to derive the PNEC_{water} or EQSs. In the EQS Directive, five hardness classes were derived which each translate into an EQS. The risk ratio has to be calculated on a dissolved basis still, using the partitioning coefficient for Cd if no measured dissolved data is available.

Hardness range (mg CaCO ₃ /L)	Cd EQS (µg Cd dissolved/L)
Class 1: < 40	≤0.08*
Class 2: 40 to <50	0.08
Class 3: 50 to <100	0.09
Class 4: 100 to <200	0.15
Class 5: ≥200	0.25

* The lower EQS is also protective for algae, invertebrates and fish in very soft waters, i.e. waters having a hardness below 40 mg CaCO₃/L (Niva, 2007a & b; Messiaen et al., 2007).

2.3.2 Risk assessment approach for chromium

In the case of chromium, a different approach has been chosen by the International Chromium Development Association (ICDA) when conducting their risk assessments. Despite an awareness of the relevance of bioavailability and the possible significance of the Biotic Ligand Model approach, there are currently no data available for chromium(III) that would allow these factors to be introduced into the assessment for chromium. Therefore, in the case of chromium, it has been decided that, until more data are available, the precautionary principle should be applied and consider that all soluble chromium(III) is bioavailable and thus contributes to toxicity. (G Darrie, pers. comm.)

3 Materials and methods

3.1 Testing the biotic ligand models

The only chronic BLMs currently available are the ones for copper and zinc, thus these two models were tested with Swedish monitoring data. For Nickel, the potential applicability was assessed by comparing the water chemistry data to the given model boundaries, but no calculations could be performed. The models used for this assessment were the following:

- The user-friendly Biotic Ligand Model for copper, version May 2007, provided by Katrien Delbeke from the European Copper Institute. This was the same model as used in the European Risk Assessment for Copper.
- A slightly modified version of the “Zinc-BLM-application-tool”, version 4a. The original version 4a was developed in February 2007, provided by Frank Van Assche from the International Zinc Association and is described by de Schampelaere et al (2005). The version used in the current assessment was slightly modified by Watts & Crane Associates in the UK, provided by Graham Merrington (WCA) and is described in UK Environment Agency (2008). The most important change in this version is that it corrects Ca-levels which lie outside the model boundaries to the lowest or highest value allowed before the calculations are performed, whereas the original model does not execute outside the ranges. To compensate, input values which are outside the boundaries are highlighted so that the user is aware of the additional uncertainty associated with these predictions.
- Because of the previously mentioned limitations in the methodology using “worst-case” reference conditions, calculations for Zn were also performed by Dr Karel De Schampelaere at Ghent University in Belgium, applying the full SSD normalization approach, which is in principle the same methodology, which will be contained in the later, updated user friendly Zn-BLMs that are under development. These results will also be commented. A detailed report on this evaluation is attached in Appendix 2.

3.1.1 Model input

The input data needed have been described previously. All data was collected from the national monitoring database of water chemistry, hosted by the Swedish University of Agricultural Sciences (http://info1.ma.slu.se/IMA/dv_program.html, September 2008). Approximately 24 samples were assessed for each site (see Appendix 1), representing as recent data as possible. When monthly measurements had been performed, the data used were from 2006 and 2007. In some cases also data from 2005 were included, to increase the number of samples and to account for internal variability. Dissolved organic carbon (DOC) is not routinely monitored within the national monitoring programme, but was estimated from TOC according to:

$$\text{DOC} = 0.8 \times \text{TOC}$$

as suggested in the EU Risk Assessment for copper (ECI, 2008). This may be a slight under-estimation of DOC levels, as some studies have indicated that DOC-levels are more likely to be in the range $0.9\text{-}0.95 \times \text{TOC}$ (e.g. Algesten 2003, Wetzel 2001), but was used as a first estimate.

Data on metal concentrations (Cu and Zn) were also derived from the same data sources. It should be emphasized here, that the desired parameter is the dissolved metal concentration. In the Swedish national monitoring programme, the samples for metal analysis are collected in separate bottles, which are acidified upon arrival to the laboratory using HNO_3 and determined by ICP-MS. The levels are referred to as “near total concentrations” and in this study they have been regarded to be total concentrations ($\text{MEC}_{\text{total}}$), which should be kept in mind. Discussions are currently held, whether the methods used can be regarded as “equivalent” to filtration with a $0.45 \mu\text{m}$ filter, but as this project was initiated, this was not clear and we have regarded them as total concentrations. In the Zn-BLM, the total concentrations are re-calculated to dissolved concentrations based on a default concentration of suspended matter (15 mg/L) as well as a default K_d -value (110000). This increases the uncertainty in the model calculations and should ideally be avoided, but was not possible in the current case.

In the full SSD approach risk ratios were calculated both assuming that total Zn = dissolved Zn, and as an alternative, with the corrections mentioned above.

For the Cu-BLM, to be consistent with the copper Risk Assessment report (ECI, 2008) no correction was done and the MEC total is considered to be equal to MEC dissolved. This is a conservative approach, but may be reasonable, as discussed previously. For consistency with the zinc approach described above, however, the median K_d value for copper of 30264 l/kg (from the copper risk assessment report, ECI, 2008) was used to calculate a MEC dissolved and subsequent risk ratios, which are provided in Appendix 1.

As the main purpose of this study is not to evaluate the risks associated to Cu and Zn, but rather to assess the model applicability, this discrepancy between the metals is not crucial. We clearly emphasize the need for measurements of dissolved concentrations within the national monitoring programme, especially considering that even the established national guidelines now refer to dissolved concentrations.

3.1.2 BLM calculations

In total 252 calculations were performed, both for Cu and Zn. In the full SSD approach for Zn, HC5 values were derived for 317 samples (i.e. also for some additional sites, other than those included here), but risk ratios calculated for 252 samples.

For copper, a sample-specific PNEC-value was derived by the model (here called $PNEC_{BLM}$), and the ratio between the measured copper concentration (MEC_{total}) and the $PNEC_{BLM}$ was calculated. For comparison, the ratio between MEC_{total} and the guidance PNEC-value recommended by the Swedish EPA ($PNEC_{rec}$) of 4 µg/L (Naturvårdsverket, 2008) was also calculated.

In the case of zinc, the model calculated bioavailability factor (BioF) was applied to the measured zinc concentration in each sample (after automatic correction to dissolved concentration as described above), yielding a concentration of bioavailable zinc (C_{BioZn}). The ratio between this concentration and the chronic ecotoxicity reference value from the EU RA (=HC5-50 or $PNEC_{added}$ without safety factor) was made. The ecotox reference values are 15.6 µg/L for hard waters, where $C_{Ca} > 5$ mg/L and 6.5 µg/L for softer waters (ECB, 2008). In parallel, a comparison of the ratio between the total measured concentration of zinc and the $PNEC_{added,rec}$ (8 and 3 µg/L; Naturvårdsverket, 2008) was also calculated for each sample. Although the $PNEC_{added,rec}$ refers to dissolved concentrations, no correction was done in this parallel assessment, as it was anticipated that a user who is not familiar with the bioavailability concept would not know which correction factors to apply and instead use the data available in the national monitoring database, the MEC_{total} . It should be emphasized here, that this comparison is purely done as an illustrative example of the outcome based on the data available in the monitoring databases. A more correct approach would be to correct total concentrations for dissolved, using K_d and suspended matter concentration. In order to reflect the impact of background concentrations, which is really the idea with the added approach (cf zinc) using a $PNEC_{added}$, the natural background levels as suggested by the Swedish EPA of 1 µg Zn/L for lakes and small rivers and 3 µg Zn/L for larger rivers (Naturvårdsverket, 2008) were also added and ratios recalculated for comparison. There is, however, an ongoing debate on how to determine natural or ambient background levels, so the current attempt should merely be regarded as an illustrative example.

In the full SSD approach for Zn (see Appendix 2) site-specific PNEC-values were derived based on HC5(50%)-values and various assessment factors (1 or 2), and risk ratios calculated based on these and reported Zn-concentrations.

3.2 Inventory of water bodies

The chronic BLMs that have been developed (and described above) have currently been validated for parameter ranges according to Table 1. This means that for these ranges, the models have been thoroughly tested and generally considered to possess a satisfactory predictive capability. It does not mean that they are not applicable outside these boundaries, only that predictions within the ranges can be guaranteed to possess a certain level of quality. Indeed, some studies show that the predictive capability of the models may be satisfactory also outside the ranges (for Zn; e.g de Schamphelaere et al., 2005; for Cu; Bossuyt et al. 2004), but predictions outside the ranges may be more uncertain.

Table 1. Abiotic boundaries for chronic BLMs developed for three different metals

Parameter	Cu – chronic	Zn – chronic	Ni – chronic ^b
pH	5.5-8.5	6-8.4 ^a	6.5-8.2
DOC (mg/L)	0-20		
Mg (mg/L)			1.4-72
Ca (mg/L)		5-150	3.8-88
CaCO ₃ (mg/L)	10-500	15-428	20-310
Ref	ECI, 2008	Van Assche (2008)	Mattelet et al. (2008)

^a)Validation range for algae: 6-8 ^b)Considers ranges for algae, daphnia and fish

Considering that the water chemistry of Sweden is different from many other parts of Europe because of climatological and geological reasons (see section 2.1), it is possible that biotic ligand models would have to be used outside their validated ranges for some parameters. Thus, it is of interest to check how well the validation ranges given in Table 1 match the current Swedish conditions in order to judge if the model is suitable for direct application in Sweden and other Scandinavian countries, or whether validation in these conditions is desirable.

This has partly been done under the EU risk assessment procedure for copper (ECI, 2007) where 145 sites were assessed, a total number of 1012 data points. The samples assessed in the risk assessment were all from 2001, and the total number of samples per site was very limited, thus internal variations such as possible seasonal dependence was not covered to any large extent. The PNEC_{BLM}-values derived for Sweden in the risk assessment were presented as 10p-50p-90p and were as follows: 13.8 – 18 – 23.3 µg/L, with the highest PNECs predicted to be located mainly along the mid-east coast (from Gävle to Skellefteå) and in the regions of Jämtland and eastern Småland. The lowest PNEC-values for Cu were predicted to be found in the northernmost subarctic areas as well as in parts of northern Värmland and around the border between Skåne/Halland. The median risk characterization ratio (RCR = MEC/PNEC) for Sweden was calculated to 0.104 and in total six out of 145 sites had an RCR > 1. Out of these six, five sites were only represented by one or two samples (ECI 2007).

In the current study, a different approach was used when choosing reference sites. Eleven sites were carefully selected, in order to cover the majority of geological (bedrock, soil types and topography), climate (temperature and precipitation) and land-use factors (vegetation type and agriculture) in Sweden, which could influence the water quality parameters determining metal bioavailability. The sites all belong to the Swedish national freshwater monitoring network which means that the water chemistry should reflect current background conditions. This means for example that the data from a reference site in Stockholm should reflect the influence from the city itself but not from any particular point sources. The selection method differs from the NiRA ecoregion approach, as it is not directly based on water chemistry parameters, but rather on the factors that influence the water chemistry.

Although there are variations in water chemistry, the sites were selected so that the specific parameters that were considered to potentially cause problems regarding the validation of the BLMs should be represented in their full range from all parts of the country. All the data were retrieved from the national monitoring program run by the Swedish Agricultural University, SLU, (<http://info1.ma.slu.se/db.html>) and financed by the Swedish Environmental Protection Agency. The catchments included in this monitoring program are not directly influenced by anthropogenic activities such as industrial point sources, but does cover various aspects of land-use, including heavily populated areas and urban regions. In these cases, the sampling points are located on suitable distance away from any emission outlets, such as e.g. STP emission pipes. The data from

this program are generated in the same way over time in order to ensure acceptable reproducibility and to allow for the detection of trends.

The sites selected were the following (see Figure 2 and Figure 3):

- **Abiskojaure**, climate zone 1, subarctic. The watershed of Abiskojaure is located in the Scandes. The watershed is mainly alpine areas with little or no soil cover.
- **Ume älv, Stornorrfors**. This site is located in one of the major rivers of the northern Boreal climate zone. The watershed covers climate zones 1, 2 and 4. The watershed is to a large extent (ca ¾) covered by forests, mainly coniferous. The rest of the land is mainly peat bogs or barren alpine areas. The only other land-use is small scale agriculture along the coast.
- **Lake Stensjön**. This site is located in a small lake in the northern Boreal climate zone (climate zone 4). The watershed is to a large extent (> ¾) covered by forests, mainly coniferous. The rest of the land is mainly peat bogs or open areas where there is small scale agriculture.
- **Näs Bruk** and **Gråda** in river Dalälven, which is a major river in the southern Boreal climate zone. These two parts of the watershed belong to climate zones 1 – 3 and 2 – 3 respectively. These parts of the watershed are to a large extent (> ¾) covered by forests, mainly coniferous. The rest of the land is mainly peat bogs, alpine areas or open area. In the latter where there is small scale agriculture. Regions with carbonate rocks are located within the watershed.
- **Bällstaån**, is a stream in a residential and industrial area in the suburbs of Stockholm City, **Centralbron** is located in central Stockholm, situated close to where Lake Mälaren flows into the Baltic Sea. Stockholm is the capital of Sweden and has around 1,5 million people including the suburbs. A city of this size naturally has an anthropogenic impact on the loads of metals, e.g. Cu, Zn, Cd, Hg and Pb (Lindström et al, 2001), on surface waters of the city. Both stations belong to the Lake Mälaren drainage basin, which constitutes the largest populated region of Sweden. Lake Mälaren is the 3rd largest lake in Sweden (1120 km²) and has a watershed which is situated in the southern Boreal zone, mainly climate zone 5. Slightly more than half of the area is forested, mainly coniferous. The rest of the land is either open areas or population centres. The clay deposits are larger than in the northern part of the country and the clay is in some parts rich in carbonates. Therefore, it is one of the most intense agricultural regions in Sweden. The post glacial gyttja clays of the Lake Mälaren drainage basin has a relatively high content of acid sulphide clays (former marine sediments) in some areas which can contribute to elevated concentrations of some metals (Ni, Cd, Zn, Co etc) in ground and surface waters (Andersson et al, 2007). The presence of carbonates in the soils can partially or totally counteract the lowering of the soil pH due to the sulphide clays and thus hinder the mobilisation of these metals.
- **Lake Fiolen** is a lake situated in the southern Boreal area, climate zone 7. Around half of the land in the watershed is covered by mainly coniferous forests. The rest is open land and peat. Small scale agriculture exists in the region. There are also extensive glaciofluvial deposits in the depressions in the landscape and areas without any or very little soil on higher ground.

- **Emån** is a river whose watershed is partly in the southern boreal, zone 7 and partly in the northern temperate zone, climate zone 5. Between 70 and 80% of the land is covered by mainly coniferous forests. The rest is open land, where small and medium scale agriculture exists. The geology and land-use is similar to Lake Fiolen above, there are however larger areas devoid of or with only very little soil cover and there are less areas of clayey till.
- **Rönneån** is a small river situated in the northern temperate climate zone, climate zone 8. 10 – 20 % of the land is covered by forests, mainly deciduous. The rest of the land is partly occupied by population centres and partly open, where large scale agriculture exists. The bedrock of the drainage basin consists both of sedimentary types (mainly clay stone and clay slates) and gneisses.
- **Kävlingeån** is a small river situated in the northern temperate zone (climate zone 8: T-sum >1300 day degrees, strongly to very strongly humid climate). Around 10 % of the land is covered by forests, mainly deciduous; the rest is divided between population centres and open land, e.g. large scale agriculture. The bedrock of the drainage basin is mainly made of limestone, sandstone, clay and clay slates but some areas of gneisses exist.

4 Results

4.1 Inventory of Swedish water bodies

The critical parameter ranges for each of the eleven reference sites were noted and checked against model validation ranges. Table 2 shows the measured ranges of the parameters as well as the boundaries for which the various BLMs have been validated.

Table 2. Measured ranges of critical BLM parameters for the eleven reference sites (<http://info1.ma.slu.se/db.html>) and BLM-specific boundaries for Zn, Cu and Ni. DOC was estimated as 0.8×TOC.

Site	pH	DOC (mg/L)	Ca (mg/L)	CaCO ₃ (mg/L)	Mg (mg/L)	N
Abiskojaure	6.8-7.3	0.6-3.3	3.6-8.3	7.6-19	0.46-1.2	14
Ume älv	6.7-7.4	2.0-6.4	3.1-5.1	7.0-13	0.55-0.81	23
Stensjön	6.0-6.7	2.7-7.5	0.8-1.5	1.6-3.6	0.24-0.44	25
Näs Bruk	6.7-7.2	4.6-7.6	3.4-5.6	6.0-14	0.56-0.91	24
Gråda	6.9-7.3	4.1-5.4	3.5-4.4	7.9-10	0.56-0.63	24
Bällstaån	7.2-7.7	5.4-12	33-90	81-200	4.6-15	24
Centralbron	7.3-8.2	5.4-7.2	18-23	44-53	4.0-7.4	24
Fiolen	6.1-7.0	3.4-8.8	1.7-3.1	2.4-4.7	0.6-1.0	25
Emån	6.7-7.3	8.1-14	7.9-12	10-25	1.8-2.7	27
Rönneån	7.2-7.9	7.0-7.9	23-36	42-90	2.5-4.3	20
Kävlingeån	7.6-8.0	5.0-12	67-95	137-200	4.3-6.9	24
Zn range	6-8.4(8)*		5-150	15-428		
Cu range	5.5-8.5	0-20		10-500		
Ni range	6.5-8.2		3.8-88	20-310	1.4-72	

* For algae, the validation range for pH in the Zn-BLM is 6-8.

In Table 3, the percentage of observations that fall within the model boundaries are given. As seen from the Table, pH and DOC normally fall within the ranges, whereas the hardness parameters (Ca, CaCO₃ and Mg) for many sites are partly too low. However, only three sites possess characteristics entirely outside model boundaries, i.e. where the hardness parameters for all samples included fall outside the ranges. These sites are Lake Stensjön, Lake Fiolen and for Zn and Ni also Gråda in river Dalälven. Gråda is also problematic for the Cu-BLM ranges, as only 4 % of the samples fall within the hardness boundaries. The same is true for Ume älv and the Zn-boundaries.

Table 3. Percentage of observations per parameter that fall within the BLM boundaries for the various metals. The total number of observations per site is given by the column to the right.

Site	pH			DOC		Ca		CaCO ₃		Mg	N
	Zn	Cu	Ni	Zn	Cu	Zn	Ni	Cu	Ni	Ni	
<i>Abiskojaure</i>	100	100	100	100	100	57	93	64	0	0	14
<i>Ume älv</i>	100	100	100	100	100	4	91	79	0	0	23
<i>Stensjön</i>	100	100	28	100	100	0	0	0	0	0	25
<i>Näs Bruk</i>	100	100	100	100	100	26	96	61	0	0	24
<i>Gråda</i>	100	100	100	100	100	0	75	4	0	0	24
<i>Bällstaån</i>	100	100	100	100	100	100	100	100	100	100	24
<i>Centralbron</i> (88 [*])	100	100	100	100	100	100	100	100	100	100	24
<i>Fiolen</i>	100	100	88	100	100	0	0	0	0	0	25
<i>Emån</i>	100	100	100	100	100	100	100	100	33	100	27
<i>Rönneån</i>	100	100	100	100	100	100	100	100	100	100	20
<i>Kävlingeån</i>	100	100	100	100	100	100	87	100	100	100	24

* For algae, the validation range for pH is 6-8, thus, 88 % of the samples from Centralbron fall within the pH-range for algae. The remaining percentage (13%) are above the pH validation range for Zn.

The above presented assessment, is anticipated to largely reflect the Swedish surface water conditions. Thus for the different regions of Sweden (climatological as well as geological) an assessment of the compatibility between the BLMs and water chemistry data can be assumed to be comparable to their respective part in Table 3. This implies that in a water body of similar type as Abiskojaure, according to the description in section 3.2, Ca-levels can be expected to fall within Zn-BLM boundaries in 57 % of measured samples etc.

4.1.1 Seasonal variation of critical input parameters

Considering that seven out of eleven sites have hardness parameters that in all or in a significant number of sampling occasions lie outside the BLM validation ranges, it is of interest to determine whether there are any seasonal patterns associated with the particular parameters. This could indicate whether samples taken at a particular season are more suitable for BLM calculations than others. Figures 6 to 8 show the seasonal variation of the five input parameters for all the eleven reference sites.

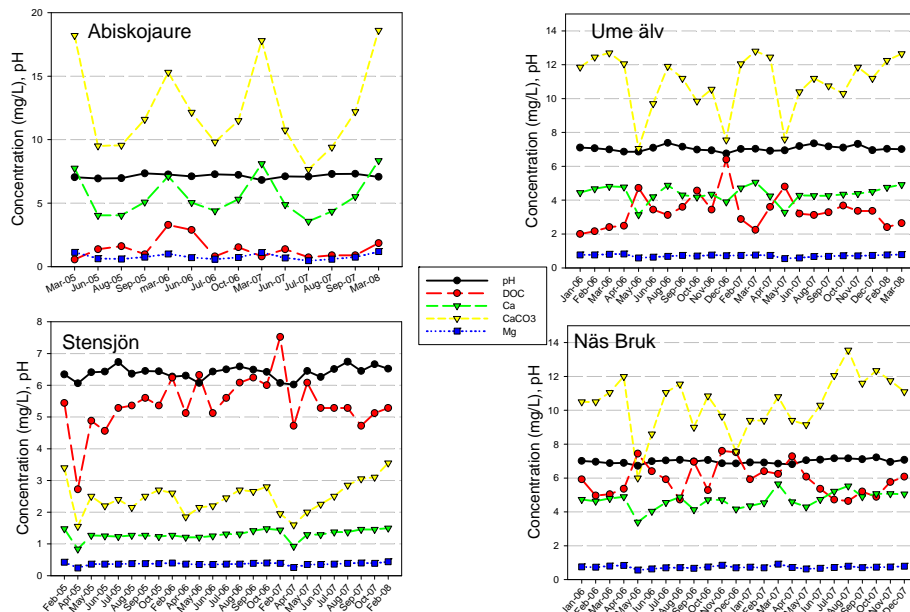


Figure 6. Seasonal variation of critical BLM parameters at the reference sites Abiskojaure, Ume älv, Stensjön and Näs Bruk in river Dalälven.

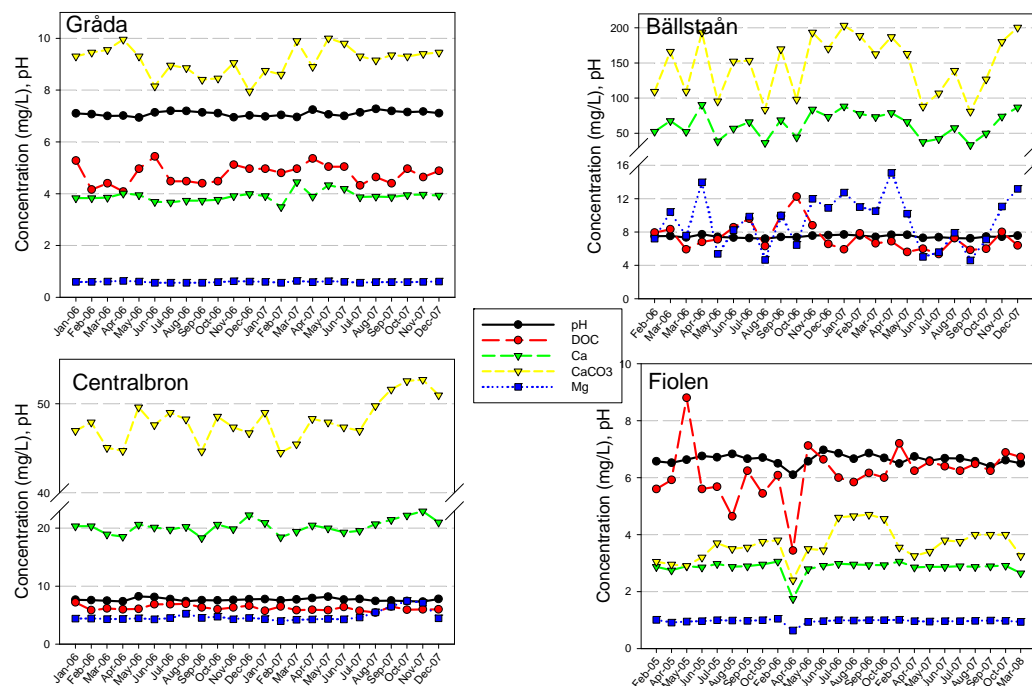


Figure 7. Seasonal variation of critical BLM parameters at the reference sites Gråda in river Dalälven, Bällstaån and Centralbron in lake Mälaren and lake Fiolen.

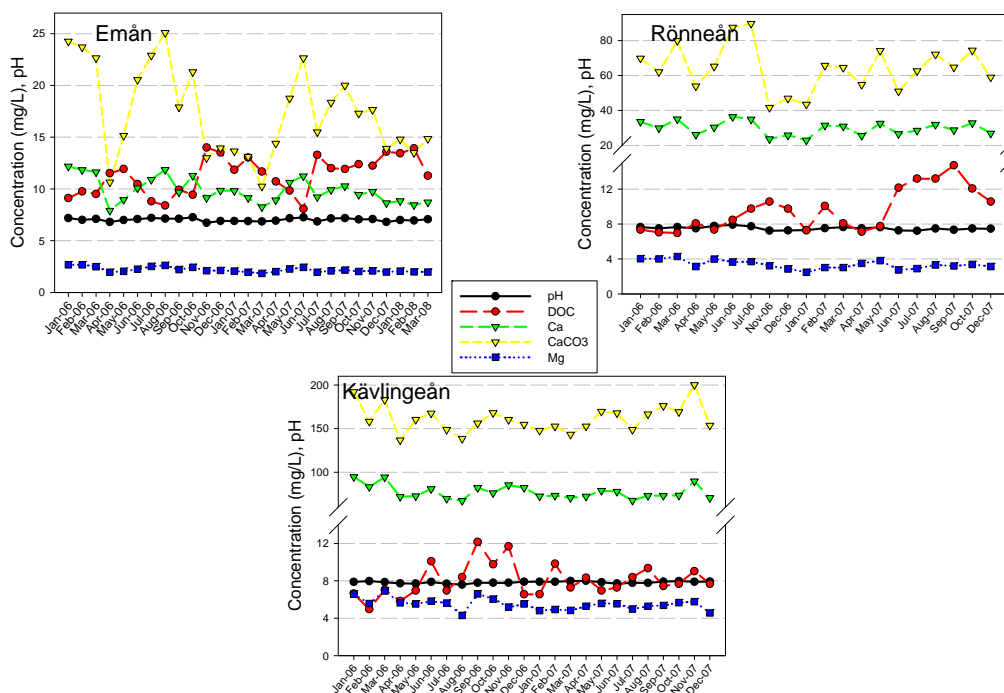


Figure 8. Seasonal variation of critical BLM parameters at the reference sites Emån, Rönneån and Kävlingeån.

As evident from the figures there seems to be a fairly clear seasonality for Ca and CaCO₃ at the northernmost site Abiskojaure with higher levels in the winter time. On the whole, however, the variation in the parameters seems to be more or less random, nevertheless pronounced, emphasizing the importance of covering the whole year in the monitoring programs, when measuring water chemistry parameters.

4.2 BLM application

4.2.1 Application of the user friendly copper-BLM

Figure 9 shows the distribution of ratios between the measured copper concentration and the predicted no-effect concentration for the eleven study sites when using the BLM-calculated site specific PNEC-values (PNEC_{BLM}) and when using the proposed limit value of 4 µg/L (PNEC_{rec}) (Naturvårdsverket, 2008). Consistent with the conclusions from the copper Risk Assessment Report, the MEC total is compared to the PNEC_{BLM}, obtained from the Hydroqual software version 2007 without applying an additional assessment factor. A ratio above 1 implies that a risk cannot be excluded. The boxes include all calculated ratios for each site, thus between 14 and 27 observations are included in each box. The plots also show the overall distribution of the ratios; whether the median MEC_{total}/PNEC ratio is >1 or whether a single value from one sampling occasion exceeds 1. It should be stressed, that the BLM-predicted PNEC-values, as well as the EPA recommended PNEC_{rec} refer to the dissolved copper concentration, whereas the measured monitoring data refer to “near total concentrations”. Thus, there is an inherent over-protectiveness in this approach, as the true dissolved concentrations should be lower than reported “near total

concentrations” (see also Appendix 1). Bearing this in mind, Figure 9 shows that three sites have some observations where the $MEC_{total}/PNEC$ ratio is > 1 , when using the recommended PNEC-value (Bällstaån, Centralbron and Emån). If the $PNEC_{BLM}$ -values are used, Abiskojaure and Bällstaån have some observations where the ratio is > 1 . However, the median $MEC_{total}/PNEC$ ratio only exceeds 1 at one site, in Bällstaån, and only if using the $PNEC_{rec}$ instead of $PNEC_{BLM}$. It is worth mentioning, that taking local bioavailability into account, by using BLM, can also result in higher risk ratios, than if adopting a single, “worst case”-PNEC throughout the country. This is exemplified in Abiskojaure (Figure 9) and in 10. The latter shows ratios estimated with the single recommended $PNEC_{rec}$ plotted against BLM-predicted ratios.

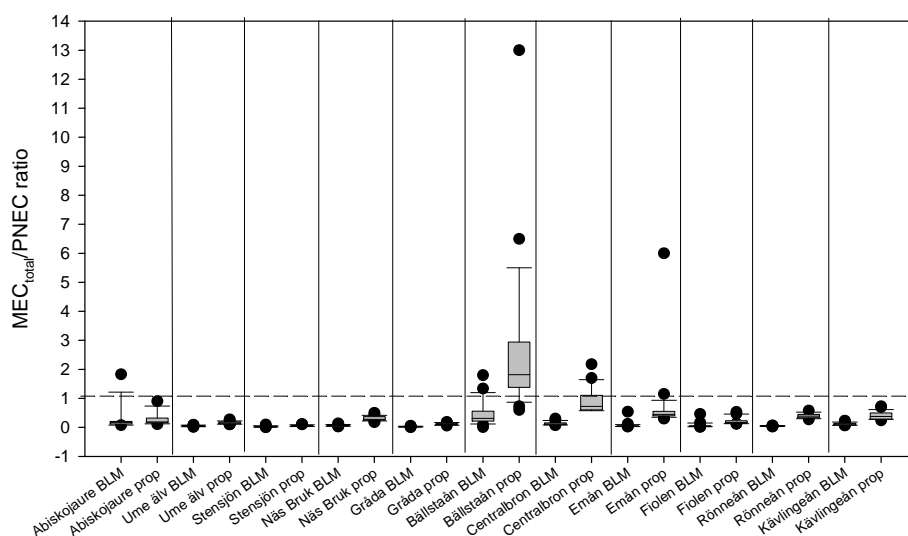


Figure 9. Ratio of MEC_{total} and PNEC for copper at the eleven reference sites as predicted by BLM and derived by using the proposed (prop) PNEC of $4 \mu\text{g/L}$.

It shows that generally, using a single PNEC value (of $4 \mu\text{g/L}$) results in overprotection of the water body, compared to using BLM-derived data, but also that for some observations (data points below the diagonal) the BLM predicts risk ratios which are higher than predicted by the single-value method. Therefore, taking local water chemistry conditions into account does not necessarily lower the predicted risk ratios, even if this is often the case in Sweden, due to the special characteristics of Swedish water chemistry as compared to the worst-case defined for Europe. The BLM-method may, however, also result in risk ratios higher than those predicted by the $PNEC_{rec}$ single-value method.

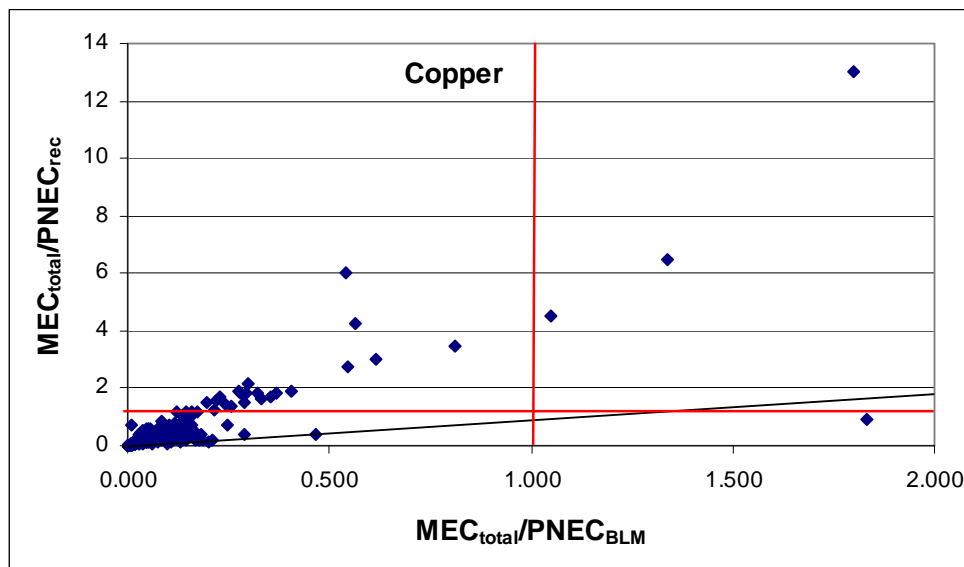


Figure 10. $MEC_{total}/PNEC_{rec}$ ratios plotted against $MEC_{total}/PNEC_{BLM}$ to highlight the differences between using site-specific water chemistry data and using one single value. The red lines show the risk ratio of 1, depending on the method used, and the diagonal represents the border where both methods estimate equal ratios. Thus, data points in the lower left square are estimated to have no risk regardless of method, whereas data points in the upper right square are predicted to exceed the risk ratios using both methods. The lower right square indicates that a risk is predicted only by BLM and the upper left that only the single PNEC-method indicates a risk.

4.2.2 Application of the Zn-BLM tool

The results from the application of the Zn-BLM tool are shown in Table 4. The table shows the min, max and average values of BLM-predicted $CBioZn/PNEC$ ratios for all reference sites as well as the exceedance percentage for each site (where measured concentration $>$ PNEC). The HC5-50 from the RA as well as the $PNEC_{rec}$ refer to “added” values, which means that this concentration should be added to the ambient/natural background concentration in order to get the true PNEC-value. There is currently an on-going debate within the EU on how to determine the background concentrations, and no consensus has so far been reached on this issue. The Swedish EPA (Naturvårdsverket, 2008) has, however, proposed preliminary suggestions on background concentrations for different water types. In order to illustrate the impact of adding background levels to the PNEC-values on the overall risk ratios, the suggested background concentrations have also been added to the PNEC-values and ratios recalculated. In Table 4 the percentage of samples exceeding risk ratio 1 are shown both for the BLM-method and for the “Total-Zn” method.

Table 4. Results from assessment of Zn bioavailability and compliance with the generic PNEC proposed in the EU risk assessment. Sites that have been written with italic letters have partly or entirely hardness conditions outside model boundaries (see Table 3). In these cases, the soft water HC5-50 of 6.5 µg/L ($PNEC_{rec} = 3.0$ µg/L) was used for comparison, rather than the HC5-50 of 15.6 µg/L ($PNEC_{rec} = 8.0$ µg/L). These calculations have somewhat higher uncertainty, thus they are highlighted in the table. "Added" indicates that natural background concentrations of 1 µg/L for lakes and small rivers and 3 µg/L for larger rivers have been added to the PNEC-value when calculating the ratio.

Site	N	$C_{BioZn}/HC5-50$ ratio			$C_{BioZn}/HC5-50 > 1$ (%)		$C_{Zntot}/PNEC_{rec} > 1$ (%)	
		<i>Min</i>	<i>Average</i>	<i>Max</i>	<i>HC5-50</i>	<i>Added</i>	<i>PNEC_{rec}</i>	<i>Added</i>
Abiskojaure	13	0.02	0.14	0.75	0	0	15	7.7
<i>Ume älv</i>	<i>23</i>	<i>0.08</i>	<i>0.22</i>	<i>0.45</i>	<i>0</i>	<i>0</i>	<i>65</i>	<i>17</i>
<i>Stensjön</i>	<i>24</i>	<i>0.04</i>	<i>0.06</i>	<i>0.19</i>	<i>0</i>	<i>0</i>	<i>8.3</i>	<i>4.2</i>
<i>Näs</i>	<i>24</i>	<i>0.11</i>	<i>0.28</i>	<i>0.46</i>	<i>0</i>	<i>0</i>	<i>96</i>	<i>75</i>
<i>Gråda</i>	<i>24</i>	<i>0.03</i>	<i>0.07</i>	<i>0.17</i>	<i>0</i>	<i>0</i>	<i>8.3</i>	<i>0</i>
Bällstaån	24	0.05	0.37	2.14	4.2	4.2	100	96
Centralbron	21	0.01	0.05	0.19	0	0	24	14
<i>Fiolen</i>	<i>23</i>	<i>0.01</i>	<i>0.03</i>	<i>0.08</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
Emån	27	0.01	0.03	0.13	0	0	3.7	3.7
Rönneån	20	0.01	0.05	0.09	0	0	35	30
Kävlingeån	24	0.01	0.02	0.08	0	0	4.2	4.2

As evident from Table 4, using the Total-Zn method applying HC5-50 with the safety factor of 2 predicts exceedance for all sites assessed at least on some occasion, apart from one (Fiolen). The added approach reduces the number of sites with exceedance by one. In essence, this would imply that *9 or 10 out of eleven* water bodies in Sweden pose a risk for effect to aquatic organisms, considering zinc toxicity, at least for some parts of the year, and would require measures to be taken. If, bioavailability is taken into account, adopting the HC5-50 but without the assessment factor of 2, the number of sites potentially posing a risk is reduced to *1 out of eleven*. In other words; applying the Zn-BLM reduces the number of potential risk sites from 91 or 81 % to 9 %, which is a significant decrease. Applying the Zn-BLM would certainly help to focus possible remediation activities to the most relevant areas.

Figure 11 shows ratios estimated using the Total-Zn method plotted against ratios predicted using the Zn-BLM.

The figure shows that for all observations, adopting the bioavailable fraction method reduces the number of identified risk observations. This is not surprising, as the bioavailable fraction can never be higher than the total Zn-concentration. The figure also shows that using the added approach slightly lowers the risk ratios, which is obvious. Considering bioavailability clearly has the biggest impact on the outcome, whereas using the added approach does not change the outcome very much.

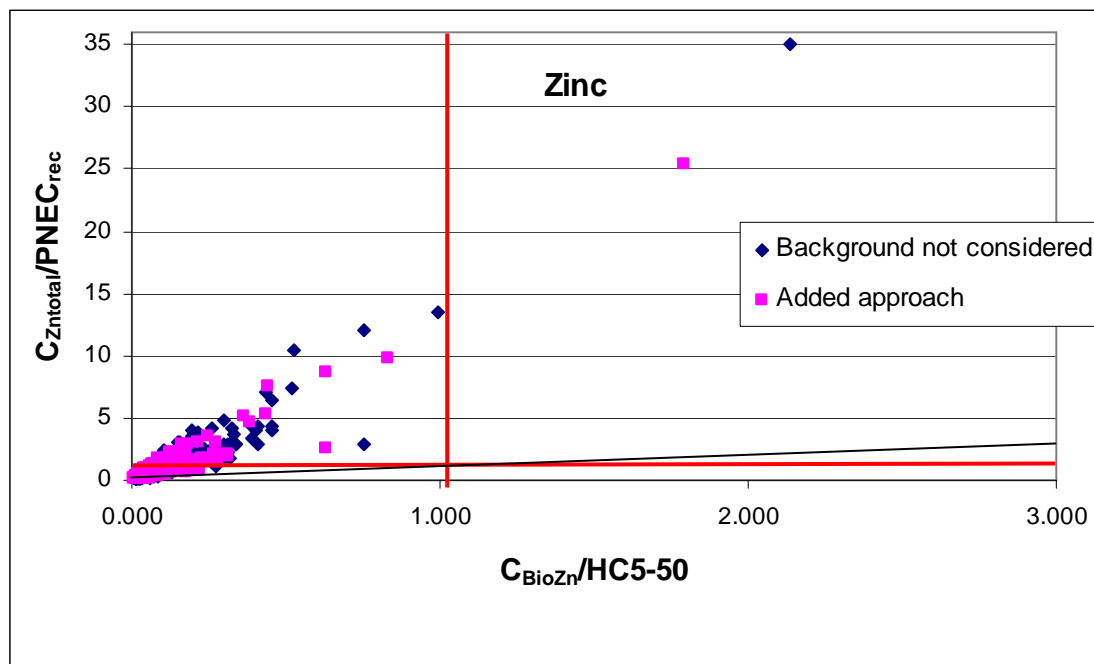


Figure 11. $C_{Zntotal}/PNEC_{rec}$ ratios plotted against $C_{BioZn}/HC5-50$ ratios to highlight the differences between accounting for bioavailability and not when calculating risk ratios. Comparison both for added and non-added approach. The red lines show the risk ratio of 1, depending on the method used, and the diagonal represents the border where both methods estimate equal ratios. Thus, data points in the lower left square are estimated to pose no risk regardless of method, whereas data points in the upper right square are predicted to exceed the risk ratios using both methods. The lower right square indicates that a risk is predicted only by the BLM-method and the upper left that only the $C_{Zntotal}$ -method indicates a risk.

4.2.3 Application of Zn-BLM using the full SSD normalization approach

The results from BLM calculations for Zn using the full normalization approach, including the min, mean and max values of HC5(50%) are described in detail in Appendix 2, but a short summary is given here.

Upon applying the full SSD normalization approach, it was noted that several water bodies have Ca-levels lower than the lower Zn BLM boundary of 5 mg/L, as mentioned previously. However, for the sites Abiskojaure, Ume Älv, Näs and Gråda, the minimum levels are still > 3 mg/L, thus results for these sites are less uncertain than for Stensjön and Fiolen.

Calculated risk ratios ($RCR_n = AF \times [Zn] / HC5(50\%)$) for four different scenarios are shown in Figure 12. Scenario 1 (RCR_1) assumes that total Zn = dissolved Zn and uses an assessment factor (AF) of 2. Scenario 2 (RCR_2) also assumes that total Zn = dissolved Zn, but applies an AF = 1. Scenario 3 (RCR_3) corrects for dissolved Zn using default values of Susp and K_D , with an AF=2, and finally scenario 4 (RCR_4) corrects for dissolved Zn and uses an AF=1. **Scenario 2** corresponds to the conditions used for calculations with the simplified Zn-BLM as described above.

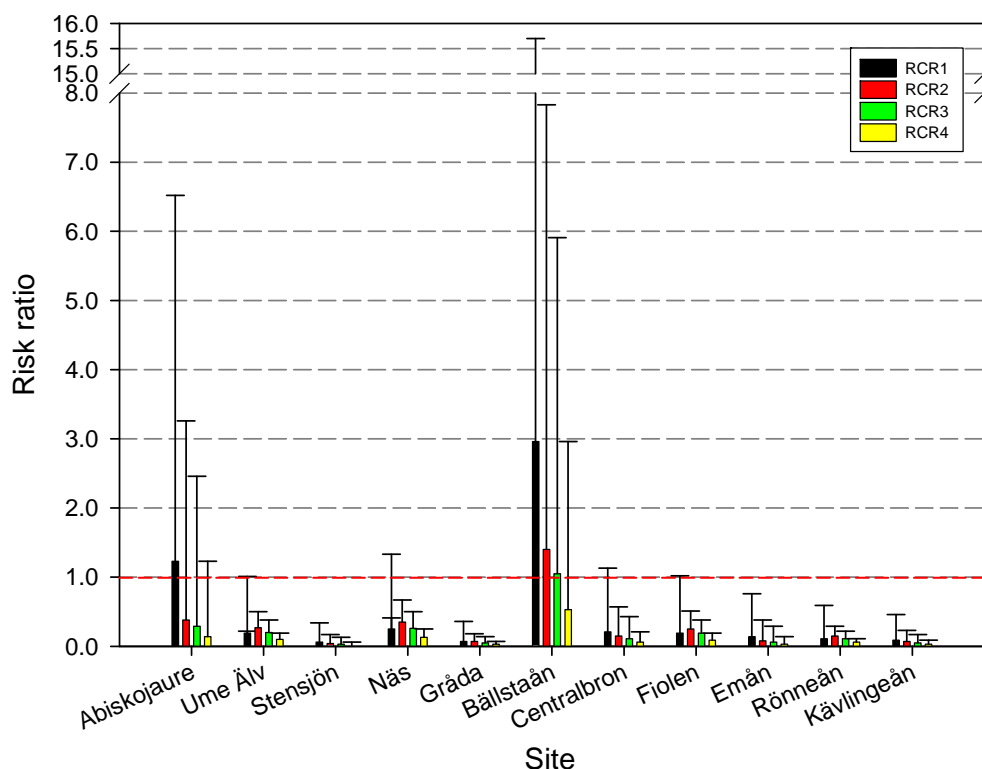


Figure 12. Summary of outcome from full SSD normalization approach regarding Zn (see Appendix 2). The filled bars show mean risk ratios for each site for four different scenarios, and the error bars shows min and max values. The red dashed line indicates a risk ratio of 1.

As evident from the figure, the mean risk ratios are generally below 1 for all scenarios, except for Abiskojaure and Bällstaån where RCR = 1 is exceeded for scenario 1 in Abiskojaure and scenarios 1-3 in Bällstaån. Overall, only 6 out of these eleven sites exceed RCR1 at all, which can be compared to 10 out of eleven when using the recommended PNEC by SEPA. The results for scenario 2 are comparable to those obtained with the simplified tool, however, it does show exceedance also in Abiskojaure, which was not captured with the simplified tool. Table 5 shows the predicted percentage of exceedance for the different sites for the four scenarios, as well as the results obtained using the simplified Zn-BLM tool and the method recommended by SEPA. The table highlights that the full BLM does capture some potential risk samples which are not captured using the simplified tool, however, it still reduces the number of potential risk sites substantially, regardless of scenario used, when compared to the method recommended by the SEPA. Using scenarios 2 to 4, RCR >1 were only found in Bällstaån and Abiskojaure.

The full SSD normalization approach also revealed a HC5(50) value of 10.3 µg/L (Abiskojaure), which is lower than the worst case reference scenario suggested in the EU RAR, clearly illustrating the need for considering site-specific PNECs when assessing risk.

Table 5. Percentage samples per site for which the RCR>1, for the four scenarios, as compared to results obtained using the simplified Zn-BLM tool as well as the recommended method by SEPA.

Site	No correction for bioavailability	BioF Approach	Full SSD normalization Approach			
	%>1 rec		%>1 BioF tool	%>1 RCR ₁	%>1 RCR ₂	%>1 RCR ₃
Abiskojaure	15	0	7.7	7.7	7.7	7.7
Ume Älv	65	0	4.3	0	0	0
Stensjön	8.3	0	0	0	0	0
Näs	96	0	8.3	0	0	0
Gråda	8.3	0	0	0	0	0
Bällstaån	100	4.2	83.3	41.7	29.2	12.5
Centralbron	24	0	4.8	0	0	0
Fiolen	0	0	4.3	0	0	0
Emån	3.7	0	0	0	0	0
Rönneån	35	0	0	0	0	0
Kävlingeån	4.2	0	0	0	0	0

4.2.4 Seasonality of risk ratios

Considering that a clear seasonality was observed for hardness parameters, in particular for Abiskojaure and possibly also for Ume Älv, it was considered interesting to see how the risk ratios for these sites vary with season. Figure 13 and Figure 14 show these variations for Zn and Cu using both calculation methods. The plots indicate that using the methods/values recommended by Swedish EPA, results in a much more variable risk ratio, whereas the BLM-method indicates a fairly consistent toxicity potential over the year. No clear seasonality is observed, indicating that the co-variation among water chemistry parameters is likely to have a larger effect on the toxicity than the impact of one single parameter. Thus, it is not possible to pinpoint a single season for which the ratio is likely to be higher or lower, and it is therefore desirable to cover all seasons when designing a monitoring program.

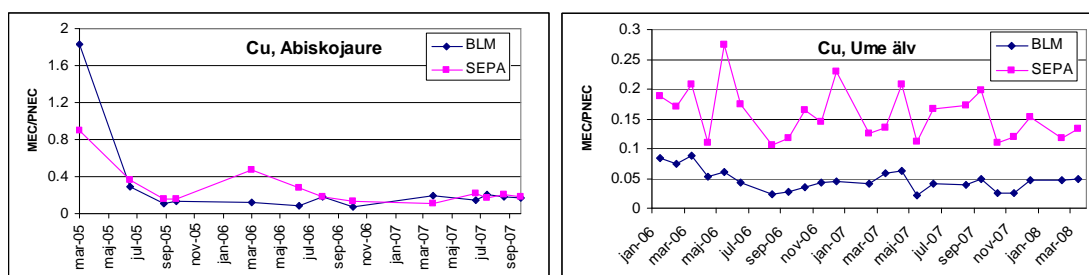


Figure 13. Seasonal variation of MEC/PNEC ratios for Copper in Abiskojaure and Ume älv.

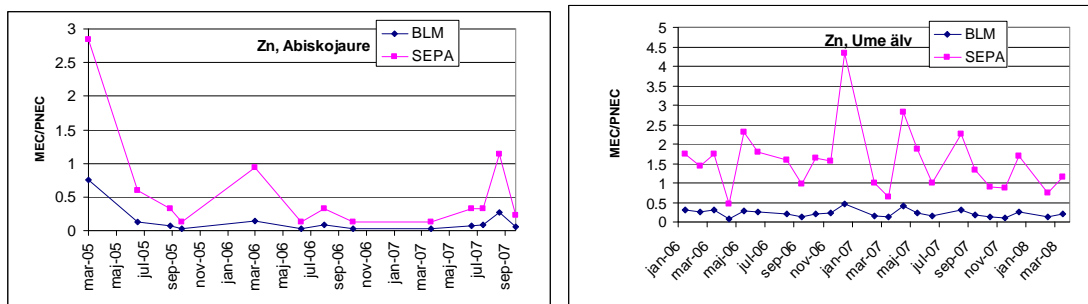


Figure 14. Seasonal variation of MEC/PNEC ratios for zinc in Abiskojaure and Ume älv

4.3 Incentives for BLM usage in Sweden, with bearing on metals such as nickel, cadmium and chromium

The applicability of the BLM methodology in Swedish freshwater systems has been exemplified with the copper and zinc BLM tools, as their development have been finalised and satisfactory validation procedures have been carried out, leading to general acceptance within the European Community. However, the metals currently on the WFD priority list are Ni, Cd, and Pb. When it concerns Ni, BLMs have been developed and validated, and a user friendly version should be released in the near future, which could directly be used for standard setting within Sweden. When it concerns cadmium, no BLM looking at chronic toxicity is available, but a hardness correction is used instead to calculate site specific EQSs. The site specific EQS has to be compared to a dissolved metal concentration which can be directly measured in the field or calculated from the total concentration using the Cd partitioning coefficient and the suspended matter concentration of the water. Concerning chromium, the international Chromium Development Association states that data are currently not available that enables the application of BLM methodology, although they acknowledge the importance of bioavailability. Thus, the precautionary principle should be applied for Cr, assuming that all dissolved metal is bioavailable.

5 Discussion

5.1 Water chemistry

Table 2 shows the general tendency of increasing DOC concentrations with decreasing latitude (i.e. higher levels in the south), as the turn-over of organic matter is increased. This general trend is influenced by the occurrence of extensive agricultural activities, e.g. in the Kävlingeån watershed, since this type of activity increases the export of TOC to the watershed (Mattson et al, 2007; Corell et al 2001). The mean TOC for all watersheds in the subarctic and Boreal climate zones (70% of the area of Sweden) are in the 3.0 to 10 mg L⁻¹ range (Algesten, 2003).

Table 2 also illustrates the general increase in water hardness, expressed as Ca, CaCO₃ or Mg, going from north to south, reflecting the increased weathering rate towards the south. The influence of regional carbonate rich soils or bedrocks in the watersheds can also be seen in e.g. Bällstaån, Rönneån and Kävlingeån.

In the following, some specific features of the reference sites are commented, and its impact on water chemistry for that particular type of water body.

- Because of the presence of carbonate rocks within the drainage basin of *Näs Bruk* and *Gråda* the hardness is higher than in the other waters of the subarctic and Boreal climate zones.
- Although the weathering rate of the bedrock is low, the presence of carbonates in the soils of *Bällstaåns* watershed increases the hardness of the water. At *Centralbron* this effect is diluted by the large volume of water in Lake Mälaren.
- The higher TOC/DOC-levels in *Emån* compared to *Fiolen* can be explained by differences in the mineralisation of TOC since the former is a river and the latter is a lake. In the case of *Fiolen* it can also be explained by the presence of areas with very little or no soil.
- Because of the occurrence of softer sedimentary bedrock in the watersheds of *Rönneån* and *Kävlingeån*, the weathering rate is higher which increases water hardness. The presence of limestone in the watershed of *Kävlingeån* makes the water here even harder.

One type of water chemistry condition which is not covered in the current assessment is found in areas located on higher ground level with only little or non-existing soil coverage. Since the Swedish bedrock mainly consists of granites, the weathering rates are low in these areas, generating water chemistry conditions of low hardness and therefore low buffering capacity. The low buffering capacity implies that only limited acidic deposition on top of that provided by the organic acids is needed in order to drive the pH down towards 5. Examples of areas where such conditions apply are parts of the Swedish west coast and along the coastline of the Bothnian Sea. The west coast of Sweden receives most of the deposition of atmospheric sulphur, which further lowers the pH of the water as a result of the low buffering capacity here. In recent years, the deposition of sulphur over Sweden has decreased, however. Between 1988 and 2000 the SO₄-S deposition at the reference site Lake Gårdsjön on the Swedish west coast decreased from 25 to 8 kg/ha/yr (Moldan et al 2004). The other sensitive area mentioned, along the Bothnian coast, contains deposits of sulphide clays. Sulphide clays are former marine sediments rich in sulphides, which have become terrestrial soils due to land uplift. Small lakes in this area of Sweden are sensitive to additional acidity because of low buffering capacity of the lake water and the acidity from the organic acids of the soils of the northern Boreal climate zones (e.g. peat). The additional acidity from the sulfide clays drives the pH further down.

The estimated total area of regions possessing this type of characteristics is small, around 1 to 2% of the area of Sweden and not considered to be representative for Swedish surface waters, which was the motive for not including them in the overall assessment. In total, around 8500 of Sweden's 92 409 lakes (9%) were estimated to have a pH<5 in 1990 (Forsberg, 1995), but area-wise the percentage is likely to be even lower. By now, this number should have decreased even more since the deposition of sulphur has decreased dramatically over Sweden.

The DOC values in this study have been estimated as 0.8×TOC, based on the risk assessment for copper. This may be a rather conservative estimate. In general for these types of environments DOC can be estimated as 0.9 -0.95×TOC (Algesten et al, 2003 c.f. Wetzel, 2001). In order to investigate the implications of such an estimate a parallel run was done using the Zn-BLM tool, and also a simplified version of the Cu-BLM (described later). It turned out that the new estimates slightly altered the risk ratios, but the overall conclusions remained the same. In general a higher

DOC-value should lead to reduced risk as it would lead to increased metal-organic matter complexation and reduced bioavailability.

5.2 BLM application

The inventory of Swedish water types show that the key parameters pH and DOC are within BLM boundaries for the all sites and sampling occasions, concerning the models validated for zinc and copper. For the nickel-BLM (which has a narrower pH validation range) two sites (Stensjön and Fiolen) fall outside model boundaries concerning pH in 72% and 12% of the assessed samples, respectively. When it comes to hardness, it seems that the Swedish surface water conditions are often too soft compared to the BLM boundaries. However, the Cu-BLM can be run outside these ranges, as can the UK modified version of the Zn-BLM tool, even though predictions are more uncertain outside these ranges (normally over-protective). Applying the full SSD normalization approach for Zinc, indicated that results for Fiolen and Stensjön are more uncertain than others, due to the low Ca-levels found here. As the user-friendly version of the Ni-BLM is not yet available, it is not possible to say whether it can be run outside model boundaries or not.

Application of the BLM methodology can lead to significant improvements in directing remediation activities, as it limits the number of identified risk sites, and thus helps focussing on relevant areas in a cost-effective manner. Application of the copper-BLM also showed that adopting a national, single PNEC-value may lead to that certain risk sites are missed, as the model predicts bioavailability from site-specific water chemistry data, which may in some cases lead to higher bioavailability than the assumed worst case EU scenario. Thus, there is a lot to gain from applying the BLM methodology in setting EQS, both in terms of producing cost-effective remediation plans, as well as obtaining a correct mapping of the ecological status of the water bodies.

5.3 Application of the BLM outside model boundaries

Considering that water hardness in Sweden is lower compared to model boundaries, it is of interest to delve a little bit deeper into this issue. What happens if the models are applied outside their ranges? In a study by Bossuyt et al. (2004), predictions performed by the acute Cu-BLM were compared to toxicity test results carried out on indigenous cladoceran species in their natural waters, of which two represented sites with chemistry conditions outside the model validation ranges (low pH, low Ca). The study showed that for these two low pH and low Ca sites, the BLM was over-protective, i.e. that toxicity was predicted to be on the average a factor of 13 higher, than what was observed. Although this concerns acute toxicity, it is still an indication that low hardness decreases the toxicity of species to copper. For zinc, Schampelaere et al. (2005) included three sites of Ca-levels < 5 in a validation exercise, showing a good predictive capability also for these waters. They also concluded that for *Daphnia magna* the model is considered applicable down to a Ca-level of 3.7 mg/L, which covers the majority of the samples assessed. UK Environment Agency (2008) cites an on-going study exploring the impact of hardness parameters and DOC levels on zinc bioavailability, which shows that DOC accounts for most of the variation in the BioF value. Furthermore, for Ca-levels below 5 mg/L, the soft water PNEC is applied, in order to reduce the risk of under protection.

In the full SSD approach, where site-specific PNECs (or HC5(50)) were derived, the results for Stensjön and Fiolen were regarded more uncertain than the others, considering the low Ca-levels.

In this assessments, HC5(50)-values were calculated for four additional sites, which were not included in the current assessment due to lack of Zn-concentrations. For these sites, HC5(50)-values were highest of all. However, these sites had extremely low Ca-levels and high pH-values, conditions for which the BLM has not been validated, and thus results for such conditions are extremely uncertain.

Deleebeeck et al. (2007a; 2008c) investigated the impact of low hardness on nickel toxicity, in order to explore if “soft water organisms” are more sensitive than organisms living in hard waters. They focused on the Scandinavian region for their assessment. One conclusion was that there are no “soft” or “hard” water species, but that the same species exist over a wide range of water chemistry conditions, even if some occur to a larger extent in hard waters. From a larger sampling set, they selected 5 soft water samples (1.26-1.98 mg Ca/L) and 4 hard water samples (11.3-16.9 mg Ca/L) from a region near Gävle where both soft and hard waters were found near each other, with low anthropogenic influence, and where background Ni levels were low. Chronic toxicity tests were performed and overall conclusions were that a) increasing hardness leads to reduced toxicity, and the concept of competition by hardness ions can be generally applied to cladoceran species, b) organisms (cladocerans and algae) from soft waters are not inherently more sensitive than organisms from hard waters and c) sensitivity of Ni to field collected cladocerans were equally sensitive to laboratory cultured *Daphnia magna* but less sensitive than *Ceriodaphnia dubia*; and d) that Ni toxicity was accurately predicted by Ni BLMs in water with hardness as low as 6 mg CaCO₃/L.

In conclusion, the studies presented above show that BLMs, at least to some extent can be applied also outside their validation ranges, without underestimation of risk. However, in order to increase and specify their accuracy in these ranges, additional validation exercises would be valuable, at least for zinc and copper. There are also some specific conditions in Sweden with low Ca-levels and high pH, where validation exercises concerning the Zn-BLM, is desirable in order to evaluate its performance in these areas.

5.4 Applicability of the BLM from a user’s perspective

The currently existing user-friendly Cu-BLM, developed in 2007, is straightforward, with a logical input format and easy-to read output. There are, however a number of issues that still leaves the model a slight bit too complicated for extensive use among non-modellers. One is that the number of input parameters is still quite large (13), although only three are said to be critical. Running the model is also fairly time-consuming (ca 30 minutes for 24 samples), and finally, the output format .txt is not easily converted to Excel. The international copper association is currently working on further simplifications addressing these issues, and a newer version has been released. The Zn-BLM in the existing format is from a user’s perspective very simple to use and gives a quick and easily interpreted output, and with the further refinement, the use of reference conditions will be removed in the near future.

6 Conclusions and recommendations

The following specific conclusions can be drawn from the current chronic BLM evaluation project:

- Applying BLM would significantly increase the accuracy in the assessment, and help focusing possible remediation activities to a more limited number of relevant areas. They give a more robust assessment procedure and less variable risk ratios, than if applying a single PNEC.
- The chemical conditions of Swedish water bodies are generally in agreement with the BLM requirements concerning the two key parameters pH and DOC, when it concerns the metals Cu, Zn, and Ni.
- Swedish monitoring programmes should focus on routine measurements of dissolved metal concentrations, and also on measurements of DOC. If the currently used method is regarded as equivalent to filtration through a 0.45 µm filter, this should be clearly stated in the national monitoring databases.
- Many Swedish waters are softer than current BLM boundaries, but it is likely that using them outside the ranges may result in overprotection of the water body, for Cu. Nevertheless, additional validation of the copper BLM at lower hardness would be useful.
- The Cu-BLM, tested in the current project is still a bit complicated, but a simplified version has been released since then.
- For Zn, the available version is user friendly, but results cannot be interpreted if the input conditions are out of the BLM boundaries, which is the case for some exceptional Swedish conditions (low Ca-levels). A full SSD normalization approach (“full BLM”) can partly solve this problem and is presented in this report, but this requires access to the full toxicity database and some additional experience. The use of the user-friendly model (BioF approach) is still recommended when the conditions met are within the boundaries. Out of the boundaries, a case-by-case evaluation is needed. Validation exercises for conditions of low hardness would be useful.
- An equivalent model for nickel is on its way, but at the time of this study, the user-friendly version had not yet been released. Thus it was not possible to apply the Ni BLM in the current project.
- Concerning Chromium, BLMs cannot be applied at present time. It is currently considered that all soluble chromium (III) is bioavailable and thus contributes to toxicity.
- Cadmium should be assessed using a hardness correction and the proposed Cd-EQSs are to be compared with dissolved monitoring data.
- Based on the above, we advocate that, when available, BLMs should be included as natural elements in EQS-setting within the Swedish implementation of the WFD.

In order to further analyze the implications of the low hardness conditions, and to determine the true need for validation exercises, it is desirable to expand the inventory performed within the

current project. However, it is important to remember, that seasonal variation should be covered in such an analysis, as levels can vary significantly over the year. The issues to address would be:

- Within the national monitoring programmes, how many of the Swedish water bodies have hardness parameter values which fall outside of model boundaries?
- What is the sampling frequency at these sites?
- How many samples per year fall outside the model boundaries?

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Appendix 1

Table A 1. Abiskojaure

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
Mar-05	0.3	7.04	0.56	0.1	7.75	1.12	1.43	0.90	8.31	1.03	18.20	3.61	22.8	1.97	11.7	1.8	1.5
Jun-05		6.94	1.36	0.1	4.04	0.62	0.80	0.63	3.46	1.13	9.50	1.46	1.8	5.05	0.85	0.29	0.27
Aug-05	11.5	6.96	1.6	0.1	4.04	0.60	0.74	0.55	4.27	0.60	9.55	0.65	<1	6.1	0.44	0.11	0.14
Sep-05	7	7.34	0.96	0.1	5.08	0.74	0.80	0.63	4.99	0.64	11.60	0.65	<1	4.97	0.50	0.13	0.064
Mar-06		7.25	3.28	0.1	7.11	1.00	0.92	0.70	6.91	0.67	15.30	1.91	7.5	15.53	2.14	0.12	0.27
Jun-06	5	7.11	2.88	0.1	5.04	0.70	0.87	0.66	4.32	1.03	12.15	1.11	<1	12.84	0.33	0.086	0.043
Jul-06	13.8	7.27	0.8	0.1	4.39	0.58	0.76	0.55	4.27	0.60	9.80	0.75	<1	4.045	0.53	0.18	0.17
Oct-06		7.22	1.52	0.1	5.31	0.72	0.78	0.70	5.23	0.60	11.50	0.54	<1	7.25	0.43	0.074	0.055
Mar-07		6.82	0.8	0.1	8.10	1.11	0.99	0.86	8.16	0.92	17.80	0.43	<1	2.16	0.47	0.20	0.060
Jun-07		7.11	1.36	0.1	4.88	0.68	0.90	0.66	4.08	1.17	10.75	0.85	<1	5.95	0.46	0.14	0.15
Jul-07	12.2	7.08	0.72	0.1	3.57	0.46	0.74	0.51	3.84	0.89	7.65	0.66	<1	3.16	0.55	0.21	0.18
Aug-07	13.5	7.29	0.88	0.1	4.34	0.58	0.74	0.59	4.27	0.64	9.40	0.81	3.4	4.56	1.76	0.18	0.57
Sep-07	6.8	7.31	0.88	0.1	5.51	0.74	0.80	0.66	5.14	0.60	12.20	0.73	1.8	4.37	0.91	0.17	0.12
Mar-08	0.2	7.07	1.84	0.1	8.34	1.18	1.13	0.86	8.02	0.96	18.60			6.95			
Average	7.8	7.1	1.4	0.1	5.54	0.77	0.89	0.68	5.38	0.82	12.4	1.1	3.5	6.1	1.62	0.27	0.26

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 2. Ume älv

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
Jan-06	0	7.1	2	0.1	4.45	0.77	1.13	0.47	2.11	1.06	11.85	0.75	5.2	8.97	2.07	0.084	0.32
Feb-06	0	7.06	2.16	0.1	4.67	0.77	1.08	0.47	2.26	1.10	12.45	0.68	4.3	9.23	1.67	0.074	0.26
Mar-06	0	6.99	2.4	0.1	4.82	0.80	1.15	0.47	2.11	1.13	12.70	0.83	5.2	9.47	1.96	0.088	0.30
Apr-06	0	6.86	2.48	0.1	4.78	0.81	1.20	0.51	2.21	1.17	12.05	0.44	1.4	8.34	0.53	0.053	0.081
May-06	6.9	6.86	4.72	0.1	3.14	0.58	1.03	0.63	2.21	0.82	7.05	1.1	6.9	17.81	1.86	0.062	0.29
Jun-06	16	7.09	3.44	0.1	4.20	0.63	1.01	0.55	2.26	0.82	9.70	0.7	5.4	15.93	1.64	0.044	0.25
Aug-06	20.9	7.38	3.12	0.1	4.88	0.68	1.22	0.70	2.30	0.96	11.90	0.42	4.8	17.89	1.40	0.023	0.22
Sep-06		7.15	3.6	0.1	4.30	0.73	1.22	0.59	2.54	1.06	11.20	0.47	2.9	17.47	0.84	0.027	0.13
Oct-06	6.6	6.98	4.56	0.1	4.18	0.69	1.08	0.55	2.64	0.92	9.85	0.66	4.9	18.91	1.31	0.035	0.20
Nov-06	0	6.94	3.44	0.1	4.34	0.75	1.10	0.51	2.40	1.06	10.55	0.58	4.7	13.29	1.49	0.044	0.23
Dec-06	0.1	6.75	6.4	0.1	3.89	0.72	1.15	0.55	2.69	0.96	7.55	0.92	13	20.32	2.95	0.045	0.45
Feb-07	0	7.02	2.88	0.1	4.71	0.73	1.03	0.51	2.35	1.06	12.05	0.5	3	11.93	1.03	0.042	0.16
Mar-07	0	7.03	2.24	0.1	5.06	0.75	1.10	0.51	2.40	1.17	12.80	0.54	5.1	9.17	1.96	0.059	0.13
Apr-07	0.3	6.91	3.6	0.1	4.24	0.73	1.06	0.59	2.30	0.96	12.45	0.83	8.5	13.35	2.64	0.062	0.41
May-07	6.4	6.94	4.8	0.1	3.28	0.55	1.36	0.51	2.50	0.74	7.60	0.45	5.6	20.1	1.46	0.022	0.22
Jun-07	15.7	7.19	3.2	0.1	4.28	0.58	0.92	0.55	2.26	0.85	10.40	0.67	3	16.18	0.92	0.041	0.14
Aug-07	18.7	7.35	3.12	0.1	4.26	0.67	1.43	0.47	2.64	1.38	11.20	0.69	6.8	17.92	2.01	0.039	0.31
Sep-07	10.3	7.17	3.28	0.1	4.26	0.68	1.06	0.51	2.26	0.89	10.75	0.79	4	16.25	1.22	0.049	0.19
Oct-07	4.6	7.1	3.68	0.1	4.34	0.72	1.13	0.55	2.35	1.13	10.30	0.44	2.7	17.13	0.79	0.026	0.12
Nov-07	0.5	7.32	3.36	0.1	4.39	0.70	1.59	0.47	2.45	1.24	11.85	0.48	2.6	18.9	0.74	0.025	0.11
Dec-07	0.5	6.95	3.36	0.1	4.51	0.73	1.10	0.47	2.35	1.24	11.20	0.61	5.1	13.03	1.63	0.047	0.25
Feb-08	0	7.03	2.4	0.1	4.75	0.77	1.08	0.47	2.26	1.13	12.25	0.47	2.2	9.95	0.82	0.047	0.13
Mar-08	0	7.01	2.64	0.1	4.92	0.78	1.15	0.51	2.35	1.21	12.65	0.53	3.5	10.68	1.25	0.050	0.19
Average	4.9	7.05	3.3	0.1	4.4	0.71	1.15	0.53	2.36	1.0	11.0	0.63	4.8	14.4	1.5	0.047	0.22

^{a)} Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 3. Stensjön

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
Feb-05	0.1	6.3	5.44	0.1	1.48	0.43	1.59	0.31	2.06	0.82	3.4	0.46	1.5	9.88	0.4	0.05	0.059
Apr-05	1.6	6.1	2.72	0.1	0.84	0.24	0.92	0.16	1.34	0.57	1.6	0.29	1.5	2.95	0.5	0.10	0.075
May-05	9.8	6.4	4.88	0.1	1.27	0.36	1.33	0.27	1.63	0.71	2.5		4.5	10.47	1.2	0.01	0.19
Jun-05	16.6	6.4	4.56	0.1	1.25	0.36	1.24	0.23	1.63	0.85	2.2		1.1	10.11	0.3	0.01	0.047
Jul-05	24.7	6.7	5.28	0.1	1.23	0.36	1.31	0.27	1.68	0.78	2.4		<1	20.11	0.3	0.00	0.040
Aug-05	17.2	6.4	5.36	0.1	1.27	0.38	1.31	0.27	1.63	0.71	2.2	0.18	<1	10.51	0.3	0.02	0.039
Sep-05	11.8	6.5	5.6	0.1	1.27	0.38	1.31	0.27	1.63	0.71	2.5	0.18	<1	13.14	0.3	0.01	0.038
Oct-05	10.1	6.4	5.36	0.1	1.23	0.38	1.36	0.27	1.58	0.67	2.7	0.16	<1	12.34	0.3	0.01	0.039
Feb-06	0.7	6.3	6.24	0.1	1.27	0.40	1.47	0.31	1.82	0.78	2.6	0.3	1.9	10.36	0.4	0.03	0.069
Apr-06	1.2	6.3	5.12	0.1	1.21	0.36	1.38	0.27	1.78	0.82	1.9	0.42	3.5	8.96	0.9	0.05	0.14
May-06	9.1	6.1	6.32	0.1	1.21	0.35	1.22	0.27	1.54	0.67	2.2	0.19	1.1	7.07	0.3	0.03	0.039
Jun-06	19.7	6.4	5.12	0.1	1.25	0.35	1.22	0.31	1.49	0.67	2.2	0.17	1.2	11.55	0.3	0.01	0.048
Jul-06	18.7	6.5	5.6	0.1	1.31	0.36	1.26	0.27	1.58	0.71	2.5	0.19	<1	14.4	0.3	0.01	0.039
Aug-06	20.6	6.6	6.08	0.1	1.31	0.36	1.38	0.31	1.58	0.74	2.7	0.15	<1	18.51	0.2	0.01	0.037
Sep-06	14.8	6.5	6.24	0.1	1.41	0.39	1.24	0.31	1.54	0.74	2.7	0.27	<1	15.67	0.2	0.02	0.036
Oct-06	10.2	6.4	6	0.1	1.48	0.40	1.29	0.31	1.54	0.74	2.8	0.14	<1	13.01	0.2	0.01	0.037
Feb-07	0.6	6.1	7.52	0.1	1.43	0.39	1.26	0.31	1.68	0.85	2.0	0.29	1.5	8.28	0.3	0.04	0.048
Apr-07	3.1	6.0	4.72	0.1	0.92	0.26	0.87	0.20	1.10	0.53	1.6	0.3	1.9	4.99	0.5	0.06	0.077
May-07	10.5	6.5	6.08	0.1	1.29	0.35	1.22	0.27	1.49	0.71	2.0	0.16	<1	14.52	0.2	0.01	0.037
Jun-07	17.2	6.3	5.28	0.1	1.29	0.35	1.20	0.27	1.58	0.78	2.3	0.15	<1	8.44	0.3	0.02	0.040
Jul-07	19.2	6.5	5.28	0.1	1.37	0.36	1.24	0.27	1.58	0.78	2.5	0.16	<1	13.62	0.3	0.01	0.040
Aug-07	17.7	6.7	5.28	0.1	1.37	0.39	1.31	0.31	1.58	0.82	2.9	0.16	<1	19.9	0.3	0.01	0.040
Sep-07	10.2	6.5	4.72	0.1	1.46	0.40	1.33	0.31	1.58	0.71	3.1	0.16	<1	10.56	0.3	0.02	0.042
Oct-07	5.9	6.7	5.12	0.1	1.46	0.39	1.31	0.31	1.63	0.85	3.1	0.16	<1	16.75	0.3	0.01	0.041
Feb-08	0.5	6.5	5.28		1.50	0.44	1.43	0.31	1.78	0.85	3.6			13.43			0.059
Average	11	6.4	5.4	0.1	1.30	0.37	1.28	0.28	1.60	0.74	2.5	0.21	1.4	12	0.36	0.02	0.06

^{a)} Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration", for Zn, detection limits were used in the calculations ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 4. Dalälven Näs Bruk

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
jan-06		7.0	5.9	0.1	4.7	0.8	2.3	0.5	3.5	1.7	10.5	1.0	8.8	25.7	2.0	0.038	0.30
feb-06	0.1	7.0	5.0	0.1	4.6	0.7	2.3	0.5	3.4	1.7	10.5	1.1	8.6	20.2	2.2	0.054	0.34
mar-06	0.1	6.9	5.0	0.1	4.8	0.8	2.4	0.5	3.6	1.7	11.1	1.1	9.9	18.4	2.6	0.060	0.39
apr-06	1.2	6.9	5.4	0.1	4.9	0.8	3.0	0.6	4.5	2.4	12.0	1.1	12.0	19.9	3.0	0.055	0.46
maj-06	10.6	6.7	7.4	0.1	3.4	0.6	1.6	0.5	2.5	1.3	6.0	1.0	8.4	23.7	1.7	0.042	0.27
jun-06	16.9	7.0	6.4	0.1	4.0	0.6	2.1	0.5	2.7	1.8	8.6	0.9	6.5	28.2	1.4	0.030	0.21
jul-06	21.0	7.0	5.9	0.1	4.5	0.7	2.6	0.6	3.5	1.9	11.1	1.0	8.3	26.7	1.8	0.037	0.28
aug-06	21.2	7.1	4.7	0.1	4.9	0.7	2.6	0.6	3.5	1.9	11.6	1.1	8.7	21.4	2.2	0.051	0.34
sep-06	15.6	7.0	7.0	0.1	4.1	0.7	2.1	0.5	2.8	1.7	9.0	1.2	7.7	30.3	1.5	0.040	0.24
okt-06	13.0	7.1	5.3	0.1	4.7	0.7	2.5	0.6	3.6	1.7	10.9	1.1	8.6	24.0	2.0	0.046	0.31
nov-06	2.7	6.9	7.6	0.1	4.7	0.9	2.3	0.6	3.9	2.2	9.7	1.7	13.0	28.2	2.5	0.060	0.39
dec-06	4.2	6.9	7.5	0.1	4.2	0.7	1.8	0.5	2.9	1.7	7.6	1.5	11.0	28.3	2.2	0.053	0.33
jan-07	2.0	6.9	5.9	0.1	4.3	0.7	2.0	0.5	2.9	1.8	9.4	1.2	9.2	23.4	2.1	0.051	0.32
feb-07	0.2	6.9	6.4	0.1	4.5	0.7	2.0	0.5	3.2	1.8	9.4	1.5	12.0	25.0	2.6	0.060	0.40
mar-07	2.2	6.9	6.2	0.1	5.7	0.9	2.6	0.8	4.8	2.7	10.8	2.0	17.0	21.6	3.8	0.093	0.24
apr-07	3.8	6.8	7.3	0.1	4.6	0.7	2.1	0.6	3.3	2.0	9.4	1.6	13.0	25.0	2.7	0.064	0.41
maj-07	11.5	7.1	6.1	0.1	4.3	0.6	2.3	0.6	3.1	2.0	9.2	0.9	8.3	28.2	1.8	0.032	0.27
jun-07	18.4	7.1	5.4	0.1	4.7	0.7	2.9	0.6	4.2	2.4	10.3	1.0	9.2	25.1	2.1	0.040	0.33
jul-07	19.2	7.2	4.7	0.1	5.2	0.7	3.1	0.7	4.4	2.3	12.1	1.4	11.0	23.2	2.7	0.060	0.17
aug-07	18.9	7.2	4.6	0.1	5.5	0.8	3.6	0.7	5.0	2.6	13.6	1.2	8.9	22.5	2.2	0.053	0.14
sep-07	14.0	7.1	5.2	0.1	4.9	0.7	2.7	0.5	3.6	1.7	11.6	0.7	5.8	24.7	1.4	0.029	0.21
okt-07	8.5	7.2	4.9	0.1	5.1	0.7	3.3	0.6	4.8	2.4	12.4	1.0	7.2	25.4	1.7	0.037	0.11
nov-07	3.1	7.0	5.8	0.1	5.1	0.7	3.1	0.6	4.5	2.5	11.8	1.0	8.1	23.1	1.9	0.042	0.12
dec-07	2.0	7.1	6.1	0.1	5.1	0.8	2.8	0.7	4.3	2.4	11.1	1.5	11.0	27.9	2.3	0.054	0.15
Average	9.1	7.0	5.9	0.1	4.7	0.7	2.5	0.6	3.7	2.0	10.4	1.2	9.7	24.6	2.2	0.050	0.4

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L, For soft waters (Ca <5 mg/L); 6.5 µg/L. Ambient background concentrations not considered in the calculation

Table A 5. Dalälven Gråda

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
jan-06		7.1	5.28	0.1	3.83	0.60	1.43	0.43	1.68	0.96	9.30	0.25	1.1	26.3	0.3	0.010	0.039
feb-06	0.6	7.1	4.16	0.1	3.83	0.60	1.43	0.39	1.97	1.10	9.45	0.46	1.2	19.7	0.3	0.023	0.051
mar-06	0.0	7.0	4.40	0.1	3.85	0.61	1.40	0.39	1.63	0.92	9.55	0.29	0.8	19.4	0.2	0.015	0.033
apr-06	1.9	7.0	4.08	0.1	4.01	0.63	1.47	0.39	1.68	1.03	9.95	0.29	1	17.9	0.3	0.016	0.044
maj-06	9.0	6.9	4.96	0.1	3.95	0.61	1.45	0.43	1.87	1.10	9.30	0.71	4.2	20.3	1.1	0.035	0.165
jun-06	14.2	7.1	5.44	0.1	3.69	0.56	1.40	0.39	1.63	0.99	8.15	0.61	2.4	28.5	0.5	0.021	0.082
jul-06	18.6	7.2	4.48	0.1	3.67	0.56	1.45	0.43	1.63	0.99	8.95	0.44	2.5	24.5	0.6	0.018	0.096
aug-06	19.9	7.2	4.48	0.1	3.73	0.56	1.47	0.43	1.63	1.03	8.85	0.41	1.5	24.3	0.4	0.017	0.058
sep-06	15.1	7.1	4.40	0.1	3.73	0.56	1.45	0.39	1.63	1.03	8.40	0.4	1.5	22.7	0.4	0.018	0.060
okt-06	12.6	7.1	4.48	0.1	3.77	0.58	1.38	0.43	1.58	0.92	8.45	0.5	2.6	22.4	0.7	0.022	0.103
nov-06		7.0	5.12	0.1	3.91	0.62	1.45	0.43	1.68	1.21	9.05	0.61	2.4	21.3	0.6	0.029	0.092
dec-06	5.1	7.0	4.96	0.1	3.99	0.61	1.38	0.43	1.63	1.03	7.95	0.5	1.7	22.5	0.4	0.022	0.065
jan-07	3.3	7.0	4.96	0.1	3.91	0.60	1.36	0.43	1.58	1.03	8.75	0.43	1.7	21.5	0.4	0.020	0.066
feb-07	0.9	7.0	4.80	0.1	3.49	0.56	1.33	0.43	1.68	1.21	8.60	0.37	1.4	22.6	0.4	0.016	0.054
mar-07	2.7	7.0	4.96	0.1	4.45	0.63	1.47	0.47	1.87	1.21	9.90	0.46	1.4	20.5	0.4	0.022	0.055
apr-07	2.8	7.2	5.36	0.1	3.89	0.58	1.29	0.39	1.63	0.99	8.90	0.41	1.6	30.4	0.3	0.014	0.053
maj-07	10.0	7.1	5.04	0.1	4.33	0.62	1.43	0.43	1.82	1.24	10.00	0.59	3.3	23.3	0.8	0.025	0.123
jun-07	19.2	7.0	5.04	0.1	4.19	0.60	1.43	0.43	1.78	1.38	9.80	0.71	3	21.9	0.7	0.032	0.115
jul-07	17.4	7.1	4.32	0.1	3.87	0.56	1.31	0.43	1.58	1.10	9.30	0.49	1.6	22.0	0.4	0.022	0.064
aug-07	19.8	7.3	4.64	0.1	3.89	0.58	1.36	0.43	1.58	1.13	9.15	0.34	1.3	26.7	0.3	0.013	0.047
sep-07		7.2	4.40	0.1	3.87	0.58	1.36	0.39	1.63	0.89	9.35	0.27	1.1	23.5	0.3	0.011	0.043
okt-07	7.7	7.2	4.96	0.1	3.95	0.58	1.38	0.43	1.68	1.17	9.30	0.27	1.2	25.6	0.3	0.011	0.044
nov-07	3.9	7.2	4.64	0.1	3.97	0.60	1.38	0.43	1.63	1.21	9.40	0.39	1.3	24.3	0.3	0.016	0.049
dec-07	3.3	7.1	4.88	0.1	3.93	0.61	1.43	0.43	1.82	1.24	9.45	0.35	2.3	24.2	0.6	0.014	0.086
Average	9.0	7.1	4.76	0.1	3.90	0.59	1.40	0.42	1.69	1.09	9.14	0.4	1.8	23.2	0.5	0.019	0.1

^{a)} Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC_{soft water} Zn= 6.5 µg/L. Ambient background concentrations not considered in the calculation

Table A 6. Bällstaån

Date	T (°C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
feb-06	1.0	7.5	7.9	0.1	52.4	7.2	253.3	6.0	40.3	449.6	109.3	17	83	30.3	8.2	0.56	0.92
mar-06	0.1	7.5	8.3	0.1	67.6	10.4	83.7	5.8	53.6	160.3	166.3	6.4	32	29.1	3.1	0.22	0.34
mar-06	0.6	7.3	5.9	0.1	52.1	7.6	131.3	5.7	34.6	251.3	109.4	18	96	17.1	11.8	1.05	1.32
apr-06	8.5	7.7	6.8	0.1	90.6	14.0	57.5	6.5	62.5	98.0	193.8	7.3	26	26.0	3.2	0.28	0.36
maj-06	14.0	7.4	7.1	0.1	38.5	5.4	31.5	4.0	27.4	47.0	95.5	52	280	28.9	33.3	1.80	3.75
jun-06	20.5	7.3	8.6	0.1	56.7	8.2	37.3	6.0	41.3	52.9	152.2	4	14	26.0	1.4	0.15	0.16
jul-06	21.0	7.3	9.6	0.1	65.9	9.9	49.5	8.8	43.8	70.0	153.3	2.4	14	26.8	1.3	0.09	0.14
aug-06	18.0	7.2	6.3	0.1	36.3	4.7	26.3	3.9	28.7	34.4	83.6	26	108	19.4	15.5	1.34	1.74
sep-06	15.2	7.4	9.9	0.1	68.6	10.0	46.9	6.9	50.5	70.3	169.8	4.6	19	31.9	1.6	0.14	0.18
okt-06	11.5	7.4	12.2	0.1	44.1	6.5	15.3	4.3	36.6	20.4	98.1	2.9	9.8	310.6	0.8	0.01	0.09
nov-06	5.1	7.6	8.8	0.1	83.8	12.0	40.6	5.9	67.5	55.3	193.5	5.9	25	30.2	2.4	0.20	0.27
dec-06	4.9	7.6	6.6	0.1	73.4	10.9	43.7	5.4	52.5	60.1	170.6	7.4	39	23.1	4.6	0.32	0.52
jan-07	0.1	7.7	5.9	0.1	88.3	12.7	45.7	6.1	65.8	68.9	203.3	5.4	20	21.1	2.7	0.26	0.30
feb-07	0.5	7.6	7.8	0.1	77.6	11.0	120.0	6.4	59.3	213.8	188.8	7.7	30	27.8	3.1	0.28	0.35
mar-07	5.5	7.4	6.6	0.1	73.2	10.5	48.0	5.4	52.6	78.8	162.7	7.6	31	18.8	3.3	0.40	0.37
apr-07	5.5	7.7	6.9	0.1	78.8	15.1	55.1	6.5	63.4	100.5	187.1	7.3	23	24.7	2.7	0.30	0.30
maj-07	10.0	7.7	5.6	0.1	66.0	10.2	42.8	5.6	56.1	68.4	163.1	6	21	20.7	2.8	0.29	0.31
jun-07	18.0	7.3	6.0	0.1	37.6	5.0	25.7	4.0	28.7	35.7	88.1	12	51	19.5	7.1	0.62	0.80
jul-07	18.5	7.4	5.4	0.1	42.0	5.6	25.8	4.1	27.1	37.5	106.8	14	59	17.3	8.1	0.81	0.91
aug-07	16.8	7.3	7.3	0.1	57.6	7.9	31.8	5.7	38.2	46.9	139.1	6.5	28	19.6	3.1	0.33	0.35
sep-07	11.0	7.2	5.8	0.1	33.2	4.6	24.5	4.1	26.9	29.7	80.9	6.7	34	18.9	5.1	0.36	0.57
okt-07	9.5	7.4	6.0	0.1	49.6	7.1	33.5	5.5	40.9	48.8	126.9	7.2	34	19.6	4.0	0.37	0.45
nov-07	3.8	7.4	8.0	0.1	73.8	11.1	48.0	6.2	63.9	63.1	180.2	5	24	23.3	2.3	0.21	0.26
dec-07	2.0	7.6	6.4	0.1	86.9	13.2	45.9	6.3	79.4	68.1	200.6	11	56	20.2	6.7	0.54	0.76
Average	9.2	7.5	7.3	0.1	62.3	9.2	56.8	5.6	47.6	92.9	146.8	10.4	48.2	35.5	5.8	0.45	0.6

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 7. Centralbron, Mälaren

Date	T (°C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
jan-06	0.7	7.65	7.2	0.1	20.3	4.4	12.2	2.7	24.3	13.5	47.0	2.4	1.7	31.6	0.2	0.076	0.02
feb-06	1	7.58	5.8	0.1	20.3	4.4	12.6	2.7	24.7	16.9	47.9			33.3			
mar-06	0.8	7.49	6.2	0.1	18.9	4.3	11.8	2.6	23.6	14.0	45.1	2.4	1.5	26.8	0.2	0.090	0.03
apr-06	3.4	7.37	6.0	0.1	18.5	4.3	11.7	2.6	23.8	15.1	44.7	2.3	1.4	25.0	0.2	0.092	0.03
maj-06	9	8.21	6.1	0.1	20.6	4.4	11.8	2.6	24.9	15.8	49.6			35.3			
jun-06	15.5	8.11	6.9	0.1	20.1	4.3	11.4	2.6	23.8	14.8	47.6	8.7	15	29.1	1.5	0.299	0.17
jul-06	21	7.76	6.9	0.1	19.8	4.5	13.0	2.7	23.5	17.4	49.0	4.1	7.3	30.2	0.9	0.136	0.10
aug-06	18	7.4	7.0	0.1	20.2	5.2	21.2	3.0	25.4	36.1	48.3	4.8	9.5	30.1	1.3	0.159	0.15
sep-06	16	7.58	6.3	0.1	18.3	4.5	15.1	2.7	22.9	20.3	44.7	2.9	3.5	28.2	0.5	0.103	0.06
okt-06	14	7.53	6.0	0.1	20.6	4.7	15.3	2.8	24.3	20.8	48.6	2.9	5	25.3	0.7	0.115	0.08
nov-06	6.2	7.62	6.3	0.1	19.8	4.3	11.3	2.6	23.1	14.6	47.4	2.3	1.5	26.8	0.2	0.086	0.02
dec-06	4.8	7.74	6.6	0.1	22.2	4.5	11.5	2.7	24.1	13.3	46.7	2.3	1.4	27.8	0.2	0.083	0.02
jan-07	3.6	7.77	5.8	0.1	20.9	4.3	11.3	2.7	22.9	13.1	49.0	2.4	1.7	23.9	0.2	0.101	0.03
feb-07	1.1	7.53	6.5	0.1	18.4	4.0	10.6	2.7	22.1	14.6	44.5	2.4	2.6	28.3	0.4	0.085	0.04
mar-07	2.2	7.71	5.8	0.1	19.4	4.2	10.9	2.7	22.3	14.5	45.5	2.5	1.8	25.2	0.3	0.099	0.03
apr-07	7.6	7.94	5.9	0.1	20.5	4.3	11.3	2.7	23.3	15.9	48.3	2.7	1.8	24.0	0.2	0.112	0.02
maj-07	10.5	8.17	5.8	0.1	20.0	4.3	12.0	2.7	23.0	13.9	47.9	3.5	3	23.3	0.4	0.150	0.04
jun-07	18.5	7.68	6.4	0.1	19.3	4.3	12.8	2.7	21.7	15.7	47.4	3.2	22	27.8	2.9	0.115	0.33
jul-07	19.6	7.78	5.8	0.1	19.5	4.6	14.0	2.8	21.8	17.1	47.0	3.4	3.9	25.5	0.5	0.133	0.06
aug-07	20.5	7.44	5.4	0.1	20.7	5.5	22.6	3.2	24.0	34.7	49.8	5.7	8.4	23.4	1.3	0.243	0.15
sep-07	16.1	7.5	6.5	0.1	21.4	6.5	31.1	3.6	27.0	49.7	51.6	6.8	13	29.9	1.8	0.227	0.20
okt-07	10.5	7.43	5.9	0.1	22.2	7.4	38.8	3.9	23.2	56.5	52.6			37.6			
nov-07	6.5	7.34	6.0	0.1	22.9	7.1	34.7	3.7	27.9	54.1	52.7	4.7	6	27.2	0.9	0.173	0.10
dec-07	4.1	7.78	6.0	0.1	21.0	4.4	12.3	2.7	23.8	15.4	51.0	3.5	3.8	24.8	0.5	0.141	0.06
Average	9.6	7.7	6.2	0.1	20.2	4.8	15.9	2.8	23.8	22.0	48.1	3.6	5.5	23.9	0.7	0.12	0.1

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 8. Fiolen

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
Feb-05	1.6	6.57	5.6	0.1	2.9	1.01	4.00	1.68	6.05	5.8	3.05	1.75	8.8	13.87	2.2	0.13	0.34
Apr-05	8.1	6.52	5.92	0.1	2.7	0.91	3.66	1.56	5.71	6.1	2.95	0.92	8.8	13.52	2.1	0.07	0.33
May-05	12.3	6.63	8.8	0.1	2.9	0.95	3.77	1.56	5.62	5.7	2.9	0.52	7	25.14	1.3	0.02	0.20
Jun-05	17.3	6.76	5.6	0.1	2.8	0.96	3.68	1.52	5.67	6.1	3.2	0.69	8	18.88	2.0	0.04	0.30
Jul-05	20.5	6.71	5.68	0.1	3.0	1.00	3.79	1.52	5.67	6.0	3.7	0.85	7.6	17.67	1.9	0.05	0.29
Aug-05	19.4	6.83	4.64	0.1	2.9	0.98	3.77	1.52	5.57	5.5	3.5	0.65	4.1	17.16	1.1	0.04	0.17
Sep-05	16.5	6.66	6.24	0.1	2.9	0.97	3.77	1.52	5.57	5.7	3.55	0.67	4.1	18.11	1.0	0.04	0.15
Oct-05	12.7	6.7	5.44	0.1	3.0	1.00	3.89	1.56	5.62	5.7	3.75	0.62	4.3	16.64	1.1	0.04	0.17
Feb-06	0.8	6.5	6.08	0.1	3.1	1.04	4.05	1.76	5.91	5.8	3.8	2.14	7.4	13.28	1.8	0.16	0.27
Apr-06	3.2	6.1	3.44	0.1	1.7	0.63	2.60	1.21	3.60	4.0	2.4	1.56	8.2	3.36	2.5	0.46	0.38
May-06	12.9	6.57	7.12	0.1	2.8	0.94	3.56	1.64	5.43	5.7	3.5	0.57	6	17.98	1.3	0.03	0.20
Jun-06	22.1	6.97	6.64	0.1	2.9	0.96	3.63	1.68	5.38	5.7	3.45	1.17	6.9	30.2	1.4	0.04	0.22
Jul-06	21	6.85	6.0	0.1	3.0	1.00	3.75	1.72	5.43	5.6	4.6	0.62	4.6	22.96	1.1	0.03	0.16
Aug-06	19.1	6.66	5.84	0.1	3.0	0.98	3.84	1.68	5.52	5.4	4.65	0.53	3	16.79	0.7	0.03	0.11
Sep-06	16.7	6.86	6.16	0.1	2.9	1.00	3.54	1.72	5.47	5.7	4.7	0.49	2.4	23.8	0.5	0.02	0.08
Oct-06	12.3	6.69	6.0	0.1	2.9	1.00	3.66	1.68	5.47	5.7	4.55	0.53	3.9	18.05	0.9	0.03	0.14
Feb-07	1	6.49	7.2	0.1	3.1	1.01	3.72	1.92	5.76	6.2	3.55	1.88	9	15.58	1.9	0.12	0.30
Apr-07	11.1	6.74	6.24	0.1	2.8	0.96	3.56	1.76	5.19	6.2	3.25	0.65	5.9	20.51	1.4	0.03	0.21
May-07	12.9	6.59	6.56	0.1	2.9	0.95	3.52	1.80	5.23	6.1	3.4	0.62	5.1	16.94	1.2	0.04	0.18
Jun-07	18.6	6.68	6.4	0.1	2.9	0.96	3.59	1.76	5.71	6.5	3.8	0.66	4.9	19.11	1.1	0.03	0.17
Jul-07	18.3	6.67	6.24	0.1	2.9	0.96	3.59	1.72	5.23	5.5	3.75	0.68	5	18.38	1.2	0.04	0.18
Aug-07	17.8	6.57	6.48	0.1	2.9	0.97	3.54	1.68	5.04	6.0	4			16.15	0.0	0.00	
Sep-07	12.9	6.39	6.24	0.1	2.9	0.98	3.68	1.72	5.14	5.9	4	0.6	3.9	11.1	0.9	0.05	0.14
Oct-07	10.7	6.61	6.88	0.1	2.9	0.97	3.61	1.76	4.99	6.0	4	0.68	4.1	18.45	0.9	0.04	0.14
Mar-08	2.5	6.5	6.72	0.1	2.6	0.94	3.56	1.68	4.70	5.6	3.25			15.05	0.0	0.00	
Average	13.3	6.6	6.1	0.1	2.9	1.0	3.7	1.7	5.4	5.8	3.7	0.87	5.8	17.65	1.31	0.07	0.21

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 9. Emån

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/ PNEC (Cu)	BioZn/ PNEC ^{d)}
jan-06	1	7.18	9.12	0.1	12.2	2.7	8.4	1.8	13.7	10.6	24.3	1.2	3.6	40.76	0.46	0.029	0.029
feb-06	0.5	7.01	9.76	0.1	11.8	2.7	8.8	1.8	13.3	10.9	23.7	4.6	4.1	38.4	0.55	0.120	0.035
mar-06	1	7.1	9.52	0.1	11.6	2.5	8.2	1.6	12.9	10.2	22.7	3.5	3.7	40.6	0.48	0.086	0.031
apr-06	7	6.81	11.52	0.1	7.9	2.0	5.9	1.5	10.7	8.6	10.7	1.6	4.3	38.48	0.60	0.042	0.039
maj-06	16	7	11.92	0.1	9.0	2.0	6.0	1.5	10.3	8.8	15.2	1.8	2.1	48.53	0.26	0.037	0.016
jun-06	22	7.08	10.48	0.1	10.1	2.2	6.8	1.6	10.8	10.1	20.6	1.5	1.9	44.2	0.24	0.034	0.015
jul-06	25	7.2	8.8	0.1	10.9	2.5	8.5	1.8	12.6	11.6	22.9	1.5	2.1	40.31	0.28	0.037	0.018
aug-06	21	7.13	8.4	0.1	11.9	2.6	8.9	1.9	13.3	12.0	25.1	1.3	3.7	35.49	0.51	0.037	0.033
sep-06	17	7.12	9.92	0.1	9.7	2.2	7.3	1.6	11.7	9.4	17.9	1.5	2.6	44.28	0.34	0.034	0.022
okt-06	12	7.26	9.44	0.1	11.3	2.4	8.4	1.8	13.5	10.7	21.3	1.4	2	45.4	0.24	0.031	0.016
nov-06	3	6.73	14	0.1	9.1	2.1	6.0	1.6	11.7	8.9	13.0	2.2	3.6	41.72	0.45	0.053	0.029
dec-06	3	6.9	13.52	0.1	9.8	2.1	6.0	1.6	11.0	8.4	14.0	1.7	2.6	49.67	0.30	0.034	0.019
jan-07	2	6.9	11.84	0.1	9.8	2.1	6.3	1.6	10.7	8.4	13.7	1.7	2.6	43.32	0.33	0.039	0.021
feb-07	2	6.89	13.04	0.1	9.1	1.9	5.9	1.5	10.6	8.9	13.1	2.2	3.5	47.73	0.42	0.046	0.027
mar-07	4	6.85	11.68	0.1	8.3	1.8	5.7	1.4	10.2	8.3	10.3	1.9	4.4	41.12	0.59	0.046	0.038
apr-07	11	6.94	10.72	0.1	8.9	2.0	6.0	1.4	10.9	9.6	14.4	1.6	2.2	40.65	0.30	0.039	0.019
maj-07	14.4	7.16	9.84	0.1	10.6	2.3	7.2	1.7	12.6	9.6	18.8	24	16	44.51	2.00	0.539	0.128
jun-07	21	7.25	8.08	0.1	11.2	2.4	8.1	1.7	13.7	11.4	22.7	1.6	1.7	37.77	0.23	0.042	0.015
jul-07	18	6.85	13.28	0.1	9.2	2.0	5.6	1.4	8.7	7.6	15.5	2.3	3.9	45.77	0.47	0.050	0.030
aug-07	17	7.15	12	0.1	9.9	2.1	6.1	1.6	8.7	8.6	18.4	1.9	2.1	55.01	0.23	0.035	0.015
sep-07	13	7.18	11.92	0.1	10.3	2.2	6.9	1.6	10.9	8.9	20.0	1.7	1.9	55.59	0.21	0.031	0.013
okt-07	8	7.06	12.4	0.1	9.4	2.0	6.2	1.7	9.5	9.3	17.3	2.1	2.3	53.27	0.26	0.039	0.017
nov-07	3	7.08	12.24	0.1	9.7	2.1	6.7	1.6	10.6	9.4	17.7	1.9	2.5	53.66	0.28	0.035	0.018
dec-07	2	6.8	13.6	0.1	8.6	2.0	5.9	1.4	9.3	8.4	13.9	1.8	3.3	44.91	0.41	0.040	0.026
jan-08	2	7	13.44		8.8	2.1	5.7	1.4	9.8	8.8	14.8	1.8	3.1	55.48	0.35	0.032	0.022
feb-08	3	6.95	13.92		8.5	2.0	5.7	1.4	9.1	7.3	13.5	1.6	2.9	55.37	0.33	0.029	0.021
mar-08	4	7.07	11.28		8.7	2.0	5.9	1.4	9.3	7.2	14.9	2.4	3.3	49.62	0.41	0.048	0.026
Average	9.37	7.02	11.32	0.1	9.9	2.2	6.8	1.6	11.1	9.3	17.4	2.75	3.4	45.62	0.43	0.06	0.03

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 10. Rönneån

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
jan-06	1.5	7.65	7.36	0.1	33.5	4.0	17.2	2.3	25.0	20.3	69.9	1.5	7.7	27.53	0.83	0.05	0.053
feb-06		7.5	7.04	0.1	29.9	4.0	15.7	2.2	26.3	20.3	62.0	1.6	8.8	27.51	1.08	0.06	0.069
mar-06	1.0	7.65	6.96	0.1	35.0	4.3	12.1	2.4	27.1	20.7	79.9	1.2	5.7	22.98	0.63	0.05	0.040
apr-06	5.5	7.5	8.08	0.1	26.1	3.1	13.0	2.1	18.8	17.2	53.9	1.6	11	32.85	1.27	0.05	0.081
maj-06	14	7.78	7.36	0.1	30.3	4.0	14.0	2.2	21.5	19.0	65.3	1.3	3.9	26.8	0.40	0.05	0.026
jun-06	20	7.91	8.48	0.1	36.4	3.6	14.5	2.5	18.9	21.2	87.5	1.1	3.4	27.37	0.32	0.04	0.020
jul-06	22	7.73	9.76	0.1	34.9	3.7	17.6	2.7	19.2	24.3	89.8	1.2	4.2	33.06	0.36	0.04	0.023
nov-06	7	7.24	10.56	0.1	23.6	3.2	11.6	2.1	20.8	15.7	41.6	2.3	12	42.54	1.34	0.05	0.086
dec-06		7.27	9.76	0.1	25.8	2.9	10.1	2.3	16.1	13.9	46.9	1.9	10	38.48	1.14	0.05	0.073
jan-07	1.0	7.3	7.28	0.1	22.8	2.5	8.4	2.1	14.4	15.2	43.5	1.8	10	28.98	1.39	0.06	0.089
feb-07	0.1	7.52	10.08	0.1	31.4	3.0	10.2	2.3	17.9	15.5	65.7	1.5	7.2	37.7	0.68	0.04	0.044
mar-07	6.0	7.64	8.08	0.1	30.9	3.0	11.0	2.2	19.2	17.2	64.5	1.7	7.5	29.5	0.78	0.06	0.050
apr-07	6.0	7.5	7.12	0.1	25.5	3.5	12.7	2.0	20.6	18.4	54.8	1.6	5.5	28.36	0.69	0.06	0.044
maj-07	14	7.63	7.76	0.1	32.5	3.8	14.2	2.3	22.2	17.2	74.2	1.3	3.4	26.77	0.36	0.05	0.023
jun-07	19	7.27	12.16	0.1	26.6	2.7	13.2	2.1	20.8	17.6	51.0	2.1	9.2	47.07	0.90	0.04	0.057
jul-07	16	7.23	13.2	0.1	28.5	2.9	8.8	2.3	12.2	11.9	62.6	1.4	1.5	45.2	0.14	0.03	0.009
aug-07	15	7.49	13.2	0.1	31.8	3.3	10.5	2.5	15.3	14.4	72.1	1.7	6.6	46.32	0.52	0.04	0.033
okt-07		7.34	14.72	0.1	28.8	3.2	9.0	2.7	14.5	12.4	64.7	2.1	9.1	53.76	0.73	0.04	0.047
nov-07	8	7.49	12.08	0.1	32.8	3.4	10.8	2.7	15.6	16.5	74.4	1.5	5.8	42.21	0.49	0.04	0.031
dec-07	2	7.46	10.56	0.1	26.9	3.1	11.7	2.1	16.5	15.3	59.0	1.5	7.3	42.34	0.71	0.04	0.046
Average	9.3	7.5	9.58	0.1	29.7	3.4	12.3	2.3	19.1	17.2	64.1	1.6	7.0	35.4	0.74	0.046	0.05

^{a)}Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 11. Kävlingeån

Date	T (C)	pH	DOC (mg/L) ^{a)}	HA %	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Alkalinity (mg/L CaCO ₃)	Cu (µg/L) ^{b)}	Zn (µg/L) ^{b)}	PNEC Cu (µg/L)	BioZn (µg/L) ^{c)}	MEC/PNEC (Cu)	BioZn/PNEC ^{d)}
jan-06	0.5	7.9	6.64	0.1	95	6.6	18.8	5.7	49.8	27.5	192.0	1.2	2.2	10.39	0.3	0.12	0.02
feb-06	0.9	8.0	4.96	0.1	83	5.6	16.6	3.4	43.9	30.8	158.2	1.5	3.1	8.26	0.53	0.18	0.03
mar-06	0.5	7.9	7.04	0.1	94	6.9	23.7	5.2	52.2	32.8	183.0	1.1	2.8	12.37	0.36	0.09	0.02
apr-06	4.9	7.7	5.84	0.1	72	5.6	12.9	3.9	36.9	22.0	136.7	1.5	2.6	11.65	0.35	0.13	0.02
maj-06	12.7	7.7	6.96	0.1	73	5.5	17.5	4.8	42.6	30.3	160.4	1.1	1.6	13.37	0.19	0.08	0.01
jun-06	20	7.9	10.08	0.1	81	5.8	18.3	4.3	45.8	31.2	167.5	1.1	1.8	19.15	0.17	0.06	0.01
jul-06	22.1	7.7	6.96	0.1	70	5.6	18.4	3.9	44.5	31.9	148.7	0.96	2.1	14.55	0.25	0.07	0.02
aug-06	16.5	7.6	8.4	0.1	67	4.3	16.7	4.2	33.4	29.6	138.5	2.9	5.2	18.49	0.51	0.16	0.03
sep-06	16	7.8	12.16	0.1	82	6.6	16.6	5.8	40.2	22.5	156.2	1.4	2.8	23.53	0.23	0.06	0.01
okt-06	12.5	7.8	9.76	0.1	76	6.1	16.0	6.6	42.3	25.7	168.1	1.2	3.2	17.81	0.3	0.07	0.02
nov-06	8.3	7.8	11.68	0.1	85	5.2	13.2	5.0	36.1	22.5	160.2	1.9	3.3	21.08	0.28	0.09	0.02
dec-06	6.5	7.9	6.56	0.1	82	5.5	12.3	5.0	36.2	19.2	154.6	1.6	2.4	10.87	0.32	0.15	0.02
jan-07	6.9	7.9	6.56	0.1	72	4.8	10.6	3.9	26.9	15.8	147.7	2.8	9.6	11.4	1.27	0.25	0.08
feb-07	2.1	7.9	9.84	0.1	73	4.9	12.8	4.6	36.8	22.5	152.6	1.7	3.4	18.34	0.33	0.09	0.02
mar-07	6	8.0	7.28	0.1	71	4.8	10.9	3.9	32.0	19.4	143.2	1.9	2.9	12.74	0.36	0.15	0.02
apr-07	9.7	8	8.32	0.1	72	5.3	13.1	5.0	37.2	23.3	152.7	1.6	1.7	14.45	0.19	0.11	0.01
maj-07	14	7.9	6.96	0.1	79	5.6	20.6	5.7	42.6	32.5	169.5	1.4	2.6	12.72	0.33	0.11	0.02
jun-07	22.3	7.7	7.28	0.1	78	5.6	18.7	5.2	44.1	31.1	167.8	2.1	3.5	13.85	0.4	0.15	0.03
jul-07	19.7	7.8	8.4	0.1	68	5.0	10.7	3.9	30.6	15.3	148.7	2.1	5.2	15.97	0.54	0.13	0.03
aug-07	20.3	7.8	9.36	0.1	73	5.3	13.8	4.6	35.6	21.3	166.6	1.3	1.7	17.22	0.16	0.08	0.01
sep-07	14	7.9	7.44	0.1	73	5.4	14.0	4.6	33.1	19.7	176.1	2	3.4	12.29	0.41	0.16	0.03
okt-07	10.1	8.0	7.68	0.1	73	5.7	13.0	6.1	31.9	21.9	169.1	1.1	1.7	12.44	0.2	0.09	0.01
nov-07	4.5	7.9	9.04	0.1	90	5.8	13.7	6.1	35.8	23.6	200.1	1.1	1.8	13.12	0.19	0.08	0.01
dec-07	5.7	7.9	7.68	0.1	71	4.6	10.2	4.1	25.9	16.2	153.6	2	4.3	13.28	0.5	0.15	0.03
Average	10.7	7.8	8.0	0.1	77	5.5	15.1	4.8	38.2	24.5	161.3	1.6	3.1	14.6	0.36	0.12	0.023

^{a)} Estimated from TOC: DOC = 0.8*TOC ^{b)} "Near total concentration" ^{c)} Estimated from TotalZn ^{d)} Added PNEC Zn= 15.6 µg/L. Ambient background concentrations not considered in the calculation

Table A 12. MEC_{diss}/PNEC ratios for copper obtained by correcting MEC_{total} using default values of K_d (=30246) and suspended material (=15 mg/L). Ratios exceeding 1 are marked in bold italic letters.

Date	Abiskojaure	Ume Älv	Stensjön	Näs Bruk	Gråda	Bällstaån	Centralbron	Fiolen	Emån	Rönneån	Kävlingeån
feb-05			0.03					0.09			
mar-05	1.26										
apr-05			0.07					0.05			
maj-05								0.01			
jun-05	0.20							0.03			
jul-05								0.03			
aug-05	0.07		0.01					0.03			
sep-05	0.09		0.01					0.03			
okt-05			0.01					0.03			
jan-06		0.06		0.03	0.01	0.39	0.05		0.02	0.04	0.08
feb-06		0.05	0.02	0.04	0.02	0.15	0.00	0.11	0.08	0.04	0.12
mar-06	0.08	0.06		0.04	0.01	0.72	0.06		0.06	0.04	0.06
apr-06		0.04	0.03	0.04	0.01	0.19	0.06	0.32	0.03	0.03	0.09
maj-06		0.04	0.02	0.03	0.02	1.24	0.00	0.02	0.03	0.03	0.06
jun-06	0.06	0.03	0.01	0.02	0.01	0.11	0.21	0.03	0.02	0.03	0.04
jul-06	0.13		0.01	0.03	0.01	0.06	0.09	0.02	0.03	0.02	0.05
aug-06		0.02	0.01	0.04	0.01	0.92	0.11	0.02	0.03		0.11
sep-06		0.02	0.01	0.03	0.01	0.10	0.07	0.01	0.02		0.04
okt-06	0.05	0.02	0.01	0.03	0.02	0.01	0.08	0.02	0.02		0.05
nov-06		0.03		0.04	0.02	0.13	0.06		0.04	0.04	0.06
dec-06		0.03		0.04	0.02	0.22	0.06		0.02	0.03	0.10
jan-07				0.04	0.01	0.18	0.07		0.03	0.04	0.17
feb-07		0.03	0.02	0.04	0.01	0.19	0.06	0.08	0.03	0.03	0.06
mar-07	0.14	0.04		0.06	0.02	0.28	0.07		0.03	0.04	0.10
apr-07		0.04	0.04	0.04	0.01	0.20	0.08	0.02	0.03	0.04	0.08
maj-07		0.02	0.01	0.02	0.02	0.20	0.10	0.03	0.37	0.03	0.08
jun-07	0.10	0.03	0.01	0.03	0.02	0.42	0.08	0.02	0.03	0.03	0.10
jul-07	0.14		0.01	0.04	0.02	0.56	0.09	0.03	0.03	0.02	0.09
aug-07	0.12	0.03	0.01	0.04	0.01	0.23	0.17	0.00	0.02	0.03	0.05
sep-07	0.11	0.03	0.01	0.02	0.01	0.24	0.16	0.04	0.02		0.11
okt-07		0.02	0.01	0.03	0.01	0.25	0.00	0.03	0.03	0.03	0.06
nov-07		0.02	0.00	0.03	0.01	0.15	0.12		0.02	0.02	0.06
dec-07		0.03	0.10	0.04	0.01	0.37	0.10		0.03	0.02	0.10
jan-08									0.02		
feb-08		0.03							0.02		
mar-08		0.03							0.03		

Appendix 2

Risk characterization of some Swedish waters using the full SSD normalization approach for effects assessment of Zn

Karel De Schamphelaere

1. Introduction

The full SSD normalization approach for effects assessment, i.e. PNEC derivation, contains following main elements, which are described in detail in Van Sprang et al. (2008):

- It assumes that the three chronic Zn-BLMs (De Schamphelaere et al., 2005), developed for algae, *Daphnia*, and fish can be extrapolated to all other algae, invertebrates, and fish, respectively. Van Sprang et al. (2008) demonstrate that this assumption is neither unreasonable nor unrealistic – on the basis of some ecotoxicological data and physiological consideration. However, at the same time they acknowledge that this assumption should be more thoroughly investigated.
- It uses the total risk approach (not the added risk approach).
- It uses an updated effects database compared to the Zn RAR (EU, 2008).

The full SSD normalization approach is in fact identical to the method used for estimating site-specific Cu PNEC values (Cu VRAR), which can be done with user-friendly software.

2. Methods

All chronic Zn NOEC data (as reported in the effects database of Van Sprang et al, 2008) were first normalized with the BLMs to the physico-chemistry of the water sample under consideration. Geometric mean NOECs per species were calculated (for the most sensitive endpoint per species) and the HC5(50%) was calculated from the NOEC distributions with the log-normal model (Aldenberg and Jaworska, 2000). The HC5(50%) is a dissolved Zn concentration. It is noted that a further refinement could have been to use the best-fitting distribution, but this option was due to time constraints, not pursued here. Risk characterization ratios (RCR) were calculated for all water samples considering four scenarios, depending on (i) the magnitude of the assessment factor (AF) for going from HC5(50%) to PNEC, which is still under debate (i.e., AF=1 or 2), and (ii) depending on whether or not there is a correction for going from measured total Zn concentration to dissolved Zn concentration:

Scenario 1 (assumes total Zn = dissolved Zn, AF=2):

$$RCR_{total,AF=2} = 2 \times [Zn_{total}] / HC5(50\%)$$

Scenario 2: (assumes total Zn = dissolved Zn, AF=1)

$$RCR_{total,AF=1} = [Zn_{total}] / HC5(50\%)$$

Scenario 3: (correction for dissolved Zn, AF=2)

$$RCR_{dissolved,AF=2} = 2 \times [Zn_{dissolved}] / HC5(50\%)$$

Scenario 4: (correction for dissolved Zn, AF=1)

$$RCR_{dissolved,AF=1} = [Zn_{dissolved}] / HC5(50\%)$$

In scenario 3 and 4, dissolved Zn is calculated from total Zn as follows:

$$[Zn_{dissolved}] = \frac{[Zn_{total}]}{(1 + K_d \cdot Cs \cdot 10^{-6})} \quad (\text{Eq. 1})$$

where $[Zn_{dissolved}]$ and $[Zn_{total}]$ are the dissolved and total Zn concentration ($\mu\text{g/L}$), K_d is the equilibrium partitioning coefficient (L/kg), and C_s is the concentration of suspended solids (mg/L). In absence of site-specific C_s and K_d values, we have used default values of $C_s = 15 \text{ mg/L}$ for C_s and $K_d = 110000$ (as suggested in the Zn RAR, EU, 2008). This results in an assumed default dissolved Zn fraction of 38%. These calculations should, however, only be considered as an example, since it should be realized that both C_s and K_d values may show considerable variation among different water bodies (and seasons) (Van Sprang et al., 2008). Applying these default conditions may actually increase the uncertainty about the estimated RCR.

3. Results

All HC5(50%) and RCRs are presented in Table 1. We also present the % of samples per river in which $RCR > 1$. We did this for the four scenarios. The raw output of all calculations can be found in the excel file.

Table 1 Overview of minimum, mean and maximum HC5 and RCR (4 scenarios) as well as the % of samples per river for which the RCR>1. RCR >1 are underlined for clarity.

River	HC5 min µg/L	HC5 mean µg/L	HC5 max µg/L	RCR ₁ min	RCR ₁ mean	RCR ₁ max	RCR ₂ min	RCR ₂ mean	RCR ₂ max	RCR ₃ min	RCR ₃ mean	RCR ₃ max	RCR ₄ min	RCR ₄ mean	RCR ₄ max	%>1 RCR ₁	%>1 RCR ₂	%>1 RCR ₃	%>1 RCR ₄
Abiskojaure	7.0	10.3	18.9	0.06	0.77	<u>6.52</u>	0.03	0.38	<u>3.26</u>	0.02	0.29	<u>2.46</u>	0.01	0.14	<u>1.23</u>	7.7	7.7	7.7	7.7
Ume Älv	12.6	18.3	25.8	0.22	0.53	<u>1.01</u>	0.11	0.27	0.50	0.08	0.20	0.38	0.04	0.10	0.19	4.3	0	0	0
Stensjön	19.3	29.6	38.5	0.03	0.08	0.34	0.01	0.04	0.17	0.01	0.03	0.13	0.01	0.01	0.06	0	0	0	0
Näs	22.0	28.0	34.0	0.41	0.70	<u>1.33</u>	0.20	0.35	0.67	0.15	0.26	0.50	0.08	0.13	0.25	8.3	0	0	0
Gråda	21.1	26.6	32.7	0.07	0.14	0.36	0.04	0.07	0.18	0.03	0.05	0.14	0.01	0.03	0.07	0	0	0	0
Bällstaån	27.1	37.6	55.7	0.35	<u>2.79</u>	<u>15.7</u>	0.18	<u>1.40</u>	<u>7.83</u>	0.13	<u>1.05</u>	<u>5.91</u>	0.07	0.53	<u>2.96</u>	83.3	41.7	29.2	12.5
Centralbron	28.3	37.0	51.7	0.07	0.30	<u>1.13</u>	0.03	0.15	0.57	0.03	0.11	0.43	0.01	0.06	0.21	4.8	0	0	0
Fiolen	16.1	23.0	32.6	0.18	0.50	<u>1.02</u>	0.09	0.25	0.51	0.07	0.19	0.38	0.03	0.09	0.19	4.3	0	0	0
Emån	34.4	43.3	74.9	0.07	0.16	0.76	0.04	0.08	0.38	0.03	0.06	0.29	0.01	0.03	0.14	0	0	0	0
Rönneån	34.1	49.2	67.7	0.05	0.30	0.59	0.03	0.15	0.29	0.02	0.11	0.22	0.01	0.06	0.11	0	0	0	0
Kävlingeån	33.6	48.9	69.9	0.06	0.13	0.46	0.03	0.07	0.23	0.02	0.05	0.17	0.01	0.03	0.09	0	0	0	0
Görväln	87.7	119.3	175.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stäketbron	124.7	171.5	256.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ringsjön	358.7	388.5	418.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Snogeholmsjön	243.1	468.0	867.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not determined because no measured Zn concentrations available

4. Discussion

Before considering the results, it is important to reiterate that several rivers have Ca concentrations that are generally lower than the lower BLM boundary of 5 mg/L. There is however a gradation in this. Indeed, Abiskojaure, Ume Älv, Näs, and Gråda have minimum Ca levels still > 3mg/L. Hence, the results for these rivers should be considered less uncertain than for Stensjön (Ca 0.8-1.5 mg/L) and Fiolen (Ca 1.7-3.1 mg/L). Although no Zn concentrations were available to us for Görväln, Stäketbron, Ringsjön and Snogeholmsjön, we did calculate HC5(50) values for these waters. These waters had the highest mean HC5(50) values of all, being between 119 and 469 µg Zn/L. Upon closer inspection of the chemistry of these waters, they all have high pH (~7.5-8.5) and extremely low Ca (<1.5 mg/L). These are very special conditions (normally a river with high pH also has a high Ca) and the BLM has not been validated for such waters. Hence, these values are extremely uncertain.

The mean HC5(50) for all other waters varied between 10.3 (Abiskojaure) and 49.2 µg/L (Rönneån). The temporal variation within a river was usually within a factor of 2 (difference between min and max). It is interesting to note that the HC5(50) of 10.3 µg/L is 1.5-fold lower than the reference HC5(50) value of 15.6 µg/L from the Zn RAR document (EU, 2008). This illustrates that there are indeed rivers for which the bioavailability is so high than the reference (worst case) HC5(50) is not necessarily conservative enough. The low HC5(50) value for Abiskojaure is likely due to a combination of low DOC and low Ca.

RCR values > 1 under the most conservative scenario (scenario 1) are found in 6 out of 11 rivers. While in Abiskojaure, Ume Älv, Näs, Centralbron, and Fiolen the RCR was > 1 in <10% of the samples, the RCR exceeded 1 in 83.3% of the samples of Bällstaån. When scenarios 2 to 4 were applied, RCR>1 were only found in Abiskojaure and Bällstaån. This analysis highlights the importance of applying additional AFs on ecotoxicity data for deriving PNECs. It is therefore recommended, to measure dissolved Zn concentrations (if correctly done) in cases where a potential risk is found based on comparing total Zn concentrations with the HC5(50).

5. Conclusion

The mean HC5(50) values varied about 5-fold among 11 rivers, i.e. between 10.3 and 49.2 µg Zn/L. Under the scenario #1 RCR values >1 were found in 6 out of 11 rivers, but only in Balstaan the %

of samples with RCR exceeding 1 was >10% (i.e. 83%). When scenarios #2 to 4 were applied, RCR>1 were only found in Abiskojaure and Bällstaån.

6. References

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