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Biogeochemistry of nickel and molybdenum in the biosphere of Forsmark and Simpevarp

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Summary

The site investigations in Forsmark and Simpevarp have resulted in a large amount of data that has been presented in a long series of SKB reports. The measurements include, for instance, concentrations in surface water (lakes, streams, sea water), suspended matter, near-surface groundwater, marine and freshwater sediments, different soil types and peat cores as well as determination of Kd values for a wide range of elements. The objective of this report was to interpret, summarise and provide a synthesis of the site investigation data with focus on Ni and Mo in the light of the current scientific knowledge of these elements. Of primary concern in the safety assessment are the artificial isotopes Ni-63 ($T_{\frac{1}{2}}$ = 76 000 a) and Mo-93 ($T_{\frac{1}{2}}$ = 4 000 a), but both elements are represented by stable isotopes in nature, which can be used to understand their long-term fate and behaviour in the environment. Of particular interest was also to assess how well the site-specific Kd values used in the dose models reflect the conclusions from the site investigation data and the general scientific understanding of these elements.

The main source of Ni in the site investigation areas is weathering of the local soils, where Ni – along with other transition metals such as Co, Cr and Zn – mainly appears to be associated with Fe-bearing minerals, e.g. hornblende. The highest Ni concentrations were found in inorganic soils such as glacial clay, in this case probably mainly in primary minerals, but the concentrations are normal for Swedish conditions in both Simpevarp and Forsmark. Although more organic soil types such as peat and gyttja sediments typically contain lower Ni concentrations, they show the clearest signs of sorption of Ni from the aqueous phase. Binding to organic matter is an important sorption mechanism for Ni, but there can also be considerable sorption onto precipitates of Fe, Mn and Al at high pH and co-precipitation with sulfide minerals. The affinity of Ni for organic matter for organic matter is also reflected in the aqueous speciation, where Ni largely can be expected to be present in organic colloids in the site investigation areas, but especially at low pH free Ni^{2+} ions can also be important. Particularly the shallow lakes in the Forsmark area undergo considerable seasonal dynamics in the chemical conditions, e.g. increasing pH and Eh during the summers, causing precipitation of $CaCO_3$ and Fe and Mn (hydr) oxides, and decreasing pH and Eh during the winters causing subsequent dissolution, but compared to other divalent transition elements, e.g. Co and Zn, Ni does not appear to be particularly strongly affected by these changes. There is a strong general resemblance between, for example, Ni and Co in terms of concentrations in soils and water, Kd values and biological uptake at both sites, but there was also a clear fractionation, for example, in the presence of Mn oxides, which causes different patterns in the surface water and, as a consequence, also in the sediment record. For example, Mn-rich sediments tend to have low Ni/Co ratios as a result of preferential scavenging of Co, while more organic sediments tend to have high Ni/Co ratios, thus emphasising the importance of organic matter for the fate of Ni.

The site-specific Kd values for Ni displayed a smooth distribution with moderately high values, ranging between 0.13 $m^3\ kg^{-1}$ and 33 $m^3\ kg^{-1}$. The highest Kd values were observed in glacial clay, mainly because of the relatively high Ni concentrations in these soils, while the lowest Kd values were associated with clay gyttja. The clay gyttja contained nearly as high concentrations in the solid phase as the glacial clay, but the concentrations in the pore water were much higher. The reason was most likely that Ni was mobilised by the high DOC concentrations in the pore water in these soils, which would be consistent with the observations of Ni from the site investigations and the current scientific understanding of the biogeochemistry of Ni.

The biogeochemistry of Mo is characterised by its redox chemistry and the large difference in mobility between sulfidic and non-sulfidic environments. Under most geochemical conditions Mo is stable as Mo(VI), which occurs as the relatively mobile oxyanion molybdate (MoO_4^{2-}). In the presence of sulfide, however, molybdate can be reduced to the immobile Mo(IV) or transformed to more reactive thiomolybdates, in which S(-II) replace one or more O atoms in the molybdate ion. As a consequence, accumulation of Mo is typically associated with sulfate-reducing environments, a pattern that also is evident in the site investigation areas.

The major source of Mo in both Simpevarp and Forsmark is probably weathering of the local soils, where some similarities between Mo and Na suggest that plagioclase could be an important mineral. Measurements of Mo in precipitation do not indicate that the Forsmark area would be affected by

substantially elevated deposition of Mo due to the vicinity to the steel industry in Sandviken. The aqueous speciation of Mo is most likely dominated by molybdate, which makes it comparatively mobile, particularly in the calcite-dominated Forsmark area. In the near-surface groundwater there are significant trends at both sites of higher Mo concentration in water with higher pH, which is consistent with a weaker sorption of molybdate at higher pH. There was also a significant trend with lower Mo concentrations in groundwater with a high fraction of the total S present as sulfide, which is consistent with the expected immobilisation of Mo in sulfidic environments. Strong accumulation of Mo could be observed in soils with high S concentrations, i.e. strongly reducing environments such as organic sediments and wetlands. In Forsmark the Mo concentration in organic lake sediments were up to two orders of magnitude higher than in the local till, which emphasises the importance of sulfidic conditions for the immobilisation of Mo in the landscape.

The Kd values for Mo varied considerably, ranging from 0.060 $m^3 kg^{-1}$ to 26 $m^3 kg^{-1}$ with a distinctly bimodal distribution, i.e. the samples were clustered at either high or low Kd values. High Kd values were associated with above all clay gyttja and wetland peat, which both contained relatively high Mo concentrations in the solid phase and low Mo concentrations in the pore water. For some samples it was noted that H_2S was produced during the incubations so the naturally reducing conditions in these soils appear to be reflected in the Kd values by low Mo concentrations in the pore water. Low Kd values were associated mainly with the more inorganic soil types, i.e. clayey till and glacial clay, where Mo can remain mobile as molybdate. Cultivated peat contained Mo concentrations similar to the wetland peat, but most likely because these soils have been ditched and oxidised the Mo concentrations in the pore water were higher, resulting in low Kd values. Hence, the bimodal Kd distribution for Mo is likely to reflect the redox chemistry of Mo, which – based both on the scientific literature and the site investigations – is so decisive for the fate of Mo. This interpretation of the Kd values of Mo is also supported by similar bimodal tendencies for other redox-sensitive elements such as Fe, Mn and Re.

Sammanfattning

Platsundersökningarna i Forsmark och Simpevarp har resulterat i stora mängder data som har presenterats i en lång rad SKB-rapporter. Mätningarna omfattar till exempel koncentrationer i ytvatten (sjöar, vattendrag, havsvatten), suspenderat material, ytnära grundvatten, havs- och sötvattensediment, olika jordtyper och torvprofiler liksom bestämning av Kd-värden för en lång rad grundämnen. Syftet med föreliggande rapport var att med tolka, sammanfatta och skapa en syntes av all platsundersökningsdata med fokus på Ni och Mo utifrån den nuvarande vetenskapliga kunskapen om dessa ämnen. Av huvudsakligt intresse för säkerhetsanalysen är de artificiella isotoperna Ni-63 ($T_{\frac{1}{2}}$ = 76 000 a) och Mo-93 ($T_{\frac{1}{2}}$ = 4 000 a), men både grundämnena förekommer naturligt som stabila isotoper som kan användas för att förstå deras beteende i miljön. Av speciellt intresse var också att bedöma hur väl de platsspecifika Kd-värdena som används i dosmodellerna avspeglar slutsatserna från platsundersökningarna och den allmänna vetenskapliga förståelsen av dessa ämnen.

Huvudkällan för Ni i platsundersökningsområdena är vittring av de lokala jordarna, där Ni tillsammans med andra övergångsmetaller såsom Co, Cr och Zn främst tycks förekomma i Fe-rika mineral, exempelvis hornblände. De högsta Ni-koncentrationerna påträffades i oorganiska jordar som glaciallera, i detta fall förmodligen främst i primära mineral, men koncentrationerna är normala för svenska förhållanden i både Simpevarp och Forsmark. Även om mer organiska jordtyper som torv och gyttjesediment ofta innehåller lägre Ni-koncentrationer uppvisar de ofta de tydligaste tecknen på sorption av Ni från vattenfas. Bindning till organiskt material är en viktig sorptionsmekanism för Ni, men det förekommer även omfattande sorption på Fe-, Mn- och Al-utfällningar vid höga pH och samutfällning med sulfidmineral. Dragningen till organiskt material avspeglas också i specieringen i vattenfasen, där Ni kan förväntas förekomma främst på organiska kolloider i plastundersökningsområdena, men i synnerhet vid låga pH kan även fria Ni^{2+}-joner vara av betydelse. Framför allt de grunda sjöarna i Forsmarksområdet genomgår en betydande årstidsstyrd dynamik i de kemiska förhållandena med exempelvis ökande pH och Eh under sommaren, vilket orsakar utfällning av $CaCO_3$ och Fe- och Mn-(hydr)oxider, och sjunkande pH och Eh under vintern, vilket leder till åtminstone delvis upplösning av dessa utfällningar. Jämfört med andra tvåvärde övergångsmetaller, till exempel Co och Zn, tycks Ni inte påverkas speciellt mycket av dessa förändringar. Det finns en stark allmän likhet mellan exempelvis Ni och Co vad gäller koncentrationer i mark och vatten, Kd-värden och upptag i biota på båda platserna, men det sker även en tydlig fraktionering till exempel i närvaro av Mn-oxider, vilket förorsakar olika mönster i ytvattnet och följaktligen i sedimenten. Mn-rika sediment tenderar till exempel att ha låga Ni/Co-kvoter till följd av en preferentiell sorption av Co, medan mer organiska sediment tenderar att ha höga Ni/Co-kvoter. Detta understryker betydelsen av organiskt material för nickels biogeokemi.

De platsspecifika Kd-värdena för Ni uppvisade en jämn fördelning med medelhöga värden mellan 0.13 $m^3\ kg^{-1}$ and 33 $m^3\ kg^{-1}$. De högsta kd-värdena observerades i glaciallera, främst på grund av de relativt höga Ni-koncentrationerna i dessa jordar, medan de lägsta Kd-värdena återfanns i lergyttja. Lergyttjan innehöll nästan lika höga Ni-koncentrationer i den fasta fasen som glacialleran, men koncentrationerna i porvattnet var avsevärt högre. Orsaken var förmodligen de höge DOC-koncentrationerna i dessa jordar, vilket skulle stämma väl med observationerna från platsundersökningarna like den rådande vetenskapliga förståelsen av nickels biogeokemi.

Molybdens biogeokemi kännetecknas av dess redoxkemi och den stora skillnaden i mobilitet mellan miljöer med respektive utan sulfid. Vid de flesta geokemiska förhållanden är Mo stabilt som Mo(VI) som förekommer som den jämförelsevis lättrörliga oxyanjonen molybdat (MoO_4^{2-}). I närvaro av sulfid kan molybdat emellertid reduceras till svårlösligt Mo(IV) eller omvandlas till mer reaktiva tiomolybdater, där S(-II) ersätter en eller flera O-atomer i molybdatjonen. Följaktligen hänger ackumulation av Mo ofta samman med sulfatreducerande miljöer, vilket också var ett påfallande mönster i platsundersökningsområdena.

Huvudkällan för Mo i både Simpevarp och Forsmark är förmodligen vittring av de lokala jordarna, där vissa likheter mellan Mo och Na tyder på att plagioklas skulle kunna vara ett viktigt mineral. Mätningar Mo i nederbörden tyder inte på att Forsmarksområdet skulle påverkas av någon betydande förhöjd deposition av Mo på grund av närheten till stålindustrin i Sandviken. Specieringen i löst fas

domineras mest troligt av molybdat, vilket gör Mo förehållandevis mobilt, i synnerhet i det kalcitrika Forsmarksområdet. I ytnära grundvatten finns signifikanta samband på båda lokalerna med högre Mo-koncentrationer i vatten med högt pH, vilket stämmer väl med en svagare sorption av molybdat vid högre pH. Det finns även en signifikant trend med lägre Mo-koncentrationer i grundvatten där en hög andel S förekommer som sulfid, vilket överensstämmer med den förväntade fastläggningen av Mo i sulfidhaltiga miljöer. Kraftig ackumulation av Mo kunde också observeras i jordar med hög S-koncentration, det vill säga starkt reducerande miljöer såsom organiska sediment och våtmarker. I Forsmark var Mo-koncentrationen i sjösediment upp till 100 gånger högre än i den lokala moränen, vilket understryker betydelsen av sulfidhaltiga miljöer för fastläggningen av Mo i landskapet.

Kd-värdena för Mo varierade kraftigt, från 0.060 $m^3 kg^{-1}$ till 26 $m^3 kg^{-1}$, med en tydligt bimodal fördelning, det vill säga jordproverna hade i regel antingen höga eller låga Kd-värden. Höga Kd-värden observerades framför allt i lergyttja och våtmarkstorv som både innehöll relativt höga koncentrationer i den fasta fasen och låga koncentrationer i porvattnet. För några av proverna noterades produktion av H_2S vid inkuberingarna, vilket tyder på att de naturligt reducerande förhållandena i dessa jordar troligen avspeglas i Kd-värdena. Låga Kd-värden hängde ihop med mer oorganiska jordar som lermorän och glaciallera där Mo troligen förblir mobilt i form av molybdat. Odlade torvjordar hade lika höga Mo-koncentrationer som våtmarkstorv, men troligtvis på grund av att de dikats ut och oxiderats vara Mo-koncentrationen i porvattnet högre, vilket resulterade i låga Kd-värden. Således tycks den bimodala Kd-fördelningen för Mo återspegla molybdens redoxkemi, vilken både utifrån den vetenskapliga litteraturen och plastundersökningarna kan anses vara avgörande för vad som händer med Mo. Denna tolkning av Kd-värdena styrks även av liknande bimodala tendenser hos andra redox-känsliga ämnen, exempelvis Fe, Mn och Re.

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1 Introduction

1.1 Background

1.1.1 Introduction

Nuclear fuel and waste contains a wide range of radioactive isotopes, the vast majority of which represent elements that also occur naturally in the environment as stable or radioactive isotopes (or both) (e.g. SKB 2014). When assessing the long-term behaviour of radionuclides in the environment, these naturally occurring isotopes can therefore function as natural analogues and provide insights about the processes that control the transport and accumulation of radionuclides in different landscape types and under different biogeochemical conditions. This knowledge about the long-term fate of key elements in the landscape is important for assessing the performance and reliability of the dose models used in the safety assessment (SKB 2014). Especially when trying to predict radionuclide mobility in a distant future, a thorough process-based understanding of the processes that govern the transport and accumulation of key radionuclides under varying biogeochemical conditions is paramount.

Over the years the site investigation programmes in the Forsmark and Simpevarp areas have resulted in large amounts of data, including Kd values and the concentrations of a wide range of major and trace elements in various media, e.g. soils, groundwater, surface water (lakes, streams, sea), sediments and biota. These results have been presented and discussed in numerous previous SKB reports, e.g. Andersson (2010), Löfgren (2010), Tröjbom and Söderbäck (2006a, b) and Tröjbom and Nordén (2010). The purpose of this study, however, was to focus specifically on two elements, Ni and Mo, that have emerged as potentially important in the on-going safety assessment for the expansion of SFR (final repository for short-lived radioactive waste) and the construction of SFL (final repository for long-lived low-level radioactive waste). The concerns regarding these elements are primarily associated with the Ni isotope ^{59}Ni ($T_{½}$ = 76 000 a) and the Mo isotope ^{93}Mo ($T_{½}$ = 4 000 a) (SKB, 2014). The ambition of the study was to go through all available biosphere data from the site investigations relating to these two elements and interpret the results in the context of both the current understanding of the biogeochemistry of Ni and Mo based on the scientific literature and the general understanding of the systems in Forsmark and Simpevarp, respectively. In order to gain more insight into the processes that govern the transport and accumulation of Ni and Mo comparisons are made to other elements with similar or in some respect contrasting biogeochemical properties. In the case of Ni this involves comparisons with, for example, Mn, Fe, Co, Cu and Zn, which permanently (like Ni) or at least under certain redox conditions occur as divalent cations. Differences in, for example, redox behaviour and affinity for organic matter can then be used to infer what processes are driving the fractionation of these elements and enhance our understanding of what sorption mechanisms are important for Ni. Similarly, Mo is related above all to other predominately anionic elements, for example, S, which is expected to be immobilised at a similar redox potential as Mo (see Section 3.1.1 for details), and W, whose oxyanion, tungstate, is stable under more reducing conditions than its Mo counterpart, molybdate. Hence, extensive accumulation of Mo and S but not W would, as an example, indicate that the sorption is related to the redox conditions, while simultaneous accumulation of Mo and W but not S would indicate otherwise. The objective was also to investigate whether the site-specific Kd values used in the dose models are consistent with the biogeochemical understanding of these elements in the site investigation areas and properly reflect the dominating sorption mechanisms.

1.1.2 Site description

Both the Forsmark area and the Simpevarp area have been extensively investigated during the course of the site investigations. Detailed descriptions of various aspects of the landscape and the ecosystems can therefore be found in previous SKB reports, e.g. Tröjbom et al. (2007), Hedenborg and Sohlenius (2008), Lindborg (2008), Sohlenius and Hedenström (2008), Andersson (2010) and Löfgren (2010).

Both sites are located by the coast and are strongly affected by glacial and postglacial processes. During much of the Holocene both sites were submerged in the Baltic Sea (and its predecessors), and the landscape is therefore young at both sites. The effects of the isostatic rebound are most apparent in the Forsmark area, both because it is more rapid there (currently ca. 6 mm a^{-1}) and because the

Forsmark area is relatively flat with the highest parts barely reaching 20 m above the current sea level (SKB 2008). As a consequence, the first parts of the Forsmark area emerged only ca. 3 000 years ago, and there is an on-going shoreline displacement in the area. The oldest lake in the in the site investigation area, Eckarfjärden, was isolated from the Baltic Sea only ca. 850 years ago (Hedenström and Risberg 2003, Hedenström et al. 2008). The isostatic rebound in the Simpevarp area is currently ca. 1 mm a^{-1}, and the oldest parts of Simpevarp area emerged from the sea ca. 11 400 BP (Sohlenius and Hedenström 2008, Söderbäck et al. 2008).

Characteristic for the chemistry of the Forsmark area is the presence of high concentrations of calcite in the soils, particularly the till and the glacial clay, which typically contain ca. 20 % calcite (Hedenström and Sohlenius 2008). This leads to generally high pH and high concentrations of Ca and carbonate in the groundwater and surface water of the Forsmark area. As a consequence, many waters are also saturated with respect to $CaCO_3$, and precipitation of $CaCO_3$ occurs in the area, for instance in the lakes during the growing season (Jaremalm et al. 2013). Locally, calcite has also been encountered in the Simpevarp area (up to 4.5 %), but its influence on the water chemistry is not as widespread and profound as in the Forsmark area (Sohlenius and Hedenström 2008, Jaremalm et al. 2013). Apart from calcite the mineralogy of the till in Forsmark area is dominated by quartz (ca. 24–26 %), K feldspar (23–32 %), plagioclase (30–36 %) and hornblende (0.5–4 %) (Sohlenius and Rudmark, 2003). The till in the Simpevarp area (n = 3) is dominated by quartz (28–36 %), K feldspar (24–26 %) and plagioclase (35–42 %) with minor fractions (< 3.2 %) of amphibole, muscovite, chlorite and in some cases small amounts of calcite (< 0.01 %) (Walger et al. 2007). The dominating clay mineral is above all illite (up to 8 % in till and up to 45 % in clay soils), but chlorite, kaolinite and vermiculite have also been detected in till and clay from the Simpevarp area (Sohlenius 2008).

The landscape in both areas is complex, consisting mainly of deciduous and coniferous forests, arable land, wetlands and lakes, albeit to different degrees in different subcatchments. The Forsmark area has a mean temperature of 5.0ºC and on average 100–125 days of snow cover, while the Simpevarp area, located further south, has a mean temperature of 6.5ºC and only 50–75 days of snow cover. The average annual precipitation in Forsmark was 589 mm during the period 2004–2010, of which ca. two thirds are lost by evapotranspiration and one third by runoff (Johansson and Juston 2009, Werner et al. 2013). In the Simpevarp area the annual average precipitation amounts to ca. 600 mm, of which nearly three fourths are lost by evapotranspiration (SKB 2009).

1.1.3 Data

All data presented in this report were taken from previously published investigations and research, generally conducted by SKB in the site investigation areas in Forsmark and Simpevarp. References to relevant SKB reports, where sampling and analyses are described in detail, are given throughout the text. Where data are presented without any specific reference, the data were taken from the general monitoring programmes at the Forsmark and Simpevarp sites as stored in the SICADA database. The key elements for this report, i.e. Mo and Ni, were analysed by ICP-AESICP-MS. In general, samples were collected in 100 mL plastic bottles, filtered and acidified by 1 mL concentrated HNO_3. For the surface waters the measurement uncertainty has been estimated to 8 % for Ni and 7–10 % for Mo, which combined with uncertainties from sampling and handling of the samples are estimated to result in uncertainties of up to 20 % (Nilsson and Borgiel 2007). These estimations are probably reasonably valid also for other sample types. Much of the data has previously been described and evaluated by Tröjbom and Nordén (2008), who present a broader description of the water quality in the site investigation areas. Thermodynamic modelling of the Mo and Ni speciation was conducted using Visual MINTEQ 3.0 (Gustafsson 2012). The full dataset will be presented in an upcoming SKB report, but a few illustrative examples are given here to help interpret and evaluate the chemistry data.

2 Nickel

2.1 The biogeochemistry of Ni

2.1.1 Overview

Nickel is a transition metal (Z = 28), which occurs exclusively as a divalent ion, Ni^{2+}, in natural waters. As such it shares many properties with other divalent ions of transition metals, particularly in the first row. Beginning with Mn these elements may occur as divalent ions, at least under the right redox conditions, and the stability of complexes with most ligands tends to increase across the period according to the so-called Irving-Williams series: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. This trend, however, peaks with Cu^{2+} so the last member of the series, Zn^{2+}, generally forms weaker complexes than Cu^{2+} (Irving and Williams 1953). In natural environments, however, this rarely results in consistent patterns because all these elements do not always occur in the divalent state. Most notably, Mn^{2+} and Fe^{2+} are normally oxidised to Mn^{4+} and Fe^{3+}, respectively, in surface water. Co^{2+} may also be oxidised to Co^{3+} in the presence of MnO_2 (Murray and Dillard 1979), whereas Cu^{2+} on the contrary can be reduced to Cu^{+} or elemental Cu. Hence, only Ni and Zn are the only consistently divalent metals in the series.

Nickel is an essential element to plants and microbes, where it is present in a number enzymes involved in various metabolic processes (Chen et al. 2009). However, the amount of Ni needed is typically small, and globally Ni toxicity therefore appears to be a bigger problem than Ni deficiency (Yusuf et al. 2011). The adverse effects of Ni are partly related to antagonistic effects between Ni and Zn (Onodera et al. 2018). (See Section 2.1.3 for further details.)

Important processes for the mobility of Ni in the surface environment include complexation with organic matter and to some extent Fe (oxy)hydroxides, particularly at high pH. Ni may also be strongly sorbed in strongly reducing environments by precipitation or co-precipitation of sulfide minerals.

2.1.2 Mobility of Ni soils and water

Boreal waters are often characterised by high concentrations of dissolved organic carbon (DOC). Several studies have demonstrated that DOC is important for the mobility of Ni in such environments. For instance, in the Kalix River in northern Sweden Dahlqvist et al. (2007) observed a preferential association of nickel with organic colloids rather than Fe colloids. Similar observations have also been made in northwest Russia, indicating that nickel has a moderately strong affinity for organic matter (Vasyukova et al. 2010). This sorption of nickel onto organic matter in river water is a relatively rapid process (Martino et al. 2003). Association of nickel with organic ligands has also been observed in lakes (Achterberg et al. 1997), and in soils the mobility of Ni is often strongly influenced by the presence of organic matter (Buerge-Weirich and Sulzberger 2004). The affinity for organic matter also affects the behaviour of nickel on the landscape level. In the Krycklan catchment the export of nickel is strongly suppressed by the presence of mires, indicating a substantial accumulation of nickel in peat (Lidman et al. 2014).

In less organic soils nickel has also been observed to bind to iron and manganese oxides (Jeske and Gworek 2012). There are no signs, however, that Ni^{2+} would be able to substitute Fe^{3+} in the matrix so the binding of nickel to ferrihydrite seems to be a pure sorption process (Xu et al. 2007). The sorption to Fe precipitates such as ferrihydrite, hematite and goethite is relatively weak at low pH, but increases steadily from pH 5 to pH 8 (Arai 2008). Since the complexation of Ni to both organic and inorganic ligands tends to become stronger at high pH so generally Ni can be expected to be more mobile at low pH and more strongly sorbed to soils and particles at high pH (Alloway 2012, Ma et al. 2013).

The importance of DOC for the mobility of Ni can be further illustrated by data from a hillslope transect in the Krycklan catchment in northern Sweden (Laudon et al. 2013, Lidman et al. 2017a). In the uphill Podzol the Ni concentration is 0.83 $\mu g\ L^{-1}$ or less, but in the more organic riparian zone it increases to > 3 $\mu g\ L^{-1}$ (Figure 2-1). The reason for the higher mobility of Ni in the riparian zone is that the riparian soil water contains higher concentrations of DOC, which Ni can bind to, thereby increasing its mobility.

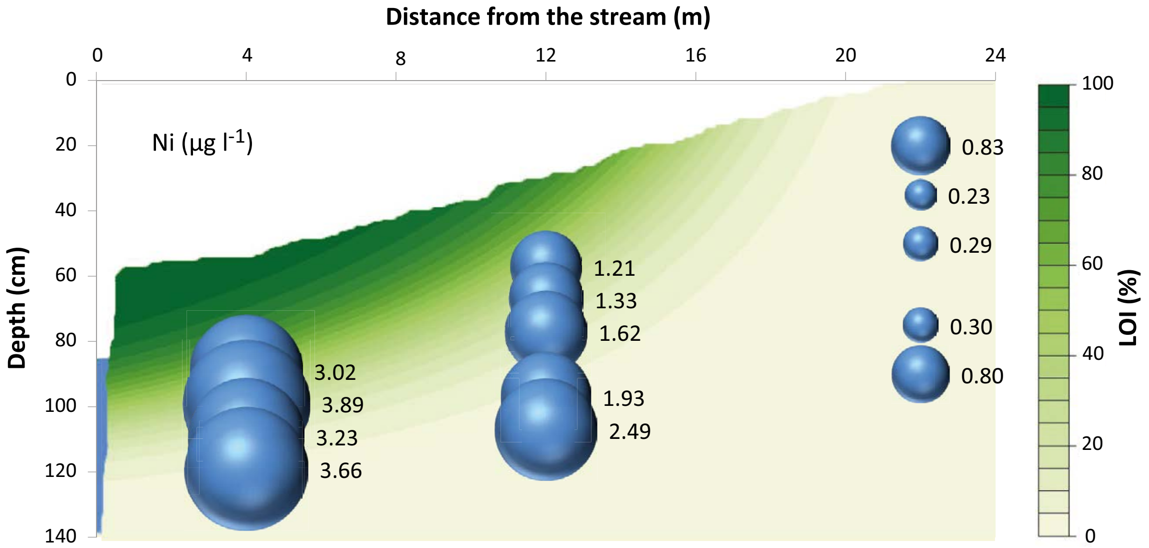

Figure 2-1. *Average Ni concentrations in soil water and groundwater from a hillslope transect in the Krycklan catchment in northern Sweden. The stream draining the transect can be seen to the left. The size of the bubbles corresponds to the concentrations given next to each observation (in µg* L^{-1}*), and the green shading shows the loss on ignition (LOI) of the soil (see the colour scale to the right). The solubility of Ni is higher in the peaty riparian zone due to the higher DOC concentrations in the soil water. Data from Lidman et al. (2017a).*

Although Ni will not be reduced itself, the redox conditions can indirectly influence the mobility of Ni, especially in sulfide-rich environments. The solubility of NiS (millerite) is low – as are the sulfide compounds of many other transition elements, e.g. Fe, Zn and Cu. This can lead to accumulation of these elements in sulfate-reducing environments such as organic sediments (Sternbeck et al. 2000). Especially in areas like Forsmark, which are affected by post-glacial rebound, later oxidation of sulfide-bearing sediments may lead to mobilisation of appreciable amounts of Ni and other chalcophile elements (Nordmyr et al. 2008). Of special interest for the Forsmark area is the fact that the Ni also can be incorporated into siderite ($FeCO_3$) (Dublet et al. 2014). This is a mineral that might occur in reducing and carbonate-rich environments in Forsmark, but more investigations are probably needed to determine whether that is the case or not (Jaremalm et al. 2013).

Judging from peat cores from ombrotrophic wetlands, the atmospheric deposition of Ni has increased considerably since the onset of the Industrial Revolution (Krachler et al. 2003). Increasing nickel concentrations in lake sediments during the last 150 years have also been observed (Augustsson et al. 2010). Locally, the use of nickel has led to severe nickel contamination (Nieminen et al. 2002, Myking et al. 2009). Yet, it is uncertain to what extent anthropogenic sources contributes to the Ni concentrations in surface waters. Recent advancements have shown that there is a measureable fractionation of nickel isotopes in nature (Gueguen et al. 2013). Possibly, this may help resolve this question and contribute to a better understanding of the transport of nickel in the various environments.

2.1.3 The biological role of Ni

Nickel is a key constituent of a number of enzymes and is therefore essential to (at least some) plants and microorganisms (Chen et al. 2009, Zamble et al. 2017). It is suspected that Ni is essential also for animals, although there are uncertainties concerning its function (e.g. Welch 1981, Hausinger 1993). In plants, Ni is present in ureases, which are involved in the decomposition of urea. Deficiency of Ni has therefore, for instance, been observed to cause accumulation of urea in leaf tips of wheat (*Tritucum aestivum*), barley (*Hordeum vulgare*) and oat (*Avena sativa*) (Brown et al. 1987). The results was ca. 30 % lower root and shoot masses. The required amounts of nickel are, however, low, and Ni limitation is therefore rare, although it has been observed in certain Ni hyperaccumulators (Küpper et al. 2001). Instead, environmental problems related to Ni are more commonly associated with its toxicity at higher concentrations (e.g. Chen et al. 2009, Tóth et al. 2016). For example, high Ni concentrations can suppress the uptake of Fe, which results in chlorosis, since Fe is required for the synthesis of chlorophyll (Rahman et al. 2005).

Typical Ni concentrations in plants have been reported in the range 0.05–10 mg kg^{-1} (dry weight) (Nieminen et al. 2007). The root uptake of Ni is believed to occur by both active transport and passive diffusion (Seregin and Kozhevnikova 2006). The bioavailability – and therefore also toxicity – of Ni has been shown to be strongly dependent on the speciation, which in turn is dictated largely by organic matter (Martino et al. 2003, Weng et al. 2004). Nickel is one of the elements that successfully has been incorporated in the biotic ligand model (BLM), which allows an assessment of the Ni toxicity under various hydrochemical conditions based on the Ni speciation (Deleebeeck et al. 2009). The uptake of Ni is also affected by the presence of certain other elements. For example, it has been demonstrated that Zn, Mn and Co inhibit the uptake of Ni, whereas Cu, Fe and Mg do not. This would suggest that the uptake of Ni can occur via transporters sensitive to the three former metals (Onodera et al. 2018). Conversely, Ni has also been demonstrated to affect the uptake of other elements. For example, increased concentration of Ni in the soil solution has been observed to increase the concentration of Fe and Cu in roots of barley (*Hordeum vulgare*), while simultaneously decreasing the concentrations in shoots (Rahman et al. 2005). For Mn and Zn the same experiment showed a consistent decrease in both roots and shoots with increasing Ni concentrations. This indicates that there is a connection between how Ni, Cu and Fe are translocated within the plant.

In boreal forests with heavy atmospheric Ni pollution the adverse effects have mainly been linked to epiphytic lichens on tree trunks and more locally also the abundance of lichens and bryophytes on the forest floor, whereas the effects on the trees themselves were limited or absent (Myking et al. 2009). For humans, some forms of Ni, e.g. nickel sulfate, nickel oxides and nickel sulfides, are known to be cancerogenic (Sterner 2010). Several other deleterious effects have also been reported in connection with elevated exposure to Ni (Das et al. 2019). A more thorough review of the biological role of Ni and its uptake mechanisms has been compiled by Yusuf et al. (2011).

2.1.4 Radioecological relevance

From a radioecological perspective there are two important Ni isotopes: the relatively long-lived Ni-59 ($T_{½}=76$ ka) and the short-lived Ni-63 ($T_{½}=96$ a). In radioactive waste both isotopes are activation products from neutron radiation in nuclear power plants, but in the case of Ni-59 there is also a cosmogenic source in nature. Both radionuclides decay to stable daughters – Co-59 in the case of Ni-59 (mainly by electron capture) and Cu-63 in the case of Ni-63 (by β^- decay) – so there is no decay chain dynamics involved in the radiation doses caused by these radioisotopes. The dose coefficient for Ni-59 (ingestion) is relatively low, $6.3 \cdot 10^{-11}$ Sv Bq^{-1}.

2.2 Ni in the site investigation areas

2.2.1 Sources of Ni

The main sources of Ni to the ecosystems in Forsmark and Simpevarp are weathering of the local soils and atmospheric deposition. The relative contribution of these sources is important because it determines whether mobile fractions of Ni will be added primarily to surface soils or below ground, which has consequences for the long-term fate of Ni and its availability to different types of biota. Historically, weathering has been the major sources, but with the industrialisation the deposition of Ni has increased substantially, the main source being oil combustion (Krachler et al. 2003, Nieminen et al. 2007, Augustsson et al. 2010). In recent decades, however, the Ni emissions have decreased significantly in both Sweden and Europe as a whole (Danielsson and Pihl Karlsson 2016). Therefore, the contribution from atmospheric deposition is likely to decline in the future, although large portions of the Ni released can be expected to remain in the ecosystems for considerable periods of time yet.

In the Forsmark area it has been estimated that the Ni deposition currently exceeds the stream water export and the accumulation in lake sediments, which would indicate a substantial accumulation of atmospherically deposited Ni in the terrestrial environment (Tröjbom and Grolander 2010). However, based on such a mass-balance it is not possible to determine from where the Ni in soils, groundwater and surface water originates. Theoretically, all Ni in the runoff could come from deposition, but it is also possible that all deposited Ni is accumulating somewhere in the systems and that the runoff is dominated by weathering-derived Ni. In the absence of isotopic evidence some conjectures can be made based on comparisons with elements of known origin and the behaviour of Ni on the landscape scale. Ni could to some degree be compared to Pb, which is another divalent ion whose origin can be traced using stable isotopes. The pollution of Pb has been worse than for Ni, in relative terms, so atmospheric deposition of anthropogenic Pb has overshadowed the weathering of geogenic Pb from local soils even in relatively remote areas such as the Krycklan Catchment in northern Sweden (Laudon et al. 2013). Most of the deposited Pb has remained in the forest soils, and the anthropogenic Pb is not expected to peak in the stream water until 200–800 years from now (Klaminder et al. 2006, 2008). Yet, the effects of the deposition of Pb can be seen in the high fluxes of Pb from wetland-dominated catchments relative to forest-dominated catchments (Wällstedt et al. 2017). The reason is that the water transport through the top soils, where Pb is deposited, is much higher in the saturated peat than in a forest soil, where there is only percolation. Metals that are derived mainly from weathering tend to show the opposite pattern – high concentrations in forest-dominated catchments and low concentrations in wetland-dominated catchments, where there are no minerals that can be weathered (Lidman et al. 2014). Although the deposition of Ni in the Krycklan catchment is high enough to support the stream water export, the highest concentrations are observed in forest-dominated streams and not wetland-dominated streams (see Section 2.2.5). This would suggest that the major source of Ni to the surface water and groundwater would be weathering of local soils rather than atmospheric deposition. Therefore, it seems likely that this would be the case also in the site investigation area. It could be argued, on the one hand, that comparing Ni to Pb is unfair, since Ni generally would be more mobile that Pb, but on the other hand the relative deposition of Pb has also been much higher than for Ni. Therefore, most Ni found in groundwater and surface water is likely to derive from weathering of local soils.

2.2.2 Ni in soils

In analysed till samples from Forsmark (n = 59) the Ni concentrations mostly varied between 2.9 µg g^{-1} and 18 µg g^{-1} (Figure 2-2). This means that the Ni concentrations in Forsmark are somewhat on the low side compared to the estimated average Ni concentration of upper continental crust (ca. 19 µg g^{-1}). However, Swedish soils generally have relatively low Ni concentrations (Wedepohl 1995, Tóth et al. 2016). The median Ni concentration in Swedish soils (n = 2 578) is 11.3 µg g^{-1}, and the median concentration of Ni in soils in Uppsala County (n = 58) is even lower, 8 µg g^{-1} with 10th and 90th percentiles of 5 µg g^{-1} and 16 µg g^{-1}, respectively (Andersson et al. 2019). Hence, the observed levels in the Forsmark area appear to be normal for this part of Sweden.

Two deep (5.7–7 m) till samples from the east side of Eckarfjärden (SFM0016), however, contained up to 32 µg g^{-1} of Ni (Figure 2-2). These samples were also characterized by high concentrations of, for example, Co, Cr, Fe, Mg and Zn. These two samples represent a harder clayey till layer found underneath a 5.7 m layer of sandy till, which is more typical for the area (Hedenström et al. 2004). Hence, it does not seem implausible that the chemical composition of this deeper clayey till would differ. It can be noted that while the bedrock of the Forsmark area largely is dominated by granite and granodiorite, there is an area with more Fe-rich rocks such as schist and gabbroid-diorite traversing Eckarfjärden, which locally could have had an impact on the mineralogical composition of the till.

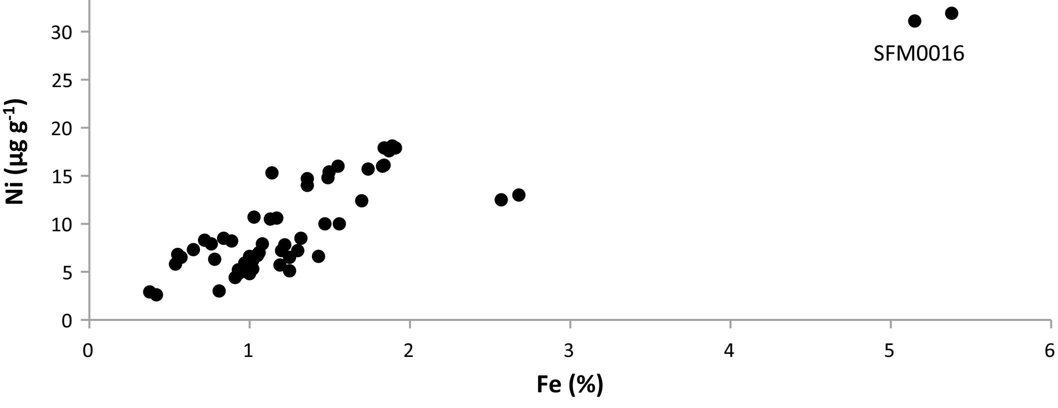

Figure 2-2. Concentration of Ni and Fe in till samples from Forsmark. Particularly high concentrations were encountered in till samples from 6.6–7.2 m in SFM0016, located just east of Eckarfjärden.

A few hundred metres northwest of Eckarfjärden there is also an abandoned 10 × 5 m pit ("Habbalsbo järngruva"), where magnetite was mined from an actinolite ore (Wik et al. 2006). Geochemically Ni can substitute for a number of different cations in minerals, but it is often associated with Fe in primary minerals (Alloway 2012). In Forsmark Ni in till correlated most strongly with Cr ($r = 0.89$, $p < 0.01$) and Fe ($r = 0.87$; $p < 0.01$) (Figure 2-2). Therefore, it is likely that this anomaly in SFM0016 is associated with a slightly different mineralogy, possibly related to the presence of Fe-rich minerals in the local bedrock.

In the Simpevarp area the Ni concentration in till ($n = 22$) is generally somewhat higher than in Forsmark; concentrations between 8.1 µg g^{-1} and 33 µg g^{-1} have been observed (Figure 2-3). The median Ni concentration in soils in Kalmar County is 8 µg g^{-1} with 10th and 90th percentiles of 4 µg g^{-1} and 21 µg g^{-1}, respectively (Andersson et al. 2019). In this context the Ni concentrations in the Simpevarp area appear somewhat high, but then Simpevarp is located in the northern parts of Kalmar County, whose Quaternary deposits and bedrock differ from the southern parts of the county, especially Öland. Nickel was positively correlated to the same group of elements as in Forsmark, e.g. Zn ($r = 0.81$), Pb (0.82), Co ($r = 0.77$) and Fe ($r = 0.72$, $p < 0.01$ for all). Therefore, it is likely that Ni mostly occurs in some Fe-bearing minerals at both sites, for instance hornblende. One soil sample with conspicuously high Ni concentration in relation to Fe and Zn had high content of organic matter (LOI = 38 %) so it represents another type of soil.

Figure 2-2 illustrated the Ni concentrations in till soils in Forsmark, but other soils types are also abundant in the area. In connection with the Kd measurements Sheppard et al. (2011) analysed different types of Quaternary deposits in Forsmark, which displayed a wider range of Ni concentrations (Figure 2-4). The clayey till samples that were used displayed Ni concentrations mostly between 10 µg g^{-1} and 20 µg g^{-1}. These observations fall within the range observed in the other till samples in Forsmark (Figure 2-2), but on average they are higher. This could be related to mineralogical differences between different particle sizes and a higher Ni content in finer material.

Even higher concentrations of Ni were encountered in clay gyttja and, above all, the glacial clay, where Ni concentrations up to 36 µg g^{-1} and 48 µg g^{-1}, respectively, were found. These high Ni concentrations are consistent with marine clay sediments sampled outside Forsmark, where Ni concentrations up to 67 µg g^{-1} have been found (PFM006062). The lowest Ni concentrations were found in the more organic peat soils – cultivated peat and wetland peat (Figure 2-4). Yet, the lowest detected Ni concentration was 0.77 µg g^{-1}, which is almost as much as the lowest concentrations observed in the till samples from the installation of the groundwater wells in Forsmark (Figure 2-2).

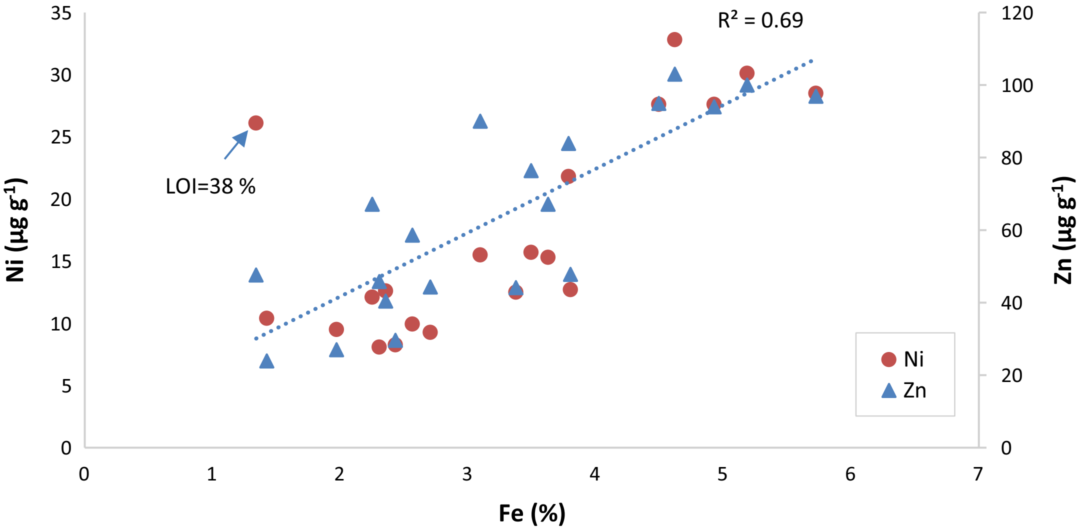

Figure 2-3. *Ni and Zn concentrations in soils from the Simpevarp area as a function of the Fe concentration. One soil sample had a high concentration of organic matter (LOI = 38 %). The regression line refers to the relationship between Zn and Fe.*

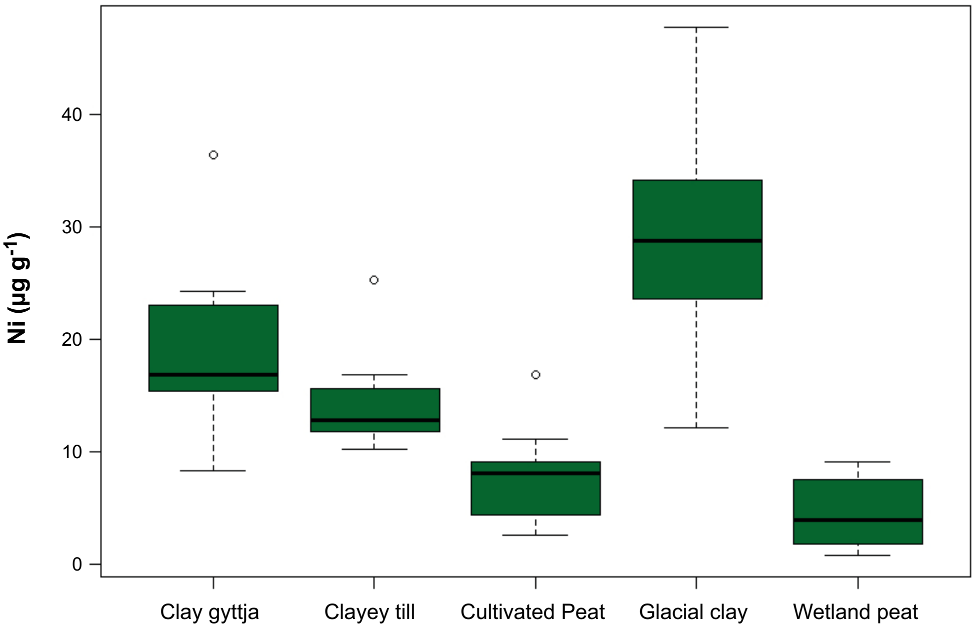

Figure 2-4. *Ni concentration in different types of soils from the Forsmark area. Data from Sheppard et al. (2011). These soil samples were used to calculate the Kd values for Ni in the safety assessment.*

The comparatively low Ni concentrations in peat soils should, however, not be interpreted as Ni having low affinity for organic matter. On the contrary, if Ti is used as an indicator of the mineral fraction, the Ni/Ti ratios suggest that accumulation of Ni from the dissolved phase in relative terms has been most important in the peat soils, i.e. in relation to the total amount of Ni found in these samples (Figure 2-5). From a biogeochemical and radioecological perspective this is the most interesting fraction to study because if natural or radioactive Ni at some point is mobilised and transported in the surface environment it is likely to be dissolved in the aqueous phase in one way or another. The low Ni/Ti ratios in the clay soils indicate that Ni predominately is present in minerals, but slightly elevated Ni/Ti ratios in some of the more organic clay gyttja samples suggest that accumulation of Ni from the dissolved phase also may have occurred in the gyttja sediments (Figure 2-5). The behaviour of Ni in sediments and wetlands will be investigated in more detail below (see Section 2.2.5).

The strong control of the mineral fraction over the Ni concentrations in different types of soils is also emphasised by the dependence on Fe (Figure 2-6). A similar relationship could be observed also for Co, which could be expected to reside largely in the same minerals as Ni. It can be noted that the clayey gyttja sediments contained less Ni and Co than expected and that some peat soils contained more Ni than expected from the overall relationship to Fe. As discussed above, this indicates that there has been some sorption processes and not just sedimentation or transport of mineral particles. The higher Ni concentration compared to the Co concentration in the more or less organic peat and gyttja soils could, for instance, reflect the fact that Ni has a higher affinity for organic matter.

Further investigations into the distribution of elements in different soil fractions have been carried out in the Simpevarp area, where in total seven soil samples from three sites were selected for sequential extraction (Lundin et al. 2006). The investigated sites represented a brown soil profile (sandy till) from an oak forest (*Quercus robur*), a peat soil with alder forest (*Alnus spp.*) and a drained peat soil with spruce forest (*Picea abies*). Soil material from 2–3 different depths (between 0 cm and 65 cm) was subjected to extraction by ammonium acetate, dithionite citrate and *aqua regia*, which resulted in a total of 21 extraction samples. Ammonium acetate is believed to mobilise the exchangeable fraction, while dithionate citrate will dissolve crystalline and amorphous Fe and Mn oxyhydroxides (Filgueiras et al. 2002). *Aqua regia*, finally, will attack the residual soil fraction, although it does not represent the total concentration because it does not dissolve, for instance, some silicates and Al and Fe minerals (Santoro et al. 2017). Digestion by *aqua regia* was also the method applied in the site-specific Kd measurements by Sheppard et al. (2011), which are used in the dose models (see Section 2.2.7).

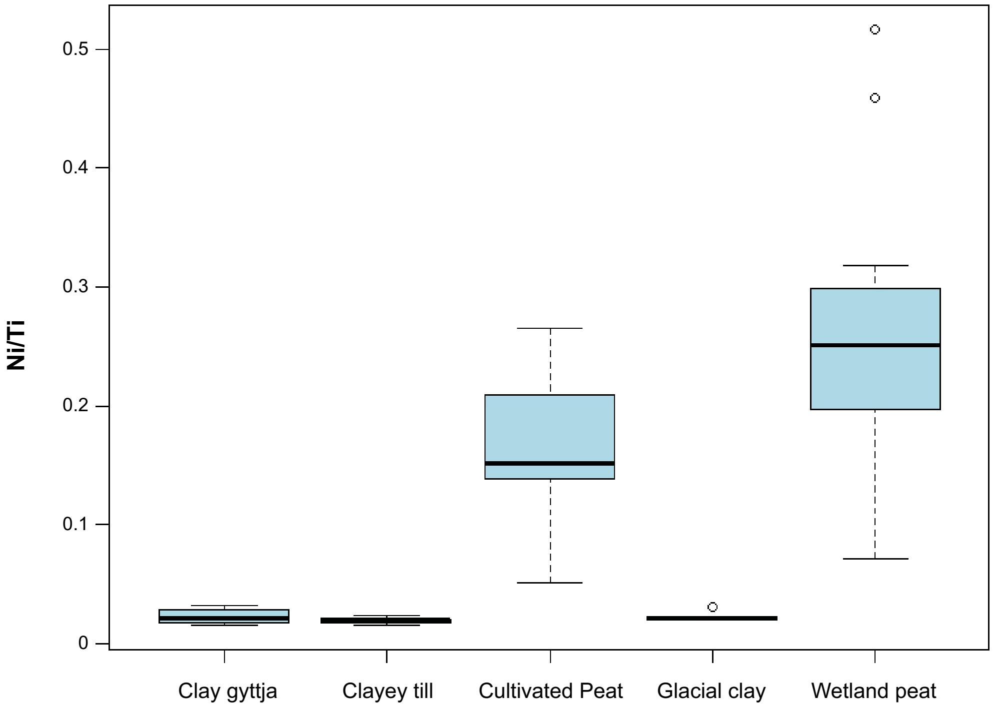

Figure 2-5. *Ni/Ti ratios (by mass) in different soil types in the Forsmark area. Data from Sheppard et al. (2011).*

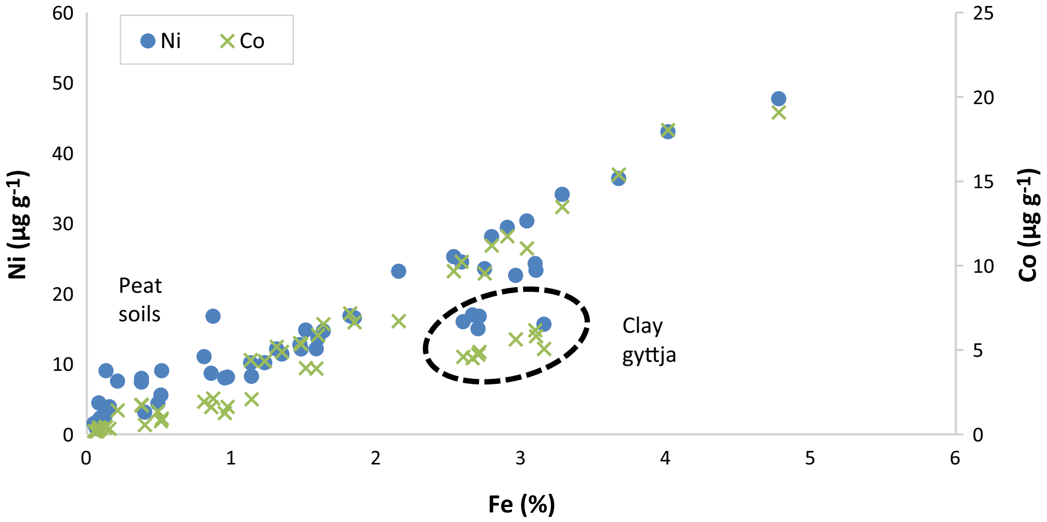

Figure 2-6. *Ni and Co concentrations in different types of soils from the Forsmark area (as in Figure 2-5) as a function of the Fe concentration. Data from Sheppard et al. (2011).*

The concentration of exchangeable Ni in the investigated soils ranged from 0.026–1.7 µg g^{-1}, which corresponded to 0.75–9.0 % of the concentration extractable by *aqua regia*. This represents the most active fraction of Ni in the soils, which is most easily mobilised and thereby potentially can become available to biota. The exchangeable fraction of Ni in the soils was most closely related to several of the other divalent transition metals like Cd, Co and Zn, but it also showed clear similarities to S (Figure 2-7). Substantially higher Ni concentrations were extracted with dithionite citrate and *aqua regia*, which indicates that most of the Ni in the soils is not readily available to organisms. The highest concentration of exchangeable Ni was found in organic soils of the alder fen. This is not surprising given the comparatively high affinity of Ni for organic matter.

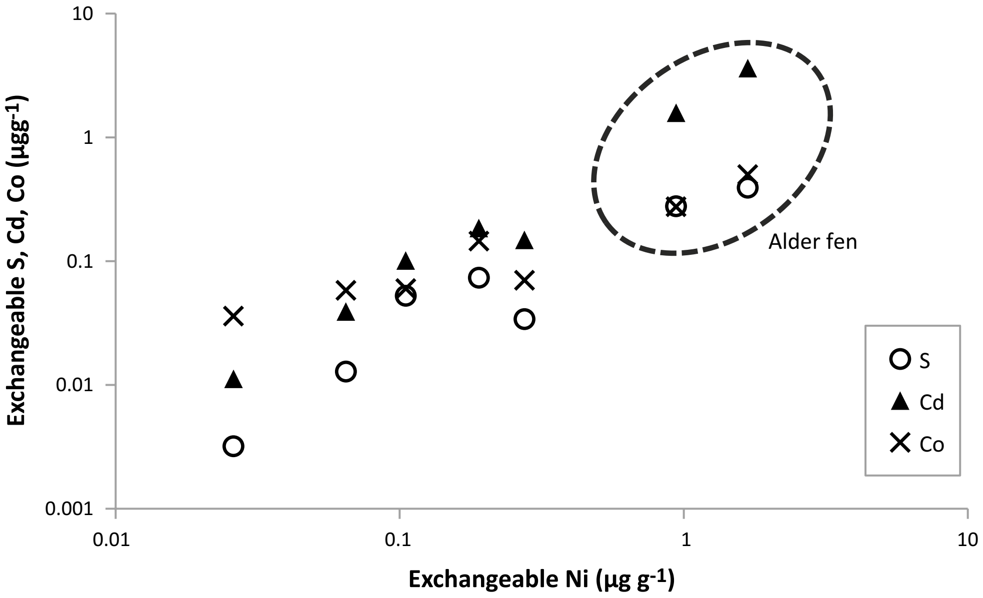

Figure 2-7. Exchangeable concentrations of Ni vs. exchangeable concentrations of S, Cd and Co, respectively, in seven soil samples from Simpevarp. Data from Lundin et al. (2006).

2.2.3 Nickel in near-surface groundwater

In near-surface groundwater (i.e. groundwater in Quaternary deposits) the observed Ni concentrations ranged over more than two orders of magnitude, from 0.15–24 µg L^{-1} in the Forsmark area (n = 135 from 24 groundwater wells). Most groundwater samples, however, had Ni concentrations < 1 µg L^{-1} with a median concentration of 0.89 µg L^{-1}. It should be noted, however, that nearly all groundwater samples were collected from till so the concentrations may not necessarily reflect groundwater in other types of Quaternary deposits in the area. All wells also collect relatively deep groundwater – the average screening depth varied between 1.6 m and 9.6 m – so the groundwater chemistry presented below may also differ from shallower groundwater in the area. In Simpevarp the Ni concentrations were generally higher than in the Forsmark area, most likely reflecting the higher Ni concentrations in the soils, and ranged from 0.26–40 µg L^{-1} with a median concentration of 3.3 µg L^{-1} (n = 101 from 31 groundwater wells).

Some of the observations of high Ni concentrations, however, might be related to analytical or sampling-related problems. For instance, the observation of 24 µg L^{-1} in Forsmark was made in a 5.1 m deep in well, SFM0051, located near Norra bassängen, as part of a time series of 11 observations. Six observations prior to this observation showed Ni concentrations < 2 µg L^{-1}, and no notable changes in the major elements, including Fe and Mn, could be observed in connection with this shift in Ni concentration. However, several other trace elements, e.g. Cd, Zn and Cr, displayed more or less drastic increases in connection with this sampling, suggesting that something extraordinary may have occurred with respect to this sample. Judging from the elements that were affected it is possible that there was some oxidisation of sulfides involved, but there are no sulfide measurements available from this well to support that. Likewise, the highest concentration of Ni in groundwater in Simpevarp, 40 µg L^{-1}, was recorded in a sample where the chemistry seems rather peculiar. This well (SSM000041, 2–4 m deep) in the Laxemar area was drilled in July 2004, and the first water sample, which had the high Ni concentration, was collected in June the following year (Johansson and Adestam 2004). The next sampling of this well was made in September 2005, and then the Ni concentration had declined by more than an order of magnitude to 3.5 µg L^{-1}. Similar trends were observed for a wide range of other trace elements, e.g. Co, Cr, Cu, Pb, V and Zn. In total, this well was sampled five times throughout 2005 and 2006, and the Ni concentration later increased to 16 µg L^{-1} again. What is most conspicuous about this well (and some other ones) were the occasionally high Al concentrations. For instance, the sample from SSM000041 with 40 µg Ni L^{-1} also contained 27 mg Al L^{-1}, which is a remarkably high Al concentration even for groundwater (Bertills 1995). At the next sampling occasion the Al concentration had declined to 1.2 mg L^{-1}, which is a more normal value. Given that pH in the well was 6.6–6.9 the solubility of Al should be low in this groundwater, and since the samples were filtered they should not be affected by particles. Peltola (2018) therefore suggested that some Al-rich colloidal phase could be present in the groundwater. This would be related to the fact that some groundwater wells in the Simpevarp area were installed without a proper bottom piece that would allow for sedimentation of suspended particles. Hence, there are reasons to be cautious, particularly concerning some of the higher observed concentrations.

Overall Ni was significantly correlated to Al in the Simpevarp area ($r = 0.77$, $p < 0.001$ for the log concentrations), which partly could be related to the artefacts discussed above (Figure 2-8). Ni and Al are generally not that similar in their chemical behaviour, but if there, for example, would be some gibbsite-like colloidal phase present in the groundwater, it is possible that this would affect Ni and also other elements (Yamaguchi et al. 2002). As a comparison, a maximum Al concentration of 0.90 mg L^{-1} was observed in groundwater in the Forsmark area, which seems more normal (Bertills 1995). Ni and Al were positively correlated also in the Forsmark area, but the correlation was noticeably weaker ($r = 0.27$, $p < 0.01$ on the logarithmic scale), suggesting that there were other factors more important for controlling the Ni concentration in the groundwater in Forsmark. Since Al is abundant in silicate minerals and its release controlled by its solubility, the differences between Forsmark and Simpevarp with respect to Al should not be related to the mineralogy.

In the Forsmark area Ni instead correlated more strongly to Ca ($r = 0.55$, $p > 0.001$ on a logarithmic scale, Figure 2-9). It is not obvious why Ni would correlate to Ca, but given the strong influence of calcite on the groundwater chemistry Ca is in most samples the dominating cation. Thus, a high concentration of Ca would enhance the mobility of Ni in the groundwater, since Ca will compete for sorption sites (Wang et al. 1997). Because many groundwater samples were saturated with respect to $CaCO_3$ Ca is also negatively correlated to pH ($r = -0.46$, $p < 0.001$), which controls the carbonate system (Jaremalm et al. 2013). Although Ni itself was not significantly correlated to pH, part of the relationship with Ca could therefore also reflect higher sorption of Ni at high pH due to less competition form H^+. Low Ca concentrations typically occur when pH and, consequently, the carbonate concentration are high.

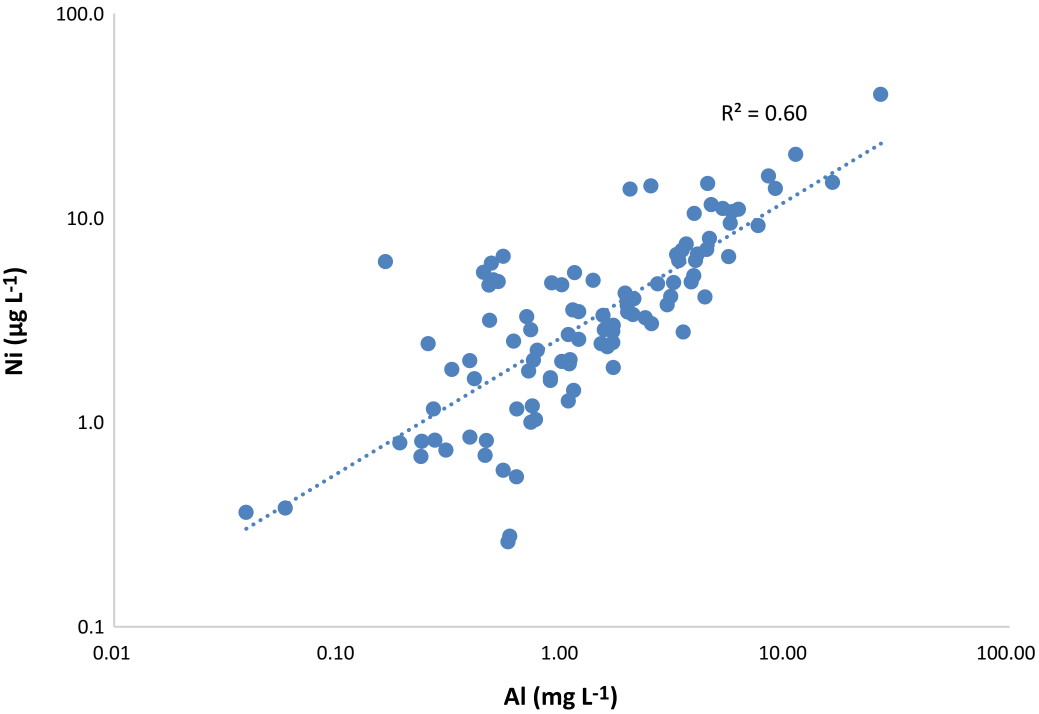

Figure 2-8. *Concentrations of Ni and Al in groundwater in the Simpevarp area. Note that the quality of some of these groundwater samples has been questioned (Peltola 2018).*

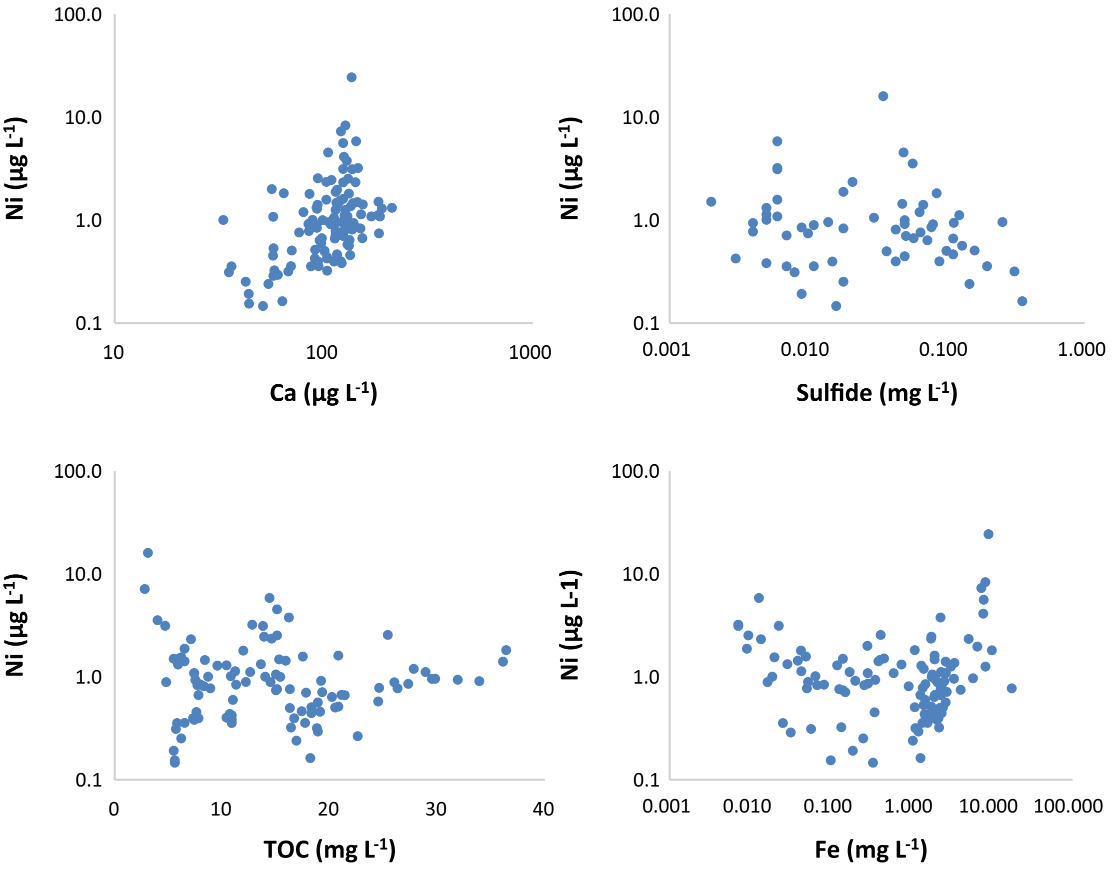

Figure 2-9. *Ni concentration in groundwater in Forsmark as a function of Ca, sulfide, TOC and Fe, respectively.*

In addition to Ca, Ni is also likely to be dependent on a number of other factors. As illustrated by Figure 2-9, the Ni concentration tended to be low when the sulfide concentration was high (ca. > 0.1 mg L^{-1}). These groundwater samples most likely represent locations where there is a precipitation of sulfide minerals, which could be expected to remove Ni from the groundwater (Åström 1998). Low Ni concentrations were, however, occasionally observed under conditions with low sulfide concentrations as well so even if this interpretation would correct, it must be acknowledged that low Ni concentrations can be caused by other factors as well. Hence, there was no significant correlation between Ni and sulfide at the 95 % confidence level – at least not before other sources of variation were taken account for. Furthermore, the mobility of Ni should generally be expected to increase in the presence of organic matter in the groundwater (Dahlqvist et al. 2007), but at first glance there was no such pattern in the groundwater (Figure 2-9). However, when combining TOC with Ca in a multiple regression a positive dependence of Ni on the TOC concentrations emerged. Adding also the sulfide concentration to the regression resulted in

$$\log(Ni) = -2.85 + 0.00801Ca + 0.0503TOC - 0.247\log(S^{2-}), \qquad \text{Equation 2-1}$$

where Ni, Ca, TOC and S^{2-} (sulfide) represent the concentration of each substance in the groundwater. Combined in this manner these variables could explain 55 % of the variation in the Ni concentration, and all coefficients were significant at the 0.001 confidence level (n = 57 due to incomplete sulfide data). Although questions could be raised concerning the distributions of these parameters, the important thing from a geochemical point of view is not primarily the coefficients themselves, but rather the general dependence of Ni on these parameters, i.e. whether there is a significant positive or negative influence on the Ni concentration. The correlation to Ca remains positive in the multiple regression, as discussed above (Figure 2-9), but, when accounting for Ca, TOC also has a significant positive influence on the Ni concentration. This is logical given that Ni has a high affinity for organic matter and often occurs as organic complexes in natural waters (Dahlqvist et al. 2007). The negative dependence on sulfide also seems logical given that Ni easily can be removed from solution when sulfide minerals are precipitating (Åström 1998). Combined these parameters can explain at least some of the variability of Ni in the groundwater and highlight some of mechanisms that could control the mobility of Ni in the groundwater (Equation 2-1).

Looking at more minor constituents of the groundwater, Ni was associated with approximately the same type of elements as in the soils, e.g. Co (Figure 2-10). The correlation (on a logarithmic scale) was stronger in Simpevarp ($r=0.89$, $p < 0.001$, $n=99$) than in Forsmark ($r=0.64$, $p > 0.001$, $n=128$). Since Co is not a very abundant element, it cannot be expected to have any major influence on the groundwater and the processes going on there. Instead, the general similarities between Ni and Co suggest that they broadly speaking are affected by the same processes, albeit to different degrees, and the fractionation between them can therefore provide some hints about what processes govern their mobility. Part of the fractionation between Ni and Co in the groundwater in Forsmark appears to be related to Mn, which correlated negatively to the Ni/Co ratio in the groundwater, again on a logarithmic scale ($r=-0.42$, $p < 0.001$, $n=121$). This is, in turn, likely to be related to the redox chemistry of Mn, which is mobile in its reduced form (as Mn^{2+}) but easily precipitates when oxidised, e.g. as MnO_2. As further discussed below (Section 3.2.4), Co has a higher affinity for Mn oxides than Ni (Appelo and Postma 1999). No data on the Mn speciation in the groundwater is available, but generally it should be expected to be present in its mobile reduced form (Mn^{2+}). The generally high pH of the groundwater in the Forsmark area would, however, favour the oxidation of Mn^{2+} relative to areas without $CaCO_3$ in the soils. There are also examples of comparatively high O_2 concentrations in the groundwater, for example the groundwater well SFM0006, which is located east of Fiskarfjärden. At a depth of 3.3 m two observations that were made two years apart showed an O_2 concentration in the groundwater of 8.7 mg L^{-1}. Mn was measured four times in this well during the same period, resulting in concentrations from 0.0027–0.11 mg L^{-1}. The wide range suggests that Mn in some cases was oxidised and in some cases not. In two of the samples – both with high relatively high Mn concentrations – both Fe^{2+} and total Fe were determined, showing that ca. 30–36 % of the Fe was oxidised (Fe^{3+}). The validity of these measurements is corroborated by the O_2 concentration of the groundwater, which was negatively correlated to the fraction of Fe^{2+} ($r=-0.92$, $p < 0.01$), as illustrated in Figure 2-11. High O_2 concentrations and a high fraction of Fe^{3+} tended to occur in groundwater wells in recharge areas. Although Mn^{2+} is not as easily oxidised as Fe^{2+}, it does not seem far-fetched to assume that also Mn could be undergoing redox reactions in some of these groundwater wells. Oxidation of both Fe and Mn would be favoured by the generally high pH in the Forsmark area. Combined these observations suggest that part of the differences observed between Ni and Co in the groundwater could be related to the oxidation and reduction of Mn even at considerable depth (i.e. several meters deep).

Principal component analysis of near-surface groundwater

A principal component analysis of near-surface groundwater in Forsmark showed that PC1 and PC2 could explain 27.5 % and 15.7 % of the variation in the groundwater chemistry (Figure 2-12). The first principal component was apparently associated with marine influences, gathering elements such Na, Mg, Sr, K, I etc., which all are abundant in sea water, in the right-hand side of the graph. More insoluble elements, like the REEs, which derive primarily from weathering of local soils, are found approximately in the opposite direction along PC1.

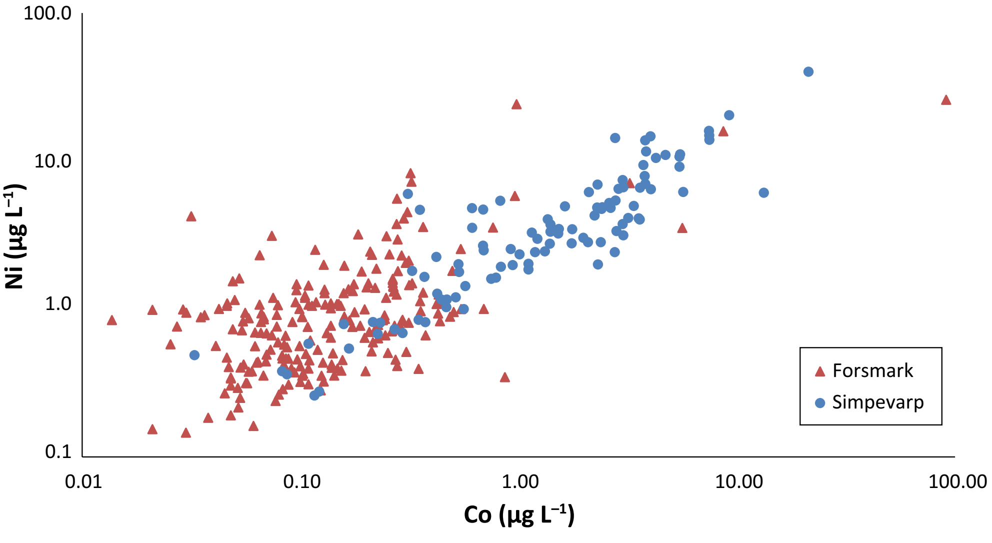

Figure 2-10. *Concentrations of Ni and Co in groundwater from Forsmark and Simpevarp, respectively.*

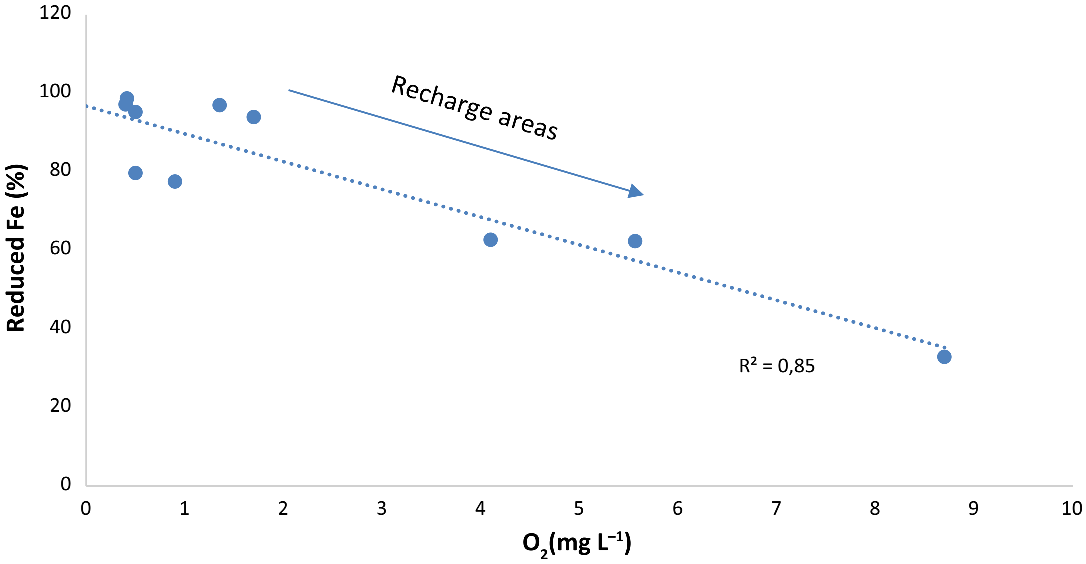

Figure 2-11. *Fraction of reduced Fe (Fe^{2+}/Fe_{tot}) as a function of the O_2 concentration in groundwater in Forsmark. Groundwater wells with high O_2 concentrations and high fractions of oxidised Fe are all found in recharge areas.*

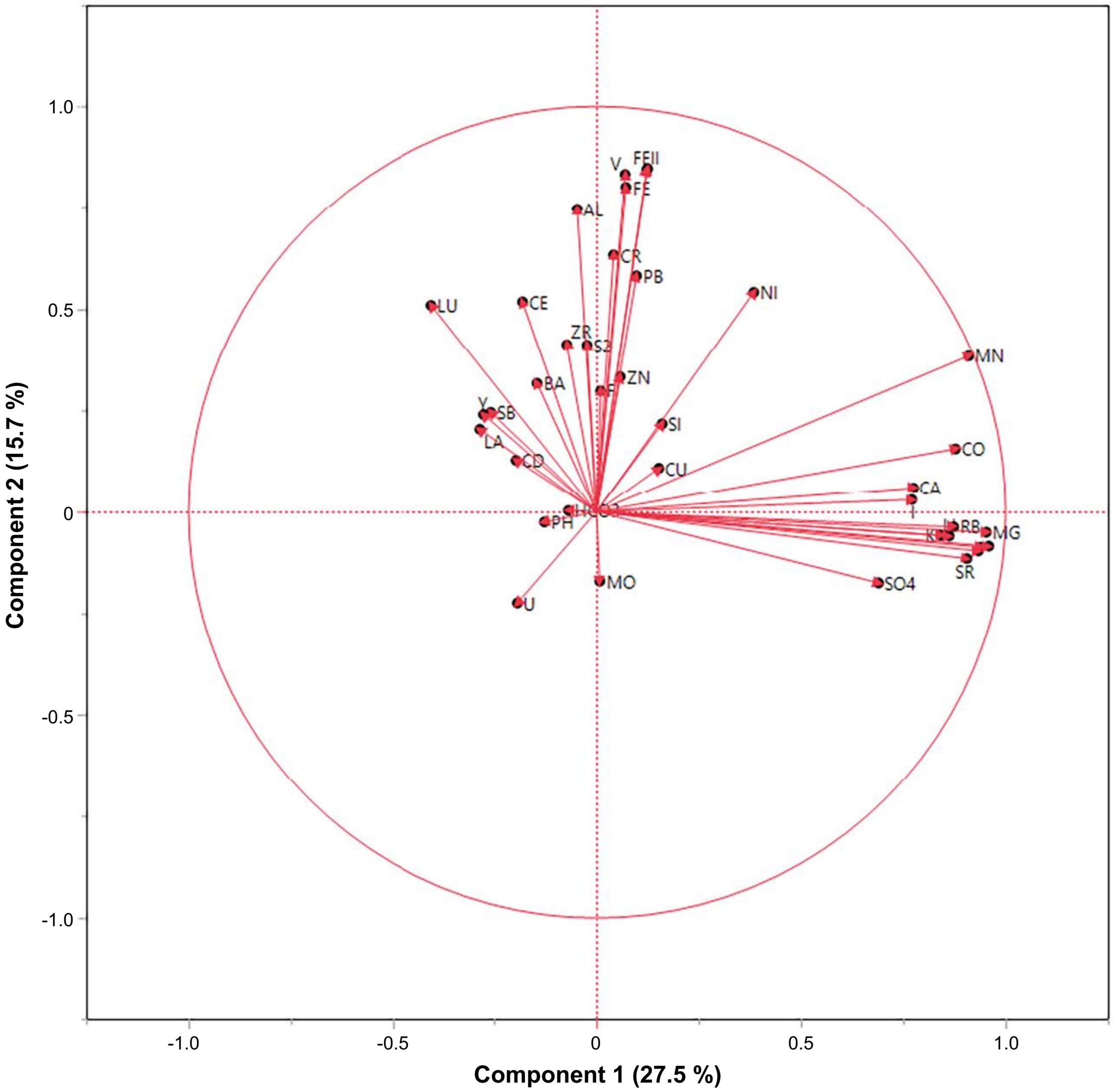

Figure 2-12. *The two first principal components of a PCA of near-surface groundwater from Forsmark. Note that not all REEs are included in the analysis, only La, Ce and Lu.*

The second principal component appears to be related to the redox conditions in the near-surface groundwater. Sulfide, Fe(II) and total Fe are, for example, found close to PC2 in the upper part of the graph. Elements like Cr, Zn and Ni, which often are associated with Fe, are also found in this area, while Mn and Co are more associated with the marine component. In the opposite direction above all Mo and U are found, which both can be immobilised under reducing conditions (see Section 3.1.1). As demonstrated below, strong accumulation of Mo and U can be observed in sulfidic lake sediments in the Forsmark area, which is entirely consistent with this pattern (see Section 3.2.5).

2.2.4 Ni in lakes

Compared to the near-surface groundwater the Ni concentration in surface water was lower in both the Forsmark and the Simpevarp area (Figure 2-13). In the Forsmark area Ni concentrations ranging from 0.14 µg L^{-1} to 2.8 µg L^{-1} were observed (n = 83 representing eight lakes). The median Ni concentration was 0.41 µg L^{-1}, and with two exceptions all observations displayed Ni concentrations < 1 µg L^{-1}. Sampling of eight streams in the Forsmark area (n = 83) showed Ni concentrations in approximately the same range, between 0.18 µg L^{-1} and 1.5 µg L^{-1} with a median of 0.48 µg L^{-1}. A main reason for the lower Ni concentrations in streams and lakes as compared to groundwater is probably that the sampled groundwater generally has been in contact with the mineral soils for longer periods of time. As previously mentioned, all groundwater wells are relatively deep (< 1.6 m) in the sense they probably do not reflect the water chemistry of near-surface soils very well. From precipitation to groundwater at 1.6 m (or below) significant changes in the water chemistry should be expected, e.g. increasing influence from weathering and higher concentrations of more soluble weathering products (e.g. Jutebring Sterte et al. 2021). Hence, there are reasons to suspect that shallower groundwater and soil water could have lower Ni concentrations. If lakes and streams mainly are fed by such shallower groundwater sources, this could explain the generally lower Ni concentrations in surface water as compared to the near-surface groundwater sampled in these comparatively deep groundwater wells (Figure 2-13; Lidman et al. 2017a).

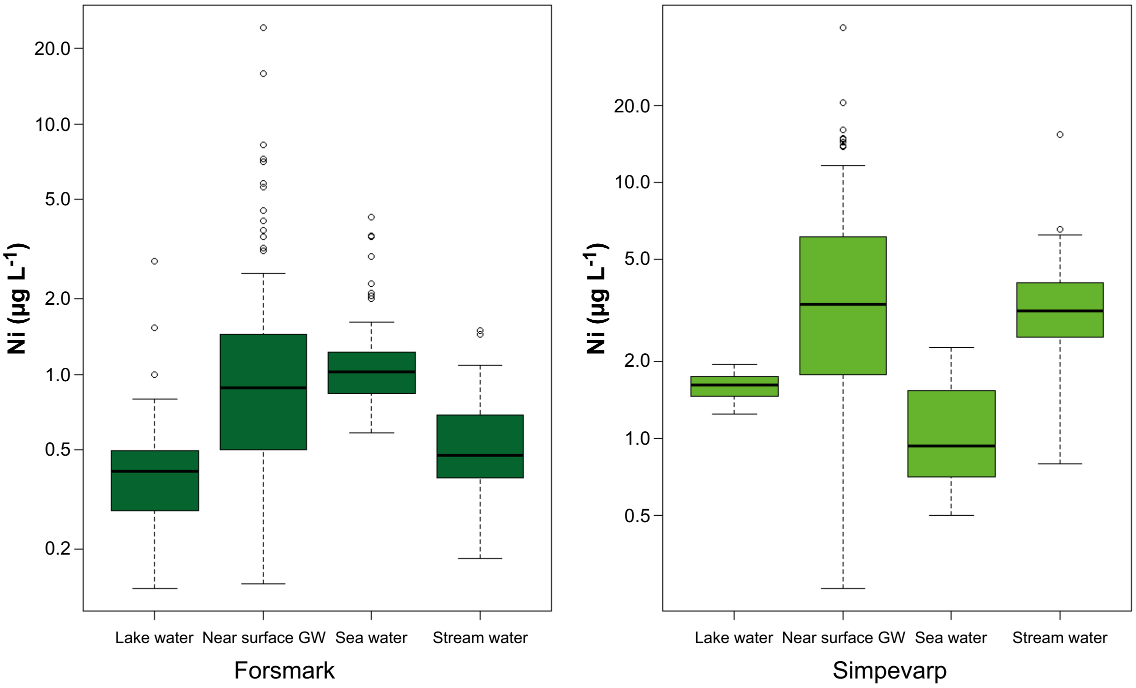

Figure 2-13. *Ni concentrations in different types of water in the Forsmark and Simpevarp areas, respectively.*

In the Simpevarp area there are fewer lakes and the only sampled lake, Frisksjön, had Ni concentrations in the range 1.2–1.9 µg L^{-1} (n = 10). In stream water (n = 27) the Ni concentrations ranged between 0.79 µg L^{-1} in a stream near Plittorp (PSM002071) and 15 µg L^{-1} in a stream near Basteböla (PSM002086), south of Laxemar. The generally higher Ni concentrations in the surface water of the Simpevarp area compared to the Forsmark area probably reflect the higher abundance of Ni in the local soils and higher weathering rates of Ni-bearing minerals in the Simpevarp area (Section 2.2.2; Figure 2-13). Compared to the Forsmark area, the streams in the Simpevarp area had Ni concentrations that were more on par with the groundwater.

The investigation of lakes and streams was conducted on a seasonal basis for trace elements like Ni, i.e. four samples per year, but higher sampling resolution is available for pH and major elements. Generally, the highest concentrations were observed during the winters, but there was considerable variation between the lakes (Figure 2-14). For instance, in Eckarfjärden the Ni concentration remained low during the winters, and the highest concentrations were instead observed during the spring. In Labboträsket, on the other hand, the Ni concentration declined throughout the year, from winter to autumn. Some of these differences can probably be explained by the characteristics of the different lakes and their catchments. All lakes in the Forsmark area are shallow with a mean depth of < 1 m, which contributes to short retention times in many cases, especially for some of the smaller lakes. For instance, the retention time in Labboträsket is seven days, which means this lake will be strongly influenced by changes in the Ni concentration of the inflowing water. The lakes in the Forsmark area are generally characterised by inflow from the groundwater to lake during the winters and outflow from the lake to the surrounding soils during the summers. Since groundwater tends to have relatively high Ni concentration, this might explain why most lakes have higher Ni concentrations during the winters (Figure 2-13). Alternatively, the increase in concentrations could also be caused by that fact that a considerable fraction of the lake water freezes during the winter. If so, this should lead to a general increase of most solutes, in particular more conservative ones. However, since no such patterns could be observed from Na, which is an example of a solute that should remain in solution when parts of the lake water freezes, this does not seem to be the main explanation to the increasing Ni concentrations observed in most lakes during the winter.

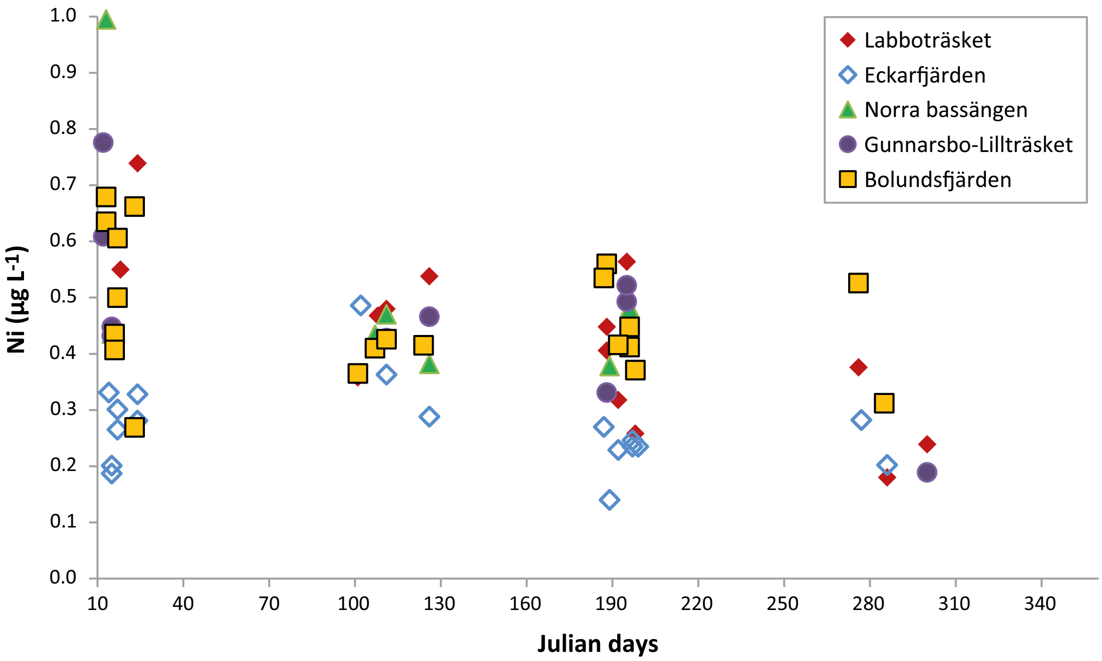

Figure 2-14. *Seasonal variation in Ni concentrations in the lakes of Forsmark (2002–2006). Not shown in the graph is one observation (2.8 µg L^{-1}) from Gunnarsbo-Lillfjärden.*

The larger lakes in the area – Eckarfjärden, Fiskarfjärden and Bolundsfjärden – have considerably longer retention times the smaller lakes, reaching nearly a year for Eckarfjärden (Table 2-1). A longer retention time implies that the lake has higher capacity to buffer chemical changes induced by inflowing water. In addition to the mixing of water volumes longer retention times also increase the potential for biogeochemical processes in the lakes to affect the water quality. For example, the biologically driven increase in pH in lakes during the growing season causes precipitation of $CaCO_3$ in the lakes in Forsmark, which could contribute to scavenging of Ni and many other trace elements (Zachara et al. 1991, Jaremalm et al. 2013). Another factor is the redox conditions in the lake and the sediments, which can vary considerably in these shallow lakes between the well-oxygenated summers and the ice-covered winters, as further discussed below.

Table 2-1. Some lake and catchment characteristics for the lakes that were analysed for trace elements. Frisksjön is located in the Simpevarp area and the rest of the lakes in the Forsmark area. The relatively large Fiskarfjärden is also shown, although no trace element data is available. Water chemistry data is also missing from Stocksjön, but a sediment core from this lake/wetland has been investigated. Data from Brunberg et al. (2004a, b).

	Elevation (masl)	Lake area (km^2)	Mean depth (m)	Retention time (d)	Catchment area (km^2)	Water (%)	Forest (%)	Wetland (%)
Gunnarsbo-Lillfjärden	1.60	0.033	0.7	7	5.12	1	73	22
Labboträsket	3.56	0.069	0.3	7	3.93	1	75	20
Norra bassängen	0.56	0.076	0.3	5	8.67	10	69	17
Bolunds-fjärden	0.64	0.61	0.6	77	8.00	9	70	16
Eckarfjärden	5.37	0.28	0.9	328	2.27	10	64	15
Fiskarfjärden	0.54	0.75	0.4	155	2.93	14	68	17
Stocksjön	2.92	0.036	0.2	9	2.48	9	65	16
Frisksjön	1.37	0.13	1.7	264	1.85	6	85	1

Part of the differences observed between the lake water chemistry are likely to be related to the characteristics of the lakes and their catchment. The lakes in the Forsmark area are shallow with a mean depth of < 1 m in all investigated lakes (Table 2-1). Partly as consequence of this, the water retention time in the smaller lakes – Gunnarsbo-Lillfjärden, Labboträsket and Norra bassängen – is short, one week or less. For the larger lakes – Eckarfjärden, Fiskarfjärden and Bolundsfjärden – the retention times are considerably longer, reaching nearly a year for Eckarfjärden (Brunberg et al. 2004). This leaves more time for processes in the lake to affect the cycling of Ni and other elements. On the landscape-scale this was most evident during the winters, when the Ni concentration in the different lakes was significantly lower in lakes with longer water retention times (Figure 2-15). There are several possible explanations to this pattern, but similar trends could be observed also for other elements, e.g. Ca, Fe, Cr, Mo, U, Si, REEs and S (sulfate). This would suggest that the lower Ni concentrations in lakes with long retention times actually could reflect removal of Ni and certain other elements from the water column. Given the relatively long retention times of the larger lakes, the removal does not necessarily have to be related to processes during the winter. For instance, in the case of Ca the responsible mechanism is most likely precipitation of $CaCO_3$, which occurs mainly during the growing season (Jaremalm et al. 2013). By fitting an exponential regression to the observations it can be estimated that the removal rate of Ni from the lake water is approximately 0.2 % per day (Figure 2-15). Extrapolated over a year this rate would imply that ca. 50 % of the Ni would be lost to the sediments (although most of the lakes in the area obviously have much shorter residence times). However, an understanding of what process might be responsible for this scavenging of Ni requires a more detailed assessment of the development of the lake water chemistry and the composition of the sediments. It should also be acknowledged that the number of observations in this case is low (n = 6) so even if the correlation (Figure 2-15) is statistically significant, some caution is warranted. There could easily be other parameters causing this pattern.

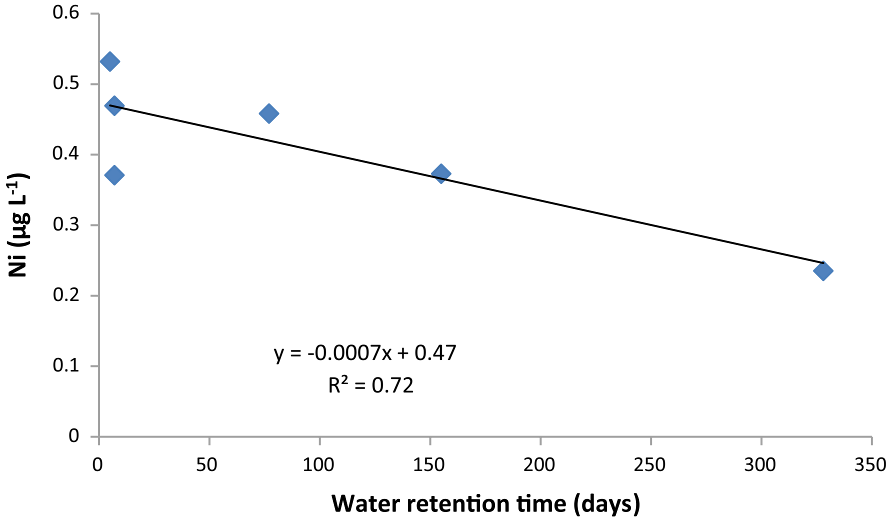

***Figure 2-15.** Average winter concentrations of Ni in the lakes of the Forsmark area as a function of the lake water retention time.*

In the case of Bolundsfjärden the Ni concentration was measured not only in the lake itself, but also in the streams flowing into the lake and out of the lake, respectively, which makes it easier to evaluate the role of water transport for the temporal variation of Ni in the lake. Figure 2-16 shows that the Ni concentration in the stream draining Bolundsfjärden agreed reasonably well with the Ni concentration in the lake at most sampling occasions. One possible deviation occurred in January 2004, when the outflowing stream water reached a Ni concentration of 0.82 µg L^{-1}, which was higher than any observation made in Bolundsfjärden itself. The Ni concentration in Bolundsfjärden was, however, also relatively high at this sampling occasion, 0.68 µg L^{-1}, so it must be concluded that the agreement overall was good. Possibly, some smaller deviations could occur mainly in wintertime when the lake is covered by ice due less mixing of the lake water. The inflowing stream water to the lake, however, often tended to have a higher Ni concentration than the lake water, at least when excluding the winter period (Figure 2-16).

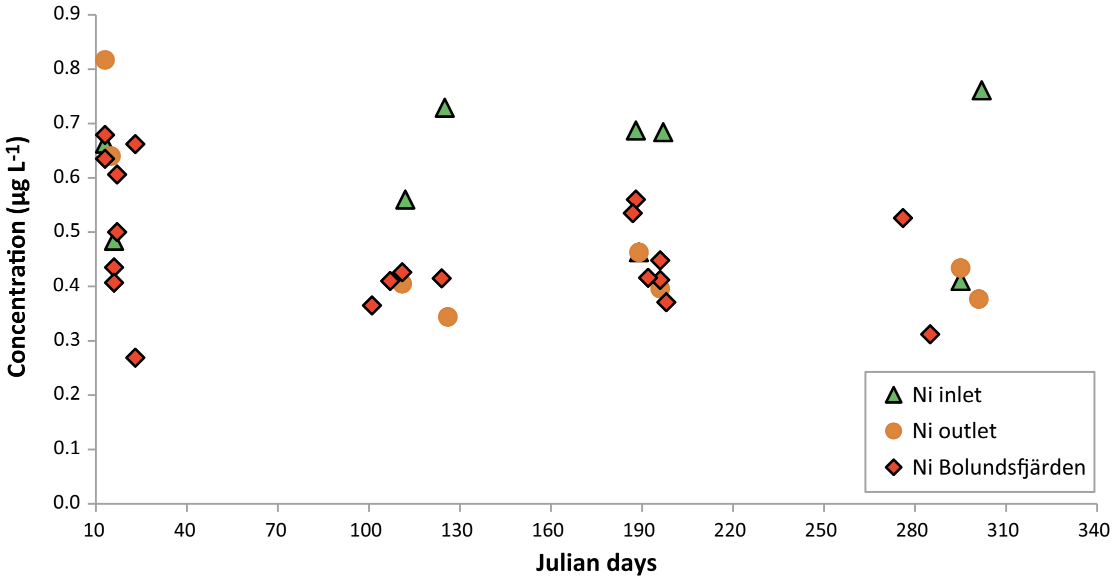

***Figure 2-16.** Ni concentrations in Bolundsfjärden and in inflowing and outflowing stream water, respectively. The data represents five years of sampling (2002–2006), but have been plotted against Julian days in order to emphasise seasonal trends in the lake water chemistry.*

A more thorough integration of chemical and hydrological data could provide a better mass balance for Ni in the lake, but the available data do not indicate that there would be any source of water with low enough Ni concentration to match what is found in Bolundsfjärden during most of the year – other than precipitation, which only is a minor input. There is another seasonally active stream feeding the lake, but it has not been monitored so its Ni concentration remains unknown. Based on the sampled streams in the area, however, stream water, if anything, tends to have higher Ni concentration than lake water (Figure 2-13). As regards the exchange with surrounding groundwater inflow should be expected to increase the Ni concentration of the lake (Figure 2-13), but during the summer the gradient is often directed from the lake to the groundwater. Hence, it appears as if there would be a removal of Ni in the lakes – both when looking at the effect of lakes on the landscape level (Figure 2-15) and when comparing the available fluxes of Ni into and out of a lake (Figure 2-16).

Looking more closely at the temporal changes in the Ni concentration, the general patterns present in Figure 2-16 remain (Figure 2-17). The temporal variation of Ni in Bolundsfjärden was largely similar to that of Co, but in some cases there were considerable difference between deep and shallow samples with respect to both Ni and Co. Lake water was as a rule collected from 0.5 m once every season, but at certain sampling occasions, typically the winter sampling, lake water was also collected from 1 m. For instance, the lowest observed Ni concentration in Bolundsfjärden (0.27 μg L^{-1}) was found in the deep sample at the same date (23 January 2006) as one of the highest observed Ni concentrations (0.66 μg L^{-1}) was recorded in the shallow samples. This indicates that there can be a substantial gradient in the Ni concentration with depth during the winters. The fact that Co displays a similar difference between deep and shallow lake water at the same sampling occasion confirms that it appears to be a real gradient and not just an artefact. This is also supported by the fact that the two water samples from January 2006 also had distinctly different $\delta^{18}O$ signatures (−9.5 ‰ at 0.5 m and −7.6 ‰ at 1 m), which shows that the lake water was not well-mixed at this point. Not all elements, however, showed any distinct differences between deep and shallow lake water, which makes it all the more conspicuous that some typically marine elements were enriched in the deeper lake water, e.g. Na (81 mg L^{-1} at 1 m and 32 mg L^{-1} at 0.5 m), Cl (150 mg L^{-1} at 1 m and 72 mg L^{-1} at 0.5 m) and Br (0.56 mg L^{-1} at 1 m and 0.39 mg L^{-1} at 0.5 m). This would suggest that the stratification in the winter of 2005/2006 may have developed due to the intrusion of sea water in this low-lying lake. Other winters the differences between deep and shallow lake water were not as clear (Figure 2-17).

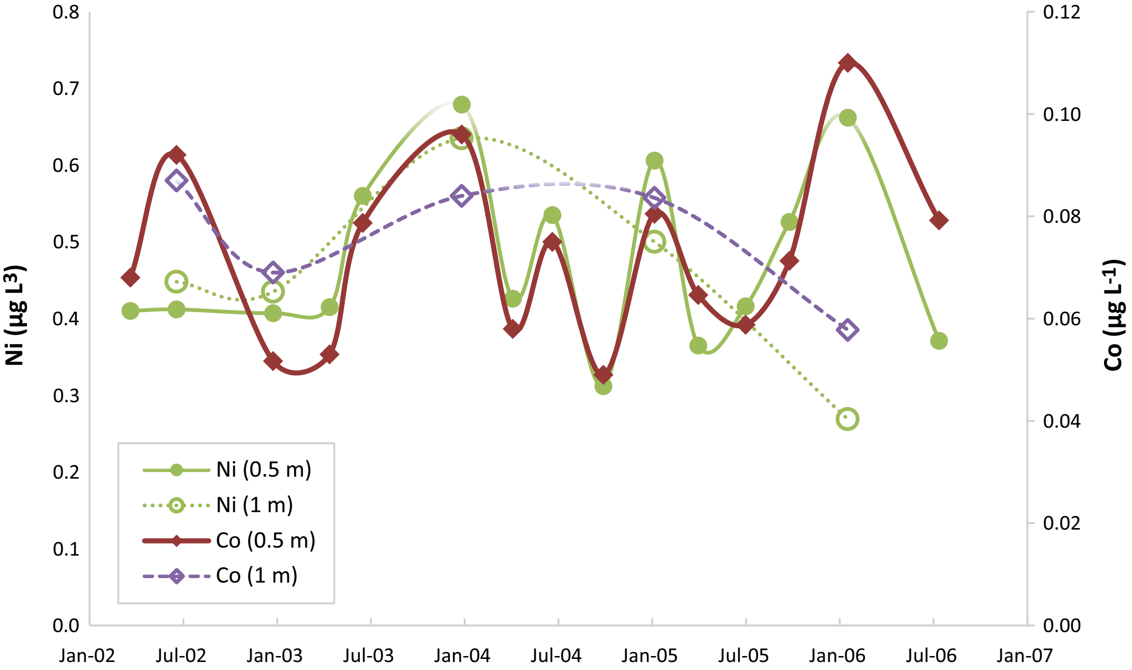

Figure 2-17. Ni (circles) and Co (diamonds) concentrations in Bolundsfjärden (for Ni same data as in Figure 2-15). Filled markers indicate shallow samples (0.5 m) and open markers deep samples (1 m), the latter of which were collected more sparsely (mostly in winter).

Given that the lake is covered by ice it does not seem unlikely that stratification of the lake water could develop, although the lakes in the Forsmark area are shallow. The stratification is also consistent with the slight differences between the outlet and the lake water discussed above (Figure 2-16). During the ice-free period, however, better mixing should be expected in these comparatively shallow lakes and, as a consequence, smaller differences between different depths. This is consistent with the observations in Bolundsfjärden, although it must be emphasised that all but one of the paired samples were collected in the winter (Figure 2-17).

Similar temporal patterns as in Bolundsfjärden can be observed in other lakes. Labboträsket, for example, displayed clear seasonal trends in the concentration of Ni (Figure 2-18). As in Bolundsfjärden, the highest Ni concentrations were associated with winter conditions, indicated by low $\delta^{18}O$ signatures in the graph, whereas the summers, indicated by high $\delta^{18}O$ values, were characterized by low Ni concentrations. This seasonal variation was not unique to Ni, as illustrated by Cu in Figure 2-18. For Cu, however, the difference between the high concentrations during the winters and the low concentrations during the summers and autumns were even more pronounced. While Ni and Cu occur in comparatively similar concentrations during the summers, Cu increases drastically from the autumn to the winter sampling. The most extreme case was the winter 2005–2006, when the Cu concentration increased by an order of magnitude, from 0.16 µg L^{-1} in early October to 1.7 µg L^{-1} in mid-April (Figure 2-18). At the same time, Ni displayed a more modest doubling of the concentration, from 0.38 µg L^{-1} to 0.74 µg L^{-1}. Given the relatively short residence time of Labboträsket, it would be tempting to attribute the differences between Ni and Cu to higher Cu concentrations in groundwater, which is likely to be the main source during the winter regardless of whether it flows directly into the lake or arrives via a stream. Judging from the available Ni and Cu concentrations in groundwater, however, the Cu concentrations are, if anything, lower than the Ni concentrations in groundwater. If these measurements of the groundwater are representative for the water entering Labboträsket, it means that this water would not be able to produce the Cu concentrations and Ni/Cu ratios observed in the lake. This indicates that even in smaller lakes with relatively short residence times there may be considerable biogeochemical processes that affect elements like Ni and Cu.

The role of $CaCO_3$

Given that the temporal variation of the concentration of Ni and other elements in the lakes appears to be affected by biogeochemical processes a key question is whether it is possible to identify what those processes might be. Since lake water samples only were analysed for trace elements four times per year, it is not that easy to sort out what happened, for example, when Cu increased tenfold from October to April 2006. However, one known processes in these lakes that potentially could affect

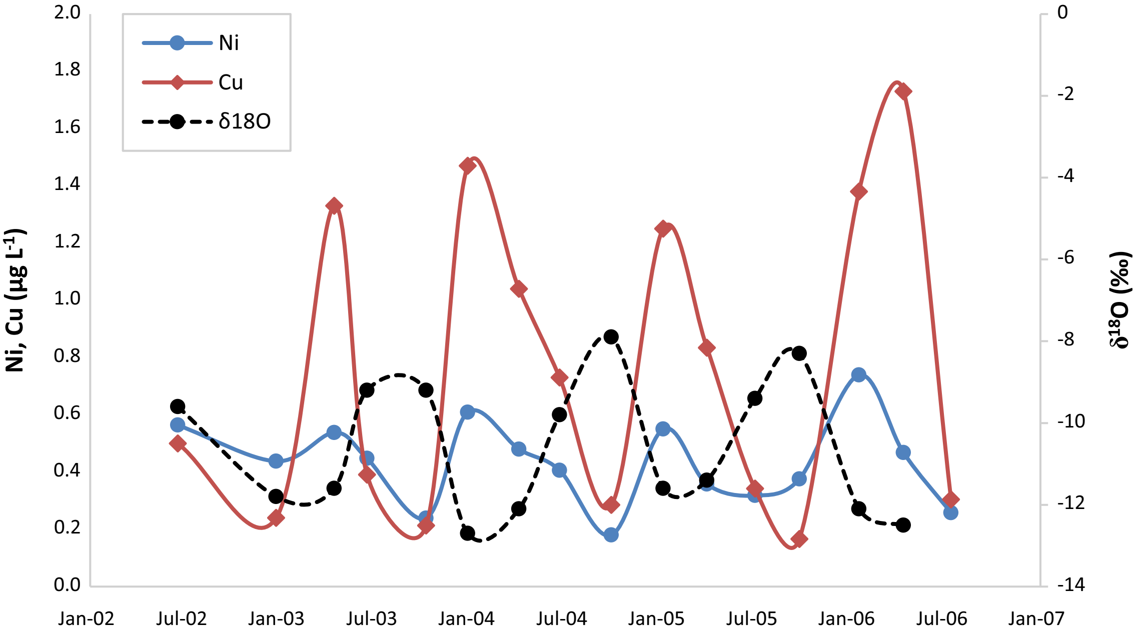

Figure 2-18. *Temporal variation in $\delta^{18}O$, Ni and Cu in Labboträsket, Forsmark, 2002–2006.*

elements like Ni is precipitation of $CaCO_3$ (Jaremalm et al. 2013). It is well-known that there can be an appreciable adsorption and coprecipitation of Ni with calcite when pH is as high as in the lakes in Forsmark (Zachara et al. 1991, Hoffmann and Stipp 2001, Andersson et al. 2014). Presence of calcite has also been observed to significantly increase the sorption of Ni in soils (Businelli 2012). In one experiment it was observed that the molar fraction of Ni in calcite was proportional to the Ni concentration in the solution, which could indicate that Ni was incorporated into the calcite (Lakshtanov and Stipp 2007). The sorption would depend on what polymorph of $CaCO_3$ that is formed in the lakes and also how the precipitation occurs. For instance, the sorption of Ni onto biogenic calcite is stronger than onto inorganically precipitated calcite (Belova et al. 2014). Compared to other similar elements such as Cd and Zn, however, the sorption of Ni onto calcite appears to be relatively weak (Hoffmann and Stipp 2001). Sorption onto calcite has been observed to decrease in the order $Cd^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > (Ba^{2+}, Sr^{2+})$. Co, for instance, sorbs more strongly onto calcite than onto aragonite (Kornicker et al. 1985), while Cd uptake in more efficient in aragonite than in calcite (Prieto et al. 2003). In Forsmark the calcareous gyttja deposits tend to have high Sr concentrations, which could indicate that it might be aragonite or amourphous $CaCO_3$ rather than calcite that is being formed (Jaremalm et al. 2013). The reason for this is that Sr^{2+} ions are too large to fit very well into the crystal structure of calcite (Curti 1999). In principle, coprecipitation or sorption onto some form of $CaCO_3$ could provide a possible explanation to the observed patterns, since $CaCO_3$ precipitates during the growing season, when the Ni concentration typically decreases, and at least partly dissolves during the winters, when the Ni concentration increases (Figure 2-18).

What speaks against that the $CaCO_3$ has major control over the Ni concentrations in the lakes, however, is the fact that neither the saturation index for calcite nor for aragonite are particularly good predictors of the concentrations of Ni and Cd (Figure 2-19). For Ni there was a tendency that the concentrations were lower when the lake water was oversaturated with respect to calcite than when it was not, but for Cd, which should be more strongly affected, no clear difference could be seen (Zachara et al. 1991, Hoffmann and Stipp 2001). Partly, this could be explained by the presence of other ligands such as DOC, which could be expected to dominate the speciation for both Ni and Cd, particularly at the comparatively high pH found in these lakes. Further clues concerning the possible role of $CaCO_3$ precipitation for removal of Ni and other elements can be found by studying sediment cores from present and former lakes in the area (see Section 2.2.5).

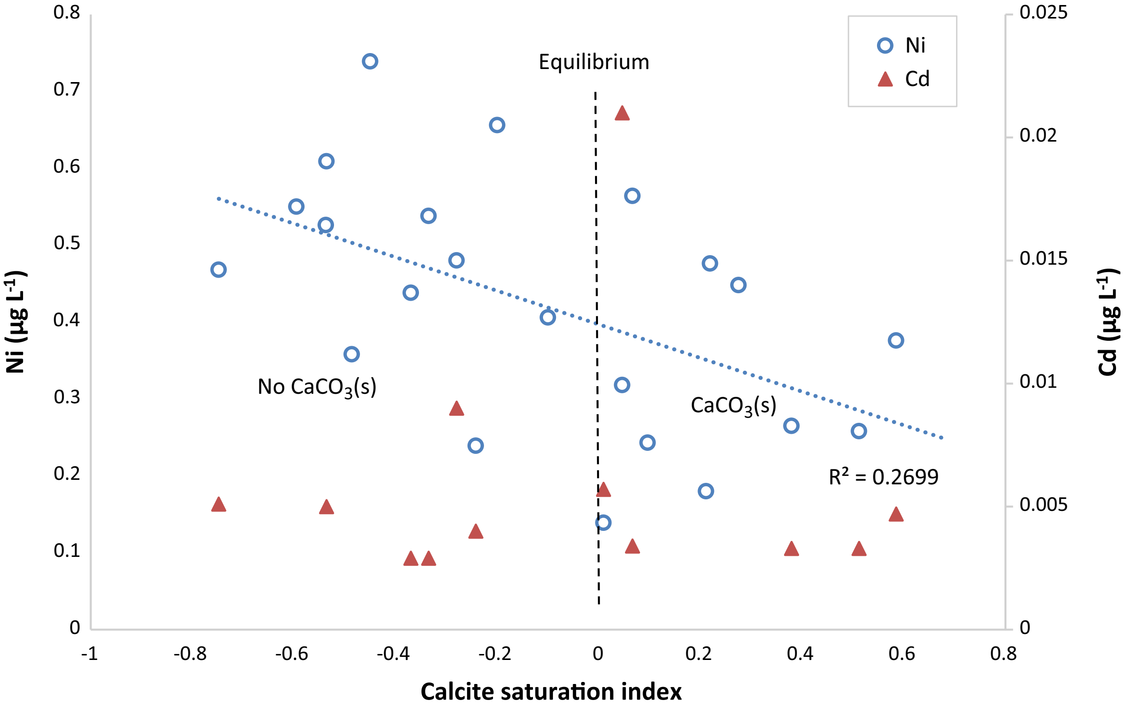

Figure 2-19. *Ni and Cd concentrations in Labboträsket as a function of the calcite saturation index. Data on the calcite saturation index was taken from Jaremalm et al. (2013). Precipitation of calcite is expected where the saturation index is positive (oversaturation), i.e. on the right side of the vertical dashed line. The graph for aragonite would look the same, but the saturation indexes would be slightly lower than for calcite.*

Redox conditions and the role of Fe and Mn

There are, however, also other changes that occur in the lakes on a seasonal basis, which must be considered. For instance, uptake of inorganic carbon from the lake water by primary producers will increase the pH of the lake water during the growing season. pH up to 9.6 has been observed in Norra bassängen in July, but all lakes listed in Table 2-1 have an average pH in the range 7.7–8.8 in the summer compared to 7.1–7.7 in the winter. This implies an average increase in pH by 0.6–1.5 pH units from winter to summer, somewhat depending on the size and residence time of the lakes, which in itself is enough to trigger a number of biogeochemical reactions involving both major and trace elements. In addition to the changes in pH, the redox conditions also vary considerably in the lakes. For instance, Eckarfjärden and Bolundsfjärden typically have an O_2 concentration of ca. 10–13 mg L^{-1} during the ice-free season (Nilsson and Borgiel 2005). This implies that the dissolved O_2 is close to equilibrium with the atmosphere. During the winters, however, the O_2 concentration has been observed to decline, occasionally reaching levels < 1 mg L^{-1}, particularly closer to the bottom of the lakes. This indicates that the redox potential decreases, as O_2 is consumed in the decomposition of organic matter, which also was supported by ORP measurements (oxidation-reduction potential) (Nilsson and Borgiel 2005). All the field measurements were made in the water body, but further down, in the sediments, the conditions can be expected to be even more reducing, as indicated by the sediment cores from lakes in the area (see Section 2.2.5).

The redox conditions will not change the oxidation state of Ni, but its mobility could still be affected by changes in the redox conditions because of the response of other elements such as Mn, Fe and S that are strongly dependent on the redox conditions. One illustration of this are the three water samples that were collected from 0.5 m, 1 m and 1.5 m, respectively, in Eckarfjärden in mid-January 2004. In this depth profile the O_2 concentration decreased from 10.6 mg L^{-1} at 0.5 m to 2.52 mg L^{-1} at 1.5 m (Nilsson and Borgiel 2004). At the same time pH declined from 8.05 to 7.34. Given that the total depth of the water column was 2.2 m very little O_2 should be expected at the water-sediment interface and, above all, in the sediment pore water at this time. Two of these depths, the 0.5 m and the 1.5 m samples, were also analysed for major and trace elements. While the concentrations of most elements were relatively similar at both depths, the Fe concentration was 0.10 mg L^{-1} in the deeper sample and only 0.030 mg L^{-1} upper sample. Both concentrations were high, however, compared to the median Fe concentration in Eckarfjärden, which is only 0.015 mg L^{-1}. Even more extreme was Mn, which had more than 20 times higher concentration at 1.5 m than at 0.5 m: 0.14 mg L^{-1} and 0.0067 mg L^{-1}, respectively. When looking at all available measurements of Fe and Mn in Bolundsfjärden, both elements displayed a considerable variation, and the same could be observed also in other lakes, e.g. Gunnarsbo-Lillfjärden (Figure 2-20). For example, the observed Mn concentration in Gunnarsbo-Lillfjärden spanned over nearly four orders of magnitude – from 0.0010 mg L^{-1} to 0.73 mg L^{-1} –, although only as few as eleven measurements of Mn were made. These large differences in the concentrations are most likely driven by reduction and oxidation of Fe and Mn. Both elements are relatively mobile in their reduced form – Mn^{2+} and Fe^{2+}, respectively –, which have many similarities with Ni^{2+}, as discussed above (Section 2.1.1). When oxidised, however, the solubility decreases and they tend to precipitate as various oxides, hydroxides and oxyhydroxides (Ingri 2012). For example, oxidation of Fe^{2+} to Fe^{3+} can often lead to precipitation of ferrihydrite, which is a common colloidal phase in oxidised water (Gustafsson and Gschwend 1997):

$$4Fe^{2+}(aq) + O_2(aq) + 8OH^-(aq) \leftrightarrow 2Fe_2O_3 \cdot xH_2O(s) + (4-x)H_2O(l) \qquad \text{Equation 2-2}$$

The x in the reaction derives from the varying water content of ferrihydrite, which therefore has an indeterminate formula. Oxidation of Mn^{2+} can, for example, lead to precipitation of birnessite or, as in the example below, pyrolusite:

$$2Mn^{2+}(aq) + O_2(aq) + 4OH^-(aq) \leftrightarrow 2MnO_2(s) + 2H_2O(l) \qquad \text{Equation 2-3}$$

Equation 2-2 and Equation 2-3 are obviously both dependent on the redox conditions, but since OH^- is consumed in the oxidation, they will also be strongly dependent on pH. During the summer both primary production (uptake of CO_2 and production of O_2) and exchange with the atmosphere (dissolution of atmospheric O_2) will push the equilibria to the right, causing precipitation and, consequently, low concentrations of Mn and Fe in the lake water. The importance of biological processes in the lakes is accentuated by the fact that the average pH of the lake water is strongly related to the lake coverage of each catchment (Figure 2-21. Average pH in lakes in the Forsmark area as a function of the lake coverage of each catchment. The increase in pH with lake coverage is probably related to uptake of CO_2 by primary producers in the lakes. High pH can lead to precipitation of $CaCO_3$ and Fe and Mn oxides/hydroxides in the lakes. During the winter ice will prevent atmospheric exchange and decomposition of the organic matter will consume O_2 and decrease pH, pushing the equilibria to the left. Dissolution of Fe and Mn precipitates can then lead to high concentrations in the lake water.

On a logarithmic scale the Mn and Fe concentrations in both Gunnarsbo-Lillfjärden and Eckarfjärden follow each other quite well (Figure 2-20), although the oxidation/reduction of Mn and Fe, respectively, does not occur at the same redox potential. Mn^{2+} is more stable than Fe^{2+} so when the redox potential increases Fe will precipitate before Mn, but when the redox potential decreases Mn will be mobilised before Fe (provided that they both had been oxidised). However, since the concentrations of both Fe and Mn are comparatively low in these lakes, the redox buffering capacity is low around the Eh where these reactions occur.

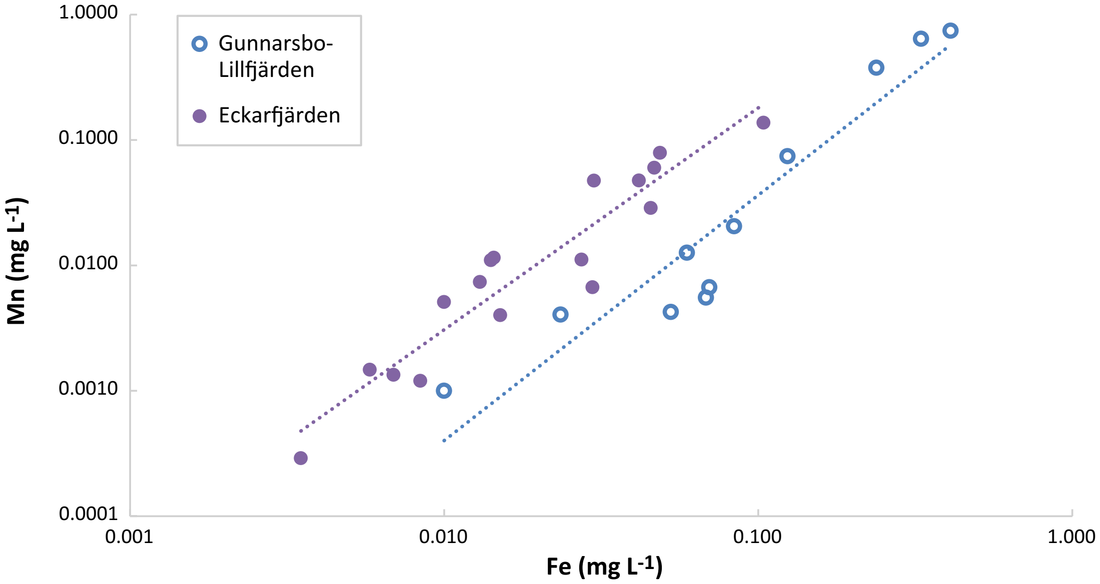

Figure 2-20. *Fe and Mn concentrations in Gunnarsbo-Lillfjärden and Eckarfjärden, respectively. Note the logarithmic scale on both axes.*

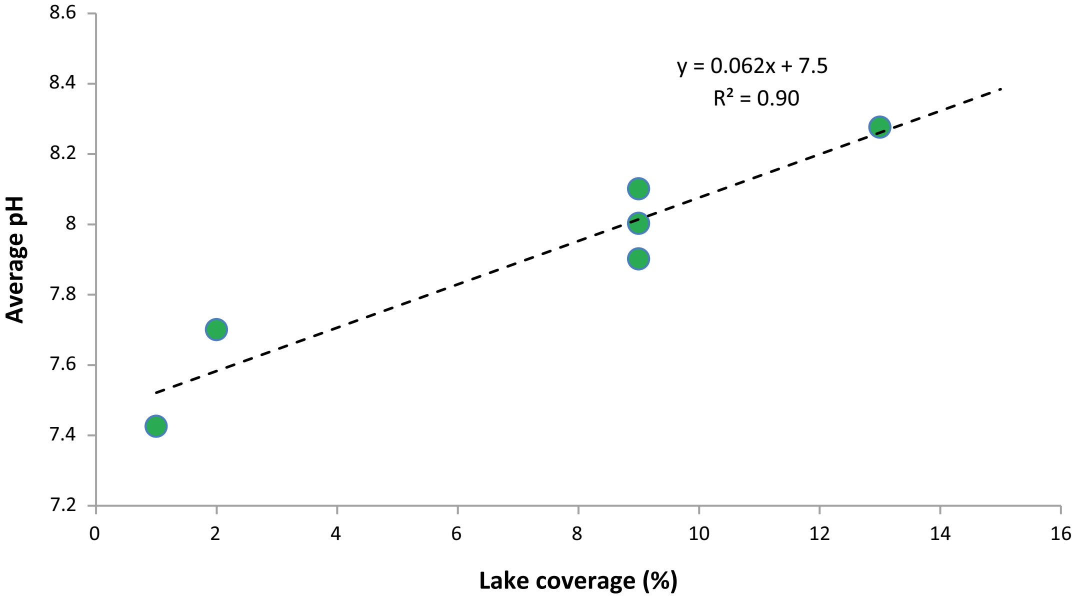

Figure 2-21. *Average pH in lakes in the Forsmark area as a function of the lake coverage of each catchment. The increase in pH with lake coverage is probably related to uptake of CO_2 by primary producers in the lakes. High pH can lead to precipitation of $CaCO_3$ and Fe and Mn oxides/hydroxides in the lakes.*

The importance of the redox conditions is also supported by comparisons with other redox-sensitive elements. In Bolundsfjärden, the Mn concentration was consistently low (< 0.02 mg L^{-1}) when the O_2 concentration was high (ca. 10–12 mg L^{-1}, which is close to equilibrium with the atmosphere), as shown in Figure 2-22. Ammonium, which is the most reduced form of N, was hardly present in the lake water when the O_2 concentration was high, but occurred in appreciable amounts (up to 0.39 mg NH_4-N L^{-1} in Bolundsfjärden) during periods with less O_2. In this respect ammonium exhibited a similar pattern as Mn, which is consistent in the sense that they both should be more abundant under reducing conditions (Figure 2-22). Ammonium could, for example, derive from the decomposition of organic N compounds during the winter. The relationship between Mn and N is, however, complicated by the fact that there could be an interaction between the two. Theoretically, MnO_2, which could be suspended in the water or present at the lake-sediment interface under anoxic conditions, could be used to oxidise ammonium to nitrate (Ingri 2012):

$$4MnO_2(s) + NH_4^+(aq) + H_2O(l) \leftrightarrow 4Mn^{2+}(aq) + NO_3^-(aq) + 6OH^-(aq) \qquad \text{Equation 2-4}$$

This reaction could lead to a loss of ammonium and increasing Mn concentration in the lake water even if all O_2 has been consumed. There are, however, observations from, for example, Mn-rich sediments in Skagerrak, where no significant oxidation of ammonium by Mn oxides could be found, although the reaction would be thermodynamically favourable (Thamdrup and Dalsgaard 2000). If these observations are valid also for the lakes in the Forsmark area, it would strengthen the relationship between Mn and ammonium shown in (Figure 2-22).

Manganese can, however, be involved also in another part of the N cycle. Nitrate could also be used to re-oxidise Mn^{2+} back to MnO_2 or, if one prefers to look at the matter from the opposite direction, Mn^{2+} can be used as a reducing agent in denitrification (Luther et al. 1997, Mogollón et al. 2016):

$$5Mn^{2+}(aq) + 2NO_3^-(aq) + H_2O(l) \leftrightarrow 5MnO_2(s) + N_2(g) + 6OH^-(aq) \qquad \text{Equation 2-5}$$

In this manner, the denitrification (Equation 2-5) could produce more MnO_2, which potentially could be used to oxidise more ammonium (Equation 2-4) – and so on. Hence, although Mn is not a particularly abundant element, this cycling of Mn can make it an efficient oxidising and reducing agent. Under slightly more reducing conditions cycling of Fe can function in a similar way (Ingri 2012).

For trace elements such as Ni the precipitation of Fe and Mn oxides can be important because they can coprecipitate or sorb onto the colloids or particles that are formed as a consequence of the oxidation. When Fe is oxidised in nature, the first step is often ferrihydrite (Equation 2-2) or amorphous $Fe(OH)_3$, but over time these precipitates are transformed into more stable minerals such as goethite and hematite (Ingri 2012). All of these Fe phases can to varying degrees sorb Ni (Buerge-Weirich and Sulzberger 2004, Xu et al. 2007, Arai 2008, Wasylenki et al. 2015). Although evidence form the Kalix River in northern Sweden indicates that Ni has a preference for organic matter over Fe colloids, this is undoubtedly dependent on the chemical conditions (Dahlqvist et al. 2007). At high pH, as in the lakes of the Forsmark area, it has been observed that the importance of ferrihydrite increases relative to organic matter (Wang et al. 2019). In Eckarfjärden, for example, there was a general agreement between Ni and Fe, although the latter varied over a much wider range, presumably due to redox transformations (Figure 2-23). In principle, this could be an indication that there is some degree of association between Ni and Fe in the lake water, although more detailed investigations would be required in order to demonstrate this more clearly, since there are so many other processes going on at the same time that display a similar seasonal pattern.

Before precipitation of Fe occurs in the lake there should, however, be precipitation of Mn. This can occur, for instance, as different forms of MnO_2 or as birnessite, another Mn oxide that often contains foreign ions such as Na^+, K^+ or Ca^{2+}. Nickel has been observed to have a substantial affinity for, for instance, MnO_2 precipitated in sea water (Balistrieri and Murray 1982), hydrous MnO_2 (Tonkin et al. 2004) and birnessite (Peacock and Sherman 2007, Peacock 2009, Peña et al. 2010), which can lead to effective scavenging of Ni from the water column. MnO_2 has also been observed to have a stronger surface affinity for Ni than both $Fe(OH)_3$ and calcite (Green-Pedersen et al. 1997). In sediments from the Bothnian Bay, for example, Ni has been observed to be enriched in the uppermost Mn oxyhydroxide layer (Ingri et al. 2014). However, compared to Pb, Cu, Co and Zn the sorption of Ni onto birnessite has been observed to be relatively weak (McKenzie 1980). The same study also concluded that the sorption of alkaline earth metals onto birnessite was fully reversible, while that was not the case for the transition metals, indicating the formation of a solid solution with birnessite in the latter case. Likewise, it has been

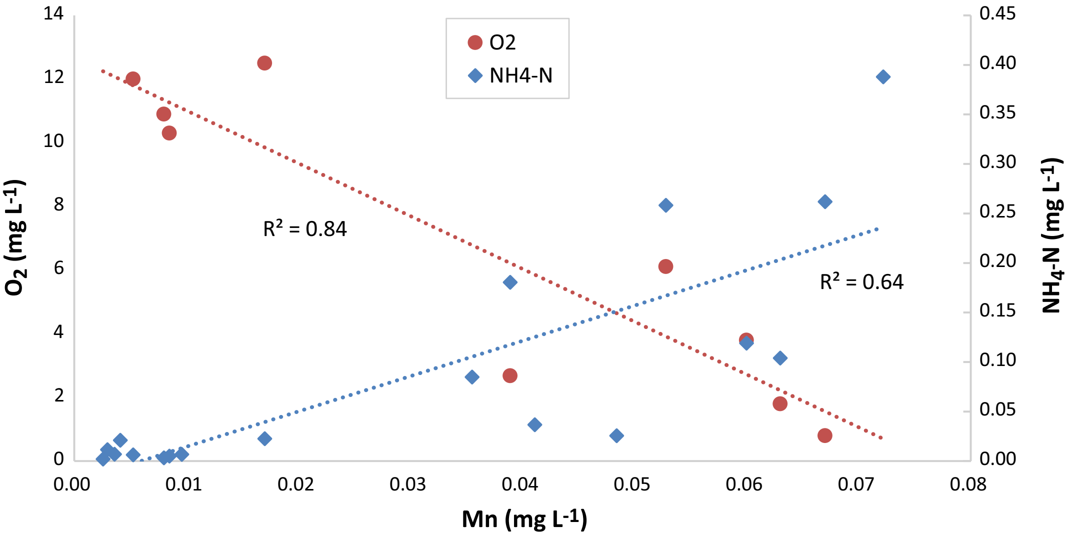

Figure 2-22. *Relationship between Mn, O_2 and NH_4-N in Bolundsfjärden, Forsmark.*

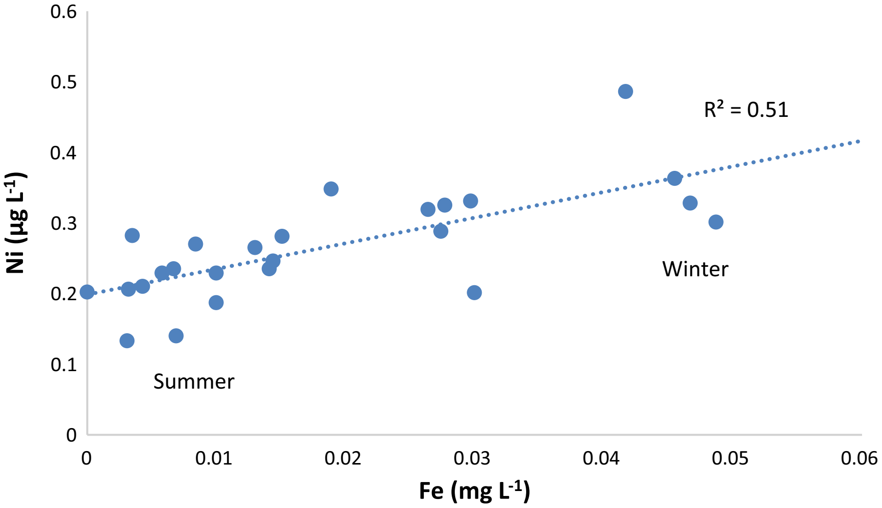

Figure 2-23. *Fe and Ni concentrations in Eckarfjärden, Forsmark.*

observed that the sorption of Ni onto biogenic Mn oxides is weaker than for Co and Zn (Tani et al. 2004). Therefore, Ni/Co and Ni/Zn ratios could be a useful indicator for assessing the role of Mn for the biogeochemistry of Ni in the lakes.

In Bolundsfjärden high Ni concentrations were typically associated with the winter and, in particular, lake water collected closer to the bottom of the lake (Figure 2-17). The Ni/Zn ratio of the lake water was, however, lower during the winter and higher during the summer, which implies that Zn was more affected by the seasonal variations in the lake water chemistry (Figure 2-24). The decline in the Ni/Zn ratio from the typically high pH and high O_2 concentration prevailing mainly during the summers to the relatively low pH and low O_2 concentration developing during the winters coincided with an increase in the Mn concentration ($r = -0.70$, $p < 0.01$). Both the Ni/Zn ratio ($r = 0.77$, $p < 0.01$) and the Mn concentration ($r = -0.91$, $p < 0.001$) were also correlated to pH, whose seasonal variation largely is driven by biological processes (Jaremalm et al. 2013). As discussed above, the trend for Mn is consistent with oxidation and subsequent precipitation of Mn in the summer and reduction and dissolution of Mn in the winter (Equation 2-3). Figure 2-24 indicates that the formation of Mn precipitates causes a preferential scavenging of Zn over Ni from the lake water, which is consistent with what should be expected based on the higher affinity of Zn for Mn birnessite and Mn oxides (McKenzie 1980, Shaw et al. 1990, Tani et al. 2004). Hence, Ni in the lake water does not appear to be particularly strongly affected by neither Fe nor Mn in Forsmark area, but a final assessment of the matter should also include the available sediment records from the area (see Section 2.2.5).

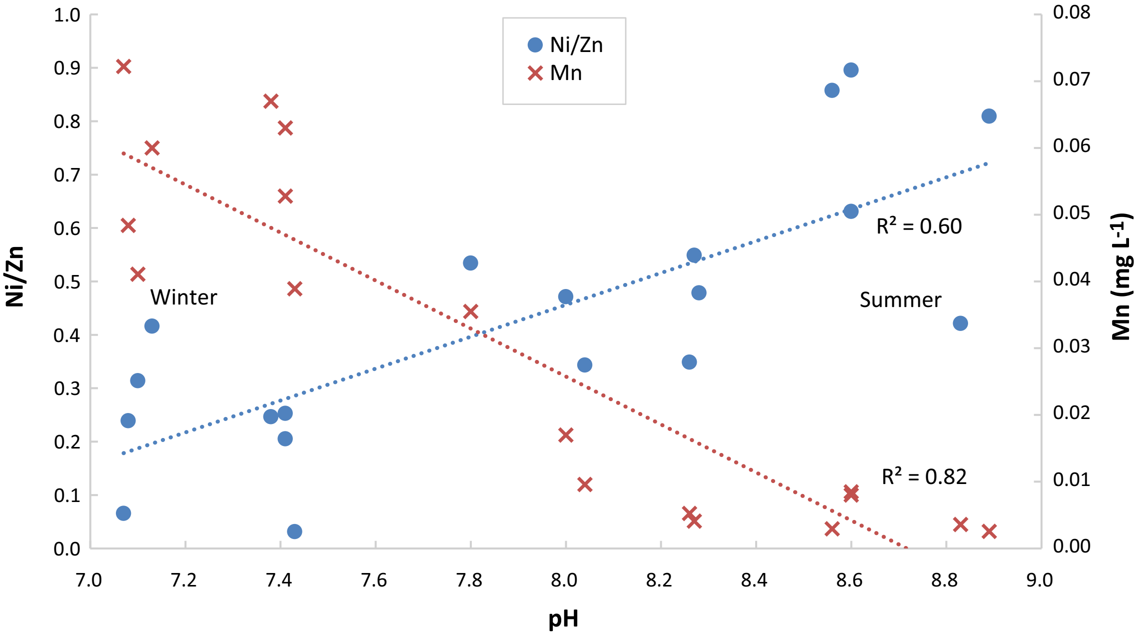

Figure 2-24. *Mn concentration and Ni/Zn ratios as a function of pH in Bolundsfjärden, Forsmark.*

Nickel in Frisksjön, Simpevarp

In the Simpevarp area Frisksjön was the only lake where trace elements were analysed. Compared to the lakes in Forsmark, Frisksjön is deeper with a maximum depth of 2.8 m and an average depth of 1.7 m, which is nearly twice as much as the deepest lake in the Forsmark area (Brunberg et al. 2004,). The catchment covers 1.8 km^2, of which the lake itself constitutes 0.13 km^2, so it has a relatively long residence time, nearly nine months (Table 2-1). The lake surface is located only 1.37 m above the current sea level, but due to the slower shoreline displacement Frisksjön was isolated from the Baltic Sea ca. 2 500–2 750 years BP, which makes it older than the lakes in the Forsmark area (Nilsson 2004). In contrast to the shallower lakes in the Forsmark area a thermocline has been observed to develop in Frisksjön both in the summers and in the winters (Ericsson and Engdahl 2005). Therefore, low O_2 concentrations (down to 0.07 mg L^{-1}) can also develop in the bottom water during the summers. For example, one profile of the water column from August 2003 shows that not much O_2 was present below 2 m (Ericsson and Engdahl 2004).

In the sampling programme lake water was collected at two different depths at each sampling occasion, one shallow sample (0–1 m or 0.5–1.5 m) and one deep sample (1.5–2.5 m or 2–3 m). During the period 2003–2006 five samplings were made, yielding a total of ten samples, with a maximum of two samplings per year. Consequently, it is not possible to assess the seasonal variation in Frisksjön, but judging from the available data the Ni concentration in the lake appears to be relatively stable over time. The lowest concentration, 1.24 µg L^{-1}, was observed in December 2005, while the highest Ni concentration, 1.94 µg L^{-1}, was observed later that winter, in March 2006. There were, however, no pronounced differences between deep and shallow samples with respect to Ni, and this was also a pattern that was consistent for most other elements.

Among the major ions, Ni in Frisksjön was mainly correlated to Ca ($r=0.79$, $p < 0.05$) and Si ($r=0.75$, $p < 0.05$). Unlike the lakes in the Forsmark area Frisksjön is not seasonally saturated with respect to calcite or aragonite, which makes the biogeochemistry of Ca in Frisksjön profoundly different (Jaremalm et al. 2013). One reason why the concentrations were increasing during the winter could simply be inflow of groundwater to the lake, since it typically has higher Ni concentration than the lake water (Figure 2-13). Even stronger correlations were observed to some transition metals like Cu ($r=0.88$, $p < 0.01$) and Cr ($r=0.85$, $p < 0.01$; Figure 2-25). There was, however, no significant correlation to Co, which was substantially more variable in the lake water (0.045–0.34 µg L^{-1}). Co was instead more closely correlated to Mn ($r=0.91$, $p < 0.01$), which points towards a significant fractionation among the transition metals also in Frisksjön. Due to the scarcity of data it is not easy to disentangle exactly what processes are driving this fractionation, but – as was discussed above with respect to the lakes in Forsmark – Mn oxides bind Co more efficiently than Ni (Shaw et al. 1990). One reason behind the preferential scavenging of Co appears to be that Co^{2+} can be oxidised to Co^{3+} and subsequently incorporated into the Mn precipitates (Kay et al. 2001).

The difference in the behaviour of Ni, Co, Cu and Zn, respectively, in Frisksjön is illustrated in Figure 2-26, where the measured concentrations of these elements at different sampling occasions and water depths are plotted against the Mn concentration. The Ni concentration was independent of the Mn concentration, while particularly Zn and Co tended to co-vary with Mn. The difference between Ni and the other transition metals can also be illustrated by the element ratios in the lake water. High Ni/Co, Ni/Cu and Ni/Zn ratios were invariably associated with low Mn concentrations in Frisksjön (Figure 2-26). As in Forsmark area, low Mn concentrations were mainly associated with summers and shallower samples, while high Mn concentrations mainly were associated with the winters. This suggests that Ni is not strongly affected by the precipitation and dissolution of Mn in Frisksjön, which also is in agreement with the observations from the Forsmark area.

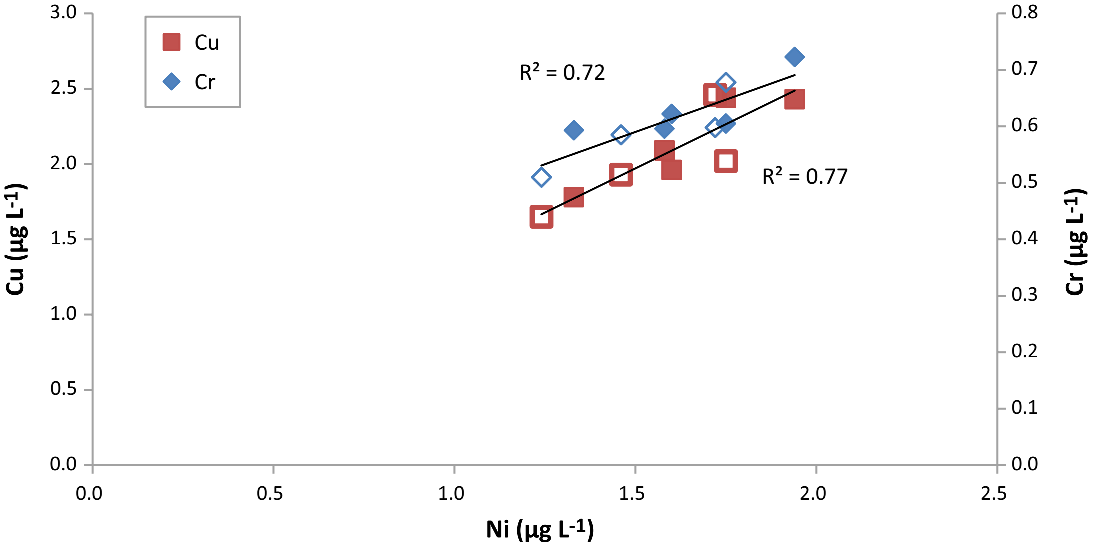

***Figure 2-25.** Concentrations of Ni vs. concentrations of Cr and Cu, respectively, in Frisksjön 2003–2006. Open markers indicate shallow samples (0–1 m or 0.5–1.5 m), while filled markers indicated deep samples (1.5–2.5 m or 2–3 m). The regression lines are based on both deep and shallow observations.*

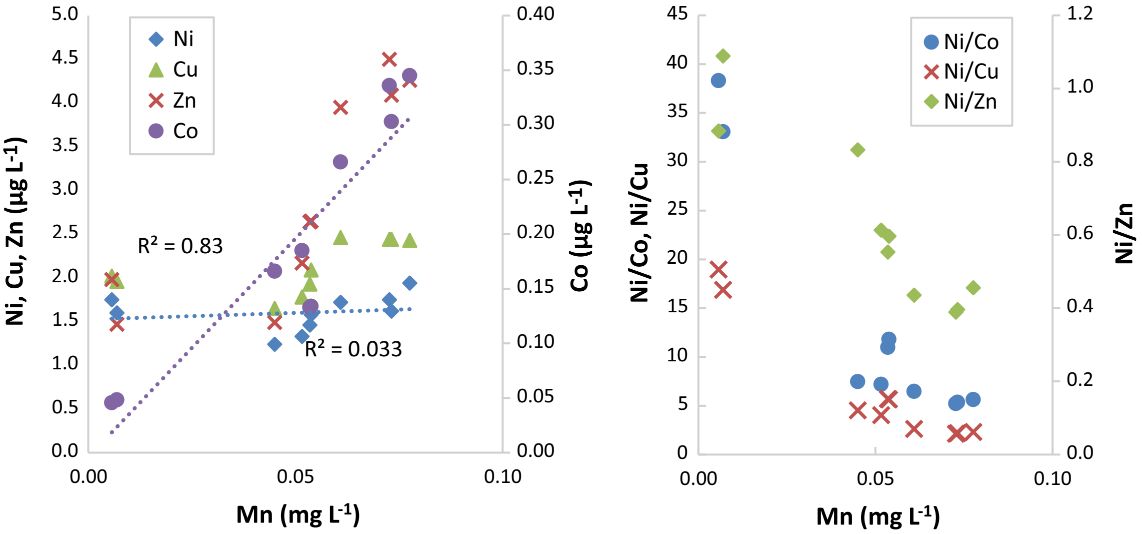

***Figure 2-26.** Left: Concentrations of Ni, Cu, Zn and Co as a function of the Mn concentration is Frisksjön, Simpevarp. Linear regressions are shown for Co ($p < 0.05$) and Ni (not significant). Right: Ni/Co, Ni/Cu and Ni/Zn ratios in Frisksjön, Simpevarp, as a function of the Mn concentration.*

As regards the cycling of Fe in Frisksjön the Fe concentration was much more stable than the Mn concentration. Fe varied between 0.55 mg L^{-1} (May 2006) and 0.99 mg L^{-1} (August 2005), while Mn varied by more than an order of magnitude, from 5.6 µg L^{-1} (July 2005) to 77 µg L^{-1} (March 2006). This indicates that Fe may not be precipitating in Frisksjön or at least that it is less prominent than in the case of Mn. From a thermodynamic perspective this is not inconceivable, since Mn is more easily reduced than Fe. The situation can be compared to Gunnarsbo-Lillträsket and Eckarfjärden in Forsmark, where both Fe and Mn varied by several orders of magnitude (Figure 2-20). In four of the samples from Frisksjön both total Fe and Fe^{2+} were measured. All samples were collected in the summer of 2005, which is a period when the conditions for oxygenation of the lake water should be beneficial. Yet, these analyses revealed appreciable amounts (30–42 %) of reduced Fe in the lake water, and no tendency of less Fe^{2+} in the shallower water could be seen. It is unclear whether the high concentrations of Fe^{2+} observed at these two sampling occasions were related to mixing periods where more reduced bottom water was brought to the surface or whether this is typical for the Fe speciation in Frisksjön during the summers. O_2 data appears to be missing for these two sampling occasions, but a distinct increase in Mn from 0.0057–0.0069 mg L^{-1} in June to 0.054 mg L^{-1} in August may indicate that there has been some mixing with more reduced water. It is not uncommon, however, to find both Fe^{2+} and Fe^{3+} in oxidising as well as reducing conditions, partly because organic matter can help stabilise the oxidation state of Fe (e.g. Sundman et al. 2014). Since only four -observations are available, one should be careful not to draw to far-reaching conclusions, but there did not appear to be any clear relationship between the distribution between Fe^{2+} and Fe^{3+} on the one hand and the total Fe concentration on the other (Figure 2-27). Although the Fe concentration increased from ca. 0.63 mg L^{-1} in first sampling in June to nearly 1 mg L^{-1} in August the fraction of Fe^{2+} essentially remained unchanged. Given that the DOC concentration remained fairly constant at ca. 14 mg L^{-1} and that there was a slight increase in pH (from 6.9–7.0 to 7.2–7.3) there seems to be no obvious reasons to think that extensive precipitation of Fe would occur during this period. It could be observed that the Ni/Pb ratio of the lake water was negatively correlated to the Fe concentration ($r = -0.95$, $p < 0.001$). Since Pb can be expected to sorb more strongly onto Fe particles than Ni (McKenzie 1980), this could be interpreted as an ongoing precipitation of Fe in Frisksjön, but, as discussed above, there are other factors that indicate otherwise. Obviously, there could be other mechanisms causing a fractionation between Ni and Pb, e.g. differences in the affinity for organic matter.

Principal component analysis of lake water

A principal component analysis of the lake water samples can be made in a number of different ways, depending on what selection criteria are used. In Figure 2-28 only components that were measured and came in over the reporting limits in all or nearly all collected samples were included. The two first principal components explained 29.4 % and 22.8 % of the variation, respectively. The first principal component is apparently closely associated with the influence of sea water, which causes high concentrations of elements like Na, Cl, S, Mg and K. It is notable that there are no elements found in the opposite direction, i.e. in the lower left quadrant. This implies that the effect of sea water intrusions is to increase the concentration of certain elements, but no so much to dilute the concentrations of others.

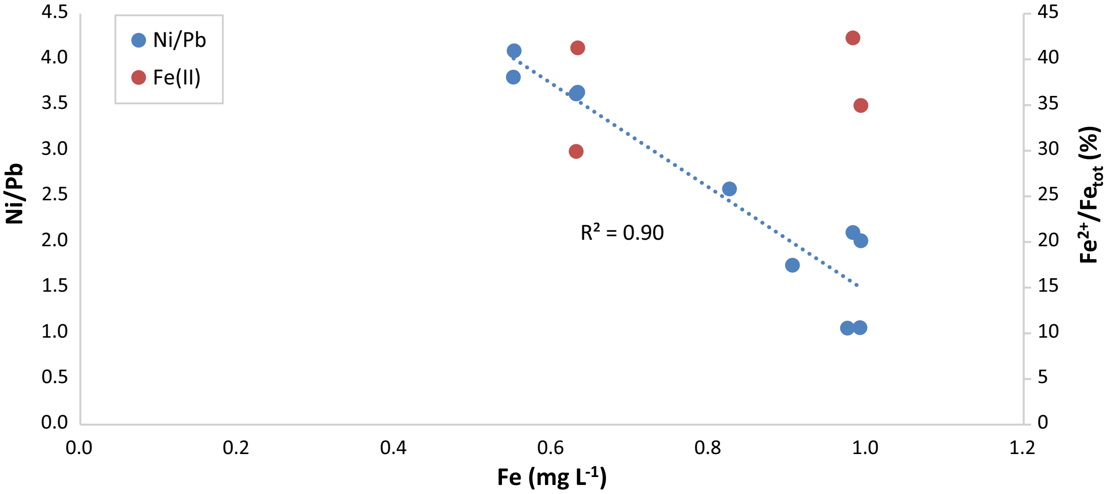

***Figure 2-27.** Ni/Pb ratios in Frisksjön and the fraction of reduced Fe as a function of the Fe concentration.*

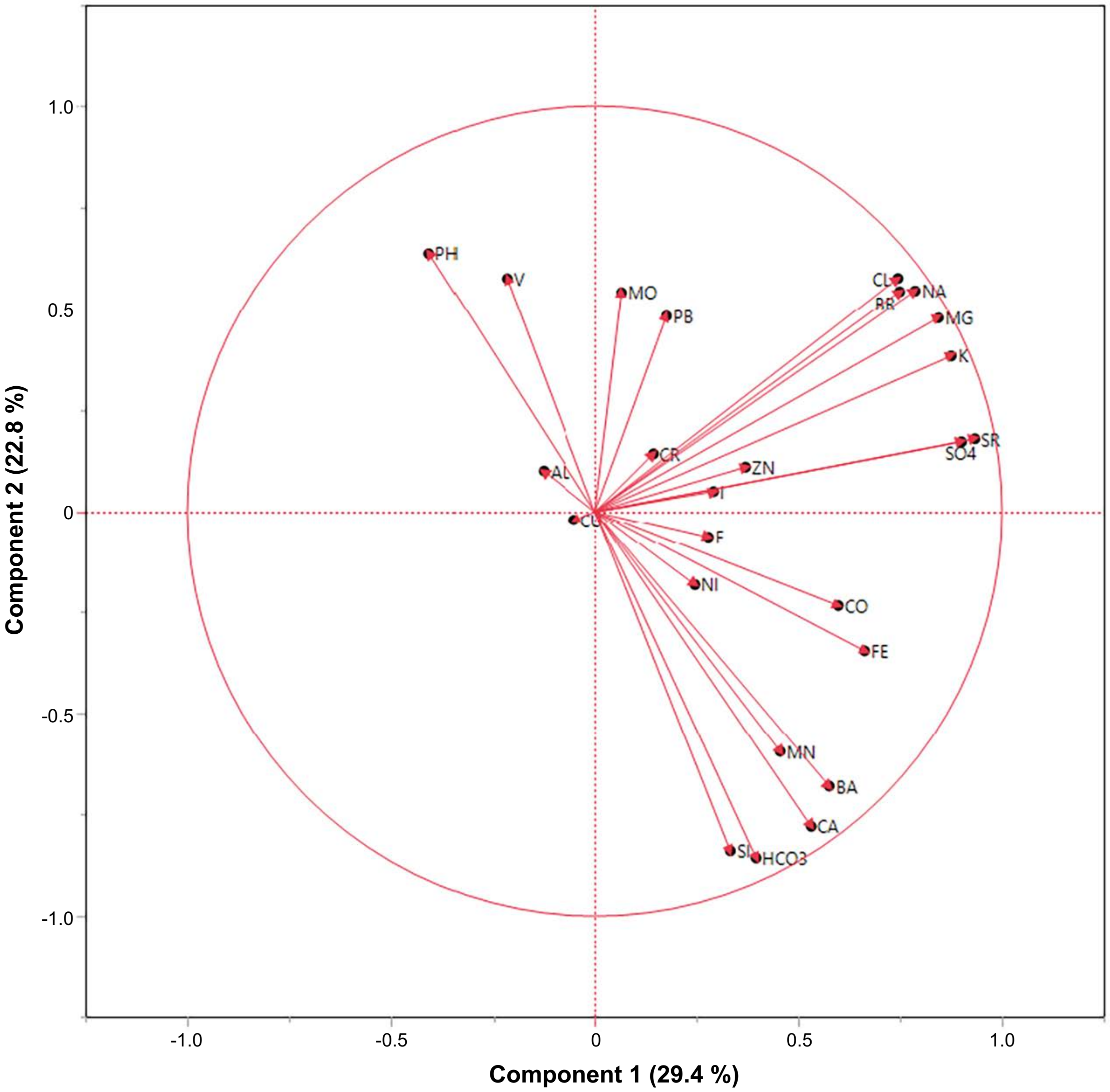

Figure 2-28. *Principal component analysis of lake water samples from Forsmark (all sampled lakes). The selection of elements was based on the available data – elements that were only infrequently analysed or often fell below reporting limits were not included.*

Among the base cations, Ca stands out, however, by falling closer to PC2, where also hydrogen carbonate, Si, Ba and other elements can be found in the lower right quadrant. Opposite to this cluster, in the upper left quadrant, pH is found along with, for example, the anionic elements V and – slightly to the right – Mo. This principal component is clearly related to $CaCO_3$. While it may be surprising at first glance to find Ca and hydrogen carbonate opposite to pH, since all these three parameters typically are associated with calcite-rich environments, it must be kept in mind that all the lakes in the Forsmark area are influenced by calcite (Jaremalm et al. 2013). The solubility of Ca and carbonate is therefore directly dependent on the pH of the lake water, which regulates that balance between hydrogen carbonate and carbonate, the latter of which determines the equilibrium with $CaCO_3$. Hence, when pH increases, the Ca concentration in the lake water will decrease due to precipitation $CaCO_3$, which is the reason why Ca and pH plot in opposite directions in Figure 2-28.

Nickel is found relatively close to the origin in the lower right quadrant of Figure 2-28. As discussed above, Ni display less variability in the lake water than, for example, Co, Mn and Fe, although they evidently all align in a similar direction in the PCA.

Suspended matter in lakes

One important link between dissolved species in the lake water and sediments is the association of different elements to particles in the lake water. This was investigated in some lake and sea water samples in the Forsmark area by analysing the concentration of various elements in suspended particles and filtered water samples (Engdahl et al. 2008). The samples were collected in in early April 2008 and therefore represent the conditions in the lakes and bays during the spring. Figure 2-29 summarises some of the results of this study by comparing the ratio between the dissolved concentrations in the water and the concentrations in the suspended particles for a number of selected elements, most of which occur as divalent ions. Theoretically these ratios can be thought of as Kd values, which can be compared to the site-specific Kd values that are used in the safety assessments (Figure 2-44). In the case of Ni the Kd values for suspended particles fell in the range 18–110 m^3 kg^{-1}, which is relatively high in comparison with the analysed soils samples. Kd values in the same range were, however, observed above all in glacial clay. There are also a number of reasons why suspended particles could be expected to be more reactive than soil particles in general. For example, the suspended matter is likely to be smaller, giving it a higher surface area per mass unit, and it may also consist of a large fraction of relatively fresh organic matter and, depending on the season, recently precipitated $CaCO_3$, Fe and Mn, making it more reactive than old soil particles.

The lowest Kd values were observed for Ca and Sr (0.067–2.1 m^3 kg^{-1}), which seems reasonable, especially given that the lake water is not yet saturated with respect to $CaCO_3$ in early April (Jaremalm et al. 2013). In contrast, the Kd values for Mn and Fe were relatively high (40–740 m^3 kg^{-1} for Mn, 150–7 100 m^3 kg^{-1} for Fe). At least the higher Kd values should reflect precipitation of Mn and Fe in the water column. The Kd values for Ni were clearly higher than for Ca and Sr, but relative to other transition metals, Cd and Pb, Ni tended to be among the more mobile elements (Figure 2-29). Based on these measurements one could therefore expect a slight depletion of Ni in relation to, for instance, Co and Zn in the sediments. It can also be noted that there were no substantial differences between Frisksjön in Simpevarp and the lakes in the Forsmark area with respect to the distribution of Ni between suspended particles and the dissolved phase, nor between fresh water and sea water (represented by Forslingens grund) in the Forsmark area (Figure 2-29).

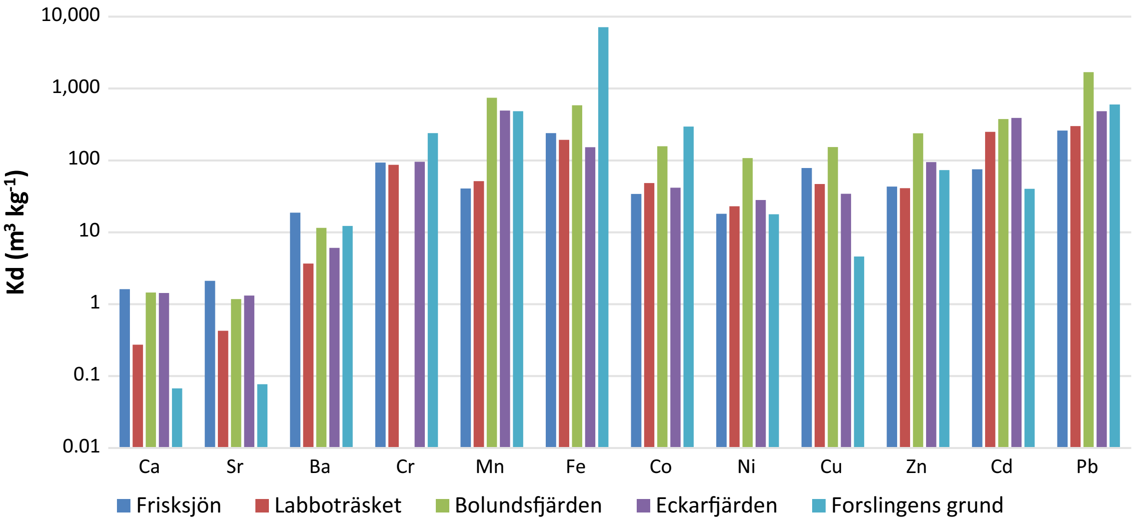

Figure 2-29. *Ratios between concentrations in suspended matter and lake water (i.e. Kd for suspended particles) in the lakes Friskjön (Simpevarp), Labboträsket, Bolundsfjärden and Eckarfjärden (all in Forsmark) and the marine site Forslingens grund (Forsmark) for some alkaline earth metals, transition metals and post-transition metals. Data from Kumbland and Bradshaw (2008) and Engdahl et al. (2008).*

2.2.5 Nickel in sediments and peat

Accumulation in peat and sediments is a potentially important retention mechanism for Ni in the landscape. Over time Ni and other elements stored in such environments can also be remobilised, e.g. as a result of land uplift, landscape evolution, ditching and cultivation, which means that peat and sediments also constitute a potentially important future source. In the Simpevarp area Ni concentrations up to 72 µg g^{-1} have been observed in sediments from Frisksjön, and in the Forsmark area Ni concentrations up to 67 µg g^{-1} have been observed in clayey marine sediments (PSM006062). This means that at both sites higher Ni concentrations have been observed in sediments than in local till (Section 2.2.2). The highest Ni concentrations were generally found in inorganic sediments, as illustrated by sediments from Eckarfjärden in Forsmark, where a maximum of 52 µg g^{-1} was encountered in sediments at 1.4 m (Figure 2-30). This depth represents the period when Eckarfjärden still was a marine bay. Relatively high Ni concentrations were also encountered in the underlying sand and clay sediments, which were deposited in the Yoldia Sea ca. 9900 years BP. As Eckarfjärden was isolated from the Baltic Sea ca. 850 years ago (Hedenström and Risberg 2003), the sediments gradually became richer in organic matter, while the concentration of Ni in the sediments decreased. In this sense, it is clear that the relative sedimentation of Ni in the freshwater environment has been lower than in the marine environment. One explanation could be a lower sedimentation of Ni-rich mineral particles in the lake as compared to the marine bay, but the higher sedimentation of organic matter has also led to a dilution of Ni and other elements that are abundant in the inorganic fraction.

From a radioecological and biogeochemical perspective, however, it is essential to distinguish between sedimentation of Ni in primary minerals and sedimentation of Ni that at some point has been dissolved in the aqueous phase. The former fraction represents particles that have been eroded and transported to the site without taking much part in any biogeochemical processes. Ni that at some point has been dissolved, however, is much more interesting for understanding the biogeochemistry of Ni and its fate in the site investigation areas. This fraction is also more relevant for understanding the behaviour of radionuclides from a deep repository, since they will be transported in the dissolved phase. One common method to study sedimentation is to normalise against elements like Zr or Ti, which are believed to occur mainly in weathering-resistant primary minerals like zircon and rutile, respectively (Boes et al. 2011). Throughout this report Ti has been the primary choice because Ti measurements were available for more samples. In the deeper sediments in Eckarfjärden the Ni/Ti ratios were around 0.01, both below and above the hiatus (Figure 2-30). This is a typical value for till in the Forsmark area, which had a median Ni/Ti ratio of ca. 0.015. It is also similar to the Ni/Ti ratios in marine sediments outside Tixlan in Forsmark (Kumbland and Bradshaw 2008). Hence, this would suggest that most of the Ni at these depths may occur in more or less locally eroded and subsequently deposited particles from land. As the sediments become more organic above ca. 1 m – in connection with the isolation of the lake – the Ni/Ti ratio increased to a maximum of 0.07. Once the lake was isolated the Ni and Ti found in the sediments should definitely derive from the catchment of the lake, but compared to what has been observed in the local till the Ni/Ti in the sediments from the freshwater stage are evidently high. The explanation could be that the Ni/Ti ratio varies with the particle size – but there is no data available to demonstrate this. A more likely explanation would be that there is a fractionation of Ni and Ti in the landscape. In practise, this would imply that there is a preferential mobilisation of Ni over Ti in the catchment and, subsequently, a scavenging of Ni from the lake water. This would also be consistent with the observation that the Ni concentration is lower in lakes the longer the water retention time is (Figure 2-15). As discussed above, Ni has a substantial affinity for organic matter (Section 2.1.2), and the increase in the Ni/Ti ratio in younger sediments coincided with a distinct increase in LOI (Figure 2-30). Furthermore, the inflow of surface water that could carry eroded particles into Eckarfjärden is limited nowadays, as witnessed by a turnover time of 328 days (Table 2-1). In comparison with the marine stage the sedimentation is now more likely to be dominated by material that as some point has been dissolved. This should favour relatively mobile elements like Ni at the expense of elements like Ti that are not easily released by weathering (Boes et al. 2011). Hence, although the sedimentation of Ni at first glance may appear to have been more efficient during the marine stage, the higher Ni/Ti ratios in the more organic freshwater sediments indicate that there most likely has been a more efficient scavenging of Ni since the lake was isolated. Given that Ni does not appear to interact particularly strongly with Fe and Mn in the lake water (e.g. Figure 2-23 and Figure 2-24), the most likely agent behind this scavenging is organic matter. As shown in Figure 2-30, the Ni/Ti ratio in the sediments largely follow the LOI.

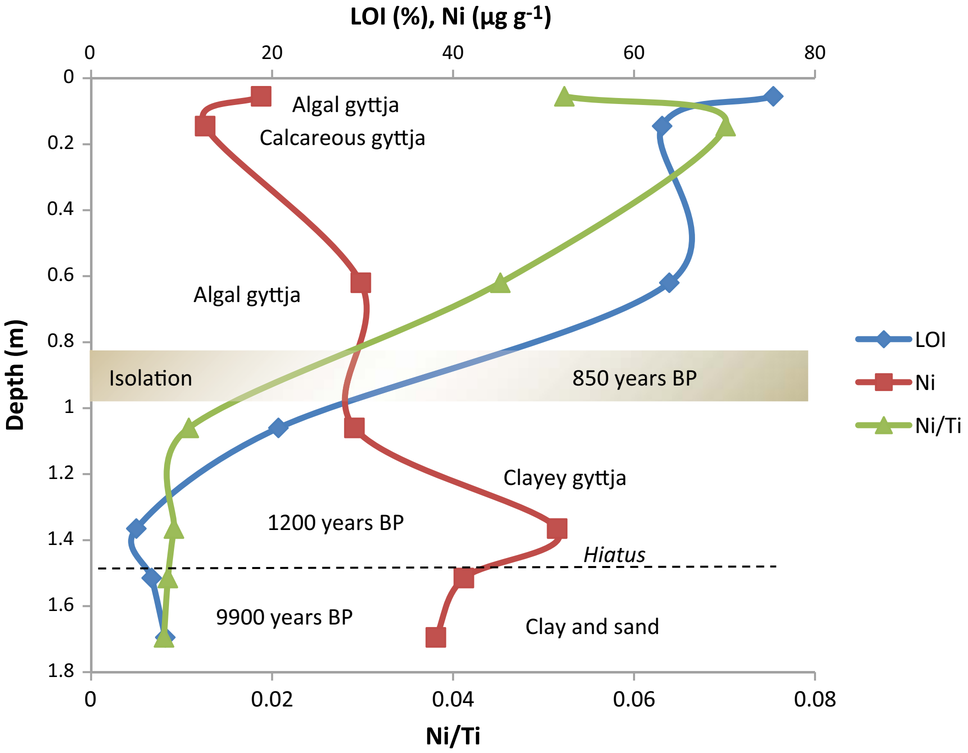

__Figure 2-30.__ Ni concentrations, LOI (loss on ignition) and Ni/Ti ratios in sediments from Eckarfjärden, Forsmark. The coloured area denotes the period when Eckarfjärden was isolated from the Baltic Sea (ca. 850 years BP). The dashed line represents a nearly 9 000 years long hiatus in the sediment record. The dating was taken from Hedenström and Risberg (2003).

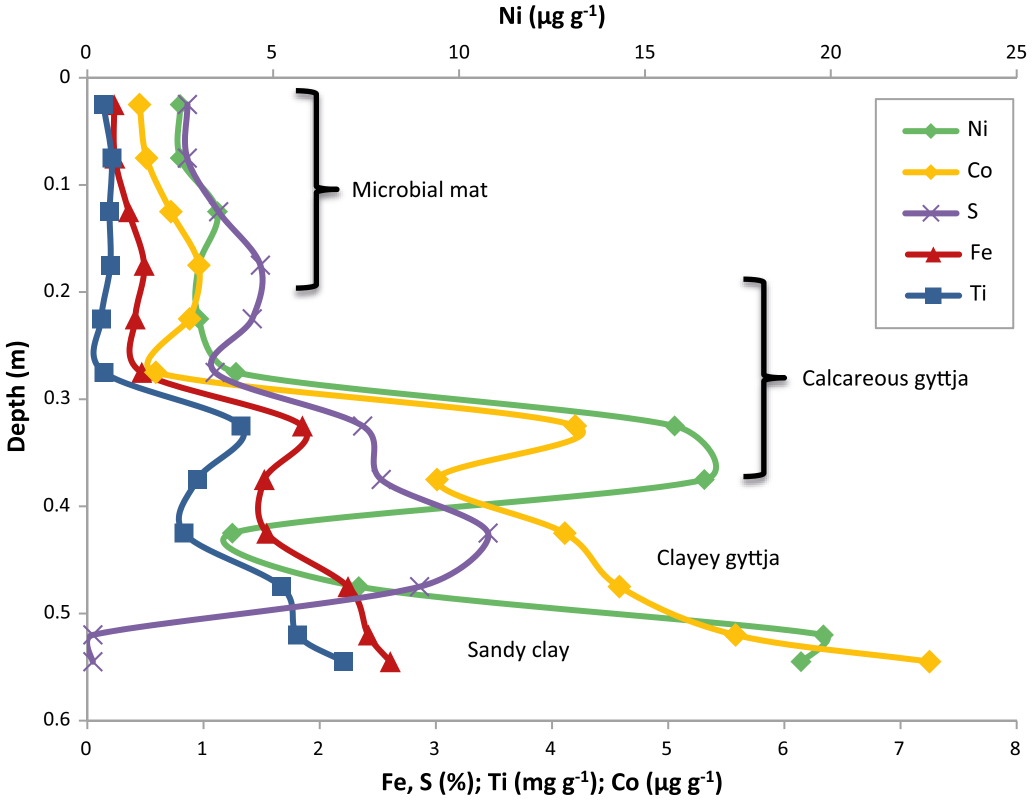

__Figure 2-31.__ Concentrations of Ni, Fe, Co, Ti and S in sediments from Stocksjön. Ni is plotted as half the reporting limit at 0–0.3 m. The core originally comprised ca. 0.7 m, but it was reportedly compressed during the transport to the laboratory (Strömgren and Brunberg 2006).

Another sediment core from the Forsmark area was sampled in Stocksjön, a small lake (0.036 km^2) downstream of Eckarfjärden (Table 2-1; Strömgren and Brunberg 2006). No lake water samples were collected at this site, but since it is fed by the stream draining Eckarfjärden, the lake water chemistry in Stocksjön should largely resemble that of Eckarfjärden. Stocksjön has a mean depth of only 0.2 m, and large parts of the lake have been transformed into a wetland. In 2002, when the sediment core was retrieved, it was estimated that 85 % of the lake area was covered by emergent vegetation (Brunberg et al. 2004). The sediments are highly organic with an ash content of 34–73 % throughout the core. Unfortunately, Ni was below the reporting limit (5–8 µg g^{-1}) in the upper 0.3 m of the sediments, leaving only six samples from 0.3–0.55 m with reliable Ni concentrations. The decline in the Ni concentration above 0.3 m appears to be typical for elements that are present mainly in eroded mineral particles, e.g. Ti (Figure 2-31). Major exceptions to this pattern were Ca and Mn, which both occurred in high concentrations in the upper 0.3 m. In the case of Ca the high concentration was undoubtedly related to precipitation of $CaCO_3$, and assuming that all Ca is present in this form, the concentrations would correspond to 28–53 % $CaCO_3$ in the upper 0.3 m. In the case of Mn the reason should be oxidation and precipitation of Mn, as discussed above (e.g. Figure 2-22). Such precipitates should be expected to be stable in the sediments only as long as Mn is not reduced, which means that it will not be conserved over time. The high pH, the relatively shallow water and the production of O_2 by the microbial mat should, however, help keep Mn oxidised in the upper sediments. In the deeper sediments the Mn concentration largely follows the mineral fraction (Strömgren and Brunberg 2004). The relatively low concentration of Ni at these depths indicates that Ni does not interact particularly strongly with neither $CaCO_3$ or Mn precipitates in these environments, which is consistent with the patterns observed in the lake water (Section 2.2.4).

Strömgren and Brunberg (2004) suggest that the change in the sediment composition around 0.3 m represents the final isolation of the lake from the Baltic Sea. Based on the general sedimentation rate in the Forsmark area they estimate the age of these sediments to ca. 230 years. Based on the elevation and the land uplift, however, Brydsten and Strömgren (2004) estimated that Stocksjön was isolated ca. 430 years ago, which is about half of the age of Eckarfjärden. Hence, the lake elevation should have been at least 1–1.5 m above the sea level when the change around 0.3 m occurred. While it may not be inconceivable that some marine influence could have occurred as late as 230 years ago in connection with high water levels and stormy weather, the change in the sediment composition at this depth could also be related to the evolution of the lake. The major source of mineral particles during the lake phase should be the inflowing stream from Eckarfjärden, but as the vegetation in the lake expanded this would have isolated parts of the lake and gradually suppressed turbulence from both wind and running water. What the decrease in Ti and similar elements around 0.3 m mainly signifies is a decrease in the sedimentation of eroded particles (Figure 2-31). With the establishment of a microbial mat across the lake bottom the potential for resuspension would also be low. Based on dating the transition from marine to freshwater conditions occurred at ca. 0.8–1 m in Eckarfjärden so assuming that the lake development has been similar the corresponding transition in Stocksjön should rather be represented by sediments around 0.4–0.5 m. This depth would be more consistent with the average sedimentation rate in Eckarfjärden, which has been estimated to ca. 1.0 mm a^{-1} (Hedenström and Risberg 2003). The S concentration in the sediments increased drastically from 0.048 % at 0.50–0.54 m to 2.9 % at 0.45–0.50 m, which indicates that sulfate-reducing conditions began to develop at the lake bottom or in the sediments around this time. This seems likely to have occurred as the area became a small sheltered bay and gradually lost all contact with the sea.

The S concentration in the sediments in Stocksjön peaked at 3.5 % at 0.40–0.45 m (Figure 2-31). As a reference, it can be mentioned that this by some margin exceeds the highest observed S concentration (2.4 %) in a survey of 110 Swedish lakes (Bindler et al. 2008). A similar accumulation of S was observed in Eckarfjärden, which in this case reached a maximum of 2.1 % around 0.6 m. The high S concentration in Stocksjön coincided with the lowest observed Ni concentration in this core, 3.9 µg g^{-1}, although Ni is known to accumulate in sulfides (Figure 2-31). For instance, Ni can precipitate directly as NiS (millerite) in the presence of sulfide, but more likely is probably coprecipitation or adsorption onto Fe sulfides, e.g. FeS (mackinawite) (Morse and Arakaki 1993, Huang et al. 2010, Wilkin and Beak 2017). When such sediments are exposed to air, e.g by land uplift and ditching, the sulfides will be oxidised, which can lead to high concentrations of Ni and other associated elements in the runoff (Nordmyr et al. 2008). However, the fact that the Ni concentration in the most S-rich sediments was so low suggests that there has not been any substantial sorption of Ni in connection with the reduction of sulfate. As will be discussed below, this is a section of the core with an appreciable accumulation of, for example, Mo and U (Section 3.2.5). Hence, Ni must have had a higher affinity for some other phase, presumably organic matter. Although it is somewhat uncertain whether this occurred under marine or freshwater conditions, it can be noted that the Ni concentration has been observed to remain constant across the O_2/H_2S redoxcline in the Baltic Sea, which then would be consistent with the sediment record in Stocksjön (Dyrssen and Kremling 1990).

Principal component analysis of sediments from Stocksjön

A principal component analysis (PCA) of the sediments from Stocksjön showed that the first principal component could explain 64.2 % of the variance in the data. As shown in Figure 2-32, the main effect of PC1 was to separate Ca from most other elements, which no doubt is related to the presence of calcite in parts of sediments. As exemplified by Fe, Ti, Ni and other elements in Figure 2-31, the concentrations in the upper 20–30 cm of the sediment cores were generally low, while higher conentrations generally were found in the deeper parts. Due to precipitation of calcite, which is common in the lakes of the Forsmark area (Jaremalm et al. 2013), Ca occurs in considerably higher concentration in the upper parts of the core so generally elements found in the right-hand side of the biplot (Figure 2-32) could be expected to have a predominately minerogenic source and in many cases also be associated primarily with sedimentation of mineral particles. This interpretation is also consistent with the occurrence of Pb in the left side of the biplot, since atmospheric deposition of anthropogenic Pb is a well-known source of Pb (e.g. Klaminder et al. 2008).

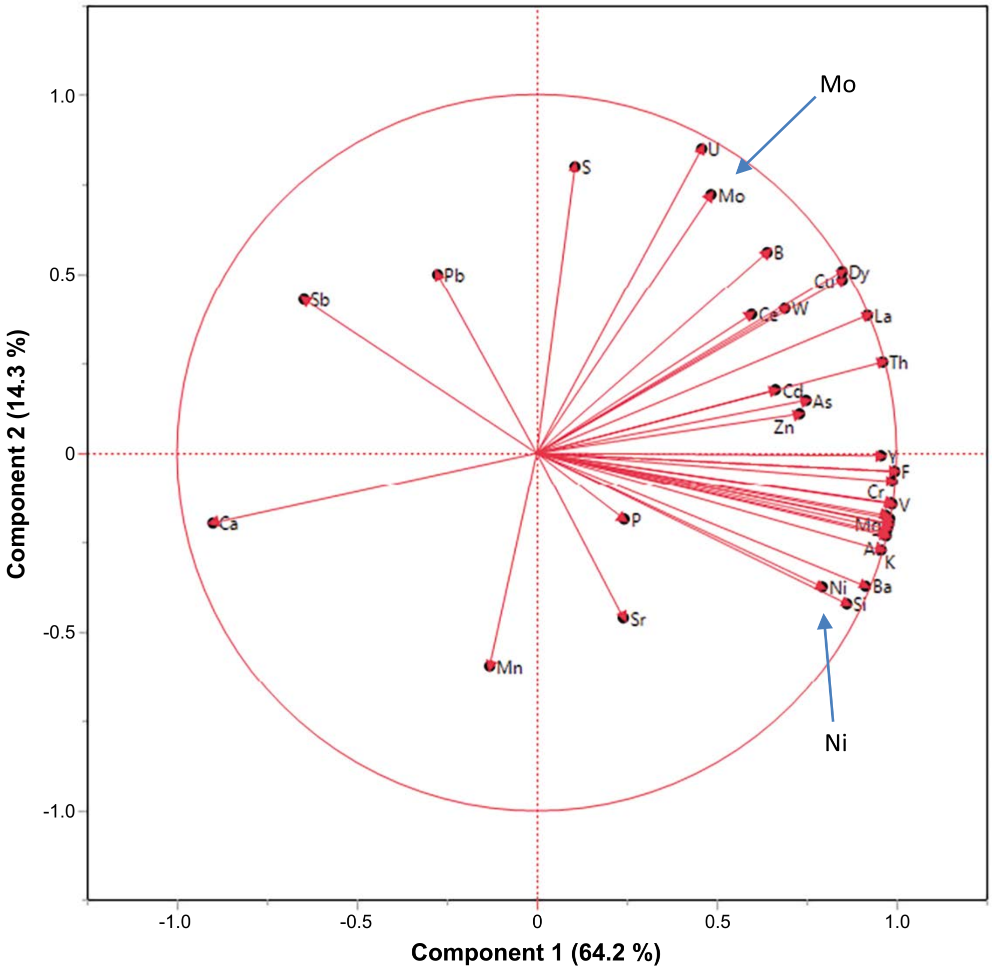

Figure 2-32. *Results of a principal component analysis of sediments from Stocksjön, Forsmark, showing how the various elements align with the first and the second principal components. The PCA includes Ni, Mo and all elements that were reported for all depths in the sediment core except the lanthanide series, for which only La, Ce and Dy were selected.*

The second principal component explained another 14.3 % of the variance, and appears to reflect the influence of redox conditions on the accumulation in the sediments. In the positive direction, S is plotted close to PC2, while Mn is plotted in the opposite direction. As discussed above, the peaks observed for S are most likely associated with sulfate reduction and precipitation of sulfide minerals. This interpretation is also supported by the fact the other elements such as Mo and U, which also tend to accumulate in reducing environments, fall close to S and PC2 (see Section 3.2.5 for more discussion on Mo in sediments). Manganese, on the other hand, exhibits the opposite behaviour, e.g. higher mobility in reducing environments, so its occurrence in the lower half of the biplot is also consistent with this interpretation. Nickel, finally, is found relatively close to PC1 along with the majority of the elements that were included in the PCA. As discussed above, this would suggest that Ni mainly is brought to the sediments by sedimentation of mineral particles, and the influence for precipitation of both carbonate and sulfide minerals has a limited effect on the total amount Ni accumulating in the sediments of Stocksjön.

Comparison between suspended matter and sediments

With respect to Ni the composition of the modern sediments in Eckarfjärden appear to agree well with the suspended matter in the lake. This would indicate that the postdepositional accumulation and activity of Ni in the sediments are limited. The Ni concentration in the suspended matter was 14 µg g^{-1}, which is comparable to the concentrations found in the two uppermost samples in the sediment core from Eckarfjärden (13–19 µg g^{-1}, see Figure 2-30). In the sediments from Stocksjön, however, the uppermost 0.1 m had a Ni concentration of only 2.5 µg g^{-1}, but this is likely to reflect the fact the sediments in Stocksjön are more organic. The suspended matter in Eckarfjärden also has a similar Ni/Ti ratio as the uppermost sediment layers, which indicates that Ni was transported to the sediments mainly by sedimentation of particles from the water column (Figure 2-33). The alternative would be that dissolved Ni in the lake would bind directly to the sediments. If Ni, for instance, was retained in the sediments mainly by sulfides, the accumulation could have been expected to occur largely in the sediments and not so much in the water column, which may not be reducing enough to contain much sulfide. It can also be noted that the Ni/Ti ratio in both suspended matter and the uppermost sediment layers are higher than in the local till. This could be related to different Ni/Ti ratios in different particles size fractions in the till, but it could also be interpreted as an indication that there is a preferential enrichment of Ni over Ti in organic particles due to the higher mobility of Ni. The Ni/Ti ratio in the dissolved phase in Eckarfjärden is ca. 1.6, i.e. approximately 20 times the Ni/Ti ratio in suspended particles in the lake (0.082). The higher Ni/Ti ratio in the dissolved phase reflects the higher mobility of Ni as compared to Ti. Sorption of dissolved Ni could therefore be expected to increase the Ni/Ti ratio of the solid phase, which was 0.052–0.070 in surface sediments from Eckarfjärden and somewhat higher, 0.12–0.19, in the more organic sediments in Stocksjön. Yet, in both cases, the Ni/Ti ratio was lower than in the dissolved phase, suggesting that much of the Ni in the sediment could be present in eroded material.

A comparison of the Ni concentration in the solid and the dissolved phase, respectively, also shows a good agreement between suspended matter and surface sediments in Eckarfjärden (Figure 2-33). This apparent Kd value for suspended matter (28 m^3 kg^{-1}) is somewhat lower than for the uppermost sediment layers (47–74 m^3 kg^{-1}), but this could be related to the comparatively high Ni concentration in the lake water at the occasion when the suspended matter was sampled – 0.50 µg L^{-1}. The sediment Kd values in Figure 2-33 were calculated using the average Ni concentration in Eckarfjärden – 0.27 µg L^{-1} (Figure 2-14). In the deeper sediments samples the apparent Kd value increased to a maximum of 110 m^3 kg^{-1}, and the increase in Kd was clearly dependent on the Ti concentration of the sediments (Figure 2-33). This could therefore reflect a higher abundance of Ni in primary minerals in these sediments rather than a higher sorption capacity. It could be discussed, however, whether it is appropriate to use the current lake water concentrations of Ni for sediments that were deposited during the marine stage, since the seawater tends to have higher Ni concentration than lake water. Using the average Ni concentration of seawater from the site investigation in Forsmark (1.2 µg L^{-1}) instead would lead to Kd values similar to the freshwater sediments. It could argued that this concentration would be more adequate, since the deeper part of the sediment core most likely was deposited in water with a higher Ni concentration, but then again the old marine pore water should have been replaced by freshwater by now, which may be better represented by the lake water concentration.

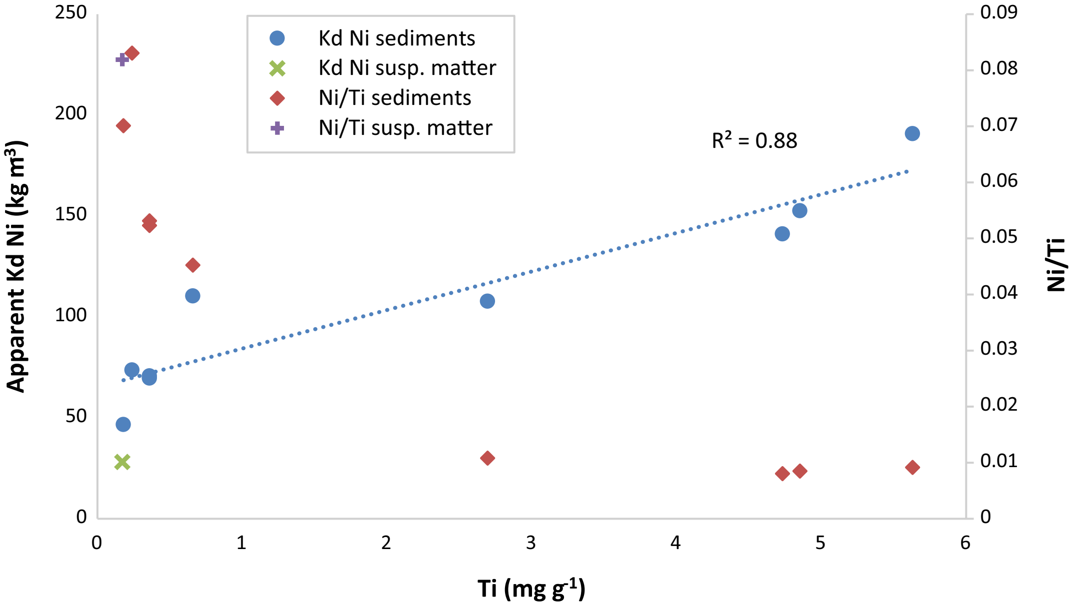

Figure 2-33. *Apparent Kd values for Ni in sediments from Eckarfjärden based on the current average Ni concentration in the lake water (0.27 µg L*$^{-1}$*) as a function of the Ti concentration of the sediments. Also shown is the Ni/Ti ratio of the sediments, a proxy for the sedimentation of Ni in primary minerals, and the Ni/Ti ratio of suspended matter in Eckarfjärden. For comparison, the observed Ni/Ti ratio in till from the Forsmark area was 0.0039–0.061. The apparent Kd value for suspended matter is the same as shown in Figure 2-29. Data from Engdahl et al. (2008).*

However, since Kd values often are compared on a logarithmic scale, the choice of lake water or seawater concentrations is not crucial in the case of Ni. Compared to the actual Kd values determined for different types of soils in the Forsmark area these apparent Kd values for sediments and suspended matter were relatively high, on average somewhat higher than glacial clay, but since the methodology was not exactly the same, one should be careful not to draw to far-reaching conclusions based on these comparisons (Figure 2-44; Sheppard et al. 2011). In Frisksjön in the Simpevarp area a similar comparison (based on an average Ni concentration in modern lake water of 1.6 µg L^{-1}) would yield apparent Kd values for the sediments in approximately the same range, 18–45 m^3 kg^{-1}.

Sediments from Frisksjön, Simpevarp

The sediment core from Frisksjön was considerably longer (4.4 m) than the cores from the Forsmark area, which at least partly might reflect the fact that Frisksjön is an older lake. Frisksjön is located 1.37 m above the current sea level and is estimated to have been isolated from the Baltic Sea 2 500–2 750 years ago (Brunberg and Carlsson 2004, Nilsson 2004). This corresponds to a depth of ca. 2 m in the sediment record (Figure 2-34). Compared to the lakes in the Forsmark area Frisksjön is deeper, on average 1.7 m, and it has a retention time nearly as long as that of Eckarfjärden, 264 days (Table 2-1). The Ni concentration in the sediments ranged between 25 µg g^{-1} and 72 µg g^{-1} (Figure 2-34). This is somewhat higher than the Ni concentration in Stocksjön and Eckarfjärden, but most likely this just reflects the generally higher Ni concentration in the Simpevarp area (Figure 2-2, Figure 2-3 and Figure 2-13).

Overall, the Ni concentration tended to follow the Ti concentration ($r = 0.86$, $p < 0.01$), which would suggest that a major fraction of the Ni found in the sediments is associated with the mineral fraction. Nevertheless, there was a slight tendency of increasing Ni/Ti ratios after the isolation of Friskjön (Figure 2-34). The Ni/Ti ratios in the sediments (0.031–0.057) were, however, considerably higher than in most samples from the local soils, which mostly had Ni/Ti ratios in the range 0.0028–0.0096. One exception was, however, the soil profile PSM007190, which had a Ni/Ti ratio similar to the sediments in Frisksjön (0.034). The sample in question was, however, a gyttja soil so it represents former sediments (Sohlenius et al. 2006). Possibly, the 20 soil samples from the Simpevarp area were not representative for the material reaching Frisksjön – only two of these soil profiles were collected within ca. 500 m of Frisksjön. Another possibility is that there has been a more considerable accumulation of once dissolved Ni in the sediments than the close relationship between Ni and Ti in the sediments would suggest. The interpretation that sorption of Ni from the dissolved phase should increase the Ni/Ti ratio (as a consequence of the low mobility of Ti in the dissolved phase) is supported by the sequential extractions that were discussed in Section 2.2.2. The most easily mobilised fraction (ammonium acetate) had an average Ni/Ti ratio of 0.12, which is higher than all sediment samples. If this is assumed to represent the exchangeable fraction, this supports that sorption from the dissolved phase should increase the Ni/Ti ratios of the sediments. The following soil fractions had fairly similar Ni/Ti ratios – 0.035 (dithionate citrate) and 0.032 (*Aqua regia*). This is similar to the ratios observed in the sediments so, consequently, it appears to be the Ni/Ti ratios in the soil samples reported by Sohlenius et al. (2006) that stand out. Hence, the interpretation of these ratios is a bit ambiguous given the currently available data. One more piece of evidence concerning the origin of the Ni in the sediments can be derived from the dating of the sediments in Frisksjön. Sternbeck et al. (2006) estimated the long-term sedimentation rate in Frisksjön to ca. 400 g m^{-2} a^{-1}. Given that the Ni concentration in the sediments was in the range 26–72 µg g^{-1} (Figure 2-34) this would imply that the accumulation rate of Ni in the sediments is ca. 10–30 mg m^{-2} a^{-1}. The amount of dissolved Ni in the water column above the sediments can be estimated to ca. 2.7 mg m^{-2} a^{-1} given that the average concentration of dissolved Ni in the lake water is ca. 1.6 µg L^{-1} (Figure 2-26) and that the average depth of the Frisksjön in 1.7 m (Table 2-1). It can be argued that the sedimentation should be focused to the deeper parts of the lake and that the estimation consequently should be increased, but nonetheless the available dissolved Ni in the lake water appears quite low compared to the flux to the sediments, especially given that the theoretical turnover time of Frisksjön is close to one year (Table 2-1). This indicates that mineral particles are important for transporting Ni to the sediments. One consequence of this is that changes in the Ni concentrations cannot uncritically be assumed to reflect the biogeochemical properties of Ni. One way to avoid this problem is to also look at the ratio between Ni and other elements.

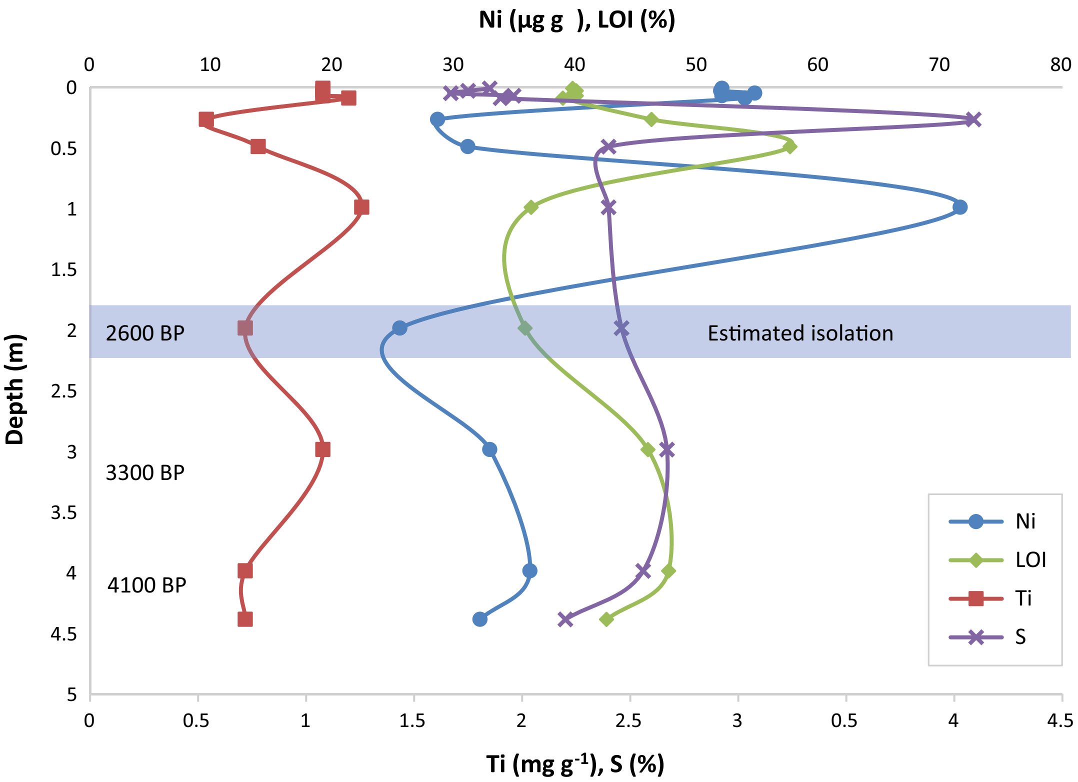

Figure 2-34. Concentrations of Ni, Ti and S, respectively, and LOI in sediments from Frisksjön, Simpevarp. The region representing the isolation from the Baltic Sea is based on the timing given by Brunberg and Carlsson (2004) and the dating of sediments from Frisksjön by Sternbeck et al. (2006).

Fractionation between Ni, Co and other transition metals

In the water of Frisksjön it was observed that Ni seemed to be fairly insensitive to changes in the redox conditions (Figure 2-26). This was also reflected in the sediment record. In the lake water Ni and Co did not covary, but in the sediments there was a positive correlation between Co and Ni ($r = 0.90$, $p < 0.01$). Again, this would suggest that both elements largely could be controlled by the mineral fraction. There was, however, a decline in the Ni/Co ratio in the sediments as Frisksjön was isolated from the sea. The main reason behind the declining Ni/Co in the freshwater sediments was that the Co concentration increased from ca. 3 $\mu g\ g^{-1}$ in the deeper sediments to ca. 40 $\mu g\ g^{-1}$ in the more recent sediments. The decrease in the Ni/Co ratio coincided with increasing Mn concentrations ($r = -0.94$, $p < 0.01$), from ca. 100 $\mu g\ g^{-1}$ in marine sediments to well above 250 $\mu g\ g^{-1}$ in the upper half metre (Figure 2-35). This trend is consistent with the correlation between Co and Mn observed in the lake water and suggests that Co could be brought to the sediments by precipitation of Mn oxides. Evidently, Ni is not affected by this nearly as much as Co. As discussed above (Section 2.2.4) one crucial difference between Ni and Co could be that Co^{2+} can be oxidised to less soluble Co^{3+} in the presence of MnO_2 (Kay et al. 2001). It was a clear pattern also in the Forsmark area that Ni was not affected by precipitation of Mn nearly as much as Co was.

The Mn concentration was particularly high in the uppermost centimetres of the sediment core, which could reflect the instability of Mn precipitates in more reducing sediments (Ingri 2012). According to Sternbeck et al. (2006) there was no oxidised layer at the top of sediment core from Frisksjön, but this does not exclude the possibility that there is a manganic zone (i.e. a zone with oxidised Mn). Below that, around 0.27 m, S displayed a distinct peak, reaching a concentration of 4.1 % (Figure 2-34). This indicates that there is a sulfate-reducing zone at some depth in the sediments so one could expect a manganous zone, where Mn is reduced to Mn^{2+} and any Mn precipitates are dissolved. It is notable, however, that the Ni concentration was comparatively low at these depths (29 $\mu g\ L^{-1}$), indicating that there is no appreciable incorporation of Ni into the sulfides, at least not in relation to other Ni fluxes. In contrast, the concentration of, for instance, Fe remained high in the S-rich sediments. This could, for example, be explained by extensive precipitation of Fe sulfides in this zone. Although the potential for substantial accumulation of Ni in sulfides is certainly there, the critical factor could be that Ni is not transported so efficiently to the sediments. Once in the sediments, most elements that are brought there by Mn or Fe precipitation could be retained as sulfides when Fe and Mn are reduced and remobilised (Tribovillard et al. 2006).

While sedimentation of Co relative to Ni appears to be favoured by high Mn fluxes to the sediments (Figure 2-35), Ni appears to be more affected by organic matter. The effect of organic matter is most evident in the sediments from Eckarfjärden, where the Ni/Co ratio declined with increasing LOI, whereas the Ni/Cu ratio increased (Figure 2-36). One possible interpretation of these trends is that Ni is more dependent on organic matter than Co is, which favours the relative sedimentation of Ni when the sediments become more organic. Copper, which tends to bind even more strongly to organic matter than Ni does, is consequently favoured even more, causing declining Ni/Cu ratios with increasing LOI. Since there are many changes occurring simultaneously, more detailed measurements would be required to definitively conclude to what extent different processes are responsible for the observed changes in the element ratios.

One such factor that complicates the interpretation of the sediment records is that all investigated lakes have undergone a transition from marine to freshwater environments, which could affect the fate of various transition metals in a number of ways. One example is the Ni/Zn ratio in the sediments from Frisksjön, which showed a strong correlation to the Cl concentration ($r = 0.98$, $p < 0.001$; Figure 2-37). The sedimentation of Cl is largely dependent on organic matter, but there is a clear gradient from seawater to freshwater in terms of Cl concentration so the sedimentation largely reflects the environment, in which the sediments were deposited. Figure 2-37 illustrates that the Ni/Zn ratio in the sediments has declined since the isolation of Frisksjön ca. 2 500–2 750 years ago (Nilsson 2004). In the water column of Frisksjön the Ni/Zn ratio was highly variable (0.39–1.1), presumably depending on the redox conditions in the lake (Figure 2-26). In Granholmsfjärden (PSM2064), a bay (marine) just outside Frisksjön, the Ni/Zn ratio was not too different, varying between 0.16 and 0.88. Because of the variation in both seawater and freshwater both types of water largely envelop the observed Ni/Zn ratios in the sediments. Hence, it is hard to draw any conclusions based on differences between seawater and freshwater. If anything, the marine Ni/Zn ratio is possibly somewhat lower than in the modern lake water, although the sediment signature for the marine stage was higher (Figure 2-37). This would suggest that the trend in the Ni/Zn ratios in the sediments is related primarily to differences in the geochemical behaviour of Ni and Zn, respectively.

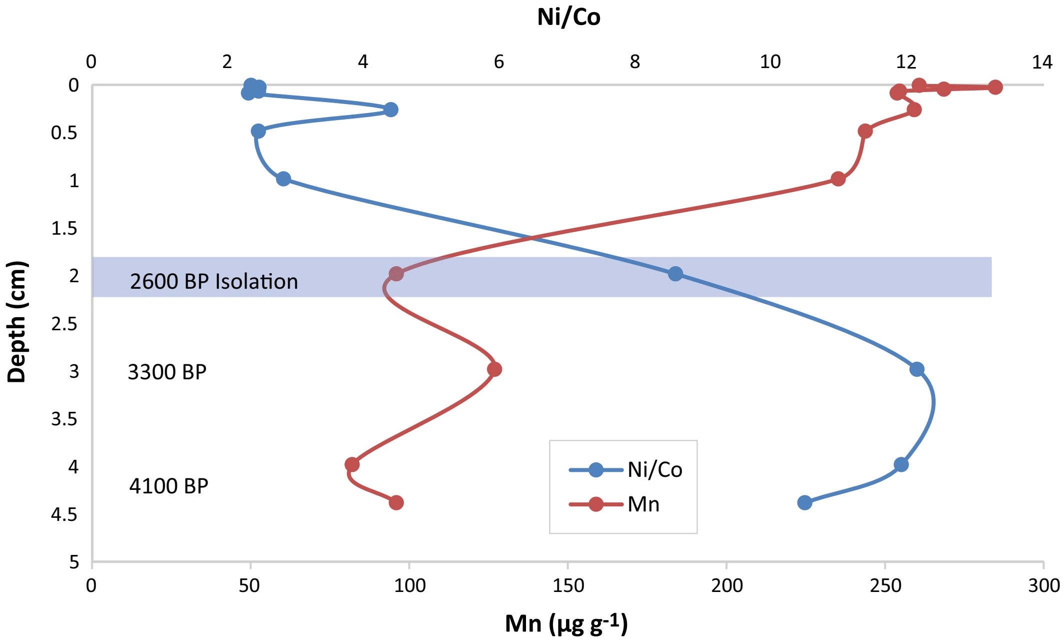

Figure 2-35. *Ni/Co ratios and Mn concentrations in sediments from Frisksjön, Simpevarp. Sediment ages are taken from Sternbeck et al. (2006).*

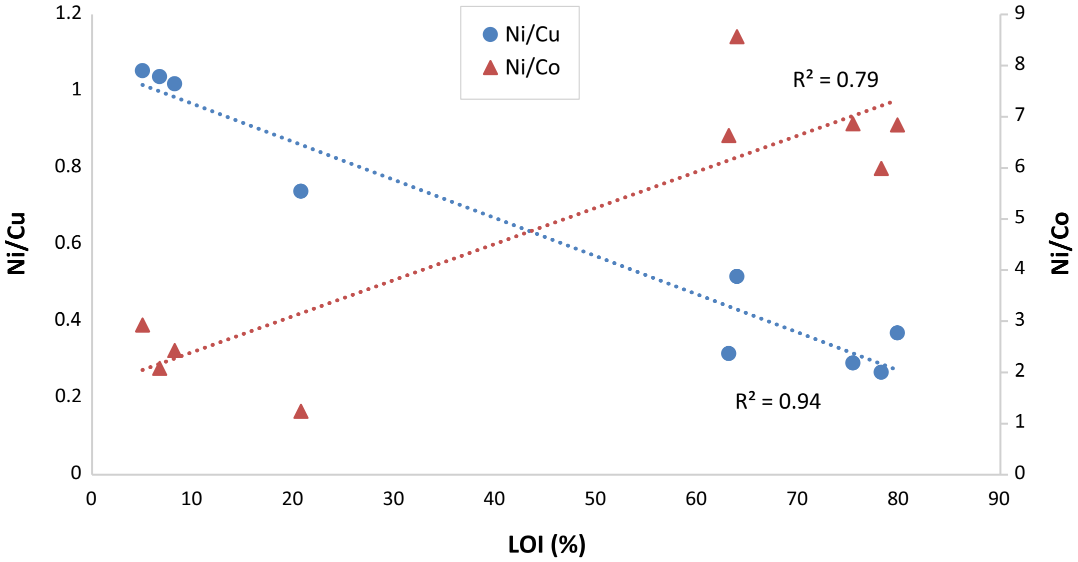

Figure 2-36. *Ni/Cu and Ni/Co mass ratios in sediments from Eckarfjärden as a function of LOI.*

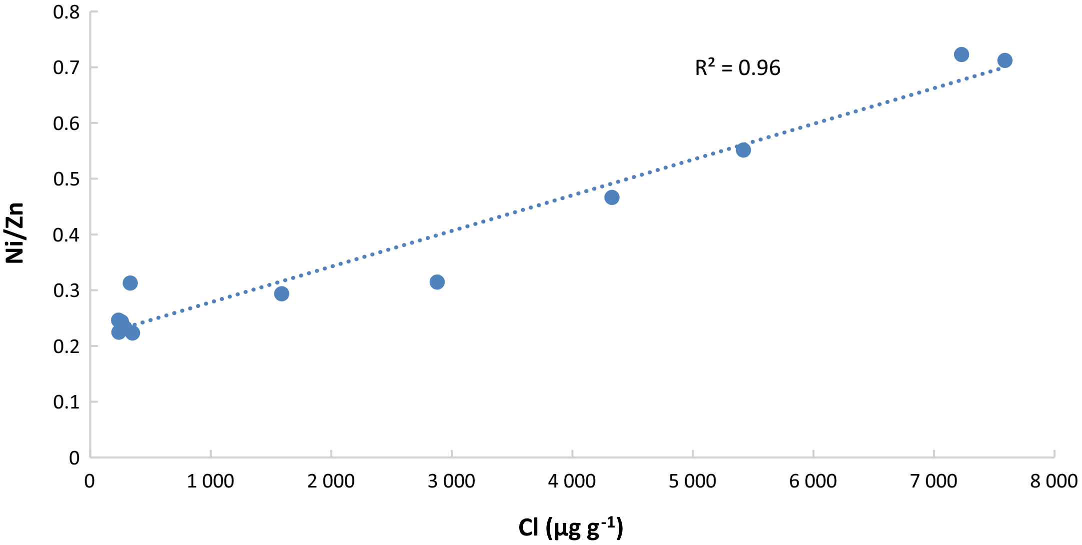

Figure 2-37. *Ni/Zn mass ratios in sediments from Frisksjön, Simpevarp, as a function of the Cl concentration.*

Nickel in peat cores

As the landscape ages, many lakes in the site investigation areas are expected to evolve into wetlands. The chemical side of this landscape evolution can be assessed by studying the peat cores from existent wetlands. In the Simpevarp area a 4.75 m deep core was collected from the bog Klarebäcksmossen and analysed for trace elements (Lidman 2009). In the underlying clay layers (< 4.6 m) the Ni concentration was relatively high, up to 32 µg g^{-1} (Figure 2-38). Compared to the levels observed in soils from the Simpevarp area this is, however, normal (Section 2.2.2). The organic content of the clay is low (< 4 %) and so is the Ni/Ti ratio (ca. 0.0068). The Ni/Ti ratio in the clay is comparable to the Ni/T ratio encountered in soils from the Simpevarp area (0.0028–0.0096) so it is likely that most Ni in the clay sediments is present in primary minerals. The transition from marine to fresh water conditions is estimated to have occurred ca. 11 250 years BP (Nilsson 2004). In connection with this the sediments gradually become more organic (above ca. 4.5 m) in a similar manner as in Eckarfjärden (Figure 2-30), but the Ni concentration initially remains high in the gyttja – up to 32 µg g^{-1}. The increasing Ni/Ti ratios in this section suggest, however, that there has been change in the source of Ni, most likely a more extensive accumulation of Ni from the lake water of the disappearing lake. This could for example, occur by sorption of dissolved Ni to the organic matter of the sediments or by direct sedimentation of organically bound Ni. Although the Ni/Ti ratios are lower in the peat than in the sediments from the transition between lake stage and wetland stage, they still remain higher than in the underlying clay sediments and in local till. Hence, this would indicate sorption of Ni from the dissolved phase.

As the lake transformed into a wetland the Ni concentration declined, remaining consistently below 3 µg g^{-1} in the peat samples. This should not be interpreted as a low affinity of Ni for peat, but rather reflects the fact that not much Ni was able to reach the central parts of the wetland once the lake had been isolated from the surrounding mineral soils by the expanding peat. It is likely that higher Ni concentrations would be encountered in peat cores close to the edge of the mire, which have been in more contact with inflowing groundwater from the surrounding mineral soils. Such patterns have, for instance, been observed for U and Th in boreal mires (Lidman et al. 2013). Furthermore, the upper part of the peat is believed to be ombrogenic (as the wetland is classified as a bog) so the Ni closer to the surface should largely derive from deposition. The higher Ni concentration in the uppermost peat sample could therefore reflect higher anthropogenic emissions of Ni since the onset of industrialisation (Krachler et al. 2003).

The fact that extensive accumulation of Ni can occur in boreal wetlands is also supported by data from the Krycklan catchment in norther Sweden. When comparing the average Ni concentrations in ten sub-catchments, there was a clear trend that the Ni concentration was lower the more wetlands there were in the catchment (Figure 2-39). The effect was partly caused the absence of mineral particles and weathering in the peat soils, but there was also a clear trend that elements with a high affinity for organic matter were more affected by wetlands than elements with little or no affinity for organic matter (Lidman et al. 2014). This indicates that there also was a sorption of these elements in the pat.

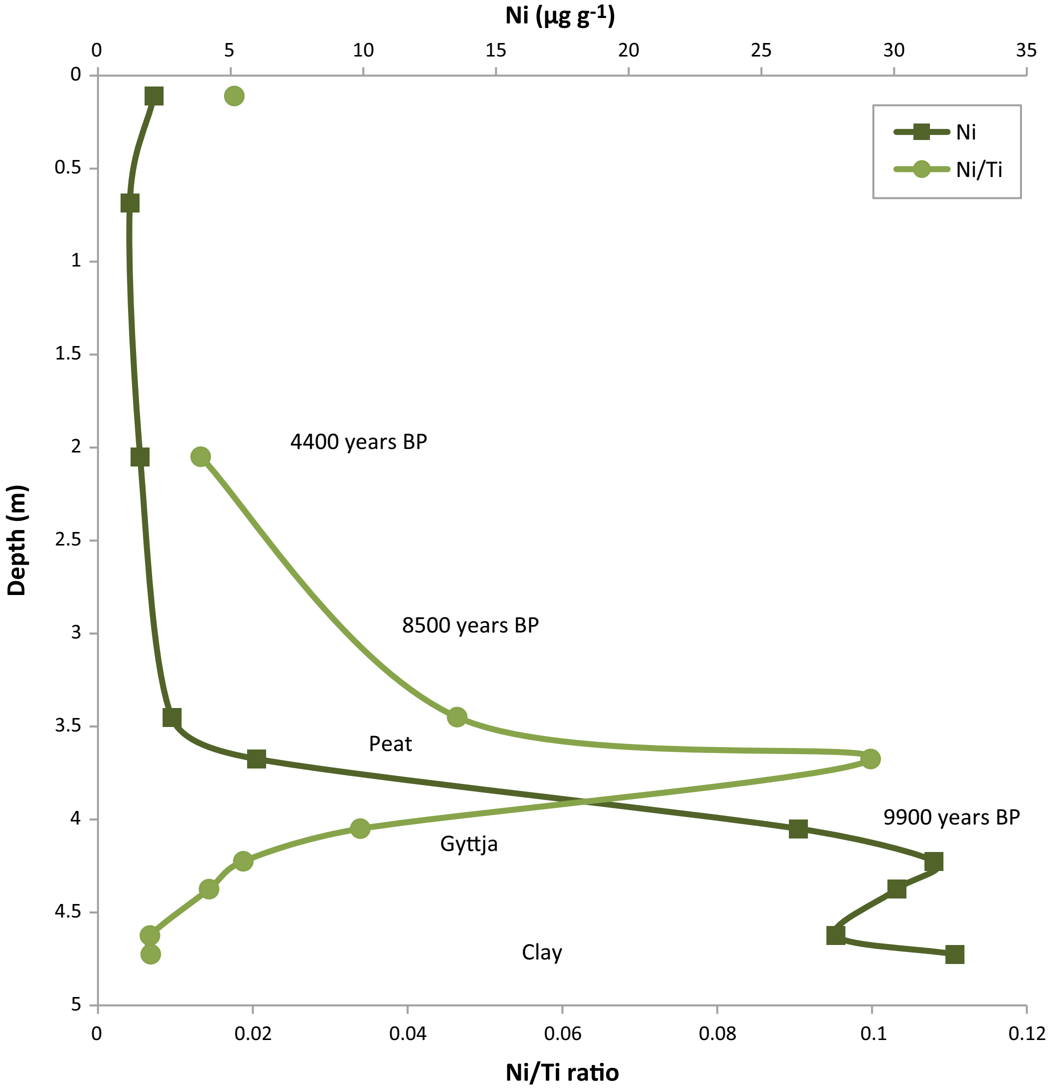

Figure 2-38. *Ni concentrations and Ni/Ti ratios in a peat core from Klarebäcksmossen, Simpevarp. The dating was taken from Sternbeck et al. (2006, P06-301).*

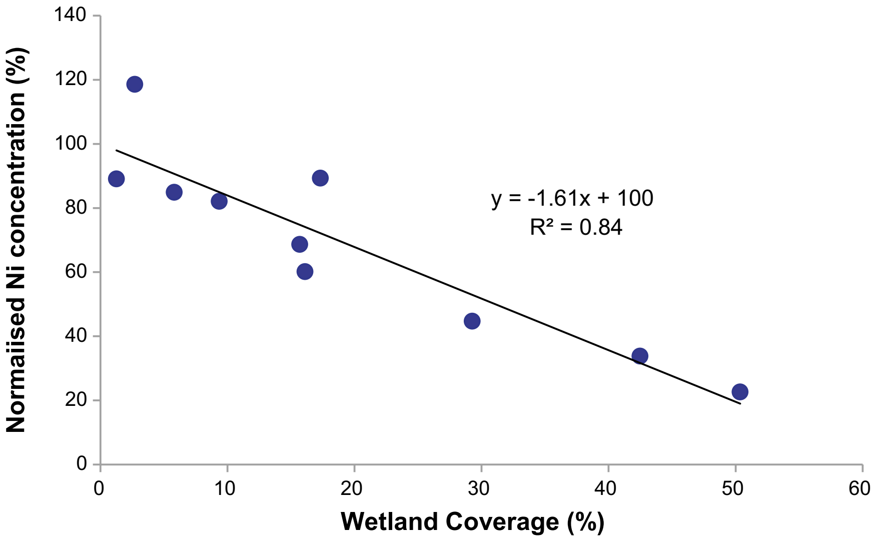

Figure 2-39. *Wetland-normalised average Ni concentrations in ten streams in the Krycklan catchment in northern Sweden as a function of the wetland coverage in each catchment (data from Lidman et al. 2014). The decline in Ni is ca. 1.6 percentage points for each percent of mineral soil that is replaced by peat, which implies that there is an accumulation of Ni in the peat.*

Since the affinity of Ni for organic matter is moderately strong, there was consequently a substantial accumulation of Ni in the peat. One should expect the wetlands in the site investigation areas to function in a similar way, perhaps even a stronger effect given the higher pH, especially in the Forsmark area. However, the catchments in the Forsmark area typically consist of ca. 10–20 % wetlands so there is no clear gradient from forest-dominated to wetland-dominated catchments, which would help make such trends more discernible. Given the complexity of the landscape the differences in wetland-coverage between the investigated catchments in the Forsmark area are probably too small to cause any statistically significant trends.

2.2.6 Speciation of Ni

One crucial parameter for understanding and predicting the behaviour of Ni in the site investigation areas is its speciation in groundwater and surface water. There are currently no direct measurements of the Ni speciation available in the site investigation areas, but the speciation has been assessed using thermodynamic modelling in Visual MINTEQ (Gustafsson 2012). The results are based on the modelling by Jaremalm et al. (2013), and the full results will be presented in an upcoming SKB report. Some key results are, however, presented here to allow a comparison with the Ni data discussed above.

Figure 2-40 shows an example of the modelled Ni speciation in Labboträsket, Forsmark, in June 2005. The speciation was dominated by nearly equal amounts of free Ni^{2+} and organically bound Ni. This is consistent with observations from other boreal waters, where organic colloids have been identified as the major carrier of Ni (Dahlqvist et al. 2007, Ilina et al. 2016). The preferential complexation with organic matter is also consistent with the behaviour of Ni in the lakes and in the sediments. Some carbonate complexes were also calculated to be present in the lake water, but since pH and carbonate concentrations never get much higher than in the Forsmark lakes during the summers, it appears as if the formation of Ni carbonate complexes would be of minor importance.

Figure 2-41 summarises the speciation calculations for all types of water samples from Forsmark except deep groundwater, i.e. groundwater from the bedrock. The dominating fraction in most samples was organically bound Ni, while free Ni^{2+} ions typically constitute ca. 20–40 % of the total Ni concentration. There was also a trend of increasing contribution from carbonate complexes with increasing pH. In the most alkaline waters there was also a minor fraction of hydroxide complexes, mainly $NiOH^{+}$, which can be seen in the upper right corner of Figure 2-41. Together with the carbonate complexes they are important only in the most alkaline waters.

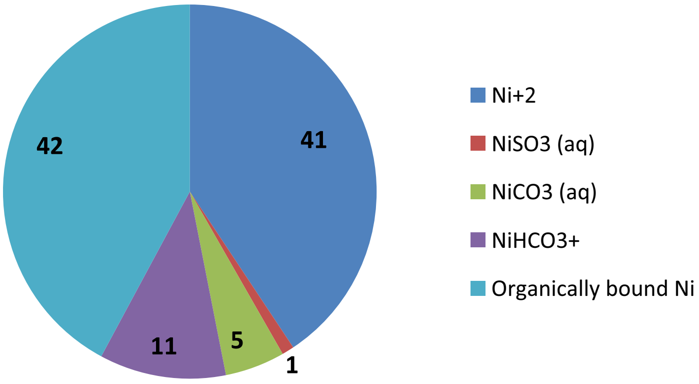

Figure 2-40. *Example of modelled Ni speciation in Labboträsket, Forsmark (11 June 2005). Fe colloids were not considered, but Ni has been observed to bind preferentially to organic matter in boreal waters (Dahlqvist et al. 2007). Generally the proportion of free* Ni^{2+} *ions decreases with increasing pH, while the proportion organically bound Ni increases.*

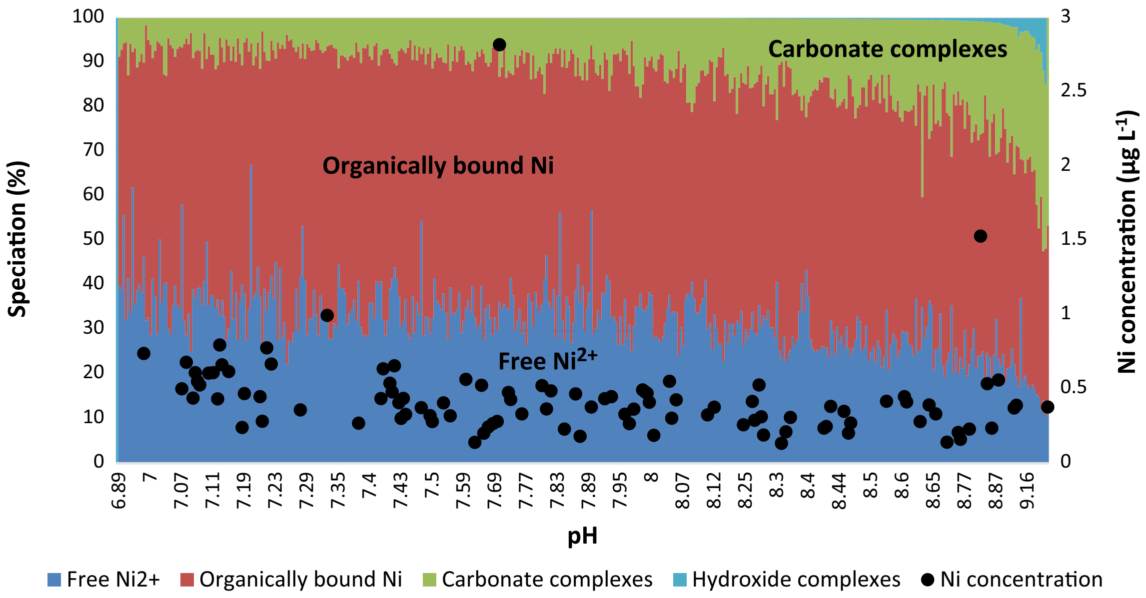

Figure 2-41. *Modelled speciation of Ni in all waters in Forsmark arranged in order of increasing pH. Data was taken from modelling by Jaremalm et al. (2013), which will be presented in detail in an upcoming SKB report. Trace elements were not analysed in all samples so where Ni concentrations are missing, the calculations were based on the available chemical parameter and typical Ni concentrations for the Forsmark area.*

In the Simpevarp area the modelling results were fairly similar in the sense that organic complexes dominated, followed by free Ni^{2+} ions (Figure 2-42). Due to the absence of calcite the carbonate complexes were apparently not nearly as important in the Simpevarp area as in Forsmark. Figure 2-42, however, only displays the speciation in lake water samples, since there are uncertainties concerning the validity of certain groundwater analyses in the Simpevarp area (Peltola 2018). As discussed above (Section 2.2.3), some groundwater wells have suspiciously high Al concentrations, which means that Al will occupy many of the available binding sites on the organic matter in the thermodynamic modelling, leaving next to nothing for Ni and other trace elements. As a consequence, Ni will be forced into solution as free Ni^{2+} or form other types of complexes. Since the high Al concentrations are questionable in the groundwater wells, there is an imminent risk that the modelling results also will be misleading, which is why only results from lake water samples are shown in Figure 2-42. The groundwater data and the modelled speciation will, however, be discussed more thoroughly in an upcoming SKB report.

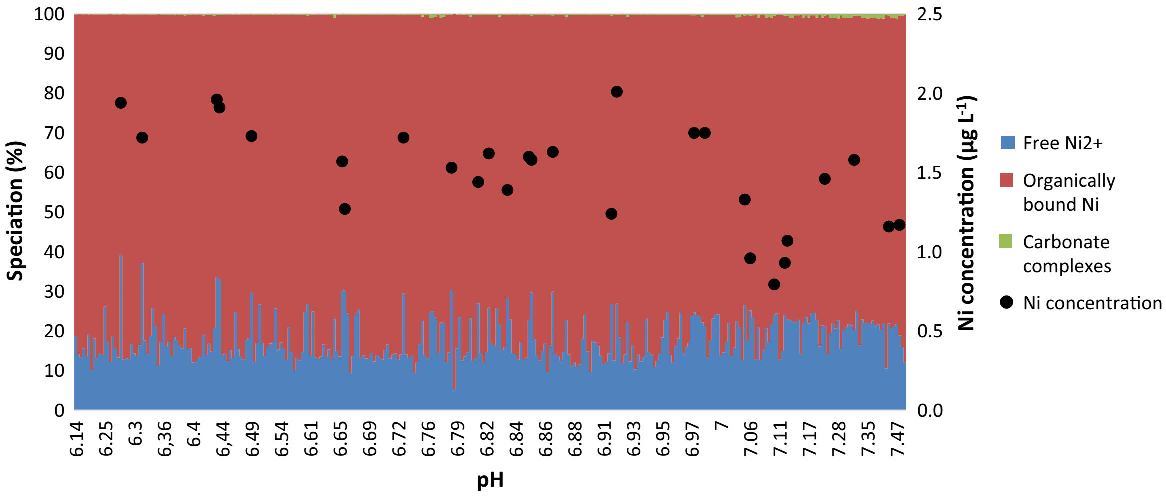

Figure 2-42. *Modelled Ni speciation in lake water from Simpevarp. Data was taken from modelling by Jaremalm et al. (2013), which will be presented in detail in an upcoming SKB report. Trace elements were not analysed in all samples so where Ni concentrations are missing, the calculations were based on the available chemical parameter and typical Ni concentrations for the Simpevarp area.*

2.2.7 Kd values for Ni

Ni was included in the site-specific Kd measurements from the site investigations presented by Sheppard et al. (2011). The overall distribution of terrestrial Kd values for all analysed elements are shown in Fig. 2-43, where Ni and Mo are highlighted in red. The Kd values for Ni were, in relative terms, low in clay gyttja (0.13–1.0 m^3 kg^{-1}), which probably was related to the high DOC concentrations observed during the analyses (Figure 2-44). The cultivated peat and the wetland peat had intermediate Kd values, ranging from 1.5–17 m^3 kg^{-1}. The mobility of Ni in these soils is likely to be enhanced by the high DOC concentrations, as predicted by the Ni speciation (Figure 2-40), but the relatively high Kd values are consistent with the accumulation of Ni that has been observed in wetlands (Figure 2-39).

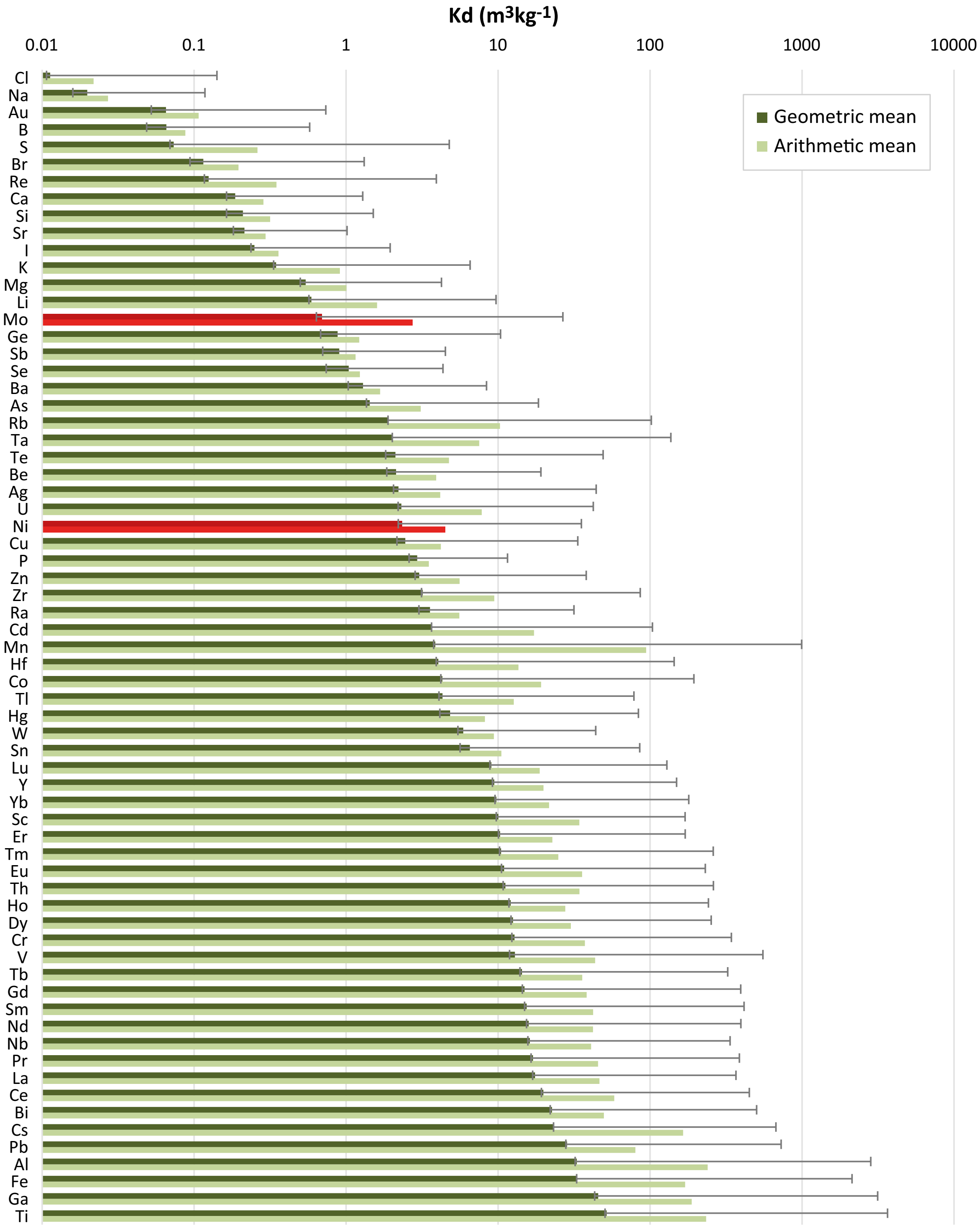

Figure 2-43. *Site specific terrestrial Kd values (clay till, clay gyttja, glacial clay, cultivated peat and wetlands) for Mo, Ni and other elements in Forsmark based on the study of Shepard et al. (2011). Both geometric and arithmetic means are shown. The error bars indicate the full observed range in Kd values.*

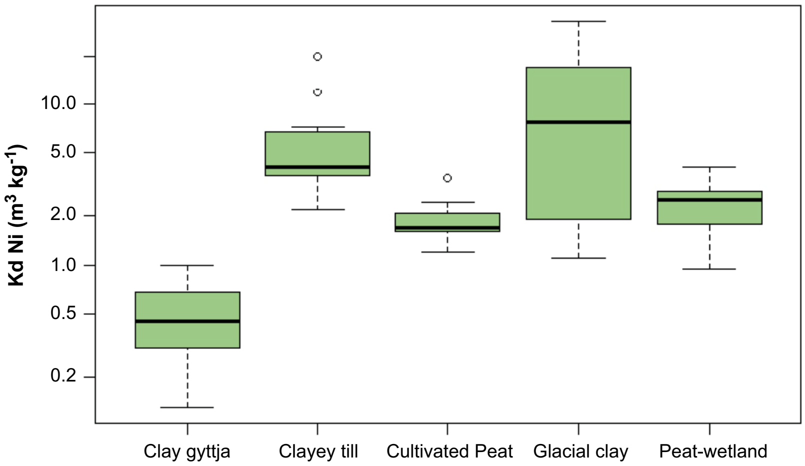

Figure 2-44. *Site-specific Kd values for Ni from the study of Sheppard et al. (2011).*

The highest – but also the most variable – Kd values for Ni were observed in the glacial clay, which displayed Kd values between 1.5 m^3 kg^{-1} and 33 m^3 kg^{-1}. These soils were characterized by large differences between shallow (20–25 cm) and deep samples (50–55 cm), approximately by an order of magnitude. Similar or even larger differences were observed for several other elements, e.g. Co, Mn and Zn, and were most likely related to differences in both particle size distribution and mineralogy. The shallow soils had lower clay content than the deeper soils (on average 37 % and 55 %, respectively) and instead higher sand content (34 % and 5.8 %, respectively). The greater surface area in the deeper soils would therefore favour sorption and lead to higher Kd values. The shallow soils also contained less Ca (1.3 %) than the deeper soils (7.7 %), suggesting a higher presence of calcite in the deeper soil horizons, which may have affected the soil water chemistry and the sorption.

Overall, the Kd values for Ni followed the same trends as those for other comparable elements (Section 2.1.1). The similarities between the Kd values for Ni and other transition metals such as Co and Zn are consistent with the results from the site investigations as outlined above (Figure 2-45). This indicates that the behaviour of Ni in the surface environment broadly is governed by the same processes as other comparable elements, albeit to different degrees, and that there are no special mechanisms involving Ni that need to be considered in the modelling of Ni. This is also consistent with the general understanding of the biogeochemistry of Ni (Section 2.1). Differences in, for example, the affinity for Mn precipitates can cause fractionation between Ni and other transition metals, but since Kd values tend to vary over logarithmic scales such differences will only lead to minor differences in the Kd values.

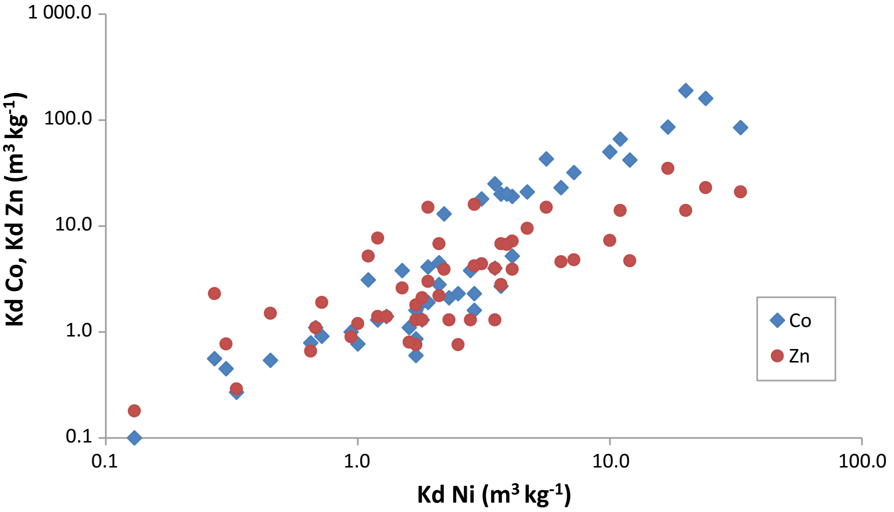

Figure 2-45. *Measured Kd values for Ni plotted against the corresponding Kd values for Co and Zn, respectively. All data were taken from Sheppard et al. (2011).*

The distribution of measured Kd values for Ni in terrestrial environments has a relatively smooth unimodal shape (Figure 2-46). This would indicate that there are no drastic differences in the mobility of Ni depending on its speciation, which also is consistent with the modelled speciation of Ni in the Forsmark area (Figure 2-41). This unimodal distribution can be compared with those of redox-sensitive elements like Mo and Fe, which show clear bimodal tendencies (see Section 3.2.6).

When investigating the underlying data more thoroughly, i.e. the pore water and soil concentrations used to calculate the Kd values, a few observations can be made. The pore water concentrations were generally well below 10 µg L^{-1} (Figure 2-47), which is in agreement with the Ni concentrations observed in different types of water in the Forsmark area (Figure 2-13). The pore water from the clay gyttja, however, stands out with Ni concentrations as high as 65 µg L^{-1} and a median concentration of 42 µg L^{-1}. This is clearly higher than any other observations that have been made in the Forsmark area (Figure 2-13), but then these gyttja sediments are not well represented in the site investigation data. The groundwater measurements are, for example, strongly biased towards till.

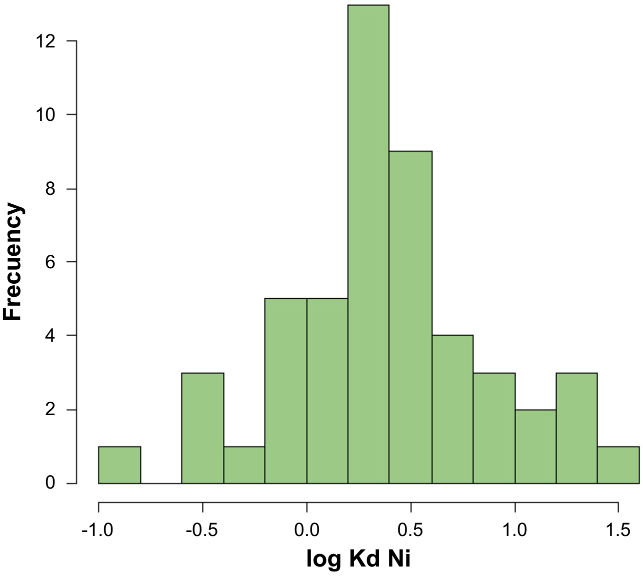

Figure 2-46. *Distribution of Kd values for Ni (m^3 kg^{-1}) in the Forsmark area.*

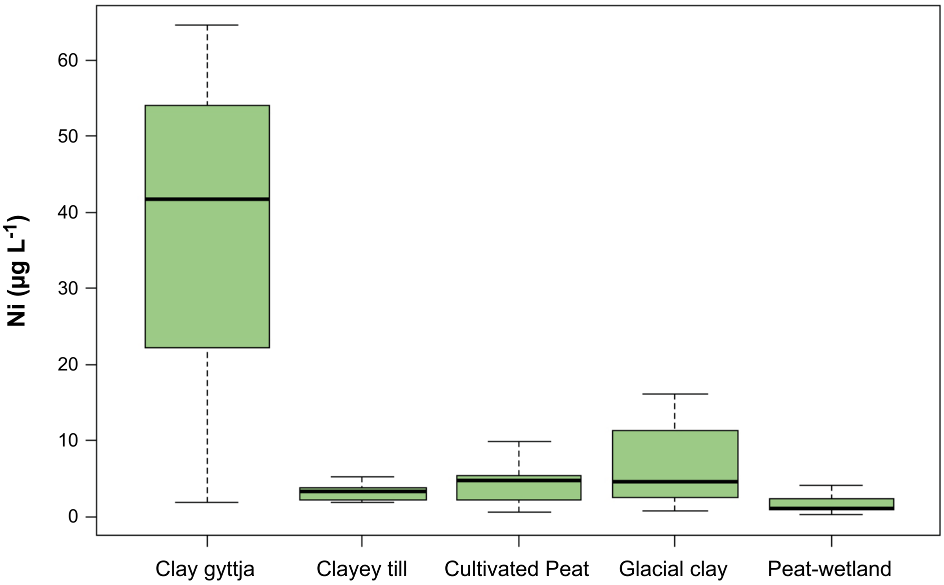

Figure 2-47. *Ni concentrations in pore water from different soil types after incubation for the Kd measurements. Data from Sheppard et al. (2011).*

Nickel is not unique in displaying markedly higher concentrations in the extracted pore water from the clay gyttja. Similar patterns can be found for, for instance, Cd, Co, Cr, Cu, Zn, the REEs and to some degree also Al, Fe and Zr. As can be seen in Figure 2-48, there is a strong correlation between observed Ni and Co concentrations, respectively, in the pore water samples ($r = 0.94$, $p < 0.01$, $n = 60$). All and all, this would suggests that the high Ni concentrations in the pore water from the clay gyttja are not related to a measurement error for Ni specifically – instead it reflects something apparently that has affected several different elements. In the protocols from the measurements it was noted for four out of ten samples that the extracted pore water was "very rich in humic material", which might explain the high concentrations of the aforementioned elements. It would also be possible that this type of organic sediments, which normally occur under strongly reducing conditions, were disturbed in connection with the sampling and the measurements, causing a mobilisation of certain elements from the solid phase, i.e. by partial oxidation, but the fact that high concentrations were observed also for elements like Th and Zr, which tend to not accumulate strongly in sulfides and normally remain comparatively insoluble except in the presence of DOC, would suggest that the key factor indeed are the high DOC concentrations present in this pore water (Dahlqvist et al. 2007, Lidman et al. 2017a). Hence, the high Ni concentrations in this pore water would reflect the high mobility of Ni in the presence of DOC.

It can also be noted that although there was a strong correlation between Ni and Co in the pore water analyses, there was also a notable trend in the Ni/Co ratios, which were discussed at some length in relation to, for example, lake water and sediments in both Forsmark and Simpevarp (e.g. Sections 2.2.4 and 2.2.5). It was argued that the fractionation between Ni and Co could be interpreted as sign of the influence of Mn. This relationship was present also in the analysed pore water samples, where samples with high Mn concentrations (predominately gyttja clay and cultivated peat) had low Ni/Co ratios, while high Ni/Co ratios were found exclusively in samples with low Mn concentrations (Figure 2-49).

When summarising the Kd measurements, most Kd values for Ni fall in the range 1–10 kg m^{-3} (Figure 2-50). Wetland peat and cultivated peat generally contained lower Ni concentrations in the solid phase, but since this was accompanied by lower concentrations also in the pore water, the resulting Kd values were fairly similar to, for example, the till soils. The lowest Kd values were associated with the clay gyttja discussed above. In this case the Ni concentrations in the solid phase were similar to other predominately minerogenic soils like clay till and glacial clay so the reason behind the lower Kd values were the higher Ni concentrations in the pore water (Figure 2-50). This seems reasonable in the sense that Ni easily can be mobilised by DOC (e.g. Lidman et al. 2017a).

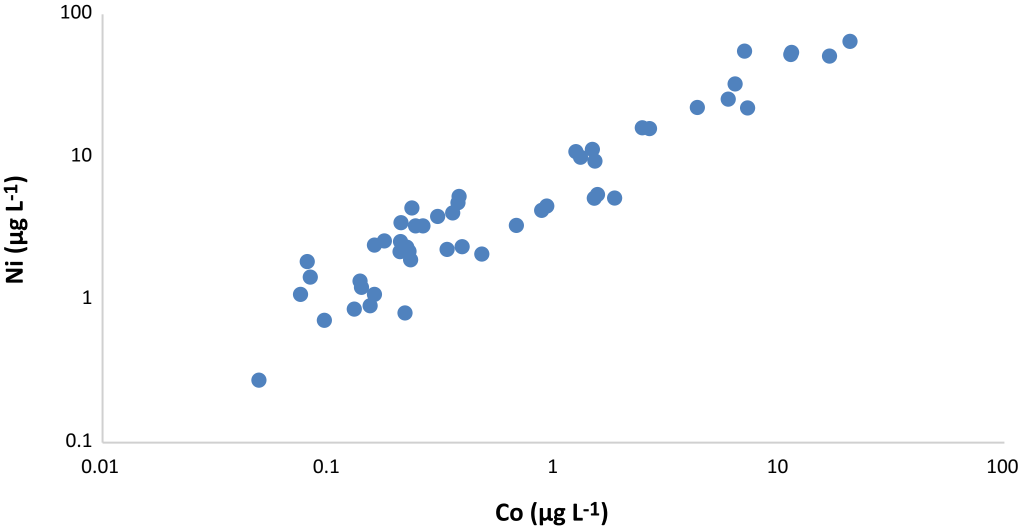

Figure 2-48. *Ni and Co concentrations in pore water from the incubated Kd samples. Data from Sheppard et al. (2011).*

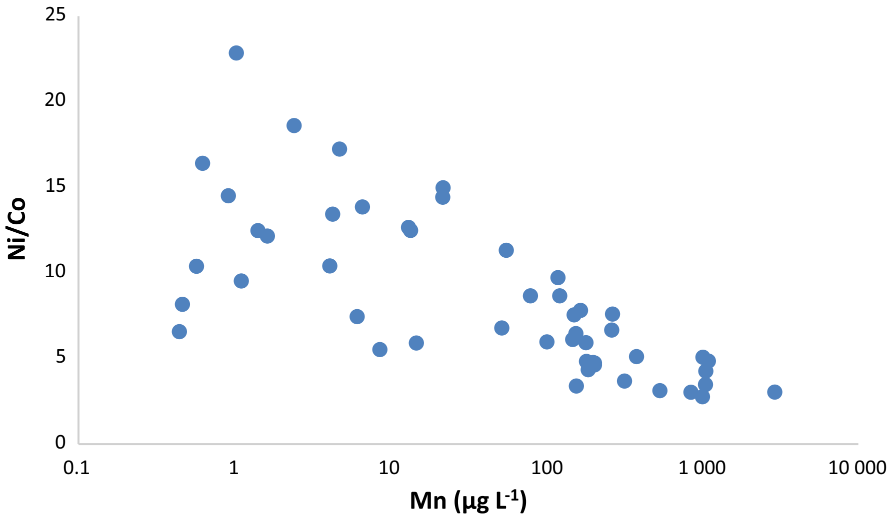

***Figure 2-49.** Ni/Co ratios in pore water from incubated Kd samples as a function of the Mn concentration. Data from Sheppard et al. (2011).*

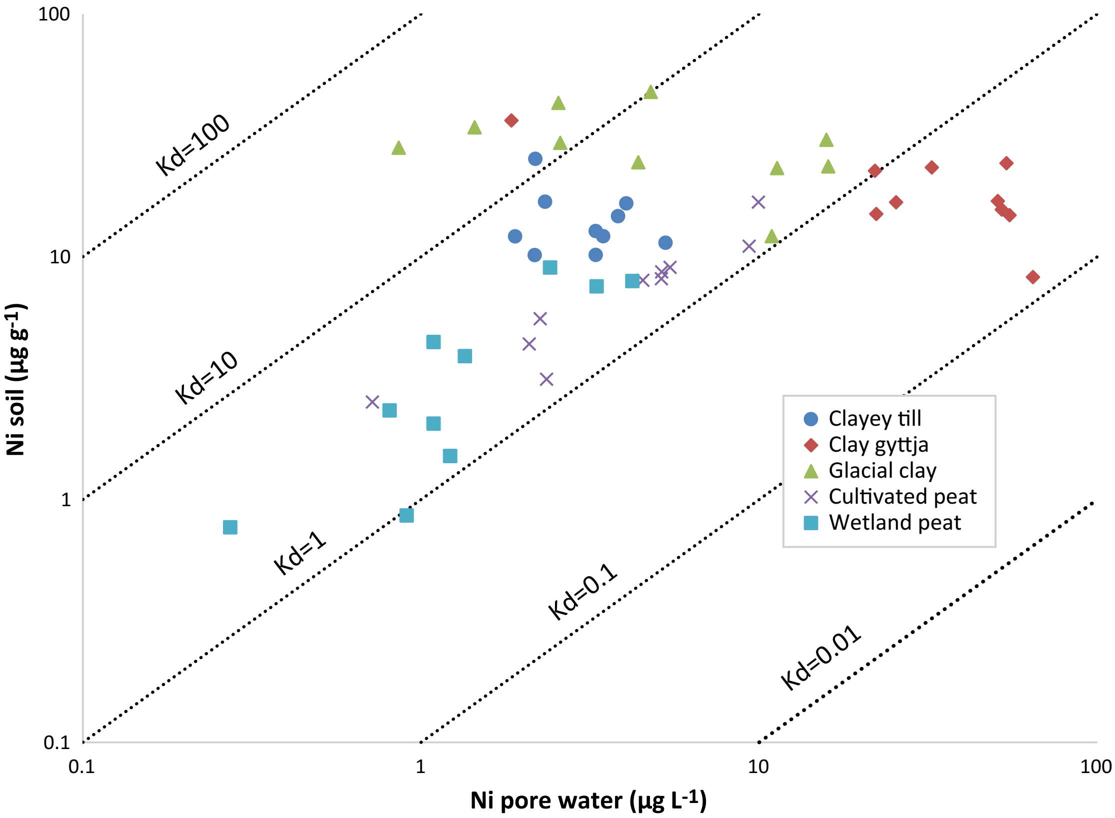

***Figure 2-50.** Concentrations of Ni in soils and pore water in different soil types from the Kd measurements in Forsmark. The diagonal lines indicate the Kd value that would result for points along each line (in kg m^{-3}). Data from Sheppard et al. (2011).*

The fact that high Ni could not be observed in pore water from the peat soils, which also should have high DOC concentration, could be explained by the low availability of Ni in these non-minerogenic soils. As discussed above, wetlands are associated with lower concentrations of Ni and many other weathering-derived elements, partly because there is little or no weathering in peat (Figure 2-39; Lidman et al. 2014). One difference between the clay gyttja and, for example, the local till is, however, that there were clear signs of considerable sorption of Ni in the former material, indicated by, for example, elevated Ni/Ti ratios compared to the till (Figure 2-30). The LOI was also appreciably higher in the clay gyttja (median 14.5 %) than in the clayey till (median 4.0 %), providing a higher potential for sorption of Ni to the organic matter. Hence, although the Ni concentrations in the solid phase of the till, the glacial clay and the clay gyttja, respectively, were relatively similar, it is possible that the Ni is present partly in different fractions of the soil, e.g. sorbed to organic matter or in primary minerals. This could have consequences for the sorption-desorption properties of Ni in these soils and the extent to which these properties are represented by the Kd values. The influence of different soil fractions on the Kd values and the use of various extraction methods for quantifying the element concentrations in the solid phase will be further investigated in on-going SKB projects.

2.2.8 Nickel in biota

The bioavailability and toxicity of Ni has been shown to depend on the presence of free Ni^{2+} ions, which in turn is largely dictated by pH and organic matter (Martino et al. 2003, Weng et al. 2004). The biological uptake of Ni is also known to be affected by competition from similar elements. For example, Mg has been demonstrated to decrease the uptake of Ni in hard waters (Deleebeeck et al. 2009). This is most likely related to the similarities in ionic radius between Ni^{2+} and Mg^{2+}. In terms of toxicity the Ni concentrations observed in the site investigation areas do not appear to constitute a problem. For example, the toxicity level (EC50) for embryos of blue mussels (*Myrtilus trossolus*) in sea water has been estimated to ca. 150 $\mu g\ L^{-1}$ (Nadella et al. 2009), which is higher than any observation in the site investigation areas.

The observed Ni concentrations in biota samples from the site investigation areas, comprising terrestrial as well as marine and limnic systems, spanned several orders of magnitude, from < 0.01 $\mu g\ g^{-1}$ DW in, for example, muscle tissue of various fish and land animals to 200 $\mu g\ g^{-1}$ in marine microphytobenthos (Figure 2-51). There was a substantial variation also within specific organism groups, which to some extent can be explained by the fact the different organism parts and sampling techniques were used in the analyses. In some matrices there were problems with the detection limits for Ni (e.g. fish muscles), while other samples (e.g. tree and macrophyte roots) possibly were affected by contamination from mineral particles.

In primary producers the observed Ni concentrations ranged from < 0.035 $\mu g\ g^{-1}$ DW in wood (*Picea abies*) to 200 $\mu g\ g^{-1}$ DW in marine microphytobenthos (Figure 2-51; Hannu and Karlsson 2006, Kumblad and Bradshaw 2008). Some of the samples with high Ni concentrations, for instance the above mentioned microphytobenthos, also had conspicuously high concentrations of metals such as Al, Hf and Zr, which are known to have generally low solubility and low biological uptake. It is therefore possible that these samples could include minerogenic matter and that the actual biological uptake of Ni may be considerably lower than indicated by some of these measurements. Apart from these anomalies, however, the observed Ni concentrations agreed with normal Ni concentrations reported for plants from non-contaminated areas, ca. 0.1–5 $\mu g\ g^{-1}$ DW (Alloway 2012, and references therein). The Ni concentrations in primary producers broadly followed the same pattern as Co and other similar elements, suggesting that there is no specific process involved in the uptake of Ni (Figure 2-52).

In animal samples from the site investigations Ni concentrations ranging from < 0.02 $\mu g\ g^{-1}$ DW in elk meat (*Alces alces*) to 3.24 $\mu g\ g^{-1}$ DW in mussels (*Cerastoderma glaucum*) were observed (Figure 2-51). Some of the variability was, however, related to differences in the analytical procedures, e.g. whole-body samples vs. muscle tissue and dissolution vs. total extraction (Hannu and Karlsson 2006, Kumblad and Bradshaw 2008). In several cases there were also problems with the reporting limits from the laboratory. For example, out of 22 samples of muscle tissue from freshwater fish including ruffe (*Gymnocephalus cernua*), roach (*Rutilus rutilus*), tench (*Tinca tinca*), northern pike (*Esox lucius*) and perch (*Perca fluviatilis*) only one sample (from a roach) had a Ni concentration above the reporting limit of the laboratory, 0.038 $\mu g\ g^{-1}$ DW. As in the primary producers there was a tendency that samples with high Ni concentrations, particularly benthic fauna, contained high concentrations of typically minerogenic elements like Al and Hf, suggesting that there may be a contribution from mineral particles also in some of the animal samples.

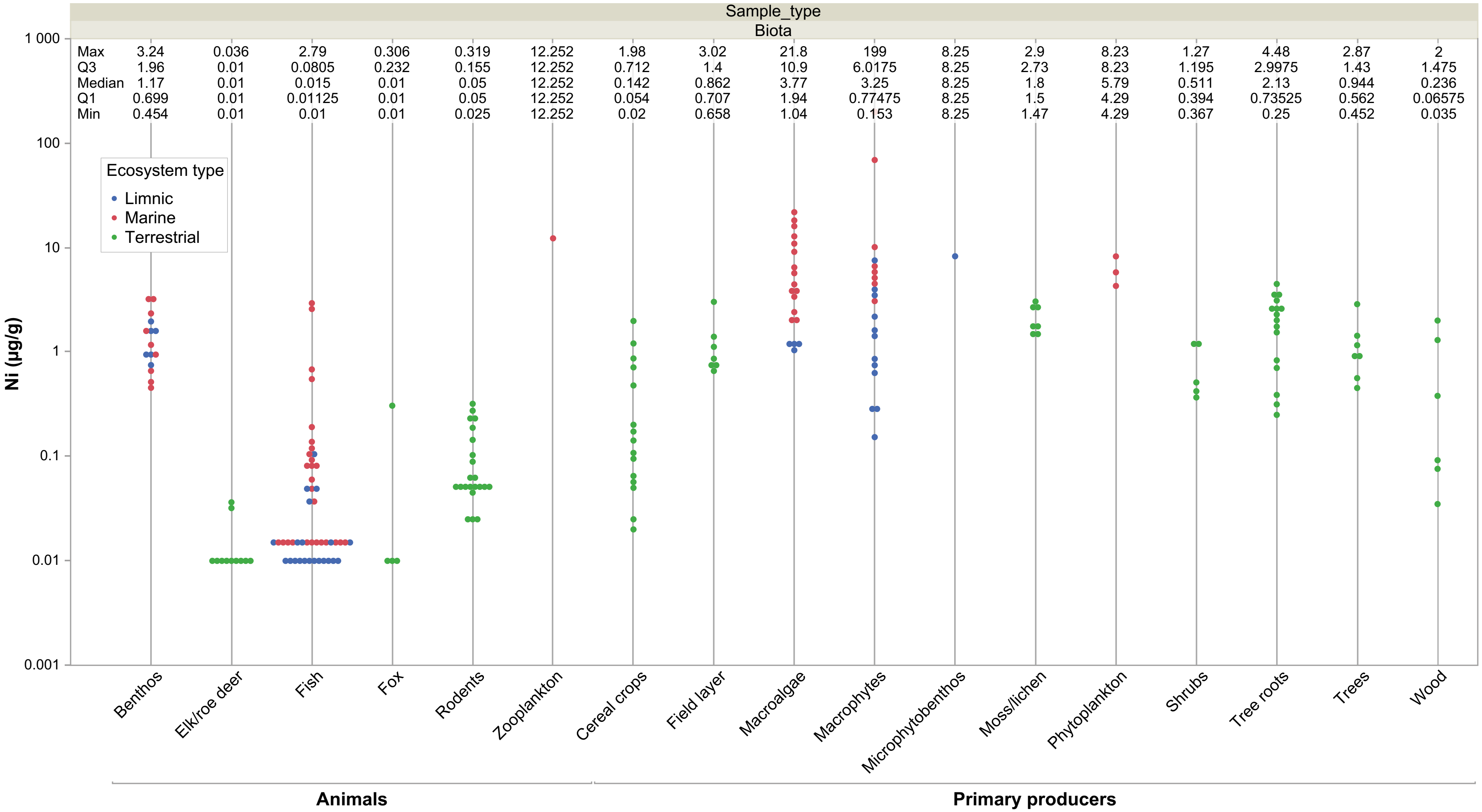

Figure 2-51. *Overview of Ni concentrations in different types of biota from the site investigation areas. Each marker represents as unique sample and is coloured according to the ecosystem type (terrestrial, limnic and marine systems) where it was collected. The upper panel shows the maximum and minimum concentrations, the median and the* 1^{st} *and* 3^{rd} *quartiles. Observations below the reporting limit are displayed at half of the reporting limit, which explains, for example, the horizontal aggregations of points for fish at 0.01 µg* g^{-1}.

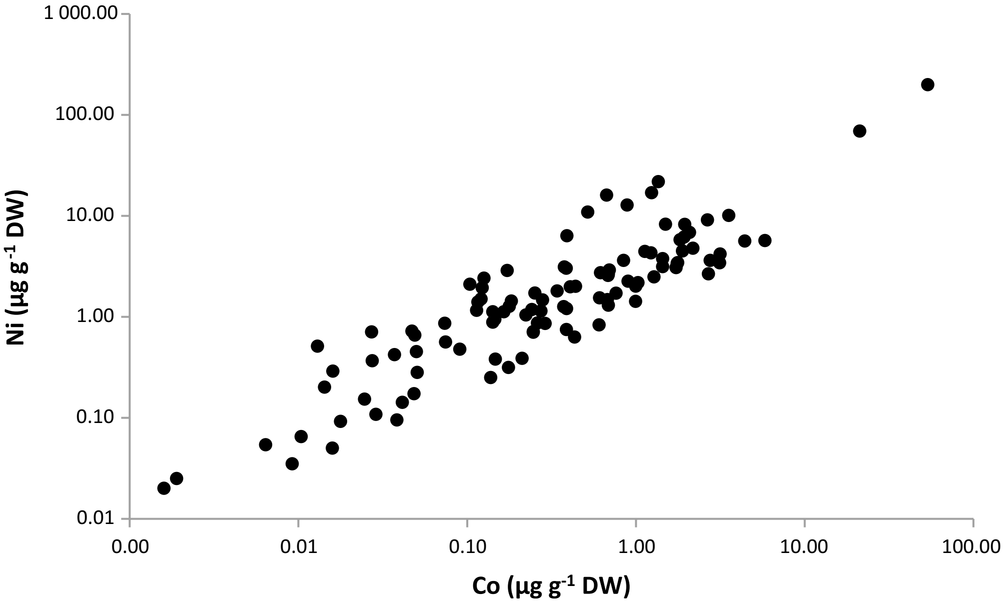

Figure 2-52. *Ni and Co concentrations in primary producers from the site investigations (data from Engdahl et al. 2006, Hannu and Karlsson 2006, Roos et al. 2007, Kumblad and Bradshaw 2008, Sheppard et al. 2011).*

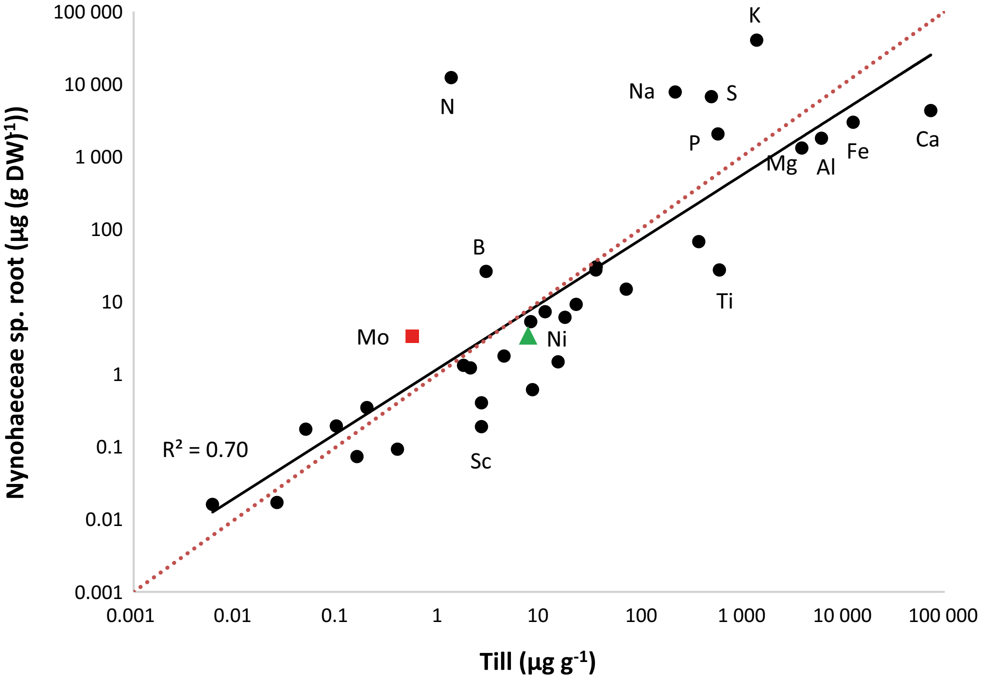

Figure 2-53. *Concentration of various elements in roots of water lilies (**Nymphaeaceae sp.**) from Forsmark as a function of the median concentration in local till. The dashed red line shows the 1:1 relationship. The red square and the green triangle denote Mo and Ni, respectively. Concentrations in biota were taken from Engdahl et al. (2007).*

Looking more broadly at the chemical composition of the biological samples, there is often a connection to the general abundance of various elements in the environment. One example are roots of water lilies (*Nyphaeaceae sp.*) from Forsmark, where the concentration of the analysed elements correlated well to their concentration in local till ($r = 0.84$, $p < 0.05$). The regression line also fell close to the 1:1 line, which indicates where the roots contain exactly the same concentration as the local till (Figure 2-53). Nitrogen was the element that deviated most from the 1:1 line, showing a substantially higher concentration in roots than in till. This is hardly surprising, since N is a primary macronutrient, which is not abundant in minerals. Other important macronutrients such as K, S and P and also some micronutrients such as Mo and B were also enriched in the roots relative to the local till, while other elements with no known biological role, e.g. Sc, Ti and Al, were depleted relative to the local till. Iron, which is a micronutrient, and Ca, a macronutrient, were also depleted in the roots relative to the local till. In the case of Ca the apparent depletion is no doubt strongly influenced by the high calcite concentrations in the till of Forsmark. Although the till may not be the most relevant soil type for water lilies, it can nevertheless be noted that the fractionation of elements in the biological samples in most cases does not exceed one order of magnitude relative to the local soils.

Biological uptake of Ni in other areas

There are some studies in the scientific literature, which have addressed the relationship between Ni in soils and biota, respectively. These studies are typically carried out in areas with elevated Ni concentration. For example, the uptake of Ni in grass, red fescue (*Festuca rubra*, 'rödsvingel' in Swedish) and rushes (*Juncus sp.*, 'tågsläktet' in Swedish), were investigated in the vicinity of a serpentine quarry in Spain (Lago-Vila et al. 2015). (Serpentine is a group of minerals rich in Mg, Fe and associated elements such as Ni and Cr.) The Ni concentration in both red fescue and rushes were found to be correlated to the concentration of extractable Ni in the soils. Relatively weak extractants such as 0.01 M $CaCl_2$ and low molecular weight organic acids were found to be the best predictors for the bioavailable Ni (Lago-Vila et al. 2015).

A somewhat similar study was performed in another area with serpentine soils in Japan, but in this case a wider range of plants were sampled (Mizuno and Kirihata 2015). Due to the serpentine bedrock the Ni concentration in the soils was high, 910–4 500 $\mu g\ g^{-1}$, which is substantially higher than the maximum Ni concentrations observed in Forsmark and Simpevarp (33 $\mu g\ g^{-1}$ and 32 $\mu g\ g^{-1}$, respectively). Only a few per mille of the total Ni concentration was, however, found in the exchangeable fraction, 1.2–12 $\mu g\ g^{-1}$. This is not too different from the exchangeable Ni found in the alder fen in the Simpevarp area, which had a maximum exchangeable Ni concentration of 1.7 $\mu g\ g^{-1}$ (Figure 2-7). In the oak and spruce forests in Simpevarp, however, the exchangeable Ni could be as low as 0.02 $\mu g\ g^{-1}$. Looking at the plants in the vicinity of this Japanese serpentine quarry, certain hyperaccumulators such as *Swertia japonica* contained notably high Ni concentrations, up to 700 $\mu g\ g^{-1}$, but most of the 75 investigated plants displayed appreciably lower concentrations with a median of 8.2 $\mu g\ g^{-1}$. This is by all means higher than the median reported for plants growing on non-serpentine soils in Japan, 1.3 $\mu g\ \mu g^{-1}$, but the given that the average Ni concentration in non-serpentine Japanese soils was more than 100 times lower than the average concentration reported for the serpentine soils the difference between the Ni concentration in plants must be characterised as comparatively modest. These concentrations can also be compared to the Ni concentration in terrestrial primary producers from the site investigation areas, which was 0.36 $\mu g\ g^{-1}$. While such comparisons may be somewhat perilous, since different species were sampled, comparisons within a single genus do provide a similar picture. Assuming that the mechanisms behind the uptake of Ni are fairly similar within the genus *Quercus*, it can be noted that leaves from *Quercus phillyraeides* growing in the Ni-rich Japanese serpentine soils had a Ni concentration of 5.8 $\mu g\ g^{-1}$, while leaves from *Quercus robur* growing in the Simpavarp area had a Ni concentration of 0.88 $\mu g\ g^{-1}$. From the reported data by Mizuno and Kirihata (2015) it is not possible to directly match the extractable Ni in the soil to the *Quercus phillyraeides* samples, but it can be noted that the lower end of the observed range in the serpentine soils (1.2–12 $\mu g\ g^{-1}$) is only ca. 10 times higher than the highest exchangeable Ni observed in the oak forest in Simpevarp (0.066–0.11 $\mu g\ g^{-1}$). Hence, while the total soil concentration of Ni was ca. three orders of magnitude higher near the Japanese serpentine quarry than in the site investigation areas, the concentration of exchangeable Ni in the soils was only ca. one-two orders of magnitude higher. The Ni concentration in the oak samples, finally, was only 6–7 times higher in the Ni-rich soils so this suggests that while the soil concentrations of Ni can vary considerably between different sites, this variation is not necessarily reflected in the plants growing there. The data appears to be relatively scarce, and direct comparisons are difficult due to different sampling and measurement techniques, differences in sampled species and other geochemical differences than the Ni concentrations (e.g. pH, concentration of competing elements etc.), but the small variation in the concentrations in biota relative to the variation in soils point to the conclusion that there should be a relatively strong biological control of the Ni uptake in plants.

When it comes to foodstuff, a large French study measured the content of Ni and other elements in 1 319 samples representing different types of viands (Noël et al. 2012). The concentrations were measured "as consumed", i.e. fresh weight, and ranged between 0.057 $\mu g\ g^{-1}$ and 0.80 $\mu g\ g^{-1}$ in the case of Ni. The food groups with the highest mean concentrations of Ni were "sweeteners, honey and confectionery", "ice cream", "tofu" and "cereals and cereal products". Other relevant food groups for the safety assessment such as "fruits and vegetables", "fish and fish products", "dairy products" and "meat and offal" had generally low Ni concentrations ($< 0.14\ \mu g\ g^{-1}$), showing no signs of high accumulation of Ni (Noël et al. 2012). For reference, the median Ni concentration in terrestrial animals from the site investigation area, for example, was 0.073 $\mu g\ g^{-1}$ (on a dry weight basis, assuming that the Ni concentration was half of the reporting limit in the 38 % of the samples were the concentration fell below the reporting limit). Hence, the observed Ni concentrations from the site investigations appear to be approximately on the same level as common eatables in France, which indicates that the reported concentrations are realistic and probably quite typical for victuals.

3 Molybdenum

3.1 The biogeochemistry of Mo

3.1.1 Overview

Molybdenum is a transition metal (Z = 42) that can occur in different oxidations states in the environment. The dominating oxidation state in most types of water is Mo(VI), which occurs as a relatively mobile oxyanion, molybdate (MoO_4^{2-}). This tendency of high-valence states to form an oxyanion is a property that Mo shares with many of its closest neighbours in the periodic table of the elements, e.g. V, Cr, Tc, Re and W. Hence, it can sometimes display similarities with these elements, but the stability of their respective oxyanions under different chemical conditions is not the same, and this can also cause large differences in their biogeochemical behaviour (e.g Crusius et al. 1996, Icenhower et al. 2010, Miller et al. 2011, Bauer et al. 2017). Among the oxyanions of the metals mentioned above – vanadate, chromate, pertechnetate, perrhenate and tungstate – molybdate belongs to the more stable ones (generally surpassed only by tungstate) and can prevail over a fairly wide range of chemical conditions. Molybdate is a weak base so considerable protonation of molybdate occurs only at low pH. Hydrogen molybdate, $HMoO_4^-$, has a pK_a of 3.47, but will never dominate the speciation because the second protonation step of molybdate, leading to the formation of molybdic acid, has a higher protonation constant, 3.74. This unexpectedly high first pK_a of molybdic acid is related to a difference in the coordination number between molybdic acid and molybdate, i.e. molybdic acid does not occur as H_2MoO_4 but probably as $MoO_3(H_2O)_3$ (Cruywagen 1999). This means that combined the protonated forms become important at pH below ca. 4. Molybdate can also be destabilised under strongly reducing conditions, where Mo(VI) is reduced to predominately Mo(IV) (Crusius et al. 1996, Smedley and Kinniburgh 2017). Mo(V) has also been observed in laboratory experiments, but it remains uncertain what role it plays in environmental systems other than as a transition state (George et al. 1989, 1999). At concentrations above ca. 100–1 000 µg L^{-1} Mo can also start to polymerise and form a range of various polymolybdate species.

The reduction of Mo has far-reaching consequences for its mobility, since it implies that Mo is transformed from a relatively mobile oxyanion to a high-valence cation with low solubility. As a consequence there can be an appreciable accumulation of Mo in strongly reducing environments such as organic sediments (Crusius and Thomson 2000, Dahl et al. 2013b, Wirth et al. 2013, Chappaz et al. 2014). Although redox is crucial for the understanding of Mo biogeochemistry, the stability of molybdate under various conditions is not fully understood. In addition to the reduction of Mo, formation of thiomolybdates are believed to be important for the immobilisation of Mo under reducing conditions. In thiomolybdates one or more O in the molybdate ion is replaced by sulfide, e.g. MoO_3S^{2-}, which renders the ion more reactive (and less soluble). The formation of thiomolybdates is therefore linked to the sulfide concentration, which in turn is linked to the redox potential. Hence, immobilisation of Mo can be expected approximately under sulfidic conditions (Smedley and Kinniburgh 2017).

In recent years improved methods to analyse naturally occurring Mo isotopes has opened up new possibilities to study the behaviour of Mo in nature (Barling and Anbar 2004, Asael et al. 2013, Hin et al. 2013, Kowalski et al. 2013, Nägler et al. 2020). This is likely to enhance our understanding of the transport and accumulation of Mo in various environments in the future.

3.1.2 Transport and accumulation of Mo

Since molybdate is stable under a fairly wide range of geochemical conditions and also much more soluble than Mo(IV), most transport of Mo can be expected to occur as molybdate. Important retention processes for molybdate include sorption onto Al and Fe (hydr)oxides, especially in acidic environments (Xu et al. 2013). In Finnish soils strong retention of Mo has been reported, particularly at pH below 4.5 (Mikkonen and Tummavuori 1993). Molybdate can form both edge-sharing and corner-sharing bidentate complexes with Al and Fe (hydr)oxides, but under certain conditions, for instance at high pH, there are also indications that outer-sphere complexes can play a significant role, at least in the case of ferrihydrite (Gustafsson and Tiberg 2015).

Molybdate has also been observed to bind relatively strongly to organic matter, and this appears to be especially important at pH below ca. 5–6. (Wichard et al. 2009, Gustafsson and Tiberg 2015). Measurements in coniferous forests in Oregon, USA, demonstrated that on average 33 % of the Mo in surface mineral soils (i.e. directly under the O horizon) was found in the organic fraction (Marks et al. 2015b). The accumulation of Mo in the soils was also correlated to the soil C pool, which suggests that the long-term fate of Mo in soils is strongly dependent on organic matter. Other measurements in American forest soils have indicated that Mo can form strong complexes with plant-derived tannins and tannin-like compounds in the leaf litter layer (Wichard et al. 2009). The binding of Mo to organic matter is hypothesised to occur through carboxylate groups, where Mo assumes a configuration similar to that of molybdic acid, allowing a distant oxygen atom to bind Mo to the carboxylate group (Gustafsson and Tiberg 2015). At lower Mo concentrations, however, thiol groups are also believed to play an important role for binding Mo to organic matter. In such cases it has been demonstrated that the formation of thiomolybdates can conserve Mo in the hexavalent state in sulfidic waters, although it will nevertheless decrease the mobility of Mo (Adelson et al. 2001, Erickson and Helz 2000). The formation of thiomolybdates is expected to occur at sulfide concentrations of ca. 1–11 mM, i.e ca. 30–300 mg L^{-1} (Helz et al. 1996, Zheng et al. 2000).

3.1.3 Accumulation of Mo in sediments

The redox properties of Mo is one reason why it has been investigated quite comprehensively in sediments. Since the mobility of Mo is so strongly affected by the presence of sulfide through the formation of thiomolybdates and also by the reduction of Mo(VI) to Mo(IV), Mo has been used as a redox tracer in both freshwater and marine sediments (Dahl et al. 2013b, Wirth et al. 2013). The idea is that high concentrations of Mo in the sediment record will indicate periods of reducing conditions because this will immobilise Mo, causing it to accumulate in the sediments. A global compilation of marine sites has demonstrated that euxinic, i.e. both anoxic and sulfidic, areas are characterised by significantly higher Mo concentrations (> 25 $\mu g\ g^{-1}$) than average continental crust (1.5 $\mu g\ g^{-1}$) and riverine suspended matter (3 $\mu g\ g^{-1}$) (Dahl et al. 2013b). Hence, it has been suggested that Mo can be used as a paleotracer for the redox potential.

To what extent the accumulation of Mo in reducing sediments is caused by reduction of molybdate to insoluble Mo(V) and Mo(IV) is still an open question, but there are indications that reduction of molybdate and subsequent precipitation of mineral phases like molybdenite (MoS_2) may not be the most common mechanism (Helz et al. 1996). As the sulfide concentration in the water increase and various sulfide minerals are precipitated, Mo may react with the minerals by forming covalent bonds to other transition metals, e.g. Fe, which also would decrease its mobility. Accordingly, precipitation of sulfide minerals like pyrite (FeS_2), sphalerite (ZnS) and galena (PbS) may be enough to immobilise molybdenum. It has been reported, for example, that significant amounts of Mo have been incorporated in pyrite in sediments (Crusius and Thomson 2000), while others have reported that formation of pyrite is not the main reason for Mo enrichment in euxinic sediment (Chappaz et al. 2014). Despite the uncertainties concerning the exact reactions that accumulate Mo in reducing sediments it is clear that sulfate-reducing conditions normally are required (Crusius et al. 1996).

3.1.4 The biological role of Mo

Molybdenum is also an important element from a biological perspective. It is an essential micronutrient, which is required in a range of different enzymes. Ultimately, this is also related to the redox properties of Mo. In eukaryotic cells Mo is needed, for instance, in enzymes responsible for the oxidation of sulfite, e.g. in the degradation of S-containing amino acids, oxidation of aldehydes and the reduction of nitrate (Mendel 2009). In most cases Mo is present in a special Mo cofactor (Moco), but in bacterial nitrogenase it is present with Fe in the FeMo cofactor. This last group of enzymes are responsible for the reduction of nitrate, which is a key step in the assimilation of inorganic N (Cole et al. 1993). Addition of Mo has been found to stimulate the N fixation by free-living bacteria in several types of ecosystems (Dynarski and Houlton 2018). For example, in tropical forests it has been demonstrated that Mo – in some cases in combination with P – constrains the asymbiotic N fixation (Wurzburger et al. 2012). Furthermore, it has been observed that asymbiotic N fixation by feather mosses can account for as much as two thirds of the N input to boreal forests and that this fixation during the middle of the growing season sometimes can be limited by Mo (Jean et al. 2013). The biological N fixation has also been observed to increase after addition of Mo to a tundra moss ecosystem in northern Sweden (Rousk et al. 2017). In ecosystems where the availability of Mo is limited it has been observed that alternative nitrogenase enzymes with V or Fe at the active sites can play an important role (Darnajoux et al. 2017). There are, however, also studies that have failed to observe any limitation by either Mo, V or P to the growth of cyanolichens and chlorolichens in forest ecosystems so this is apparently not a universal pattern (Marks et al. 2015a). There is also evidence that Mo can limit the primary production in certain oligotrophic lakes (Glass et al. 2013).

Because of the importance of Mo as micronutrient and its relatively high mobility in oxidising environments one can expect a high biological uptake and cycling of Mo in organic litter (Nägler et al. 2020). It is known that certain bacteria actively can release ligands that mobilise Mo from organic matter (Wichard et al. 2009). The biological uptake of Mo occurs as molybdate and requires specific systems to distinguish molybdate from competing anions (Mendel 2009). Uptake of molybdate in eukaryotes is not well understood, but it is known that at least bacteria have special protein transporters that target molybdate (Sigel and Sigel 2002). In plants no specific uptake system for Mo is known, but it has been hypothesised that the uptake of Mo could be mediated by sulfate transporter, since molybdate and sulfate have a similar structure (Zimmer and Mendel 1999). The uptake of Mo in cucumber (*Cucumis sativus*) is known be affected by the access to Fe, which is another essential micronutrient (Vigani et al. 2017). Moreover, the uptake of Mo by cyanobacteria and phytoplankton has been observed to be inhibited by tungstate (WO_4^{2-}) and high sulfate concentrations (Cole et al. 1993). As a consequence of the high sulfate concentrations in sea water, Mo is less available in sea water than in fresh water (Howarth and Cole 1985). In the pelagic zone along the German Bight the biological uptake of Mo has been observed to be high enough to locally cause notably lower Mo concentrations in the sea water (Kowalski et al. 2013). A study of Mo in Californian rivers, USA, however, showed no signs of biomagnification of Mo in the aquatic food chain (Saiki et al. 1993). Algae and detritus typically had higher Mo concentrations than invertebrates and fish.

In too high concentrations, however, Mo is toxic, which appears to be because it can inhibit the uptake of Cu, thereby causing Cu deficiency (Vunkova-Radeva et al. 1988, van Gestel et al. 2012). In humans Mo poisoning may lead to various symptoms such as diarrhea, anemia, fatigue, lack of appetite and joint pains. The requirement for Mo in adults has been estimated to 75–250 $\mu g\ day^{-1}$, and current WHO guidance recommends that Mo concentrations in drinking water should not exceed 70 $\mu g\ L^{-1}$ (WHO 2022). In practice, however, high Mo concentrations in water does not appear to be a widespread problem (Smedley et al. 2014).

3.1.5 Mo in radioecology

Molybdenum has traditionally not been given particularly much attention in radioecology, but the concern for primarily Mo-93 is likely to increase as more countries are preparing final repositories for nuclear fuel and waste. Mo-93 ($T_{½} = 3\,500$ a) is produced mainly by neutron irradiation of stable Mo-92 in nuclear power plants. This can occur, for example, as result of the use of Mo alloys in reactors or because of Mo impurities in reactor materials (Lidman et al. 2017b). Mo-93 decays by electron capture to stable Nb-93 so it is not involved in any decay chain dynamics. The dose coefficient for Mo-93 is comparatively high, $3.1 \cdot 10^{-9}$ Sv Bq^{-1}, which is an important reason for its radioecological relevance.

3.2 Mo in the site investigation areas

3.2.1 Sources of Mo

The major sources of Mo in the site investigation areas is expected to be weathering of local soils and atmospheric deposition. According to estimations by Tröjbom and Grolander (2010) the contribution of Mo from atmospheric deposition is nearly as important as weathering in the Forsmark area, but the numbers are somewhat uncertain as no measurements of Mo in precipitation from the Forsmark area was available at the time. More recent measurements of Mo in precipitation in Forsmark (2018–2019) showed concentrations from < 0.05 $\mu g\ L^{-1}$ to a maximum of 0.28 $\mu g\ L^{-1}$ (Wallin et al. 2019, Wallin et al. 2020). The occasionally higher concentrations could possibly be influenced by the relative vicinity to ironworks in south Gästrikland, ca. 100 km northwest of Forsmark (Lidman et al. 2017b).

In a national survey of metals in mosses, which is used as a proxy for the atmospheric deposition, the highest Mo concentration (2.4 µg g^{-1} DW) was encountered in Uppsala County (Danielsson and Pihl Karlsson 2016). The Mo concentration in mosses suggest that the deposition of Mo should be lower in the Simpevarp area.

On larger scales it has been observed that the atmospheric deposition of Mo has increased significantly since the onset of the Industrial Revolution (Krachler and Shotyk 2004). Molybdenum is nowadays used by society in various applications – it is, for instance, common in alloys. Recent data from the Krycklan catchment in northern Sweden, however, showed no clear trend for Mo in precipitation during the past decades (2002–2019) (Figure 3-1). The monthly average Mo in bulked, volume-weighted precipitation ranged from 0.011 µg L^{-1} to 0.69 µg L^{-1} with a median of 0.052 µg L^{-1} (n = 200; Lidman, unpublished data). These concentrations are low compared to the typical concentrations in groundwater and surface water in the site investigation areas (see Figure 3-16 below), which would indicate that weathering is a more important source than precipitation. In the light of these measurements the observed Mo concentrations in precipitation in Forsmark do not markedly stand out, which would indicate that the influence from anthropogenic contribution probably is limited in the area.

3.2.2 Mo in soils

The average Mo concentration in the upper continental crust has been estimated to 1.4 µg g^{-1} (Wedepohl 1995). Most of this is believed to reside in feldspars and plagioclase, although it may also occur in minerals such as quartz and biotite (Ahrens et al. 2013). In Sweden the median Mo concentration in soils (n = 2 578, a*qua regia* extraction) is 0.43 µg g^{-1} with 10th and 90th percentiles of 0.16 µg g^{-1} and 1.43 µg g^{-1}, respectively (Andersson et al. 2019). In till samples from the Forsmark area, covering depths from 0.4 m to 11.5 m, Mo concentrations between 0.060 µg g^{-1} and 1.4 µg g^{-1} have been observed (n = 59). This is approximately in the same range as typical Mo concentration in other parts of Uppsala County, where the 10–90 interpercentile range was 0.2–0.9 µg g^{-1} based on 58 samples (Andersson et al. 2019).

In the till samples from Forsmark Mo correlated most strongly with Na (r = 0.62, $p < 0.05$) so it possible that weathering of albite (a Na-rich type of plagioclase) could be a major source of Mo in the area (Figure 3-2). The till samples from SFM0057, which is located near Gällsboträsket, stand out by having notably higher Na concentrations, but although the Mo concentrations were high too, the difference to the other observations were not as conspicuous as for Na. As dicussed above, Mo may reside in different minerals so this probably only reflects a somewhat deviating mineralogy at this site. Another group of samples that also stand out with Na concentrations > 400 µg g^{-1}, but still relatively normal Mo concentrations, derive from SFM0002, SFM0011, SFM0017 and SF002581. Molybdenum also correlates significantly to Ti (r = 0.56, $p < 0.05$), and when plotting Mo versus Ti, this latter group of till samples does not deviate in the same manner as when plotting Mo versus Na (Figure 3-3). A possible explanation is that biotite, where substitution by both Ti and Mo can occur, also might be an important source of Mo (Douce 1993, Ahrens et al. 2013). However, the soil samples from SFM0057 near Gällsboträsket still stand out, and the deviation is even more conspicuous for SFM0017, located just south of Eckarfjärden. In the latter case, the mineralogical difference could be related to the same geological formation that caused high concentration of Ni, Fe and other elements in SFM0016, which is located in the vicinity of SFM0017 (Figure 2).

In the Simpevarp area slightly higher Mo concentrations, between 0.35 µg g^{-1} and 2.0 µg g^{-1}, were observed in the till (n = 18). These somewhat higher concentrations are not reflected throughout Kalmar County, where 76 soil samples displayed the same 10–90 interpercentile range as in Uppsala County, 0.2–0.9 µg g^{-1} (Andersson et al. 2019). This is probably related to differences between the northern parts of Kalmar County, where Simpevarp is located, and in particular its southeast parts. As in Forsmark, there was a correlation to Na (r = 0.49, $p < 0.05$), albeit weaker.

In another sampling campaign in the Simpevarp area a wider range of soil types were included. In addition to till both glacial and postglacial sorted soils were collected, including size fractions from sandy gravel to clay, and also more organic soils such as surface soils (0–2.5 cm and 2.5–10 cm deep) and gyttja (Sohlenius 2006). Particularly gyttja and organic surface soils contained higher Mo concentrations (up to 8.7 µg g^{-1}) than the till. Overall, there was a positive correlation to S (r = 0.68, $p > 0.001$), but it should be noted that this correlation was entirely dependent on the inclusion of the S-rich gyttja and organic surface soils (Figure 3-4). In the more inorganic soil types Mo and S appear

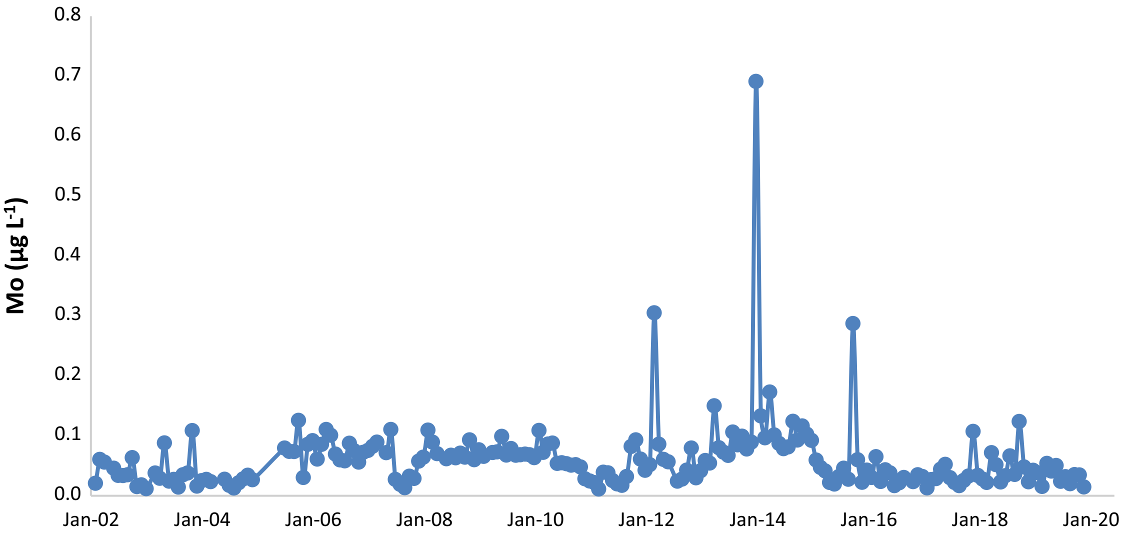

Figure 3-1. *Monthly average Mo concentration in volume-weighted bulked precipitation from the Krycklan catchment in northern Sweden.*

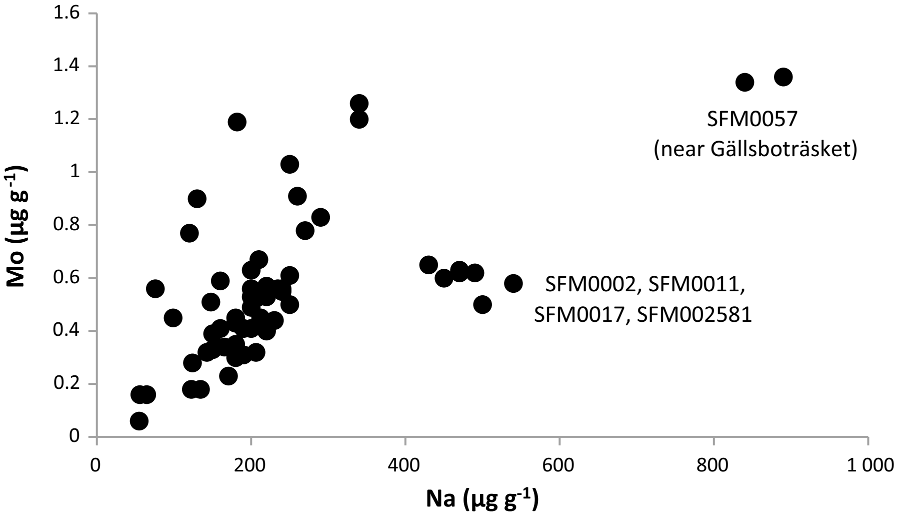

Figure 3-2. *Mo concentration in till (Forsmark) as a function of the Na concentration.*

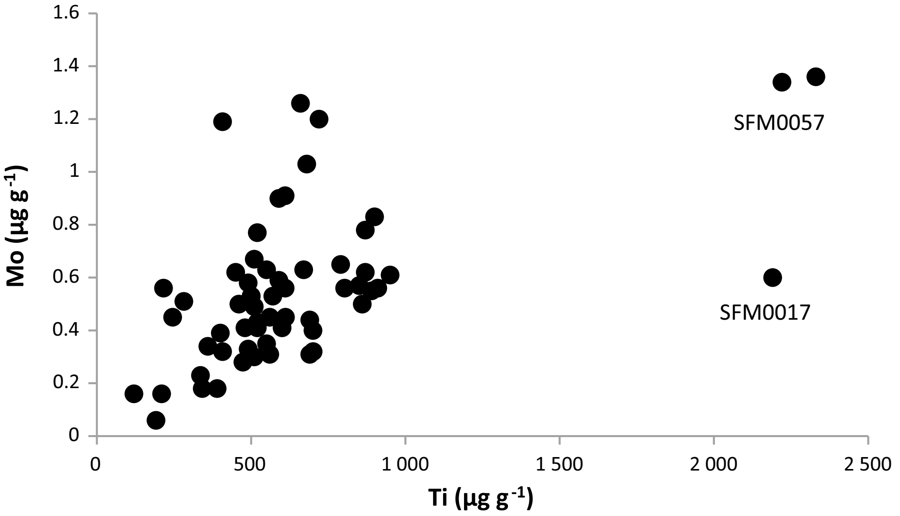

Figure 3-3. *Mo concentration in till (Forsmark) as a function of the Ti concentration.*

to be independent, which indicates that these two elements are not typically present in the same minerals. Instead, the relationship between Mo and S should be understood as a tendency to accumulate in similar environments. The Mo and S concentrations in surface soils are likely to reflect a biologically driven enrichment of nutrients, while the accumulation of Mo and S in the gyttja sample probably is caused by the reducing conditions (see Section 3.2.5 below).

Five of the samples included in Figure 3-4 derived from a single 3.2 m soil profile (PSM007171), comprising a sequence of soil types often found in both the Forsmark and the Simpevarp area (Figure 3-5). Overlying the bedrock there was first till, followed by glacial clay and, closer to the surface, postglacial sediments. The highest Mo concentration was encountered in the clay gyttja (2.1 µg g^{-1}), but the underlying postglacial sand was also rich in Mo (2.0 µg g^{-1}). The deeper soil layers, however, contained relatively low Mo concentrations, 0.81 µg g^{-1} in the coarse till and a minimum of 0.43 µg g^{-1} in the glacial clay. In three of these samples more detailed X-ray diffraction analyses of the mineralogy were conducted, showing clear differences between the till, on one hand, and the glacial clay and the clay gyttja on the other (Sohlenius et al. 2006). The till was dominated by above all quartz, K feldspar and plagioclase (> 20 % each) and other primary minerals, although it also contained considerable amounts of secondary clay minerals like illite, chlorite and vermiculite (up to 8 % each). The clayey soils had, not surprisingly, a higher content of clay minerals, above all illite – 27 % in the clay gyttja and 33 % in the glacial clay – but lower content of primary minerals (< 10 % quartz, < 10 % K feldspar, < 20 % plagioclase). Secondary clay minerals like illite, chlorite and not least vermiculite tend to have negatively charged surfaces and are therefore important cation exchangers. They are less important, however, for the retention of anions like molybdate. Since Mo will be relatively mobile as molybdate when released by weathering, there are no reasons to expect an extensive incorporation of Mo into these secondary minerals. Although the till and the glacial clay may originate from different types of bedrock, the low Mo concentrations in the glacial clay do not seem unreasonable given that Mo is not likely to be enriched in the type of secondary minerals that are common in the glacial clay. The higher Mo concentrations in the clay gyttja, on the other hand, are more likely to be related to a higher content of organic matter and, at least in some cases, sulfides rather than the clay fraction (Figure 3-5). It can be noted, however, that this clay gyttja contained less Mo than the gyttja sample marked in Figure 3-4. This sample was less organic – 11 % vs. 38 % – and showed less signs of sulfate reduction. The S concentration in the clay gyttja from PSM0071717 was 810 µg g^{-1}, while the Mo-rich gyttja (from PSM007190) had a S concentration of nearly 20 000 µg g^{-1} (i.e. 2 %).

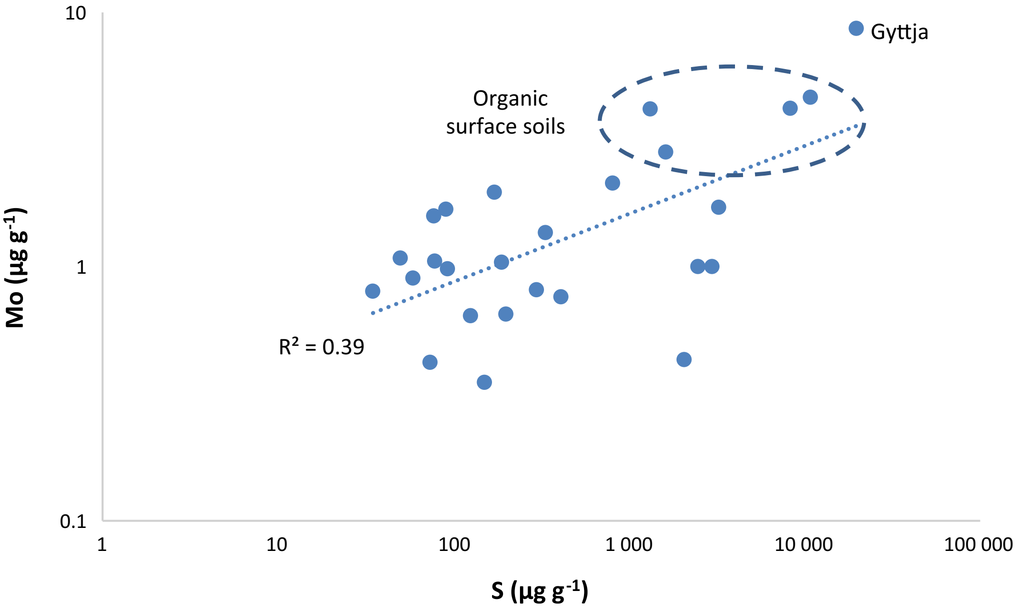

***Figure 3-4.** Mo and S concentrations in different soil types from the Simpevarp area. The samples comprise a wide range a soil types, both till and sorted sediments of glacial or postglacial origin, including grain sizes from clay to sandy gravel. More organic soils such as gyttja and surface soils are also included. The regression line refers to the logarithm of the concentrations.*

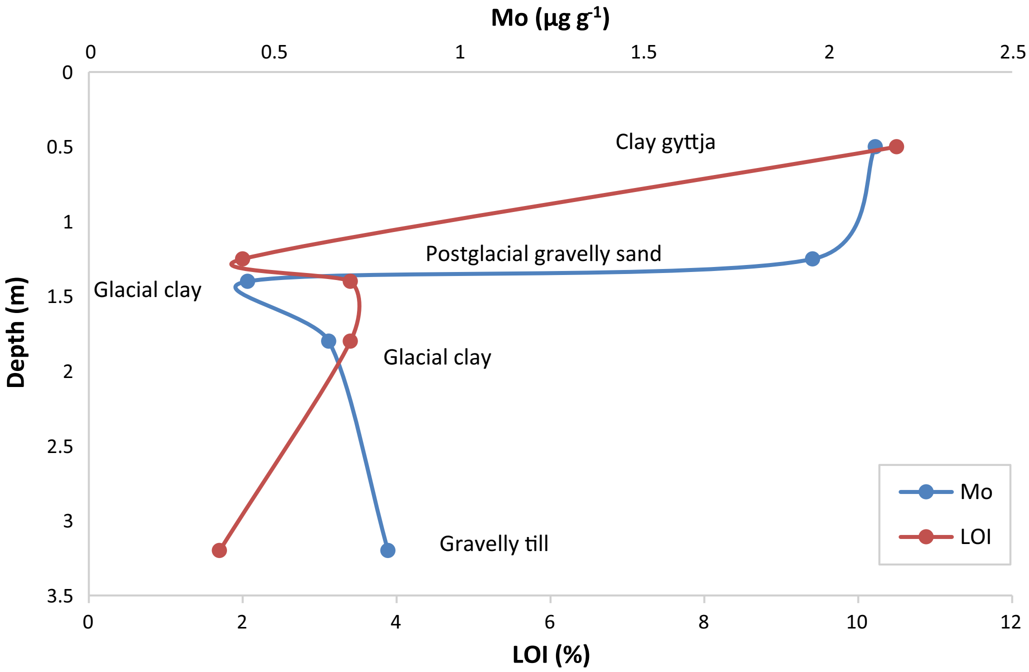

Figure 3-5. *Mo concentration and LOI in a soil profile from Simpevarp (PSM007171) comprising different soil types. Data from Sohlenius et al. (2006).*

A similar difference between different soil types can be observed in the Forsmark area. In the soil samples that were used for Kd measurements (see Sheppard et al. 2009) – including clayey till, glacial clay, clay gyttja, cultivated peat and wetland peat – significant differences in Mo concentrations could be observed between different soil types (Figure 3-6). The more inorganic soil types, clayey till and glacial clay, both had low Mo concentrations in comparison with the more organic soil types, clay gyttja, cultivated peat and wetland peat. The relatively high Mo concentration in gyttja agrees well with the observations from Simpevarp, as do the relatively low Mo concentrations in till and glacial clay (Figure 3-5). The Mo concentrations in clay gyttja, cultivated peat and wetland peat by far exceed what was observed in the numerous till samples collected throughout the Forsmark area (Figure 3-2). Yet, even higher Mo concentrations have been encountered in gyttja from lake sediments (see Section 3.2.5 below).

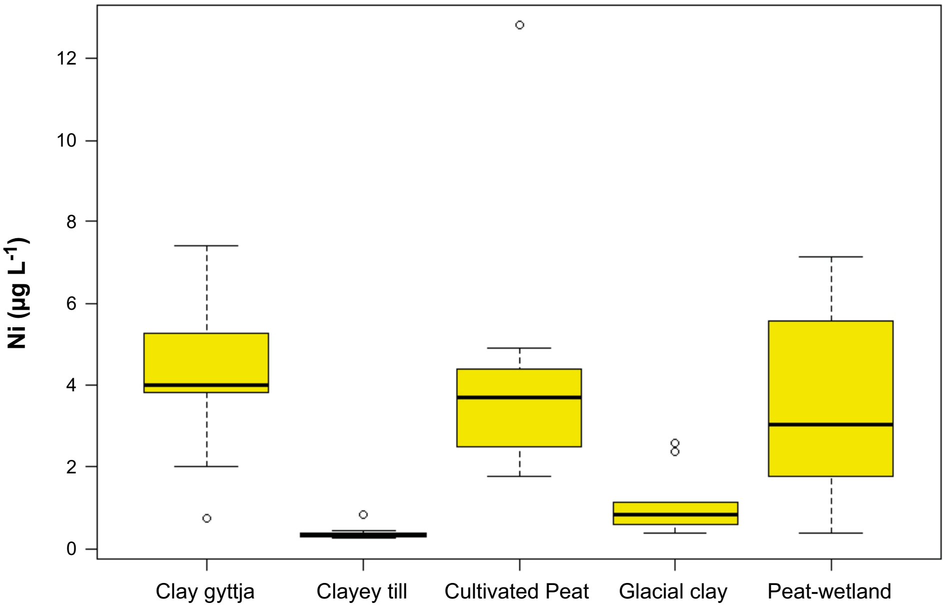

Figure 3-6. *Mo concentration in different types of soils from the Forsmark area. Data from Sheppard et al. (2011). n = 10 for each soil type.*

As in Simpevarp, there was a general tendency that soils with high S concentrations also had high Mo concentrations (Figure 3-7). Partly this may be related to the fact that both elements are important nutrients and that clay gyttja as well as peat soils are rich in organic matter, but all the soil types with high Mo concentrations also represent reducing or, in the case of the cultivated peat, formerly reducing environments. Therefore, it is likely that reduction of sulfate, formation of thiomolybdates and reduction of molybdate is involved in the accumulation of the high Mo concentration in these soils (e.g. Helz et al. 2011, Dahl et al. 2013a).

The importance of reducing conditions for acquiring high Mo concentrations is implied when comparing Mo to W, which occurs as an oxyanion, tungstate (WO_4^{2-}), that is analogous to molybdate. Tungsten will, however, not be reduced and will therefore remain more mobile than Mo, for example, in wetlands, although tungstate otherwise in general tends to be somewhat less mobile than molybdate (Gustafsson 2003, Bauer et al. 2018). When plotting the Mo/W ratio in the Kd soil samples as a function of the S concentration the till and the glacial clay tend to display relatively low and mostly uniform Mo/W ratios of ca. 0.01–0.03 regardless of the S concentration (Figure 3-8). Tungsten was not analysed in the larger set of till samples shown in Figure 3-2, but the Mo concentrations coincided well so presumably this ratio is representative for most of the minerogenic material in the Forsmark area. The more organic soil types – clay gyttja and the peat soils – displayed Mo/W ratios that were substantially elevated in comparison with the till and the glacial clay. The difference was approximately one order of magnitude for the clay gyttja and up to two orders of magnitude for wetland peat (Figure 3-8). In these soil types there was also a clear relationship between the S concentration and the Mo/W. A plausible interpretation is that there has been an accumulation of S in these soils by reduction of sulfate and precipitation of sulfides because of the reducing conditions. This would also lead to an immobilisation of Mo, but not of W, which would explain the high Mo/W ratios.

Another relevant element to compare Mo to is Re, which is also neighbour of Mo in the periodic table of the elements. Rhenium was also absent in the larger dataset of till soils, but it was included in the Kd analyses. In oxidising environments Re normally occurs as heptavalent Re^{7+} in the form of the oxyanion perrhenate, ReO_4^-. Just like molybdate, perrhenate can be reduced, whereupon Re will be immobilised as Re^{4+}, analogously to Mo^{4+}. Perrhenate is, however, less stable than molybdate and can be expected to be reduced at somewhat higher Eh (Crusius et al. 1996, Morford et al. 2012). Accumulation of Re has also been observed in anoxic sediments (Koide et al. 1986). In the cultivated peat and the wetland peat from Forsmark there was a tendency that samples with high Mo concentrations also had high Re concentrations, which is consistent with the hypothesis that Mo is accumulating because of the reducing conditions (Figure 3-9). Some of the clay gyttja samples, however, contained high Mo concentrations, but still relatively low Re concentrations. This does not necessarily contradict the hypothesis because the reduction of Mo and Re cannot be expected to occur at exactly the same Eh. In other soil types there was no clear relationship between Mo and Re, but the effects of reduction on these elements should become visible only when the conditions are sufficiently reducing, which probably is not the case in the till and glacial clay samples. Consequently, the comparisons with both W, Re and S suggest that the occurrence of high Mo concentrations in more organic soil types is linked to the reducing conditions in these environments.

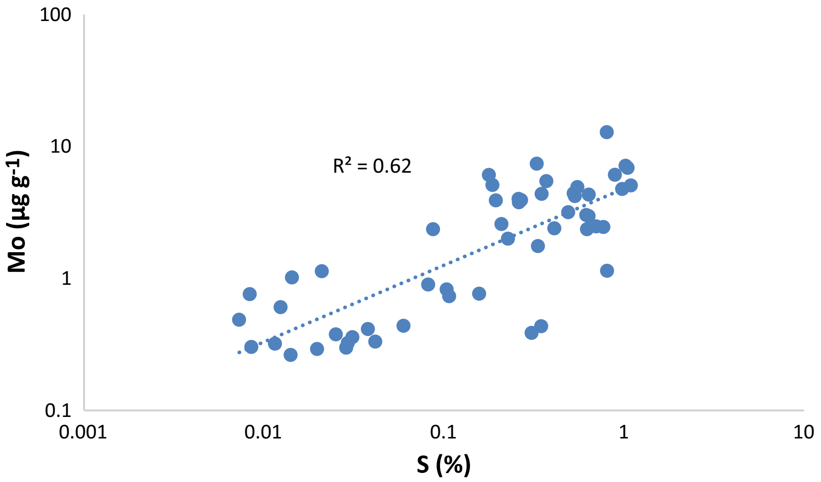

Figure 3-7. *Mo and S concentrations in the Kd soil samples. The regression line and the* R^2 *value refer to the logarithm of the concentrations. Data from Sheppard et al. (2011).*

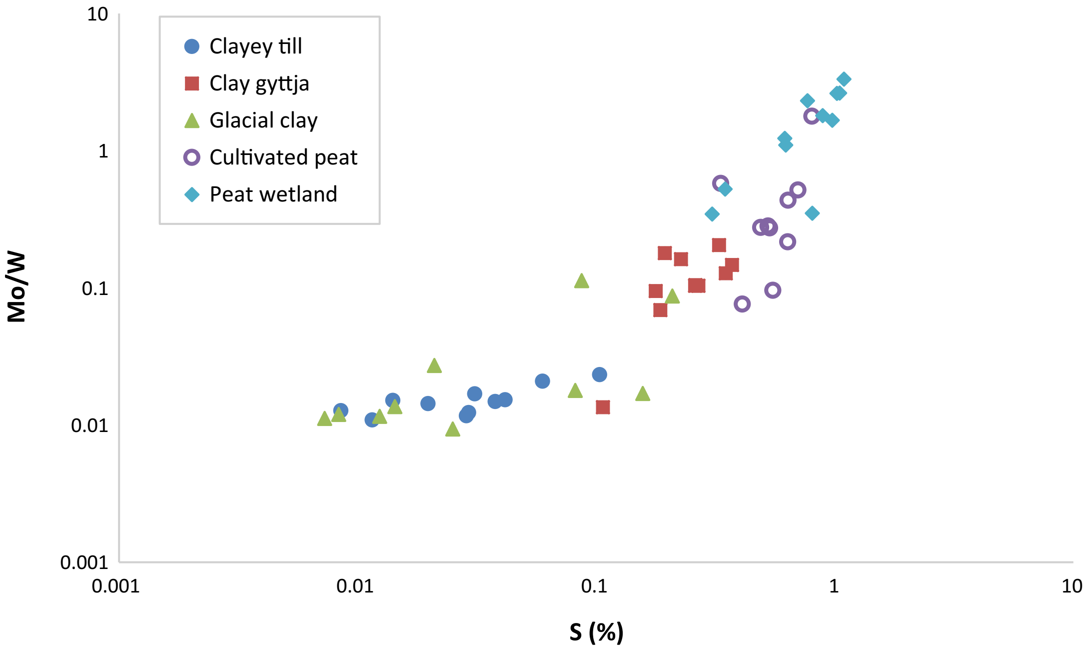

Figure 3-8. *Mo/W (mass) ratios in different types of soils from the Forsmark area as a function of the S content. Data from Sheppard et al. (2011).*

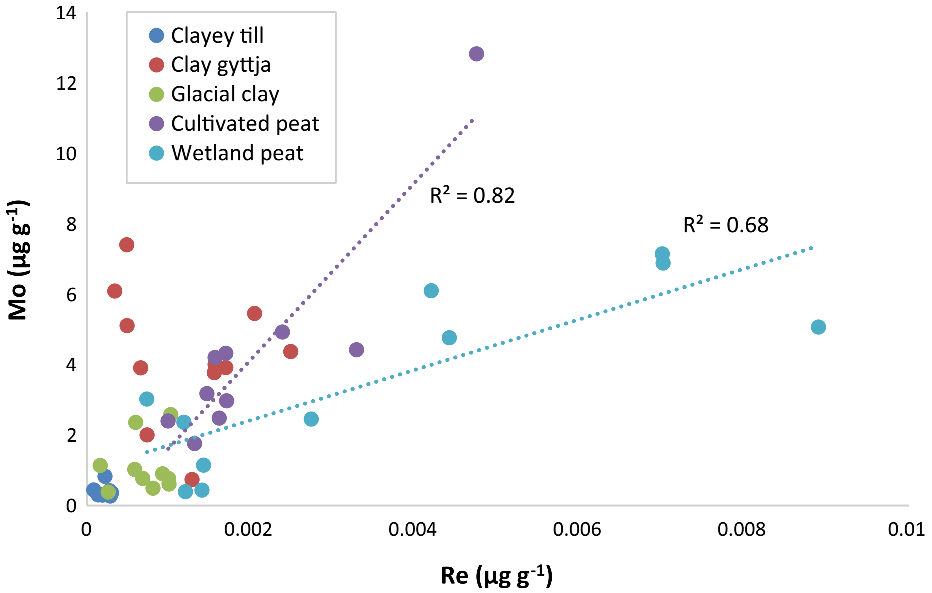

Figure 3-9. *Concentrations of Mo and Re in different types of soils from the Forsmark area. Data from Sheppard et al. (2011).*

As described for Ni (see Section 2.2.2 for details), different extraction methods were applied to a number of soil samples from Simpevarp representing a spruce forest, an oak forest and an alder fen (Lundin et al. 2006). In these analyses the concentration of exchangeable Mo, i.e. the least strongly bound soil fraction, ranged from 0.0065 µg g^{-1} in the mineral soil of the oak forest to 5.9 µg g^{-1} in the peat soil of alder forest (Figure 3-10). This means that these few samples envelop the entire range of Mo concentrations observed in the local till, which were measured using a much stronger extractant (*Aqua regia*). Since these extractions by ammonium acetate only represent a fraction of weakly bound Mo in the soils, it is not surprising that it can result in low Mo concentrations in some cases. It is not obvious, however, that the exchangeable Mo in certain soils would exceed the concentration in till determined by *Aqua regia*. The observation is, however, fully consistent with the high Mo concentrations that have been observed in other soil types, and demonstrate that a substantial fraction of the Mo in these soils derive from sorption of dissolved Mo (Figure 3-4). In the soils from the extraction experiments the concentrations of exchangeable Mo corresponded to between 1.9 % and 47 % of the Mo extractable by *aqua regia*, and the number is likely to be higher in soils where there has been an appreciable accumulation of Mo from the pore water. In this case the high exchangeable Mo concentrations are associated with relatively nutrient-rich peat soils where sulfide also is likely to be present. Figure 3-10 also shows that the peat samples that contain high concentrations of exchangeable Mo also contain high concentrations of exchangeable U and V. Both U and V are redox-sensitive elements that easily can be immobilised when reduced, just like Mo.

There are, however, other mechanisms than reduction or association with thiol groups that could lead to considerable sorption of Mo from the pore water. For example, Gustafsson and Tiberg (2015) have pointed at the importance of Al and Fe (hydr)oxides for retention of molybdate in forest soils. When looking at all the three extraction techniques that were applied to the three soil profiles, the concentration of extractable Al was high in some of the samples that also contain high concentrations of extractable Mo (Figure 3-11). This mainly concerned the deeper sample (40–60 cm) from the spruce forest, where both the dithionite citrate and the aqua regia extractions resulted in high concentrations of both Mo and Al. This site (ASM001440) was, however, relatively wet so the soil was not classified as Podzol, which is typical for most coniferous forests, but a Histosol, i.e. an organic soil (Lundin et al. 2005). The C content at 50 cm was ca. 20 % so the analysed sampled also represented a relatively organic soil. Since Al can bind strongly to organic matter and precipitation of any Al mineral would be suppressed by the presumably high DOC concentrations in the pore water, it is unclear in what form the extracted Al was present and whether the high Mo concentrations were associated with the Al. In the alder fen high concentrations of both Al and Mo were extracted by aqua regia, but although high Al concentrations were extracted also by dithionite citrate in these samples relatively little Mo was mobilised by this extractant (Figure 3-11). High concentrations of Mo were instead mobilised by ammonium acetate, which, conversely, did not dissolve much Al. Hence, at least the exchangeable Mo appears not be associated to Al, while the data is more ambiguous for the more strongly bound fractions.

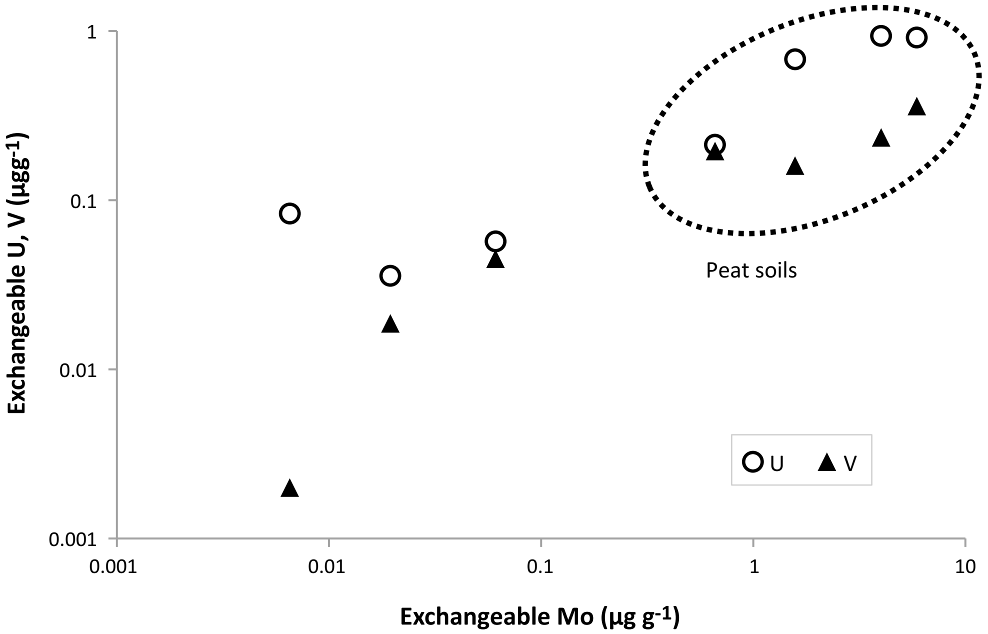

__Figure 3-10.__ Exchangeable Mo vs. exchangeable U and V, respectively, in peat soils and mineral soils from Simpevarp. Notably higher concentrations were found in the peat soils (alder fen) compared to the mineral soils (spruce forest and oak forest. Data from Lundin et al. (2006).

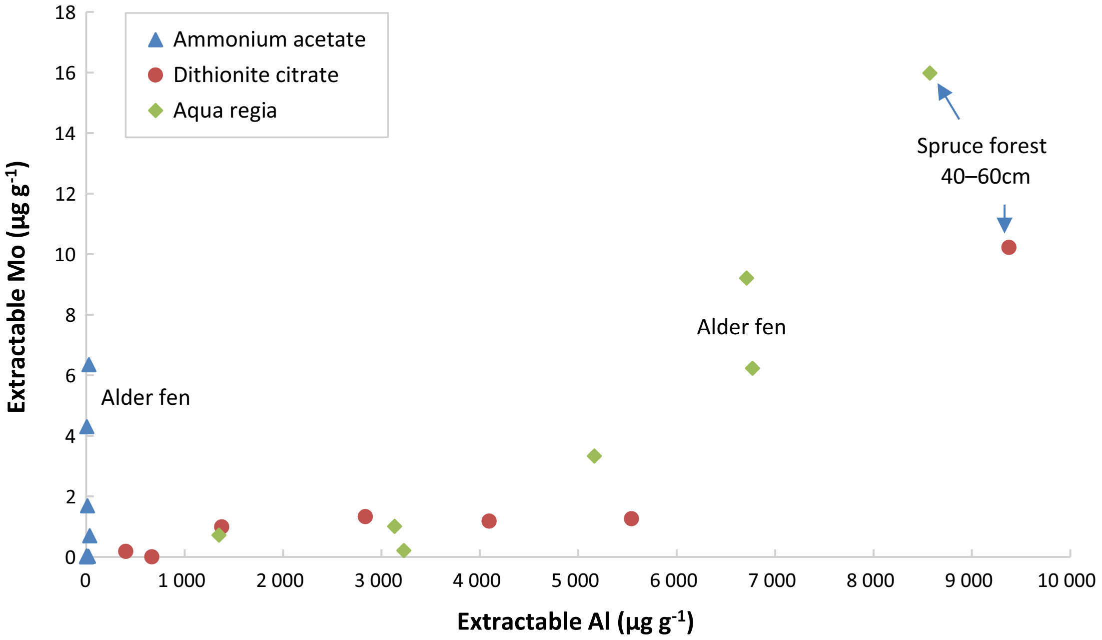

Figure 3-11. *Concentrations of extractable Al and Mo in seven soil samples from Simpevarp using three different extraction methods. Data from Lundin et al. (2016).*

3.2.3 Mo in near-surface groundwater and surface water

In near-surface groundwater (i.e. groundwater in the Quaternary deposits) in Forsmark Mo concentrations between 0.063 µg L^{-1} and 31 µg L^{-1} have been observed (n = 135). The Mo concentration tended to be higher in groundwater with high pH, which could be related to a generally weaker sorption and higher mobility of anions like molybdate in more alkaline water (Figure 3-12). Particularly low Mo concentrations were encountered in a groundwater well with high concentrations of sulfide (SFM0049). The recorded sulfide concentrations in this groundwater well were in the range 0.15–0.35 mg L^{-1}, which is well above the concentrations were removal of Mo from the aqueous phase should be expected (Zheng et al. 2000). The low Mo concentrations in this groundwater well was therefore consistent with the expected immobilisation of Mo in sulfate-reducing environments (see Section 3.1.3). It was also consistent with the trend observed in the soils, namely that Mo often tends to accumulate in the same environments as S (e.g. Figure 3-7).

Figure 3-13 shows the relationship between the average concentrations of three redox-sensitive elements – Mo, S and Fe – in the groundwater wells were sulfide was analysed. It is clear that in these groundwater wells Mo never occurs in high concentration when sulfide does. Likewise, when the Mo concentration is high, there is never much sulfide in the groundwater. A plausible explanation is that Mo is immobilised in the presence of high sulfide concentrations. The absence of sulfide, however, does not necessarily imply that there must be high Mo concentrations – this would require the presence of a suitable source for Mo – so there are no reasons to expect any strong correlation in this case. One groundwater well (SFM0027) stands out in Figure 3-13 with a Mo concentration of 9.6 µg L^{-1}. This 6.7 m deep well is located near the outlet of Fiskarfjärden and at the screening depth the groundwater comes from a confined aquifer with silty till.

The redox conditions implied by the sulfide concentrations are largely consistent with the Fe speciation. In the groundwater Fe is mostly dominated by ferrous Fe (Fe^{2+}), particularly in groundwater with high sulfide concentrations. Appreciable contribution from Fe^{3+} was found in some wells, but in those cases the sulfide concentration was mostly low. This is reasonable, since Fe^{3+} is reduced before sulfate as the water becomes more reducing. As shown in Figure 2-11, Fe^{3+} is present in groundwater with sufficiently high O_2 concentrations, mainly in recharge areas. The relationship between Fe and Mo is not particularly clear, which is not unexpected, since Fe is more easily reduced than Mo. Hence, a predominance of ferrous Fe does not necessarily imply that the redox conditions are reducing enough to also immobilise Mo.

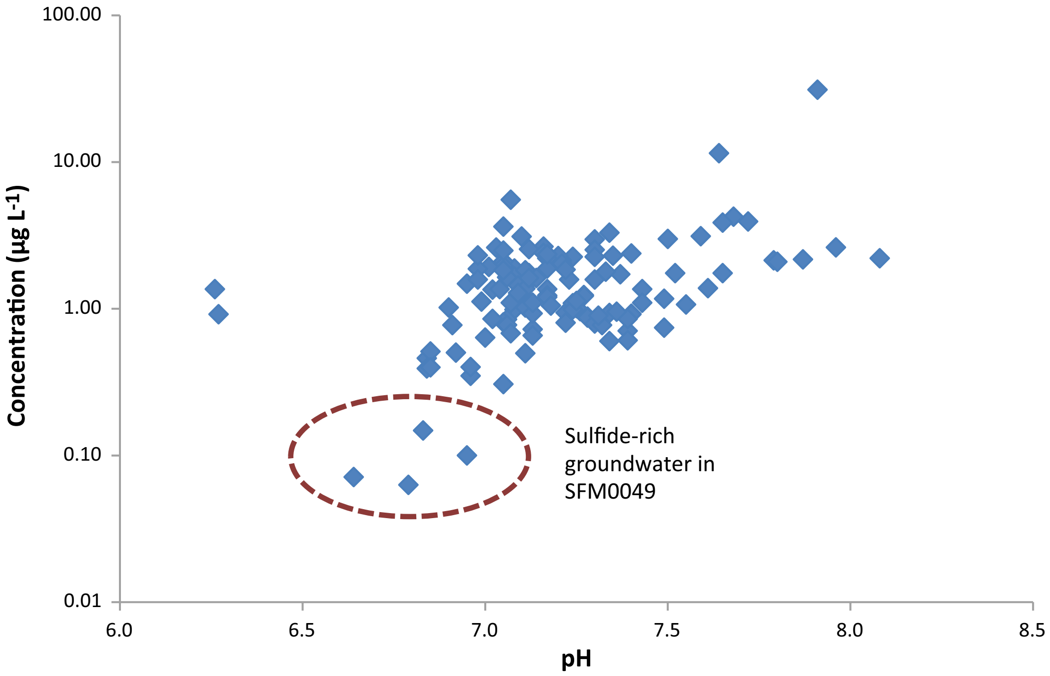

Figure 3-12. *Mo concentrations in groundwater in Forsmark as a function of pH. The lowest concentrations were encountered in the groundwater well SFM0049, which was characterised by high concentrations of sulfide (0.16–0.35 mg L^{-1}).*

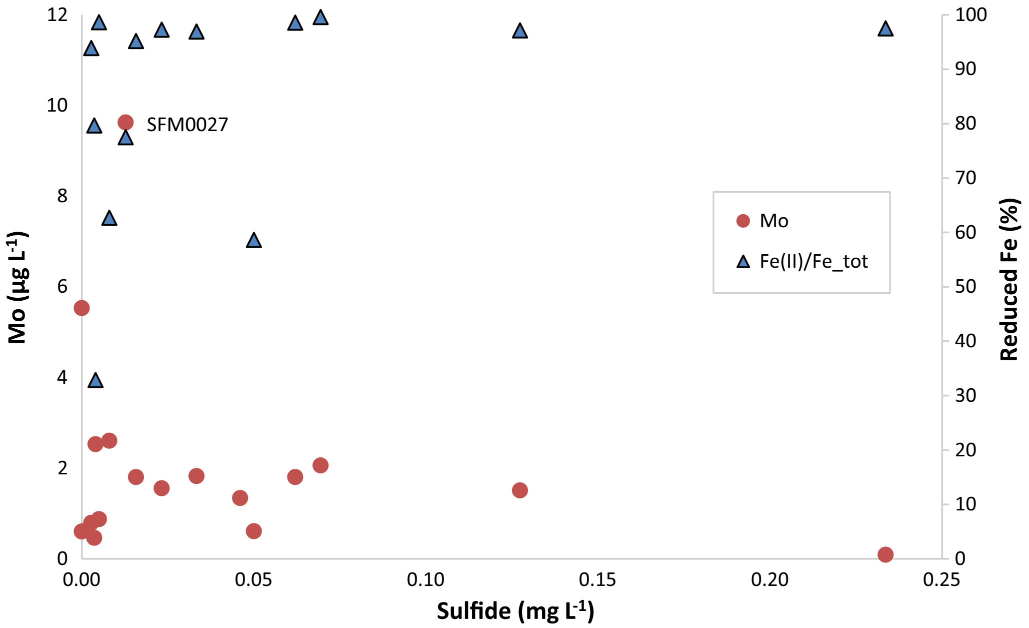

Figure 3-13. *Mo concentration and the fraction of reduced Fe in groundwater wells in Forsmark as a function of the sulfide concentration.*

In the Simpevarp area the Mo concentrations in near-surface groundwater also display a high variation, ranging from < 0.05 µg L^{-1} to 14 µg L^{-1} (n = 101). There was a significant correlation between log Mo and the pH (r = 0.50, p> 0.001), which, as in Forsmark, could reflect a higher mobility of molybdate in more alkaline water (Figure 3-14). Alternatively, this could be related to differences in mineralogy, soil types or other chemical parameters. As can be seen in Figure 3-14, much of the linearity in the relationship is dependent on a quite limited number of observations at the higher and lower ends, respectively, of the pH range, while the relationship is weaker in the pH range 6–7.5, which encompasses most of the sampled groundwater.

Molybdenum in groundwater is not correlated to sulfide in Simpevarp, but the groundwater chemistry is complex because the installations cover a relatively large area with different soil types. In some cases there are also marine influences on the groundwater chemistry, which, for instance, has a major impact on the sulfate concentrations in the groundwater. For example, the highest sulfate concentration in groundwater from Simpevarp, 480 mg L^{-1}, was encountered in SFM000241, which is located in Borholmsfjärden (a marine bay). Therefore, a better proxy for the redox conditions might be the fraction of inorganic S present as sulfide. In this case there is a negative correlation to log Mo ($r = -0.38$, $p > 0.01$), which again is consistent with the expected immobilisation of Mo in sulfate-reducing environments (Figure 3-15).

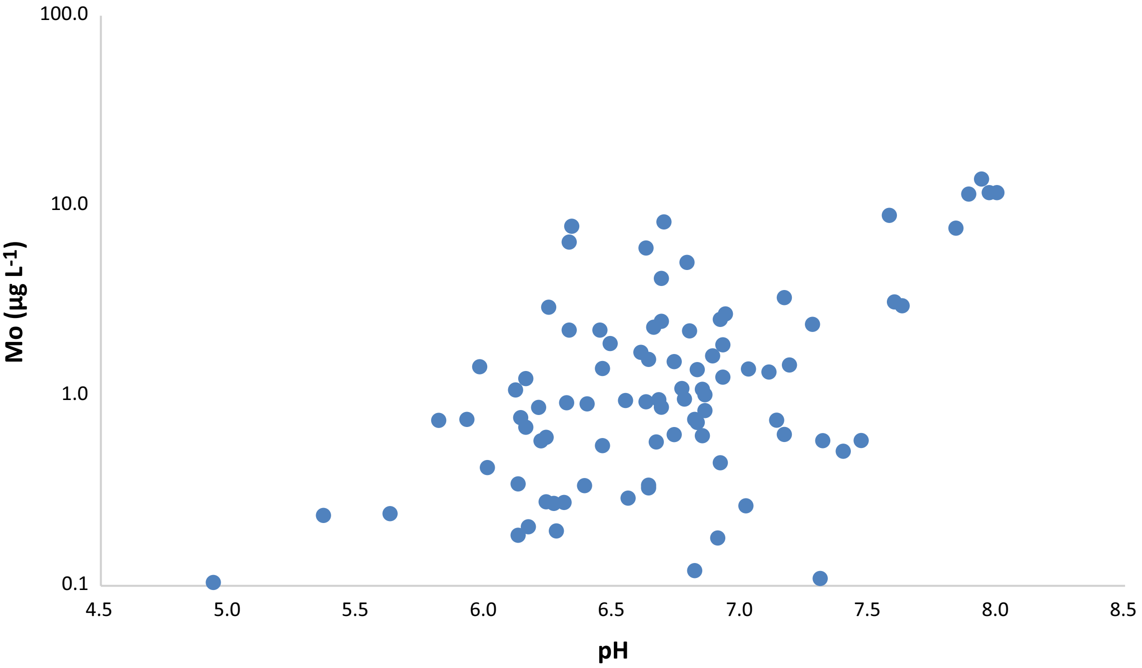

Figure 3-14. *Mo concentrations in groundwater in Simpevarp as a function of pH.*

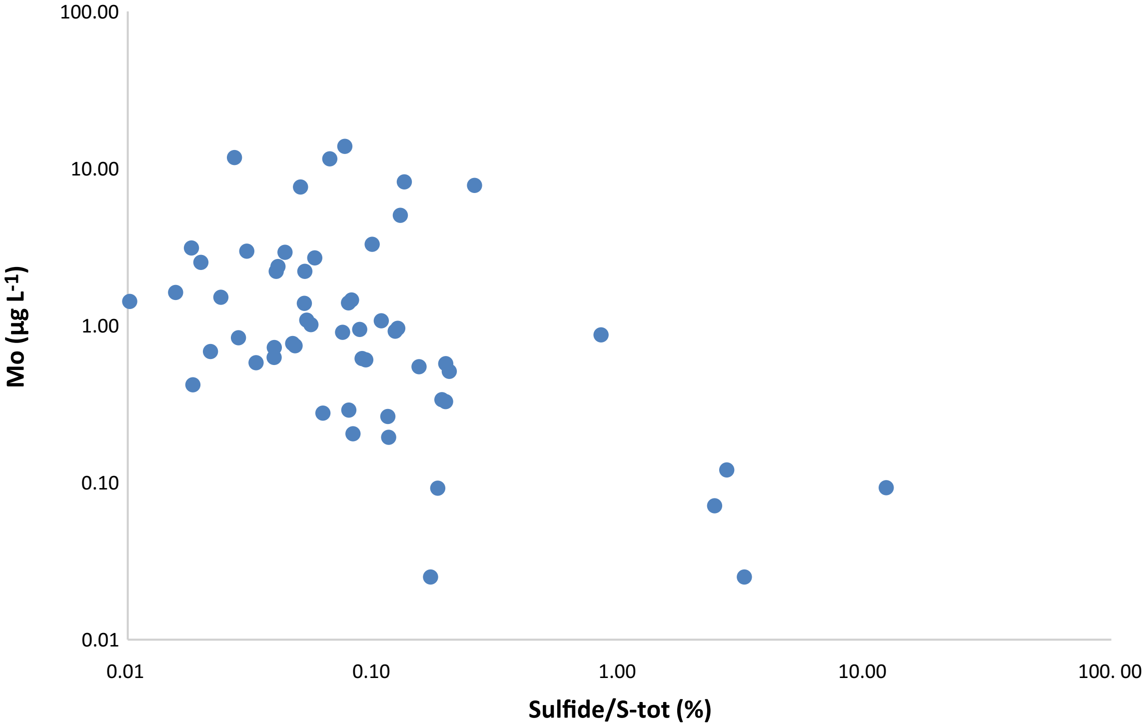

Figure 3-15. *Mo in groundwater in Simpevarp as a function of the sulfide fraction of the total inorganic S.*

Statistically, the effects of pH and redox potential on the mobility of Mo in the groundwater are independent in the sense that these two parameters are uncorrelated. It is, for example, possible to explain 41 % of the variation of log Mo in the groundwater in Simpevarp based on pH and the fraction of sulfide:

$$\log Mo = -8.77 - 0.346\frac{S^{2-}}{S_{tot}} + 1.31pH, \qquad \text{Equation 3-1}$$

where Mo, S^{2-} and S_{tot} denote the concentrations of Mo, sulfide and total inorganic S, respectively. All coefficients are significant at the 99.9 % confidence level ($R^2 = 0.41$; $n = 56$). The multiple regression could be further improved, e.g. by introducing a Cl as proxy for the marine influence because sea water tends to have higher Mo concentration than freshwater (see Figure 3-16 below), but what is perhaps more interesting is that a strikingly similar equation is valid in the Forsmark area. Using the same parameters as in Equation 3-1 the corresponding regression for near-surface groundwater in Forsmark is

$$\log Mo = -9.75 - 0.124\frac{S^{2-}}{S_{tot}} + 1.41pH. \qquad \text{Equation 3-2}$$

All denotations remain the same as in Equation 3-1, and the coefficients are significant at the 99.9 % confidence level ($n = 60$). The number of observations is lower than given above (e.g. Figure 3-12) because sulfide was not analysed in all samples. It is generally precarious to imply causation from regressions, but the fact that two datasets from two different sites, Simpevarp and Forsmark, display so similar relationships between Mo, pH and the sulfide fraction should strengthen the interpretation that the Equation 3-1 and Equation 3-2 do reveal something about what processes control the mobility of Mo in the groundwater. As discussed above, the mobility of molybdate – as an anion – should be favoured by higher pH. Conversely, the mobility of Mo should decrease under strongly reducing conditions where sulfide is common – and at least partly directly due to the presence of sulfide. More importantly, however, this interpretation is also supported not only by the accumulation of Mo in S-rich soils in the site investigation areas, but also by the scientific literature (see chapter 3.1).

3.2.4 Mo in lakes and sea water

In the Forsmark area the surface waters as a rule had notably lower Mo concentrations than the near-surface groundwater, ranging from 0.19–1.1 µg L^{-1} in lake water ($n = 83$) and from 0.082–1.9 µg L^{-1} in stream water ($n = 48$) (Figure 3-16). In the Simpevarp area the differences between near-surface groundwater and surface water were smaller with Mo concentrations between 0.92 µg L^{-1} and 1.3 µg L^{-1} in Frisksjön ($n = 10$) and between 0.069 µg L^{-1} and 6.8 µg L^{-1} in stream water ($n = 27$).

The sampling programme for Mo (and most other trace elements) in lake water included four samplings per year, one for each season. Most lakes in the Forsmark area displayed recurring seasonal patterns with the highest concentrations during the summer or the spring (Figure 3-17). In the smaller lakes Gunnarsbo-Lillfjärden and Labboträsket the highest Mo concentrations were observed in April-May, while the larger Bolundsfjärden and Norra bassängen, which is located downstream of Bolundsfjärden, peaked in July. One plausible reason for the more rapid response in Labboträsket and Gunnarsbo-Lillträsket is that the retention time in these lakes only amounts to 7 days, whereas Bolundsfjärden has a retention time of 77 days (Table 2-1). Although Norra bassängen also has a short retention time, it will unavoidably be affected by the Bolundsfjärden, from which it receives the lion's part of its water. In Eckarfjärden, however, the Mo concentration remained relatively stable throughout the entire sampling period regardless of season. It is possible that the even longer retention time of Eckarfjärden – 328 days – suppresses the seasonal trends that are observed in the other lakes. It can also be noted that the seasonal pattern, where present, is opposite to that of, for example, Ni, which tended to peak during the winters (Figure 2-14). There may be several explanations why Ni and Mo behave differently in the lakes, but as a cation and an anion, respectively, they are clearly not affected by the same mechanisms.

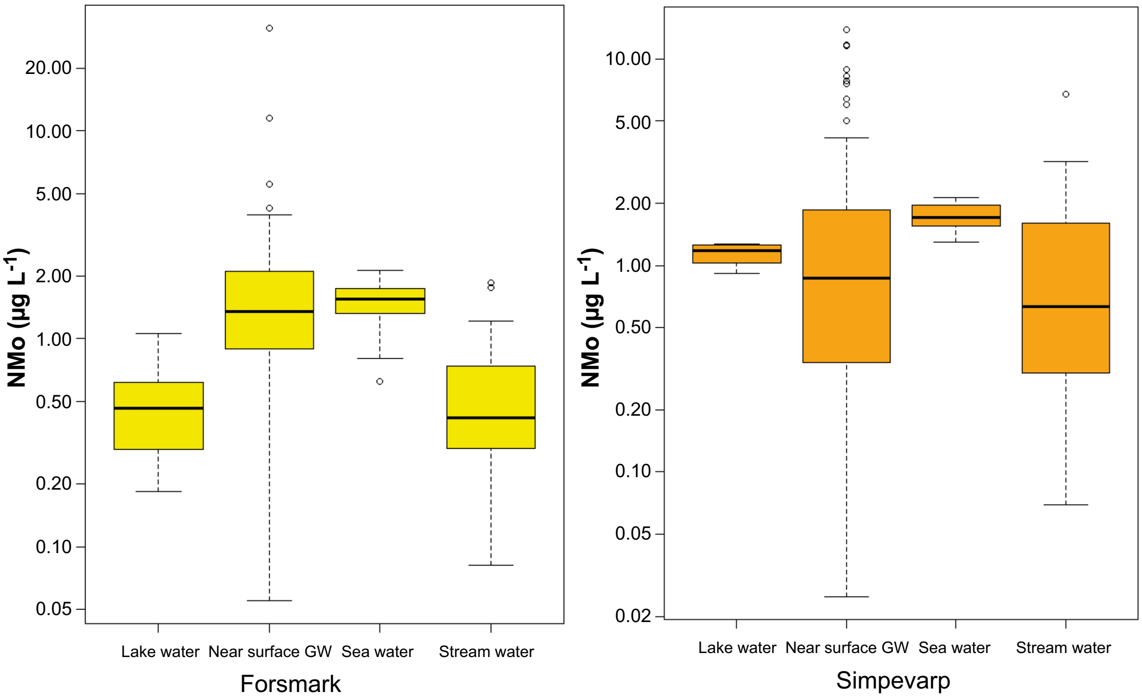

Figure 3-16. *Mo concentrations in different types of water in the Forsmark and Simpevarp areas, respectively. Note that the graphs have different scales on the y axis.*

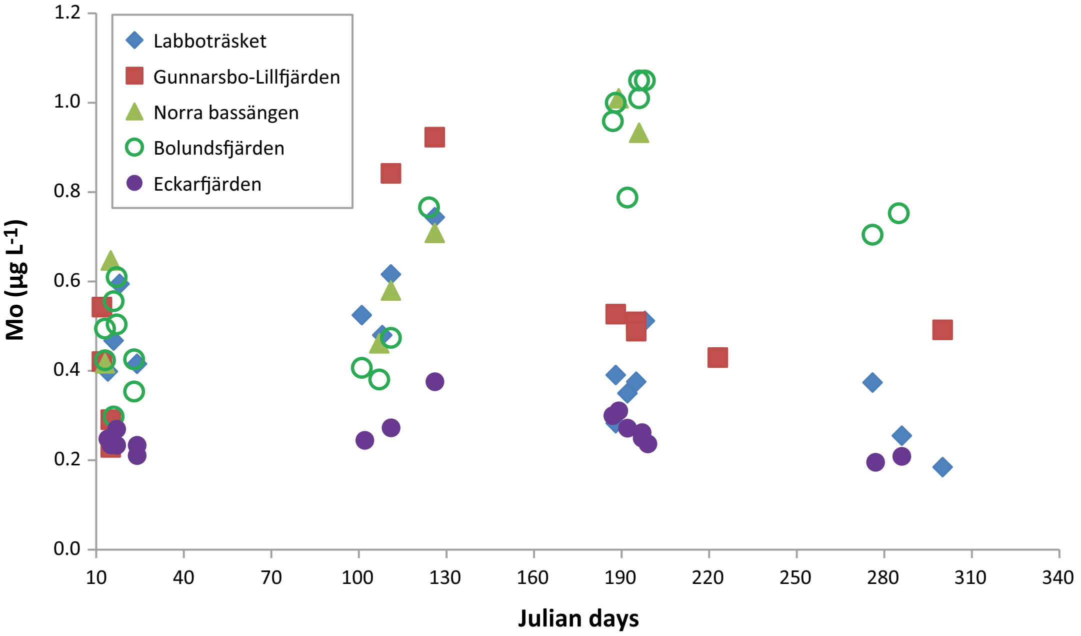

Figure 3-17. *Seasonal variation in Mo concentrations in the lakes of Forsmark (2002–2006).*

When comparing the lakes in the Forsmark area Eckarfjärden did not only lack the seasonal pattern that to varying degrees could be observed in the other lakes; it also tended to have the lowest Mo concentrations overall (Figure 3-17). Looking at the landscape scale, there was a trend that lakes that are situated higher up in the landscape had lower average Mo concentrations (Figure 3-18). Given the on-going shore line displacement the elevation is in this case also directly related to the age of the lakes, i.e. younger lakes tend to have higher Mo concentration than older lakes. As there are only data for six lakes, some caution is required, but there appears to be an appreciable difference between low-lying lakes like Bolundsfjärden with average Mo concentrations > 0.6 µg L^{-1} and, in particular, Eckarfjärden with an average Mo concentration of 0.25 µg L^{-1} (Figure 3-18). High Mo concentrations in the Forsmark area are typically associated with either groundwater or sea water (Figure 3-16). High Mo concentrations could therefore in some cases be related to intrusion of sea water, which also has been recorded in Bolundsfjärden. Another possible explanation would be that this gradient represents a gradual loss of marine Mo from the soils. This would also be consistent with the occurrence of similar trends for other elements that also are enriched in sea water, e.g. S and Sr (Figure 3-18 and Figure 3-19). However, the Sr isotope signature of the lake water does not resemble that of the local sea water. In sea water the ^{87}Sr/^{86}Sr ratio is relatively constant, varying between 0.7069 and 0.7107 with an average of 0.7094 (n = 23). This is substantially lower than the ^{87}Sr/^{86}Sr ratios observed in the lake water, and it is therefore clear that at least Sr is not primarily of marine origin (Figure 3-19). There is possibly a slight increase in the Sr isotope ratio with elevation, as indicated by the regression line in Figure 3-19, but it should be emphasised that with the currently available data there is no significant correlation between the average ^{87}Sr/^{86}Sr ratio of the lake water and the elevation at the 95 % confidence level. In any case, the major source of Sr in the lake water is most likely weathering of local soils rather and not marine Sr. Although Sr, S and Mo all can be categorised as relatively mobile elements in most environments, there are clearly differences in how they are retained in the landscape. Yet, the comparison with S and Sr indicates that it is unlikely that the decreasing Mo concentration with lake elevation would have anything to do with lingering marine Mo in the system. First, the isotope data clearly demonstrate that the corresponding pattern observed for Sr is not caused by a marine influence. Second, the differences in concentration between lake water and sea water is relatively modest for Mo, especially when compared to S and Sr. Hence, stronger effects should be expected for S and Sr unless the retention of Mo in the landscape is not substantially stronger. Combined this suggests that these trends are not related to marine sources. If this conclusion is correct, it would imply that the retention time of Mo in the groundwater system does not exceed the age of the landscape. For example, Eckarfjärden is estimated to have been isolated from the Baltic Sea ca. 850 years ago (Hedenström and Risberg 2003). This does, however, not exclude the possibility that Mo retained in older sediments etc. could be of marine origin. The matter could probably be unequivocally resolved by looking at the Mo isotopes.

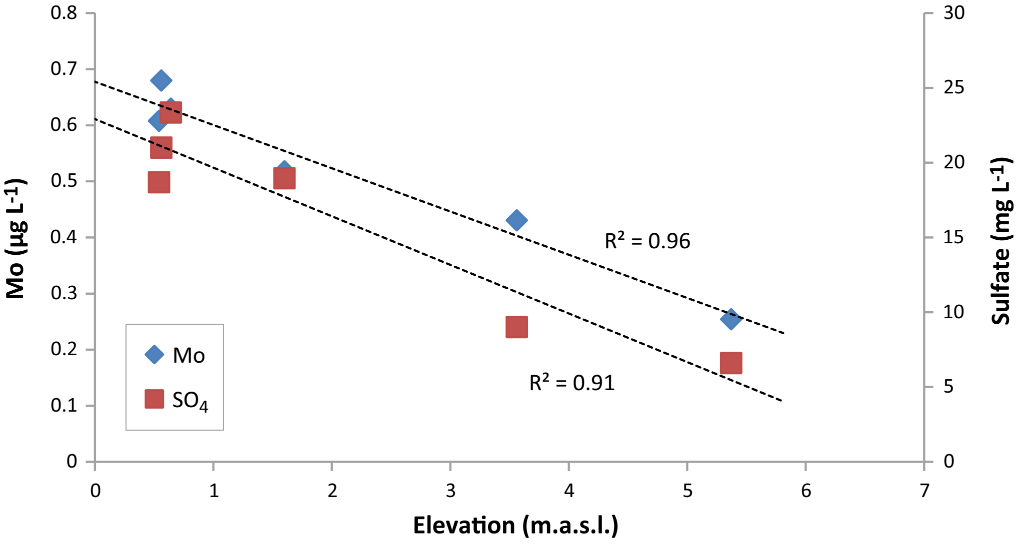

Figure 3-18. Average Mo and sulfate concentrations in the lakes of Forsmark as a function of the lake elevation (metres above current sea level). Due to the isostatic rebound the elevation is also indirectly a measure of the age of the lakes.

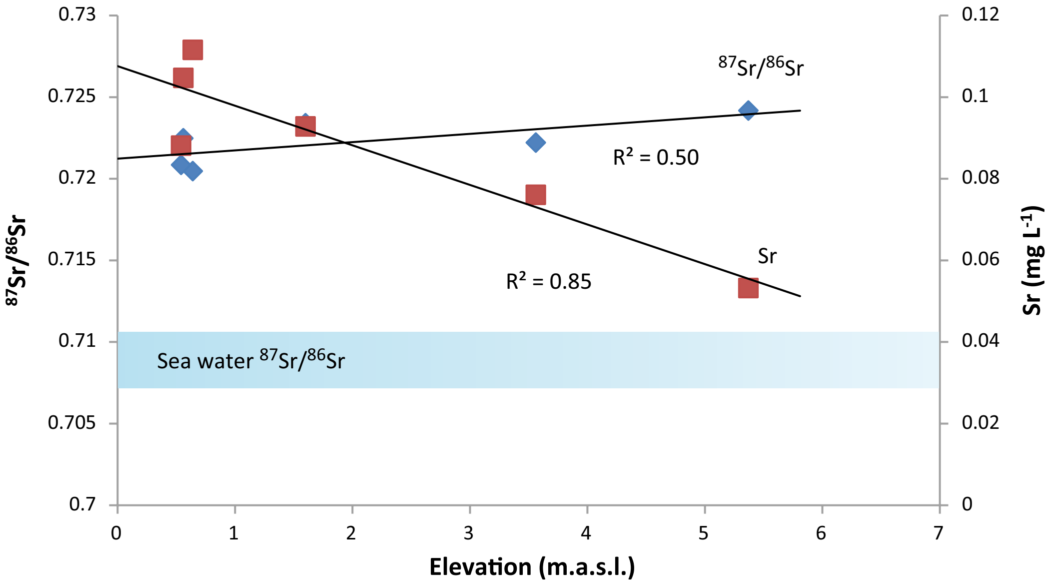

Figure 3-19. *Average concentration (red squares) and isotopic signature of Sr (blue diamonds) in lakes in the Forsmark area as a function of the elevation above sea level. The isotopic signature of local sea water is indicated by the blue area. The regression line suggests that the Sr isotope ratio could increase slightly with elevation, but the note that the correlation is not significant at the 95 % confidence level with the currently available data.*

Since the higher Mo concentrations in the lakes with lower elevation in the landscape do not seem to be related to any marine Mo, the most likely source of Mo for the lakes appears to be weathering of local soils. An alternative explanation to the differences in Mo concentration between the lakes could therefore be that lakes that are situated lower in the landscape receive older or deeper groundwater that has acquired higher concentrations of various weathering products like Mo. This would also explain why similar patterns are observed for, for instance, Sr and S. The hydrological understanding of the area and, more specifically, the available hydrological models could be used to further explore the validity of this hypothesis.

Looking more closely at Bolundsfjärden, which was one of the lakes with the most distinct seasonal variation, the highest Mo concentrations (up to 1.1 µg L^{-1}) were observed during the summer (Figure 3-20). The temporal resolution of the data is not sufficient to follow in detail what happens in the lake, but there is one observation suggesting that the Mo concentration starts to increase during the late part of the spring (May). The observations from the inlet to Bolundsfjärden are scarce, but there appears to be a trend that the inflowing stream water during this period has higher Mo concentrations than the lake water, which could provide an explanation to why the Mo concentration in the lake increases. Some precaution is advisable, however, as the inlet drains only ca. 15–20 % of the catchment area of Bolundsfjärden (Sonesten 2005). Although most water consequently reaches Bolundsfjärden from other sources, it nevertheless indicates the possibility that there could be an inflow of Mo-rich groundwater to the lake during the spring period. Especially if much of the inflow of water occurs as groundwater, this would be expected to increase the Mo concentration of the lake (Figure 3-16). Although water from the groundwater wells are denoted as near-surface groundwater (as in contrast to the deeper groundwater from the bedrock), many of the groundwater wells are relatively deep in comparison with the lakes and the streams. A plausible explanation to the generally lower Mo concentrations in lakes and streams is therefore that much of their water comes from more superficial hydrological pathways that do not allow as much time for weathering as in the groundwater found in most of the wells. Hence, periods when deeper groundwater reaches the surface systems could be expected to cause higher concentrations of weathering-derived solutes like Mo. During all other seasons apart from the spring, however, the inlet has similar or, in most cases, lower Mo concentration than the lake. Thus, it would not increase the Mo concentration of the lake water, but dilute it. Furthermore, Bolundsfjärden is believed to be a groundwater source during the summer, i.e. water is flowing from the lake and out into the surrounding soils. This seems inconsistent with the idea that high Mo concentrations would build up in Bolundsfjärden during the summers as a result of the inflow of deeper groundwater with high Mo concentration.

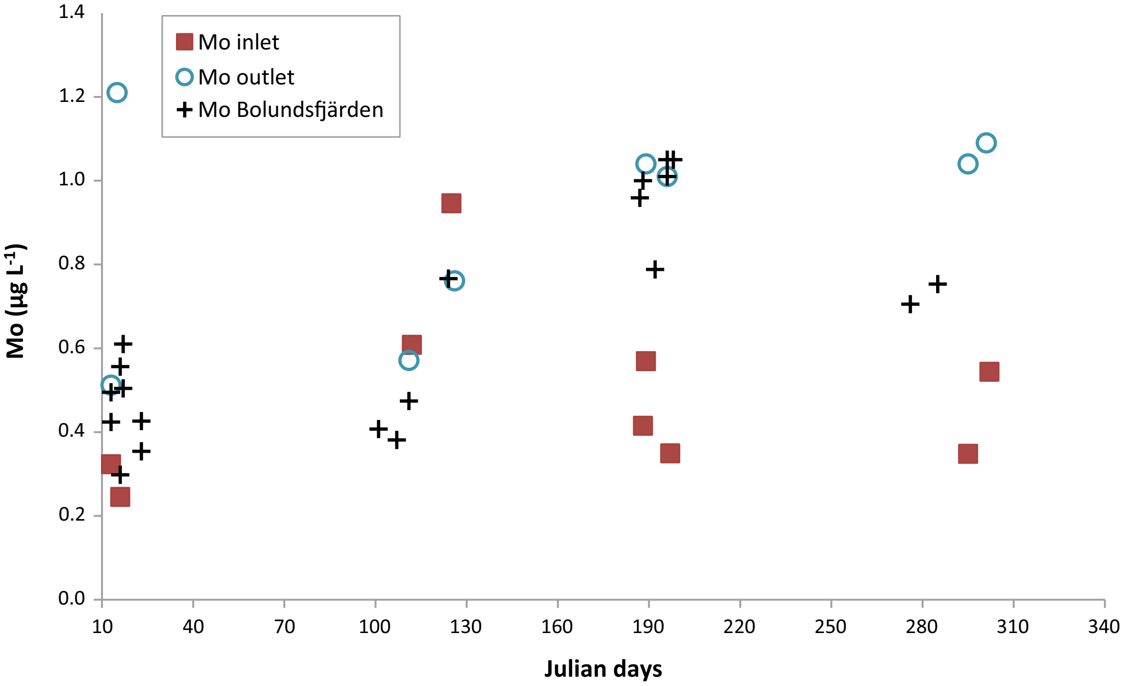

Figure 3-20. *Seasonal variation in the concentrations of Mo in Bolundsfjärden, its outlet and one of its inlets.*

It can also be noted that the Mo concentrations at the outlet of Bolundsfjärden mostly agree well with the concentrations observed in the lake, but particularly during the autumn and at one occasion in the winter there were substantially higher Mo concentrations at the outlet (Figure 3-20). As discussed with respect to Ni and specifically redox-sensitive elements like Mn and Fe (e.g. Figure 2-20 and Figure 2-24), the stratification of the lake water appears to be well-developed during the winters despite the shallowness of the lakes. With respect to, for example, redox conditions, pH and calcite saturation the lake water chemistry in the Forsmark area undergoes quite drastic changes as the seasons change, all of which can have far-reaching consequences for the fate of various trace elements in the lakes. Therefore, it is also possible that the varying Mo concentrations in the lakes are related mainly to internal biogeochemical processes in the lake water.

The perhaps most obvious parameter that has the potential to strongly affect the solubility of Mo is the redox potential of the lake water or at the water-sediment interface. As the lakes become covered by ice in the autumn and decomposition of organic matter consumes the oxygen, the redox potential is likely to drop considerably in the lake (Figure 2-22). Unfortunately, sulfide was not analysed in the lake water samples, but other redox parameters such as Fe, Mn, NH_4 and – for that matter – O_2 concentrations in the lake water consistently indicate that above all winters are associated with more reducing conditions (e.g. Figure 2-20, Figure 2-22 and Figure 2-24). Sulfide would, however, be a better indicator of whether the redox potential becomes reducing enough to also affect molybdate. Yet, there is, a significant correlation ($r=-0.63$, $p < 0.01$) between the concentration of Fe and Mo, respectively, in Bolundsfjärden (Figure 3-21). The negative correlation could be interpreted as a redox effect, since Fe generally is more mobile in reducing water, while Mo is more mobile in oxidising water. The meaning of this relationship is, however, called into question by the absence of any similar trend in other lakes, e.g. Eckarfjärden and Labboträsket. Molybdate can also adsorb to Fe (oxy)hydroxides, but given the high pH in these lakes, especially during the summers when Fe appears to be oxidised, it should not be particularly important (Gustafsson 2003).

Besides the redox conditions, the other parameter that appeared to be important for the mobility of Mo in groundwater was pH (Equation 3-2). The lakes in the Forsmark area are characterised by high pH (Figure 2-21). Particularly high pH can be observed during the summer due the biological uptake of CO_2. In Bolundsfjärden and Eckarfjärden, for example, pH values up to 8.9 and 8.8, respectively, have been observed. In Norra bassängen even higher pH has been encountered, up to 9.6. All these observations were made during the summer, but in the winter the pH of the lake water can decrease by nearly

2 pH units (and in some cases even more). In Bolundsfjärden Mo was positively correlated to pH ($r = 0.81$, $p < 0.001$), which is in agreement with the observations in the near-surface groundwater in Forsmark (Figure 3-12 and Figure 3-22). Despite the low variation in the Mo concentration there was a significant, albeit weaker, correlation to pH also in Eckarfjärden ($r = 0.55$, $p < 0.05$). Although the pH of both lakes span approximately the same range, the response of Mo to the changes in pH in the two lakes appears quite different (Figure 3-22); if pH would be a major driver behind the varying Mo concentrations in the lakes, it is unclear why the response in Bolundsfjärden would appear so much stronger than in Eckarfjärden.

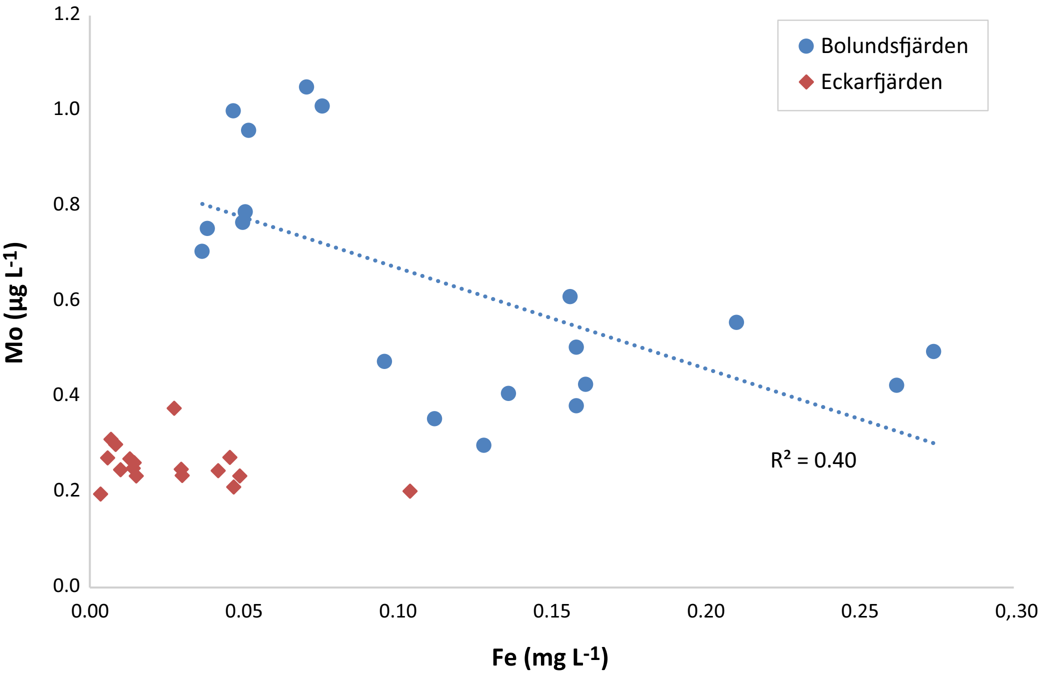

Figure 3-21. *Mo and Fe concentration in Bolundsfjärden and Eckarfjärden.*

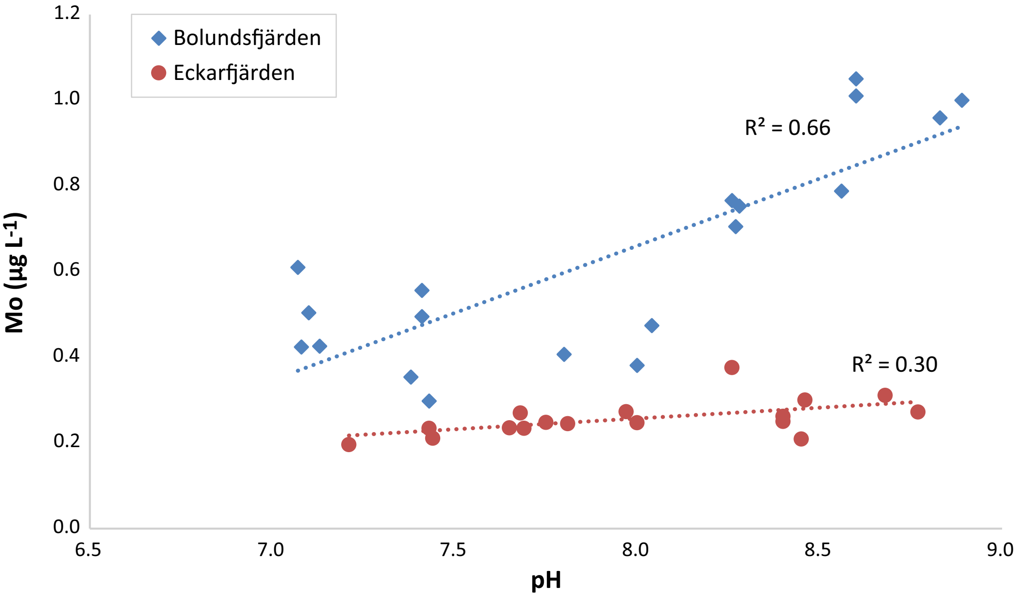

Figure 3-22. *Mo concentrations in Bolundsfjärden and Eckarfjärden as a function of pH.*

In the soils Mo was compared to other elements with similar – but in some key aspects different – properties like W and Re (Figure 3-8 and Figure 3-9). Neither W nor Re is available in the lake water, but another neighbour of Mo in the periodic table that also should be expected to occur as an oxyanion, at least during the ice-free period when the lake water is well oxidised, is V. The stable oxidation state of V in oxidising environments is normally V(V), which will occur as vanadate, either protonised as $H_2VO_4^-$ when pH is below 8.8 or as HVO_4^{2-} at higher pH (Gustafsson 2019). At lower Eh, vanadate will be reduced either to V(IV), which occurs as the oxycation vandyl (VO^{2+}), or to V^{3+}. Vanadyl is mainly stable under acidic conditions so in the lakes of Forsmark reduction directly to the relatively immobile V(III) would be most likely. Some similarities between Mo and V could be observed in the extraction of soils from Simpevarp (Figure 3-10).

In both Eckarfjärden and Bolundsfjärden there was a clear resemblance between Mo and V, although V tended to vary over a wider range in both lakes (Figure 3-23). The correlation between Mo and V was significant in both cases, $r = 0.81$ in Bolundsfjärden and $r = 0.75$ in Eckarfjärden ($p < 0.05$ for both). Particularly in Bolundsfjärden, summers were typically associated with higher concentrations of Mo and V, while winters were associated with low concentrations. For both elements the redox conditions are fundamental for their behaviour, and the mobility of both would be expected to decrease if they undergo reduction. In the presence of sulfide, for example, V would be expected to be stable as V(III) (Gustafsson 2019). Hence, the seasonal patterns observed in the lakes would be consistent with a redox-controlled mobilisation and immobilisation of Mo and V.

There are, however, also important differences between vanadate and molybdate. For example, vanadate tends to be more reactive than molybdate. In a study of colloids and trace elements in Kalixälven V was found to be associated mainly with Fe colloids, whereas no Mo at all could be detected in the colloidal phase (Dahlqvist et al. 2007). Presumably, Mo was present as free molybdate ions in the river water. The pH of Kalixälven was arguably lower than in the lakes of the Forsmark area – ca. 6.5–7.5 –, which would favour the adsorption of anions. Yet, vanadate is one of oxyanions that is known to adsorb most strongly to ferrihydrite, which would suggest that the association of V with Fe colloids could be important also at higher pH (Gustafsson 2019). Precipitation of ferrihydrite or other forms of Fe(III) minerals would, however, be expected mainly during the ice-free period, when the lake water is well oxidised. Summers are typically associated with low concentrations of Fe and Mn, which suggests that there is a precipitation during this period (Figure 2-20). This is, however, also the period when the V concentrations are highest in the lake so it does not appear as if V is scavenged from the lake water when Fe precipitates. Still, as will be further discussed in Section 3.2.5, accumulation of V in the lake sediments appears to be strongly related to Fe (see Figure 3-32), while the accumulation of Mo is more associated to S (e.g. Figure 3-31). If V is more associated with Fe, that might explain why V appears to be more active in the lakes, since precipitates of Fe(III) can re-dissolve as soon as the lake becomes more reducing, e.g. during the winters. Sulfide, however, would remain insoluble as long as sufficiently reducing conditions persist, which should be the case in the organic lake sediments (Figure 3-31). When comparing the Mo/V ratios in different lakes in the Forsmark area there was a significant trend of lower Mo/V ratios in lakes with the longer retention times (Figure 3-24). Again, the number of lakes is limited, but one possible interpretation is that there is a more permanent accumulation of Mo in the lake sediments. The sediments are discussed in more detail in Section 3.2.5.

In Frisksjön in the Simpevarp area both Mo and V were positively correlated to Fe ($r = 0.92$ for Mo, 0.95 for V, $p > 0.01$ for both), see Figure 3-25. This means that among all analysed chemical parameters in Frisksjön Fe showed the strongest relationship to Mo. This positive correlation between Fe and Mo in Frisksjön is contrary to the negative correlation observed in Bolundsfjärden in Forsmark (Figure 3-21). However, there are some differences between these lakes, which could explain why. The Fe concentrations in Frisksjön were notably higher, 0.55–0.99 mg L^{-1}, as compared to 0.037–0.27 mg L^{-1} in Bolundsfjärden and even less in Eckarfjärden. The Fe concentrations were also more stable in Frisksjön, which suggests that the lake water has a more stable redox potential with less oxidation/reduction of Fe. Analyses of Fe(II) in four of the ten lake water samples confirm that even during the summers – the samples were taken at 0–1 m and 1.5–2.5 m in June 2003 and August 2005 – a substantial fraction of the Fe was present as Fe(II), between 30 % and 42 %. As Fe(II) has not been analysed in Forsmark, no direct comparison can be made. Nevertheless, it can be noted that with a maximum depth of 3.2 m Frisksjön is significantly deeper than the lakes in Forsmark, which should moderate the mixing of the lake and, consequently, the oxygenation of the lake water compared to the shallower lakes in Forsmark

(Engdahl and Ericsson 2004). This is also confirmed by measurements in Frisksjön, demonstrating that below 2 m not much O_2 was present even in the summer (Ericsson and Engdahl 2004). The presumably more reducing conditions in Frisksjön would favour the solubility of Fe. Likewise, pH was also appreciably lower in Frisksjön, 6.3–7.3, which also favours the solubility of Fe due to lower hydroxide concentrations. However, based on the measurements of Ericsson and Engdahl (2004) suspended matter from Frisksjön is also enriched in Fe, which suggests that there at times could be precipitation of Fe also in Frisksjön.

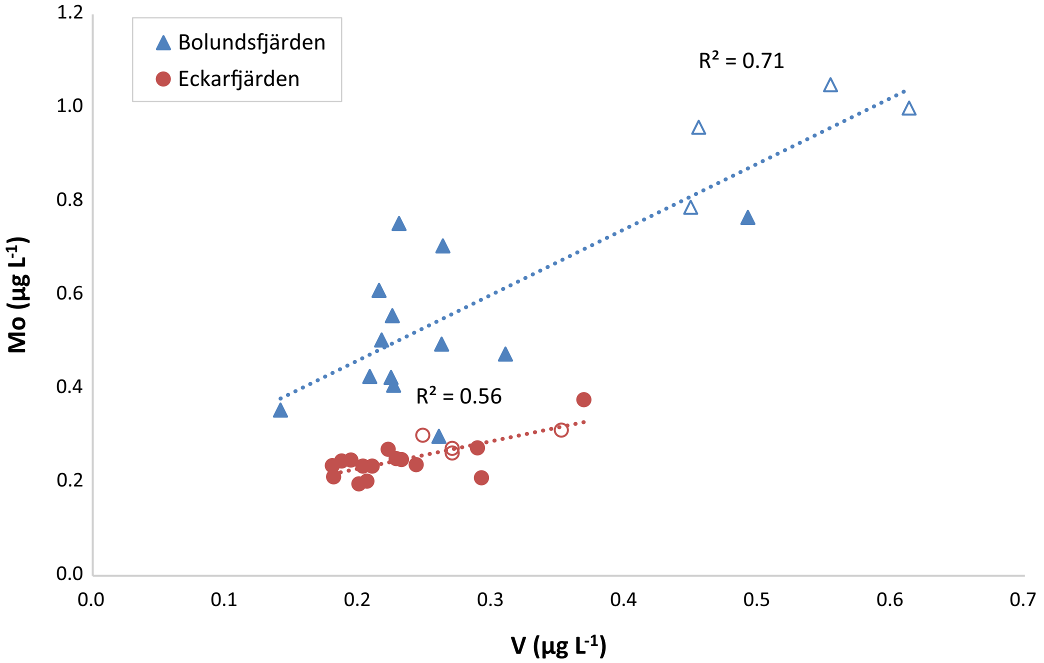

Figure 3-23. *Mo and V concentrations in Bolundsfjärden and Eckarfjärden. Summer values (July) are indicated by open markers.*

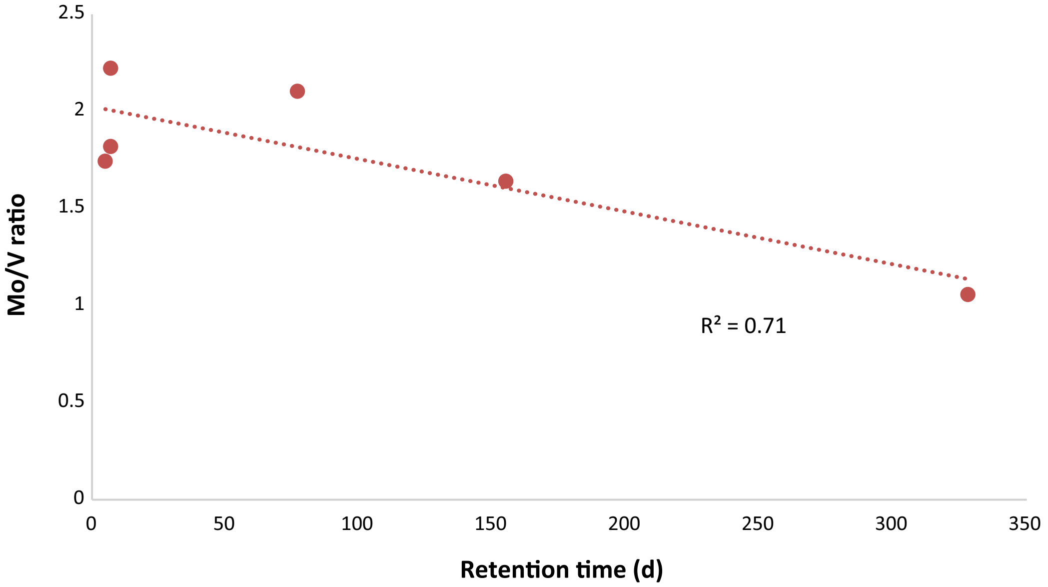

Figure 3-24. *Average Mo/V ratios in six lakes in the Forsmark area as a function of the retention time of the lakes.*

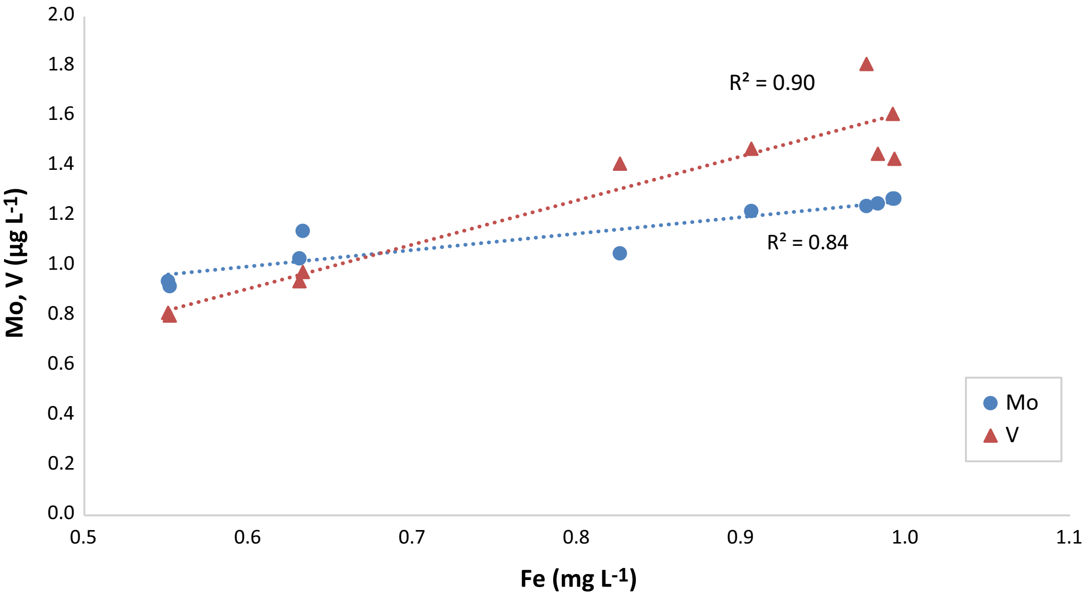

Figure 3-25. *Mo, V and Fe concentrations in Frisksjön, Simpevarp.*

In comparison with Fe and V, the Mo concentration was relatively stable in Frisksjön, ranging from 0.92–1.3 µg L^{-1}. These concentrations fall well within the range observed in near-surface groundwater in Simpevarp (Figure 3-16). If there is ferrihydrite or some other Fe(III) phase present in the lake water, it would be reasonable to expect V to be more affected than Mo, since V binds stronger to the precipitates (Gustafsson 2019). As discussed above, Mo would, however, be more strongly affected by the presence of high sulfide concentrations than by Fe precipitates. Sulfide was not at all measured in the lakes in Forsmark, but in Frisksjön four of the samples were. The sulfide concentration ranged from 0.004–0.011 mg L^{-1}. These were the same samples that were analysed for Fe(II) so they represent summer conditions at 0–1 m and 1.5–2.5 m, respectively. In both cases the sulfide concentration was 0.003 mg L^{-1} higher in the deeper sample, which could indicated more reducing conditions closer to the bottom, but sulfide never constituted more than 0.27 % of the total inorganic S in the lake. Compared to, for example, the near-surface groundwater, where low Mo concentrations could be observed, the sulfide concentration in the lake water of Frisksjön is low so there are no clear signs of removal of Mo related to sulfide (e.g. Figure 3-15). Things could, however, be different in the sediments or closer to the water-sediment interface. Sediments from Frisksjön are discussed in Section 3.2.5.

Another relationship that deserves to be mentioned is the comparatively strong correlation between Mo and POC, particulate organic C, in Bolundsfjärden (Figure 3-26). Excluding one outlier with anomalously high POC concentration (1.52 mg L^{-1}), the correlation was $r=0.89$ ($p > 0.01$). Other related parameters also correlated well to the Mo concentration, e.g. chlorophyll A ($r=0.77$, $p < 0.01$) and particulate N and P ($r=0.87$, $p < 0.01$; $p=0.80$, $p < 0.01$, respectively). POC is only a minor fraction of the organic carbon present in the lake water, typically < 1 mg POC L^{-1} as compared to ca. 17 mg DOC L^{-1} in Bolundsfjärden, but it comprises various types of organic particles, including phytoplankton, which could explain the connection to chlorophyll A. It is not clear, however, how the POC could cause higher Mo concentrations in the lake water. As Mo is a micronutrient, increased biomass in the lake water should, if anything, decrease the concentration of dissolved Mo. Such effects of biomass growth on the Mo concentration have been observed, for example, in the pelagic environments in the German Bight (Kowalski et al. 2013). Based on the Mo isotope fractionation it was hypothesised that Mo was scavenged by algae-derived organic matter in the water column during the early summer. Since no similar relationships could be found in any of the other lakes in Forsmark, the most likely explanation is probably that the strong seasonal variation of Mo concentrations in Bolundsfjärden coincides with the increase in phytoplankton and other types of POC during the growing period.

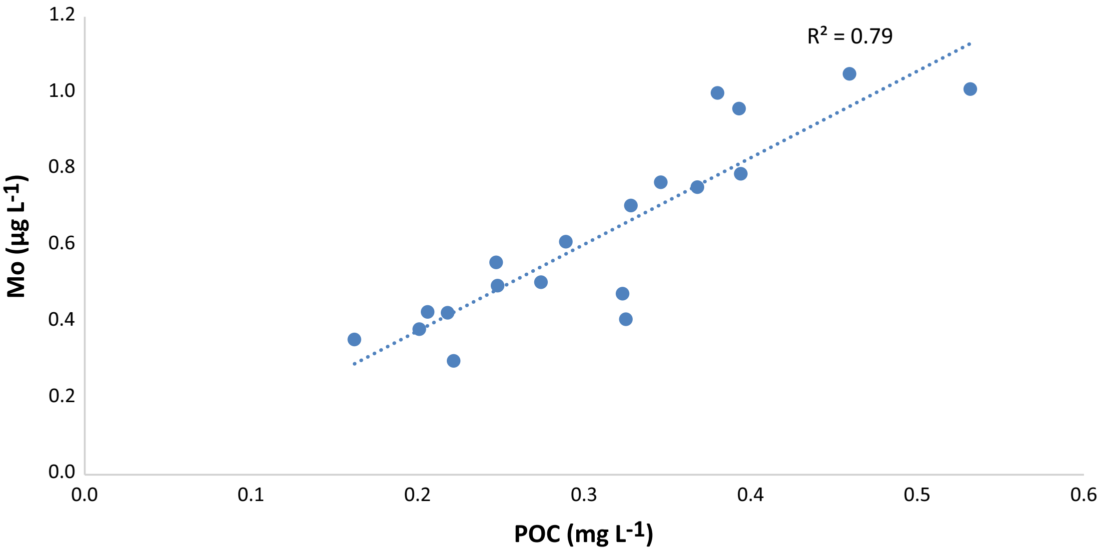

Figure 3-26. *Mo concentration in Bolundsfjärden, Forsmark, as a function of POC. One observation with an uncommonly high POC concentration (1.5 mg L^{-1}) is not shown in the graph, nor included in the regression.*

Molybdenum in suspended matter

In the investigation of suspended material from the lakes and the sea in the Forsmark area Mo concentrations between 0.65 µg g^{-1} at Forslingens grund (marine) and 11 µg g^{-1} in Bolundsfjärden were observed (Bradshaw and Kumblad 2008). The Mo concentration was consistently higher in freshwater environments than in the sea, and the concentration in the lakes also exceeded the concentrations observed in the local till. The number of samples was low, but samples with high Mo concentrations also seemed to have high S concentrations, up to 2.0 % in Bolundsfjärden. By comparing the concentrations in the suspended matter to the concentrations in the filtered water apparent Kd values for the suspended material can be determined. Figure 3-27 shows these Kd values for Frisksjön in Simpevarp; Labboträsket, Bolundsfjärden and Eckarfjärden in Forsmark; and Forslingens grund in the sea outside Forsmark.

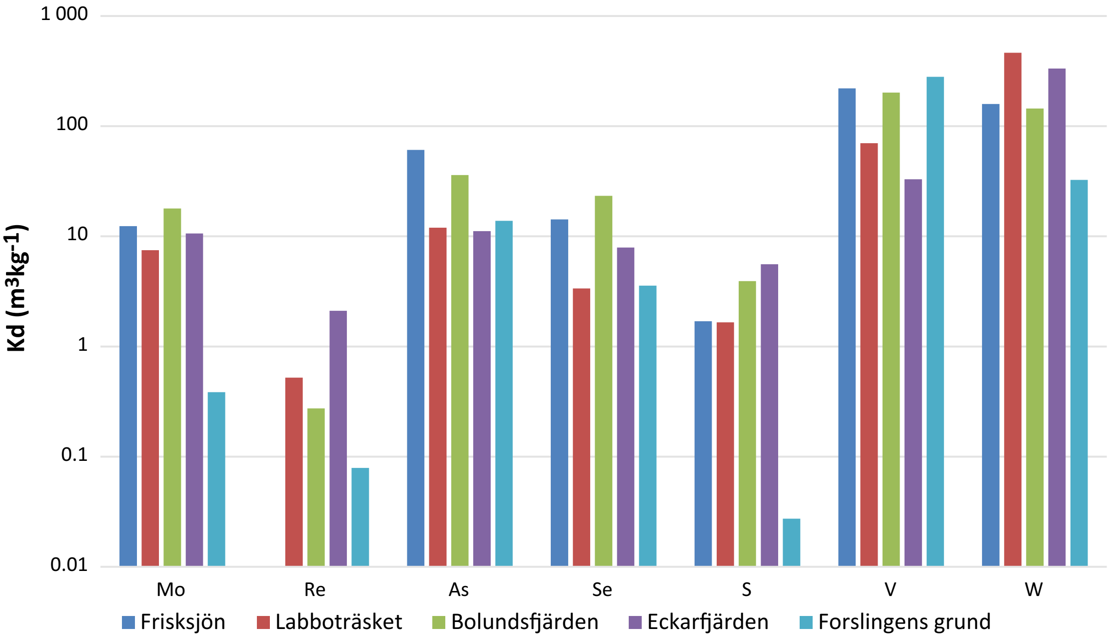

Figure 3-27. *Ratios between concentrations in suspended matter and water (i.e. Kd value) for the lakes Friskjön (Simpvarp), Labboträsket, Bolundsfjärden and Eckarfjärden (all in Forsmark) and the marine site Forslingens grund (Forsmark) for Mo and some other at least occasionally anionic elements. Data from Kumbland and Bradshaw (2008).*

The apparent Kd values for Mo were close to 10 m^3 kg^{-1} except in the sea water, where it was considerably lower. These Kd values were comparable to the site-specific Kd measurements that were conducted in the Forsmark area, although there were large differences between different soil types (see Figure 3-37). The most relevant comparison for the suspended material is probably clay gyttja, which the soil type these particles most likely eventually would form once they settle on the lake bottom. The Kd values for clay gyttja tended to be up to ca. one order of magnitude higher for the clay gyttja than for the suspended matter. Although the measurements are not entirely comparable, there appears to be a general agreement, both in terms of solid phase concentrations and Kd values (Figure 3-6 Figure 3-37). Higher Kd values for the actual sediments could indicate that there is an accumulation of Mo directly from the lake water to the sediments, but the relatively high Mo concentrations in the suspended matter in, for instance, Bolundsfjärden suggests that the material that is added to the sediments already may contain appreciable amounts of Mo.

When comparing Mo to other elements that also can occur as oxyanions – Re (perrhenate), As (arsenate), Se (selenite and selenite), S (sulfate), V (vanadate) and W (tungstate) – Mo is approximately on the same level as As and Se. As expected Re – and to some extent S – appear to be more mobile, while above all V and W appear to be more reactive. These patterns are consistent with the notion that Mo is relatively mobile in surface water. Based on thermodynamic modelling of groundwater and surface water in the site investigation areas the speciation of Mo is believed to be dominated by molybdate and its complexes with Mg and Ca, as exemplified by lake water from Labboträsket (Forsmark) in Figure 3-28.

The predominance of molybdate appears to be valid for all types of waters sampled in the Forsmark area (Figure 3-29). It also appears to increase slightly at higher pH, while the influence of complexes with Ca decreases. The prevalence of mobile Mo species is consistent with dialysis measurements of Mo in some “excessively limed” lakes in Sweden (Sjöstedt et al. 2009). The pH of these lakes was in the range 7.1–7.7, i.e. generally lower than in lakes in Forsmark, but the mobility of Mo should generally be expected to increase with pH. In some of the bottom waters some Mo could, however, be found in the > 1 kDa fraction, i.e. the colloidal fraction. Based on thermodynamic modelling this Mo was believed to be bound to ferrihydrite, which possibly also is important for controlling the Mo concentrations above all in Frisksjön (Figure 3-25).

3.2.5 Mo in sediments and peat

Molybdenum is expected to remain relatively mobile as long as it is present as molybdate, but, as outlined above, its mobility is expected to decrease considerably if it is reduced or at least exposed to high sulfide concentrations. It is well-establish that reduction of molybdate can cause significant accumulation of Mo in both marine and freshwater sediments (e.g. Dahl et al. 2010, Helz et al. 2011, Chappaz et al. 2014).

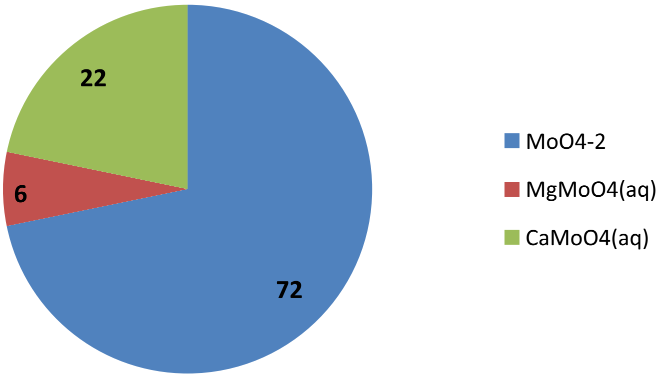

Figure 3-28. *Example of modelled Mo speciation in Labboträsket (June 11th 2005) using Visual MINTEQ. The speciation does not appear to vary appreciably throughout the year.*

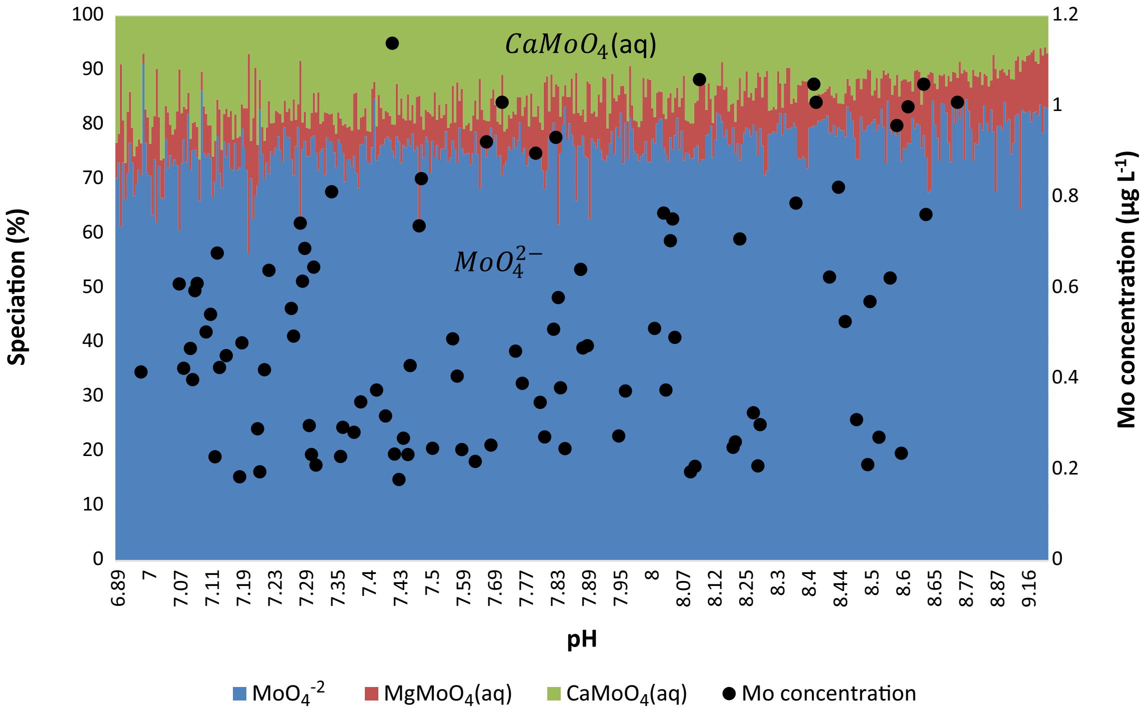

Figure 3-29. *Modelled Mo speciation for all water samples from Forsmark arranged in order of increasing pH. For samples where trace elements were not analysed the Mo speciation was calculated assuming typical Mo concentrations for the Forsmark area.*

Figure 3-30 shows the concentrations of Mo, U, S and Ti in a sediment core from Stocksjön in Forsmark. Stocksjön is a small, largely terrestrialised lake (0.036 km^2) located downstream of Eckarfjärden. The sediment profile is not complete for Mo, but the uppermost sediment samples with detectable Mo concentrations (0.1–0.25 m) were in the range 3.9–8.0 µg g^{-1}, which already is well above what has been observed in the local till (Figure 3-2). The Mo concentration increases further down in the sediments, reaching a maximum of 76 µg g^{-1} at 0.4–0.45 m. This is the highest Mo concentration that has been observed in the solid phase in the Forsmark area. The high Mo concentrations coincided with high concentrations of S (up to 3.5 %), which suggests that there has been an accumulation of sulfide in the sediments. The peak also coincides with high concentrations of U (up to 93 µg g^{-1}). Uranium normally occurs as U(VI) in surface water, where it forms the oxycation uranyl UO$_2^{2+}$), but similar to Mo U can be reduced, for example in organic sediments, to immobile U(IV). Therefore, the accumulation of U also supports that the high concentrations of Mo and S are related to the reducing conditions in these organic sediments. These three elements also showed large similarities in the PCA that was made for the Stocksjön sediments (Figure 2-32), largely aligning with PC2, so the accumulation of certain elements in reducing environments clearly represents an important process for understanding the fractionation between different elements in these sediments. Figure 3-30 also shows the Ti concentration in the sediment core, which can be used as a proxy for the mineral content of the sediments. Evidently, the peak in Mo, S and U is not associated with a corresponding peak for Ti, which indicates that these elements most likely are not present in the form of primary minerals from the catchment of Stocksjön. The Mo/Ti in the sediment core were ca. 100 times higher than in the local till, which indicates that there has been a substantial accumulation of Mo from the sea water or sediment pore water.

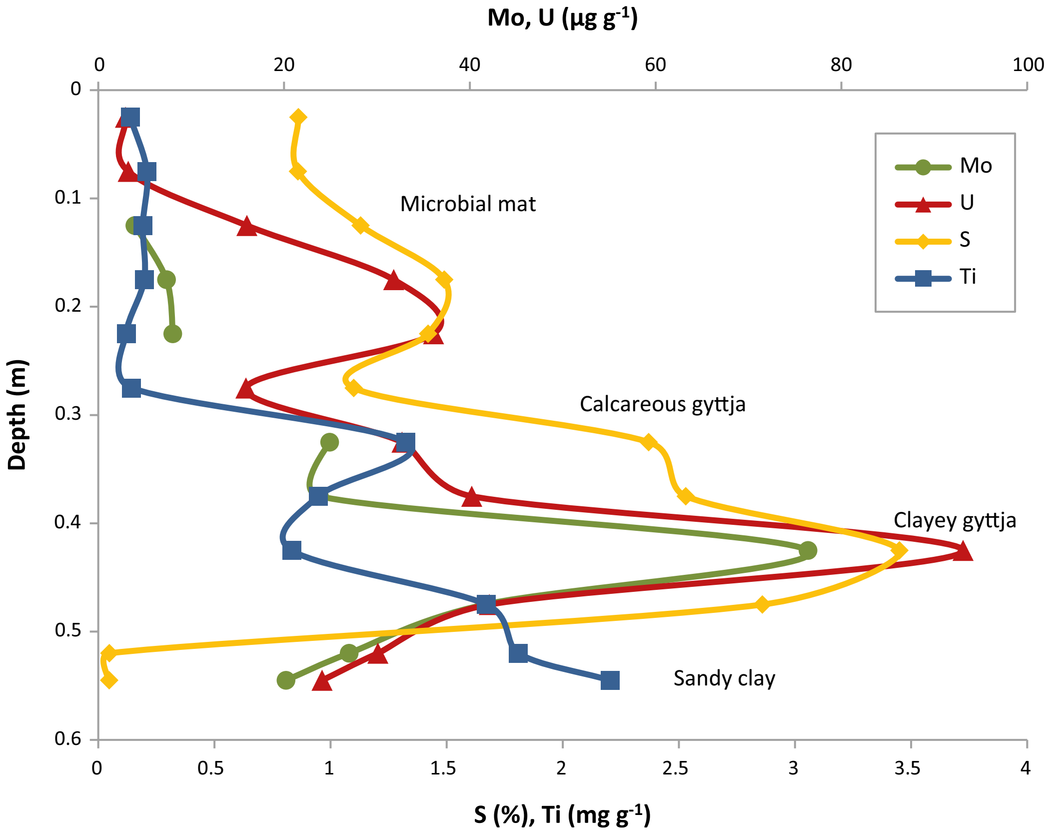

Figure 3-30. *Concentrations of Mo, U, S and Ti in sediments from Stocksjön, Forsmark. For reference, the median Mo concentration in local till is 0.53 µg g^{-1}.*

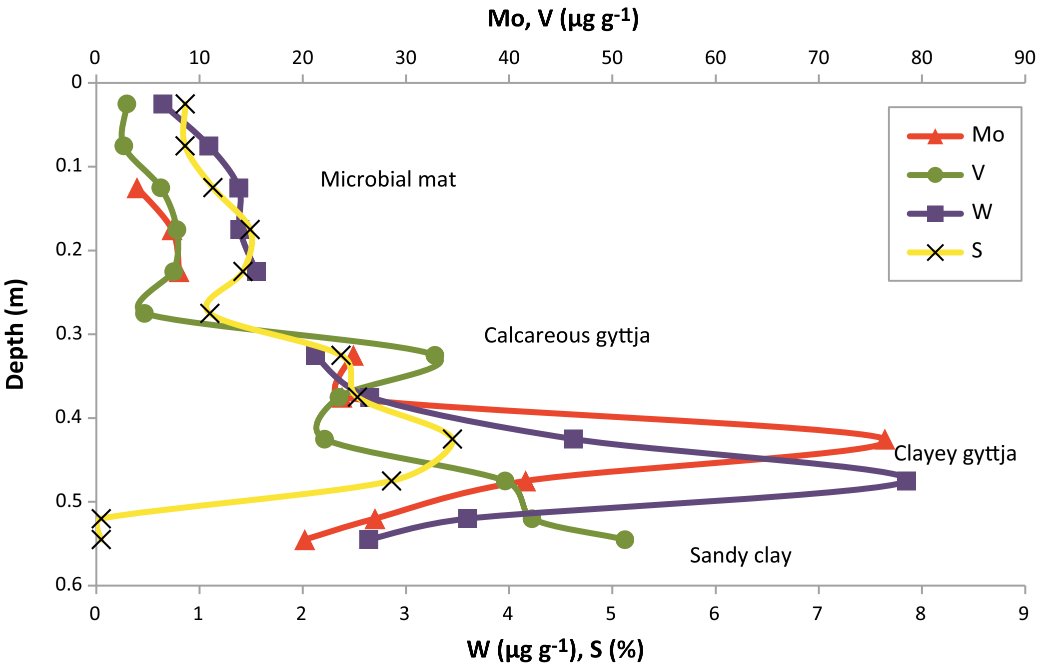

Figure 3-31. *Concentrations of Mo, V, W and S in sediments from Stocksjön, Forsmark.*

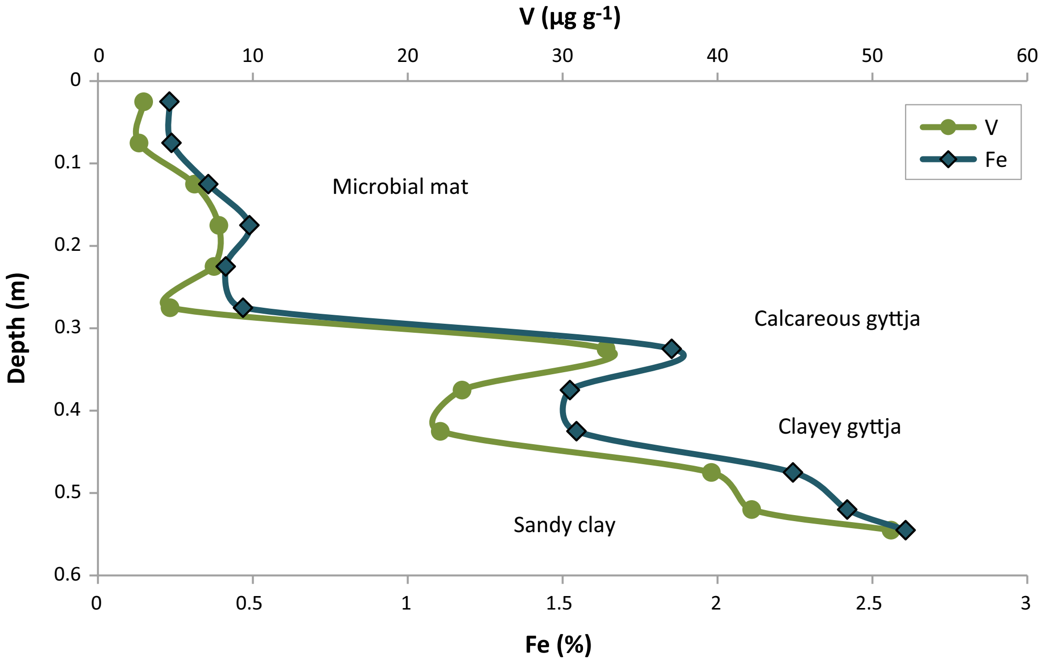

Figure 3-32. *Concentrations of V and Fe in sediments from Stocksjön, Forsmark.*

Further comparisons can be made to V and W, which have been discussed previously. Tungsten does display a distinct peak in the sediment core, but unlike Mo and S the W peak occurs deeper (45–50 cm). It has been suggested that formation of thiotungstate, i.e. when one (or more) O in tungstate is replaced by sulfide (WO_3S^{2-}), could be important in sulfidic water (Johannesson et al. 2013, Mohajerin et al. 2014). This could possibly explain the peak in W, since the S concentration is high also at this depth. Formation of thiotungstates is not believed to occur as easily as formation of thiomolybdates, i.e. higher sulfide concentrations are required, but since tungstate is unlikely to be reduced in the lake or in the sediment pore water and still accumulates in high concentrations in the sediments, it suggests that reduction of molybdate may not be required to build up high Mo concentrations in the sediments (Erickson and Helz 2000, Mohajerin et al. 2014). Instead, formation of thiomolybdates could be enough – or at least the first step – in the sorption of Mo in these sediments.

Vanadium, however, which exhibited some similarities to Mo in the lake water (Figure 3-23), appears to follow a rather different trend in the sediments. As shown in Figure 3-32, this trend closely resembles that of Fe, which is consistent with the high affinity of V for Fe precipitates (Gustafsson 2019).

Although the Mo concentration in the sediments from Stocksjön were the highest that have been observed (so far) in the Forsmark area, it is not unique to find high Mo concentrations in this type of soils. For example, concentrations up to 7.4 µg g^{-1} were found in clay gyttja from the Kd analyses (Figure 3-6). High Mo concentrations have also been encountered at certain depths in sediment cores from other sites in the Forsmark area, e.g. 14 µg g^{-1} in gyttja from a wetland near Bolundsfjärden (PFM006023) and up to 18 µg g^{-1} in marine sediments outside Forsmark (PFM002560) (Hannu and Karlsson 2006). In a sediment core from Eckarfjärden gyttja sediments with Mo concentrations up to 8.0 µg g^{-1} were found (Figure 3-33). Although this is nearly an order of magnitude lower than the highest Mo concentration observed in Stocksjön, it still represents a high Mo concentration in relation to the local till (Figure 3-2). The Mo concentration in the most recent sediments (0–0.3 m) were in the range 2.7–6.5 µg g^{-1}, which is not far from the Mo concentration in suspended material from Eckarfjärden observed by Engdahl et al. (2008), 2.7 $µg^{-1}$. This suggests that an appreciable sorption of Mo can occur already in the water column. In this case the samples were collected in the beginning of April near the bottom of the lake (2 m) so it is uncertain to what extent the water had been mixed and oxygenised after the winter. Unfortunately, no sulfide concentrations are available from the lakes in Forsmark. Nevertheless, as in Stocksjön, Mo in the sediments of Eckarfjärden displayed a trend that clearly resembled that of S, once again emphasising the importance of reducing condition for the accumulation of high concentrations of Mo (Figure 3-33). Tungsten, however, did not follow the same trend, varying within a relatively narrow interval of 1.1–2.6 µg g^{-1}. Although the Mo concentrations in the sediments of Eckarfjärden and Stocksjön, respectively, in largely are on the same level, it can be speculated why the accumulation in Stocksjön during certain periods has been more intense than in Eckarfjärden. There may several explanations to this, but one obvious difference is that that represent different stages in the evolution of a lake. Large portions of Stocksjön are now covered by peat so the transport of particles to the open water surface is limited. This can, for example, be seen in the lower Ti concentrations in the sediments from Stocksjön. As consequence, the sediments will become more organic and the concentration of the elements that are accumulated in these sediments will not be “diluted” as much by sedimentation of mineral particles from the catchment. The fact that W has not accumulated to the same extent in Eckarfjärden also indicates that the sulfide concentrations may have been lower there, since there are not as obvious signs of formation of thiotungstates. This could possibly be related to the difference in size between the lakes, which favours mixing and oxygenation of the lake water in the larger Eckarfjärden, or other mechanisms related to biological and/or chemical processes in these lakes. Investigations in an American lake has demonstrated that one limiting factor for the rate of the sulfate reduction in sediments can be the access to sulfate so it also matters where the reduction takes place, e.g. in the water column or deeper down in the sediments (Urban et al. 1994).

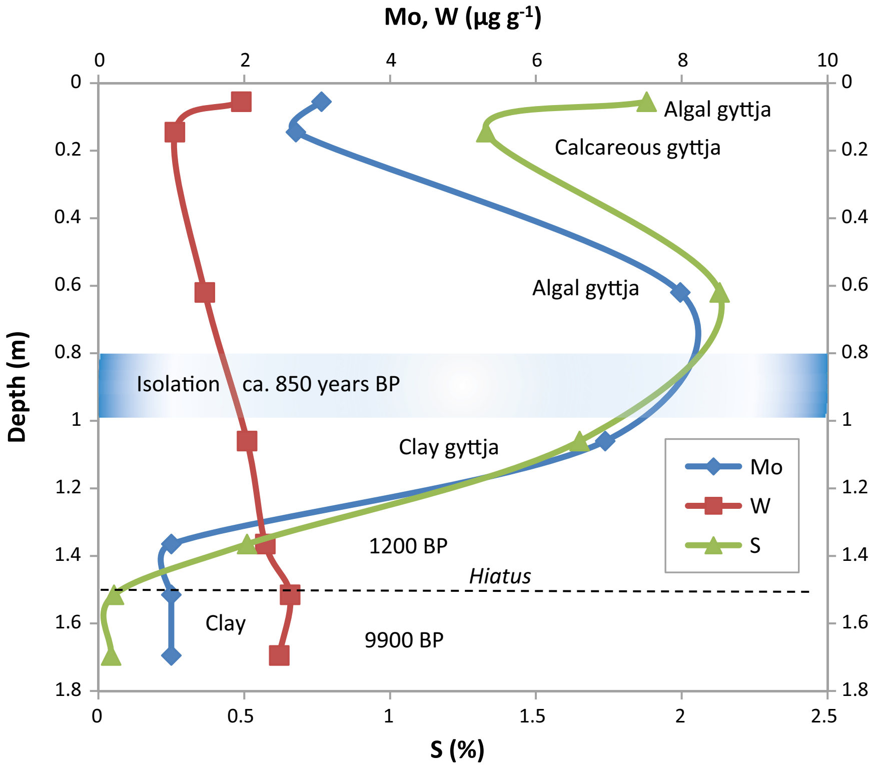

Figure 3-33. *Mo, W and S in a sediment core from Eckarfjärden, Forsmark. The approximate period of isolation from the Baltic Sea ca. 850 years BP is indicated by the blue area. Sediment ages were taken from Hedenström and Risberg (2003). The dashed line represents a nearly 9 000 year long hiatus in the sediment record.*

Molybdenum in sediments from Frisksjön, Simpevarp

In the Simpevarp area a 4.4 m deep sediment core from Frisksjön was analysed (Figure 3-34). In seven of the twelve sediment samples Mo was below the (relatively high) detection limit of 6 µg g^{-1}, but in the samples where Mo could be quantified the concentrations were significantly higher than the maximum of 2 µg g^{-1} observed in the local till. There was a distinct peak at 0.25–0.28 m with a maximum Mo concentration of 24 µg g^{-1}. This coincided with a peak for S as well, reaching a maximum of 4.1 %. Hence, it seems likely that the accumulation of Mo also in this case would be related to sulfide and reducing conditions. Apart from this peak, however, the Mo concentration in the sediments appear to have declined after the isolation of the lake. In suspended matter from Frisksjön (collected at 3 m depth in mid-April 2008) the Mo concentration was 11 µg g^{-1} (Engdahl et al. 2008). In the light of this it is a bit peculiar that the Mo concentration in the surface sediments would be so lower (< 6 µg g^{-1}) than in the suspended matter. Enrichment of Mo is often used as an indicator for the presence of sulfide near the sediment-water interface (Sulu-Gambari et al. 2017). In this case the S concentration at the sediment surface was 1.9 %, which was more than twice as much as was found in the suspended matter, 0.91 %, suggesting that there indeed could be reduction of sulfate close to the sediment surface. One explanation could be that the suspended Mo is associated with some type of particle that does not reach the sediments. An obvious candidate would be Fe, e.g. in the form of ferrihydrite, which according to the same measurements make up nearly 12 % of the suspended matter in Frisksjön. Ferrihydrite would be expected to dissolve as soon as Fe(III) is reduced, which would explain why the Fe concentration in the surface sediments is substantially lower, ca. 3 %. As shown in Figure 3-25, Mo was correlated to Fe in the lake water so if molybdate is sorbed onto these Fe particles that could explain that pattern. A similar but stronger relationship was also observed between V and Fe in Frisksjön. It can therefore be noted that the V concentration in the suspended matter was 200 µg L^{-1}, which was considerably higher than the 43 µg g^{-1} that was found in the surface sediments. Hence, this interpretation is also consistent with the behaviour of V in the lake water and in the sediments. Tungsten was, however, below the reporting limit (< 60 µg g^{-1}) in all sediment samples from Frisksjön.

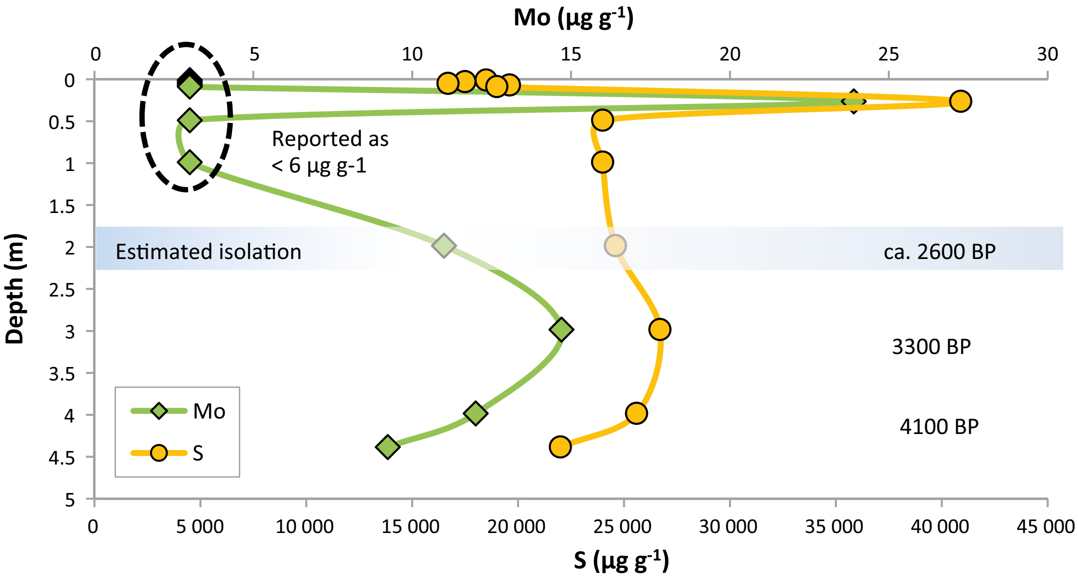

Figure 3-34. *Mo and S in sediments from Frisksjön, Simpevarp. Mo was reported as < 6 µg g^{-1} in the majority of the samples. These observations are plotted as half of the reporting limit (3 µg g^{-1}) in the graph to illustrate the approximate Mo profile in the core.*

Concerning the accumulation of S and the apparently associated accumulation of Mo in the sediments in both Forsmark and Simpevarp it should pointed out that from a national perspective the S concentrations in the investigated sediments appear comparatively high. In a survey of surface (0–1 cm) and deep (ca. 25–35 cm) sediments from 111 lakes across Sweden only 12 % of the surface sediments had S concentration > 0.8 % (Bindler et al. 2008). Similarly, only 15 % of the deep sediments had S concentration > 0.9 %. The S concentration in the sediments was found to be correlated to the content of organic matter, but there was also a clear tendency that areas with high S deposition, mainly in southern Sweden, had higher S concentrations in the lake sediments. To what extent these lakes will continue to accumulate these relatively high amounts of Mo in the sediments is therefore dependent on how the lakes will evolve in the future.

Molybdenum in a peat core (Klarebäcksmossen, Simpevarp)

One not uncommon fate for lakes is that they eventually develop into wetlands. Such a site is represented by Klarebäcksmossen, a bog in the Simpevarp area. In the underlying inorganic clay (below ca. 4.5 m in the profile) the Mo concentration was below the reporting limit (< 2 µg $^{-1}$), but as the sediments became more organic (i.e. gyttja) Mo concentrations up to 7.4 µg g^{-1} were detected at a depth of ca. 4 m (Figure 3-35). Again, this is well above the Mo concentrations observed in the local till (Figure 3-4). The enrichment of Mo in the gyttja sediments coincided with high S concentrations (up to 1.6 %), similar to what has been observed in lake sediments in both the Forsmark and the Simpevarp areas (e.g. Figure 3-30 and Figure 3-34). Hence, accumulation of high concentrations of Mo appears to be related to sulfidic environments also at this site. As the gyttja gradually is followed by peat, marking the terrestrialisation of the site, both the Mo and the S concentrations decline. The reason is not that the conditions become less reducing – as witnessed by the continued accumulation of peat – but rather that the transport of Mo and S is limited by the surrounding peat. Neither Mo nor S can be expected to be particularly mobile under the reducing conditions that prevail in a wetland. The lowest concentrations of both elements – 0.020 µg g^{-1} Mo and 0.088 % S – were found at ca. 0.7 m. This depth reflects the bog stage, where the peat no longer receives any weathering products from the surrounding mineral soils. The concentrations increase in the upper decimetres of the peat core, which could be caused both by increased atmospheric deposition of Mo and S in modern times and biological uptake.

Contrary to Mo, the highest W concentrations were found in the deep layers of inorganic clay (Figure 3-35). A comparison with other soil samples from Simpevarp indicates that 2–3 µg g^{-1} is a normal concentration for W in local mineral soils so this is probably mainly W in primary minerals. As the sediments become increasingly organic, the W concentration decreases. There is a minor peak at 4.2 m, where the highest Mo and S concentrations are found, possibly due some formation of thiotungstates, but further up in the peat the W concentration remains low. The higher accumulation of Mo in the peat should therefore be interpreted as generally higher mobility of Mo in groundwater and more extensive accumulation of Mo in reducing environments. In the Krycklan catchment in northern Sweden the Mo concentrations were considerably higher in a stream draining a forest than in a streams draining a mire, which suggests that there is a substantial immobilisation of Mo in the peat (Bauer 2018). For W, however, the differences between the two streams were smaller, and temporarily the W concentration in the stream draining the mire was even higher than in the forest stream. This suggests that there is less accumulation of W in mires, which is consistent with the observations from Klarebäcksmossen (Figure 3-35). Consequently, one should expect a similar accumulation of Mo in wetlands in the site investigation areas, but due to the heterogeneity of the landscape it is hard to discern any clear influence from the wetlands on the Mo concentrations based on the existing data.

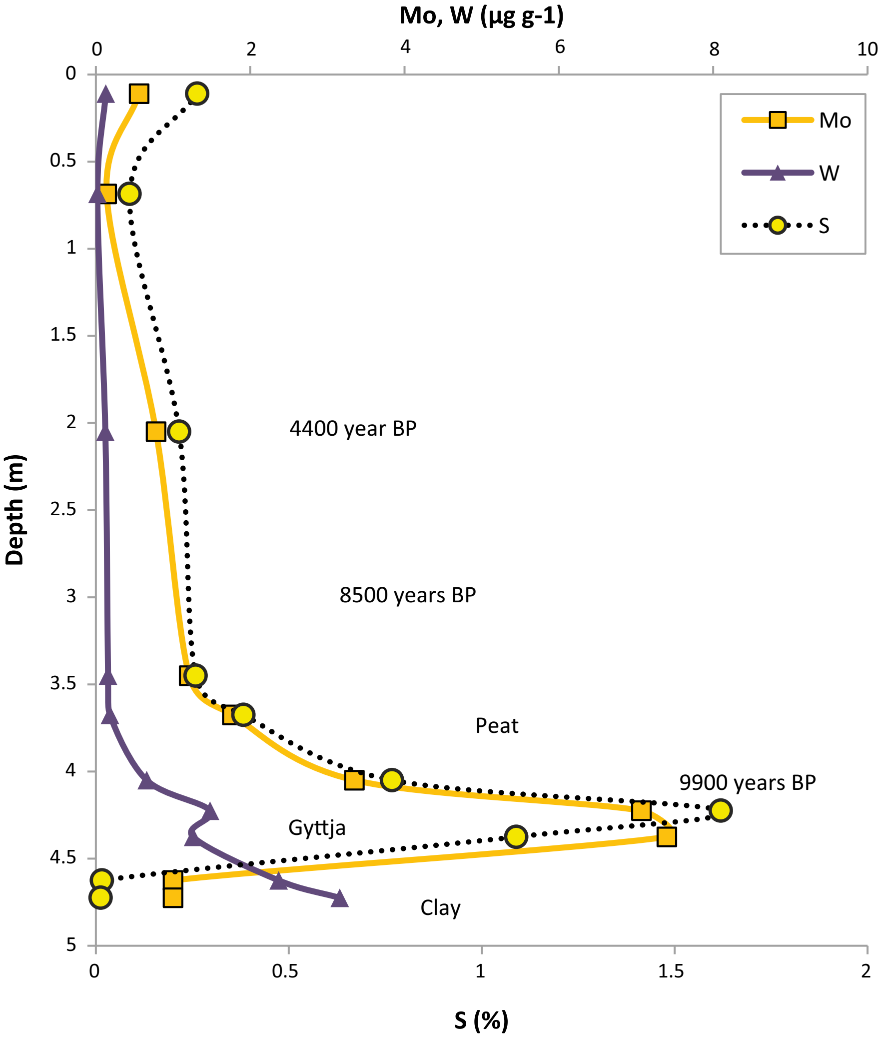

Figure 3-35. *Concentrations of Mo, W and S in a core from Klarebäcksmossen, a bog in the Simpevarp area. The dating was taken from Sternbeck et al. (2006)*

3.2.6 Kd values for Mo

As perviously mentioned, Mo was included in the site-specific Kd measurements reported by Sheppard et al. (2011). The Mo concentrations in different soil types from these measurements were shown in Figure 3-6, and the pore water concentrations after the incubations are shown in Figure 3-36 below.

The pore water concentrations after incubation were in the range 0.12–27 µg L^{-1}, which coincides well with the range observed in near-surface groundwater in Forsmark, 0.063–31 µg L^{-1}. The highest Mo concentrations in pore water after incubation were found in cultivated peat and glacial clay, while low Mo concentrations were found above all in wetland peat (Figure 3-36). It was noted in the protocols from the incubations that three out of a total of ten wetland samples smelled of H_2S, which is a clear sign of the presence of sulfide in at least these samples. Hence, the low Mo concentration in the pore water from the wetland peat (0.12–3.0 µg L^{-1}) seem to be related to the presence of sulfide. The low Mo concentrations in sulfide-rich water are consistent with the observations from Forsmark site investigation (Figure 3-12). Consequently, there are reasons to believe that the reducing conditions that typically prevail in wetlands are reflected in the Kd measurements. This is important particularly for redox-sensitive elements like Mo, where the large differences in mobility can be expected depending on its oxidation state. No comments concerning H_2S were made for the clay gyttja samples, but it was noted for four of the ten samples that the pore water was rich in humic material. Judging from the generally high accumulation of Mo in organic sediments (e.g. Figure 3-30), strongly reducing conditions should be expected also in the clay gyttja.

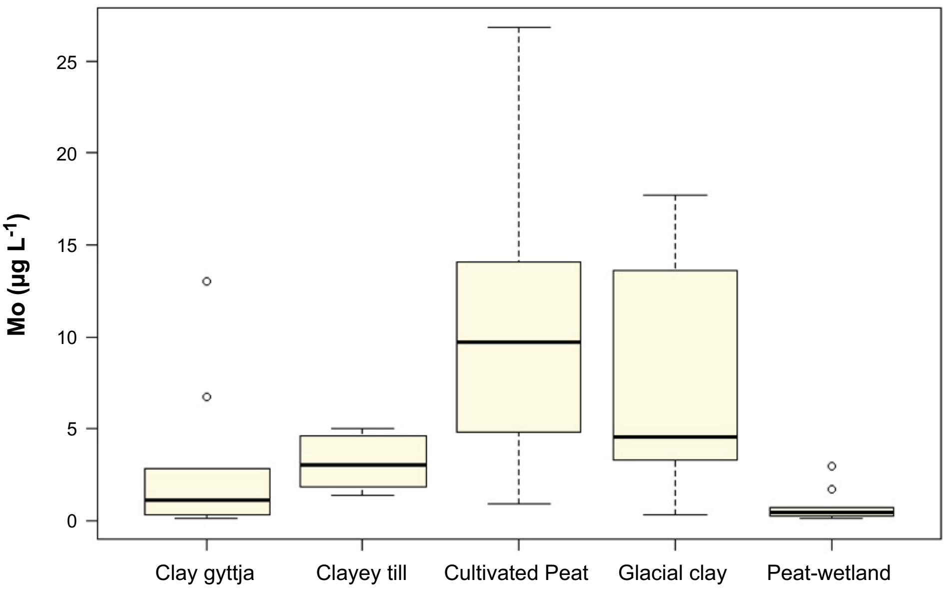

Figure 3-36. *Mo concentrations in pore water from incubated Kd samples from different soil types (n = 10 for each soil type). Data from Sheppard et al. (2011).*

The relatively large differences in Mo concentrations in both the solid and the aqueous phase between different soil types unavoidably resulted in large differences in the calculated Kd values (Figure 3-37). The general pattern was that Mo exhibited low Kd values in inorganic soils such as clay till and glacial clay, mostly in the range 0.06–0.26 m^3 kg^{-1}, while higher Kd values were found in more organic soils such as clay gyttja and peat (up to 26 m^3 kg^{-1}). For comparison, the median LOI was 91 % in wetland peat, 83 % in cultivated peat, 15 % in clay gyttja, 4.1 % in glacial clay and 4.0 % in clay till. The accumulation of organic matter is related to lower redox potential so these differences are consistent with the general understanding of the biogeochemistry of Mo and, in particular, the accumulation of Mo that has been observed in such environments in the site investigations (Section 3.2.5). The low Kd values in the till and glacial clay would support that Mo mainly is present as molybdate in these soils, while there is a preferential accumulation of Mo in more organic soils, i.e. in lake sediments and wetlands. The measured Kd values therefore seem to reflect the redox behaviour of Mo, which is central for predicting the fate of Mo in the surface environment.

The underlying reasons for the differences in the calculated Kd values can also be illustrated by plotting the Mo concentration in soils vs. the Mo concentration in the pore water (Figure 3-38). The diagonal lines show all combinations of concentrations that would lead to equal Kd values. Clay gyttja and wetland peat typically contained relatively high Mo concentrations in the solid phase, and the concentrations in the pore water were also relatively low, presumably because the solubility of Mo is suppressed by the reducing conditions. Hence, these soils tended to have high Kd values. Cultivated peat contained equally high Mo concentrations in the solid phase, but probably since Mo is more mobile under oxidising conditions, the Mo concentration in the pore water was considerably higher, thereby causing higher mobility for Mo and lower Kd values. In the more inorganic soil types, clayey till and glacial clay, the Mo concentrations were generally low in the solid phase, which in combination with high pore water concentrations led to low Kd values. Since the concentrations in both soils and pore water seem to agree well with other data from the site investigation in Forsmark, it seems likely that the Kd measurements at least qualitatively reflect the differences in mobility between the different oxidation states of Mo.

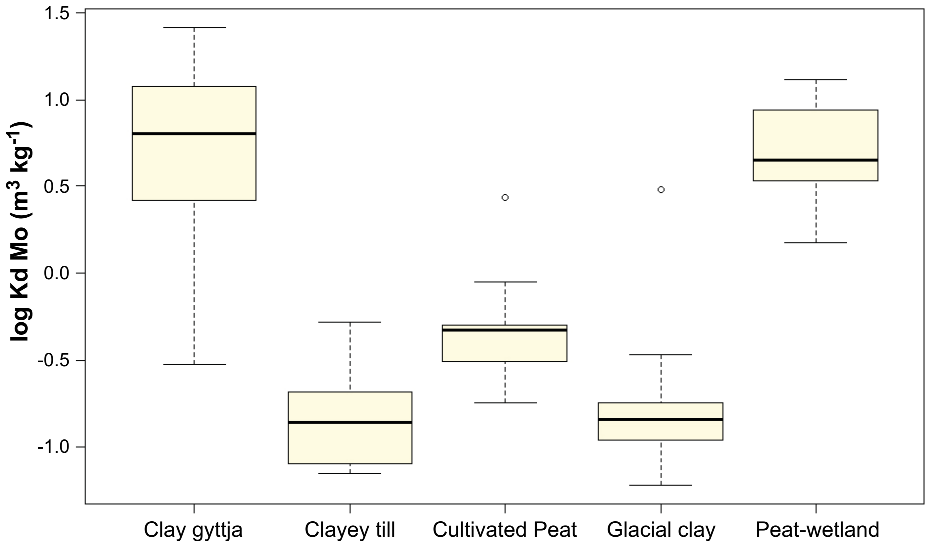

***Figure 3-37.** Kd values for Mo in different soil types in Forsmark (Sheppard et al. 2011). n = 10 for each soil type.*

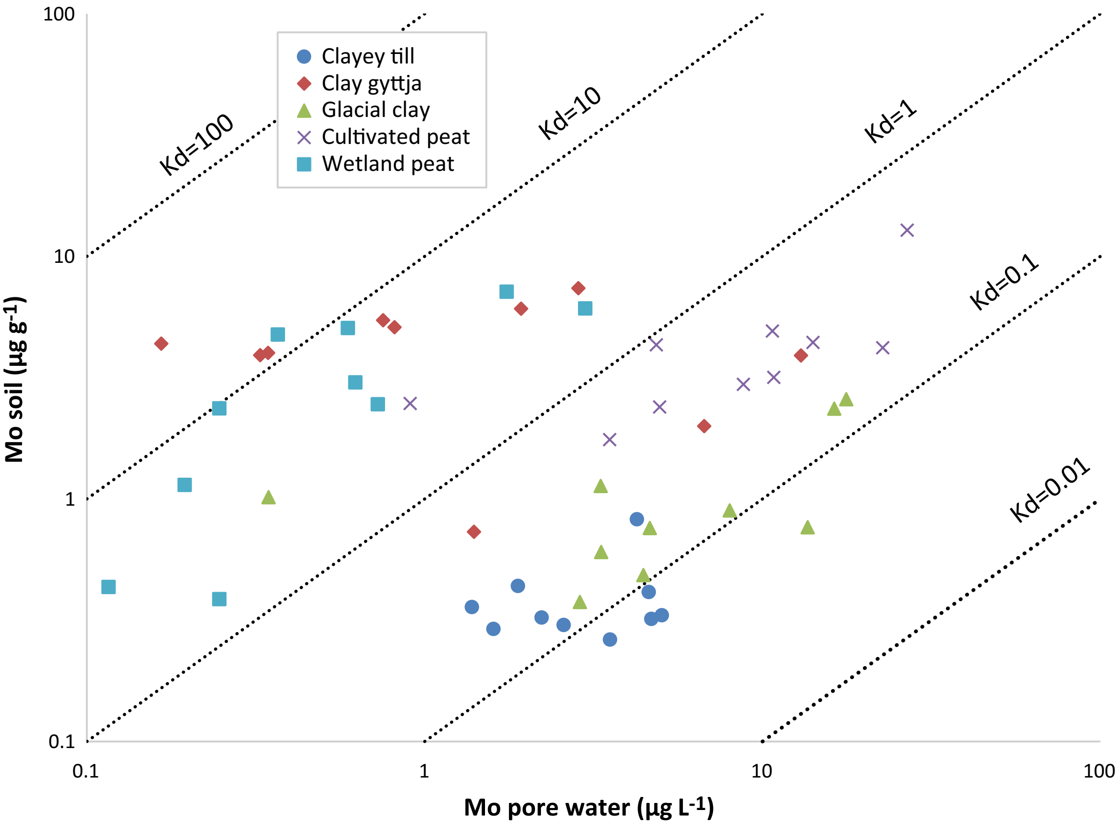

***Figure 3-38.** The soil and pore water concentrations that were used to calculate the Kd values for Mo in different soil types. High concentrations in the soil and low concentrations in the pore water cause high Kd values, while low concentrations in the soil and high concentrations in the pore water cause low Kd values. Data from Sheppard et al. (2011).*

It can be noted in Figure 3-38 that the observations tend to fall close to either the Kd = 10 isoline or the Kd = 0.1 isoline with relatively few observations close to the Kd = 1 isoline. As a result, when plotting the total distribution of Kd values for Mo in the Forsmark area, the distribution will have a conspicuously bimodal appearance, i.e. a distribution with two peaks (Figure 3-39). It is tempting to interpret this bimodality as a result of the redox-chemistry of Mo, especially since the high Kd values are associated primarily with reducing environments such as wetland peat and clay gyttja. The variation in the Kd values for Mo did not closely resemble that of any other analysed element in the Kd study of Sheppard et al. (2011), which indeed may be explained by its special redox properties. However, the bimodal tendency in the frequency distribution was not unique for Mo, and Sheppard et al. (2013) initially proposed that such tendencies could be related to differences in mobility between different oxidation states of an element. Figure 3-39 displays the frequency distributions for four redox-sensitive elements, where large differences in mobility for geochemical reasons could be expected between different oxidation states – Fe, Mn, Mo and Re. All these elements display clear bimodal tendencies, which can be compared to, for example, the unimodal distribution for Ni (Figure 2-46). It can further be noted that although the Kd distribution of Fe, for example, may resemble that of Mo, Fe and Mo do not exhibit high Kd values in the same type of soils. As shown in Figure 3-40, Fe has high Kd values primarily in clay till and glacial clay and low Kd values in clay gyttja, cultivated peat and wetland peat, which is almost the complete opposite of Mo (Figure 3-37).

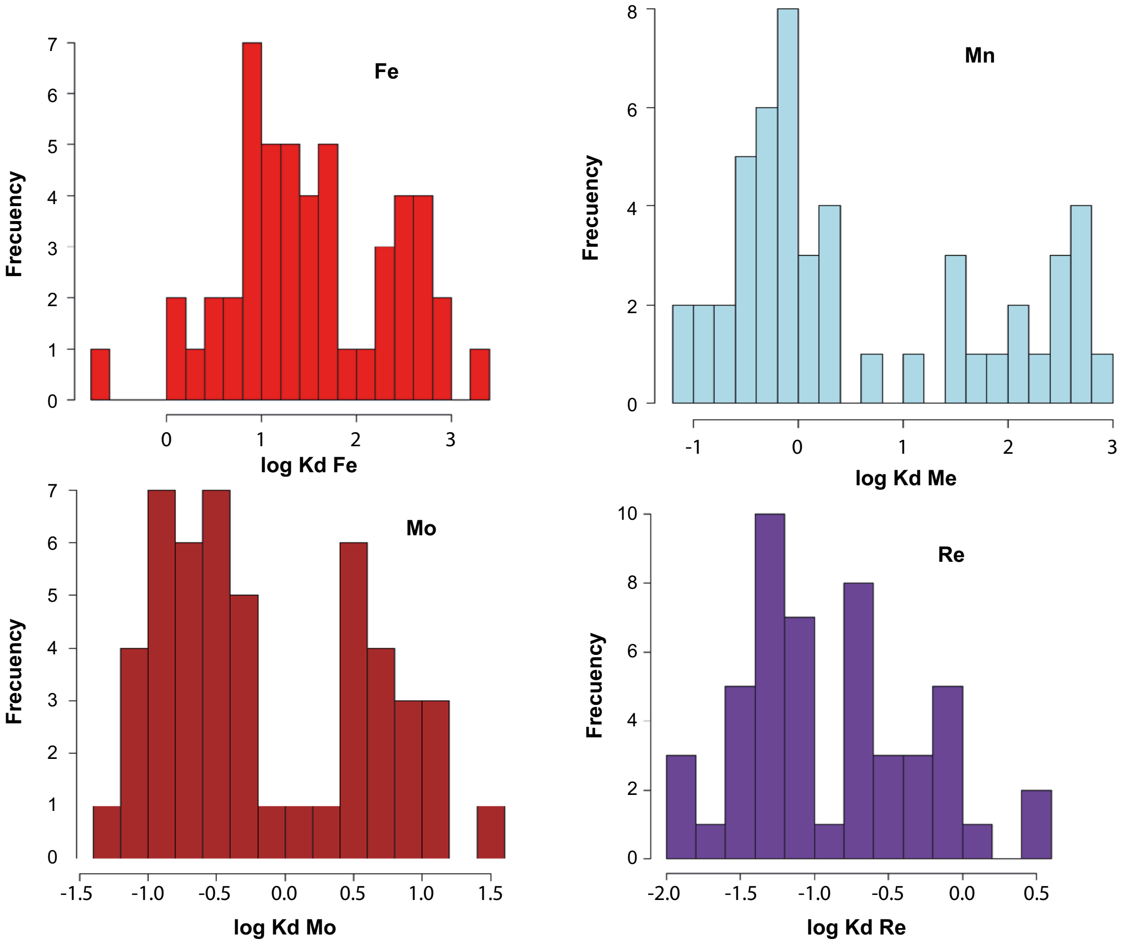

Figure 3-39. *Distributions of site-specific Kd values for Fe, Mn, Mo and Re from the Forsmark area (data from Sheppard et al. 2011). All four elements are redox sensitive and are expected to display large differences in mobility between reduced and oxidised forms, which could be reflected in the bimodal tendencies in the distributions. The distributions can be compared to the unimodal distribution of Ni, which is not redox sensitive (Figure 2-44).*

Geochemically Fe is expected to be more mobile in its reduced form so from that perspective it makes sense that Fe would have lower Kd in reducing environments such as organic sediments and wetlands. The groundwater samples, which mainly were collected from till, showed that although Fe mostly is present as Fe(II), a substantial fraction of Fe(III) can be found especially in recharge areas (Figure 2-11). It is possible that the till for the Kd analyses were collected from such sites, but it is also possible that Fe was oxidised and immobilised in connection with the measurements in the more inorganic soil types. Similar to Fe, Mn is also more mobile in its reducing form so it seems consistent that Mn would have low Kd values in the same environments as Fe. The main difference is that Mn is reduced at higher Eh than Fe. Hence, there is no trend that certain soil types display high Kd values and others low for all elements. Instead, the apparent similarities in the Kd distributions of Fe, Mn, Mo and Re reflect the fact that they behave differently and partly even oppositely in different soil types.

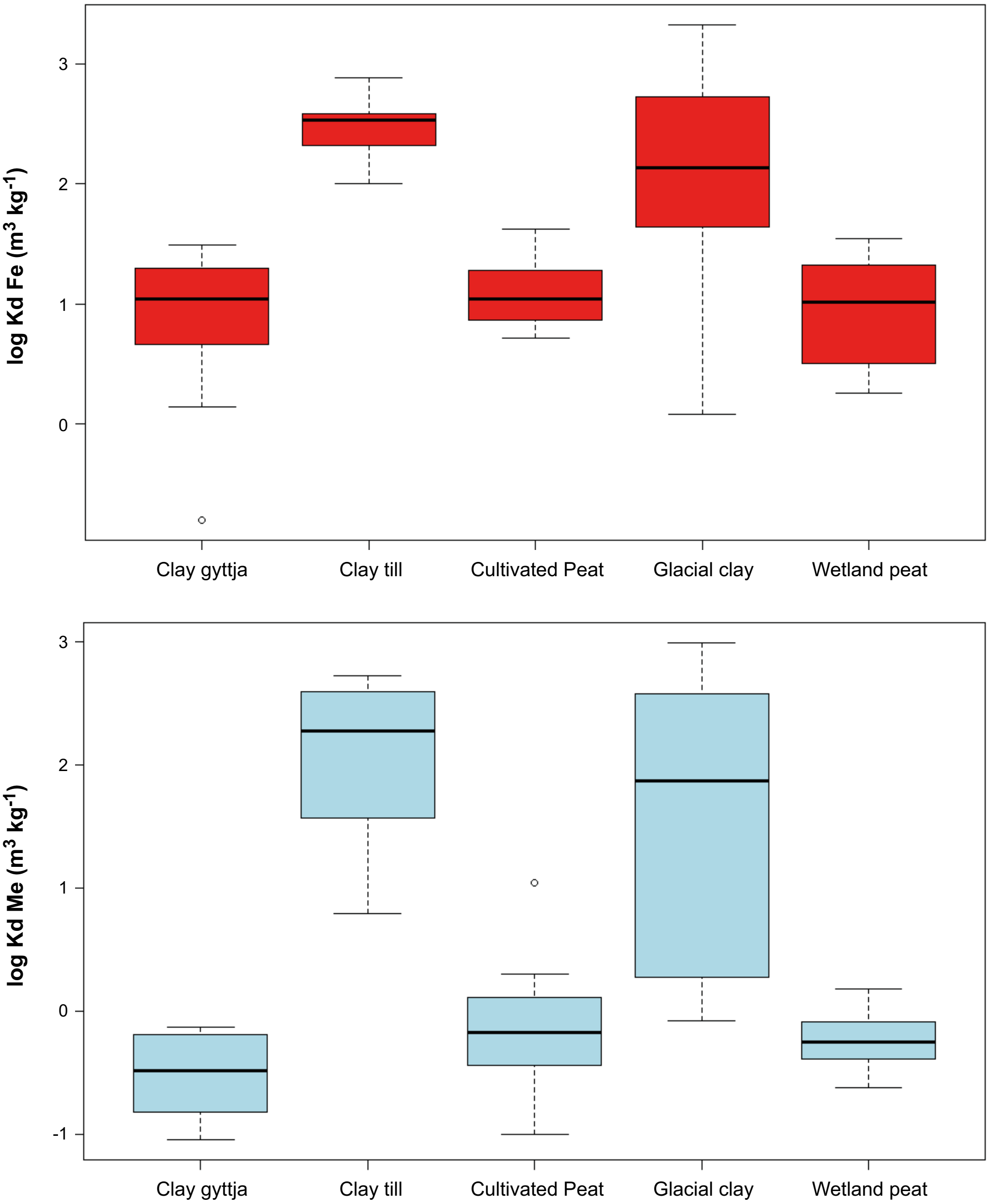

Figure 3-40. *Kd values for Fe (upper panel) and Mn (lower panel) in different soil types in Forsmark. Data from Sheppard et al. (2011).*

3.2.7 Mo in biota

The available data for Mo in biota from the site investigations is compiled in Figure 3-41. The Mo concentrations span a wide interval, from < 0.01 µg g^{-1} DW in muscle tissue from a ruffe (*Gymnocephalus cernuus*) caught in Forsmark to 18 µg g^{-1} DW in marine microphytobenthos sampled in the Forsmark area. The latter sample is described as an 'algal mat', sampled at a depth of ca. 2 m outside Tixlan (Kumblad and Bradshaw 2008). This is the same term as was used from the upper layers of the sediment core from Stocksjön, which also contained high Mo concentrations (Figure 3-30). In that case the accumulation of Mo was most likely caused by the reducing conditions in the organic sediments, resulting in sulfate reduction and most likely also reduction of U and Mo. Hence, it is not obvious that the high Mo concentrations in this algal mat really represents biological uptake. Kumbland and Bradshaw (2008) also discuss the possibilities of contamination in more details.

In addition to the above-mentioned marine microphytobenthos, high Mo concentrations were also observed, for instance, in tree roots (up to 5.7 µg g^{-1} DW) and roots of waterlilies (*Nymphaeaceae sp.*; 4.6 µg g^{-1}). As was noted for Ni, many of these samples are characterised by high concentrations of poorly soluble metals with no known biological function, e.g. Ti, Zr and Al, which makes it likely that there could have been some sort of minerogenic material present in the samples. The risk for unintentional inclusion of such material is obviously higher when collecting biological samples from mineral soils and minerogenic sediments than when sampling, for instance, above-ground parts. Given the high density of mineral particles relative to biota and their relatively high concentrations of certain elements even minor inclusions of mineral grains or accretions on the surface of the roots could contribute with significant amounts of elements that are not taken up by the root to any substantial degree. While this certainly calls for caution when interpreting the data, it does not necessarily imply that the results need to be discarded. As exemplified by the *Nymphaeaceae sp.* roots from Forsmark (Figure 2-53), the elemental composition of some samples is not too different from the composition of the local till. While this at some level obviously reflects the general abundance of various elements in nature, certain elements were clearly more abundant in biota than in the local till, and these elements included important nutrients such as N, P, K, B and – as indicated by the red square in Figure 2-53 – Mo. Hence, this would suggest that there is an active accumulation of Mo in these roots.

In animals from terrestrial, marine and freshwater environments the highest Mo concentrations were observed in mussels (*Anodonta sp.*), reaching a maximum of 1.34 µg g^{-1} (classified as benthos in Figure 3-41; Hannu and Karlsson 2006). In this case the samples were not characterised by suspiciously high concentrations of elements like Ti and Zr, which makes it more likely that the high Mo concentrations actually reflect some sort of biological uptake. The mussel samples with high Mo concentrations were also the muscles rather than the shells. Given the relatively high Mo concentrations of Mo in sea water and also in the lake water of the Forsmark area plus the habit of mussels to sift large amounts of water does not seem unlikely that they might accumulate considerably higher Mo concentrations than, for example, fish.

As indicated by the assemblages of observations at certain concentrations in Figure 3-41, there were also problems at the other side of the concentration spectrum, namely that certain samples had Mo concentration close to or below the reporting limits of the responsible laboratories. This is perhaps most conspicuous for the analyses of muscular tissue from fish (Figure 3-41). As a result, these numbers are associated with a substantial uncertainty. Yet, the situation is notably better than for Ni, where most of the fish samples fell below the reporting limits. Despite these uncertainties concerning the Mo concentrations in certain types of biota, it could be argued that the most important thing is to get the right order of magnitude for the Mo concentration in various types of biota. Hence, even if only one significant digit with substantial uncertainty is reported, that is valuable information and considerably more useful that values below the reporting limits. Regrettably, data for Mo is, however, missing entirely for mushrooms (Johansson et al. 2004).

The variation in Mo concentration was large also within different types of biota (Figure 3-41). For all classes, for which a fair selection of samples were analysed, the observed range tended to span approximately an order of magnitude or more. In this case some of the variation can probably be ascribed to slight differences in the sampling techniques (e.g. sampling fish muscles with or without bones, the time of year when the samples were collected etc.) as well as analytical techniques (e.g. total vs. partial extraction). As is apparent from the tree samples, for example, there can be significant

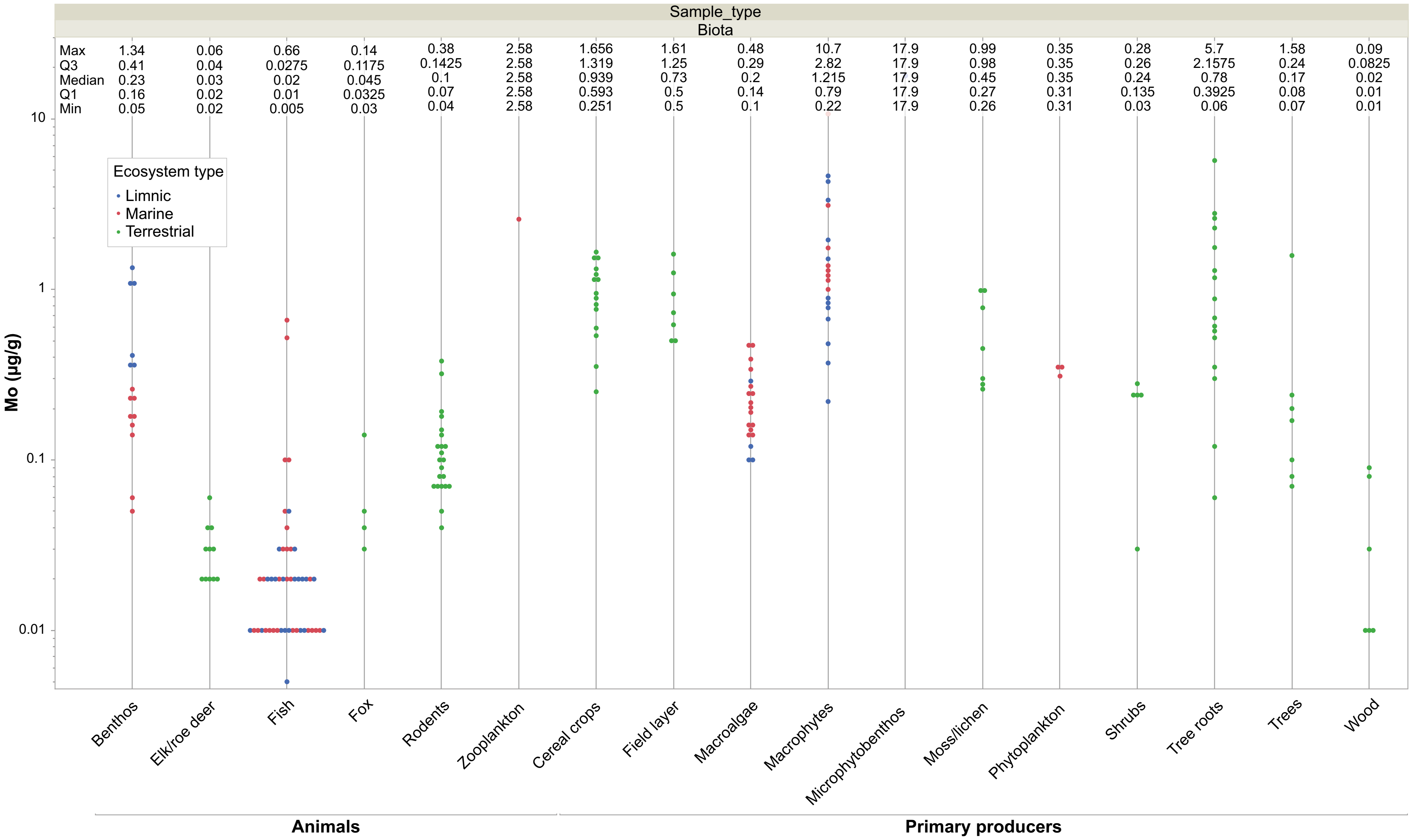

Figure 3-41. *Overview of observed Mo concentrations in biota from the site investigation areas. Each marker represents a unique observation and is coloured according to the ecosystem type (terrestrial, limnic or marine system). The observations are ordered by organism groups and divided into animals and primary producers. No observations for mushrooms were available. The upper panel displays the maximum and minimum concentrations, the median and the 1st and 3rd quartiles. Observations below the reporting limit are shown at half the value. Horizontal aggregations of points at low concentrations, for example, for fish at 0.01 µg g^{-1} and 0.02 µg g^{-1} are typically caused by concentrations close to or below the reporting limit of the responsible laboratory.*

differences also between different parts of an organism (Figure 3-41); in tree roots Mo concentrations up to 5.7 µg g^{-1} were observed, while the maximum in wood was only 0.09 µg g^{-1}. In general, there appears to be no obvious differences between the Mo concentration of limnic and marine biota, respectively. In benthos, however, limic systems had consistently higher Mo concentrations than marine systems.

When comparing Mo to other elements, there was a resemblance to above all W in animal samples from Forsmark and Simpevarp (Figure 3-42). Similar to Mo, which tends to occurs as molybdate (MoO_4^{2-}), W also occurs as an oxyanion, tungstate (WO_4^{2-}). Tungsten is known to be used by some prokaryotes, where it plays a similar role as Mo in certain enzymes, particularly for reactions at low redox potentials, but it has no known biological role for eukaryotes (Kletzin and Adams 1996). As in the animal samples, there was a correlation between Mo and W on a log-log scale also in the primary producers ($r = 0.90$, $p < 0.01$). There is some evidence suggesting that W could have a synergistic effect on the uptake of Mo. Application of W to soils has been demonstrated to increase not only the W concentration in plant tissue of wheat (*Triticum aestivum*) but also the concentration of Mo (Kumar and Aery 2011). Hence, although W should play no biological role for the sampled organisms, it is possible that there are similarities in the uptake mechanisms of Mo and W, respectively, which, accordingly, would explain the correlation between these two elements in biota.

Biological uptake of Mo in other areas

Different studies have shown incongruous results as to whether plant uptake can be related to various fractions of Mo in soils. For instance, observations across coniferous forests in Oregon, USA, did not show any correlation between foliar Mo concentrations and any extractable Mo fraction or the total Mo concentration in the soils (Marks et al. 2015b). This would suggest that the uptake of Mo either is actively controlled by the trees or that neither of the measured Mo fractions in the soils accurately represent the bioavailable Mo pool. On the other hand, the Mo concentration in needles from Norway spruce (*Picea abies*) in Bavaria, Germany, has been observed to correlate to the ion exchange extractable Mo fraction in the soils (Lang and Kaupenjohann 1999). One factor that also complicates comparisons between soils and biota is, however, that the Mo concentration has been observed to increase with the age of the needles (Lang and Kaupenjohann 2000).

Kasimov et al. (2016) reported a correlation between W and Mo in soils and trees (*Larix sibirica* and *Betula platyphylla*), respectively, in the vicinity of a W-Mo mine in Russia. The highest trace elements concentrations were generally found in larch needles, which was hypothesised to be related to fixation of dust particles onto their wax layer. Hence, it is not certain that these results reflect actual biological uptake of W and Mo.

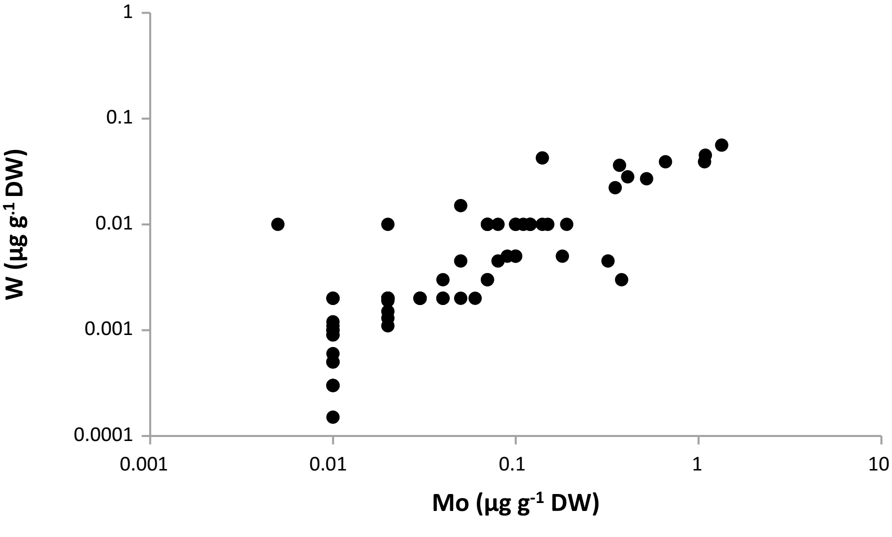

Figure 3-42. *Mo and W concentrations in animal samples from Forsmark and Simpevarp. The assemblages of observations at certain levels reflect the analytical difficulties of measuring Mo and W in these matrices. Observations below the reporting limits are plotted at half of that the value, which explains why some observations tend to fall along vertical or horizontal lines.*

An investigation of the effects of Mo deficiency in maize seedlings (*Zea mays*) grown in either nutrient solutions or real soils in both cases showed increased Mo concentrations in both roots and shoots when adding additional Mo (Kovács et al. 2015). The increase in the Mo concentrations in the maize seedlings was, however, not in proportion to the Mo added to the nutrient solution and the soils, respectively; when increasing the Mo supply by a factor 100 the increase in Mo concentration in roots and shoots increased approximately by a factor 10. In addition, the extra supply of Mo led to clear effects on the N concentration and the balance between nitrate, nitrite and ammonium in the plants, which most likely is attributable to the role of Mo in nitrate reductase (Kovács et al. 2015).

Elevated Mo concentrations in plants following Mo addition to soils have also been reported from a long-term field experiment in Hungary (Puskás-Preszner and Kovács 2009). In this case the focus was on maize (*Zea mays*) and peas (*Pisum sativum*) grown on calcareous black soils. Up to 810 kg ha^{-1} of Mo were added to the soils, which led to increased Mo concentrations in maize kernels and maize stems as well as peas and pea stems (Figure 3-43). Both the response and the initial conditions, however, varied strongly between different parts of the plants. In general, pea plants had higher Mo concentrations than maize plants, but the Mo was in both cases preferentially distributed to the stems rather than to the edible parts. In maize, the stem initially contained ca. 40 times higher Mo concentration than the kernels, while in peas, the stems contained only twice as much Mo as the peas. The response was also strongest for the lowest doses added Mo, particularly in peas, where the no clear increase in Mo could be observed either in the stems or in the peas for Mo doses > 300 kg ha^{-1} (Figure 3-43). It is not clear from the data, however, whether this is caused by an active limitation of the Mo uptake by the plants or whether the excessive Mo was converted into non-bioavailable forms, e.g. by sorption in the soils. It is clear, however, that both species tended to not to allocate the Mo evenly throughout the plants.

As regards the uptake of Mo in fish, a study of Chinook salmon (*Oncoryncthus tshawytscha*) exposed the fish to elevated concentrations of B, Se and Mo (up to 193 µg L^{-1} for Mo) in both brackish water and freshwater. However, no effects were observed for either Mo or B, while the whole-body concentration of Se increased with increasing exposure (Hamilton and Wiedmeyer 1990). This would indicate that these fish have an active control of the uptake of Mo.

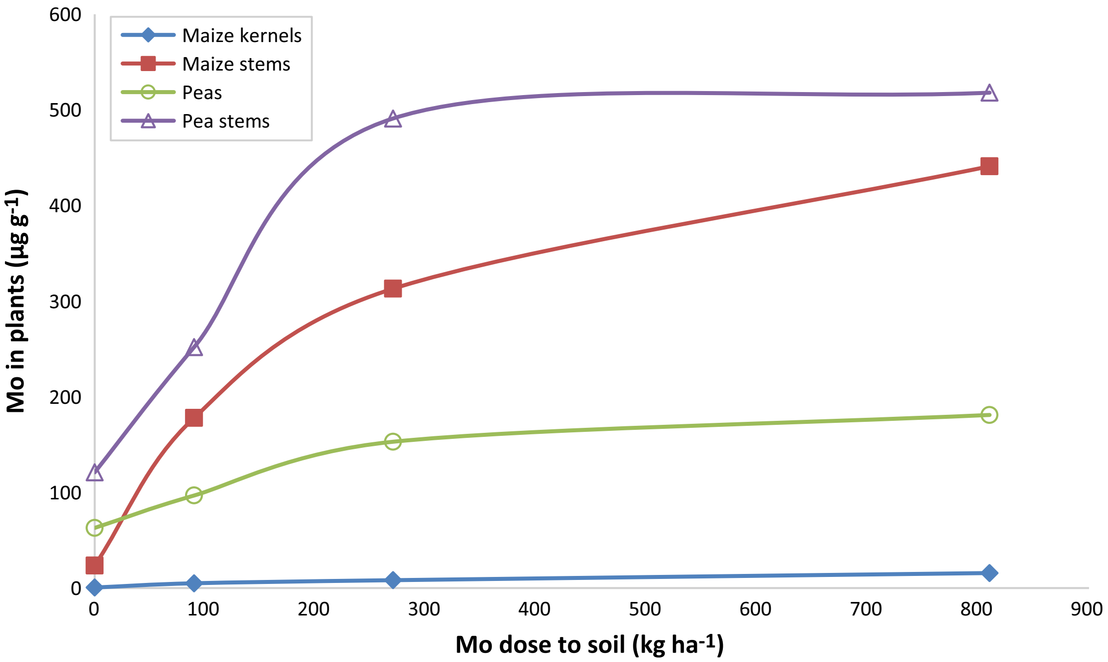

Figure 3-43. *Mo concentration in maize kernels (blue diamonds), maize stems (red squares), peas (open green circles) and pea stems (open purple squares) as a function of the Mo dose added to a long-term field experiment on a Hungarian calcareous black soil. Data from Puskás-Preszner and Kovács (2009).*

In study of the dietary exposure to various trace elements in France, 1 319 food samples “typically consumed by the French population” were analysed for Mo (Noël et al. 2012). Looking at food groups defined in the study, the highest average Mo concentration was found in “tofu”, 0.44 µg g^{-1}, followed by “fish and fish products” with an average of 0.14 µg g^{-1}. In this latter group particularly high Mo concentrations were found in “shellfish”, not least mussels with a maximum Mo concentration of 3.1 µg g^{-1}. The average Mo concentration in “shellfish” was ca. 10 higher than in “fish”, which is pattern similar to what was observed in the site investigations (Figure 3-41). In limnic fish from Forsmark and Simpevarp, for example, the Mo concentration was consistently low (from < 0.01 µg g^{-1} to 0.05 µg g^{-1}), while mussels (*Anodonta sp.*) displayed substantially higher concentrations (from 0.35 µg g^{-1} to 1.3 µg g^{-1}). It should be noted, however, that the concentrations from the SKB data refers to dry weight, while the French data refers to fresh weight. Other food groups of relevance for the safety assessment, e.g. “cereals and cereal products”, “fruit and vegetables”, “meat and offal” and “dairy products” all had lower average Mo concentrations (< 0.20 µg g^{-1}), although certain samples and sub-groups stood out, e.g. lentils (1.2 µg g^{-1} on average) and liver (1.0 µg g^{-1} on average). To what extent the relatively high Mo concentrations in these viands reflect a preferential uptake and accumulation of Mo or high levels of Mo in the environment where they were produced is unfortunately not possible to assess based on the data presented by Noël et al. (2012).

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Arkitektkopia AB, Bromma, 2023

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