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Micronutrient Distribution in Relation to Waste Emission from Aquaculture Activities

A field study in Trondheimsfjorden

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To my amazing family for all your support in everything that I do, I can always count on you. And finally to Lars Erik for keeping up with me when I'm hungry, cold, warm, tired, excited, stressed and bored. You are the best!

Samandrag

Bioaktive spormetall, eller mikronæringsstoff, er avgjerande som kofaktorar i enzym som brukast i forskjellige makronæringstoffsyklusar i det marine system. Akvakultur slepp ut store mengder makronæringsstoff, som kan føre til ei forandring i fordelinga av spormetall. Ved Norskekysten er det fleire områder med akvakultur aktivitet, men det er ingen historiske data over metallkonsentrasjonen.

I denne avhandlinga har eg sett på fordelinga av mikronæringsstoff nær oppdrettsanlegg, samanlikna med referansestasjonar utan noko kjent aquakultur. For å gjer dette vart prøvar av sjøvatn samla inn i Trondheimsfjorden i løpet av to tokt, eit i februar og eit i april. Prøvane vart so analyserte av ein HR-ICP-MS ved bruk av tre teknikkar: direkte prøvetaking, chelex-100 og DGT. Følgjande metall vart fokusert på: Fe, Mo, Mn, Cu, Co, Zn og Cd.

Det var ein generell sesongbasert trend med reduksjon i konsentrasjonane frå det første til det andre toktet, men ikkje ein klar trend mellom dei forskjellige stasjonane. Sidan det ikkje finnes bakgrunnsdata for metallkonsentrasjonen er det vanskeleg og seie om desse verdiane er naturlege eller på grunn av akvakulturaktivitet. Uansett so kan desse verdiane bli brukt som baselinje for både resten av CINTERA prosjektet og i framtida.

Abstract

Bioactive trace metals, or micronutrients, are crucial as cofactors in enzymes used in various macronutrient cycles in marine systems. Aquaculture releases large quantities of macronutrients, which may lead to a shift in the distribution of micronutrient. At the coast of Norway there are several areas with aquaculture activity, but there are no historical data on the metal concentrations in the Norwegian coastal system.

In this thesis, the distribution of micronutrients close to fish farms, has been compared to a location whiteout any known aquaculture activity. To do this, samples of seawater was collected in the Trondheimsfjord in two cruises, one in February and one in April. The samples were analysed with an HR-ICP-MS with the techniques of direct sampling, chelex-100 and DGT units. The following metals were focused on: Fe, Mo, Mn, Cu, Co, Zn and Cd.

There was a general seasonal trend of decrease from the first to the second cruise, but not a clear trend between the different locations and it did not seem like the distribution of micronutrients was significantly affected by aquaculture activities. The lack of background value of the micronutrients makes it difficult to decide whether the current values are natural or due to aquaculture activities. However, the data obtained in this thesis can be used as a baseline for both the rest of the CINTERA project and more importantly for the future.

Table of Contents

1. Introduction

This study has been done as a part of Gemini Center's project: A Cross-disciplinary Integrated Eco-Systemic Eutrophication Research and Management Approach – CINTERA. The objective of the project is to improve knowledge of ecosystem response to eutrophication and management of eutrophication in different marine fjord ecosystems and zones in Norway and Chile (CINTERA, 2011).

Earlier there has been done a project with WAFOW that has looked at how the waste from fish farms can change the structure of marine food webs. This was done with mesocosms experiments. However, in the CINTERA project we would go in situ and take samples in fjords with fish farming and compare those results to reference stations without any known aquaculture.

In the WAFOW project, Annie Vera Hunnestad, a master student, wrote her thesis on the effects of macronutrient enrichment (ammonium) on the distribution of four bioactive trace metals (Cd, Mo, Ni and Cu) in seawater and planktonic biomass. The design of the experiment was to measure the changes in different variables as a gradient of ammonium was added to different bodies of water (mesocosm) (Hunnestad, 2012).

In this master thesis work it was found that the enrichment in ammonium concentrations and other macronutrients caused an increase in the total amount of biomass. The particulate concentrations of all the considered trace metals (Cd, Mo, Ni and Cu) increased with the increase of ammonium due to the increasing biomass (Hunnestad, 2012). The general trend was that with chelex and DGT labile metal concentration decreased with higher ammonium flux. (Hunnestad, 2012).

Nicolas Sanchez was also a master student with the WAFOW project where he studied the distribution and variation of iron in the mesocosm experiment. He found that the addition of ammonium led to an either increase or decrease in the iron concentration, depending on the form the iron was in (Sanchez, 2012).

The fish farming industry in fjords are growing, and Norway and Chile are two of the major fish producers (Food and Agriculture Organization, 2011). The amount of waste produced and released from fish farming increases with the industry, however the knowledge on how this nutrient enrichment can affect the coastal ecosystem is scarce (Cloern, 2001, Olsen et al., 2006).

The effect a fish farm and its waste can have on its environment depends on the size and type of fish farm. The waste from salmon farming contains a direct loss of uneaten feed and large amounts of dissolved inorganic macronutrients from fish excretion and urine (NH_4^+, PO_4^{2-} and urea-N), particulate organic nitrogen (PON) and

phosphorus (POP) through defecation, and its dissolved components (dissolved organic N and dissolved organic P) through re-suspension from the particulate fractions. The feed losses and the larger faeces particles will sink and affect the sediments whilst the dissolved nutrients will affect the quality of the water column (Olsen and Olsen, 2008).

Marine microorganisms are a major component of global nutrient cycles, and are responsible of approximately half of the earths primary production (Arrigo, 2004, Morel and Price, 2003). Algae accounts for more than 90% of the ocean's plants and a vast majority of these are phytoplankton (Pinet, 2009). For marine and estuarine phytoplankton it is assumed that nitrogen (N) is the limiting nutrient for the growth (Hecky and Kilham, 1988, Zehr and Ward, 2002). The nitrogen cycle is therefore important when looking at waste from fish farms. Nitrogen is also contributed to the surface water through runoff from agricultural fertilization or from nutrient rich deep water, mainly in the form of nitrate (NO_3^-) (Zehr and Ward, 2002).

The nitrate, nitrite and ammonium are all dissolved inorganic nitrogen (DIN). These can be taken up and assimilated via membrane transporters by many microorganisms. Nitrate can be taken up by phytoplankton, and after series of metabolically processes, the final assimilated substance is ammonium (NH_4^+). This is possible through a sequential reduction from nitrate to nitrite (NO_2^-) by the assimilatory nitrate reductase enzyme, and from nitrite to ammonium by the assimilatory nitrite reductase enzyme. However, the reason why phytoplankton in general prefers ammonium to nitrate, is most likely due to the additional energy and the reductant necessary to reduce nitrate to ammonium (Zehr and Ward, 2002).

All nitrogen transformation in the nitrogen cycle involve metalloenzymes (see Figure 1), therefore the metal availability is crucial. Since the available nitrogen goes from mainly nitrate to ammonium, the need and hence the uptake of the different trace metals may be affected. For example, when one has nitrate as nitrogen substrate instead of ammonium, the algae needs to use nitrate and nitrite reductase, where iron and molybdenum are cofactors. If the algae then get an ammonium source, they might not need iron and molybdenum as much anymore. Through the nitrogen cycle, the trace metals can also influence the carbon cycle. In addition, trace metals do also have a direct effect on photosynthesis and respiration at the cellular and ecosystem levels (Morel and Price, 2003).

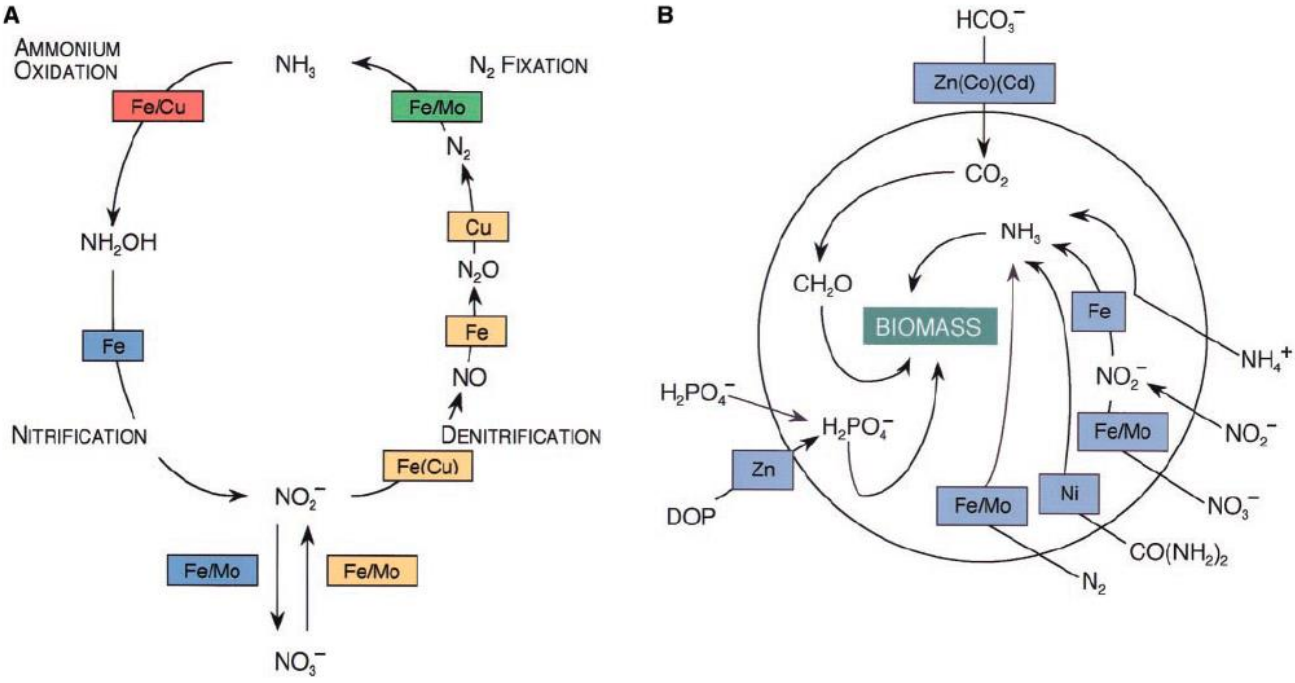


Figure 1.1: (A) Model of the nitrogen cycle showing how metals are involved in the enzymatically catalysed steps. The colours identify the reactions involved in nitrogen fixation (green), denitrification (yellow), nitrification (blue), and ammonium oxidation (red). (B) Shows the main metal requirements for nitrogen, carbon and phosphorous acquisition and assimilation by marine phytoplankton (Morel and Price, 2003).

As seen in Figure 1.1, Iron is the most important trace metal in the nitrogen cycle as it has a role in both nitrate and nitrite reductase as well as in the nitrogen fixation. Molybdenum can in some cases be used as well as iron. This tells us that in lack of availability of these two metals, the enzymes that reduce nitrate and nitrite to ammonium will not be working. Therefore the phytoplankton cannot get bioavailable nitrogen, and will suffer of nitrogen limitation. In that way, the lack of Fe and Mo will induce nitrogen limitation and this is why it is so important to study bioactive trace metals together with macronutrients.

2. Objective and hypothesis

The objective of this thesis is to see whether aquaculture activities have any direct or indirect effects on the bioactive trace metals (micronutrients) distribution. I have worked closely together with another master student, Cathrine Solli, who has looked at the distribution of macronutrients. Our studies may therefore together contribute to a better understanding on how micronutrients together with macronutrients from aquaculture activities can affect the costal marine ecosystem.

Aquaculture activities might through the release of excess macronutrients and organic matter to the environment change the chemistry of the water column and sediment water interface, and thereby also the biological activities around the fish cages. These changes may have an effect on the distribution of biological active trace metals (micronutrients).

3. Background Theory

3.1 What are micronutrients?

A micronutrient is a substance that organisms need a small amount of for proper growth (Millero, 2009) and metabolism. Micronutrients can be vitamins, minerals, organic acids or bioactive elements in trace amounts (Challem, 1999). Any micronutrient can be toxic to an organism if it receives too much of it. This limit varies for the different organisms and the micronutrient in question (Millero, 2009). Whilst micronutrients only are needed in small amounts, macronutrients are needed in large amounts to withstand proper growth and metabolism.

We differ between essential and non-essential elements. A simple definition of an essential element is a metabolic or functional nutrient. Another definition is that an essential element is an element that is required for the maintenance of life and its deficiency causes an impairment of a function from optimal to suboptimal. Impairment can lead to diseases, metabolic anomalies or perturbation development (Reilly, 2004).

Some metals are essential micronutrients (Fisher and Reinfelder, 1995) and they will be the focus in this thesis. Trace metals are of environmental interest both as its position as a limiting micronutrient, and as a toxicant in larger quantities (Sunda and Huntsman, 1998). Trace metals exist in nanomolar to picomolar quantities in the worlds oceans (Vraspir and Butler, 2009).

For example, phytoplankton needs the following macronutrients: Nitrogen, phosphorus, silicon, calcium, carbon, magnesium, oxygen and potassium. And of micronutrients they need cobalt, iron, molybdenum, vanadium, zinc, manganese, copper, nickel and even cadmium. They also need organic nutrients like biotin, cobalamine and thiamine (Kennish, 2001).

3.2 Fish farming and the environment

According to the Food and Agriculture Organisation (FAO), the overall global capture fisheries production has been kept stable since 2006 at about 90 million tonnes per year. However, since the 1980s, the fish production by the means of aquaculture has expanded by almost twelve times. The total amount of production from the worlds fisheries was 148,5 million tonnes in 2010, where of 59,9 million tonnes came from aquaculture activities (excluding plants and non-food products). Of the produced amount in the Americas and in Europe, Chile and Norway are both the main producers respectively. In the Americas, Chile has 27,21% of the production, whilst in Europe, Norway has 39,95% of the production. This makes Norway the seventh largest producer in the world and it is the second largest exporter (Chile is the tenth). In this thesis the focus is marine water, and marine water aquaculture is

accounted for 29,2% of the total aquaculture production by value (Food and Agriculture Organization, 2011).

In 2010, 3,6 million tonnes of the fish produced in the world, or 6,0 per cent, were diadromous fish. Of these, 1,9 million tonnes are Atlantic salmon (Salmo salar). Norway is the main producer of Atlantic salmon, whilst Chile is the second (Food and Agriculture Organization, 2011).

The salmon fish farming is seen as an intensive aquaculture production, that is, a high concentration of fish kept in small areas, where feed is introduced with artificial pellets. There are several environmental issues to consider when looking at intensive fish farming. Salmon that escapes might affect the gene pool of the wild salmon, and bring parasites and diseases. The discharge of organic waste from the fish farming is also a large issue, since it can affect the local marine environment (Tveterås, 2002).

The effect of nutrient input due to intensive aquaculture activity can be measured in the water column and on the nearby seabed. This is caused by fish excretion and uneaten feed. As the nutrients sink to the bottom, microorganisms will decompose it leading to oxygen depletion. If the fish farms are located in areas with poor water currents and circulation, this may cause a change in the conditions and the fauna on the seabed may be damaged (Soto and Norambuena, 2004). If the sediment-water interface has anoxic conditions, this will cause for iron, manganese, cobalt and other surface-active toxic metals such as lead to undergo reduction and dissolution (Stumm and Morgan, 1996). Any changes in the sediment-water may therefore cause changes in the biogeochemistry of trace elements.

The environmental impact from salmon farming has become a general concern around the world. These include, as mentioned, the general conditions on the seabed, the increased amount of nutrition in the costal waster that can lead to algal blossom. It also includes the harvest of wild fish population for the production of fish feed for the carnivore fish. In the fish production there is also a use of chemical and medicine, and some farmed salmon escape into the wild (Buschmann et al., 2006).

The release from fish farms varies with the season (see Figure 3.1), as the fish grows more in the summer, this is also the time when the sewage release is the greatest (Fiskeri- og kystdepartementet i samråd med Miljøverndepartementet, 2011) and the most feed is supplied (Wang et al., 2012). This is also when the primary producers will be more active, due to more sun energy (Paffenhöfer, 2009).

Waste from aquaculture

The results are varying for different aquaculture systems, but on average the amount of nitrogen that the target organism in a pond of aquaculture can recover is about 25% (Hargreaves, 1998). Olsen and Olsen (2008) calculated an annual mass balance of carbon, nitrogen and phosphorous waste from a hypothetical salmon cage aquaculture system producing 1000 metric tonnes net weight per year to correspond to emissions from a community of 7500 to 10.000 people (2g P per person per day, 13g N per person per day, Norwegian standard). Figure 3.1 shows how N and P from feed are distributed between loss, uptake, excretion, POP, PON and resuspended DON or POP.

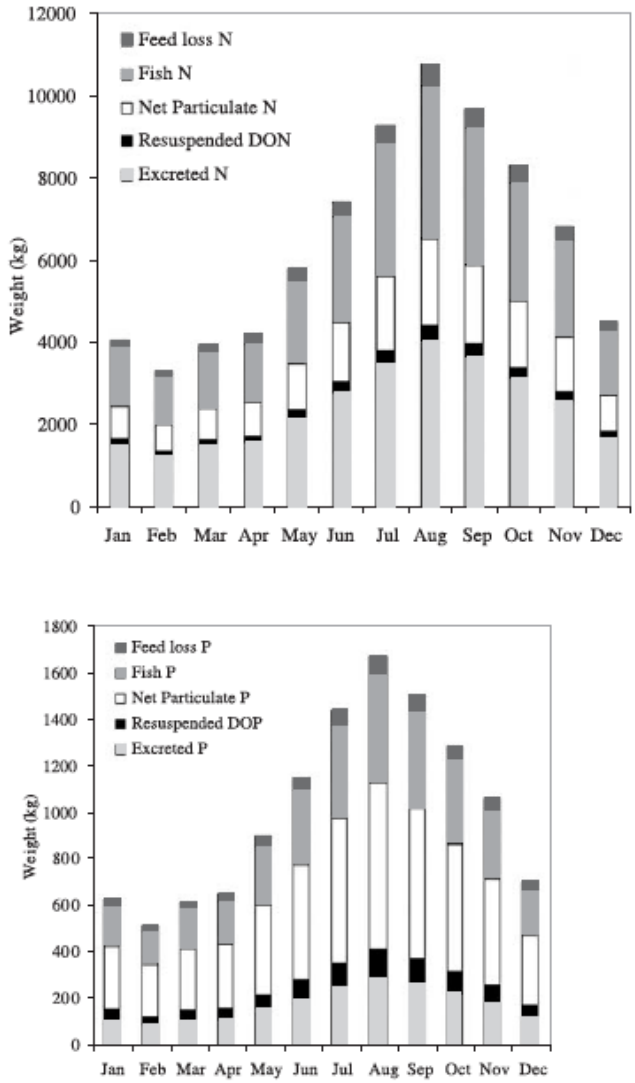


Figure 3.1: Annual variation in nitrogen (upper panel) and phosphorus (lower panel) deposition in fish biomass and waste components for a hypothetical CAS producing 1000 tonnes salmon per year. The sum of the fractions equals the food nitrogen and phosphorus supplied (Olsen and Olsen, 2008).

It has been measured that there is an increase in total nitrogen and ammonia, and a decrease of nitrate in the effluent from marine fish and shrimp ponds (Ziemann et al., 1992). Ammonia is excreted as an end product of protein metabolism (Hargreaves, 1998).

Phytoplankton is the primary pathway for nitrogen removal in the water column of aquaculture ponds due to their uptake of dissolved inorganic nitrogen (DIN). Ammonia is the preferred N-substrate for phytoplankton since nitrate assimilation and incorporation is done by an enzymatic reduction to ammonia within the phytoplankton cell before it can be incorporated into cellular amino acids. This is a process that requires energy and is therefore undesirable (Hargreaves, 1998). In aquaculture ponds the concentration of dissolved inorganic nutrients in the water column has an inverse relationship with the density of phytoplankton (Krom et al., 1989).

Effects on benthic zone

There is an expected flux for several dissolved constituents between sediment pore waters and the overlaying waters. Electron acceptors, like oxygen, will diffuse down to the sediments from the overlaying waters and electron acceptors, like ammonium, will go from the sediments and into the overlaying waters. However, if the oxygen demand caused by the input of organic matter is greater than the oxygen diffusion rate, the sediments will become anoxic and anaerobic processes will dominate. If the sediment layer becomes anoxic, this will change the redox chemistry in the sediment water interface. In the start of a suboxic environment, manganese oxides will be reduced and manganese ions will be released from the sediment into the water. If environment becomes even more anoxic, the same thing will happen with iron oxides, and subsequent to the release of other particle reactive metals (Ardelan et al., 2012, Stumm and Morgan, 1996). Therefore the manganese to iron ratio can be used to check if the sediments are becoming anoxic (Stumm and Morgan, 1996). The areas where waste from aquaculture, either feed or feces accumulate on the seabed they can deplete the oxygen level and release noxious gases that will suffocate the benthic organisms. This can lead to a dramatic change in the community of organisms that live beneath salmon production nets, and may reduce the diversity of the species, allowing only a few to thrive in the polluted conditions (Weber, 1997).

The scientific literature on the impact on the sediments and benthic ecosystems from the waste from aquaculture is very comprehensive. This is due to the fact that feed and feces falls directly to the seabed and is easy to detect. There is also a general scientific understanding on the requirements to base assessment of state and dynamic, management and monitoring measures (Olsen and Olsen, 2008).

Effects on the pelagic zone

The potential impact on the water column from waste from aquaculture is far less studied that the impact on the sediments. The pelagic ecosystems are primarily

affected by the inorganic nutrients (NH_4 and PO_4), which cause phytoplankton-, macro algae- and bacterial-growth. Whilst the majority of N is released into the water column (68%), the majority of P is accumulated in the sediments (63%) (Olsen and Olsen, 2008).

The occurrence of harmful algal blooms in one of the large concerns when it comes to salmon production, and in Chile algal blooms have been reported to affect human health as well as natural and cultural resources (Buschmann et al., 2006). Whether the algal bloom is caused by nutrients from salmon production or from other sources, it can damage the salmon production in several ways. It may cause oxygen depletion, which salmon and other animals and organisms depend on, but it can also produce toxins and cause disease among farmed salmon and other species in the area (Weber, 1997).

The pelagic ecosystems have an inherent capacity of persistence, and smaller changes in nutrient input are moderated through adaptive responses. However, there is an upper assimilation limit to its capacity. This can lead to changes or a complete shift of the dominant type of microalgae. The assimilation capacity of the pelagic ecosystems is mediated by two main mechanisms: the incorporation of nutrient in the organisms and a dilution process driven by hydrodynamics (Olsen and Olsen, 2008).

Primary producers

The first step in the marine food chain is known as plankton, which also has a major role in cycling chemical elements in the ocean. Plankton can be divided into smaller groups based on size and functionality (Mullin, 2009), and in this thesis the focus is on the primary producers such as phytoplankton and cyanobacteria. Phytoplankton are single-celled plants or colonies, they depend on sunlight for photosynthesis, and exists therefore mostly at the surface to 50-200m depth (Mullin, 2009). There are about 25000 known species of phytoplankton, and they are responsible for the photosynthetic fixation of around 50×10^{15} g carbon each year, which is almost half of the Earths primary production. The cell size of phytoplankton is highly variable, from a volume of 0,1µm^3 for the smallest cyanobacteria, to 10^8 µm^3 for the largest diatom (Marañón, 2009). During algal bloom, phytoplankton can take up metals, which leads to increased metal bioavailability to the food chain (Luengen et al., 2007, Luoma et al., 1998).

3.3 Cycling of macronutrients

Nutrients like silicate, phosphate, nitrate and nitrite follow a seasonal cycle (Clarke and Leakey, 1996), but marine microorganisms have also a very important role to play in the global cycling of nutrients. They are responsible for about half of the world's primary production, (Arrigo, 2004) and nitrogen, phosphorus and silicon have the greatest role in the growth of phytoplankton. Of these, nitrate and sometimes

phosphate are the limiting nutrients. Other elements are needed as well, but these usually do not limit growth (Kennish, 2001).

Algal uptake of macro- and micronutrients in the surface layer is followed by regeneration back into solution in deeper waters due to the sinking of biogenic particles and the microbial degradation (Pinet, 2009, Stumm and Morgan, 1996). This cycle depletes the concentration of the nutrients in the surface waters in the ration they occur in phytoplankton and enriches the deeper waters in the same ratio (Stumm and Morgan, 1996). This ratio is known as the Redfield ratio and one assumes that the phytoplankton uptake of nutrients is proportional to this ration (C:N:P = 106:16:1) (Hargreaves, 1998).

An idealised model can be used to show the principal fluxes of nutrients (see Figure 3.2).

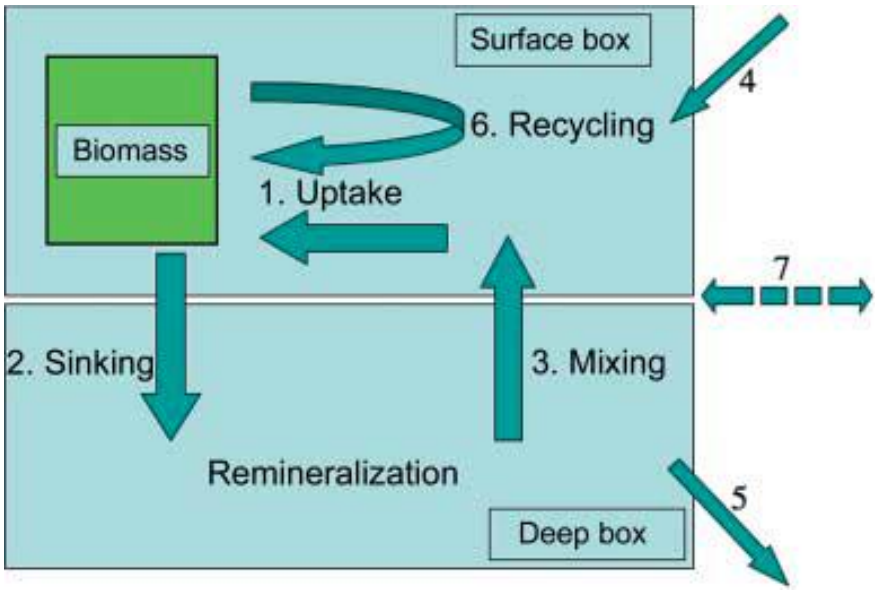


Figure 3.2: Diagram of a two box model of the open ocean showing the principal fluxes of nutrients (Morel, 2008).

The top box represents the euphotic zone at the surface where the phytoplankton will take up all the essential nutrients that it needs to sustain the photosynthetic generation of planktonic biomass. The lower box represents the deep ocean waters where the nutrients are sinking with the biomass and resuspended in solution. As seen in the model, the nutrients goes through a six step cycle: (1), uptake at the surface by the biota, (2) sinking and resuspension of the biomass, (3) mixing (diffusion and advection) of the resuspended nutrients to the surface, (4) input to the surface layer (mainly from the atmosphere), (5) output to the outside (mainly to the atmosphere and sediments) from the deeper water and (6) recycling at the surface. The lateral fluxes are represented by the dashed arrow (7), they stand for the distant influence of the rivers and hydrothermal sources which provide the main inputs of most elements to the global oceans (Morel, 2008).

The nitrogen cycle in the oceans

Of all the essential nutrients, nitrogen is the only one whose seawater concentration is clearly controlled biologically (Morel, 2008). The nitrogen cycle consists of several reduction-oxidation reactions transforming several nitrogenous compounds. It is primarily catalysed by microbes that uses specific enzymes and the cycle controls the bioavailability of nitrogenous nutrients and biological productivity in the marine systems. The main source of nitrogen in the oceans comes from the nitrogen rich deep waters and both physical- and biological forces controls are involved in the upward moving of the nitrogen (Zehr and Ward, 2002).

However, the Redfield ratio discussed earlier is not always true. To stabilise the forces of the nitrogen cycle there is a series of negative feedback, which therefore selects for a narrow range of plankton species assemblages. This feedback is illustrated in Figure 3.3. The upwelling water at present day has an N:P ratio of less than 16. In regions with this type of water has a high primary production and distributes large amounts of particulate organic matter (POM). The resuspension of the POM in the subsurface waters leads to oxygen depletion, which supports the denitrification and anammox. This leads to a net loss of fixed nitrogen and therefore the N/P ratio is lower in the subsurface waters. When the nitrogen depleted water returns to the surface, this supports nitrogen fixers that can overcome their nitrogen limitation, and therefore producing more POM. Since POM has a N:P ratio greater than 16, its export and resuspension in the deep waters leads to an N:P ratio in the long-term to an average of 16 in the surface waters (Arrigo, 2004, Libes, 2011).

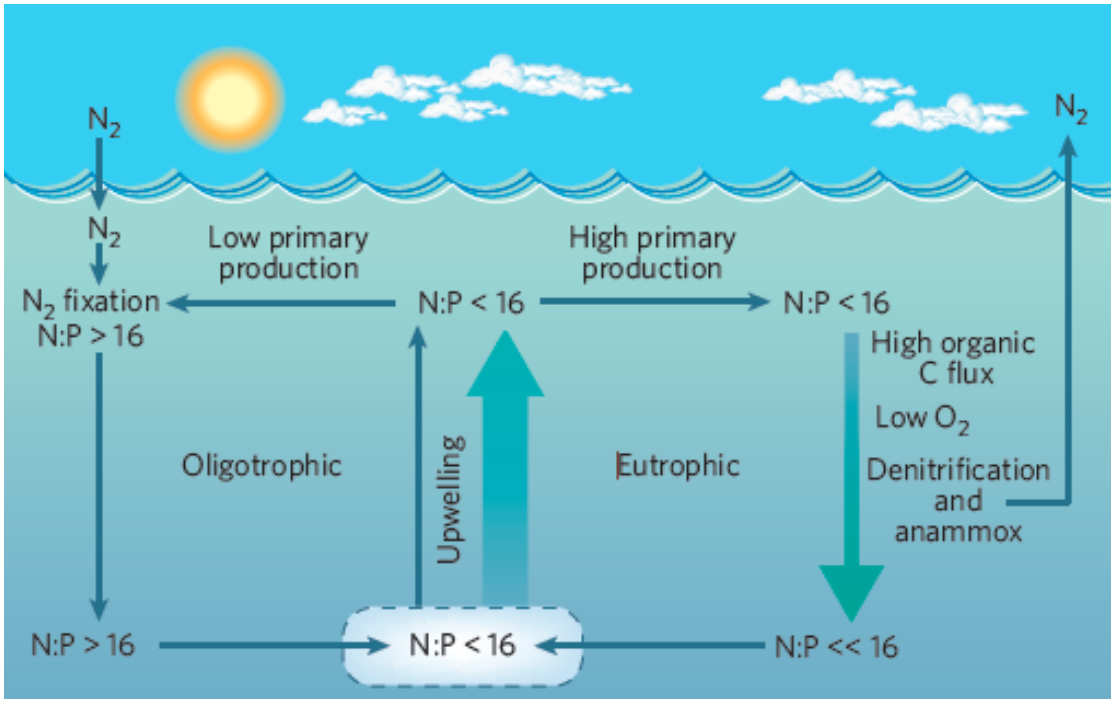


Figure 3.3: The global ocean balance between N_2 fixation and the loss of fixed nitrogen through anammox and denitrification (Arrigo, 2004).

Nitrogen uptake in phytoplankton

All organisms depend on nutrients to grow and one of the most important element is nitrogen (Barsanti and Gualtieri, 2005). It is often assumed that the lack of nitrogen limits the productivity of phytoplankton (Arrigo, 2004, Dugdale and Goering, 1967), and it is the third most abundant constituent in algal biomass. Amongst the numerous species of nitrogen compounds present in marine waters, ammonium (NH_4^+) and nitrate (NO_3^-) are the preferred ones (Thompson et al., 1989), together with nitrite (NO_2^-) they make up a group of dissolved inorganic nitrogen (DIN). They can be taken up via cell membranes and assimilated by many organisms (Zehr and Ward, 2002). Ammonium is seen as the favourable one, since it costs more energy and reductant to reduce nitrate to ammonium (Thompson et al., 1989, Zehr and Ward, 2002, Dortch, 1990). This leads to the importance of bioactive trace metals since to reduce nitrate and nitrite to ammonium, enzymes are required, and iron and molybdenum are used as metal cofactors in these enzymes. Iron is also used in nitrification and together with molybdenum used in the nitrogen fixation, whilst copper is together with iron important for ammonium oxidation and denitrification (Morel and Price, 2003). However, there are results that show that growth rates on nitrate usually is equal, or even exceeds the growth rates of ammonium (Dortch, 1990, Dugdale and Goering, 1967, Thompson et al., 1989). In other words, the reductant requirement for nitrate does not necessarily lead to decreased growth and preference to ammonium is not universal (Zehr and Ward, 2002).

One of the roles to bacteria is to recycle N, by transforming organic matter into inorganic N (NH_4^+) (and other nutrients) that phytoplankton can take up. However, sometimes bacteria can use inorganic nitrogen too, and therefore compete with phytoplankton. This seems to be related to the carbon:nitrogen ratio (Zehr and Ward, 2002).

3.4 Trace metals: the biological role as micronutrients

In living organisms, metal ions regulate several physiological mechanisms with considerable selectivity and specific (Reilly, 2004). A variety of borderline trace metals are essential micronutrients for biological processes, as cofactors of metalloenzymes and proteins (Hunter et al., 1997, Stumm and Morgan, 1996, Morel et al., 1991, Morel and Price, 2003). The reason why d-block metals play such an important part in the enzymatic activities in living organisms is due to their chemical flexibility, variety of oxidation states and extensive bonding patterns, they can participate extensively as cofactors in catalysts (Reilly, 2004).

In the surface of the ocean, the microorganisms are dependent on several biochemically significant elements. These are manganese, iron, nickel, cobalt, copper, zinc and cadmium (Millero, 2009, Morel and Price, 2003). The vertical profile from the sea is similar as the ones you can find with macronutrients. The concentration of trace metals is lower close to the surface, because of algal uptake, whilst at greater

depths, the concentration will increase due to partial release from mineralisation (Stumm and Morgan, 1996).

All invertebrates take up trace metals, either from the aquatic medium it is surrounded by or from food. Which of these routs are most prominent varies from the different vertebrates and the bioavailable trace metals in the surrounding water and diet (Rainbow, 2002, Wang, 2002). A trace metal can be limiting or toxic, dependent on the metal and the concentration. All the essential elements have a window of essentiality with different concentration limits for different organisms, which are needed for the organism to grow and reproduce normally (see Figure 3.4) (Walker et al., 2006).

In the biomass of all living organisms one can find around 30 of the 92 naturally occurring elements (Moore et al., 2013). It has been concluded that in addition to C, H, O and N, all animals need seven macronutrients: Ca, Ph, K, Mg, Na, Cl and S. There are thirteen micronutrients that have been found to be required: Fe, I, Cu, Mn, Zn, Co, Md, Se, Cr, Ni, V, Si, As. Some metals are nonessential eg. mercury. These are not only toxic above a certain concentration, but they may also cause deficiencies of essential elements by competing at active sites in biologically important molecules (Walker et al., 2006).

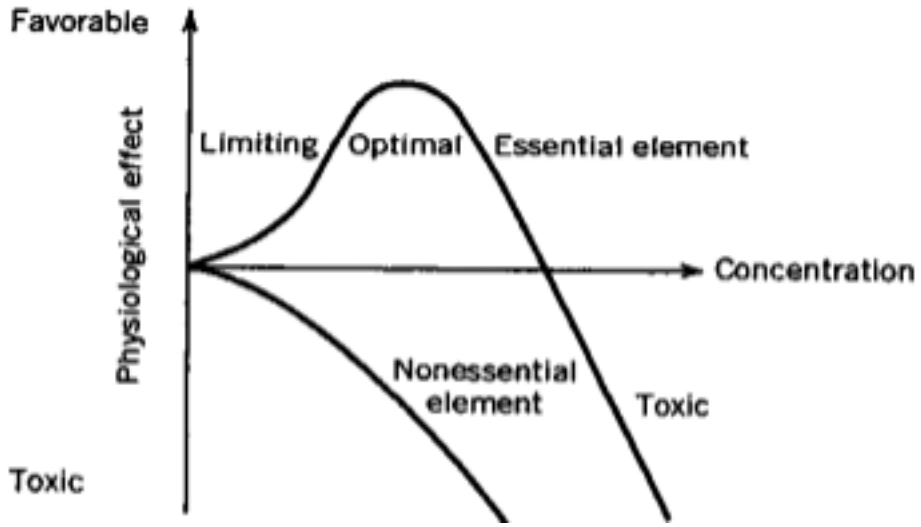


Figure 3.4: Relationships between the concentration of an element and its physiological effect (Stumm and Morgan, 1996).

Following a table presents the metals studied in this thesis, and some of the enzymes they are cofactors in.

Table 3.1: Enzymes and redox proteins containing the following trace metal cofactors; Fe, Mo, Mn, Co, Zn, Cd and Cu (Lane et al., 2005, Stumm and Morgan, 1996)

Metal	Enzyme	Function
Fe	Cytochrome *f* Cytochrome *b* and *c* Ferredoxin Iron-sulfur proteins Catalase Peroxidase Chelatase	Photosynthetic electron transport Electron transport in respiration and photosynthesis Electron transport in photosynthesis and nitrogen fixation Photosynthetic and respiratory electron transport H_2O_2 breakdown to H_2O and O_2 H_2O_2 breakdown to H_2O Porphyrin and phycobiliprotein synthesis
Fe and Mo	Nitrogenase Nitrate and nitrite reductase	Nitrogen fixation Nitrate reduction to ammonia
Mn or Fe	Superoxide dismutase	Disproportionation of $O_2^{-\bullet}$ radicals to O_2 and H_2O_2
Mn	O_2 evolving enzyme	Oxidation of water to O_2 in photosynthesis
Cu	Plastocyanin Cytochrome c oxidase	Mitochondrial electron transport Ascorbic acid oxidation and reduction
Co	Vitamin B_{12}	Carbon and hydrogen transfer reactions
Zn	DNA and RNA polymerase Alkaline phosphatase	Nucleic acid replication and transcription Hydrolysis of phosphate esters
Zn or Co or Cd	Carbonic anhydrase	Hydration and dehydration of CO_2

Iron (Fe)

Iron is the second most abundant metal (Rayner-Canham and Overton, 2006, Reilly, 2004) and the fourth most abundant element in the earths crust (Haese, 2006, Sunda and Huntsman, 1995, Turner et al., 2001, Reilly, 2004). It is an essential element for all known living organism, and in phytoplankton it has been suggested that it limits growth in major ocean regions (Turner et al., 2001). In the biological systems it is often found in the forms of ferrous (+2) and ferric (+3) (Klaassen, 2008), but can also be found as ferryl (+4) (Reilly, 2004). Iron is transported to the marine system by four major pathways: fluvial (the most important one in coastal areas), aeolian submarine hydrothermal and glacial input (Haese, 2006). Iron has a rich redox chemistry (Reilly,

2004) that makes it able to be an important metal in several enzymes like nitrogenase (nitrogen fixation) and nitrate and nitrite reductase (Morel and Price, 2003, Stumm and Morgan, 1996). The concentration of Fe is found at a range of 0,1-2,5 nmol/Kg (Glasby, 2006)

Molybdenum (Mo)

Molybdenum is the eighteenth metal in order of abundance in seawater. It is said to be the most biologically important element in group six, and it is present in several enzymes, usually as the molybdate ion $[MoO_4]^{2-}$. One of the reasons for why molybdenum is so biologically important is that the molybdate ion has a high aqueous solubility at pH values near neutral. Thus makes it easy to transport by biological fluids. The ion also has a negative charge, and this makes it suitable for different environments in addition to its wide oxidation states, +4, +5 and +6. It has been argued that molybdate might be transported by the same mechanisms as the sulphate ion, SO_4^{2-} (Rayner-Canham and Overton, 2006). These are very similar in size, charge and stoichiometry, which may lead to sulphate being a potential competitive inhibitor (Cole et al., 1993). One of many enzymatic functions, Mo is a part of pterin-containing enzymes, like nitrate reductase which catalyses the reduction of nitrate to nitrite and which is converted to ammonia by nitrite reductase (Kisker et al., 1997, Rayner-Canham and Overton, 2006). In addition, Mo is also a cofactor in a large number of N_2-fixation systems (Cole et al., 1993). Since Mo is so biologically important, one would assume that the depth profile would have some correlation with the depth profile of nitrogen or phosphorus, however this is not the case. Molybdenum seams to be distributed homogenously thorough the water column, this leads to the conclusion that Mo does not limit the primary production in seawater (Collier, 1985). In natural waters the Mo concentration is in a range of ~1 to ~100 nmol/L, however, values closer to 100 nmol/L is more commonly observed (Cole et al., 1993, Collier, 1985, Howarth et al., 1988, Marino et al., 1990).

Manganese (Mn)

Manganese is the tenth most abundant element in the Earth's crust (Glasby, 2006) and it is a crucial element in several plant and animal enzymes (Rayner-Canham and Overton, 2006). It is important in O_2 evolving enzymes, which is used in the oxidation of water to O_2 in photosynthesis (Morel and Price, 2003, Stumm and Morgan, 1996). Manganese can exist in many valence forms, but the divalent cation is by far the most common species within cells (Klaassen, 2008). In natural waters the +II oxidation state can be found as both soluble and particulate phases (Santschi et al., 1990). It is also a redox reagent, cycling between the +2 and +4 oxidation states (Morel and Price, 2003, Rayner-Canham and Overton, 2006). Manganese oxides, which are often present in natural waters, have a high absorption capacity due to a large surface area and cation exchange capacity and can scavenge other cations from the natural waters, such as Ni^{2+}, Cu^{2+}, and Zn^{2+}. Therefore, redox cycling of manganese in natural waters can have a large effect on the fate of other trace metals (Glasby, 2006, Santschi et al.,

1990). In open ocean, the concentration of dissolved Mn is in a range of 0,2-3 nmol/Kg (Glasby, 2006).

Copper (Cu)

Copper is found as both +1 and +2, but in aqueous solutions, the +2 oxidation state dominates. After iron and zinc, copper is the most biologically important *d*-block metal and there is several parallel iron and copper compounds for many biological functions. However, an excess of copper can be highly poisonous (Rayner-Canham and Overton, 2006). In open oceans, Cu tends to have a high concentration in the surface, and the depth profile has been found to be almost linear, slowly increasing in concentration as you go deeper. This increase is not as great as for other bioactive trace metals, and a reason for that might be that copper is absorbed onto particles and therefore a greater part of the dissolved copper may be removed from the water (Bruland, 1980, Nolting et al., 1991). Studies from San Francisco Bay show that even though other elements, such as nickel, zinc and cadmium, had a clear reduction of the dissolved fraction in the surface water during algal bloom, this was not the case for copper, which in the study by Luoma et al., 1998, actually increased its dissolved concentration by 20% (Luengen et al., 2007, Luoma et al., 1998). The strong complexation of Cu also means that even though the dissolved concentration is in nanomoles, only sub-pico moles are available for the marine planktonic algae (Rijstenbil et al., 1998). Copper is important in enzymes involved in denitrification (Morel and Price, 2003, Ye et al., 1994). Whilst some oceanic diatoms are limited by copper, it is toxic to some cyanobacteria (Morel and Price, 2003). The concentration of dissolved copper in surface marine waters vary from 0,4 – 4,1 nmol/liter, however much higher concentrations are found but these probably result from pollution (Stumm and Morgan, 1996).

Cobalt (Co)

Cobalt is a relatively rare metal (Klaassen, 2008) and the highest concentrations are found in ores in the earths crust. Cobalt ends up in the marine system through weathering (Hamilton, 1994). The form of cobalt varies from where it is found (Collins and Kinsela, 2010), and in seawater it can be found in more than one oxidation state and is involved in a redox cycle (Morel and Price, 2003). It may also be found as an ion complexed with inorganic or organic ligands, or it may be bound to suspended colloidal material (Collins and Kinsela, 2010). Cobalt is important in the vitamin B_{12} (Croft et al., 2005, Croft et al., 2006, Kobayashi and Shimizu, 2001), which has a function in carbon and hydrogen transfer reactions (Stumm and Morgan, 1996). Cobalt has also been observed replacing zinc in Carbonic anhydrase, a metalloenzyme that catalyses the equilibrium between HCO_3^- and CO_2, which makes it possible for phytoplankton to get inorganic carbon for photosynthesis (Lane et al., 2005, Morel and Price, 2003). This replacement of one essential element by another may be common in marine plankton, and may also occur in other zinc metalloenzymes (Morel and Price, 2003). The biological activity is probably one of the reasons for the relationship between cobalt and other nutrients, that are depleted at

surface waters and the concentration increases with the depth of the ocean related to organic productivity. The average concentration of cobalt in the oceans is 0,3µg/L (Hamilton, 1994).

Zinc (Zn)

The zinc ion has a d^{10} electron configuration, and it is the second most important trace element after iron (Rayner-Canham and Overton, 2006). Over 2000 zinc-dependent transcription factors and 300 catalytically active zinc metalloenzymes have been identified (Klaassen, 2008). Zinc is a strong Lewis acid and this function is used in the enzymes were Zn is present. Unlike most other trace metals, zinc is resistant to redox changes and will therefore not be affected by the change of redox potential in an organism. Zinc is also able to undergo very rapid ligand exchange, which is good for its role in enzymes (Rayner-Canham and Overton, 2006). Zinc has a depth profile that shows a relationship with other macronutrients, especially silicate. When zinc is depleted in the surface waters, there has been evidence that cadmium and cobalt can take its place in some enzyme like carbonic anhydrase (Lane et al., 2005, Saager et al., 1992). The distribution of dissolved zinc in surface marine waters vary from 0,04-2,4 nmol/L, however much larger concentrations can be found, but these are believed to come from pollution (Stumm and Morgan, 1996). Unfortunately, zinc is very easy to contaminate as it settles on dust particles, and can then be transferred to the sample through air (Doner and Ege, 2004).

Cadmium (Cd)

Cadmium has long been seen as a toxic metal and a pollutant (Klaassen, 2008), however we can now see evidence showing that cadmium can be a micronutrient (Lane et al., 2005). Just like zinc, cadmium has filled *d* orbitals and +2 as oxidation number in all simple compounds, this gives cadmium and zinc similar properties (Rayner-Canham and Overton, 2006). Cd is depleted in the surface, and the concentration increases with depth and this behaviour correlate with phosphate and nitrate (Bruland, 1980, Saager et al., 1992, Nolting et al., 1991). One of the reasons for this nutrient-like behaviour is that diatoms can use cadmium, like cobalt, instead of zinc in carbonic anhydrase (Lane et al., 2005, Xu et al., 2008). The concentration of cadmium in open waters is about 0,013 nmol/L (Howarth et al., 1988).

Trace metal uptake by phytoplankton

The trace metal uptake in phytoplankton is important due to the nutritional and potential toxicological effects of the metals and on the biogeochemical cycling in the marine systems (Fisher and Reinfelder, 1995). Phytoplankton cells can be considered to take up trace metal in three stages: (1) Transport of metal species to the cell surface through diffusion, (2) binding to a biologically produced ligand through sequestration or capture and (3) transfer of complex across cell membrane through internalisation (Whitfield, 2001). In general the overall process for uptake follows the Michaelis-Menten kinetics, typical for enzyme-mediated reactions (Morel et al., 1991, Stumm and Morgan, 1996):

$$p = \frac{p_{max}[M']}{K_p + [M']} \qquad (3.1)$$

Where p is the uptake rate, p_{max} is the maximum uptake rate and K_p is the half saturation constant. M' is the available metal concentration, that is, the concentration of free metal ions and kinetically labile complexes adjacent to the cell surface. The K_p value is assumed to be fixed for a given trace metal with a given species of phytoplankton. The value depends upon the ligand exchange rates (k_{-L}, k_L) and the rate of transport into the cell (k_{in}) (Whitfield, 2001):

$$K_p = \frac{k_{-L} + k_{in}}{k_L} \qquad (3.2)$$

If the trace metal is limited, the surface will be undersaturated. The M' value will then be smaller than the value of K_p. At steady state:

$$p^{55} = \frac{k_{in}[L1]^{max}}{K_p}[M'] \qquad (3.3)$$

Where $[L1]^{max}$ is the maximum concentration that the cell can produce of surface ligands (Whitfield, 2001).

Examples

A study from south San Francisco Bay showed that the concentration of dissolved cadmium decreased with about 50% during the height of algal bloom, and a decrease were also seen for nickel and zinc. It was assumed that the cadmium was taken up by the phytoplankton, leading to bioaccumulation of the metal (Luoma et al., 1998). One reason for this cadmium uptake is that cadmium is found to be able to substitute zinc in metalloenzymes (Lane et al., 2005, Morel and Price, 2003, Morel et al., 1991). A study by Wang et al. (2001) showed that the uptake of cadmium increased considerably under nutrient rich conditions. There was also a correlation between cell growth rate of the phytoplankton and the metal uptake, and with an increased cellular metal concentration, the herbivores will have a higher risk be exposed to metals by

ingestion. However there was not enough to conclude that the metal uptake was dependent on the cell growth (Wang et al., 2001) and the concentration of cadmium is generally decreasing at higher trophic levels in classic planktonic food chains (Wang, 2002). The study published in 2001 also showed that under nitrogen-limiting conditions, the cadmium cycle seamed to be depressed in the marine planktonic food chain, whilst at nitrogen enrichment there was registered a cadmium uptake in both phytoplankton and zooplankton. From this perspective one may say that algal bloom and local eutrophication does not only affect the macronutrient cycles, but also they do also have a great impact on the micronutrient cycles (Wang et al., 2001).

Luoma et al. (1998) also showed that even though cadmium, zinc and nickel was depleted in the surface during algal bloom, the copper concentration increased with 20% and the increased particulate copper during the bloom seamed to be primarily influenced by resuspension. In other cases, like with open ocean species, Morel and Price (2003) shows that oceanic diatoms require extremely little iron, but is very easily limited by copper. It is believed that copper might have replaced iron in some very important biological functions. In some species of arthropods and molluscs, the iron in haemoglobin is substituted with copper, forming haemocyanin, this makes the blood blue instead of red (Rainbow, 2002, Reilly, 2004). Then again, a high copper concentration can be toxic to some species of cyanobacteria (Morel and Price, 2003).

Trophic transfer of trace metals

Aquatic invertebrates will accumulate trace metals independent of whether it is essential or not (Rainbow, 2002). Phytoplankton can concentrate metals out of seawater, and since they are the main food source for most marine herbivores, phytoplankton have a critical role in introducing metals into the food chain. Therefore, phytoplankton bioaccumulation can lead to a trophic transfer of metals in the aquatic food chain. (Fisher and Reinfelder, 1995). Very simplified we can say that the marine food chain consists of the following: phytoplankton – zooplankton – nekton. Nekton include active swimmers like fish, squids, reptiles, birds and mammals (Pinet, 2009).

Classification of metals

Chemists define metals as an element that is lustrous. They enter reactions as either cations or anions, and it is a good electrical conductor (Walker et al., 2006). Metals are also toxicologically important since they can react in biological systems by losing one or more electrons to form cations (Klaassen, 2008).

In aqueous solutions, metals exist in a variety of forms, but the most common categorisation is to separate them into “dissolved” and “particulate” by filtration. Dissolved metals can be free metal ions (bound to water molecules), inorganic complexes, organic complexes or large polymers. Particulate metals can be colloids, surface bound or a solid bulk phase (Stumm and Morgan, 1996).

We can classify metals as type “A” and “B” metals, or “hard” and “soft” metals respectively and those in between are referred to as borderline metals (Stumm and Morgan, 1996).

A-type metals have a noble gas type (d^0) electron configuration. This configuration is associated with low polarisabilities: high spherical symmetry and electron sheaths that are not readily deformed by electric fields. In a more descriptive way one can call these for “hard” metals (Stumm and Morgan, 1996). The class A metals has also often high charge densities (Rayner-Canham and Overton, 2006). All macronutrients belong to class A (Nieboer and Richardson, 1980, Stumm and Morgan, 1996).

B-metals or “soft” metals on the other hand, have in general a higher polarisability, and are found to have an increased strength of covalent bonding. These metal cations have electron clouds more readily deformable bye electric fields of other species. B-type metals have electron numbers that corresponds to Ni^0, Pd^0, and Pt^0, that is ten or twelve outer shell electrons (Stumm and Morgan, 1996). The B class metals have a low charge density (Rayner-Canham and Overton, 2006).

Transition-metal cations are those who have one to nine electrons in their outer shell and are not spherically symmetric. This is the group were the micronutrients belong (Nieboer and Richardson, 1980, Stumm and Morgan, 1996). These are found on the divide between A and B class metals, and have intermediate values as charge densities (Rayner-Canham and Overton, 2006).

This categorisation also tells us something about the different affinity metals have for various ligands and functional groups, which is important for our understanding of the biological system. A-type metal ions prefer to form complexes with fluoride and having oxygen as the donor atom. They will not form any precipitates or complexes with sulphides in aqueous solutions; this is because OH^- ions readily displace HS^- and S^{2-}. However, B-type metal ions will preferably coordinate with bases containing I, S, or N as donor atoms (Stumm and Morgan, 1996).

When we look at toxicity: B-type metal ions are more toxic than the transition-metal ions, which in turn are more toxic than the A-type metal ions (Nieboer and Richardson, 1980, Stumm and Morgan, 1996).

The significance of speciation

Chemical speciation describes which form a molecule or particles is present as in a solution (Stumm and Morgan, 1996) and is defined as the distribution of an individual element between different chemical species or groups of species (Turner, 1995). In aquatic environment it is fundamental to know the speciation of a metal to predict its impact on the biota (International Network for Acid Prevention, 2002). Speciation affects the bioavailability, and there also the possible toxicity (Vraspir and Butler, 2009, Franklin et al., 2000). There is much more variability in speciation in fresh

water than in seawater since seawater has a much larger buffer capacity for pH (Turner, 1995).

Generally, most elemental metals tend to form ionic bonds (Klaassen, 2008). Factors that can influence speciation is the concentration of the metal and ligands, pH, pE, the hardness of the water (amount of calcium and magnesium) and the characteristics of the water (International Network for Acid Prevention, 2002, Valavanidis and Vlachogianni).

Usually when a metal forms complexes with organic ligands, the bioavailability of the metal will be reduced since most of the organic-metal complexes are not easily transported across cell membranes. On the other hand, when metals form complexes with inorganic ligands (such as carbonates etc.), which are easily dissociated, one will get more of the free metal form. This is crucial when considering the Free-Ion Activity Model (FIAM) (International Network for Acid Prevention, 2002).

This model stipulates that the biological response of an organism to trace metals in natural water is proportional to the free-ion activity of the metals (Campbell, 1995), and not the total dissolved concentration (which also includes the metal bound in complexes) (International Network for Acid Prevention, 2002).

However, it is not always the case that organic metal complexes are nontoxic. An example is methyl mercury, which can cross the blood brain barrier relatively easy. An other example is tributyltin was used on boats to kill of algae, and is therefore also toxic to organisms in the marine environment (Klaassen, 2008, Stumm and Morgan, 1996, Manahan, 2009).

Metal complexation to organic ligands

Complexation by organic ligands dominates the speciation to a variety of trace metals (Vraspir and Butler, 2009), and this is one of the most important environmental qualities of humic substances. Humic substances are a mixture of compounds with different molecular weight. The different humic substances are divided into three fractions: Fulvic acids that are soluble in both acid and alkaline solutions, humic acids that are soluble in alkaline solutions, but precipitates at pH 2 and humin, which is insoluble in water at all pH values. In water, the humic substances come from two sources: From degradation of vegetation (Manahan, 2009) and excretion of organic material from the aquatic organisms (Turner, 1995).

The complexation reaction will be carried out by the functional group of the humic substance (Manahan, 2009). The binding can occur as a chelation by phenolic and carboxylic groups (Stumm and Morgan, 1996), as chelation between two carboxyl groups or as a complexation reaction with a carboxyl group (Manahan, 2009). The carboxylic groups are ionised at low pH, whilst the phenolic groups are ionised at higher pH (Turner, 1995).

It is debated whether humic substances have an influence on the overall picture of metal speciation in seawater, because of the high concentration of calcium and magnesium, which might compete with the metals over the organic ligands (Mantoura et al., 1978, Stumm and Morgan, 1996). However, for some trace metals, the complexation with humic substances has important consequences for the geochemical cycle, the bioavailability and toxicity (Ellwood and van den Berg, 2001, Sunda and Huntsman, 1998).

Bioavailability and toxicity of trace metals

Both the bioavailability and the toxicity of a metal, is strongly dependent on the metals speciation (International Network for Acid Prevention, 2002). Equilibrium models have been developed to predict the role of chemical speciation on the bioavailability of metals. From this we have learned that complexation or competition will decrease the interaction between the uptake sites on the surface of the organism and the metal (Worms et al., 2006). Any free metal ions can be potentially toxic, due to its reactive potential (Klaassen, 2008). Free trace metals and metals in complexes diffuse from their external medium and to the surface of the organism via mass transport. The complexes are often dynamic and can dissociate and form a complex again in the time it takes to diffuse on the surface (Worms et al., 2006).

For the metal to have an effect (desired or toxic) it must go through adsorption or desorption on an active site on the biological membrane, and often, however not necessarily must this step be followed by biological transport (Fisher and Reinfelder, 1995, Worms et al., 2006).

4. Materials and methods

In this thesis, the sampling sites were in various locations in the Trondheim fjord and several methods were used to get different fractions of metals in order to get a broader picture of the bioactive trace metal distribution.

4.1 Study area

The samples were collected in the Trondheim fjord, which in situated in central Norway. Fjords were created when the sea lever rose it flooded the glacial moraines, and the basins were filled with seawater (Pinet, 2009). The fjord is 135km long with an average depth of 195m (maximum depth is 617m) and has a total volume of 235km^2 and a total area of 1420km^2. The sill separating the fjord from the costal water has a minimum depth where of 195m, which means that there is little restriction for the coastal water to go into the fjord (Öztürk et al., 2002). In fjords the seawater that comes from the ocean will be mixed with freshwater from the rivers, which will lower the salinity in the top layer of the coastal water.

Following there is a map of the aquaculture in the area reported by Fiskeridirektoratet in the end of May 2013 (Figure 4.1a), and maps from the two cruises which show the sampling sites (Figure 4.1b and 4.1c):

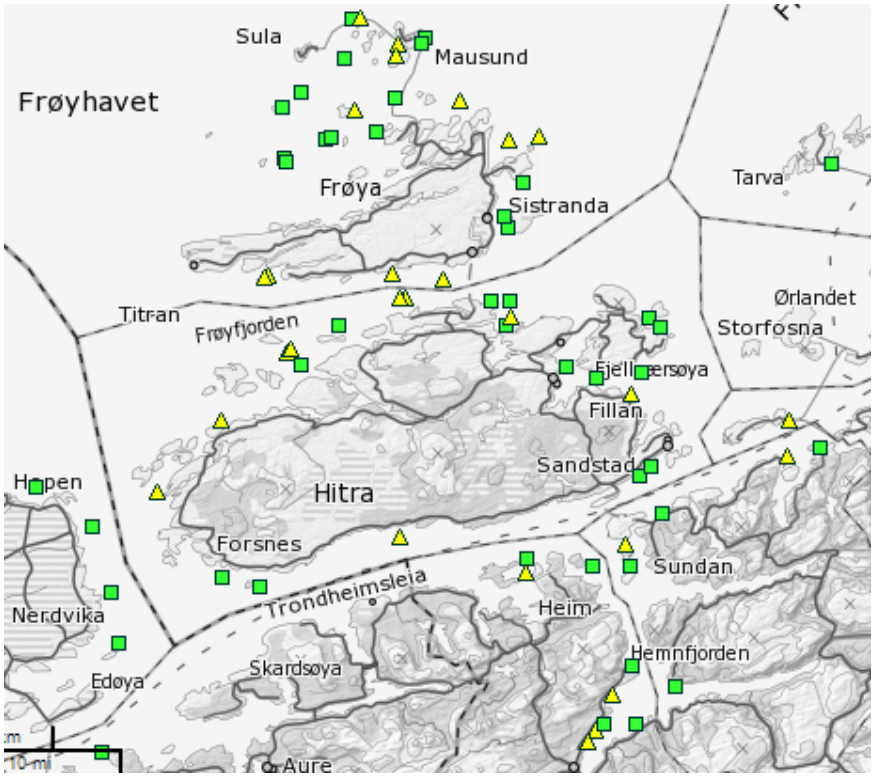


Figure 4.1a: Aquaculture activity reported in the end of May 2013 (Fiskeridirektoratet, 2013). (Green squares: fish at reporting. Yellow triangles: no fish at reporting)

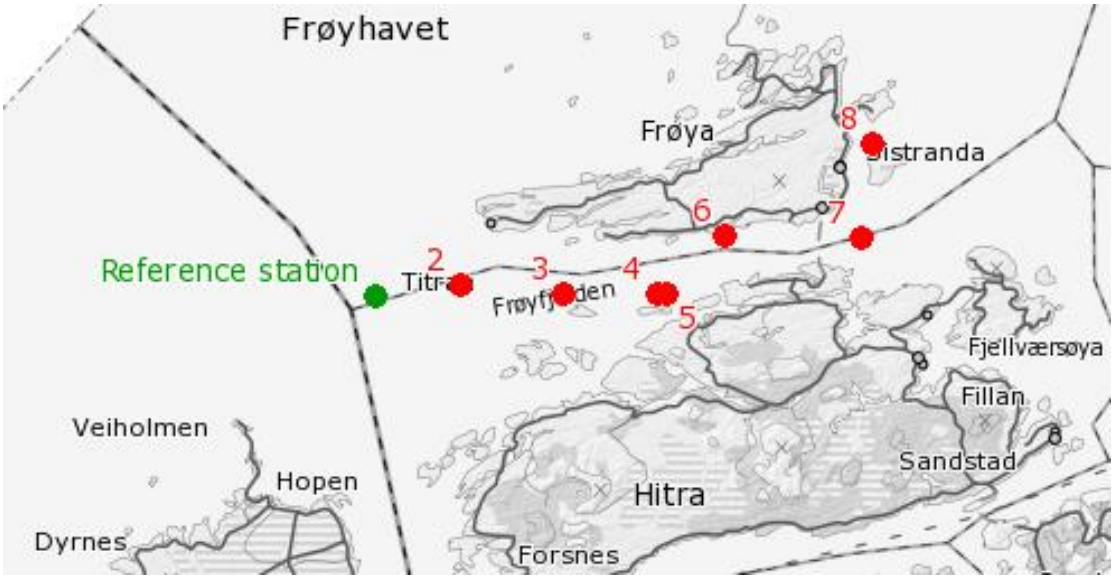


Figure 4.1b: Sampling stations during the first cruise (12-13 Februrary). (2) Vest Frøyfjorden, (3) Vest Torsøya, (4) Vest Langøya, (5) Øst Langøya, (6) Storhallaren, (7) Inntian Nord Frøya, (8) Øst Frøyfjorden.

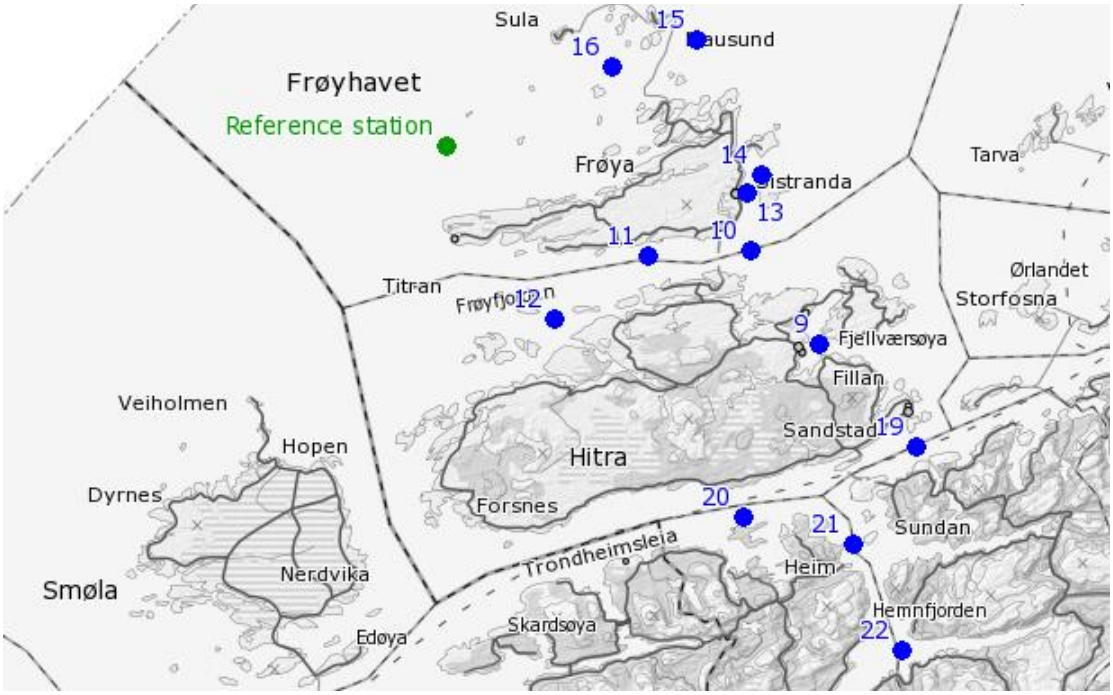


Figure 4.1c: Sampling stations during the second cruise (16-18 April). (9) Fillfjorden, (10) Inntian Nord Frøya, (11) Inntian Frøya, (12) Øst Frøyfjorden, (13) Øst Torsøya, (14) Midt. Frøyfjorden, (15) Sørvest Mausen, (16) Øst Mausen, (19) Nordøst Hemskjel, (20) Nord Røstøya, (21) Vest Jamtøya/Hemnefjorden, (22) Midt. Snillfjord.

At station 21 (Figure 4.1c, Vest Jamtøya/Hemnefjorden, only mentioned as Hemnefjorden from now) the tide was coming in when we took the sample (Kartverket, 2013), therefore we know that this sample is downstream.

4.2 Washing of sample tubes, bottles, chelex resin and DGT units

Direct sample tubes

The Teflon test tubes used for direct sampling of seawater were washed thoroughly with acid. This was done to prevent that contaminants would have bound themselves to the surface of the tube. When you lower the pH, they will release themselves as free ions, and be easier to get out. The tubes were filled with ultrapure (UP) acid (65% HNO_3 distilled from HNO_3 Supur Milestone, approximately 0,6 M) and the acid was kept in the tubes until sampling. Straight before sampling the tubes were emptied and rinsed in sampling water three times, gradually increasing the amount of sampling water.

Chelex bottles, syringe and filter

The bottles (250mL) used for Chelex-100 had been used for seawater samples earlier, and was first rinsed with Milli-Q (MQ) water (18,2 Ω). Then the bottles were filled with ultrapure acid (65% HNO_3 distilled from HNO_3 Supur Milestone, approximately 0,7 M) and left standing over night. The next day the acid was taken out, and the bottles were rinsed with MQ-water three times in a stepwise way, gradually increasing the amount of MQ-water used in the rinsing process. After rinsing the bottles were double bagged to keep them clean till sampling. The bottles were rinsed with the sample prior to filling.

The syringe was filled with UP acid (0,7 M UP HNO_3) and left standing over night. Then it was rinsed three times with MQ-water. The filter was run through with acid (0,7 M UP HNO_3) three times before being rinsed with MQ-water.

Chelex-100 resin

Chelex-100 resin was taken out from its original bottle with a plastic stick and put into and acid cleaned bottle. Ultra pure HNO_3 (3M) was added till it filled the bottle, and the bottle was left on a shaker for 2 hours, since the resin can loose its chelating capacity if left hydrogenated for more than a few hours. The UP acid was emptied and the chelex was rinsed two times in MQ-water. This process was repeated and a little MQ-water was added together with NH_4OH (1M, about 10 mL) till the ammonium smell was present in order to convert it to the NH_4 form. Then just enough MQ-water was added so that it had the right slurry consistence (Ardelan et al., 2010, Öztürk et al., 2002).

DGT bottles

The bottles that the DGTs would be in with the sampled water were also, like the chelex bottles, filled with ultrapure acid (65% HNO_3 distilled from HNO_3 Supur Milestone, approximately 0,7 M) and left standing over night. The next day the bottles were rinsed with MQ-water three times in a stepwise way, gradually increasing the amount of MQ-water used in the rinsing process. After rinsing the bottles were double bagged to keep them clean till sampling. The bottles were rinsed with the sample prior to filling.

DGT units

First two boxes with lids were filled with ultrapure acid (65% HNO_3 distilled from HNO_3 Supur Milestone, approximately 0,7 M) and left standing over night. The next day bottles were rinsed with MQ-water three times in a stepwise way, gradually increasing the amount of MQ-water used in the rinsing process. Then the DGTs were added into the boxes, and UP HNO_3 (approximately 1M) was added. This was placed on a shaker at 60 rpm for two hours and 45 min., followed by rinsing with MQ-water three times. Then the DGTs were treated with ammonium hydroxide (NH_4OH, approximately 0.5M) for an hour on the shaker at 60 rpm. The NH_4OH was used to remove any magnesium and calcium that might have been present in the gel in the DGTs. Then the DGTs were rinsed with MQ-water three times, before being bagged and refrigerated.

Polypropylene centrifuge tubes

When washing the polypropylene centrifuge tubes there is a three-step procedure. First the tubes were put in an acid bath (3M HNO_3), and left standing for three days. Then, in a certified clean lab, the tubes were rinsed gradually four times with MQ-water and filled with ultrapure acid (65% HNO_3 distilled from HNO_3 Supur Milestone, approximately 0,5 M) and left standing for two days. Finally the tubes were rinsed gradually five times with MQ-water prior to use.

4.3 Sampling- and lab procedure

All water sampling was done from the R/V Gunnerus in two cruises. The first cruise was from the 11th of February to the 13th of February. The second cruise was from the 16th of April to the 18th of April. The water samples were collected with an acid-cleaned Teflon-lined GO-FLO (General Oceanic, Florida) bottle for micronutrient determination. The GO-FLO bottles were deployed on trace metal clean polymer 1/400 Sta-Set X linen (New England ropes) line using a dedicated winch (see Figure 4.2). The samples were taken form 10 meters depth to represent the upper layer, where there can be algal growth. The samples from the GO-FLO bottle were drained into UP acid cleaned bottles and tubes.

For macronutrient determination, Niskin (12 x 2,5 liter) bottles were deployed on a CTD-rosette. In addition to collect water samples for measurements, the CTD-rosette also measured conductivity, temperature, and density.

Figure 4.2: Collecting samples with the GO-FLO

Direct samples

The UP acid washed Teflon tubes were pre-conditioned by gradually adding more and more sample water. Direct samples were collected, transferring about 9 mL of seawater from the GO-FLO to acid washed Teflon tubes, and then stored. In the laboratory, three drops of UP 65% HNO_3 was added for a total concentration of about 0,1M HNO_3. Twelve tubes were run for blank analysis. The blanks were made by using Milli-Q water and adding three drops of UP HNO_3.

Chelex-100 samples

UP acid washed plastic bottles (250 mL) were pre-conditioned by gradually adding more and more sample water. Samples of seawater were transferred from the GO-FLO into plastic bottles. Then five drops of Chelex-100 resin was added. The containers were gently shaken (73 rpm) for three days in room temperature before being stored in a refrigerator until extraction to prevent bacterial growth.

The bottles with seawater with Chelex-100 weighed before the content was transferred to funnels and into acid washed Poly-Prep chromatographic columns (see Figure 4.3). The empty bottles were weighed again to find the volume collected. The samples were transferred into separate columns that were washed thoroughly between the applications. The water was tapped out by dripping through plastic tubes and thrown away, whilst the metal containing chelex resin was restrained in the column by the filter.

After most of the water had been removed from the column, it was run through with Milli-Q (5 mL), then with ammonium acetate (0,1M 5 mL) and again with Milli-Q (5 mL). Then a cork was attached to the bottom and UP HNO_3 (2M, 1 mL) was applied. This was left for five minutes, before the column with Chelex-100 was shaken carefully so that all the Chelex-100 was resuspended in the acid. Then the column was left for 15 minuets before the acid was transferred to a new polypropylene centrifuge tube. Then UP HNO_3 (0,25M, 4 mL) was added to the column and left fore five minuets, and the column was again shaken carefully so that all the Chelex-100 was in contact with the acid. After another five minuets the acid was transferred to the tube for a total of 5mL, and the tube was sent to analysis (Ardelan et al., 2010, Öztürk et al., 2002). In total 16 tubes were run for blank analysis, however one of these was a clear outlier and was not used. The blanks were made by using Milli-Q instead of seawater.

Figure 4.3: Chelex-100 samples run through chromatographic columns

Filtration of Chelex-100 samples

At one station, filtration of the samples was performed with a Sartobran cartridge (double layer Sartorius filter with 0.4–0.2 µm pore size). This was done to see if there was a great difference between the concentration of unfiltrated and filtrated samples, since only the smaller particles would get through the pores in the filter. The sample water was sucked in a syringe, and placed on the filter, which was again place over the sample container. After the water had been filtrated through, the same procedure was done as for the other chelex samples.

DGT

Samples of seawater were transferred from the GO-FLO into plastic bottles (2L) that had been were pre-conditioned by gradually adding more and more sample water. In each bottle, a small number of DGT units were placed inside the containers, and the containers were placed on a shaker (73 rpm) for three days. The start and stop time for the shaking process was recorded. The DGTs were taken out of the water sample and stored in a refrigerator till extraction (Ardelan et al., 2009).

In the extraction face the DGTs were opened over a Teflon sheet. The membrane and the gel were removed before the Chelex resin was transferred to an acid washed polypropylene centrifuge tube. Then UP HNO_3 (3M, 1 mL) was added and the samples were placed on a shaker (78 rpm) for 20 hours. Then the acid was transferred to a new acid washed polypropylene centrifuge tube, while the Chelex resin was left in the old tube. Milli-Q water was then added in two steps (first 1 mL, then 3 mL) to the old tube and transferred to the new tube. The tubes were sent to analysis. In total 12 tubes were run for blank analysis. The blanks were made by using DGTs that had been through the same washing procedure, and then opened and had the Chelex resin extracted.

Analysis

For determination of the metal concentration was performed on a HR-ICP-MS (Thermo Finnigan Element 2) by Syverin Lierhagen. Details for the instrument is found in appendix A.

4.4 Diffusive Gradients in Thin film

Diffusive gradients in thin film (DGT) are used to measure labile metal species quantitatively in aquatic systems and the flux (the rate of supply of material over a given time) (Zhang and Davison, 1995). DGT is a suited technique for in situ measurement since it can be configured as a simple, robust plastic device and the concentration is calculated from the measured mass and deployment time (Buffle and Horvai, 2000, Zhang, 2003). Also problems with contamination from filtration processes and collection of the samples are eliminated (International Network for Acid Prevention, 2002, Munksgaard and Parry, 2002). Even though it is not common to acid wash the DGT units, earlier thesis work has shown that the blanks for un-treated DGT units are much higher than for acid washed units, whilst there is no significant difference in the accumulation ability (Slinde, 2011). When the DGT is placed in an aqueous solution, water with its dissolved species will diffuse through a membrane and a gel. Under these two layers there is a Chelex-100 gel, which will then complex with the metal ions (International Network for Acid Prevention, 2002, Munksgaard and Parry, 2002, Zhang, 2003, Zhang and Davison, 1995). The Chelex-100 is a chelating resin that selectively binds to divalent and trivalent metal ions in high concentrations of alkali metals, such as in marine environment (Garmo et al., 2003).

Calculations

In the DGT units, the elements have to pass a film before being able to bind to the resin gel, therefore the laws of diffusion can be applicable to the flux of the ions present in the solution (International Network for Acid Prevention, 2002). Between any solid and liquid, in this case, between the membrane surface and the bulk solution, there is a zone of laminar flow, a diffusive boundary level (DBL). DBL has a thickness of δ and this is where transport of ions is dominated by molecular transport. The DBL adds to the defined length of the sampler, and the form and thickness varies with the shape and dimension of the samples (Buffle and Horvai, 2000, Garmo et al., 2003, International Network for Acid Prevention, 2002, Zhang, 2003). A few minuets after applying the DGTs to the sample, a steady-state linear concentration gradient will be established between the solution and the membrane surface. The flux, J (mol x cm^{-2} x s^{-1}), of an ion though the gel is given by Fick's first law of diffusion (equation 4.1), where D is the diffusion coefficient (cm^2 x s^{-1}) that is unique for each ion, and dC/dx (mol x cm^{-4}) is the concentration of the gradient (Buffle and Horvai, 2000, Zhang, 2003).

$$J = D\frac{dC}{dx} \qquad (4.1)$$

Next is a table presenting the diffusion coefficients used in this thesis.

Table 4.1: Diffusion coefficients of metal ions in the DGT gel at 20°C. No coefficient for molybdenum was found so the coefficient for chromium was used (Zhang, 2003).

Element	D (E-06 cm^2/sec)
Cd	5,30
Co	5,17
Cu	5,42
Fe	5,32
Mn	5,09
Ni	5,02
Zn	5,29
Mo (Cr)	4,39

If the diffusion coefficients of ions through the diffusive gel are the same as in the water, the flux can be described as in equation 4.2, where C (mol x cm^{-3}) is the concentration in the bulk solution of an ion, whilst C´ is the concentration between the Chelex-100 and the diffusive gel (Buffle and Horvai, 2000, Zhang, 2003). This is also shown in Figure 4.4.

$$J = D\frac{C - C'}{\Delta g + \delta} \qquad (4.2)$$

Δg (0,093 cm in this thesis) is the thickness of the diffusive gel layer and the membrane. Equation 4.2 can be simplified if following criteria are met. The solution is well stirred, and then the DBL thickness, δ, is negligibly small compared to the thickness of the diffusive layer. Also if the resin gel is not saturated, the concentration between this and the diffusive gel will be effectively zero (Buffle and Horvai, 2000, Zhang, 2003). This gives equation 4.3:

$$J = \frac{DC}{\Delta g} \qquad (4.3)$$

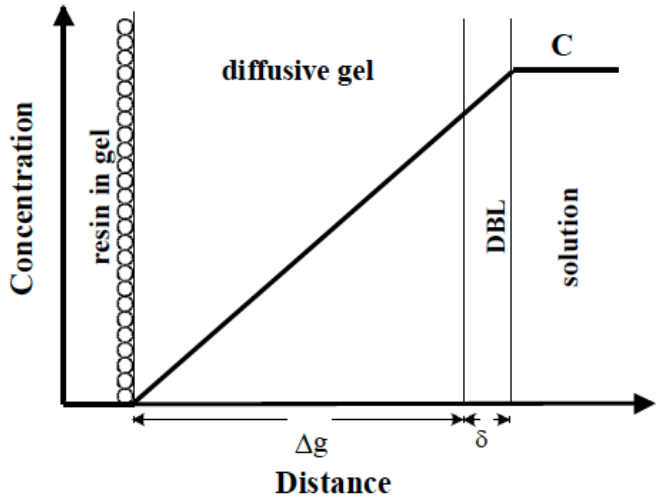


Figure 4.4: Schematic presentation of the DGT device in contact with analyte solution (Buffle and Horvai, 2000, Zhang, 2003).

When the resin gel is collected from the DGT unit after being exploited to the sample, it can be calculated how much of the target compounds were present in the sample. The ions in the resin gel can be eluted with a known volume (V_e, mL) of nitric acid (HNO_3). The concentration of the ions in the eluent (C_e) is measured with a suitable analytical technique (Buffle and Horvai, 2000, Zhang, 2003), in this thesis HR-ICP-MS. The C_e value can be related to the actual concentration of ions in the gel, however, since only a certain ratio of ion will be eluted from the gel during extraction, it must be calculated how much of the analyte ions that are actually extracted. The calculation can be done by using the elution factor (f_e), this factor is found through practical determination and varies for different elements. For Zn, Cd, Cu, Ni and Mn has f_e values of 0,8, and Fe has a reported value of 0,7, when using 1M or 2M HNO_3 to elute from Chelex-100 resin. The accumulated mass (M, in moles) of ions in the binding gel can be theoretically calculated as follows (Buffle and Horvai, 2000, Zhang, 2003):

$$M = \frac{C_e(V_g + V_e)}{f_e} \qquad (4.5)$$

Were V_g (mL) is the volume of binding gel. Using the value of accumulated mass it is possible to calculate the flux through the gel (Buffle and Horvai, 2000, Zhang, 2003):

$$J = \frac{M}{At} \qquad (4.6)$$

Where A (3,14 cm^2) is the area of the diffusive layer and *t* (sec) is the deployment time. From equation 4.3 and 4.6 it is possible to calculate the concentration in the bulk solution, using the known values for Δg, D, A, *t* and M (Buffle and Horvai, 2000, Zhang, 2003):

$$C = \frac{M\Delta g}{DtA} \qquad (4.7)$$

The deployment time of the DGT is important, since it needs to be in contact with the sample long enough for the metals to diffuse, but not too long since the DGT unit then can be susceptible for bacteria growth, which may lead to a biofilm on the outer membrane. This would increase the thickness of the diffusive path, and the DGT-labile metal concentrations calculated would be underestimated proportionally (Dunn et al., 2003).

The construction of a DGT unit

In order to fully understand the how DGTs work, one must be to understand how they are assembled. In Figure 4.5, a schematic view of a DGT water samples is presented.

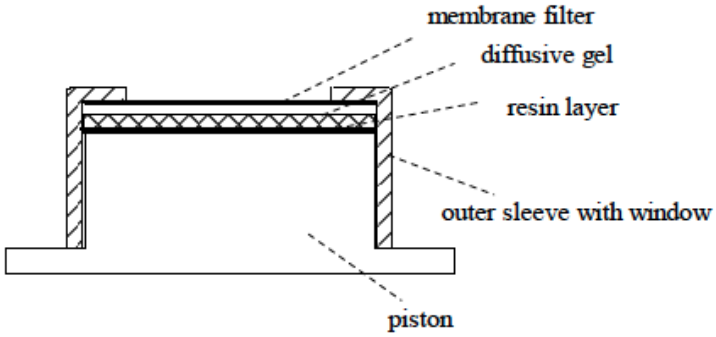


Figure 4.5: Schematic representation of a water sampling DGT unit (Buffle and Horvai, 2000, Zhang, 2003).

The DGT device consists of a plastic piston that keeps the device together. This plastic base is 2,5 cm in diameter, and is filled with a resin gel (0,4 mm), a diffusive gel (0,8 mm) and a membrane filter (0,135 mm) with a pore size of 0,45µm. This is all covered by a plastic cap (outer sleeve), which leaves a window of 2 cm in diameter. The diffusive gel and resin gel comes in discs form (2.5 cm in diameter), and for metals chelex-100 gel is used as resin gel (Zhang, 2003).

4.5 Solid state extraction and pre-concentration of micronutrients with Chelex-100

Stumm and Morgan (1996) define a complexation reaction as a reaction where central atom binds to one or more ligands. The binding of metal to the Chelex-100 is a complexation reaction, where the metal is the central atom and the Chelex-100 resin is the ligand. In this thesis, the Chelex-100 resin is used both as the binding gel inside the DGT units, and as a direct binding agent added to seawater (only non-filtrated in the first cruise, and two filtrated samples in the second cruise). The Chelex-100 is made of styrene divinylbenzene copolymers that contains paired iminodiacetate ions that act as chelating groups in binding polyvalent metal ions (Bio-Rad Laboratories, 2011).

In this complexation, the ligand group (iminodiacetate) is a weak acid, and is therefore dependent on the pH. A change in the pH value may lead to structural change (see Figure 4.6), which may affect its ability to bind metal. The best conditions for absorption of metal ions is above pH 4 and below pH of 10 to 13 (Garmo et al., 2003). In seawater the average pH is around 8,1 (Stumm and Morgan, 1996).

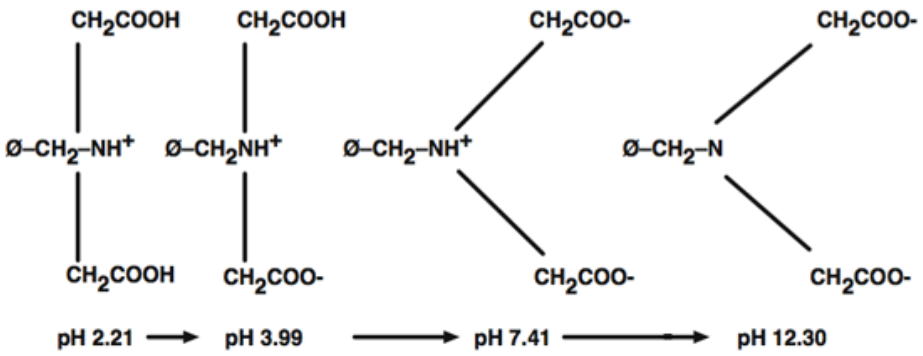


Figure 4.6: Structural change in the Chelex-100 resin with different pH (Bio-Rad Laboratories, 2011).

When using Chelex-100, the principle behind the complexation is ion exchange. Any metal that is taken up by the Chelex-100 from the solution will be replaces with an equal amount of ions that originally was attached to the Chelex-100 resin. The most common is to use sodium, but other alkali metals like potassium can be used as well. These are weakly held ions that can readily be exchanged for ions with higher affinity to the Chelex-100 resin (Bio-Rad Laboratories, 2011).

The following reactions (4.8 – 4.10) for the complexation between metal, metal-ligand complex and Chelex-100 are discussed in Zhang and Davidson (1995). With a simple equilibrium, the speciation between a free metal (M) and a ligand (L) can be represented:

$$M + L \leftrightarrow ML \qquad (4.8)$$

The ligand exchange can be very rapid, so both the metal and the metal-ligand complex can react with the resin (Res):

$$M + Res \rightarrow MRes \quad (4.9)$$

$$ML + Res \rightarrow MRes + L \quad (4.10)$$

The Chelex-100 inside the DGT units will complex with free metal ions and the metal complexes that are both labile and mobile. Before the Chelex-100 is able to react with the metal, the species has to be able to diffuse through the membrane and the gel layer (Warnken et al., 2005). The free metals will diffuse through the membrane and the gel layer and react with the resin as seen in reaction (4.9). The smaller complexes that are able to go past the diffusive gel layer and the membrane will go through an ion exchange as described in reaction (4.10) when it binds to the Chelex-100 resin. Chelex-100 is a strong binding agent, and therefore it can "induce" lability because of its functional group, iminodiacetic acid. The metals will then generally prefer binding to iminodiacetic acid that to its natural ligand (Zhang and Davison, 1995). The most effective way to remove the metals from the Chelex-100 is to elute them from the resin with acids (Bio-Rad Laboratories, 2011).

4.6 ICP-MS

Inductively coupled plasma-mass spectrometry (ICP-MS) is an analytical technique for determining elements (Taylor, 2001, Wolf, 2005). This technique is often used for trace metals due to its wide detection limits, from the lower end at sub parts per trillion (ppt) to the higher end with parts per million (ppm) (Thomas, 2004).

The use of high resolution allows the user to eliminate or reduce the interferences due to mass overlap. Figure 4.7 shows a typical instrumental configuration used in high resolution (HR) ICP-MS.

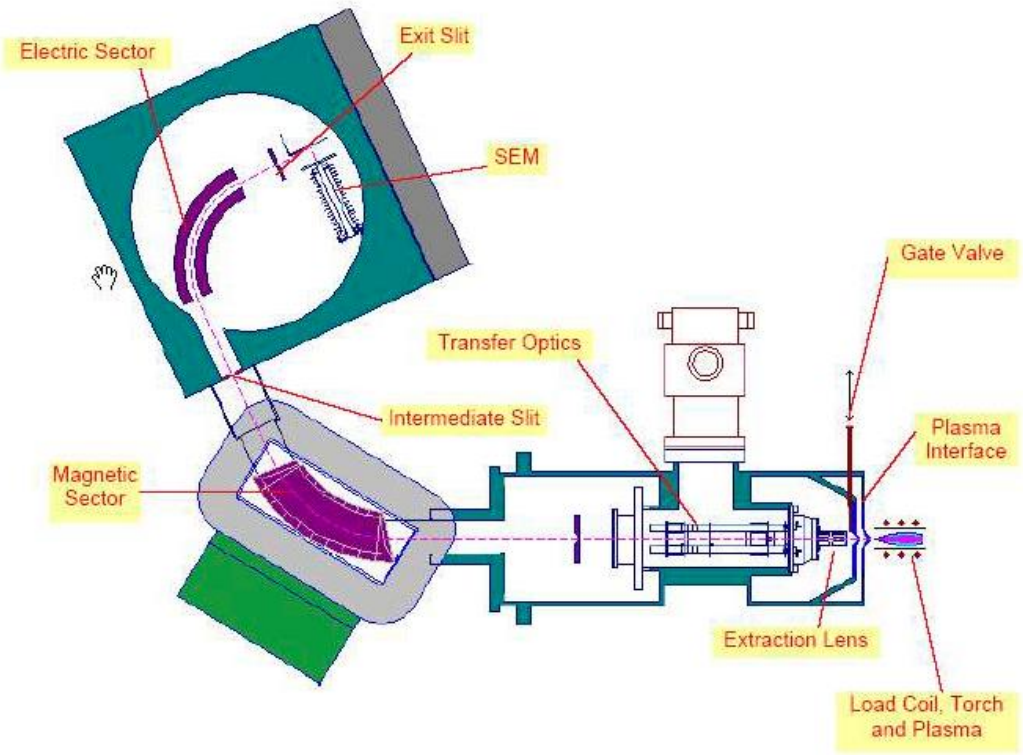


Figure 4.7: Model of the HR-ICP-MS system showing the different components (Wolf, 2005).

Sample Introduction

When using the ICP-MS the samples must be converted to a suitable form before being introduced to the plasma where the ionisation takes place (Taylor, 2001).The first step in the mass spectrometric analysis of compounds is to produce gas-phase ions of the compound by electron ionisation (Hoffmann and Stroobrant, 2007):

$$M + e^- \rightarrow M^{\bullet +} + 2e^- \qquad (4.11)$$

In this thesis, all the samples where liquid. A nebulizer converts the liquid samples in to an aerosol that consists of finely divided droplets. A spray chamber is used to narrow the distribution of droplet sizes being introduced to the plasma (Taylor, 2001). The large droplets (10 µm) will be removed by gravity and exit through a drain tube at the end of the spray chamber (Thomas, 2004), this is because the plasma is inefficient at dissociating large droplets (Thomas, 2001). The smaller droplets (<10 µm) are transported to the plasma carrier gas (Taylor, 2001).

Plasma

Inductively coupled plasmas are one of the most used plasmas today. A gas, usually argon, is used to form the plasma. While the gas is flowing thorough the torch, a high voltage spark is applied and some electrons will be stripped from the atom. These electrons will be caught up and accelerated by the magnetic field, colliding with other atoms, which will form more ions. This collision-induced ionisation will continue in a

cascade reaction, breaking the gas into atoms, electrons and ions forming the inductively coupled plasma discharge (Thomas, 2001).

The plasma has zones with different temperatures and the sample is ionised when passing through the plasma. First the sample enters the preheating zone where the solvent in the aerosol is stripped away and the sample is left as a small solid particle. Moving further in the plasma the particle will change into a gaseous form before it changes into a ground state atom. Then the atoms will be transformed into ions due to the collision with free energetic argon electrons present in the plasma (Thomas, 2004).

Introduction to the analysing region

In the interface region the ions produced in the plasma should be transported to the mass spectrometer analysing area. The interface consists of two cones with very small orifices. The first cone is called the sampler cone and has an orifice between 0,8 – 1,2 mm in diameter, this makes a beam of ions that travel a short distance before reaching the skimmer cone with an even smaller diameter (0,4 – 0,8 mm). When the ions have passed through the skimmer cone they are directed through the ion optics before being led into the mass separation device. Since the orifices are so small, it is important that the total dissolved solids (TSD) is not grater than 0,2% (Thomas, 2004). If samples with higher TSD are run, the cones will eventually be blocked causing the instrument to be shut down for maintenance due to decreased sensitivity and detection capability (Wolf, 2005). A dual vacuum system is used to reduce the pressure from the plasma to the required working pressure for the mass spectrometer. Between the sampler and the skimmer cone there is a pressure of about 1 Torr with a mechanical vacuum pump. Behind the skimmer cone the pressure is reduced to 10^{-5} Torr (the normal working pressure for the mass spectrometer) with an oil diffusion or turbomolecular pump (Taylor, 2001).

To assist the transport of positively charged ions from the interface region, ion lenses are used. The ion beam enters the mass spectrometer and a negatively charged extraction electrode is used to attract the positive ions and transport them into the electrostatic lens assembly. The first component of an ion lens set is often a metal disk called a photon stop. This component prevents photons and energetic neutral species produced by the plasma to enter the mass analyser, and therefore reduces the background signal. The assembly will the further focus the ion beam and prepare it for ion analysis by the mass spectrometer (Taylor, 2001).

Mass analyser

In a mass analyser the ions of different atomic masses are separated to produce a mass spectrum (Skoog et al., 2004). In this thesis a double focusing instrument was used, which means that ions passed through both a magnetic sector and an electrostatic sector, which leads to a significant improvement in resolution (Taylor, 2001) by reducing interference due to mass overlap (Wolf, 2005).

First the magnetic sector will separate ions according to their m/z (mass to charge ratio) (Taylor, 2001). This is done by varying the magnetic field over time with a fixed acceleration voltage (Thomas, 2004). After that an electrostatic analyser will filter the ions according to their kinetic energy. The result is narrow and separated peaks, which makes it possible to detect very small quantities (Taylor, 2001).

Interference

In all analytical techniques there is interference and in ICP-MS there are two basic categories: spectroscopic and non-spectroscopic interference. Spectroscopic effects impact the measurement of specific isotope ion currents in the mass spectrum (see Table 4.3), whilst non-spectroscopic effects are various physical and chemical interference that can seriously impact the accuracy of ICP-MS analyses (Taylor, 2001).

Table 4.3: Examples of overlapping species in ICP-MS (Wolf, 2005).

Analyte	Interference
$^{75}As = 74.92160$	$^{40}Ar\,^{35}Cl = 74.93123$
$^{52}Cr = 52.94065$	$^{37}Cl\,^{16}O = 52.96081$
$^{56}Fe = 55.93494$	$^{40}Ar\,^{16}O = 55.95729$
$^{40}Ca = 39.96259$	$^{40}Ar = 39.96238$
$^{87}Sr = 86.90889$	$^{87}Rb = 86.90918$

There are four main types of mass spectrometric interferences: isobaric spectral overlap, multiple charged species, background contributions to the measurement of the ion current and one of the most common types, the polyatomic molecular spectral overlap (Taylor, 2001). This interference is caused by the combination of two or more atomic ions. For example, even though argon is an inert gas and is one of the most used gasses for the plasma, the spectral overlaps caused by argon ions and argon combined with other ion species is very common. In argon gas the major isotope has m/z 40, which is the same as both $^{40}K^{+}$ and $^{40}Ca^{+}$. This will make the determination of these elements impossible, even when using HR-ICP-MS (Taylor, 2001, Thomas, 2004).

However, as mentioned earlier the spectral interference is greatly reduced or eliminated when using an HR-ICP-MS compared to a quadrupole ICP-MS (Wolf, 2005). One can also compensate for spectral interference by eliminating the matrix or by mathematical corrections (Thomas, 2004).

There are two main types of non-spectrometric effects: matrix effects and physical effects. The matrix effect can be seen when the concentration of the target compounds is low compared to the concentration of matrix constituents. The effect can be shown

as a suppression of the ion current of analyte species. These suppression effects can be reduced to an insignificant level by reducing the absolute concentration of the matrix. There are several physical effects like excess of total dissolved solids and cross-contamination of samples. Dissolved solids may build up and block the system, while cross-contamination of different samples may cause problems when detecting contamination in one sample that was originally a major component in the precious sample run on the system (Taylor, 2001).

4.7 Blanks and limits of detection

The limit of detection or sensitivity is a part of the quality control and is defined as the lowest concentration level that is statistically different from the instrumental blank value. The limit of detection is rarely limited by the sensitivity of the analytical instrument, but rather by the level and variability of the blank value, that might have been contaminated by impurities introduced with reagents, apparatus, air, procedural steps and/or the instrumental variation (Grasshoff et al., 1983). The detection limit used in this thesis was calculated by multiplying the standard deviations obtained from the blank values by three.

In this thesis it was chosen to report all values that lie above the blank value detected. The reported values are therefore the values obtained from the HR-ICP-MS subtracted the blank values and then calculated to nanomoles per liter. The detection limits are given as an addition to the method evaluation. Both the blank values, standard deviation and detection limits are presented in table 4.3 – 4.8. The detection limits for the direct samples was found by taking three times of standard deviation for the blanks, times ten (due to a ten times dilution). The methodical detection limits for the chelex-100 was found by taking three times of standard deviation for the blanks, divided by fifty (due to preconcentration factor of 50 (metals in 250mL samples were preconcentrated to final volume, 5mL). The methodical detection limit for DGT are calculated from equation 4.7, based on three times standard deviation of the blanks and three days exposure time for the DGT units (Ardelan et al., 2009).

Table 4.3: First cruise, Direct samples

Element	Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]
Fe	0,3987	0,4082	12,246
Mo	0,0173	0,0699	2,097
Mn	0,0336	0,0521	1,563
Cu	0,3896	0,6147	18,441
Co	0,0173	0,0189	0,567
Zn	1,1310	1,4063	42,189
Cd	0,0261	0,0105	0,315

Table 4.4: First cruise, Chelex

Element	Methodical Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]
Fe	3,6614	2,6142	0,1569
Mo	0,0146	0,0089	0,0005
Mn	1,4707	1,0392	0,0624
Cu	0,0929	0,0400	0,0024
Co	0,0083	0,0058	0,0003
Zn	3,4058	2,7300	0,1638
Cd	0,0011	0,0011	0,0001

Table 4.5: First cruise, DGT

Element	Methodical Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]	Diffusion coefficient at 20° Celsius (cm^{-2} s^{-1}) 10^{-6}
Fe	1,5851	0,5816	0,19	5,32
Mo	0,0105	0,0044	0,0054	4,39
Mn	0,1325	0,0772	0,0199	5,09
Cu	0,3213	0,2692	0,0578	5,42
Co	0,0125	0,0026	0,0188	5,17
Zn	3,7431	2,1965	0,5615	5,29
Cd	0,0003	0,0003	0,0007	5,3

Table 4.6: Second cruise, Direct samples

Element	Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]
Fe	0,5874	0,6709	20,127
Mo	0,0413	0,0287	0,861
Mn	0,0692	0,0662	1,986
Cu	0,0646	0,6304	18,912
Co	0,0254	0,0178	0,534
Zn	0,8739	1,4063	42,189
Cd	0,0001	0,0080	0,024

Table 4.7 Second cruise, Chelex

Element	Methodical Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]
Fe	0,5426	0,3459	0,0208
Mo	0,0033	0,0024	0,0001
Mn	0,0948	0,1119	0,0067
Cu	0,0672	0,0300	0,0018
Co	0,0020	0,0018	0,0001
Zn	1,6200	0,8803	0,0528
Cd	0,0346	0,0174	0,0010

Table 4.8: Second cruise, DGT

Element	Methodical Blank [nM]	Standard Deviation [nM]	Detection Limit [nM]	Diffusion coefficient at 20° Celsius (cm^{-2} s^{-1}) 10^{-6}
Fe	3,4396	0,6488	0,41	5,32
Mo	0,0180	0,0038	0,0092	4,39
Mn	0,6010	0,1964	0,0902	5,09
Cu	0,1369	0,0217	0,0246	5,42
Co	0,0026	0,0010	0,0039	5,17
Zn	3,1401	1,4570	0,4710	5,29
Cd	0,0010	0,0004	0,0023	5,3

Washing method and Clean lab

Before using any equipment is was properly acid washed. This was to prevent particles stuck to the surface of the equipment to contaminant the samples. The protons in the acid would compete with the particles so the particles would be suspended in the solution. The acid was poured out and the equipment was rinsed gradually with Milli-Q water. This was done to first, remove suspended particles, and then it was rinsed in case not all particles were removed the first time. The reason for the rinsing process to be gradually is so that the pH will not increase too rapidly, causing the particles to reattach, but to still keep it low so that the particles will be rinsed out.

The samples were processed at a Class-100 clean lab at the chemistry department at NTNU, since dust particles can be a great contamination source.

5. Results

All the results are presented in nanomoles per liter (nM). All samples had parallels, but if some of the parallels were clear outliers, they were removed before the results were presented. This was done to reduce contamination in the result presentation. For samples were the parallels are available, standard deviations are presented with the results.

The results for the DGT samples from the ICP-MS in both µg/L and nmol/L can be found in tables in appendix B.1. For the DGT samples, 6 blanks were run for both cruises. For the first cruise blank 2 was removed for zinc due to a very high value.

The results for the chelex-100 samples from the ICP-MS in both µg/L and nmol/L can be found in tables in appendix B.2. For the chelex samples, 7 blanks were run for the first cruise and 9 were run for the second cruise. Following blanks were removed due to very high values: For the first cruise blank 1 was removed for Mn and Zn, whilst blank 2 was removed for Mn, blank 6 removed for Mn and blank 7 removed for Zn. For cruise two blank 3 was a clear outlier and removed all together. Blank 4 was also removed for Fe.

The concentrations found with the chelex-100 and DGT samples can be viewed as a snapshot of the concentration of labile metals at the time and location of sampling. Since the chelex-100 sample water is not filtrated, particles in the water sample might be competing with the chelex-100 resin to remove the dissolved fraction of particle reactive metals from sample. This will create an uncertainty in the results, and the results may be lower that the actual concentration in the water sample.

The results for the direct samples from the ICP-MS in both µg/L and nmol/L can be found in tables in appendix B.3. For the direct seawater samples, 5 blanks were run for the first cruise and 7 in for the second cruise. One blank value for zinc was removed for the second cruise due to a very high value.

5.1 Metals

Here the results for the metals are presented, individually.

Iron

DGT: The concentrations decreased from the first to the second cruise and all values were below the reference station in the first cruise. The DGT labile concentration fluctuates from 1 nM (Fillfjorden, 16.04) to 9,5 nM (reference station, 12.02), (Figure 5.1).

Chelex-100: The concentration decreased from the first to the second cruise and in the second Cruise, all values were higher than the reference value. The chelex-100 labile concentration ranged from 0,3 nM (reference station, 17.04) to 17,2 nM (Vest Frøyfjorden, 12.02), (Figure 5.2).

Direct: The concentrations decreased from the first to the second cruise. The acid leachable concentration varied from 9,6 nM (Øst Mausen, 17.04) to 93,5 nM (Øst Frøyfjorden, 13.02), (Table 5.1).

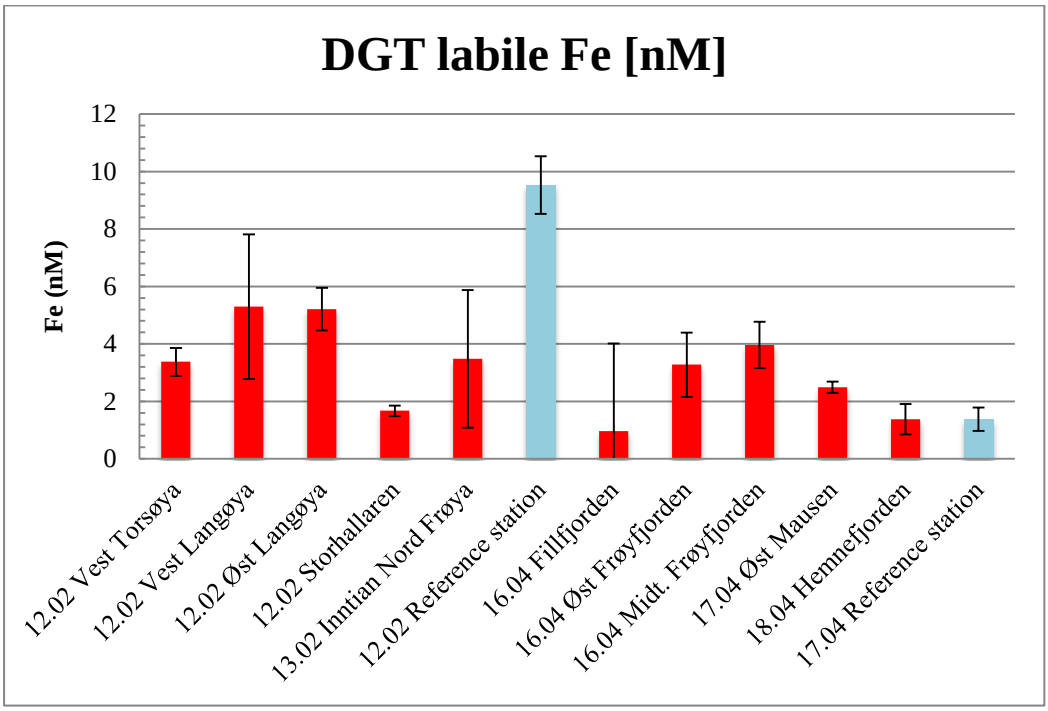


Figure 5.1: The concentration of DGT labile iron

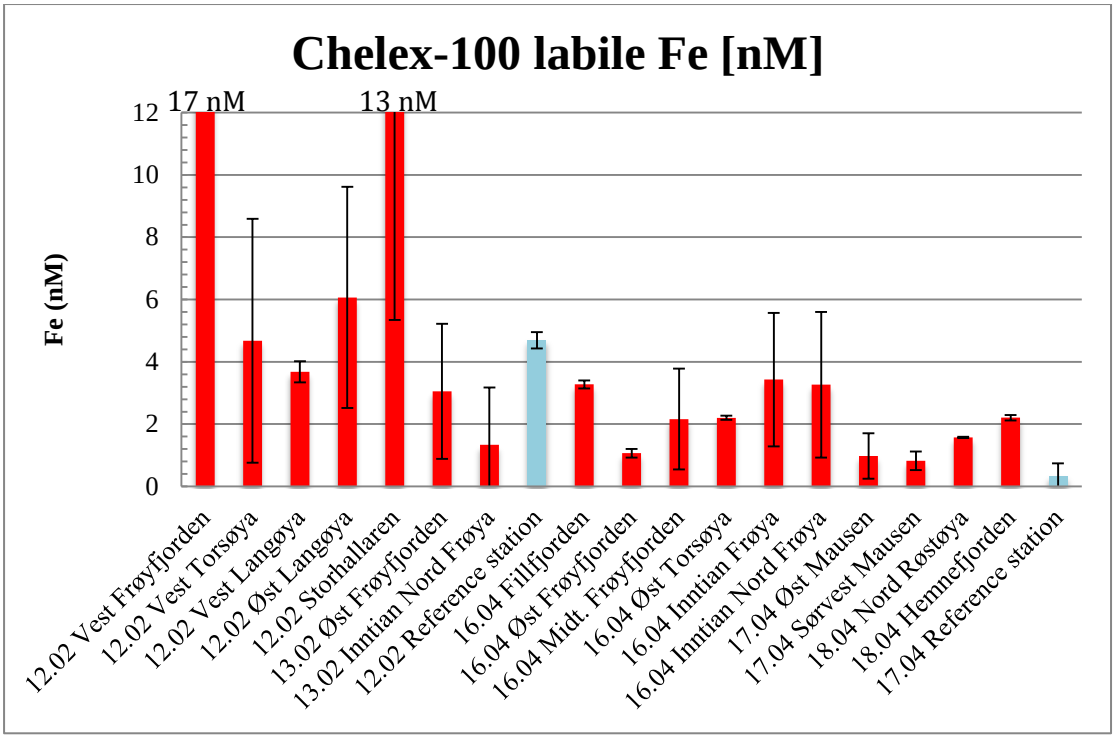


Figure 5.2: The concentration of chelex-100 labile iron

Molybdenum

DGT: The concentrations were fairly similar for both the first and the second cruise. All values are below the reference station in the first cruise. The DGT labile concentration fluctuates from 0,3 nM (Hemnefjorden, 18.04) to 0,5 nM (Fillfjorden 16.04), (Figure 5.3).

Chelex-100: There was a decrease in the concentration from the first to the second cruise. The chelex-100 labile concentration ranged from 0,01 nM (Øst Torsøya, 16.04) to 0,16 nM (Vest Frøyfjorden, 12.02), (Figure 5.4).

Direct: There was a slight decrease in concentration from the first to the second cruise. The acid leachable concentration varied from 104,9 nM (Nordøst Hemskjel, 18.04) to 120,4 nM (Vest Langøya, 12.02), (Table 5.1).

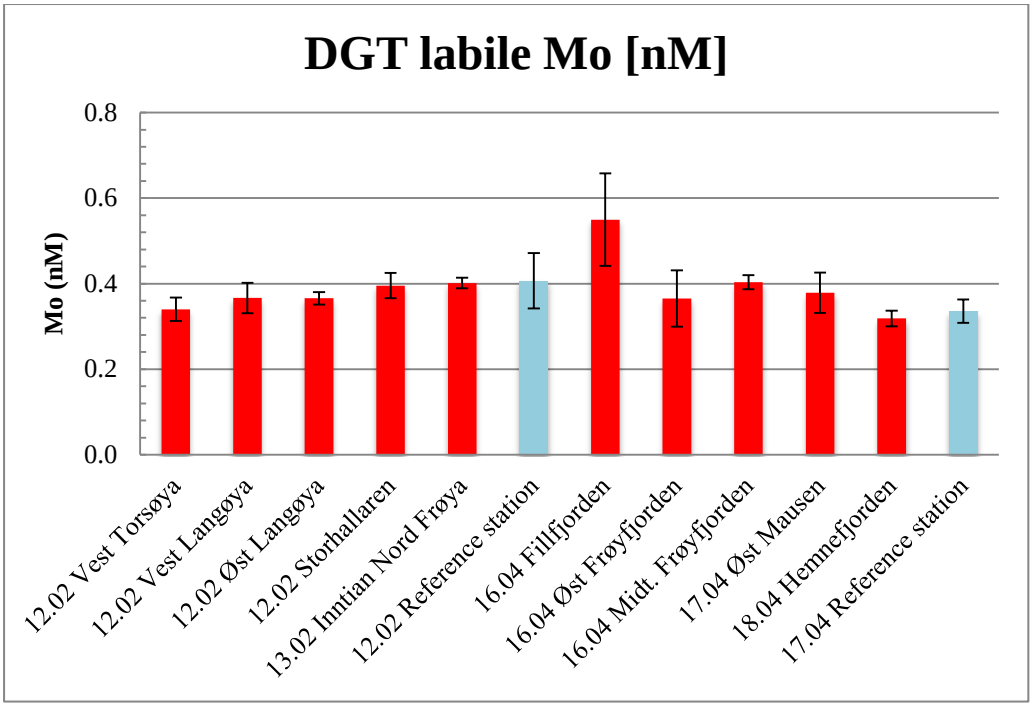


Figure 5.3: The concentration of DGT labile molybdenum

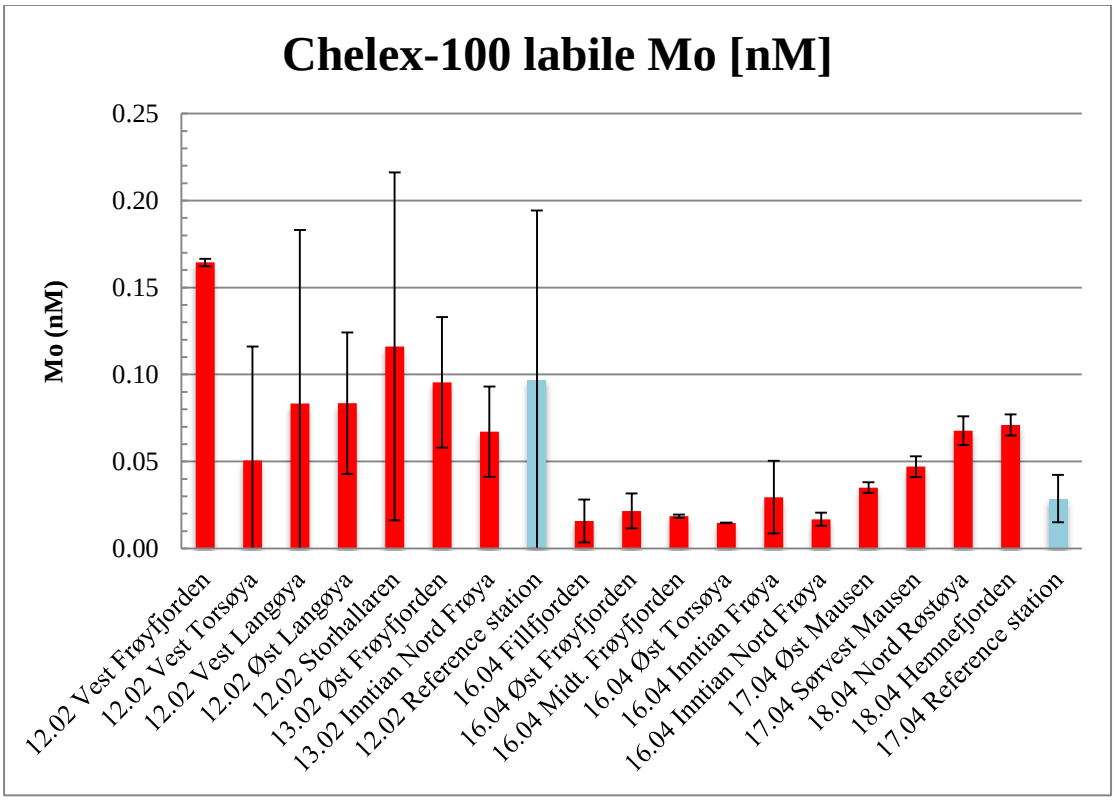


Figure 5.4: The concentration of chelex-100 labile molybdenum

Manganese

DGT: The concentrations were fairly similar for both the first and the second cruise. All values were below the reference station in the first cruise, and above in the second. The DGT labile concentration fluctuates from 2,2 nM (Vest Torsøya, 12.02) to 6,7 nM (Hemnefjorden 18.04), (Figure 5.5).

Chelex-100: Station Vest Frøyfjorden was removed due contamination. The concentration had a slight visual increase from the first to the second cruise. In the second cruise, all values were higher than the reference value. The chelex-100 labile concentration ranged from 0,5 nM (Vest Langøya, 12.02) to 6,0 nM (Inntian Nord Frøya, 13.02), (Figure 5.6).

Direct: With some exceptions there is a general decrease in concentration from the first to the second cruise. In the second cruise, all values were higher than the reference value. The acid leachable concentration varied from 8,2 nM (Reference station, 17.04) to 16,3 nM (Midt. Snillfjord, 18.04), (Table 5.1).

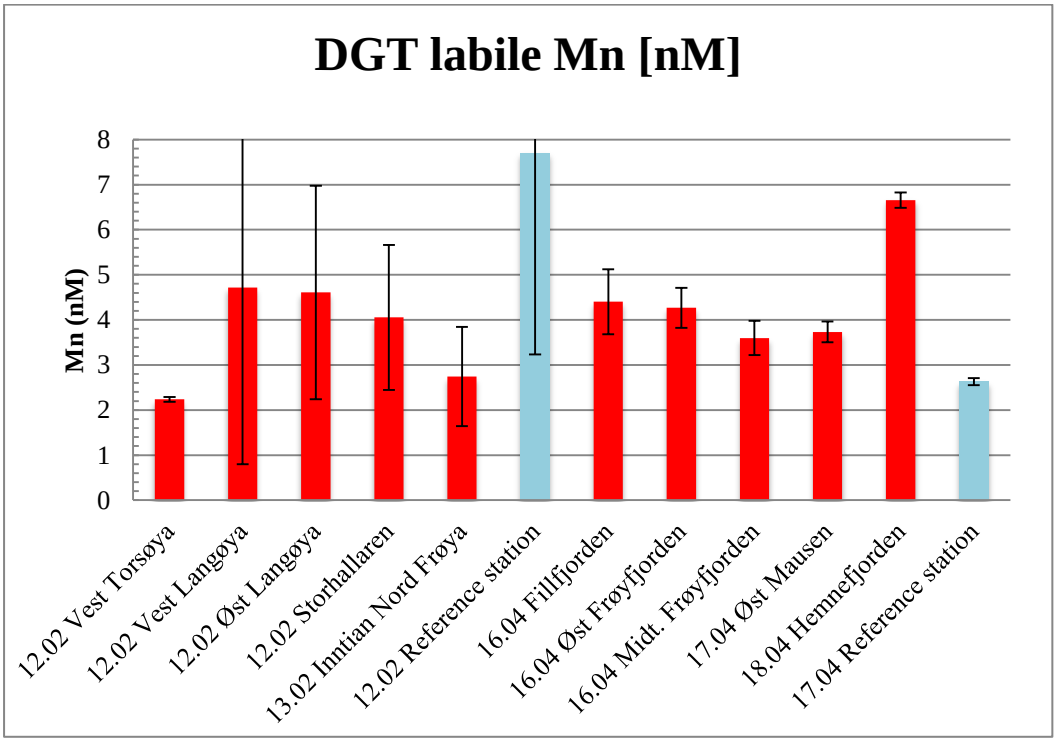


Figure 5.5: The concentration of DGT labile manganese

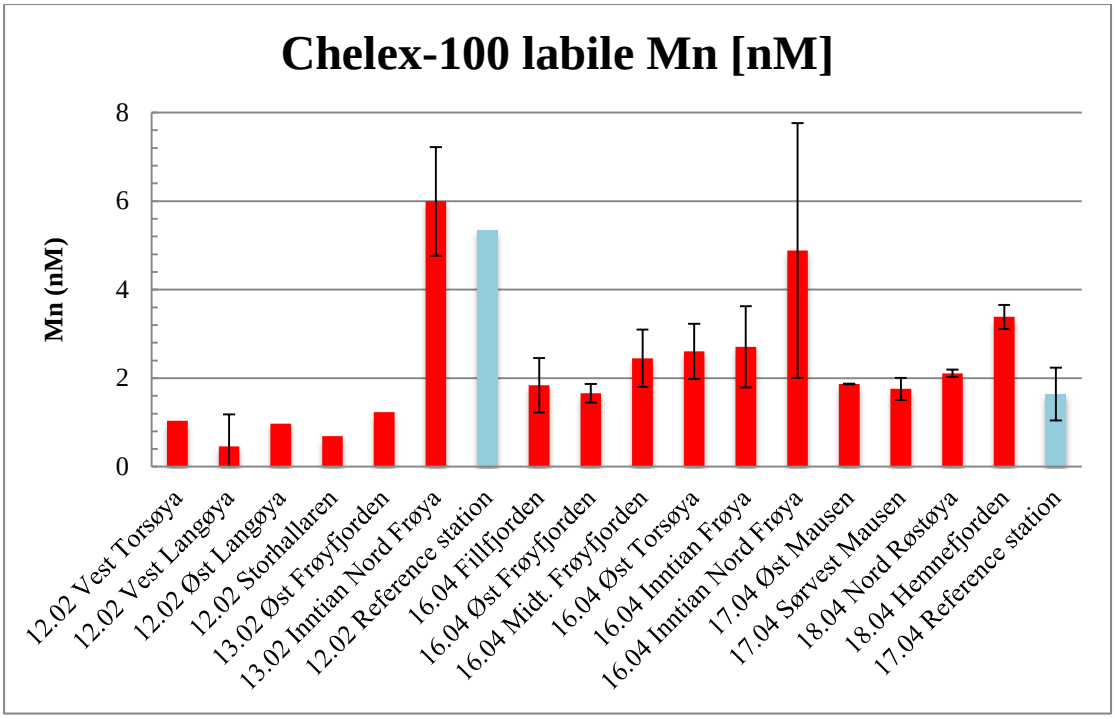


Figure 5.6: The concentration of chelex-100 labile manganese

Copper

DGT: The concentrations decreased from the first to the second cruise and all values were below the reference station in the first cruise and above in the second. The DGT labile concentration fluctuates from 0,5 nM (Reference station 17.04) to 1,6 nM (Fillfjorden, 16.04), (Figure 5.7).

Chelex-100: Fairly similar concentrations with some exceptions. In the second cruise, all values were higher than the reference value. The chelex-100 labile concentration ranged from 0,3 nM (reference station, 17.04) to 1,2 nM (Inntian Frøya, 16.04), (Figure 5.8).

Direct: Fairly varying values with a slight visual decrease from the first to the second cruise, and a visual decrease from the first to the last station within the first cruise. All values were greater than the reference in the first cruise. The acid leachable concentration varied from 0,4 nM (reference station, 12.02) to 9,2 nM (Øst Langøya, 12.02), (Table 5.1).

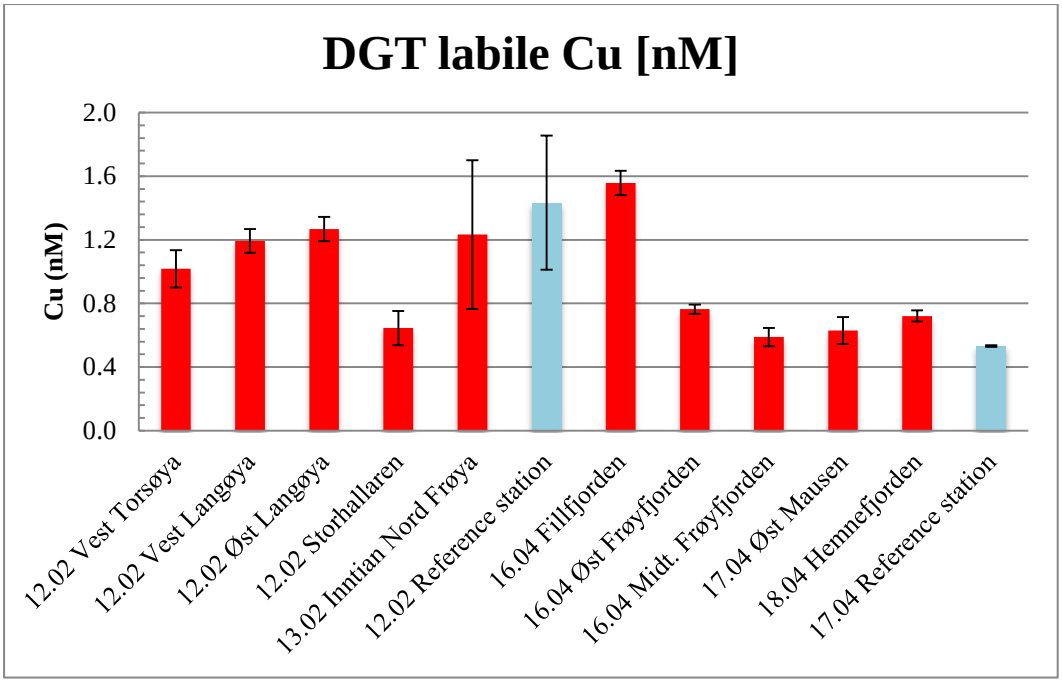


Figure 5.7: The concentration of DGT labile copper

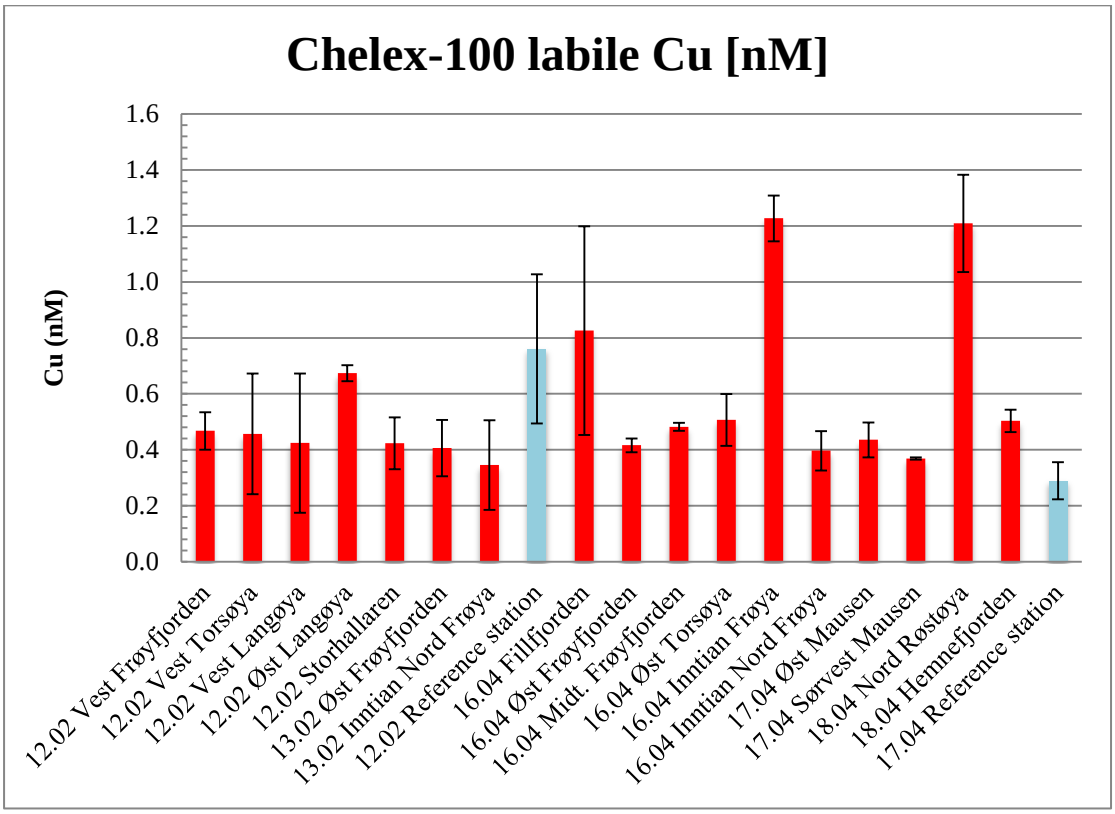


Figure 5.8: The concentration of chelex-100 labile copper

Cobalt

DGT: Fairly similar values. Most values were below the reference station in the first cruise, and above the reference station in the second. The DGT labile concentration fluctuates from 0,06 nM (Reference station 17.04) to 0,13 nM (Vest Langøya, 12.02), (Figure 5.9).

Chelex-100: Varying results with no clear trend. The chelex-100 labile concentration ranged from 0,03 nM (Vest Langøya, 12.02) to 0,16 nM (Inntian Nord Frøya, 16.04), (Figure 5.10).

Direct: There is a slight decrease from the first to the second cruise and all stations except one is has values below the reference station in the first cruise. The acid leachable concentration varied from 0,3 nM (Inntian Frøya, 16.04) to 0,7 nM (reference station, 12.02), (Table 5.1).

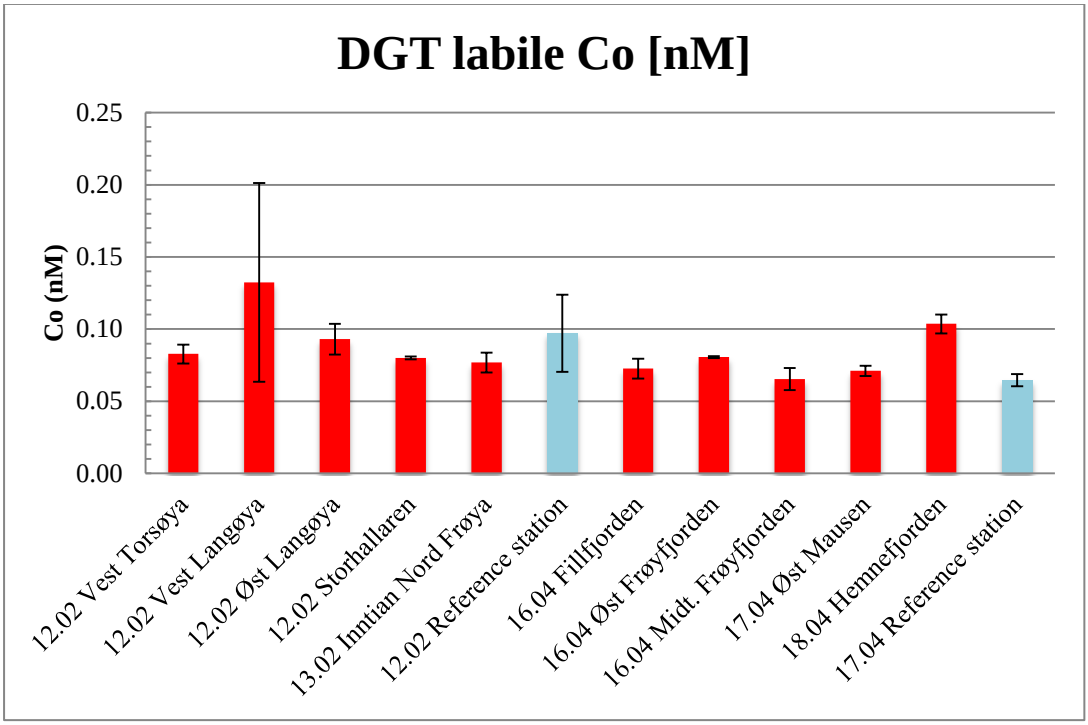


Figure 5.9: The concentration of DGT labile cobalt

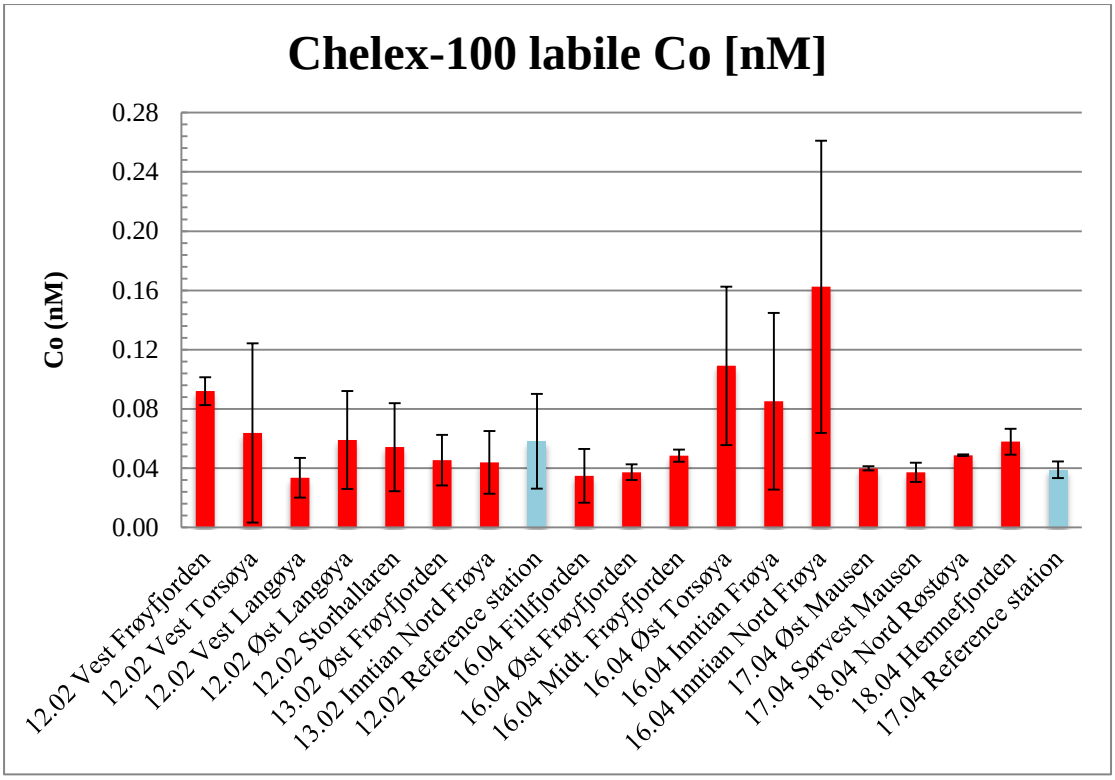


Figure 5.10: The concentration of chelex-100 labile cobalt

Zinc

DGT: Very varying results, but overall the values are lower in the second cruise. Most samples are below the concentration for the reference station in the first cruise, and above in the second. The DGT labile concentration fluctuates from 1,0 nM (Reference station 17.04) to 19,2 nM (Øst Frøyfjorden, 16.04), (Figure 5.11).

Chelex-100: Samples for station Øst Torsøya, Inntian Frøya and Inntian Nord Frøya were removed due to contamination. In the first cruise, the highest value were the same as the reference value. The chelex-100 labile concentration ranged from 0,7 nM (Vest Langøya, 12.02) to 8,3 nM (Midt. Frøyfjorden, 16.04), (Figure 5.12).

Direct: There is a decrease from the first to the second station. The acid leachable concentration varied from 2,9 nM (Øst Mausen, 17.04) to 20,5 nM (Vest Frøyfjorden, 12.02), (Table 5.1).

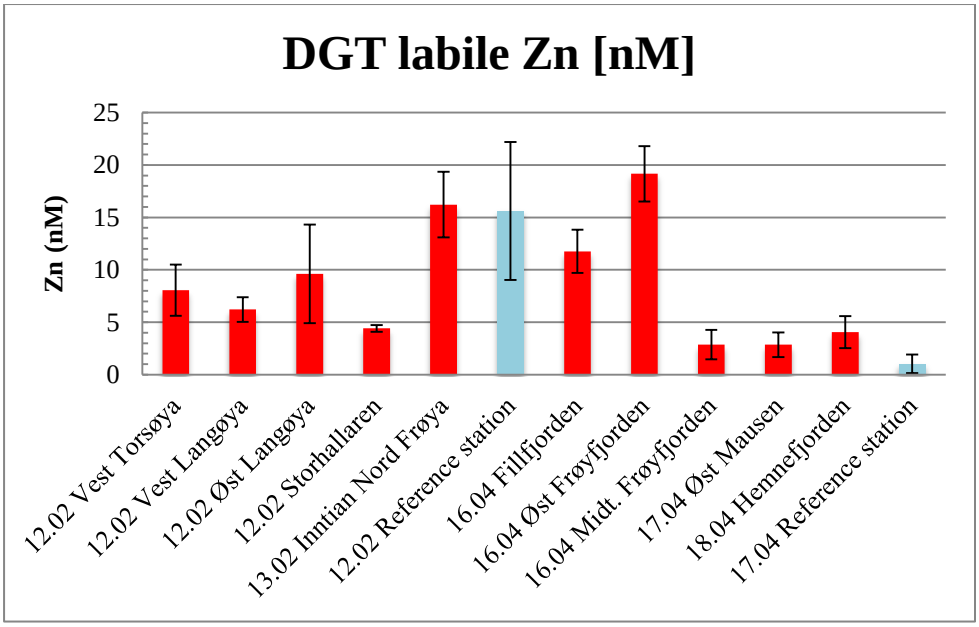


Figure 5.11: The concentration of DGT labile zinc

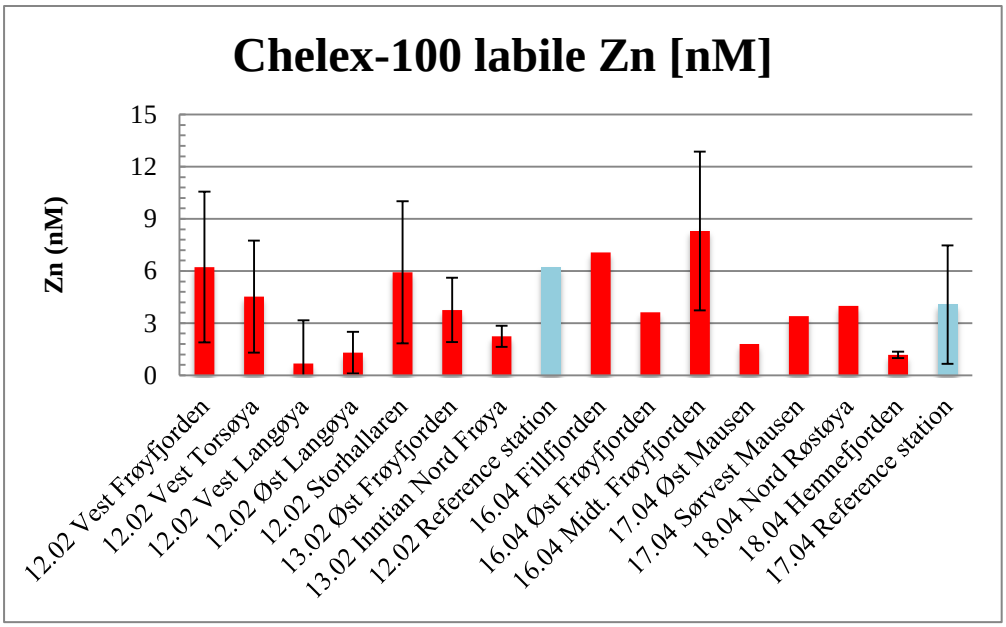


Figure 5.12: The concentration of chelex-100 labile zinc

Cadmium

DGT: There is a slight increase in the concentration from the first to the second cruise. In the first cruise, the highest values are the same as the reference station. In the second cruise, all values were higher than the reference value. The DGT labile concentration fluctuates from 0,07 nM (Vest Langøya 12.02) to 0,09 nM (Øst Frøyfjorden, 16.04), (Figure 5.13).

Chelex-100: The value for the second reference station was removed due to contamination. In the first cruise, the highest values were the same as the reference station. The chelex-100 labile concentration ranged from 0,01 nM (Øst Frøyfjorden, 16.04) to 0,04 nM (reference station, 12.02), (Figure 5.14).

Direct: There was a clear increase in the concentration from the first to the second cruise. The acid leachable concentration varied from 0,3 nM (Øst Langøya, 12.02) to 0,7 nM (Fillfjorden, 16.04), (Figure 5.15).

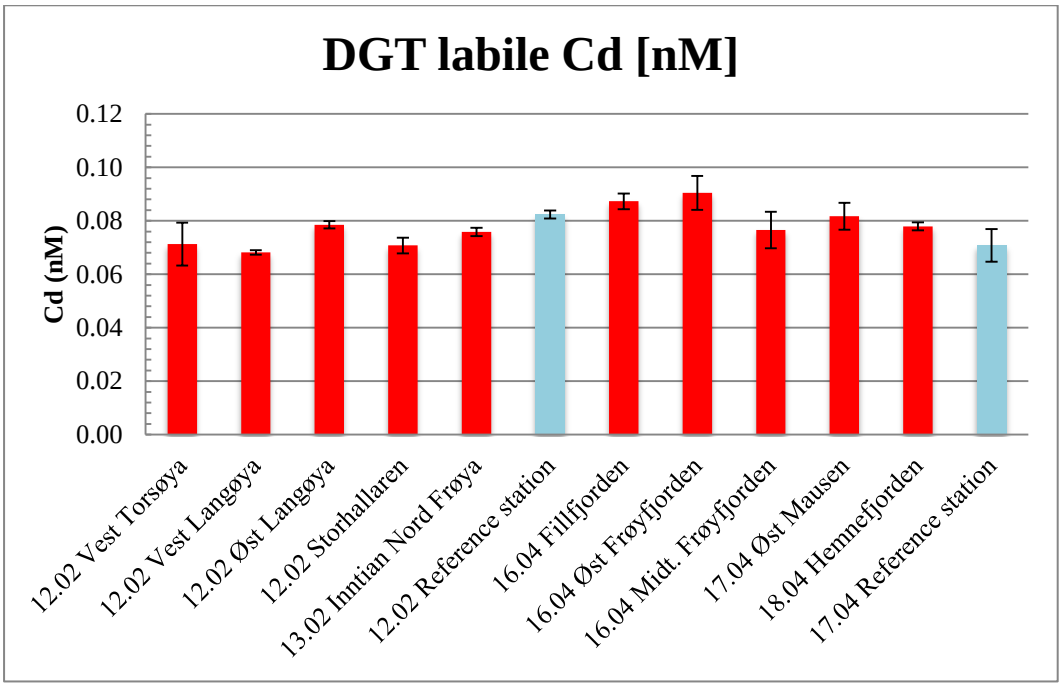


Figure 5.13: The concentration of DGT labile cadmium

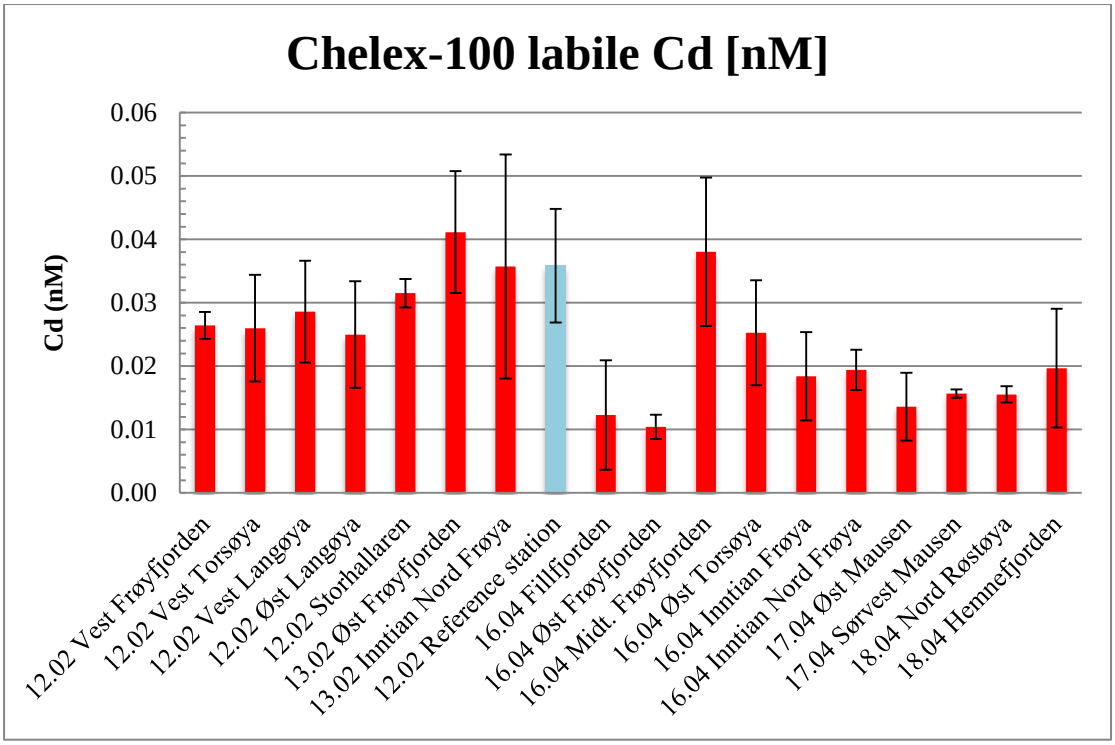


Figure 5.14: The concentration of chelex-100 labile cadmium

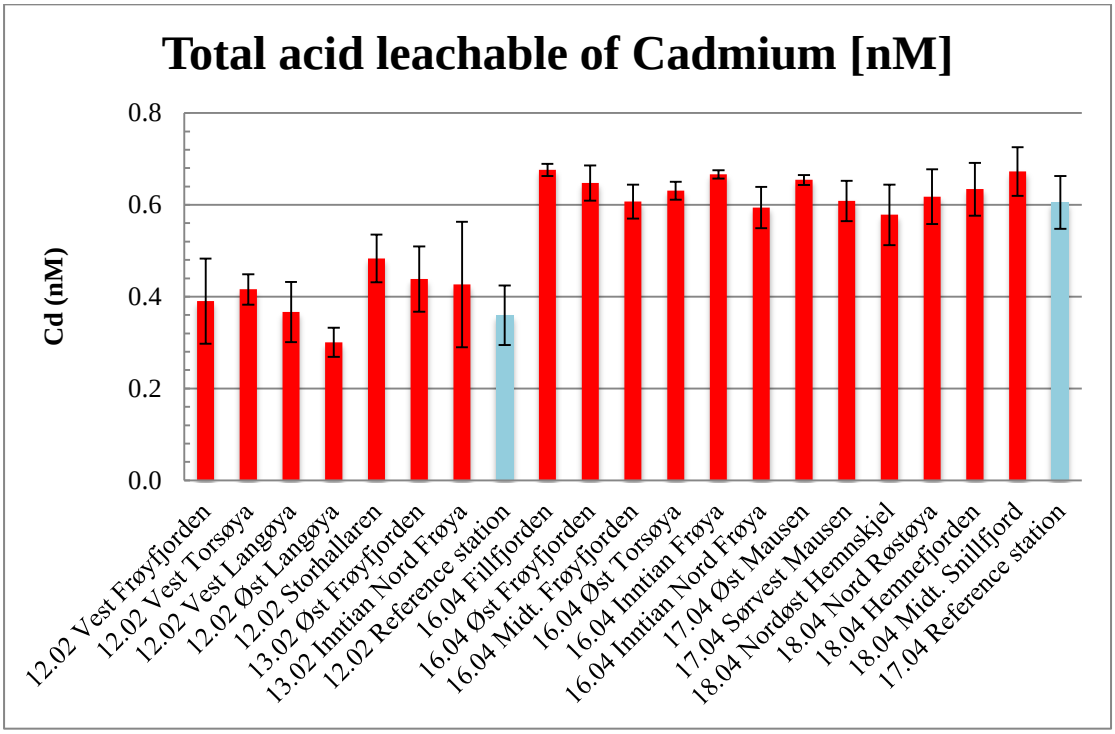


Figure 5.15: The concentration of total acid leachable cadmium

The results for total acid leachable metals are given in Table 5.1.

Table 5.1: Concentrations for total acid leachable metals (Cd, Mo, Mn, Fe, Co, Cu and Zn) at the different stations

Element	Cadmium		Molybdenum		Manganese		Iron		Cobalt		Copper		Zinc	
Station	Average [nM]	SD	Average [nM]	SD	Average [nM]	SD	Average [nM]	SD	Average [nM]	SD	Average [nM]	SD	Average [nM]	SD
12.02 Vest Frøyfjorden	0,4	0,09	116	5,0	10	0,5	46	5,3	0,5	0,05	9	0,9	20	1,8
12.02 Vest Torsøya	0,4	0,03	119	3,7	10	0,4	41	8,0	0,5	0,13	8	0,4	16	2,3
12.02 Vest Langøya	0,4	0,07	120	5,1	10	0,3	39	3,9	0,5	0,08	8	0,7	9	2,4
12.02 Øst Langøya	0,3	0,03	115	3,4	10	0,5	57	11,3	0,7	0,17	9	3,3	8	0,9
12.02 Storhallaren	0,5	0,05	117	0,2	10	0,8	53	6,0	0,5	0,14	6	0,9	14	1,1
13.02 Øst Frøyfjorden	0,4	0,07	119	6,9	12	1,0	94	4,4	0,5	0,17	4	1,0	13	2,0
13.02 Inntian Nord Frøya	0,4	0,14	113	3,6	11	0,8	56	3,7	0,4	0,06	1	0,7	8	0,2
12.02 Reference station	0,4	0,06	112	4,7	10	0,2	43	3,0	0,7	0,02	0	0,4	10	4,0
16.04 Fillfjorden	0,7	0,01	114	3,4	12	0,3	36	4,3	0,4	0,03	6	0,6	19	2,8
16.04 Øst Frøyfjorden	0,6	0,04	115	2,4	9	0,4	13	1,0	0,4	0,07	4	0,7	6	1,9
16.04 Midt.	0,6	0,04	111	3,3	9	0,6	16	1,1	0,4	0,07	4	0,5	4	0,7

Frøyfjorden														
16.04 Øst Torsøya	0,6	0,02	113	1,6	9	0,1	16	1,8	0,4	0,02	5	0,5	5	0,8
16.04 Inntian Frøya	0,7	0,01	116	1,1	10	0,3	30	1,1	0,3	0,08	7	0,6	4	0,5
16.04 Inntian Nord Frøya	0,6	0,04	113	3,1	9	0,5	20	2,1	0,4	0,05	4	0,4	6	1,4
17.04 Øst Mausen	0,7	0,01	112	1,1	9	0,3	10	1,1	0,3	0,06	4	0,5	3	1,6
17.04 Sørvest Mausen	0,6	0,04	108	2,3	9	0,3	14	8,8	0,4	0,09	3	0,1	3	1,5
18.04 Nordøst Hemnskjel	0,6	0,07	105	3,9	9	0,2	20	0,3	0,4	0,07	4	0,2	3	1,2
18.04 Nord Røstøya	0,6	0,06	110	3,1	9	0,4	20	3,1	0,4	0,04	4	0,4	7	0,1
18.04 Hemnefjorden	0,6	0,06	111	2,8	11	0,8	20	0,8	0,4	0,17	7	1,2	10	1,2
18.04 Midt. Snillfjord	0,7	0,05	113	0,8	16	0,4	79	5,5	0,5	0,21	6	2,3	11	8,9
17.04 Reference station	0,6	0,06	105	1,4	8	1,1	11	9,1	0,4	0,08	3	0,1	4	3,8

6. Discussion

There was a general difference between the cruises with lower values in the first than in the second cruise, despite the increasing freshwater input because of spring melting of snow. On the other hand, there was no clear trend between the different locations. Most values are also above the average values set in the theory, however this may be because these values are from coastal waters, not open sea, and the theoretical values are rarely true. There are differences even between the large oceans like the Atlantic and Pacific Ocean, since the Pacific is a much older water.

6.1 Oceanography

Before beginning this project we thought that the current system brought water from southwest to northeast. At first the hypothesis was to find differences in a transect line, and to see how the current system affected the concentrations. However, after seeing the result, a trend has been hard to find. During a new cruise conducted by CINTERA, the currents were measured and it was found that the current system was much more complex than expected. The current could go one way at five meters depth, and then in ten meters depth go 180 degrees the other way. Our reference stations, taken west in relation to the sample stations, could therefore be contaminated by nutrients from aquaculture activities located in the east. For example, station Vest Frøyfjorden, had some of the highest chelex-100 concentrations in the first cruise (see Figure 6.1), and it is possible the current went from areas with aquaculture activities in the east, towards the west and thereby supplied this station with nutrients. However, this station lies very close to the reference station in the first cruise and the reference could therefore also easily have been contaminated by nutrients from aquaculture activities.

It is also important to look at the depth of the ocean where the samples are collected. Most samples are collected at locations where there is at least 100 meters to the sea floor. However, some samples are collected at places as shallow as 30 meters. Then it is needed to take into account that the sediment may affect the whole water column and therefore have affected the samples. For the same reason it is also important to take into account how far away from the shore the samples are collected. Some of the samples are collected from the middle of the fjord, whilst others are quite close to the coast.

6.2 General trends for micronutrients

Seasonal trend

The first cruise was in February, which is wintertime. Whiteout enough sunlight, the phytoplankton cannot bloom. The second cruise was in April, which is early spring. It was not the height of bloom and we couldn't see any phytoplankton in the samples. Still the chlorophyll a results show that there had been a small increase in phytoplankton mass from the first to the second cruise (see appendix D, the concentration of chlorophyll a was determined by Tale Skrove (Skrove, Unpublished)). Also during spring, melted snow water from the mountains will go into the rivers, which have their outlet in the fjord. This river water may contain a higher metal concentration and will also lower the salinity in the fjord.

The general trend for the DGT results seam to be either decreasing concentrations or unchanged from the first to the second cruise. Iron is not surprising one of the metals that has decreased in concentration. This metal is highly important for phytoplankton to get the nitrogen from nitrate/nitrite to an available nitrogen source, ammonium.

The general trend for chelex-100 is also either decreasing or unchanged concentrations from the first to the second cruise. Iron and zinc are the only metals with the same seasonal trend in both the chelex-100 results and the DGT. Zinc does not show any clear trend, and it has high standard deviations.

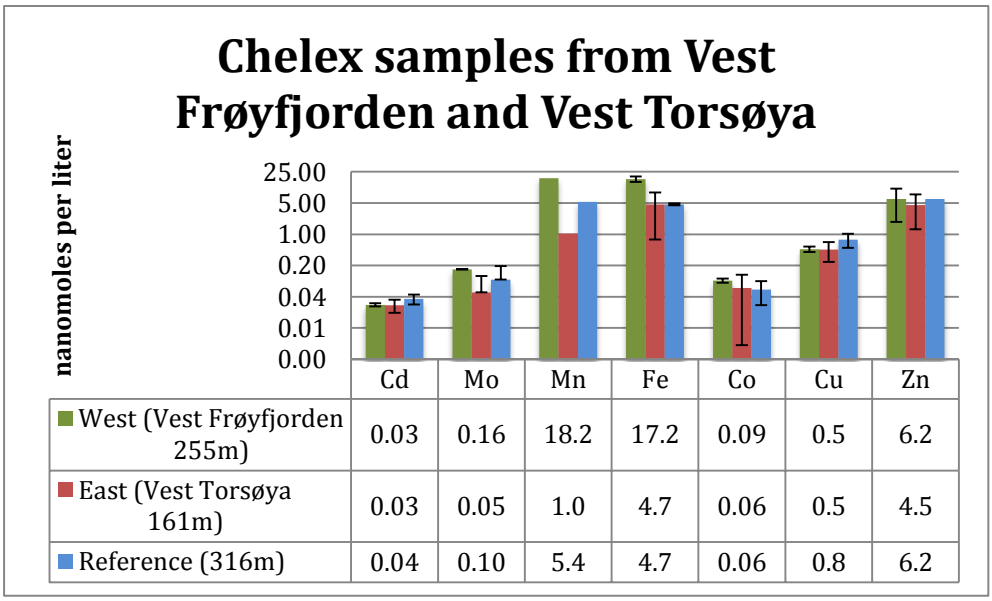
In the direct sample, all metals except for cadmium shows a decrease in concentration from the first to the second cruise. A reason for this might be that cadmium is not crucial for algae if they have zinc and cobalt available. Extra cadmium might have been brought to the fjord by the melted snow water in the rivers, and therefore increased the concentration. However, the cadmium concentration is very low for all the different techniques.

The overall decrease seeing all three techniques together is expected since it was early spring and some of the algae had started to grow in volume.

General trends for the different stations

For the DGT results, the first reference station seams to have the highest results for most metals, whilst the lowest values were on the second reference station. A reason for this may be that since there is little aquaculture here, and not as much addition of nutrients. There might also be fewer algae in the open ocean, which means there are a lot of nutrients here during the winter, however, when the algae start to grow, all nutrients will be depleted here. For the other stations, no one stood out with neither high nor low concentrations of DGT labile metals and no other station showed any specific trend.

In the chelex-100 samples the reference stations did show the same trend as in the DGT results, but not as clearly. Instead Vest Frøyfjord stood out with relatively high values. In Figure 6.1 this station is compared with Vest Torsøya, which was in the same geographical area. This figure is presented in a logarithmic scale so that all the metals could be presented in the same graph.



	Cd	Mo	Mn	Fe	Co	Cu	Zn
West (Vest Frøyfjorden 255m)	0.03	0.16	18.2	17.2	0.09	0.5	6.2
East (Vest Torsøya 161m)	0.03	0.05	1.0	4.7	0.06	0.5	4.5
Reference (316m)	0.04	0.10	5.4	4.7	0.06	0.8	6.2

Figure 6.1: Comparison of the concentration for chelex-100 labile metals at Vest Frøyfjorden , Vest Torsøya and reference station

At Vest Frøyfjorden there were only taken direct and chelex-100 samples, and the chelex-100 sample shows the highest values for all elements in the first cruise, except cadmium and cobalt (the manganese value is removed in the results as it is most likely contaminated). Cathrine Solli, who looked at macronutrients, found that the ammonium- and silicate levels were low in this station, whilst phosphorus and nitrate/nitrite were fairly similar to other stations. The nitrogen:phosphorous ratio was also low, suggesting that the system is nitrogen limited (Solli, 2013). Since it was wintertime, Vest Frøyfjorden had a low concentration of chlorophyll a, even though it was the largest concentration for the first cruise (Skrove, Unpublished). The increased ammonium emissions from the fish farm may cause a small increase in the phytoplankton production, therefore lowering the ammonium levels compared to the nitrate and nitrite. However, a low phytoplankton level means that there are no organisms there to take up all the available trace metals. Vest Torsøya on the other hand, the molybdenum concentration was the lowest one for the first cruise, and the other metal concentrations were also fairly low. These two stations are therefore very different from each other even though both are in the same area and with over a hundred meters in depth. However, such high iron and manganese concentration as found in Vest Frøyfjorden, can also be a result of contamination or methodical bias, and with such a small sample number, few parallels and no DGT samples, the results are very uncertain.

For the low values it was interesting to notice that Øst Frøyfjord and Sørvest Mausen stood out together with the second reference station. These were low on both iron and manganese, which are crucial in transforming unavailable nitrogen into nitrogen that is useful for the organism and to oxidate water into oxygen for the photosynthesis. The ammonium concentration in Øst Frøyfjorden, was the highest one reported, and it was also relatively high in Sørvest Mausen. However, the system is still nitrogen limited (Solli, 2013) and the phytoplankton concentration is only around average for the second cruise at these stations (Skrove, Unpublished).

Except for these stations, no other showed any particular trend of neither high nor low concentration of chelex-100 labile metals.

In the result for the direct samples there is not the same trend with high concentrations for the first reference station. In fact, there is only one element (Co) with a high concentration here, whilst another element (Cu) has one of its lowest concentrations. However, there are some other stations that stand out. Fillfjorden has some high concentrations together with Øst Frøyfjorden. This contradicts the results for chelex-100, where Øst Frøyfjorden had some of the lowest concentrations. However, it is important to remember that whilst the chelex-100 only accumulates metals that are in a chelex-100 labile form, whilst the direct samples is acidified and all acid-leachable metals are released, even though they are not bioavailable.

For low concentrations the chelex-100 and direct results agree, since they both show in general low concentrations at Sørvest Mausen.

There is one other result that is special for the direct samples. Whilst Øst Frøyfjorden had the highest concentration for iron in the first cruise, the same station had one of the lowest concentrations for iron in the second cruise. This is no surprise when looking at the results for chlorophyll a, which had an increase over 525%.

Trends of metal distribution being dependent on aquaculture

The DGT results show the clearest trend of the metal concentration being dependent on the aquaculture. For all metals, the highest concentration in the first cruise is either lower or the same as the reference station. In the second cruise, most metals have concentrations above the reference station.

Some of the chelex-100 shows similar a similar trend as the DGT. Whilst nearly all of the metals in the DGT results showed both lower values in the first cruise and higher in the second than the respective reference stations, the results are more split with the chelex-sample. Two metals (Cd, Zn) show lower concentrations in the first cruise than the reference samples, whilst three metals (Fe, Mn and Cu) show a higher concentration in the second cruise than the reference sample.

The direct samples show little signs of this trend. Only three metals show a difference in concentration in relation to the reference station, and one of these are different that what we would expect. Cobalt shows a lower value in the first cruise than the reference station, and manganese show a higher value in cruise two, compare to the reference station. Copper shows a higher value than the reference station in the first cruise. As mentioned in the theory, Morel and Price (2003) has shown that in Open Ocean, some diatoms require very little iron, and it is believed that copper has taken its place in several enzymes. This may be a reason for why there is so little copper in the reference station for the first cruise. But again it is important to remember that this is the total acid leachable concentration.

Since the only difference between the reference stations and the sample stations is that the sample stations are taken in areas close to fish farming activity, it seams that the aquaculture has at least a part to play in these different concentrations. However, with lack historical data makes it difficult to decide whether these values are the natural values for the fjord or due to aquaculture activities.

In general, Cathrine Solli found that macronutrient distribution had a significant increase in concentration that may have been due to aquaculture activity (Solli, 2013).

6.3 Effects on and from sediments

Some of the stations were taken at relatively shallow water. Then it is needed to take into account that the sediment-water interface may affect the whole water column and therefore have affected the samples. Also, if there is a short distance from the fish farm to the bottom of the seafloor, accumulated organic matter from fish cages can lead to a suboxic environment in the surface sediments that could also affect the release of trace elements into the water column. When the sediment water interface turn suboxic or anoxic, a significant fraction of the deposited manganese oxides (III, IV) will be reduced and released into the water as free Mn^{2+} ions. On the other hand, the reduction of iron oxides (III) and release of Fe^{2+} ions is not as drastic (Stumm and Morgan, 1996). There is a constituent flux from the sediments to the water, and if there is an oxygen depletion this may lead to changes such as the solubilisation of iron and manganese and subsequent the release of other particle reactive metals (Ardelan et al., 2012).

From this we would expect a large manganese to iron ratio at Inntian Frøya (30m), and Inntian Nord Frøya (45m) if the sediment-water interface was anoxic. Inntian Frøya was only collected in the second cruise with chelex-100 and direct samples, whilst Inntian Nord Frøya was collected in both cruises, in the first cruise with DGT, chelex-100 and direct, and chelex-100 and direct in the second cruise. To compare the ratios I have also looked at the ratios for deeper stations; Vest Torsøya (161m), first reference station (316m), Fillfjorden (179m) and the second reference station (211m). See appendix C for calculations.

After analysing the results by looking at the Mn:Fe ratio for all three techniques, it did not seam as the samples were affected by any suboxic sediment-water flux. However, the sample number is far too small to say anything for certain, and the water-sediment interface was not sampled.

6.4 Iron

All values were above the theoretical average concentration for iron in open ocean. However, this is coastal water and extra input can come from sediments, rivers and coastlines.

The DGT samples show a visual trend of a decrease from the first to the second station, despite the extra input due to melting snow. All samples are below the reference station in cruise one. As iron is very important in the nitrogen cycle and is used by phytoplankton and cyanobacteria in nitrate and nitrite reductase it is expected that the concentration will decrease with algal blooms. The decrease in the concentration could therefore be due to algae using nitrate or nitrite as their nitrogen source. As seen in Figure 6.2, there seams to be an opposite correlation between the chlorophyll a and the DGT labile iron.

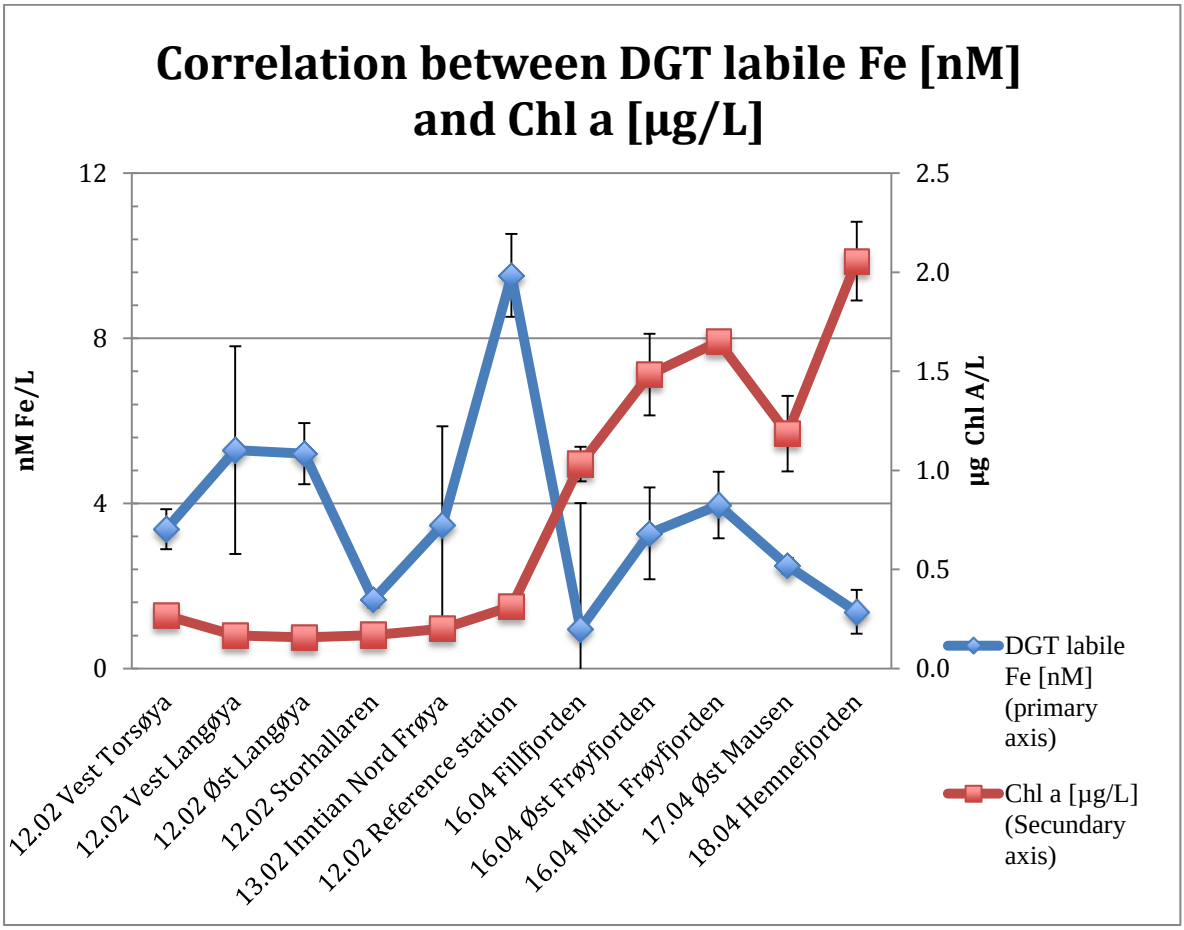


Figure 6.2: Correlation between DGT labile iron and chlorophyll a

The chelex-100 samples show a decrease from the first to the second cruise. However, two of the stations in the first cruise have relatively high values, which may be due to contamination or methodical bias. Even though if we rejected these, there is still a visual trend showing a decrease. As seen in Figure 6.3, there seams to be an opposite correlation between the chlorophyll a and chelex-100 labile iron:

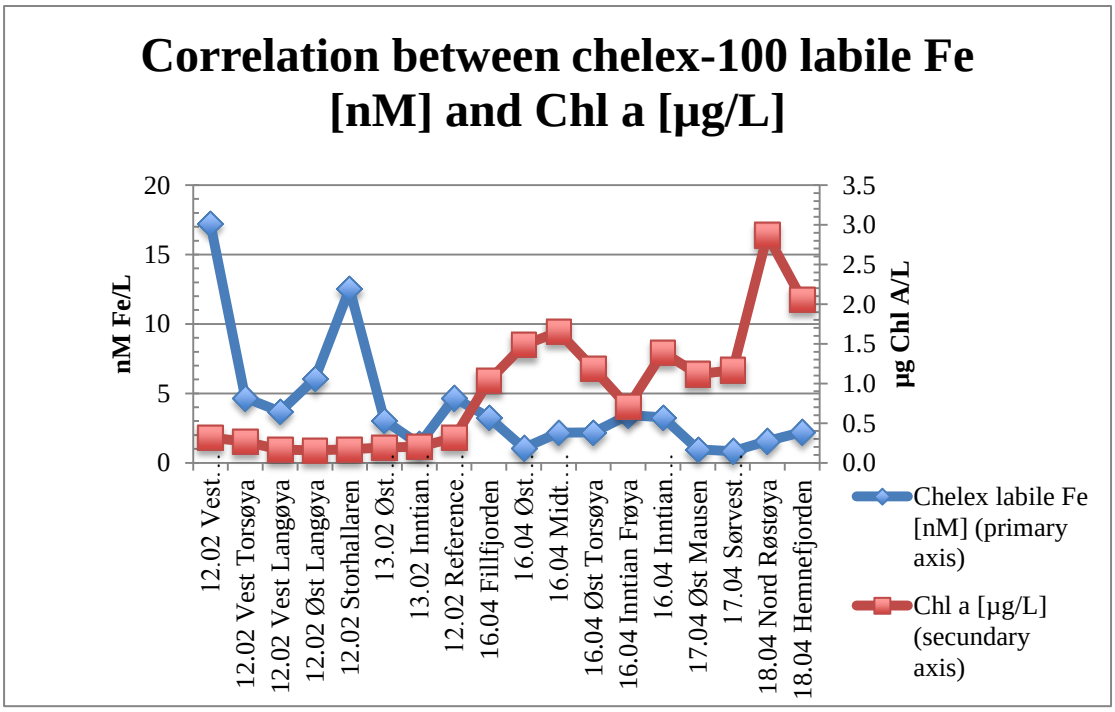


Figure 6.3: Correlation between chelex-100 labile iron and chlorophyll a

The direct samples show a decrease from the first to the second cruise. Some of the direct sample concentrations are higher than we would expect from any biological activity, and is more likely to be due to contamination or due to the acid added to the sample, leaching all of the metal. However, there is a clear decreasing trend and as seen in Figure 6.4, there seams to be an opposite correlation between the chlorophyll a and the total acid leachable iron.

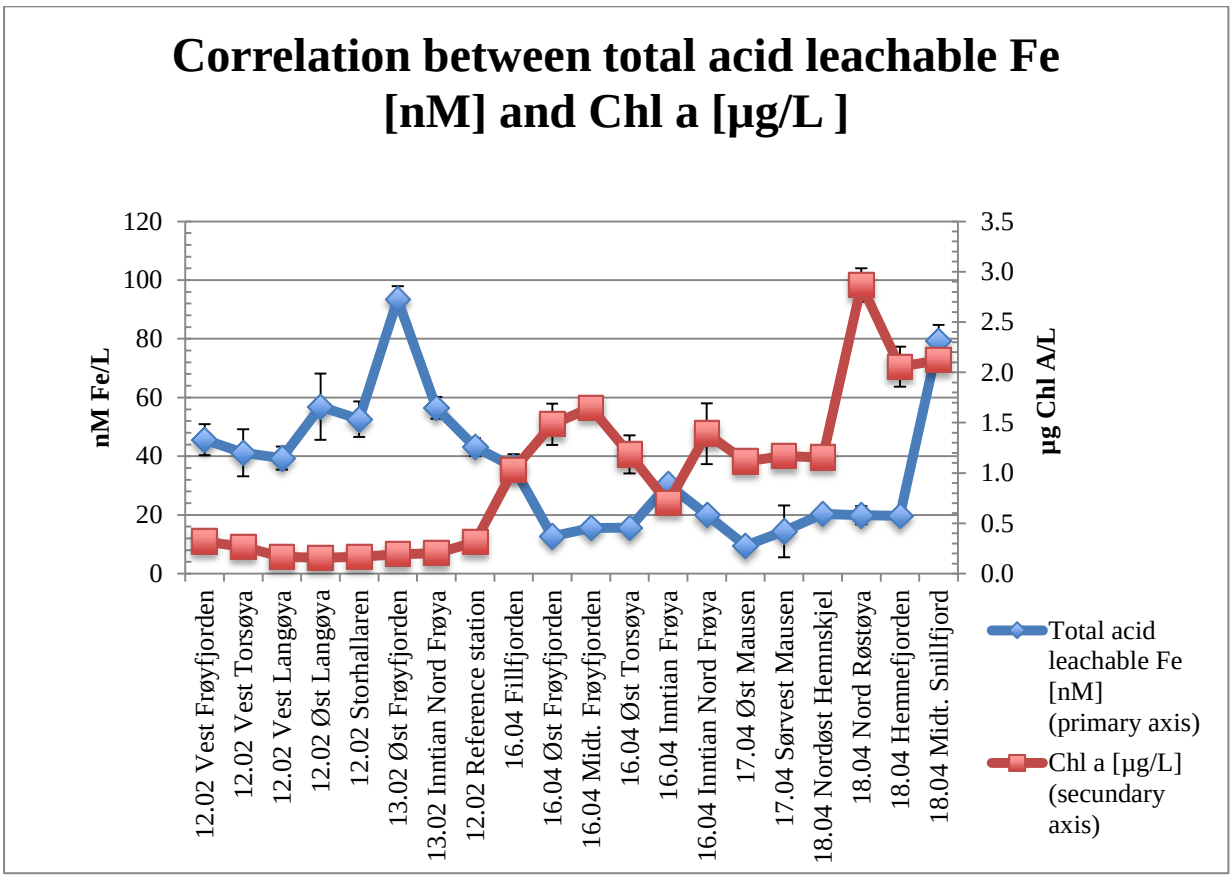


Figure 6.4: Correlation between total acid leachable iron and chlorophyll a

6.5 Molybdenum

The fraction of DGT labile- and chelex-100 labile molybdenum is very low compared to the total acid leachable concentration (Figure 5.3, 5.4 and Table 5.1), and the DGT and chelex-100 results show concentrations around the same as the theoretical average value for open ocean.

The DGT labile molybdenum results show similar concentrations for all samples in both cruises including the reference samples. As mentioned in the theory, molybdenum seams to be distributed homogenously thorough the water column, and changes in concentration due to bioactivity is not registered even though it is an important bioactive trace metal.

For the chelex-100 results in the first cruise the standard deviations are very high, probably due to methodical bias or contamination, and these results are therefore uncertain. The results show a decrease from the first to the second cruise.

The direct samples show a decrease from the first to the second cruise. All the molybdenum results are very high in the direct samples compared to the chelex-100 and DGT labile results, but consistent. The values are in average 113nM, and theory states that in open ocean the values are usually around 100nM. It is important to remember that the DGT and chelex-100 only accumulate the metal that is available to the chelex-100 resin. Some of the molybdenum might have been in complexes that the acid added to the sample has dissolved. This molybdenum would then in the true biological system not be available for the phytoplankton.

6.6 Manganese

Both the DGT labile- and the chelex-100 labile concentrations show values similar to the theoretical average concentration for open ocean. The total acid leachable concentration is higher.

When comparing the DGT labile results to the reference stations, all samples in the first cruise are below, whilst they are above in the second cruise. The first reference station has a high standard deviation together with all the other stations in the first cruise, except for the first one. There is a slight visual trend of an increase in concentration from the first to the second cruise. Manganese is important in O_2 evolving enzymes, but is also capable of scavenge other cations from the water when in form of oxides. Larger particles will not be able to be accumulated by DGT units, so a reason for the slight increase in concentration may be due to more free ions and smaller particles in the water. However, since there were so high standard deviations in the first cruise these results are uncertain.

The results for chelex labile manganese are generally poorly, and several parallels were taken out due to contamination. This is a problem that has been encountered previously (Ardelan, 2013). The reference station value is relatively high in the first cruise and low in the second.

The direct samples show a slight visual trend of a decrease from the first to the second station. Manganese is often present as oxides, and this might be the reason for a higher concentration in the direct samples than in chelex-100 and DGT.

6.7 Copper

Both the DGT labile- and the chelex-100 labile concentrations show values similar to the theoretical average concentration for open ocean. The total acid leachable concentration is higher.

When comparing the DGT labile results to the reference stations, all samples in the first cruise are below, whilst they are above in the second cruise. At the same time, a slight decrease trend can be seen visually. This may be due to biological activity as it can be used by phytoplankton in denitrification and ammonium oxidation and other enzymes.

The chelex-100 results seams fairly similar except for two stations in the second cruise, where all the values are above the reference value.

For the direct sample results, all values are higher than the reference values, and there is visually a slight decrease from the first to the second cruise, and within the first cruise from the first to the last station.

6.8 Cobalt

Both the DGT labile- and the chelex-100 labile- and the total acid leachable concentrations show values lower than the theoretical average concentration in the open ocean.

When comparing the DGT labile results to the reference stations, all samples in the first cruise are below, whilst they are above in the second cruise. At the same time, a slight decrease trend can be seen visually. This may be due to biological activity as it is important in vitamin B_{12}, and can also be used, like cadmium, as a replacement for zinc in Carbonic anhydrase. However, the difference between the cruises is very small and with such a little sample group one should be careful to draw any conclusions.

The chelex-100 results were very varying, and the results had relatively high standard deviations, so the uncertainty is quite high. Some stations had relatively high concentrations in the second cruise, however these also had a high standard deviation.

The direct samples were very varying, but there was a slight decrease from the first to the second cruise.

6.9 Zinc

All techniques showed higher values than the theoretical average concentration in the open ocean. The results, however, were generally poor, however zinc is very easy to contaminate as it attaches itself easily to dust particles (Doner and Ege, 2004).

The DGT labile results showed very varying concentrations with no clear trend and some of the stations had high standard deviations. Most samples are below the concentration for the reference station in cruise one, and above in cruise two.

For the chelex-100 results, a lot of the stations had a high standard deviation, which makes the results uncertain. In cruise one, the highest value was the same as the reference value, but several stations had to be removed due to contamination and there were no clear trend.

In the direct samples one can se a slight decrease from the first to the second station.

6.10 Cadmium

Both the DGT labile- and the chelex-100 labile results in the first cruise and the total acid leachable results in both cruises had concentrations show values higher than the theoretical average concentration in the open ocean. The chelex-100 labile concentrations in the second cruise show values similar to the theoretical value.

The result for DGT labile cadmium shows that the highest value in the first cruise is the same as the reference station. In the second cruise however, all samples are higher than the reference station. Overall the results are fairly similar, with a slight increase in the concentration from the first to the second cruise.

For the chelex-100 results, several of the stations had relatively high standard deviations. The reference sample for the second cruise was removed due to contamination. These results are therefore highly uncertain. When the results were rounded up to two decimals, the highest levels in the first cruise were the same as the reference station. This confirms the results from the DGT samples. However, there is a decrease in the concentrations from the first to the second cruise.

The direct samples show a clear increase in concentration from the first to the second cruise. Cadmium may be used in the enzyme carbonic anhydrase in the carbon cycle, when cobalt and zinc are depleted. Therefore some phytoplankton might have taken up cadmium, before releasing it due to acidification when sampling. The increase in relationship to the reference stations may also be due to cadmium containing freshwater that enters the system from snow melting and than be led to the fjords with rivers and streams.

6.11 Evaluation of the analytical method

Blanks

In general the blank values, see appendix B.1 – B.3, are high for all the sample types with exception for the direct samples in the first cruise. This creates an uncertainty since we cannot know if they are genuine, or random contamination. Therefore, the average of the blank values were subtracted from the samples. When a blank value is very high, this leads to a small concentration in the sample.

For the chelex samples it was important to transfer all the chelex to the chromatographic column, however some of the chelex may have been left in the bottle. It was also important to transfer all the acid from the column to the test tube, if a drop missed the test tube, a large proportion of the metals might have been lost.

Even though the experimental part has been carried out in a clean lab, and all plastic equipment has been washed thoroughly, there are still some results that show error due to contamination. Several of the direct samples for an example, has much higher concentrations than what would be estimated to be caused by biological processes, and are much more likely to be contaminants from the surrounding environment.

For the polyethylene centrifuge tubes that the samples where stored before analysis with the HR-ICP-MS was washed together in the first step, in a large container. Therefore, it is difficult to know if they were all washed equally, and in addition to this, some of the tubes might have had traces of metals in them, even though they were washed with acid in two steps.

In the clean lab there was a positive pressure, which allowed air to flow out, but not in. This made the air flow inside the lab minimal, reducing the amount of dust particles in the room, compared to a normal lab. However on the research vessel, when pouring sample water from the go-flo into sample bottles, there was sometimes a rather turbulent airflow, due to the door being open from the lab to the open deck. This would increase the risk of contamination of the samples, particularly for the chelex and the direct samples.

Direct sampling

The direct sampling is generally a poor technique which is most used to give a picture, rather than specific values. The reason for this is that the samples are easy to contaminate, but at the same time the initial metal concentration present may be to low. It is also important to notice that acid is added straight to the direct sample, and this technique is therefore destructive and particles will be soluble after a short while. The direct method can be said to represent the total metal concentration, included acid leachable metals. Whilst the direct samples only contain the concentration of the metal at the time of sampling in a small volume, Chelex-100 and DGT on the other hand accumulate metal from a larger volume of sample water. On the other hand, DGT and chelex-100 will only collect the chelex-100 labile metals.

Chelex-100 compared to DGT

In this thesis both Chelex-100 added directly to the sample as well as chelex-100 gel inside DGT units have been used. As stated previously, with the direct chelex-100 and DGT method you get a snapshot of the labile metal concentration in the water at the time that the chelex-100/DGT is deployed. In addition to that the chelex-100 will compete with other ligands as shown in equation 4.8 – 4.10, the chelex-100 in the DGT units will only be able to get metals that are in small enough complexes to pass

through the membrane and the diffusion gel. However, some particles and larger molecules attached on the surface on the DGT units may gradually release DGT labile metals over time.

Overall, the result from this thesis shows that it is much more efficient to use only DGT samples compared to Chelex-100 direct in sample water. The results seam better in the DGT, the SD is smaller and there are fewer steps where human errors and contaminations could be made. In addition this technique could save time, money and equipment. However, the small number of samples and few parallels makes the results obtained in this thesis makes the accuracy uncertain and this also affects the possibility for statistical analysis.

Filtration

Filtration was only carried out in one station, and after reviewing the results, which were slightly higher for the filtrated, than for the non-filtrated samples filtrated samples have most likely been contaminated. Since R/V Gunnerus is not made for trace metal studies, there was very high contamination risk to filter the samples as well as time consuming. This was therefore not prioritised.

DGT

Here I will discuss the deployment time, diffusion coefficients and the acid wash procedure that were chosen.

DGT deployment time

There are many different deployment times used in literature (Ardelan et al., 2009, Garmo et al., 2003, Zhang and Davison, 1995). In collaboration with Murat van Ardelan, the deployment time of the DGT units were set to three days as this has been found in Ardelans previous work to be a good timeframe. The DGT units need time for the metals in the sample to diffuse through the membrane and the diffusion gel before reaching the chelex-100 gel, but at the same time one must be careful to not leave the DGT units too long, since this can cause a biofilm to be formed on the outer membrane by bacteria. This would cause the diffusion path to be thicker than in the calculations, and so the concentration of the DGT-labile metals would be underestimated (Dunn et al., 2003).

DGT Diffusion Coefficients

The diffusion coefficients used in this thesis was found in Zhang (2003), but the value for molybdenum was not found so instead the value for chromium was used since they are in the same periodic group. All values were for 20 degrees Celsius, since the deployed DGT units were always kept at room temperature. However, this is only the average temperature, since it would change some degrees plus/minus on the vessel, and also during transport to the lab. One could also question if the movement on the shaker was enough to ensure that the diffusion coefficients were accurate. This creates an uncertainty for the results since small changes could change a lot in the

calculations of the metal flux to the chelex gel and therefore the final DGT-labile metal concentration. However, this would not affect trends seen in the results.

Acid wash of DGT units

Although it is not common to acid wash the DGT units, it was chosen to do so in this thesis. As with all other equipment, we don't know how the DGT units have been prepared and how the conditions are during the production and contaminations seen in the blank values may not be the same for each unit. This is why we find it essential to acid wash the DGT units, to reduce the contamination risk from the production process. In another master thesis, the difference between acid washed and non-treated DGT units were looked into and there were no difference in the accumulation ability, but the blanks were higher for the non-treated DGT units (Slinde, 2011). However, it is important to remember that there is a possibility that the acid washing induces deformation to the gel and may change the pore size. This needs further research, and is the reason for why the acid washing is not exceeded over three hours.

7. Conclusion and further work

There was a general seasonal trend of decrease from the first to the second cruise, most likely due to the beginning of phytoplankton bloom. Since iron is possibly the most important bioactive trace metal, involved in several enzymes, it was interesting to see the clear decrease in its concentration from the first to the second cruise due to increasing phytoplankton growth.

There was not a clear trend between the different locations and it didn't seem like the distribution of micronutrients was significantly affected by aquaculture activities. However, a better selection of reference stations, or more importantly, long term comparison of micronutrient distribution in the coastal system of Norway where aquaculture activity is important, could give a much better idea about the effects of aquaculture on the distribution of micronutrients.

Unfortunately there are no historical data on the metal concentrations in the Norwegian coastal system. The lack of background value of the micronutrients makes it difficult to decide whether the current values are natural or due to aquaculture activities. However, the data obtained in this thesis can be used as a baseline for both the rest of the CINTERA project and for the future. It is also important to remember that these data were collected during winter and early spring. The CINTERA project is still going on till 2015, and since the fish grows more during the summer, and that is when the algae blooms are on its height, it would be interesting to see these results when available.

For further projects, samples should be taken several times during the whole year, for several years. This should be done to get historic data. There should be taken more parallels to make the results more certain, and sediment-water interface samples should be taken at places where fish farms could have an impact through particulate organic waste as well as macronutrients. In addition it would be interesting to look at the different speciation to see the distribution of the different forms of metals. It is also important that the reference station is far away from the aquaculture activities, so that currents cannot bring significant amounts of nutrients from fish cages to the reference station.

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Appendix A: ICP-MS settings

Parameter	Value
Sample flow/pumping speed	200 µL
Sample loop	500 µL

Equipment	Type
Nebuliser	PFA-ST with approx. volume range from 50-700µl/min.
Spray chamber	Quarts baffled micro cyclonic, with dual gas inlet type ESI – ES-3452-111-11
Cooling	PC^{3x} - Peltier cooling and heated inlet system
Torch	Quarts Demountable with o-rings
Injector	Quarts 2.5 mm with o-rings, ES-1024-0250
Sample cone	Aluminium ES-3000-18032
Skimmer cone	Aluminium type X-skimmer ES-3000-1805 X
RF-power in W	1350

Gas flows

In addition to ordinary setup for sample gas, there was used both splitting of gas lines for the sample gas, and use of methane as additional gas to argon.
Splitting of sample gas - makes it possible to optimize both nebulizer gas flow (PFA-ST 0.7 -0.8 l/min), and gas flow in the plasma (1.2 – 1.4 ml/min). This lowers the RSD with approx. 50%. Sample gas line 1 is connected to the nebulizer, while sample gas line 2 is connected to a T-connection between the spray chamber and the injector.

Addition of CH_4 - to the sample gas is used because of many advantages, as lower oxides, increased sensitivity of Se and As.

Gas flow	Value (L/min)
Cooling gas	15,5
Auxiliary gas	1,1
Sample gas 1 (nebuliser)	0,75
Sample gas 2 (T-connection)	0,55
Additional gas	10% methane in Argon- approx 0.0004 CH4, corresponds to approx. 0.04% in the sample gas

Determination	Value
Resolutions	Low (400), Medium (5 500) and High (10 000)

Appendix B: ICP-MS results

In the results shown, the µg/L is given directly from Syverin Lierhagen, and the relative standard deviation (RSD%) is also shown for each sample. This is a sign of the variation of three analysis of the sample, and the values are shown coloured by the following limits: <5, 5-10, >10. The concentrations shown are the average of the three values. The calculated values used in this thesis (nM) are also included.

All values have been subtracted the average blank value by Syverin Lierhagen, except for the direct samples first cruise, as these blank values were very low.

B.1 DGT results

Table B.1: Blank values DGT labile iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Iron	0,55	3,7	0,05
222	Blank	Iron	1,32	2,6	0,12
223	Blank	Iron	0,97	2,4	0,09
224	Blank	Iron	0,88	1,2	0,08
225	Blank	Iron	0,55	5,2	0,05
226	Blank	Iron	0,65	4,9	0,06

Table B.2: Results for DGT labile iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
201	1	Iron	5,53	3,3	0,4955	
202	1	Iron	4,66	1,4	0,4169	
203	1	Iron	4,62	2,8	0,4133	
204	1	Iron	15,01	4,2	1,3439	Fe removed
205	3	Iron	1,73	5,8	0,1547	
206	3	Iron	2,10	1,7	0,1885	
207	3	Iron	1,64	4,2	0,1471	
208	3	Iron	1,52	1,4	0,1360	
209	4	Iron	3,46	3,7	0,3102	
210	4	Iron	1,24	5,2	0,1106	
211	4	Iron	3,52	2,6	0,3156	
212	5	Iron	5,70	4,3	0,5108	Fe removed
213	5	Iron	1,47	2,6	0,1313	
214	5	Iron	0,92	3,1	0,0826	
215	6	Iron	12,18	1,9	1,0903	Fe removed
216	6	Iron	0,80	1,4	0,0713	
217	6	Iron	0,93	5,4	0,0835	

218	8	Iron	3,23	5,4	0,2890	
219	8	Iron	1,20	4,0	0,1076	
220	8	Iron	0,98	3,0	0,0875	

Table B.3: Blank values DGT labile molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Molybdenum	0,008	20,7	0,0004
222	Blank	Molybdenum	0,015	7,6	0,0008
223	Blank	Molybdenum	0,012	17,2	0,0006
224	Blank	Molybdenum	0,005	28,4	0,0002
225	Blank	Molybdenum	0,006	11,8	0,0003
226	Blank	Molybdenum	0,009	17,2	0,0005

Table B.4: Results for DGT labile molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
201	1	Molybdenum	0,414	1,8	0,022
202	1	Molybdenum	0,369	5,0	0,019
203	1	Molybdenum	0,410	4,2	0,021
204	1	Molybdenum	0,343	10,4	0,018
205	3	Molybdenum	0,274	5,2	0,014
206	3	Molybdenum	0,300	4,8	0,016
207	3	Molybdenum	0,333	5,6	0,017
208	3	Molybdenum	0,304	2,3	0,016
209	4	Molybdenum	0,292	7,4	0,015
210	4	Molybdenum	0,355	2,8	0,019
211	4	Molybdenum	0,331	6,3	0,017
212	5	Molybdenum	0,311	0,6	0,016
213	5	Molybdenum	0,332	3,6	0,017
214	5	Molybdenum	0,334	6,7	0,017
215	6	Molybdenum	0,357	6,4	0,019
216	6	Molybdenum	0,323	1,3	0,017
217	6	Molybdenum	0,376	8,7	0,020
218	8	Molybdenum	0,365	1,6	0,019
219	8	Molybdenum	0,345	8,6	0,018
220	8	Molybdenum	0,362	11,4	0,019

Table B.5: Blank values DGT labile manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Manganese	0,03	9,8	0,003
222	Blank	Manganese	0,12	3,6	0,011
223	Blank	Manganese	0,11	3,2	0,010
224	Blank	Manganese	0,06	8,6	0,006
225	Blank	Manganese	0,03	6,5	0,003
226	Blank	Manganese	0,04	10,9	0,004

Table B.6: Results for DGT labile manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
201	1	Manganese	26,62	2,6	2,4228	Mn removed
202	1	Manganese	5,06	4,9	0,4601	
203	1	Manganese	3,09	3,4	0,2815	
204	1	Manganese	6,37	1,1	0,5798	
205	3	Manganese	1,17	1,7	0,1068	
206	3	Manganese	1,12	2,0	0,1015	
207	3	Manganese	1,12	1,2	0,1018	
208	3	Manganese	1,15	4,1	0,1046	
209	4	Manganese	1,27	3,4	0,1159	
210	4	Manganese	1,23	4,3	0,1118	
211	4	Manganese	4,71	3,0	0,4289	
212	5	Manganese	3,74	1,4	0,3402	
213	5	Manganese	1,74	2,6	0,1585	
214	5	Manganese	1,57	0,9	0,1426	
215	6	Manganese	2,02	2,2	0,1841	
216	6	Manganese	1,27	1,6	0,1156	
217	6	Manganese	2,91	1,1	0,2646	
218	8	Manganese	2,05	0,8	0,1863	
219	8	Manganese	1,10	2,9	0,1003	
220	8	Manganese	1,05	0,2	0,0953	

Table B.7: Blank values DGT labile copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Copper	0,18	2,9	0,014
222	Blank	Copper	0,51	3,9	0,040
223	Blank	Copper	0,14	4,2	0,011
224	Blank	Copper	0,11	0,7	0,009
225	Blank	Copper	0,11	2,6	0,009
226	Blank	Copper	0,09	3,7	0,007

Table B.8: Results for DGT labile copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
201	1	Copper	1,15	5,2	0,0908
202	1	Copper	1,02	2,8	0,0801
203	1	Copper	0,70	0,8	0,0552
204	1	Copper	0,82	4,1	0,0647
205	3	Copper	0,53	1,3	0,0415
206	3	Copper	0,66	2,8	0,0519
207	3	Copper	0,66	0,8	0,0518
208	3	Copper	0,55	2,2	0,0435
209	4	Copper	0,67	5,3	0,0526
210	4	Copper	0,69	3,4	0,0542
211	4	Copper	0,75	4,0	0,0593
212	5	Copper	0,75	1,6	0,0589
213	5	Copper	0,70	1,0	0,0552
214	5	Copper	0,79	3,7	0,0623
215	6	Copper	0,43	1,6	0,0339
216	6	Copper	0,40	1,9	0,0315
217	6	Copper	0,31	4,9	0,0243
218	8	Copper	0,80	1,1	0,0633
219	8	Copper	0,42	4,1	0,0331
220	8	Copper	0,96	0,9	0,0752

Table B.9: Blank values DGT labile cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Cobalt	0,005	14,9	0,0005
222	Blank	Cobalt	0,009	14,5	0,0008
223	Blank	Cobalt	0,006	32,1	0,0005
224	Blank	Cobalt	0,008	3,1	0,0007
225	Blank	Cobalt	0,006	8,0	0,0005
226	Blank	Cobalt	0,007	7,0	0,0006

Table B.10: Results for DGT labile cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
201	1	Cobalt	0,078	5,0	0,0066
202	1	Cobalt	0,050	5,6	0,0043
203	1	Cobalt	0,044	7,8	0,0037
204	1	Cobalt	0,052	5,9	0,0044
205	3	Cobalt	0,041	7,5	0,0035
206	3	Cobalt	0,044	4,3	0,0038
207	3	Cobalt	0,050	3,6	0,0042
208	3	Cobalt	0,046	5,8	0,0039
209	4	Cobalt	0,051	4,4	0,0043
210	4	Cobalt	0,116	2,5	0,0098
211	4	Cobalt	0,051	4,4	0,0043
212	5	Cobalt	0,057	10,0	0,0049
213	5	Cobalt	0,047	1,5	0,0040
214	5	Cobalt	0,048	3,1	0,0041
215	6	Cobalt	0,044	2,1	0,0037
216	6	Cobalt	0,043	2,8	0,0037
217	6	Cobalt	0,044	5,8	0,0037
218	8	Cobalt	0,046	7,8	0,0039
219	8	Cobalt	0,038	15,8	0,0032
220	8	Cobalt	0,042	6,7	0,0036

Table B.11: Blank values DGT labile zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
221	Blank	Zinc	0,81	7,3	0,06	
222	Blank	Zinc	8.84	5,0		Zn removed
223	Blank	Zinc	3,90	5,5	0,30	
224	Blank	Zinc	1,93	3,8	0,15	
225	Blank	Zinc	1,31	7,3	0,10	
226	Blank	Zinc	3,41	0,9	0,26	

Table B.12: Results for DGT labile zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
201	1	Zinc	9,97	2,5	0,7623
202	1	Zinc	13,74	1,8	1,0506
203	1	Zinc	10,49	1,0	0,8018
204	1	Zinc	10,27	3,0	0,7847
205	3	Zinc	2,87	3,9	0,2195

206	3	Zinc	6,41	1,3	0,4903
207	3	Zinc	5,24	2,3	0,4004
208	3	Zinc	5,04	3,0	0,3854
209	4	Zinc	4,55	5,9	0,3482
210	4	Zinc	3,61	3,3	0,2757
211	4	Zinc	3,15	3,0	0,2409
212	5	Zinc	4,37	1,3	0,3337
213	5	Zinc	9,13	1,9	0,6977
214	5	Zinc	4,00	1,6	0,3061
215	6	Zinc	2,85	2,4	0,2182
216	6	Zinc	2,72	1,7	0,2080
217	6	Zinc	2,46	1,3	0,1878
218	8	Zinc	11,68	1,0	0,8928
219	8	Zinc	7,88	2,7	0,6024
220	8	Zinc	9,97	2,8	0,7620

Table B.13: Blank values DGT labile cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
221	Blank	Cadmium	0,0002	120,3	7,0E-06
222	Blank	Cadmium	0,0005	26,0	2,3E-05
223	Blank	Cadmium	0,0001	177,6	5,4E-06
224	Blank	Cadmium	0,0000	108,9	
225	Blank	Cadmium	0,0002	22,7	1,1E-05
226	Blank	Cadmium	0,0009	49,2	3,9E-05

Table B.14: Results for DGT labile cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
201	1	Cadmium	0,0848	1,2	0,0038
202	1	Cadmium	0,0859	2,3	0,0038
203	1	Cadmium	0,0880	10,3	0,0039
204	1	Cadmium	0,0849	1,0	0,0038
205	3	Cadmium	0,0643	6,2	0,0029
206	3	Cadmium	0,0766	5,9	0,0034
207	3	Cadmium	0,0721	3,6	0,0032
208	3	Cadmium	0,0843	2,3	0,0038
209	4	Cadmium	0,0721	3,5	0,0032
210	4	Cadmium	0,0708	5,7	0,0031
211	4	Cadmium	0,0704	5,8	0,0031
212	5	Cadmium	0,0828	4,5	0,0037
213	5	Cadmium	0,0803	9,1	0,0036
214	5	Cadmium	0,0826	2,8	0,0037

215	6	Cadmium	0,0707	8,4	0,0031
216	6	Cadmium	0,0768	3,8	0,0034
217	6	Cadmium	0,0738	5,3	0,0033
218	8	Cadmium	0,0808	8,3	0,0036
219	8	Cadmium	0,0790	5,9	0,0035
220	8	Cadmium	0,0776	3,0	0,0035

Table B.15: Blank values DGT labile iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Iron	2,33	4,6	0,21
246	Blank	Iron	1,65	3,9	0,15
247	Blank	Iron	1,36	5,6	0,12
248	Blank	Iron	1,58	6,0	0,14
249	Blank	Iron	1,94	1,2	0,17
250	Blank	Iron	1,83	6,2	0,16

Table B.16: Results for DGT labile iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Iron	-0,76	3,5	-0,0679
228	9	Iron	0,41	1,2	0,0371
229	9	Iron	1,34	2,4	0,1201
230	10	Iron	1,04	4,4	0,0931
231	10	Iron	1,92	3,2	0,1718
232	10	Iron	2,13	3,3	0,1908
233	11	Iron	2,32	2,6	0,2081
234	11	Iron	1,57	2,5	0,1405
235	11	Iron	2,26	2,7	0,2026
236	15	Iron	1,39	6,0	0,1243
237	15	Iron	1,30	1,6	0,1162
238	15	Iron	1,19	4,6	0,1065
239	17	Iron	0,80	5,0	0,0714
240	17	Iron	0,48	4,8	0,0428
241	17	Iron	0,87	2,2	0,0777
242	21	Iron	1,03	2,1	0,0923
243	21	Iron	0,58	5,1	0,0521
244	21	Iron	0,53	3,0	0,0473

Table B.17: Blank values DGT labile molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Molybdenum	0,021	7,7	0,001
246	Blank	Molybdenum	0,012	9,7	0,001
247	Blank	Molybdenum	0,016	34,5	0,001
248	Blank	Molybdenum	0,016	2,8	0,001
249	Blank	Molybdenum	0,012	22,4	0,001
250	Blank	Molybdenum	0,018	39,8	0,001

Table B.18: Results for DGT labile molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Molybdenum	0,396	0,3	0,0207
228	9	Molybdenum	0,312	8,1	0,0162
229	9	Molybdenum	0,271	6,8	0,0141
230	10	Molybdenum	0,292	3,7	0,0152
231	10	Molybdenum	0,393	10,3	0,0205
232	10	Molybdenum	0,291	6,5	0,0152
233	11	Molybdenum	0,375	11,0	0,0196
234	11	Molybdenum	0,348	4,9	0,0181
235	11	Molybdenum	0,354	2,8	0,0184
236	15	Molybdenum	0,324	1,6	0,0169
237	15	Molybdenum	0,384	9,1	0,0200
238	15	Molybdenum	0,304	9,4	0,0158
239	17	Molybdenum	0,325	7,9	0,0169
240	17	Molybdenum	0,277	6,9	0,0144
241	17	Molybdenum	0,294	6,1	0,0153
242	21	Molybdenum	0,302	5,8	0,0157
243	21	Molybdenum	0,272	7,6	0,0142
244	21	Molybdenum	0,277	11,4	0,0144

Table B.19: Blank values DGT labile manganese, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Manganese	0,36	2,0	0,03
246	Blank	Manganese	0,24	3,6	0,02
247	Blank	Manganese	0,20	6,7	0,02
248	Blank	Manganese	0,25	1,1	0,02
249	Blank	Manganese	0,48	3,3	0,04
250	Blank	Manganese	0,31	1,7	0,03

Table B.20: Results for DGT labile molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Manganese	1,23	1,8	0,1121
228	9	Manganese	1,54	2,2	0,1402
229	9	Manganese	1,71	4,9	0,1560
230	10	Manganese	1,94	3,5	0,1764
231	10	Manganese	2,20	3,7	0,2002
232	10	Manganese	2,39	2,4	0,2172
233	11	Manganese	1,99	3,1	0,1811
234	11	Manganese	1,62	0,7	0,1471
235	11	Manganese	1,89	3,0	0,1724
236	15	Manganese	1,89	3,5	0,1719
237	15	Manganese	1,79	5,6	0,1630
238	15	Manganese	2,03	4,0	0,1845
239	17	Manganese	1,38	4,0	0,1257
240	17	Manganese	1,30	1,1	0,1183
241	17	Manganese	1,34	0,7	0,1218
242	21	Manganese	3,46	2,8	0,3153
243	21	Manganese	3,42	1,2	0,3112
244	21	Manganese	3,30	4,3	0,3000

Table B.21: Blank values DGT labile copper, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Copper	0,10	9,9	0,008
246	Blank	Copper	0,09	13,0	0,007
247	Blank	Copper	0,07	14,8	0,005
248	Blank	Copper	0,07	10,6	0,006
249	Blank	Copper	0,09	10,9	0,007
250	Blank	Copper	0,07	10,7	0,006

Table B.22: Results for DGT labile copper, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Copper	0,62	0,9	0,0487
228	9	Copper	0,58	4,5	0,0456
229	9	Copper	0,64	4,5	0,0502
230	10	Copper	0,44	7,8	0,0349
231	10	Copper	0,44	8,0	0,0345
232	10	Copper	0,47	1,8	0,0370
233	11	Copper	0,37	2,2	0,0290

234	11	Copper	0,31	4,2	0,0243
235	11	Copper	0,37	2,4	0,0288
236	15	Copper	0,33	5,4	0,0261
237	15	Copper	0,35	3,8	0,0278
238	15	Copper	0,43	3,7	0,0336
239	17	Copper	0,31	5,3	0,0246
240	17	Copper	0,32	2,7	0,0250
241	17	Copper	0,31	3,9	0,0246
242	21	Copper	0,44	3,4	0,0343
243	21	Copper	0,44	4,4	0,0345
244	21	Copper	0,40	2,9	0,0316

Table B.23: Blank values DGT labile cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Cobalt	0,001	28,6	0,0001
246	Blank	Cobalt	0,002	52,7	0,0002
247	Blank	Cobalt	0,001	86,6	0,0001
248	Blank	Cobalt	0,001	66,7	0,0001
249	Blank	Cobalt	0,002	70,0	0,0002
250	Blank	Cobalt	0,001	87,4	0,0001

Table B.24: Results for DGT labile cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Cobalt	0,025	15,5	0,0021
228	9	Cobalt	0,025	13,7	0,0021
229	9	Cobalt	0,029	9,3	0,0025
230	10	Cobalt	0,044	6,1	0,0037
231	10	Cobalt	0,044	8,4	0,0038
232	10	Cobalt	0,044	4,8	0,0037
233	11	Cobalt	0,039	15,8	0,0033
234	11	Cobalt	0,031	10,9	0,0026
235	11	Cobalt	0,037	8,3	0,0032
236	15	Cobalt	0,039	9,2	0,0033
237	15	Cobalt	0,037	15,0	0,0031
238	15	Cobalt	0,041	2,3	0,0035
239	17	Cobalt	0,034	21,2	0,0029
240	17	Cobalt	0,038	5,4	0,0032
241	17	Cobalt	0,034	10,2	0,0029
242	21	Cobalt	0,053	4,5	0,0045
243	21	Cobalt	0,060	3,4	0,0051
244	21	Cobalt	0,057	9,7	0,0048

Table B.25: Blank values DGT labile zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Zinc	2,12	2,5	0,16
246	Blank	Zinc	2,75	5,0	0,21
247	Blank	Zinc	1,16	3,1	0,09
248	Blank	Zinc	0,88	7,7	0,07
249	Blank	Zinc	3,06	4,9	0,23
250	Blank	Zinc	1,45	5,2	0,11

Table B.26: Results for DGT labile zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
227	9	Zinc	3,84	4,4	0,2936	
228	9	Zinc	4,95	1,9	0,3786	
229	9	Zinc	5,48	1,3	0,4188	
230	10	Zinc	9,86	0,6	0,7540	
231	10	Zinc	12,04	0,7	0,9206	
232	10	Zinc	12,97	1,8	0,9918	
233	11	Zinc	2,71	3,8	0,2075	
234	11	Zinc	1,31	3,2	0,0999	
235	11	Zinc	1,18	1,8	0,0899	
236	15	Zinc	2,23	3,9	0,1705	
237	15	Zinc	1,23	3,2	0,0943	
238	15	Zinc	23,73	2,4	1,8140	Zn removed
239	17	Zinc	0,56	1,1	0,0429	
240	17	Zinc	0,12	6,4	0,0090	
241	17	Zinc	1,19	4,5	0,0913	
242	21	Zinc	2,16	4,8	0,1649	
243	21	Zinc	1,73	1,7	0,1320	
244	21	Zinc	3,50	2,7	0,2678	

Table B.27: Blank values DGT labile cadmium, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
245	Blank	Cadmium	0,002	49,4	6,8E-05
246	Blank	Cadmium	0,001	72,2	4,0E-05
247	Blank	Cadmium	0,000	22,7	1,4E-05
248	Blank	Cadmium	0,001	18,8	4,0E-05
249	Blank	Cadmium	0,001	48,3	4,3E-05
250	Blank	Cadmium	0,001	37,3	6,0E-05

Table B. 28: Results for DGT labile zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
227	9	Cadmium	0,061	7,8	0,0027
228	9	Cadmium	0,059	2,7	0,0026
229	9	Cadmium	0,063	8,5	0,0028
230	10	Cadmium	0,087	8,6	0,0039
231	10	Cadmium	0,095	3,8	0,0042
232	10	Cadmium	0,100	5,3	0,0045
233	11	Cadmium	0,085	3,2	0,0038
234	11	Cadmium	0,072	11,1	0,0032
235	11	Cadmium	0,083	2,2	0,0037
236	15	Cadmium	0,079	8,0	0,0035
237	15	Cadmium	0,086	3,3	0,0038
238	15	Cadmium	0,090	9,5	0,0040
239	17	Cadmium	0,078	6,0	0,0035
240	17	Cadmium	0,077	3,9	0,0034
241	17	Cadmium	0,067	1,8	0,0030
242	21	Cadmium	0,081	2,7	0,0036
243	21	Cadmium	0,083	5,5	0,0037
244	21	Cadmium	0,080	0,8	0,0036

B.2 Chelex-100 results

Table B.29: Blank values chelex-100 labile iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
17	Blank	Iron	15,28	2,4	6,68
18	Blank	Iron	13,72	1,4	5,44
19	Blank	Iron	3,57	3,1	1,43
20	Blank	Iron	-0,02	43,6	-0,01
21	Blank	Iron	16,28	2,7	6,44
22	Blank	Iron	5,19	8,2	2,08
23	Blank	Iron	9,28	4,6	3,56

Table B.30: Results for chelex-100 labile iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
1	1	Iron	12,76	0,4	4,51
2	1	Iron	13,94	4,1	4,87
3	2	Iron	41,15	4,5	15,53
4	2	Iron	52,39	4,5	18,95
5	3	Iron	20,70	2,8	7,44

6	3	Iron	5,20	1,5	1,91
7	4	Iron	9,37	4,8	3,44
8	4	Iron	10,87	0,4	3,92
9	5	Iron	9,87	4,1	3,56
10	5	Iron	23,94	3,1	8,58
11	6	Iron	20,90	1,5	7,45
12	6	Iron	48,11	4,1	17,65
13	7	Iron	12,91	0,5	4,59
14	7	Iron	4,34	1,2	1,52
15	8	Iron	0,07	1,3	0,03
16	8	Iron	7,30	4,2	2,64

Table B.31: Blank values chelex-100 labile molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
17	Blank	Molybdenum	0,08	1,5	0,02
18	Blank	Molybdenum	0,09	6,5	0,02
19	Blank	Molybdenum	0,04	1,6	0,01
20	Blank	Molybdenum	0,00	135,5	0,00
21	Blank	Molybdenum	0,10	4,1	0,02
22	Blank	Molybdenum	0,04	7,5	0,01
23	Blank	Molybdenum	0,09	11,6	0,02

Table B.32: Results for chelex-100 labile molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
1	1	Molybdenum	0,137	4,2	0,028
2	1	Molybdenum	0,815	6,4	0,166
3	2	Molybdenum	0,755	4,6	0,166
4	2	Molybdenum	0,774	4,7	0,163
5	3	Molybdenum	0,463	9,2	0,097
6	3	Molybdenum	0,020	16,3	0,004
7	4	Molybdenum	0,719	3,6	0,154
8	4	Molybdenum	0,061	15,2	0,013
9	5	Molybdenum	0,261	2,0	0,055
10	5	Molybdenum	0,538	2,1	0,112
11	6	Molybdenum	0,219	3,3	0,045
12	6	Molybdenum	0,875	7,3	0,187
13	7	Molybdenum	0,333	3,9	0,069
14	7	Molybdenum	0,597	3,9	0,122
15	8	Molybdenum	0,393	1,6	0,086
16	8	Molybdenum	0,232	7,6	0,049

Table B.33: Blank values chelex-100 labile manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
17	Blank	Manganese	8,65	6,1	3,85	Mn removed
18	Blank	Manganese	15,50	3,8	6,25	Mn removed
19	Blank	Manganese	2,01	0,8	0,82	
20	Blank	Manganese	0,00	20,8	0,00	
21	Blank	Manganese	4,57	2,8	1,84	
22	Blank	Manganese	6,15	2,3	2,51	
23	Blank	Manganese	5,62	6,1	2,19	

Table B.34: Results for chelex-100 labile manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
1	1	Manganese	14,90	2,5	5,35	
2	1	Manganese	110,37	1,0	39,21	Mn removed
3	2	Manganese	47,38	1,4	18,18	Mn removed
4	2	Manganese	79,24	4,1	29,14	Mn removed
5	3	Manganese	107,31	1,0	39,22	Mn removed
6	3	Manganese	2,79	4,1	1,04	
7	4	Manganese	2,59	2,4	0,97	
8	4	Manganese	-0,15	4,2	-0,05	
9	5	Manganese	2,66	3,3	0,97	
10	5	Manganese	63,12	0,2	22,98	Mn removed
11	6	Manganese	1,91	1,1	0,69	
12	6	Manganese	36,05	2,3	13,45	Mn removed
13	7	Manganese	28,43	5,6	10,27	Mn removed
14	7	Manganese	3,45	2,6	1,23	
15	8	Manganese	13,51	4,0	5,13	
16	8	Manganese	18,69	0,9	6,86	

Table B.35: Blank values chelex-100 labile copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
17	Blank	Copper	0,52	3,0	0,20
18	Blank	Copper	0,25	3,0	0,09
19	Blank	Copper	0,19	4,6	0,07
20	Blank	Copper	-0,03	28,9	-0,01
21	Blank	Copper	0,30	3,0	0,11
22	Blank	Copper	0,34	3,7	0,12
23	Blank	Copper	0,24	7,7	0,08

Table B.36: Results for chelex-100 labile copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
1	1	Copper	1,84	2,7	0,5722
2	1	Copper	3,09	2,6	0,9494
3	2	Copper	1,55	2,8	0,5146
4	2	Copper	1,32	1,5	0,4201
5	3	Copper	1,93	0,7	0,6093
6	3	Copper	0,94	1,5	0,3045
7	4	Copper	1,86	4,6	0,5994
8	4	Copper	0,78	1,2	0,2482
9	5	Copper	2,19	4,8	0,6936
10	5	Copper	2,08	4,3	0,6535
11	6	Copper	1,14	1,8	0,3581
12	6	Copper	1,52	2,2	0,4892
13	7	Copper	1,53	2,5	0,4768
14	7	Copper	1,08	3,7	0,3346
15	8	Copper	0,71	3,8	0,2325
16	8	Copper	1,44	0,8	0,4586

Table B.37: Blank values chelex-100 labile cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
17	Blank	Cobalt	0,02	10,1	0,008
18	Blank	Cobalt	0,05	13,9	0,017
19	Blank	Cobalt	0,01	5,4	0,004
20	Blank	Cobalt	0,00	121,8	0,000
21	Blank	Cobalt	0,04	14,2	0,014
22	Blank	Cobalt	0,02	10,7	0,006
23	Blank	Cobalt	0,02	20,5	0,008

Table B.38: Results for chelex-100 labile cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
1	1	Cobalt	0,106	12,0	0,0356
2	1	Cobalt	0,244	4,4	0,0808
3	2	Cobalt	0,239	6,5	0,0854
4	2	Cobalt	0,288	2,6	0,0987
5	3	Cobalt	0,313	7,1	0,1065
6	3	Cobalt	0,060	4,8	0,0210
7	4	Cobalt	0,123	1,8	0,0430
8	4	Cobalt	0,071	7,2	0,0241
9	5	Cobalt	0,104	9,3	0,0356
10	5	Cobalt	0,243	3,4	0,0825
11	6	Cobalt	0,099	8,7	0,0333
12	6	Cobalt	0,217	4,3	0,0753
13	7	Cobalt	0,171	6,4	0,0575
14	7	Cobalt	0,100	9,7	0,0334
15	8	Cobalt	0,082	4,3	0,0289
16	8	Cobalt	0,172	2,2	0,0589

Table B.39: Blank values chelex-100 labile zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
17	Blank	Zinc	51	1,0	19,0	Zn removed
18	Blank	Zinc	9,81	3,9	3,3	
19	Blank	Zinc	10,63	3,3	3,6	
20	Blank	Zinc	-0,01	34,8	0,0	
21	Blank	Zinc	19,75	3,0	6,7	
22	Blank	Zinc	72	1,1	24,6	Zn removed
23	Blank	Zinc	58	3,5	19,0	Zn removed

Table B.40: Results for chelex-100 labile zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
1	1	Zinc	51,5	0,6	15,53	Zn removed
2	1	Zinc	20,8	2,1	6,21	
3	2	Zinc	9,8	4,8	3,16	
4	2	Zinc	30,1	1,0	9,29	
5	3	Zinc	22,2	6,0	6,81	
6	3	Zinc	7,2	4,8	2,24	
7	4	Zinc	7,7	4,5	2,43	

8	4	Zinc	-3,5	0,9	-1,09	
9	5	Zinc	1,5	2,0	0,45	
10	5	Zinc	7,0	2,3	2,15	
11	6	Zinc	10,0	3,7	3,04	
12	6	Zinc	28,1	2,8	8,81	
13	7	Zinc	16,7	2,2	5,07	
14	7	Zinc	8,2	3,3	2,45	
15	8	Zinc	5,7	3,4	1,81	
16	8	Zinc	8,7	3,4	2,68	

Table B.41: Blank values chelex-100 labile cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
17	Blank	Cadmium	0,014	4,4	0,003
18	Blank	Cadmium	0,002	35,6	0,000
19	Blank	Cadmium	0,003	5,3	0,001
20	Blank	Cadmium	0,000	105,6	0,000
21	Blank	Cadmium	0,004	5,4	0,001
22	Blank	Cadmium	0,013	9	0,003
23	Blank	Cadmium	0,003	11,9	0,001

Table B.42: Results for chelex-100 labile cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
1	1	Cadmium	0,2404	0,9	0,0422
2	1	Cadmium	0,1700	6,8	0,0295
3	2	Cadmium	0,1489	3,6	0,0279
4	2	Cadmium	0,1387	1,8	0,0249
5	3	Cadmium	0,1787	2,8	0,0319
6	3	Cadmium	0,1098	0,6	0,0200
7	4	Cadmium	0,1876	6,0	0,0343
8	4	Cadmium	0,1280	8,1	0,0229
9	5	Cadmium	0,1726	3,3	0,0309
10	5	Cadmium	0,1070	4,9	0,0190
11	6	Cadmium	0,1688	4,7	0,0299
12	6	Cadmium	0,1816	2,1	0,0331
13	7	Cadmium	0,2716	2,2	0,0480
14	7	Cadmium	0,1968	2,9	0,0343
15	8	Cadmium	0,1250	3,2	0,0232
16	8	Cadmium	0,2686	2,9	0,0482

Table B.43: Blank values chelex-100 labile iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
48	Blank	Iron	3,41	2,0	1,20	
49	Blank	Iron	1,04	1,7	0,35	
51	Blank	Iron	9,06	5,7	3,14	Iron removed
52	Blank	Iron	0,92	3,2	0,31	
53	Blank	Iron	1,39	3,3	0,47	
54	Blank	Iron	1,81	3,4	0,62	
55	Blank	Iron	0,85	2,2	0,30	
56	Blank	Iron	1,77	0,9	0,61	

Table B.44: Results for chelex-100 labile iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Iron	10,20	3,1	3,36	
25	9	Iron	9,87	3,7	3,18	
26	10	Iron	2,93	6,9	0,97	
27	10	Iron	3,53	2,5	1,17	
28	11	Iron	3,08	5,4	1,02	
29	11	Iron	10,25	2,1	3,31	
30	12	Iron	6,54	2,6	2,16	
31	12	Iron	6,87	6,2	2,25	
32	13	Iron	5,79	3,3	1,91	
33	13	Iron	15,19	1,3	4,94	
34	14	Iron	4,86	0,8	1,61	
35	14	Iron	15,21	5,8	4,92	
36	15	Iron	4,41	4,4	1,50	
37	15	Iron	1,36	2,6	0,46	
38	16	Iron	1,88	3,9	0,61	
39	16	Iron	3,13	0,6	1,03	
40	17	Iron	1,90	5,3	0,62	
41	17	Iron	0,13	4,3	0,04	
42	20	Iron	4,72	3,9	1,59	
43	20	Iron	4,57	7,4	1,56	
44	21	Iron	6,01	3,0	1,94	Filtrated
45	21	Iron	5,30	6,6	1,74	Filtrated
46	21	Iron	7,01	4,2	2,27	
47	21	Iron	6,59	3,8	2,15	

Table B.45: Blank values chelex-100 labile molybdenum second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Molybdenum	0,013	41,2	0,003
49	Blank	Molybdenum	0,005	47,9	0,001
51	Blank	Molybdenum	0,035	25,3	0,007
52	Blank	Molybdenum	0,006	48,0	0,001
53	Blank	Molybdenum	0,008	36,5	0,002
54	Blank	Molybdenum	0,013	40,9	0,003
55	Blank	Molybdenum	0,017	17,5	0,003
56	Blank	Molybdenum	0,011	42,7	0,002

Table B.46: Results for chelex-100 labile molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Molybdenum	0,128	5,2	0,0246	
25	9	Molybdenum	0,038	28,3	0,0071	
26	10	Molybdenum	0,075	9,2	0,0145	
27	10	Molybdenum	0,149	16,5	0,0287	
28	11	Molybdenum	0,100	9,8	0,0192	
29	11	Molybdenum	0,096	6,4	0,0180	
30	12	Molybdenum	0,076	4,2	0,0146	
31	12	Molybdenum	0,078	6,5	0,0148	
32	13	Molybdenum	0,076	17,8	0,0147	
33	13	Molybdenum	0,234	4,5	0,0443	
34	14	Molybdenum	0,100	9,2	0,0194	
35	14	Molybdenum	0,075	17,3	0,0141	
36	15	Molybdenum	0,167	11,9	0,0329	
37	15	Molybdenum	0,188	9,1	0,0371	
38	16	Molybdenum	0,273	3,9	0,0513	
39	16	Molybdenum	0,223	3,4	0,0429	
40	17	Molybdenum	0,202	3,1	0,0384	
41	17	Molybdenum	0,101	21,7	0,0191	
42	20	Molybdenum	0,375	1,7	0,0735	
43	20	Molybdenum	0,311	7,0	0,0619	
44	21	Molybdenum	0,214	3,4	0,0402	Filtrated
45	21	Molybdenum	0,365	6,5	0,0699	Filtrated
46	21	Molybdenum	0,400	9,0	0,0753	
47	21	Molybdenum	0,352	6,9	0,0667	

Table B.47: Blank values chelex-100 labile manganese second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Manganese	0,93	5,1	0,33
49	Blank	Manganese	0,08	3,6	0,03
51	Blank	Manganese	0,44	8,2	0,15
52	Blank	Manganese	0,05	1,1	0,02
53	Blank	Manganese	0,06	8,8	0,02
54	Blank	Manganese	0,10	15,0	0,04
55	Blank	Manganese	0,06	9,0	0,02
56	Blank	Manganese	0,10	8,3	0,04

Table B.48: Results for chelex-100 labile manganese, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Manganese	4,20	0,5	1,41	
25	9	Manganese	6,94	3,2	2,27	
26	10	Manganese	4,50	1,2	1,51	
27	10	Manganese	5,40	2,2	1,81	
28	11	Manganese	5,94	3,3	1,99	
29	11	Manganese	8,85	2,8	2,91	
30	12	Manganese	6,46	4,3	2,17	
31	12	Manganese	9,15	2,3	3,05	
32	13	Manganese	6,14	2,6	2,06	
33	13	Manganese	10,16	0,8	3,36	
34	14	Manganese	8,45	4,7	2,85	
35	14	Manganese	21,05	2,2	6,92	
36	15	Manganese	5,40	2,7	1,86	
37	15	Manganese	5,43	3,6	1,87	
38	16	Manganese	5,89	3,1	1,94	
39	16	Manganese	4,73	3,3	1,58	
40	17	Manganese	6,23	4,6	2,07	
41	17	Manganese	3,70	2,4	1,22	
42	20	Manganese	5,99	5,1	2,05	
43	20	Manganese	6,24	2,9	2,17	
44	21	Manganese	10,71	5,7	3,51	Filtrated
45	21	Manganese	12,34	2,2	4,12	Filtrated
46	21	Manganese	10,88	4,2	3,58	
47	21	Manganese	9,65	5,4	3,19	

Table B.49: Blank values chelex-100 labile copper second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Copper	0,22	4,3	0,067
49	Blank	Copper	0,12	12,2	0,037
51	Blank	Copper	0,32	2,1	0,098
52	Blank	Copper	0,17	7,5	0,051
53	Blank	Copper	0,11	9,7	0,031
54	Blank	Copper	0,16	10,9	0,048
55	Blank	Copper	0,36	1,4	0,110
56	Blank	Copper	0,18	3,4	0,054

Table B.50: Results for chelex-100 labile copper, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Copper	1,94	0,3	0,56	
25	9	Copper	3,85	1,7	1,09	
26	10	Copper	1,50	3,1	0,43	
27	10	Copper	1,37	8,6	0,40	
28	11	Copper	1,63	5,7	0,47	
29	11	Copper	1,73	5,7	0,49	
30	12	Copper	1,97	5,6	0,57	
31	12	Copper	1,53	2,7	0,44	
32	13	Copper	4,03	4,6	1,17	
33	13	Copper	4,49	3,3	1,28	
34	14	Copper	1,53	3,4	0,45	
35	14	Copper	1,22	4,7	0,35	
36	15	Copper	1,31	8,5	0,39	
37	15	Copper	1,61	1,1	0,48	
38	16	Copper	1,29	3,5	0,37	
39	16	Copper	1,28	4,1	0,37	
40	17	Copper	1,17	2,3	0,34	
41	17	Copper	0,85	3,5	0,24	
42	20	Copper	3,67	3,1	1,09	
43	20	Copper	4,43	1,4	1,33	
44	21	Copper	1,91	1,7	0,54	Filtrated
45	21	Copper	2,10	5,9	0,61	Filtrated
46	21	Copper	1,87	1,5	0,53	
47	21	Copper	1,66	3,9	0,47	

Table B.51: Blank values chelex-100 labile cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Cobalt	0,007	5,9	0,002
49	Blank	Cobalt	0,001	26,6	0,000
51	Blank	Cobalt	0,015	14,0	0,005
52	Blank	Cobalt	0,002	47,9	0,001
53	Blank	Cobalt	0,002	48,5	0,001
54	Blank	Cobalt	0,004	18,9	0,001
55	Blank	Cobalt	0,002	28,6	0,001
56	Blank	Cobalt	0,003	57,3	0,001

Table B.52: Results for chelex-100 labile cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Cobalt	0,070	2,2	0,0220	
25	9	Cobalt	0,156	1,8	0,0476	
26	10	Cobalt	0,131	3,1	0,0411	
27	10	Cobalt	0,107	3,6	0,0336	
28	11	Cobalt	0,146	8,1	0,0456	
29	11	Cobalt	0,168	7,4	0,0514	
30	12	Cobalt	0,228	6,8	0,0713	
31	12	Cobalt	0,473	1,4	0,1469	
32	13	Cobalt	0,138	8,4	0,0431	
33	13	Cobalt	0,413	5,5	0,1274	
34	14	Cobalt	0,295	4,7	0,0927	
35	14	Cobalt	0,758	5,1	0,2322	
36	15	Cobalt	0,127	6,7	0,0409	
37	15	Cobalt	0,121	4,2	0,0389	
38	16	Cobalt	0,137	4,1	0,0418	
39	16	Cobalt	0,105	3,3	0,0327	
40	17	Cobalt	0,139	6,3	0,0430	
41	17	Cobalt	0,114	8,6	0,0349	
42	20	Cobalt	0,154	2,0	0,0491	
43	20	Cobalt	0,149	3,7	0,0484	
44	21	Cobalt	0,203	2,8	0,0620	Filtrated
45	21	Cobalt	0,216	1,1	0,0673	Filtrated
46	21	Cobalt	0,209	6,4	0,0642	
47	21	Cobalt	0,168	1,9	0,0517	

Table B.53: Blank values chelex-100 labile zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Zinc	8,6	4,5	2,59
49	Blank	Zinc	2,4	2,6	0,70
51	Blank	Zinc	8,6	0,7	2,54
52	Blank	Zinc	1,9	1,2	0,55
53	Blank	Zinc	2,7	3,4	0,76
54	Blank	Zinc	6,7	7,0	1,95
55	Blank	Zinc	4,6	6,1	1,35
56	Blank	Zinc	6,6	5,0	1,92

Table B.54: Results for chelex-100 labile zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Zinc	25,07	2,4	7,06	
25	9	Zinc	78,49	2,3	21,61	Zn removed
26	10	Zinc	40,51	1,5	11,41	Zn removed
27	10	Zinc	12,89	2,2	3,63	
28	11	Zinc	17,97	1,9	5,07	
29	11	Zinc	41,83	3,4	11,54	
30	12	Zinc	578,56	2,5	163,02	Zn removed
31	12	Zinc	3 184,66	3,9	890,75	Zn removed
32	13	Zinc	109,00	3,0	30,74	Zn removed
33	13	Zinc	3 103,08	4,6	862,25	Zn removed
34	14	Zinc	1 685,61	3,4	477,76	Zn removed
35	14	Zinc	11 759,98	2,3	3247,68	Zn removed
36	15	Zinc	6,25	2,0	1,81	
37	15	Zinc	100,33	5,6	29,07	Zn removed
38	16	Zinc	12,35	3,0	3,41	
39	16	Zinc	44,94	6,1	12,64	Zn removed
40	17	Zinc	23,24	2,1	6,47	
41	17	Zinc	5,99	3,3	1,66	

42	20	Zinc	49,22	1,2	14,17	Zn removed
43	20	Zinc	13,71	1,9	4,00	
44	21	Zinc	7,70	2,4	2,12	Filtrated
45	21	Zinc	8,32	2,2	2,33	Filtrated
46	21	Zinc	3,76	4,5	1,04	
47	21	Zinc	4,68	2,0	1,30	

Table B.55: Blank values chelex-100 labile cadmium, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
48	Blank	Cadmium	0,20	5,3	0,04
49	Blank	Cadmium	0,13	3,2	0,02
51	Blank	Cadmium	0,29	2,7	0,05
52	Blank	Cadmium	0,14	6,2	0,02
53	Blank	Cadmium	0,36	3,9	0,06
54	Blank	Cadmium	0,08	4,7	0,01
55	Blank	Cadmium	0,12	8,3	0,02
56	Blank	Cadmium	0,14	6,5	0,02

Table B.56: Results for chelex-100 labile cadmium, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
24	9	Cadmium	0,038	0,8	0,0062	
25	9	Cadmium	0,115	2,5	0,0184	
26	10	Cadmium	0,055	5,7	0,0090	
27	10	Cadmium	0,072	4,0	0,0118	
28	11	Cadmium	0,181	0,5	0,0298	
29	11	Cadmium	0,289	3,4	0,0463	
30	12	Cadmium	0,118	2,4	0,0194	
31	12	Cadmium	0,191	1,8	0,0311	
32	13	Cadmium	0,082	3,0	0,0135	
33	13	Cadmium	0,144	2,0	0,0233	
34	14	Cadmium	0,131	1,5	0,0216	
35	14	Cadmium	0,107	6,9	0,0171	
36	15	Cadmium	0,103	2,4	0,0174	
37	15	Cadmium	0,058	1,0	0,0098	
38	16	Cadmium	0,095	0,9	0,0152	
39	16	Cadmium	0,098	5,6	0,0161	
40	17	Cadmium	0,863	2,1	0,1398	
41	17	Cadmium	0,101	3,2	0,0163	
42	20	Cadmium	0,098	0,7	0,0164	

43	20	Cadmium	0,086	2,6	0,0146	
44	21	Cadmium	0,133	1,6	0,0213	Filtrated
45	21	Cadmium	0,185	4,3	0,0302	Filtrated
46	21	Cadmium	0,164	5,0	0,0263	
47	21	Cadmium	0,081	4,1	0,0131	

B.3 Direct samples

Table B.57: Blank values for direct samples iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Iron	-0,01	14,1	-0,16
126	Blank	Iron	0,04	29,4	0,78
127	Blank	Iron	0,01	29,7	0,11
128	Blank	Iron	0,03	20,0	0,51
129	Blank	Iron	0,04	31,2	0,74

Table B.58: Results for direct samples iron, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Iron	2,83	4,60	50,66
101	1 (reportest)	Iron	2,90	5,20	52,00
102	1	Iron	2,24	1,70	40,14
102	1 (reportest)	Iron	2,40	5,40	42,90
103	1	Iron	2,38	9,20	42,64
104	2	Iron	2,77	2,90	49,59
105	2	Iron	2,25	5,70	40,36
106	2	Iron	1,88	6,20	33,59
107	3	Iron	2,09	3,80	37,46
108	3	Iron	2,06	5,50	36,82
109	3	Iron	2,45	3,60	43,83
110	4	Iron	3,74	2,70	66,91
110	4 (reportest)	Iron	3,70	7,50	66,33
111	4	Iron	2,62	8,30	46,98
112	4	Iron	2,64	4,70	47,20
113	5	Iron	3,29	6,60	58,94
114	5	Iron	2,91	2,90	52,10
115	5	Iron	2,62	7,50	46,88
116	6	Iron	5,50	2,70	98,49
117	6	Iron	5,14	3,80	92,01
118	6	Iron	5,03	5,30	90,13
119	7	Iron	2,91	6,40	52,19
120	7	Iron	3,29	6,50	59,00
121	7	Iron	3,25	2,20	58,24

122	8	Iron	2,47	7,10	44,24
123	8	Iron	2,22	12,00	39,77
124	8	Iron	2,53	4,80	45,38

Table B.59: Blank values for direct samples molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Molybdenum	0,00	59,0	0,00
126	Blank	Molybdenum	0,00	43,5	0,02
127	Blank	Molybdenum	-0,01	172,4	-0,06
128	Blank	Molybdenum	0,00	197,3	0,00
129	Blank	Molybdenum	0,01	46,6	0,13

Table B.60: Results for direct samples molybdenum, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Molybdenum	11,5	4,00	119,64
101	1 (reportest)	Molybdenum	10,6	6,60	110,74
102	1	Molybdenum	10,8	4,60	112,43
102	1 (reportest)	Molybdenum	11,2	6,70	116,62
103	1	Molybdenum	11,8	1,50	123,01
104	2	Molybdenum	11,8	4,00	122,73
105	2	Molybdenum	11,1	1,30	115,32
106	2	Molybdenum	11,4	7,80	119,24
107	3	Molybdenum	12,1	3,30	126,27
108	3	Molybdenum	11,2	9,90	117,02
109	3	Molybdenum	11,3	5,40	117,79
110	4	Molybdenum	11,1	6,30	115,23
110	4 (reportest)	Molybdenum	10,8	5,90	112,29
111	4	Molybdenum	11,4	8,40	119,16
112	4	Molybdenum	10,7	1,40	111,90
113	5	Molybdenum	11,2	3,20	116,94
114	5	Molybdenum	11,2	2,40	116,87
115	5	Molybdenum	11,3	3,00	117,27
116	6	Molybdenum	10,9	4,70	114,07
117	6	Molybdenum	11,1	8,10	115,45
118	6	Molybdenum	12,1	6,70	126,64
119	7	Molybdenum	10,6	8,80	110,60
120	7	Molybdenum	11,3	7,70	117,34
121	7	Molybdenum	10,7	9,30	111,69
122	8	Molybdenum	10,6	8,30	109,97
123	8	Molybdenum	11,3	7,90	117,56

124	8	Molybdenum	10,5	3,20	109,02

Table B.61: Blank values for direct samples manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Manganese	0,00	107,9	-0,028
126	Blank	Manganese	0,00	5,1	0,067
127	Blank	Manganese	0,00	48,9	0,070
128	Blank	Manganese	0,00	91,7	-0,019
129	Blank	Manganese	0,00	35,3	0,077

Table B.62: Results for direct samples manganese, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Manganese	0,58	6,10	10,63
101	1 (reportest)	Manganese	0,52	1,20	9,42
102	1	Manganese	0,55	8,50	10,03
102	1 (reportest)	Manganese	0,53	4,80	9,59
103	1	Manganese	0,51	9,70	9,33
104	2	Manganese	0,57	8,60	10,30
105	2	Manganese	0,52	12,10	9,49
106	2	Manganese	0,55	3,50	10,07
107	3	Manganese	0,55	4,60	9,96
108	3	Manganese	0,53	7,10	9,65
109	3	Manganese	0,56	1,80	10,18
110	4	Manganese	0,52	2,30	9,53
110	4 (reportest)	Manganese	0,57	5,70	10,44
111	4	Manganese	0,55	9,30	9,94
112	4	Manganese	0,59	1,90	10,75
113	5	Manganese	0,52	8,30	9,44
114	5	Manganese	0,60	11,50	10,97
115	5	Manganese	0,58	11,90	10,49
116	6	Manganese	0,60	7,40	10,98
117	6	Manganese	0,71	2,10	12,98
118	6	Manganese	0,64	9,60	11,57
119	7	Manganese	0,57	12,50	10,39
120	7	Manganese	0,61	12,10	11,13
121	7	Manganese	0,66	3,00	11,93
122	8	Manganese	0,52	5,40	9,55
123	8	Manganese	0,52	3,90	9,49
124	8	Manganese	0,54	8,60	9,80

Table B.63: Blank values for direct samples copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Copper	0,03	27,6	0,40
126	Blank	Copper	0,03	7,8	0,43
127	Blank	Copper	0,00	27,6	0,01
128	Blank	Copper	0,09	24,5	1,36
129	Blank	Copper	-0,02	24,2	-0,25

Table B.64: Results for direct samples copper, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Copper	0,63	2,80	9,91
101	1 (reportest)	Copper	0,56	9,60	8,74
102	1	Copper	0,47	10,10	7,34
102	1 (reportest)	Copper	0,57	10,50	8,97
103	1	Copper	0,55	6,30	8,61
104	2	Copper	0,49	1,60	7,66
105	2	Copper	0,52	7,30	8,21
106	2	Copper	0,54	15,60	8,47
107	3	Copper	0,49	11,30	7,72
108	3	Copper	0,56	6,80	8,88
109	3	Copper	0,49	5,80	7,70
110	4	Copper	0,49	11,40	7,66
110	4 (reportest)	Copper	0,55	6,10	8,69
111	4	Copper	0,89	9,60	14,01
112	4	Copper	0,41	2,60	6,49
113	5	Copper	0,29	9,30	4,57
114	5	Copper	0,37	6,00	5,83
115	5	Copper	0,41	4,20	6,42
116	6	Copper	0,31	9,50	4,87
117	6	Copper	0,22	4,10	3,39
118	6	Copper	0,19	4,30	2,92
119	7	Copper	0,06	0,70	0,97
120	7	Copper	0,11	9,50	1,73
121	7	Copper	0,02	8,50	0,28
122	8	Copper	0,02	5,80	0,31
123	8	Copper	0,05	16,70	0,86
124	8	Copper	0,00	16,70	0,04

Table B.65: Blank values for direct samples cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Cobalt	0,000	0,0	0,00
126	Blank	Cobalt	0,002	173,2	0,03
127	Blank	Cobalt	0,000	0,0	0,00
128	Blank	Cobalt	0,001	173,2	0,01
129	Blank	Cobalt	0,003	173,2	0,04

Table B.66: Results for direct samples cobalt, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Cobalt	0,03	24,10	0,45
101	1 (reportest)	Cobalt	0,03	36,80	0,49
102	1	Cobalt	0,03	24,10	0,48
102	1 (reportest)	Cobalt	0,03	16,40	0,56
103	1	Cobalt	0,03	26,20	0,43
104	2	Cobalt	0,02	34,00	0,38
105	2	Cobalt	0,04	9,40	0,62
106	2	Cobalt	0,02	27,30	0,42
107	3	Cobalt	0,03	17,80	0,45
108	3	Cobalt	0,04	22,90	0,60
109	3	Cobalt	0,03	36,30	0,47
110	4	Cobalt	0,03	36,30	0,47
110	4 (reportest)	Cobalt	0,03	31,10	0,56
111	4	Cobalt	0,05	15,50	0,83
112	4	Cobalt	0,04	30,20	0,75
113	5	Cobalt	0,03	24,80	0,56
114	5	Cobalt	0,04	41,10	0,67
115	5	Cobalt	0,02	6,90	0,38
116	6	Cobalt	0,02	9,10	0,29
117	6	Cobalt	0,03	9,10	0,59
118	6	Cobalt	0,03	30,70	0,58
119	7	Cobalt	0,02	37,10	0,41
120	7	Cobalt	0,02	25,00	0,38
121	7	Cobalt	0,03	5,60	0,50
122	8	Cobalt	0,04	23,50	0,66
123	8	Cobalt	0,04	26,30	0,65
124	8	Cobalt	0,04	21,40	0,69

Table B.67: Blank values for direct samples zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Zinc	0,02	86,6	0,25
126	Blank	Zinc	0,20	18,2	3,11
127	Blank	Zinc	0,01	56,8	0,11
128	Blank	Zinc	0,06	44,4	0,95
129	Blank	Zinc	0,08	36,5	1,24

Table B.68: Results for direct samples zinc, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
101	1	Zinc	1,16	16,50	17,66	
101	1 (reportest)	Zinc	1,41	12,80	21,55	
102	1	Zinc	1,33	21,30	20,28	
102	1 (reportest)	Zinc	1,47	9,20	22,41	
103	1	Zinc	1,34	26,70	20,51	
104	2	Zinc	0,90	19,70	13,74	
105	2	Zinc	1,20	13,70	18,28	
106	2	Zinc	1,11	22,20	17,00	
107	3	Zinc	0,45	0,00	6,85	
108	3	Zinc	0,76	5,90	11,58	
109	3	Zinc	0,66	29,60	10,04	
110	4	Zinc	0,55	33,80	8,48	
110	4 (reportest)	Zinc	0,50	10,30	7,66	
111	4	Zinc	0,49	23,70	7,43	
112	4	Zinc	0,62	18,70	9,42	
113	5	Zinc	0,90	12,50	13,73	
114	5	Zinc	1,02	11,20	15,62	
115	5	Zinc	0,90	17,40	13,83	
116	6	Zinc	3,63	8,70	55,55	Zn removed
117	6	Zinc	0,73	2,00	11,21	
118	6	Zinc	0,92	16,00	14,05	
119	7	Zinc	0,48	29,40	7,41	
120	7	Zinc	0,49	24,00	7,48	
121	7	Zinc	0,51	7,50	7,85	
122	8	Zinc	0,53	50,80	8,08	
123	8	Zinc	0,93	8,70	14,18	
124	8	Zinc	0,44	13,10	6,77	

Table B.69: Blank values for direct samples cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
125	Blank	Cadmium	0,004	59,0	0,039
126	Blank	Cadmium	0,001	43,5	0,011
127	Blank	Cadmium	0,003	172,4	0,027
128	Blank	Cadmium	0,002	197,3	0,022
129	Blank	Cadmium	0,003	46,6	0,031

Table B.70: Results for direct samples cadmium, first cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
101	1	Cadmium	0,037	15,5	0,3279
101	1 (reportest)	Cadmium	0,045	28,1	0,4037
102	1	Cadmium	0,038	13,2	0,3344
102	1 (reportest)	Cadmium	0,032	52,2	0,2851
103	1	Cadmium	0,050	45,7	0,4468
104	2	Cadmium	0,033	36,3	0,2910
105	2	Cadmium	0,046	20,5	0,4047
106	2	Cadmium	0,053	19,6	0,4751
107	3	Cadmium	0,051	10,4	0,4508
108	3	Cadmium	0,046	19,1	0,4117
109	3	Cadmium	0,043	13,0	0,3849
110	4	Cadmium	0,049	11,1	0,4389
110	4 (reportest)	Cadmium	0,040	27,9	0,3524
111	4	Cadmium	0,044	38,2	0,3911
112	4	Cadmium	0,032	32,0	0,2841
113	5	Cadmium	0,038	3,6	0,3370
114	5	Cadmium	0,031	40,9	0,2796
115	5	Cadmium	0,032	20,7	0,2847
116	6	Cadmium	0,055	17,9	0,4904
117	6	Cadmium	0,060	25,3	0,5313
118	6	Cadmium	0,048	6,8	0,4278
119	7	Cadmium	0,057	20,2	0,5041
120	7	Cadmium	0,050	16,3	0,4481
121	7	Cadmium	0,041	28,9	0,3630
122	8	Cadmium	0,043	16,9	0,3820
123	8	Cadmium	0,065	53,6	0,5800
124	8	Cadmium	0,036	25,4	0,3176

Table B.71: Blank values for direct samples iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Iron	0,01	22,4	0,18
170	Blank	Iron	0,10	17,8	1,75
171	Blank	Iron	0,00	14,0	0,05
172	Blank	Iron	-0,01	18,6	-0,19
173	Blank	Iron	0,05	12,4	0,92
174	Blank	Iron	0,05	8,3	0,96
175	Blank	Iron	0,02	18,0	0,44

Table B.72: Results for direct samples iron, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
130	9	Iron	1,93	13,6	34,54	
131	9	Iron	1,85	1,6	33,21	
132	9	Iron	2,31	1,9	41,30	
133	10	Iron	0,67	5,6	12,09	
134	10	Iron	0,78	11,8	13,95	
135	10	Iron	0,68	8,4	12,22	
136	11	Iron	0,90	6,5	16,10	
137	11	Iron	0,91	6,5	16,22	
138	11	Iron	0,80	11,5	14,25	
139	12	Iron	0,96	5,8	17,26	
140	12	Iron	0,90	3,3	16,08	
141	12	Iron	0,76	7,8	13,67	
142	13	Iron	1,66	1,0	29,73	
143	13	Iron	1,77	7,8	31,67	
144	13	Iron	1,66	5,5	29,66	
145	14	Iron	1,21	6,3	21,65	
146	14	Iron	0,99	3,8	17,65	
147	14	Iron	1,16	10,8	20,78	
148	15	Iron	0,54	13,7	9,67	
149	15	Iron	0,47	5,4	8,42	
150	15	Iron	0,60	6,7	10,71	
151	16	Iron	0,58	1,2	10,34	
152	16	Iron	1,37	4,8	24,59	
153	16	Iron	0,47	11,1	8,40	
154	17	Iron	1,23	12,7	21,94	
155	17	Iron	0,35	15,5	6,21	
156	17	Iron	0,35	7,5	6,20	
157	19	Iron	1,12	6,6	20,11	

158	19	Iron	1,14	7,2	20,41	
159	19	Iron	1,15	1,7	20,62	
160	20	Iron	1,29	21,5	23,07	
161	20	Iron	1,10	3,9	19,71	
162	20	Iron	0,95	5,7	16,94	
163	21	Iron	1,14	5,0	20,34	
164	21	Iron	1,05	6,2	18,85	
165	21	Iron	1,12	11,2	20,01	
166	22	Iron	6,68	2,1	119,56	Fe Removed
167	22	Iron	4,64	7,4	83,18	
168	22	Iron	4,21	10,3	75,41	

Table B.73: Blank values for direct samples molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Molybdenum	0,00	138,9	0,012
170	Blank	Molybdenum	0,01	32,3	0,082
171	Blank	Molybdenum	0,00	121,1	0,022
172	Blank	Molybdenum	0,00	169,3	0,009
173	Blank	Molybdenum	0,01	59,7	0,072
174	Blank	Molybdenum	0,00	141,3	0,048
175	Blank	Molybdenum	0,00	87,6	0,045

Table B.74: Results for direct samples molybdenum, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Molybdenum	10,65	6,1	110,97
131	9	Molybdenum	11,29	2,7	117,68
132	9	Molybdenum	10,92	3,2	113,81
133	10	Molybdenum	10,79	1,9	112,42
134	10	Molybdenum	11,24	2,0	117,12
135	10	Molybdenum	11,05	6,0	115,20
136	11	Molybdenum	10,63	8,1	110,76
137	11	Molybdenum	11,03	4,3	115,02
138	11	Molybdenum	10,42	2,5	108,56
139	12	Molybdenum	10,65	8,9	110,98
140	12	Molybdenum	10,83	4,4	112,86
141	12	Molybdenum	10,96	6,5	114,22
142	13	Molybdenum	11,24	1,4	117,17
143	13	Molybdenum	11,19	4,4	116,67
144	13	Molybdenum	11,05	5,6	115,15
145	14	Molybdenum	11,19	5,7	116,65

146	14	Molybdenum	10,65	2,9	110,96
147	14	Molybdenum	10,71	2,3	111,68
148	15	Molybdenum	10,66	3,2	111,11
149	15	Molybdenum	10,81	6,1	112,71
150	15	Molybdenum	10,87	7,7	113,32
151	16	Molybdenum	10,55	3,0	110,00
152	16	Molybdenum	10,52	3,1	109,65
153	16	Molybdenum	10,15	4,1	105,83
154	17	Molybdenum	10,05	1,5	104,75
155	17	Molybdenum	9,97	4,9	103,91
156	17	Molybdenum	10,22	2,4	106,57
157	19	Molybdenum	10,19	3,2	106,25
158	19	Molybdenum	9,64	10,4	100,50
159	19	Molybdenum	10,36	5,6	107,99
160	20	Molybdenum	10,30	1,6	107,32
161	20	Molybdenum	10,84	4,1	113,04
162	20	Molybdenum	10,39	10,9	108,31
163	21	Molybdenum	10,39	0,4	108,34
164	21	Molybdenum	10,89	3,1	113,46
165	21	Molybdenum	10,81	2,6	112,67
166	22	Molybdenum	10,94	2,3	114,03
167	22	Molybdenum	10,79	2,1	112,41
168	22	Molybdenum	10,90	0,2	113,66

Table B.75: Blank values for direct samples manganese, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Manganese	0,00	94,4	0,04
170	Blank	Manganese	0,01	41,7	0,18
171	Blank	Manganese	0,00	107,9	0,04
172	Blank	Manganese	0,00	97,2	0,02
173	Blank	Manganese	0,01	33,3	0,14
174	Blank	Manganese	0,00	37,8	0,05
175	Blank	Manganese	0,00	14,4	0,01

Table B.76: Results for direct samples manganese, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Manganese	0,63	6,6	11,44
131	9	Manganese	0,65	9,0	11,89
132	9	Manganese	0,66	8,5	12,01
133	10	Manganese	0,53	3,3	9,72
134	10	Manganese	0,50	7,2	9,03

135	10	Manganese	0,50	1,8	9,14
136	11	Manganese	0,52	6,8	9,40
137	11	Manganese	0,48	6,1	8,80
138	11	Manganese	0,45	8,1	8,14
139	12	Manganese	0,48	10,5	8,79
140	12	Manganese	0,48	10,2	8,81
141	12	Manganese	0,48	4,4	8,71
142	13	Manganese	0,58	4,8	10,54
143	13	Manganese	0,55	10,9	10,06
144	13	Manganese	0,55	6,7	10,04
145	14	Manganese	0,51	5,5	9,37
146	14	Manganese	0,46	1,5	8,45
147	14	Manganese	0,47	4,1	8,62
148	15	Manganese	0,52	10,6	9,52
149	15	Manganese	0,49	7,4	8,95
150	15	Manganese	0,49	5,1	8,90
151	16	Manganese	0,49	7,9	8,92
152	16	Manganese	0,47	3,2	8,47
153	16	Manganese	0,46	9,2	8,38
154	17	Manganese	0,51	1,5	9,20
155	17	Manganese	0,46	7,9	8,32
156	17	Manganese	0,38	6,4	6,98
157	19	Manganese	0,51	10,9	9,33
158	19	Manganese	0,50	7,5	9,04
159	19	Manganese	0,49	2,4	8,84
160	20	Manganese	0,49	5,5	8,84
161	20	Manganese	0,50	8,9	9,13
162	20	Manganese	0,53	10,4	9,65
163	21	Manganese	0,55	4,2	9,98
164	21	Manganese	0,57	5,7	10,33
165	21	Manganese	0,64	10,0	11,59
166	22	Manganese	0,87	8,4	15,84
167	22	Manganese	0,90	4,1	16,45
168	22	Manganese	0,91	2,6	16,65

Table B.77: Blank values for direct samples copper, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Copper	0,00	27,6	0,00
170	Blank	Copper	0,06	13,1	1,02
171	Blank	Copper	0,00	16,2	-0,02
172	Blank	Copper	0,00	32,7	-0,06
173	Blank	Copper	-0,01	21,2	-0,17
174	Blank	Copper	0,00	18,8	-0,06
175	Blank	Copper	-0,02	45,3	-0,25

Table B.78: Results for direct samples copper, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Copper	0,37	4,0	5,88
131	9	Copper	0,44	11,3	6,96
132	9	Copper	0,38	10,1	5,91
133	10	Copper	0,30	10,1	4,69
134	10	Copper	0,29	7,1	4,49
135	10	Copper	0,22	9,2	3,47
136	11	Copper	0,29	6,2	4,59
137	11	Copper	0,23	14,0	3,65
138	11	Copper	0,25	6,2	3,96
139	12	Copper	0,28	9,8	4,45
140	12	Copper	0,33	11,7	5,23
141	12	Copper	0,27	15,2	4,31
142	13	Copper	0,51	6,6	8,03
143	13	Copper	0,43	7,3	6,83
144	13	Copper	0,45	6,8	7,08
145	14	Copper	0,26	13,8	4,11
146	14	Copper	0,24	16,4	3,77
147	14	Copper	0,21	4,6	3,29
148	15	Copper	0,24	22,7	3,74
149	15	Copper	0,24	4,8	3,70
150	15	Copper	0,30	10,9	4,65
151	16	Copper	0,21	16,9	3,37
152	16	Copper	0,21	15,3	3,36
153	16	Copper	0,21	13,1	3,25
154	17	Copper	0,20	10,7	3,17
155	17	Copper	0,20	16,6	3,18
156	17	Copper	0,22	4,8	3,39
157	19	Copper	0,23	19,9	3,55
158	19	Copper	0,22	9,5	3,49

159	19	Copper	0,25	19,6	3,95
160	20	Copper	0,27	17,2	4,25
161	20	Copper	0,27	11,0	4,30
162	20	Copper	0,31	15,1	4,90
163	21	Copper	0,36	13,0	5,63
164	21	Copper	0,48	4,4	7,57
165	21	Copper	0,49	15,3	7,72
166	22	Copper	0,53	4,3	8,40
167	22	Copper	0,30	22,9	4,67
168	22	Copper	0,26	8,5	4,15

Table B.79: Blank values for direct samples cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Cobalt	0,001	173,2	0,013
170	Blank	Cobalt	0,001	173,2	0,015
171	Blank	Cobalt	0,002	89,2	0,030
172	Blank	Cobalt	0,001	173,2	0,016
173	Blank	Cobalt	0,004	173,2	0,062
174	Blank	Cobalt	0,002	87,7	0,029
175	Blank	Cobalt	0,001	173,2	0,013

Table B.80: Results for direct samples cobalt, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Cobalt	0,022	41,8	0,38
131	9	Cobalt	0,019	13,9	0,33
132	9	Cobalt	0,023	30,0	0,39
133	10	Cobalt	0,024	29,6	0,41
134	10	Cobalt	0,019	50,0	0,33
135	10	Cobalt	0,027	21,6	0,46
136	11	Cobalt	0,022	52,9	0,37
137	11	Cobalt	0,018	15,1	0,31
138	11	Cobalt	0,027	28,4	0,45
139	12	Cobalt	0,020	58,1	0,35
140	12	Cobalt	0,021	58,1	0,35
141	12	Cobalt	0,023	33,3	0,39
142	13	Cobalt	0,014	16,7	0,24
143	13	Cobalt	0,024	10,0	0,40
144	13	Cobalt	0,018	20,8	0,30
145	14	Cobalt	0,024	17,3	0,41
146	14	Cobalt	0,021	17,6	0,35
147	14	Cobalt	0,026	24,1	0,45

148	15	Cobalt	0,017	34,3	0,29
149	15	Cobalt	0,023	57,0	0,40
150	15	Cobalt	0,017	14,3	0,29
151	16	Cobalt	0,026	66,5	0,44
152	16	Cobalt	0,031	48,2	0,53
153	16	Cobalt	0,020	42,1	0,35
154	17	Cobalt	0,016	85,3	0,28
155	17	Cobalt	0,025	17,3	0,42
156	17	Cobalt	0,024	48,9	0,40
157	19	Cobalt	0,017	37,8	0,29
158	19	Cobalt	0,026	31,1	0,43
159	19	Cobalt	0,022	33,3	0,38
160	20	Cobalt	0,027	30,1	0,45
161	20	Cobalt	0,022	69,6	0,37
162	20	Cobalt	0,025	43,6	0,42
163	21	Cobalt	0,036	16,1	0,61
164	21	Cobalt	0,018	34,3	0,31
165	21	Cobalt	0,019	39,8	0,33
166	22	Cobalt	0,041	9,4	0,70
167	22	Cobalt	0,016	9,1	0,27
168	22	Cobalt	0,028	9,1	0,47

Table B.81: Blank values for direct samples zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)	Comment
169	Blank	Zinc	-0,03	63,0	-0,41	
170	Blank	Zinc	0,520	19,9	7,95	Zn removed
171	Blank	Zinc	0,02	20,0	0,25	
172	Blank	Zinc	-0,01	62,4	-0,17	
173	Blank	Zinc	0,18	15,7	2,70	
174	Blank	Zinc	0,17	46,5	2,62	
175	Blank	Zinc	0,02	52,9	0,25	

Table B.82: Results for direct samples zinc, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Zinc	1,07	13,6	16,34
131	9	Zinc	1,23	15,8	18,74
132	9	Zinc	1,43	10,0	21,91
133	10	Zinc	0,34	25,4	5,17
134	10	Zinc	0,56	14,8	8,50
135	10	Zinc	0,34	27,0	5,27

136	11	Zinc	0,33	26,0	5,10
137	11	Zinc	0,28	4,2	4,26
138	11	Zinc	0,25	39,6	3,75
139	12	Zinc	0,24	9,6	3,67
140	12	Zinc	0,34	5,6	5,13
141	12	Zinc	0,31	11,5	4,79
142	13	Zinc	0,26	15,1	4,03
143	13	Zinc	0,31	2,2	4,72
144	13	Zinc	0,24	21,3	3,69
145	14	Zinc	0,29	18,5	4,39
146	14	Zinc	0,47	23,7	7,25
147	14	Zinc	0,36	35,7	5,44
148	15	Zinc	0,28	19,1	4,32
149	15	Zinc	0,07	26,2	1,12
150	15	Zinc	0,22	35,6	3,38
151	16	Zinc	0,16	53,1	2,40
152	16	Zinc	0,33	31,4	5,06
153	16	Zinc	0,18	45,8	2,71
154	17	Zinc	0,58	9,8	8,83
155	17	Zinc	0,14	59,2	2,10
156	17	Zinc	0,17	38,6	2,54
157	19	Zinc	0,15	10,8	2,28
158	19	Zinc	0,17	31,8	2,64
159	19	Zinc	0,30	16,4	4,58
160	20	Zinc	0,43	19,9	6,61
161	20	Zinc	0,45	19,3	6,88
162	20	Zinc	0,44	12,4	6,71
163	21	Zinc	0,56	6,4	8,49
164	21	Zinc	0,65	15,4	10,00
165	21	Zinc	0,71	13,8	10,90
166	22	Zinc	1,37	10,1	20,93
167	22	Zinc	0,41	26,4	6,31
168	22	Zinc	0,31	17,4	4,72

Table B.83: Blank values for direct samples cadmium, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
169	Blank	Cadmium	0,000	6,5	-0,003
170	Blank	Cadmium	-0,001	89,2	-0,008
171	Blank	Cadmium	-0,001	166,1	-0,008
172	Blank	Cadmium	0,000	186,7	-0,003
173	Blank	Cadmium	0,001	102,6	0,005
174	Blank	Cadmium	0,002	84,9	0,015
175	Blank	Cadmium	0,000	261,0	-0,001

Table B.84: Results for direct samples cadmium, second cruise

Sample nr.	Station	Element	Conc. (µg/L)	RSD (%)	Conc. (nM)
130	9	Cadmium	0,074	12,7	0,66
131	9	Cadmium	0,077	9,5	0,69
132	9	Cadmium	0,076	9,2	0,68
133	10	Cadmium	0,078	1,6	0,69
134	10	Cadmium	0,069	16,5	0,62
135	10	Cadmium	0,072	8,6	0,64
136	11	Cadmium	0,073	3,0	0,65
137	11	Cadmium	0,065	2,3	0,58
138	11	Cadmium	0,067	9,8	0,59
139	12	Cadmium	0,072	10,1	0,64
140	12	Cadmium	0,072	13,9	0,64
141	12	Cadmium	0,068	8,4	0,61
142	13	Cadmium	0,075	10,9	0,66
143	13	Cadmium	0,076	6,5	0,68
144	13	Cadmium	0,074	15,3	0,66
145	14	Cadmium	0,062	11,5	0,55
146	14	Cadmium	0,072	23,9	0,64
147	14	Cadmium	0,067	11,2	0,60
148	15	Cadmium	0,074	1,8	0,66
149	15	Cadmium	0,072	3,9	0,64
150	15	Cadmium	0,074	10,7	0,66
151	16	Cadmium	0,068	10,9	0,61
152	16	Cadmium	0,074	3,9	0,65
153	16	Cadmium	0,064	7,7	0,57
154	17	Cadmium	0,066	16,0	0,59
155	17	Cadmium	0,075	9,2	0,67
156	17	Cadmium	0,063	15,3	0,56
157	19	Cadmium	0,059	13,1	0,53
158	19	Cadmium	0,073	4,2	0,65

159	19	Cadmium	0,062	18,4	0,55
160	20	Cadmium	0,065	3,6	0,57
161	20	Cadmium	0,067	12,6	0,59
162	20	Cadmium	0,077	1,8	0,69
163	21	Cadmium	0,064	2,7	0,57
164	21	Cadmium	0,077	13,2	0,69
165	21	Cadmium	0,072	9,5	0,64
166	22	Cadmium	0,074	9,2	0,66
167	22	Cadmium	0,071	4,8	0,63
168	22	Cadmium	0,082	2,1	0,73

Appendix C: Manganese to iron ratio

Table C.1: Manganese:iron ratio in stations with deep and shallow water, first cruise

	First cruise			
Station	Shallow water			
		Mn [nM]	Fe [nM]	Mn/Fe ratio
Inntian Nord Frøya (44m)	DGT	2,74	3,47	0,8
	Chelex-100	5,99	1,33	4,5
	Direct	11,15	56,47	0,2
	Deep water			
Vest Torsøya (161m)	DGT	2,23	3,37	0,7
	Chelex-100	1,04	4,67	0,2
	Direct	9,95	41,17	0,2
Reference station, first cruise (316m)	DGT	7,69	9,52	0,8
	Chelex-100	5,35	4,69	1,1
	Direct	9,61	43,13	0,2

Table C.2: Manganese:iron ratio in stations with deep and shallow water, second cruise

	Second cruise			
Station	Shallow water			
Inntian Nord Frøya (44m)	Chelex-100	4,88	3,23	1,5
	Direct	8,81	20,02	0,4
Inntian Frøya (30m)	Chelex-100	2,71	3,42	0,8
	Direct	10,21	30,35	0,3
	Deep water			
		Mn [nM]	Fe [nM]	Mn/Fe ratio
Fillfjorden (179m)	DGT	4,4	0,96	4,6
	Chelex-100	1,84	3,24	0,6
	Direct	11,78	36,35	0,3
Reference station, second cruise (211m)	DGT	2,62	1,37	1,9
	Chelex-100	1,64	0,33	5,0
	Direct	8,16	11,44	0,7

Appendix D: Chlorophyll a results

Table D.1: Chlorophyll a results

200 µm filter				
Station	A1 [µg chl a/L]	A2 [µg chl a/L]	B1 [µg chl a/L]	B2 [µg chl a/L]
12.02 Vest Frøyfjorden	0,2976	0,3264	0,3096	0,3432
12.02 Vest Torsøya	0,2544	0,2424	0,2784	0,2904
12.02 Vest Langøya	0,1656	0,156	0,1704	0,1776
12.02 Øst Langøya	0,1536	0,168	0,1608	0,1488
12.02 Storhallaren	0,168	0,1896	0,156	0,1584
13.02 Øst Frøyfjorden	0,192	0,2088	0,1848	0,1896
13.02 Inntian Nord Frøya	0,204	0,2088	0,192	
12.02 Reference station	0,3096	0,3216	0,3096	0,312
16.04 Fillfjorden	1,0944	1,0968	1,0248	0,912
16.04 Øst Frøyfjorden	1,7016	1,6104	1,2648	1,3584
16.04 Midt. Frøyfjorden	1,5936	1,6704	1,6848	1,6512
16.04 Øst Torsøya	1,0728	0,9792	1,3128	1,3776
16.04 Inntian Frøya	0,744	0,7752	0,6768	0,6288
16.04 Inntian Nord Frøya	1,668	1,6368	1,1112	1,1472
17.04 Øst Mausen	1,0584	1,0656	1,2168	1,1256
17.04 Sørvest Mausen	1,2216	1,1952	1,1472	1,1064
18.04 Nordøst Hemnskjel	1,1592	1,1784	1,1352	1,1448
18.04 Nord Røstøya	2,7336	2,7168	3,0192	3,0048
18.04 Hemnefjorden	2,1264	2,2992	1,9512	1,848
18.04 Midt. Snillfjord	2,2248	2,016	2,1264	2,112

Appendix E: Overview of the stations

Table E.1: Overview for the stations with respective coordinates, depth, name and sampling date

Date	Station	Coordinate	Depth (m)	Name
12.02.13	2	N 63°37.427` E 8°15.977	255	Vest Frøyfjorden
12.02.13	3	N 63°37.541` E 8°25.468	161	Vest Torsøya
12.02.13	4	N 63°37.888` E 8°34.131	131	Vest Langøya
12.02.13	5	N 63°37.912` E 8°34.815	145	Øst Langøya
12.02.13	6	N 63°40.544` E 8°39.562	89	Storhallaren
13.02.13	7	N 63°40.979` E 8°52.059	102	Øst Frøyfjorden
13.02.13	8	N 63°44.771` E 8°52.412	44	Inntian Nord Frøya
12.02.13	1	N 63°36.634` E 8°08.379	316	Reference station
16.04.13	9	N 63°36.605` E 9°00.709	179	Fillfjorden
16.04.13	10	N 63°40.979` E 8°52.059	103	Øst Frøyfjorden
16.04.13	11	N 63°40.148` E 8°40.509	108	Frøyfjorden
16.04.13	12	N 63°36.524` E 8°30.403	82	Torsøya
16.04.13	13	N 63°43.790` E 8°51.018	30	Inntian Frøya
16.04.13	14	N 63°44.771` E 8°52.412	45	Inntian Nord Frøya
17.04.13	15	N 63°51.334` E 8°43.462	132	Øst Mausen
17.04.13	16	N 63°49.548` E 8°34.149	91	Sørvest Mausen
18.04.13	19	N 63°31.856` E 9°12.735	168	Nordøst Hemskjel
18.04.13	20	N 63°27.441` E 8°54.001	170	Nord Røstøya
18.04.13	21	N 63°26.595` E 9°06.699	207	Vest Jamtøya/Hemnefjorden
18.04.13	22	N 63°21.473` E 9°13.332	400	Midt. Snillfjord/Hemnefjorden
17.04.13	17	N 63°44.636` E 8°16.109	211	Reference station