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Distribution of metals and organic material along a Norwegian river - ocean transect

Fordeling av metaller og organisk materiale langs
en norsk elv – hav transekt

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Environment and Natural Resources

Preface

With this thesis, I am completing my master studies in environment and natural resources, with a specialization in environmental toxins and ecotoxicology, at the Norwegian University of Life Sciences (NMBU). This project was a collaboration between NMBU and Norwegian Institution of Water Research (NIVA) and is a part of the project "DOMseason" led by Anne Deininger and funded via Center for Coastal Research, University of Agder (UiA). Additional funding was provided from the Faculty of Environmental Sciences and Natural Resource Management at NMBU.

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Abstract

The distribution of metals in aquatic systems is crucial for bioavailability and toxicity. Metals are transported from catchment to oceans through rivers. During this transport, the properties of metals (e.g., charge, size, and toxicity) are often strongly altered by chemical, physical and biological transformational processes. Specifically, terrestrial organic matter (ter-OM) may be a significant vector for trace metal transport across the land-to-sea continuum. According to the European Commission, integrative comprehension of the fate and effects of contaminants in different compartments of these transitional environments (estuarine sediment, water, biota) is still required to better establish, assess, and monitor the good ecological and chemical status targeted by the Water Framework Directive.

Questions remain as to which role salinity and associated increased ter-OM precipitation play along this gradient, i.e., when, how, and why metals and organic material distribute as they do along the river to sea transect. This thesis considers the distribution of 15 different metals (Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo, Ca, Pb, Mg, Na) in surface water along a river-ocean transect situated in southern Norway (Storelva – Sandnesfjorden transect).

After collecting water surface samples at 10 different sites along the transect, laboratory analysis of *in-situ* samples was conducted to assess the quantity and quality of organic material (OM), metal contribution, and size distribution (dissolved versus particulate fraction). Additional UV/VIS spectrophotometric analysis at specific wavelengths was conducted to determine the properties of dissolved organic matter (DOM) (< 0.22 μm).

In sum, there was detected a decrease in ter-OM and associated river-borne particle reactive metals (Al, Pb, Fe, Mn and, Si) along the river-ocean transect (i.e., highest values at riverine site, lowest at the marine site). The opposite trend, an increase along the gradient, was observed for ocean-associated metals (Ca, Mg, Na, Mo, As, but also Cr). There was detected a sudden change in element concentration at the mixing zone of fresh and saltwater. However, the location of the mixing zone varied between samplings due to variations in river flow and tidal water. Analysis of OM properties analysis indicated a decrease in color, aromaticity, humic content, and size, indicating a greater portion of terrestrial input of organic matter at the river site compared to the marine site.

Coastal zones are discussed as important zones for blue economy, especially in Norway. To achieve sustainable use of coastal resources, it is necessary to obtain knowledge of pollution in these areas. This study provides important new insights regarding the distribution, transformation, and cycling of organic matter and metals, with a special focus on ter-OM and associated metals, along river-ocean transects.

Sammendrag

Distribusjonen av metaller i akvatiske systemer er avgjørende for biotilgjengelighet og toksisitet. Metaller transporteres fra nedbørsfelt til hav gjennom elver. Under denne transporten endres egenskapene til metaller (f.eks. ladning, størrelse og toksisitet) sterkt ved kjemiske, fysiske og biologiske transformasjonsprosesser. Spesielt kan terrestrisk organisk materiale (ter-OM) være en viktig vektor for spormetalltransport over land-til-sjø-kontinuum. Ifølge EU-kommisjonen er det nødvendig med bedre forståelse av skjebnen og effektene av forurensninger i disse overgangsmiljøene (estuariesediment, vann, biota) for å bedre etablere, vurdere og overvåke den gode økologiske og kjemiske statusen som kreves av EUs vanndirektiv.

Det mangler fortsatt kunnskap om hvilken rolle salinitet og ter-OM spiller langs denne gradienten, dvs. når, hvordan og hvorfor metaller og organisk materiale fordeler seg som de gjør langs elv-hav gradienter. Denne oppgaven vurderer fordelingen og konsentrasjonen av 15 forskjellige metaller (Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo, Ca, Pb, Mg, Na) i overflatevann langs en elv - hav transekt i Sør-Norge (Storelva - Sandnesfjorden transekten).

Etter å ha samlet prøver fra 10 stasjoner av overflatevann langs transekten ble laboratorieanalyse av in-situ prøver utført for å kvantifisere mengde og kvalitet av organisk materiale (OM), metallbidrag og størrelsesfordeling (oppløst versus partikkelfraksjon). Ytterligere UV/VIS spektrofotometrisk analyse ved spesifikke bølgelengder ble utført for å bestemme egenskaper av løst organisk materiale (DOM) (<0,22 μm).

I sum ble det oppdaget en reduksjon i ter-OM og assosiert elvebårne, partikkelreaktive metaller (Al, Pb, Fe, Mn og Si) langs elv – hav transekten (dvs. høyeste verdier ved elveområdet, lavest på marint område). Den motsatte trenden, en økning langs gradienten, ble observert for havassosierte metaller (Ca, Mg, Na, Mo, As, men også Cr). Det ble oppdaget en plutselig endring i elementkonsentrasjonen ved blandesonen mellom ferskvann og saltvann. Plasseringen av blandesonen varierte imidlertid mellom prøvetakinger på grunn av variasjon i elvestrøm og tidevann. OM-egenskapsanalyse avdekket reduksjon i farge, aromatisitet, humusinnhold og størrelse, indikerte større andel allokton tilførsel av organisk materiale i elveområdet enn havområdet.

Kystsoner blir diskutert som viktige soner for blå økonomi, spesielt i Norge. For å oppnå bærekraftig bruk av kystressurser er det nødvendig med kunnskap om forurensning i disse områdene. Denne studien gir viktig ny innsikt angående distribusjon, transformasjon og sirkulasjon av organisk materiale og metaller, med et spesielt fokus på ter-OM og tilknyttede metaller, langs elv-hav transekter.

Abbreviations and definitions

Mo: Molybdenum

Al: Aluminum

Fe: Iron

Pb: Lead

Cr: Chromium

Si: Silicon

Ca: Calcium

Mn: Manganese

Ni: Nickel

Cu: Copper

Zn: Zinc

As: Arsenic

Cd: Cadmium

Mg: Magnesium

Na: Sodium

O: Oxygen

N: Nitrogen

CO_2: Carbondioxide

HCO_3^- : Bicarbonate

HA: Humic acid

FA: Fulvic acid

OM: Organic matter/organic material

NOM: Natural organic matter

Ter-OM: terrestrial organic material

TOC: Total organic carbon

DOC: Dissolved organic carbon

POC: Particulate organic carbon

SPM: Suspended particulate matter

PP: Polypropylene

Chl-a: Chlorophyll a

LOD: Limit of detection

LOQ: Limit of quantification

NMBU: Norwegian University of Life Sciences

NIVA: Norwegian Institution of Water Research

UiO: University of Oslo

UiA: University of Agder

WFD: Water Fame Directive

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1. Introduction

1.1. Coastal pollution

Water running through a catchment carries loose material with it (Goel, 2011). These substances are located in the catchment, either naturally or introduced by anthropogenic activity, and may be further transported through the water cycle, towards rivers and eventually the ocean (Bianchi, 2007). During recent years, an increased runoff of material from land to sea has been hypothesized (Deininger et al., 2020; Gundersen et al., 2020), with potentially large effects on downstream coastal zones (Friggstad et al. 2013, Deininger et al., 2019, McGovern et al., 2020). The properties of ter-OM make is a vector in transportation of metals. To assess the risks ter-OM and associated metals may pose to nature, ecosystems, or individuals, it is necessary to obtain information of how they are distributed and transformed by the changing environmental factors during land to ocean transport.

1.2. Today's issues

Traditionally inland waters and oceans have been studied as two different systems, with a lack of attention to the transition between them. However, during the transport from land to rivers, brackish water, and eventually saltwater, a substance enters different systems that each affect the substance's physicochemical properties (e.g., charge, reactivity, and solubility) (Schlesinger & Bernhardt, 2012). The determination of the exact effects of chemical, biological and environmental factors on metal and NOM distribution and properties has been a challenge. Especially for metals, it is crucial to obtain more knowledge on their size and distribution along the transport through the landscape to assess their potential risk in coastal areas, as it can range from severely toxic to harmless, e.g., due to speciation.

The large Norwegian sea and coastal areas are rich in resources and are predicted to be important for Norwegian future blue economy (Norwegian ministries, 2019). Coastal areas are affected by pollution transported with air and ocean currents from distant and/or offshore activities. In addition, land-based activities and leakage from old pollution pose a great contributor to Norwegian coastal pollution (Miljøstatus 2021c).

The consequences of coastal pollution can lead to:

- Change and destruction of habitats.
- Reduced biodiversity.
- A decline in stocks.
- Increased strain on vulnerable species.

Coastal areas are also important to reduce the effects of climate change. Blue carbon is the carbon stored in coastal and marine ecosystems and is an integral part of global carbon storage (Lovelock & Duarte, 2019). However, if the ecosystems are degraded or damaged, their carbon sink capacity is lost or adversely affected. The carbon stored is released, resulting in emissions of carbon dioxide (CO_2) that contribute to climate change (IPCC, 2019). To obtain a good coastal environment, i.e., develop the Norwegian blue economy, and reduce CO_2-induced climate change, sustainable management of coastal areas is essential (Norwegian ministries, 2019). A key step in this direction is a better understanding of land to ocean pollution, here with a focus on ter-OM and metals.

1.3.   Aim of this study

The aim of this study is to determine the quantity and quality of ter-OM, trace metal contribution, as well as the size distribution of dissolved versus particulate fractions of ter-OM. This was done by detailed analysis of *in situ* samples from a natural river-ocean transect located in boreal southern Norway (Storelva – Sandnesfjorden transect) during fall 2020. By considering the metal and organic matter distribution, compared with coastal physical and biological conditions, this thesis will be contributing to improving the knowledge of the dynamics and transformation processes within the transect. Comparison of the result from this study with existing literature will be conducted to conclude which environmental factors are of main importance for the distribution of the chosen substances. In detail, this study addresses 15 different metals chosen due to their importance in coastal systems. (Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo, Ca, Pb, Mg, Na)

The hypothesis of the study is that there will be a reduction in river-borne ter-OM and associated metals along the surface water of the river-ocean transect, to a great extent caused by the introduction of saltwater. Simultaneously there is expected an increase in ocean-associated metals. Regarding properties of organic matter, the highest contribution of terrestrial-associated properties is expected closest to the river.

2. Theory

2.1. Land – ocean transects.

The physiochemical properties of a substance are to a great extent affected by environmental factors (e.g., pH, temperature, competing ions, and redox conditions). During the transport from catchment to the ocean, substances enter both soil, freshwater, brackish water, and eventually saltwater. The changes in environments are known to affect the physicochemical properties of both organic matter and metals and are crucial to their faith in the environment (Bianchi, 2007). To assess the risk of metals and organic material, and ensure sustainable management of coastal areas, it is necessary to obtain information on the properties of both the substances and the environment.

2.2. Natural organic matter

Natural organic matter (NOM) is degraded products of biomolecules such as plants and animals (VanLoon & Duffy, 2011). Other common names used for the same substances are organic material or organic matter (OM). Because analytical quantification has historically for a long time been based on measuring the amount of organic carbon, NOM has also often been referred to as organic carbon (OC). Organic material is produced wherever there are living organisms, both on land and in water (VanLoon & Duffy, 2011). Terrestrial organic matter (ter-OM) is organic material produced in the terrestrial environment and is of particular interest in the study of material transport from land to the ocean.

All life on earth consists of carbon. When an organism dies, it is broken down by microbial activity and eventually ends up as small portions of a wide variety of components consisting of mainly carbon, but also hydrogen, oxygen, and smaller amount of nitrogen and other trace elements (VanLoon & Duffy, 2011). Even though NOM also are produced within rivers and coast, a great portion is from terrestrial vegetation/soil in boreal areas due to the nature of the water cycle. (Alling et al., 2008; Malcolm & Durum, 1976; Sillanpää, 2015). The properties of organic matter are often different for different sources (e.g., terrestrial vs. aquatic) (Helms et al., 2008). Based on these differences, it is possible to determine the source of NOM.

The different forms of organic matter have a wide variety of different properties. However, in aquatic environments, soluble fractions are often of particular interest. Fulvic acid (FA) and humic acids (HA) are the two primary components of NOM, which both have complex structures, with various functional groups like hydroxyl, carboxylic, and phenolic groups (Deng & Dixon, 2002). One important difference is that fulvic acids are water-soluble across the entire pH range, while humic acid is not soluble below pH 2 (VanLoon & Duffy, 2011).

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Additionally, NOM might also be operationally divided by size. Dissolved organic matter (DOM) and particulate organic matter (POM) are typically differentiated by which can pass through a membrane. Historically, as well as discipline dependent (e.g., marine versus freshwater), a filter with pore size 0.45 μm has been used. However recent years 0.22 μm has been more common, for better filtering out bacteria (Pawlowicz, 2013). Filter size 0.22 μm was operationationally chosen in this study.

NOM can be recognized in water by the characteristic brown/yellow color caused by CDOM, the fraction of DOM that absorbs UV and visible light (blue end of VIS-spectra). This fraction is largely responsible for the optical properties of most natural waters (Haaland et al., 2010). By adsorbing radiation in the lower specter of UV light, it protects biota from harmful radiation. However, it can also block out light important for photosynthesis (Nevalainen et al., 2020; Walsh et al., 2013). CDOM is therefore crucial in many photochemical and biogeochemical processes.

The functional groups of organic material are usually negatively charged and are highly reactive with cationic metals (VanLoon and Duffy, 2011). This results in the formation of both soluble and insoluble NOM–metal complexes (Eshwar et al., 2017; Redman et al., 2002). Both humic and fulvic acid can form water-soluble and insoluble complexes with a wide variety of metals. The solubility is correlated with the valence, first hydrolysis constants, and effective hydrated ionic diameter of the metal ions (Schnitzer & Kerndorff, 1981)

2.3. Metals

Of all the elements in the periodic table, 61 are metals. The word trace is used when metals occur in low amounts, which in aqueous environments is between 10^{-15} mol/L (10 fM) and 10^{-5} mol/L (1 μM) (Robbins et al., 2019). Earth's crust consists of all the different metals in different proportions. When rocks and soil are exposed to forces of nature, some of the metals are eroded and can be transported to new places by wind and water. Human activity that moves metals out of their natural habitat may enhance this process. In their new environment, metals can engage in reactions and cause chemical changes, and when sufficient amounts of metals enter a new system, it can lead to severe changes and/or cause problems for organisms and ecosystems.

Metals are typically electropositive, which means they donate one or more electron(s). In a chemical reaction, there needs to be an element to accept these electron(s) (electron acceptor). In these reactions, the metal ends up with an increased charge (positive charge), while the electron acceptor ends up with a reduced charge (negative charge). The transfer of

electrons can either be complete (ionic bonding) or be shared between elements (e.g., covalent bonding or hydrogen bonding). Organic matter is one reactant especially of interest in natural waters. Natural organic matter contains functional groups (e.g., carboxyl, phenol, amine, thiols) that form complexes with trace metals. There is a wide variety of organic matter and metals, and the complexes they form have a wide variety of properties; however, size, charge, and solubility are especially important in biogeochemistry.

Some metals in the environment are associated with toxicity but are still necessary for biological functions. The bioavailability and load of the metal will determine the toxicity. The oxidation state is of primary importance for toxicity. A common example is arsenic, where the inorganic. As(III) is severely toxic, while As(V) is far less toxic to aquatic organisms (Oremland & Stolz, 2013). When redox condition changes, the toxicity of arsenic changes, even though the concentration is unchanged (Sharma & Sohn, 2009). The toxicity of metals in nature largely dependent on pH. Solubility and charge increase when pH is reduced (Walker et al., 2012). In river-ocean systems where pH is expected to increase towards the ocean (Schlesinger & Bernhardt, 2013), there would be expected a general decrease in toxicity.

2.4.   Size distribution

The size of a substance (e.g., metal-OM complex) is of great importance for its distribution in aquatic environments, determining whether the substance stays in the water column (dissolved fraction) or sinks to the sediments (particulate fraction). The dissolved fraction in this study contains both "truly dissolved" ions and colloids that float.
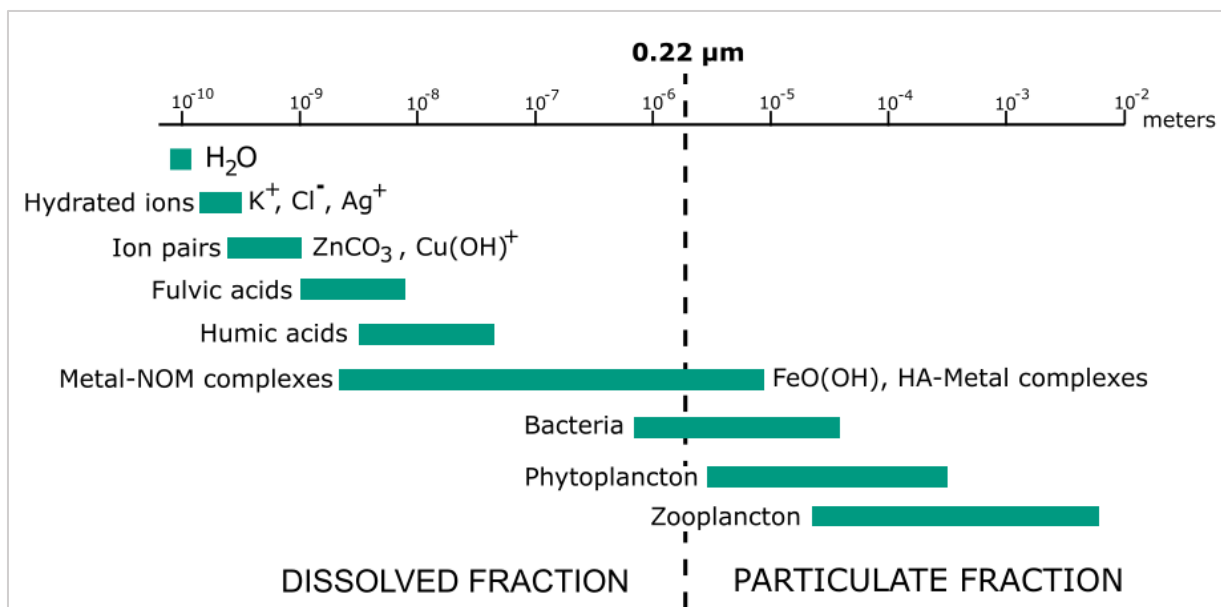
Figure 1 *The average size distribution of different substances. The dotted vertical line marks the critical separation between dissolved and particulate fractions at 0.22 μm. This is an operationally set size limit, and 0.45 μm is also commonly used in this context.*

2.5. Mobility of metals and NOM in aquatic environments

The most important environmental change during river–ocean transport occurs in estuaries which is the area providing an interface between river freshwater and ocean saltwater. These areas have strong gradients in many variables, both physical and chemical. Examples are pH, temperature, dissolved salt, nutrients, dissolved oxygen, amount, and particle composition (Schlesinger & Bernhardt, 2013). In many estuaries, salinity is the controlling factor for portioning and distribution of particles (Asmala et al., 2014; Santschi, 1988; Turner, 1996) and is, therefore, a key variable controlling bioavailability and toxicity of metals bound to particles. The mixing zone, where river freshwater is mixed with ocean saltwater, is of particular interest in particle distribution as it is an area for many transformational processes. The placement of this zone is largely dependent on precipitation/river flow and tidal water.

When organic matter is transported from fresh to saltwater, it tends to flocculate at the river-sea mixing zones. When the electrolyte concentration increase, it neutralizes the negative surface charge of NOM molecules, which results in riverine particles destabilizes and coagulate (Bianchi et al., 2007). Hence, NOM is general less hydrophilic in more saline environments. When becoming large enough, they flocculate before being integrated into sediments. (fig. 2) (Marcovecchio et al., 2016). Flocculation mainly depends on salinity (Asmala et al., 2014; Santschi, 1988; Turner, 1996). When organic matter flocculates, associated metals tend to flocculate as well. This is an essential mechanism of removing both metals and OM from surface water in river-ocean transects.

The same process appears to many (oxy)hydroxides (Daneshvar, 2015). Iron hydroxides are of particular importance because of the abundance in natural waters and the chemical nature (Turner et al., 1996). Similar to NOM, the negative surface charge of metal (oxy)hydroxides is balanced out by an "ionic cloud" in river freshwater. When ion concentration increases, the "cloud" is disturbed, and the oxide attracts other elements, coagulate and flocculate (fig, 2). Increasing pH is another important factor, reducing the solubility of metals and thereby causing precipitation (Walker et al., 2012).
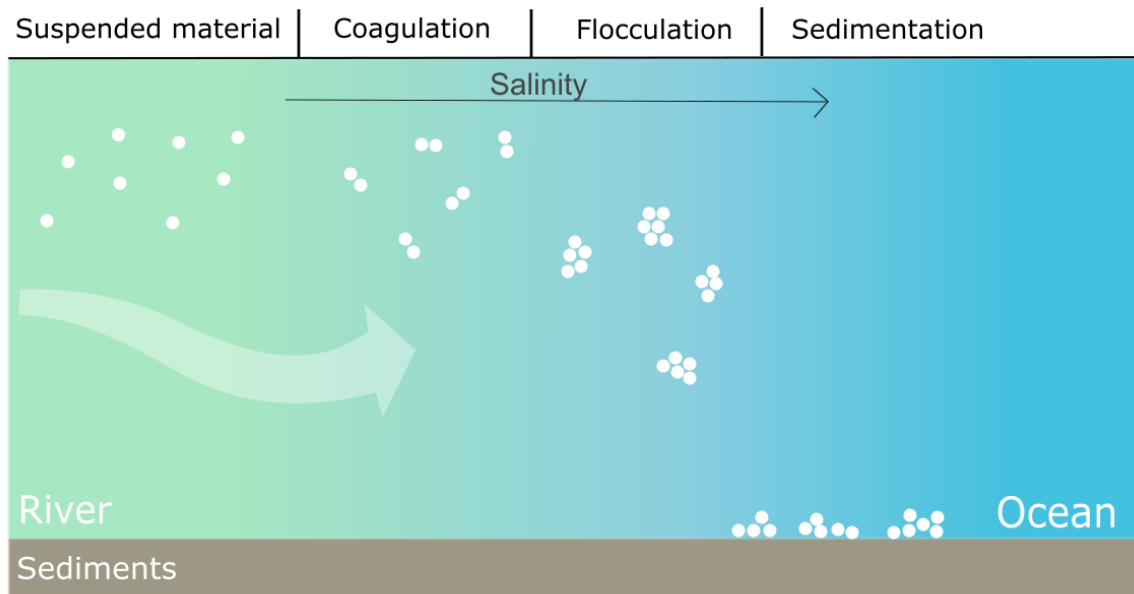
Figure 2 *The salt-induced transformational process of suspended material in river–ocean transects. The increasing salinity/ion concentration destabilizes suspended material which causes them to coagulate, then flocculate, and eventually sediment.*

Despite the fact that salinity variation is highlighted as one of the regulator mechanisms (Asmala et al., 2014; Santschi, 1988), other environmental factors are also important in material distribution on river-ocean transects. Catchment exposed to acid rain is one example (Haaland et al., 2010), where pH drop caused oxidation and leakage of toxic aluminum, causing fish death in the 1980s (Miljøstatus, 2020b). The overall input to the system is controlled by the climate and properties of the catchment, which determines the amount within the system. In addition, biology is of great importance, both in the decomposition of NOM and the transport of metals. Uptake in plankton cause metals to follow the same distribution as the plankton. This phenomenon is especially important for nutrients (e.g., Si, Mg, Na) but also metals with similar properties of nutrients, e.g., Cd, which is similar to phosphorus (Machado et al., 2016; Santschi, 1988). Dilution of river water by ocean water is another effect, which will cause the abundance of river-borne substances to decrease.

So far, river-borne, flocculating, decreasing metals have been the focus. However, metals also increase along the transect, like those abundant in saltwater (e.g., Na, Mg, Ca). Other causes for increase are addition along the transect due to either pollution from land, upwelling from sediments, or desorption from particles due to increasing complexation with seawater anions and/or increasing competition for particle adsorption sites with seawater cations (Schlesinger & Bernhardt, 2013).

2.6. Environmental issues

2.6.1. Organic material

In addition to being an essential transporter for metals, NOM affects water systems in several ways, both directly and indirectly. A small selection of essential effects will be discussed in the following part.

Increasing concentrations of CDOM in the water column leads to brownification, decreases UV light penetration, and thus decreases the water transparency (Colbe, 2007). These properties make it a possible limiting factor in photosynthesis production. The effect of ter-OM addition has been illustrated to affect primary production (Deininger et al., 2017; Jones, 1992; Klug, 2002), which is the basis of aquatic food webs. The decreased light penetration causes more of the warmth generated by sun radiation to be trapped in the upper part of the water column. This leads to higher surface temperature and a subsequent rise of the thermocline, an effect that is often observed in lakes (Caplanne & Laurion, 2008; Read & Rose, 2013)

Decreased photosynthesis might decrease the O_2 concentration. Increased input of ter-OM can also increase O_2 demand for microbial-driven decomposition of NOM (VanLoon & Duffy, 2011). An abundance of NOM is known to cause anoxic sediment (Kristensen, 2000). This might have substantial effects on benthic communities, and especially the distribution between anaerobic and aerobic organisms (Vasconcelos et al., 2018)

2.6.2. Metals

Metals have different properties and roles in the environment. Some are essential nutrients, while others are highly toxic. The basic principle of toxicology states that any substance can be harmful, and toxicity is dependent on the administered dose. It needs to be bioavailable to affect an organism, which means it exists in a form and location where an organism can take it up. Living organisms need many metals, i.e., for building cells or energy production; however, all metals are toxic at certain levels. What determines the toxicity is the amount, the

form, and availability. The toxic effects can cause harm to both individuals as well as entire ecosystems, and examples of effects are oxidative stress, hormonal distribution, increased risk of cancer, or death. (Walker et al., 2012)

Metal complexation with ligands and size distribution is also important for bioavailability. Generally, toxicity is reduced with larger size (Walker et al., 2012), which makes the order: Free ions ≥ colloids > particles.

Free ions can be adsorbed on gills or other surface areas of negatively charged cells and are taken up more easily in the intestine and stored in organs. Particles are generally less bioavailable as they need to swallow and are more easily regulated and excreted (Walker et al., 2012; Yancheva et al., 2014).

The distribution also determines which parts of the ecosystem the metals will affect. If buildup in the sediments, metals are more available to benthic organisms, while in surface water, they are more available to phytoplankton or swimming organisms. Biomagnification, the process of accumulation upwards in the food chain, is relevant to some metals; however, bioconcentration, uptake from the surrounding water, is the main pathway of metals to most animals (Gray, 2002).

Uptake and toxicity of one element are strongly affected by the presence of other elements in the same solution. The presence of different components in the same solution can either be synergistic, antagonistic, or additive (Walker et al., 2012). A synergistic effect is when exposure to two or more chemicals at one time results in effects that are greater than the sum of the effects of the individual chemicals. An antagonistic effect is when hen the presence of another chemical decrease toxicity of a chemical. An additive effect is when to chemicals do not affect the toxicity of each other. The presence of several substances can enhance or reduce the impact of each other. Therefore, determining the risk of one metal is highly challenging, and a vast amount of information about the total mixture is needed.

Even though metal pollution is still a problem today, most toxic metals have been major reduced due to governmental regulations. One example is the banning of lead in gasoline, which has been a great contributor to the 90% reduction of lead emissions from 1995 – 2021 (Miljøstatus, 2021). However, because metals are not broken down as organic compounds, they can be stored in soil or sediments over long periods and be a risk in the future.

3. Method

The study was designed to determine the distribution of organic matter and metals along the Norwegian fjord - Storelva and to detect how metals and organic material are affected by the environmental changes along the transect. In addition, there were conducted analyzes to assess the properties of the organic material.

Fieldwork was carried out during fall of 2020. Laboratory analyzes were performed at the Norwegian University of Life Sciences (NMBU), Norwegian Institute of Water Research (NIVA), University of Oslo (UiO), and the University of Agder (UiA)

3.1. Fieldwork
3.1.1. Study area

Storelva is a river in southern Norway, which runs through Vegårdshei and Tvedestrand in Agder and ends up in Sandnesfjorden before entering the Skagerak coast (Fig 3).

An upstream location in the fjord is included in the Norwegian river monitoring program, and some information about the area is collected from NIVA reports (Gundersen et al. 2020). Through the monitoring program, there has been detected elevated levels of As, Pb, and Zn (Gundersen et al., 2020). The flow dynamics in Storelva are characterized by rapid responses to precipitation events with a relatively quick return to the baseline level after the flood peak. There is no distinct seasonal pattern, and flood events can occur in all seasons, also during winter.

The catchment consists of mostly pine vegetation, and there is not much settlement. Storelva is probably affected by runoff from historical mining in the catchment area (Gundersen, 2020)

Figure 3 *Map of the study area Storelva - Sandnesfjorden in southern Norway. The map is retrieved from www.norgeskart.no*

3.1.2. Sampling

Sampling was performed twice in 2020 (12th October and 4th November 2020).
10 sites along Storelva were chosen (fig. 4). More sites were chosen in the upper section of the transect compared to the marine section, due to the expected higher concentration of ter-OM associated metals in this area. The sampling procedure started with station A and followed the fjord until station J.

At each sapling spot, both unfiltered and filtered samples were collected. All containers and equipment were pre-rinsed three times with the same water (i.e., natural or distilled). The samples were collected by the following procedure:

Unfiltered samples: A plastic bucket was lowered to approximately 0.5 m and filled. Two polypropylene (PP) bottles were filled with water collected from the bucket.

Filtered samples A syringe and 0.22 μm filter was rinsed with 70 ml ($\pm$10 mL) distilled water. Water collected from the bucket was filtered into a PP bottle.

All samples were stored in black plastic bags until reaching land, then stored dark at 4°C until analysis.
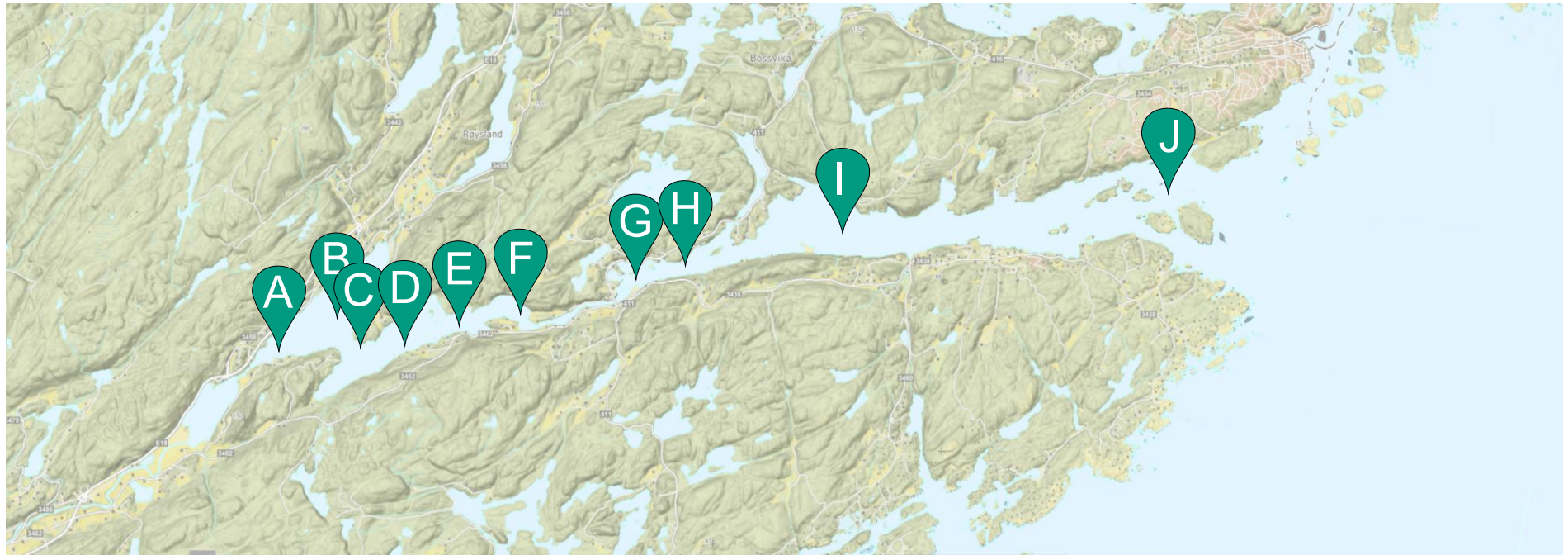
Figure 4 *The different sampling stations A – J along the river – ocean transect Storelva-Sandnesfjorden. The map is retrieved from www.norgeskart.no*

3.2. Instrumental analysis

3.2.1. Organic carbon analysis

Total organic carbon (TOC) was measured from unfiltered samples, while dissolved organic carbon was measured as TOC in filtered (< 0.22 μm) samples. Both were determined in unfiltered and filtered samples from both sampling campaigns.

TOC was analyzed with a Shimadzu organic carbon analyzer TOC-V CPN with ASI-V automatic pump, according to the Norwegian standard method NS-EN 1484 IR. The instrument works by inserting HCL through the sample with synthetic (Hydrocarbon free) air. This removes the inorganic carbon. The sample is then heated by a platina catalysator to transform the organic carbon into CO_2. The amount of CO_2 is then measured by an infrared detector. The Analysis was performed at NMBU.

3.2.2. Fluorescence spectroscopy

Phytoplankton biomass can be estimated by the photosynthetic pigment, chlorophyll a, which is found in all phytoplankton cells. The procedure consists of isolating the cells, extracting the chlorophyll, and measuring the fluorescence. The analysis was performed on samples collected during the first sampling campaign (October) at stations A, C, G, I, and J.

Preparation of the samples was conducted at the NIVA Grimstad laboratory the same day as sampling. Preparation consisted of filtering natural water collected in the field through GF/F glass fiber filters by using a vacuum pump. This filtering was performed in dim light.

Chlorophyll a was determined fluorometrically on a Turner 10-AU fluorometer after methanol extraction. Fluorometry works by molecules of the analyte being excited by irradiation at a certain wavelength, and emitted radiation at longer wavelengths is detected (Skoog et al., 2014). The Analysis was performed at UiO.

3.2.3. UV/VIS spectrophotometry

To determine the properties of the organic material, absorbance at specific wavelengths was measured. The aim was to determine the amount and properties of CDOM and assess how the organic material is affected by changing environmental factors along the transect. This method was used on both filtered (< 0.22 μm) samples collected in field during the first sampling (October).

The analysis was performed on a Cary UV-Vis-NIR spectrophotometer. The analytical method works by measuring the intensity of light that passes through a sample with respect to the intensity of light through a reference sample or blank (Skoog et al., 2014). Absorption was measured at wavelengths between 190 and 900 nm, however absorption measured at 204, 250, 254, 365, 375, 420, and 435 were extracted and used. All samples were analyzed in 10 mm cuvettes and blank correlated with distilled water. Analysis was performed at NIVA.

3.2.4. ICP-MS and ICP-OES

ICP-MS and ICP-OES were performed to determine the quantity of the chosen metals in the samples. Dissolved metals were measured as the total in filtered ($< 0.22 \ \mu m$) water, and total fraction was measured in unfiltered samples. The analysis was conducted on both unfiltered and filtered samples collected from the ten stations during both sampling campaigns.

Inductively coupled plasma mass spectroscopy (ICP – MS) was used in the analysis for Al, Si, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo, Ca, and Pb, on an Agilent 8800 ICP-MS instrument. ICP-MS is mass spectroscopy using inductively coupled plasma to ionize the samples. It atomizes the sample and creates atomic and small polyatomic ions, which are differentiated by their mass to charge ratios (Skoog et al., 2014). The technique is widely used and known for its ability to detect metals (and several non-metals) in liquid samples in very low concentrations. Limits of detection (LOD) and quantification (LOQ) were calculated as 3x and 10x the standard deviation in the control samples. Analysis was performed at NMBU.

Inductively coupled plasma optical emission spectroscopy. (ICP – OES) was used for determining Mg and Na, on a PerkinElmer Optima (5300 DV ICP-OES) Instrument. The instrument produces exited atoms and ions. Because each element has its own characteristic set of energy levels, which reflects the transition between one energy level to another, it is possible to determine both the quality and quantity of atoms and ions by using this method (Skoog et al., 2014). This instrument has a higher detection limit than the MS and was therefore used on elements with higher concentrations. Analysis was performed at NMBU.

Samples that contained saltwater, collected at G, H, I, and J were analyzed in 1+9 dilution, to reduce the ion concentration and thereby interference, caused by saltwater. The other samples, A – F, were not diluted. LOD and LOQ are therefore different for station A – F and station G – J.

3.3.   Physical parameters

Conductivity was measured by WTW Cond 3310 Set 2 and pH by WTW pH 3110 Set 2. The measurements were performed a few hours after sample collection. Conductivity is measured as the specific conductivity (siemens/meter). However, for simplicity reasons, it was converted to grams of salt per kg water with unit ‰.

Precipitation data were collected from the nearest weather station in Arendal. Tidal water data was collected from kartverket.no, Risør station.

3.4.   Calculations

The particulate organic fraction was calculated by subtracting the measured dissolved fraction (< 0.22 μm) from the measured particulate fraction.

$$POC = TOC - DOC \qquad\qquad \textit{Eq. 1}$$

Where: POC = Particulate organic carbon
TOC = Total organic carbon
DOC = Dissolved organic carbon

The particulate metal fraction was calculated by subtracting the measures dissolved fraction (<0.2 μm) from the measures particulate fraction.

$$PMet = TMet - DMet \qquad\qquad \textit{Eq. 2}$$

Where: PMet = Particulate metal fraction
TMet = Total metal fraction
DMet= Dissolved metal fraction

Different properties of dissolved organic material were determined using the equations in Table 1.

Table 1 *Relation between different absorption values at specific wavelengths used to determine a selection of organic matter properties. Abs(x) is the measured light absorbance at wavelength* x (nm)

Purpose	Equation	Explanation	Reference	Equation number
Watercolor	$Abs(450) * 5 * 500$	UV light absorption capacity	(Højerslev, 1980)	*Eq. 3*
Size	$\dfrac{Abs(250)}{Abs(365)}$	Protein-like or humic-like properties	(De Haan & De Boer, 1987)	*Eq. 4*
Aromaticity	$\dfrac{Abs(254)}{Abs(204)}$	Aromatic properties	(Summers et al., 1987) (Weishaar et al., 2003)	*Eq. 5*
SUVA(254)	$\dfrac{Abs(254)}{DOC}$	Aromatic/humic properties	(Hansen et al., 2016)	*Eq. 6*

3.5. Statistical analysis

Microsoft Excel (version 2103) were used for data organization and simple calculations.

Rstudio (version 1.3.1073) were used to conduct statistical analysis. There was conducted one- and two-way ANOVA, linear regression, and principal component analysis (PCA).

Figures were made in Rstudio and edited in incskape.

Groups with detected levels under LOQ, where the values below LOQ < 15% of the population was set to half of the LOQ. Confidence levels was set to 95%

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4. Results

4.1. Observation in field

There were observed higher water levels and higher currents during the second sampling. This was detected by the boat being more challenging to maneuver and more easily drifted off the sampling site.

4.2. Physical properties

4.2.1. Precipitation

There was 'more precipitation during the week before the October sampling (34mm) than the week before the November sampling (24mm). However, the was more precipitation close to the sampling day in November.
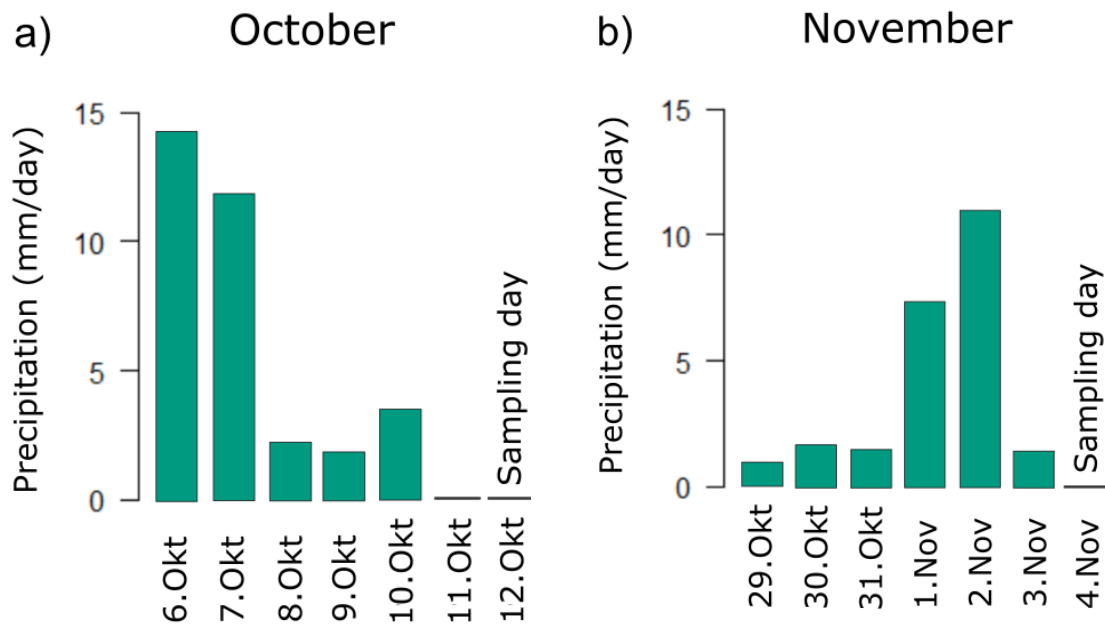
Figure 5 *Precipitation in mm/day during the week before a) The October sampling campaign and b) The November sampling campaign of surface water along Storelva - Sandnesfjorden river-ocean transect.*

4.2.2. Salinity

There were detected higher salinity levels and steeper salinity increase during the October sampling than the November sampling.
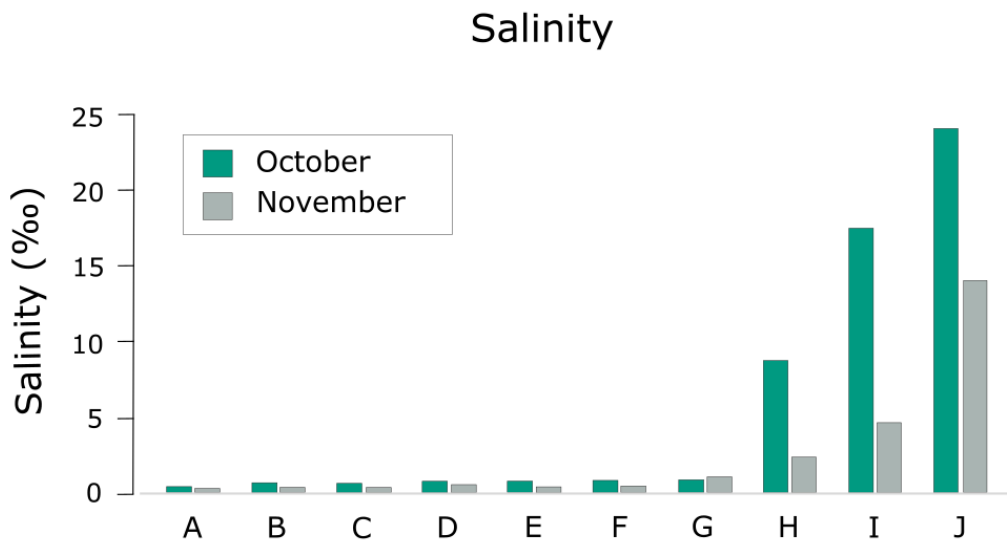
Figure 6 *Salinity at the different stations along the river-ocean transect Storelva-Sandnesfjorden where A is closest to the river and J is closest to the ocean.*

4.2.3. Tidal water

During the October sampling (11.30 – 16.00, 12. October 2020), tidal water increased and then decreased. During the November sampling (09.30 – 14.00, 4. November 2020), there was a tidal decrease before a tidal increase. In addition, the water level was significantly higher during the November sampling. There were also observed significantly higher water levels than predicted during the November sampling.
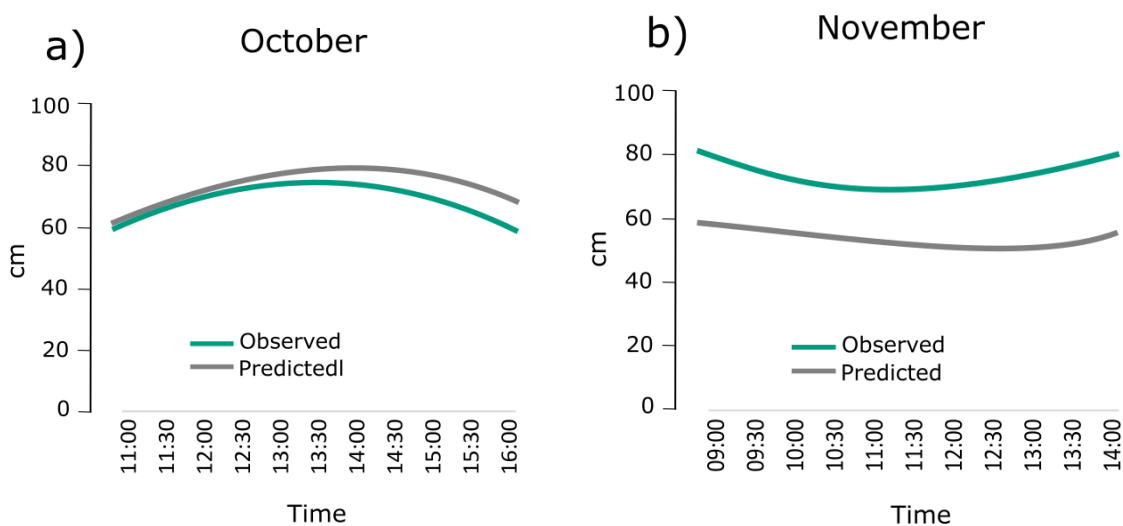
Figure 7 *Tidal water during sampling in the river-ocean transect Storelva - Sandnesfjorden during sampling in a) October, and b) November. Data is collected from katrverket.no*

4.2.4. pH

There was detected a slight, however, insignificant increase in pH along the transect during both samplings.
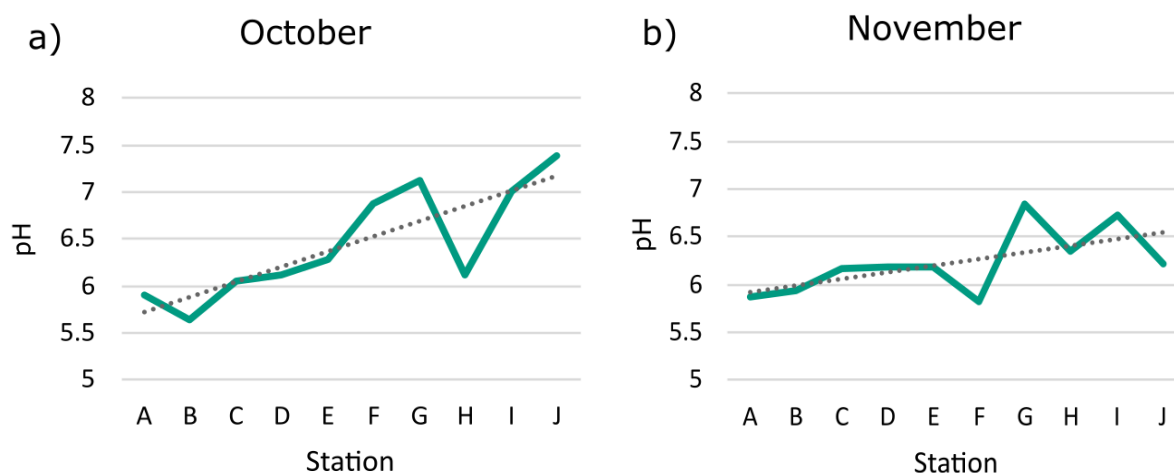
Figure 8 *pH in surface water at the different sites A - J (where A is closest to river and J is closest to the ocean) along the river-ocean transect Storelva – Sandnesfjorden*

4.3. Organic material

Both TOC and DOC decreased along the salinity gradient. There was no significant difference between samplings, either for DOC or TOC.
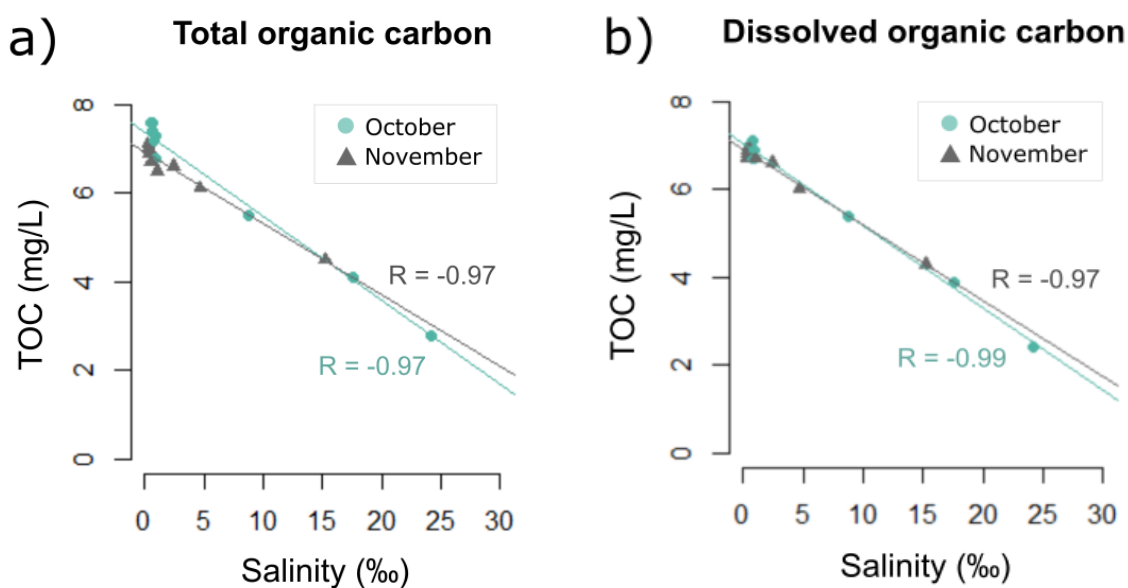
Figure 9 *Correlation between a) Total organic carbon (TOC) (> 0.22 μm) and salinity and b) Dissolved organic carbon (DOC) (< 0.22 μm) and salinity, along the river-ocean transect Storelva – Sandnesfjorden*

The dissolved fraction (DOC) makes up most of the organic carbon along the river-ocean transect (86% - 100%). There was detected a higher DOC/TOC ratio than during the November sampling, which means more of the organic carbon content was in dissolved form in November than in October. There was detected DOC levels higher that the total fraction station F and G during the second sampling, which indicates an interference.
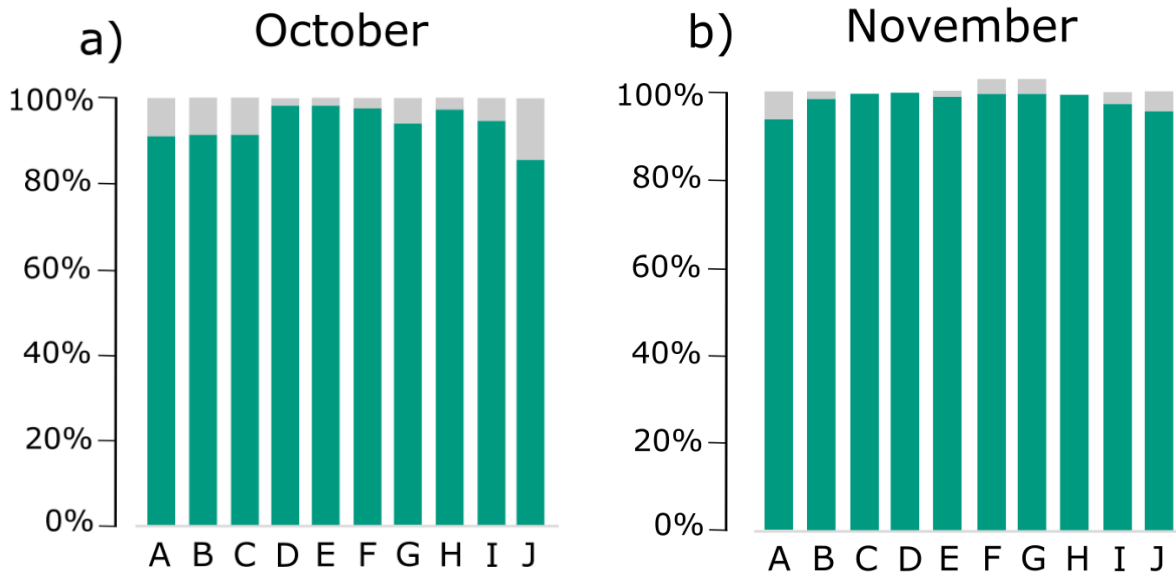
Figure 10 *The size distribution (in %) between green: dissolved organic carbon (DOC) (< 0.2 μm) and grey: particulate organic carbon (POC) (> 0.2 μm) during a) the October sampling and b) the November sampling.*

4.4. Metal distribution

To determine the distribution of metals along the transect, there was conducted linear regression (least square method) for each metal and salinity.

Figure 11a *Correlation between aluminum (Al) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*

Figure 13b *Correlation between silicon (Si) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
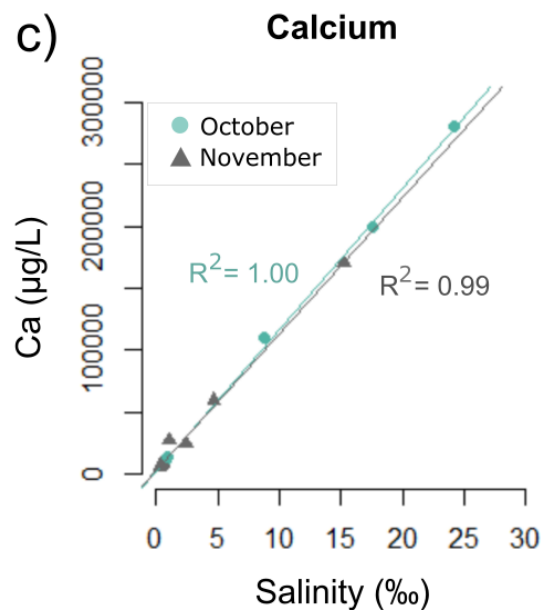
Figure 11c *Correlation between calcium (Ca) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
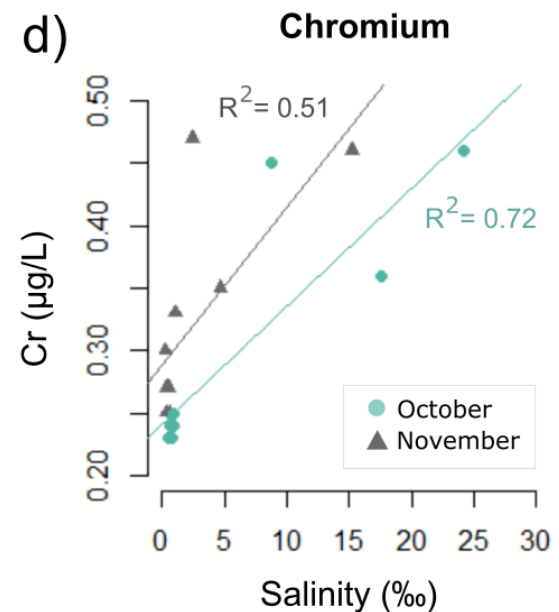
Figure 11d *Correlation between chromium (Cr) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
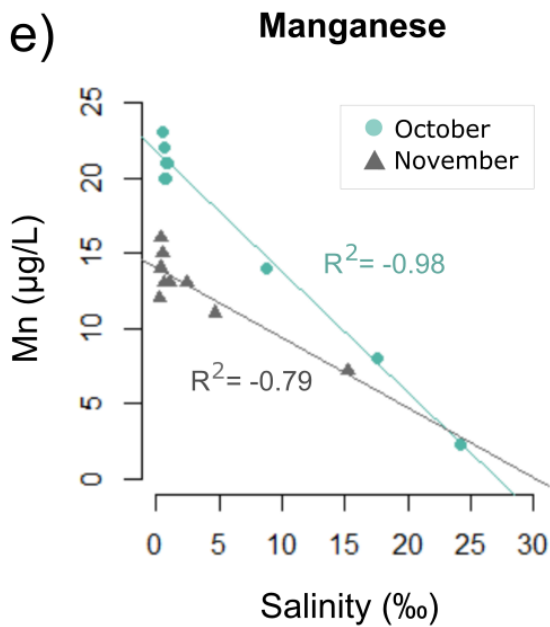
Figure 11e *Correlation between manganese (Mn) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
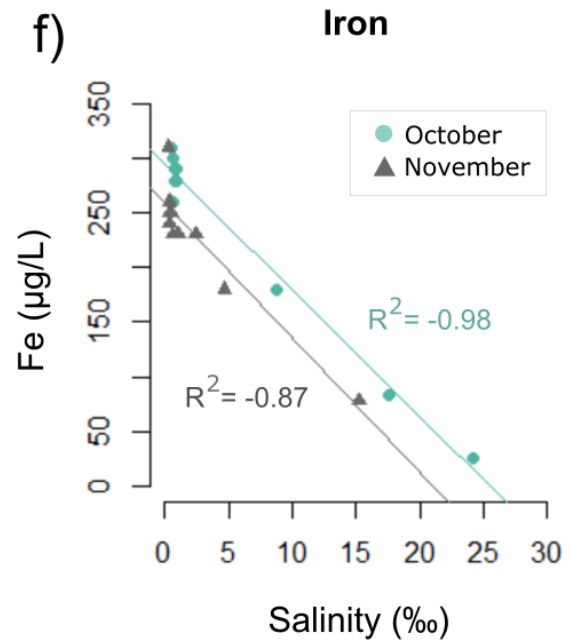
Figure 11f *Correlation between iron (Fe) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
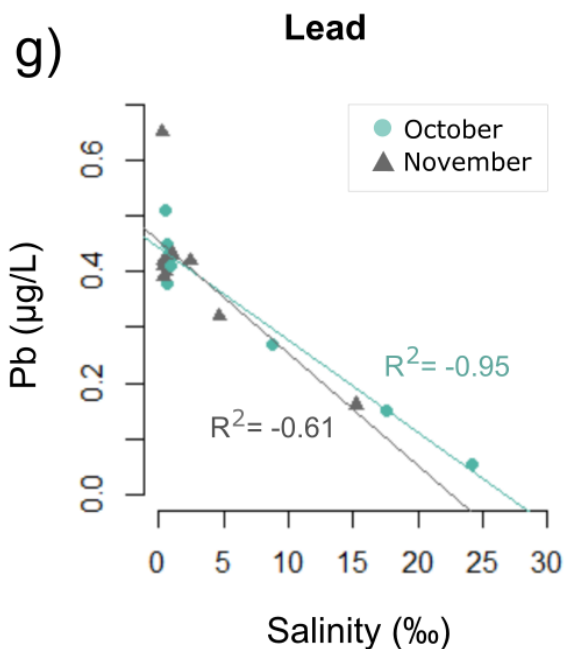
Figure 11g *Correlation between lead (Pb) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
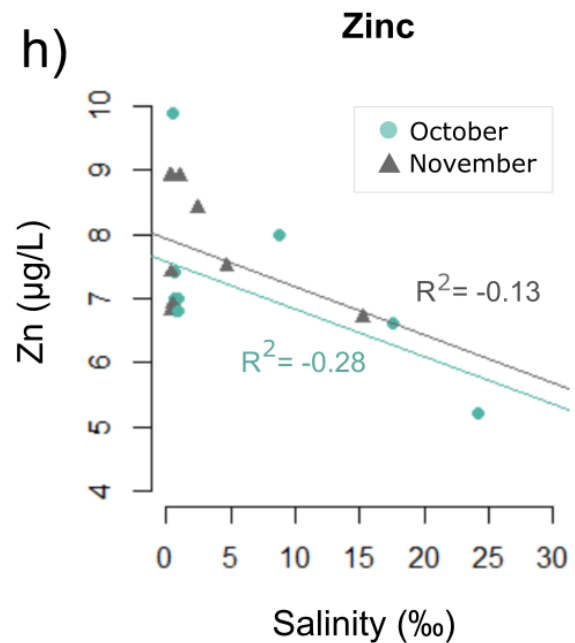
Figure 11h *Correlation between Zinc (Zn) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
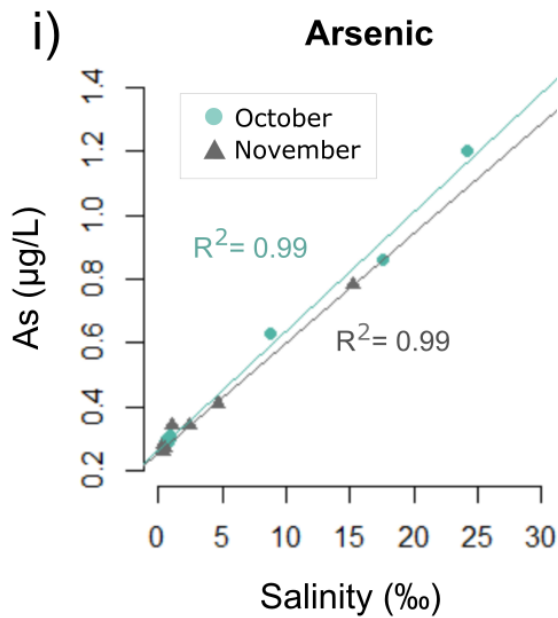
Figure 11i *Correlation between arsenic (As) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
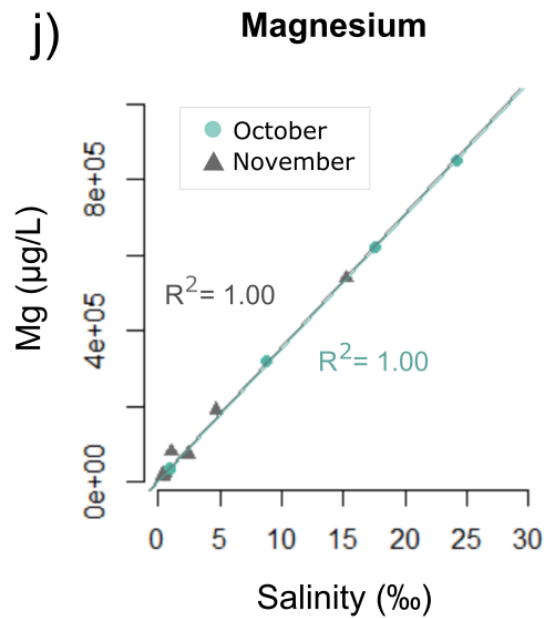
Figure 11j *Correlation between magnesium (Mg) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
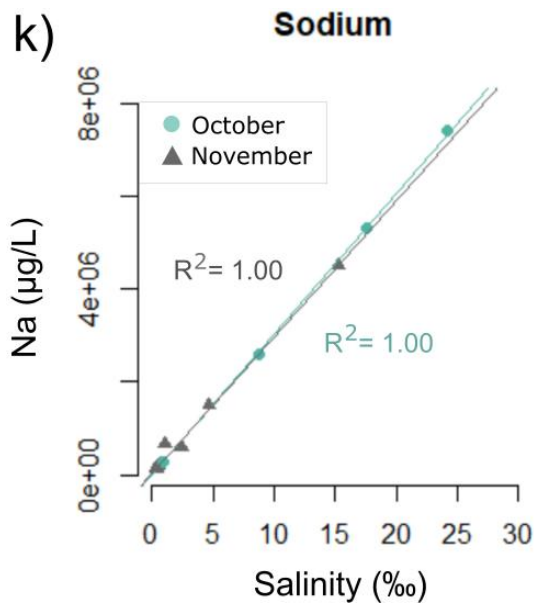
Figure 11k *Correlation between sodium (Na) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*
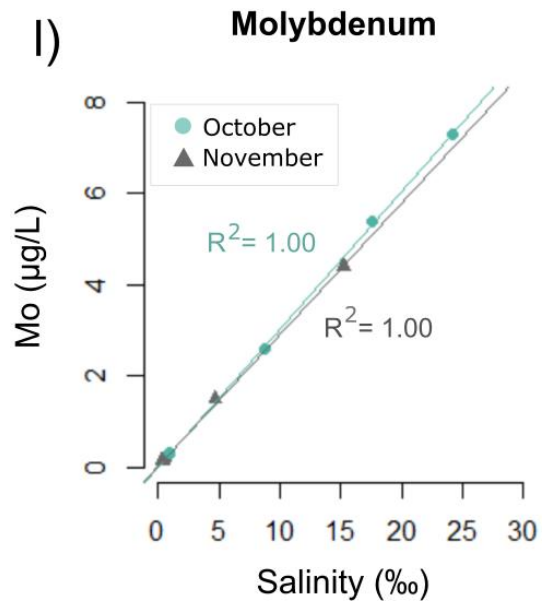
Figure 11l *Correlation between molybdenum (Mo) and salinity along the river-ocean transect Storelva – Sandnesfjorden.*

m)

Cadmium

$R^2= -0.07$

$R^2= -0.16$
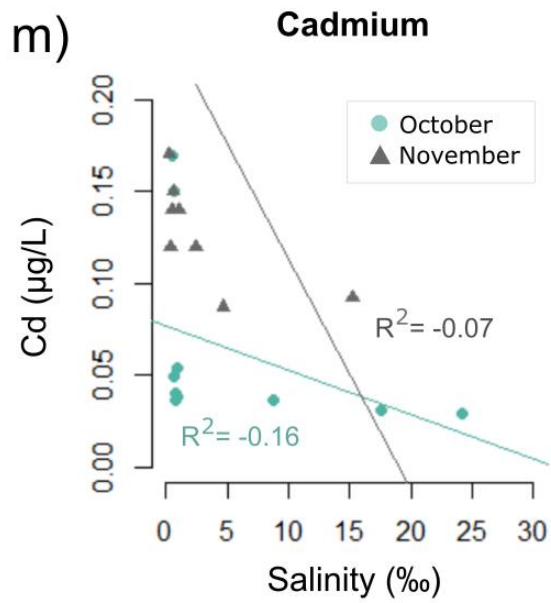
Figure 11m Correlation between cadmium (Cd) and salinity along the river-ocean transect Storelva – Sandnesfjorden.

n)

Copper

$R^2= 0.15$

$R^2= -0.04$
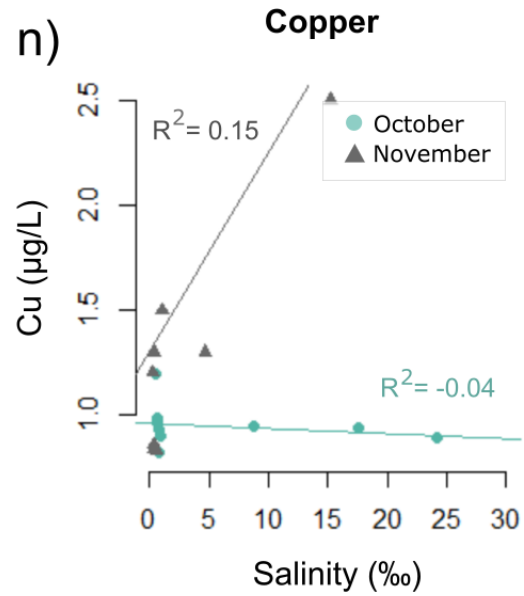
Figure 11n Correlation between copper (Cu) and salinity along the river-ocean transect Storelva – Sandnesfjorden.

o)
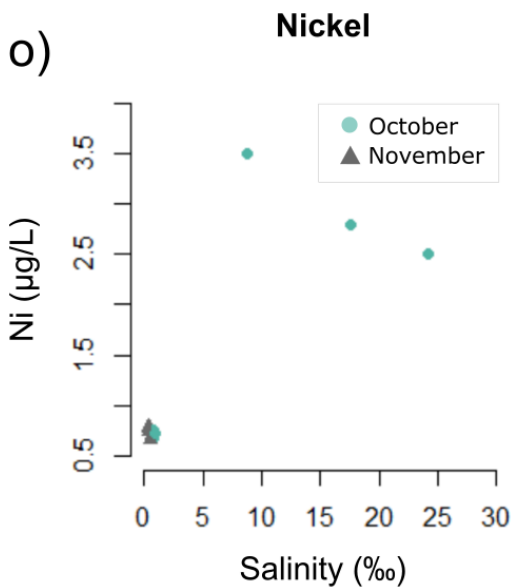
Nickel

Figure 11o Correlation between nickel (Ni) and salinity along the river-ocean transect Storelva – Sandnesfjorden.

4.5.   Size distribution of metals

There was no significant change in the ratio dissolved:particulate phase of any metals along the salinity gradient. Therefore, the average of each metal along the entire gradient was calculated and is presented here. Cadmium and Copper samples were contaminated and are therefore excluded from the model.

Fe, Pb, and Al were the metals with the highest particulate fraction, all with less particulate fraction in November than October.
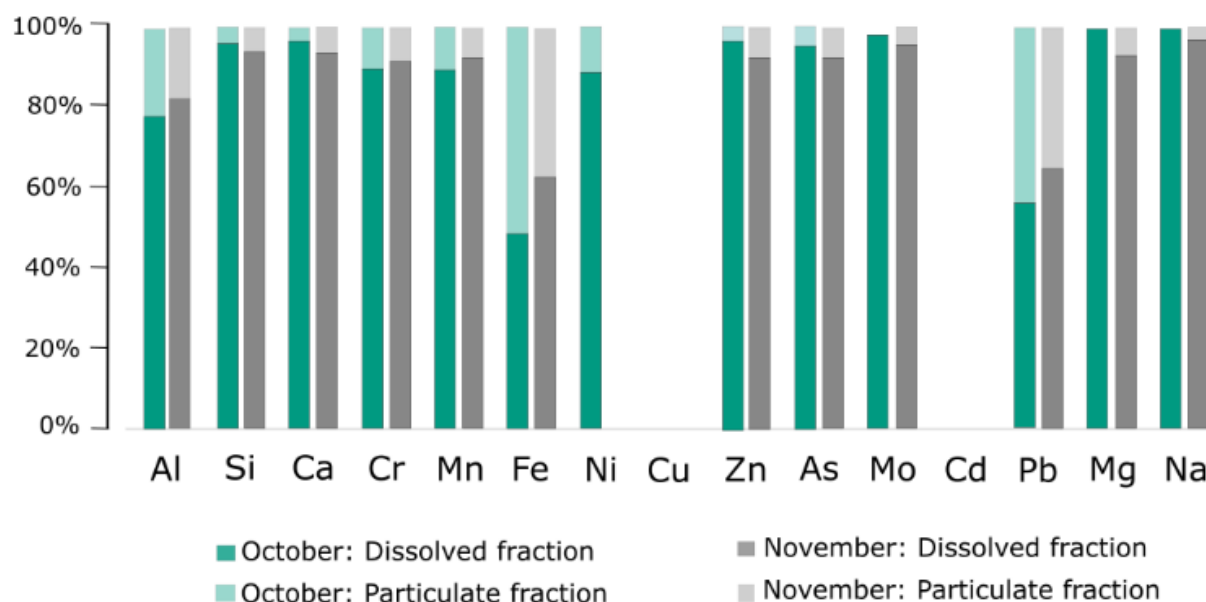
Figure 12 *The distribution (in %) of metals between green: dissolved (< 0.22 μm) and grey: particulate (> 0.22 μm) fraction for the different metals Al, Si, Ca, Cr, Mn, Fe, Ni, Zn, As, Mo, Cd, Pb, Mg, and Na.*

4.6. Fluorescence

Chlorophyll a concentration increased along the salinity gradient (fig 13a). There was also detected a negative correlation between Chlorophyll A and TOC (fig. 13b).
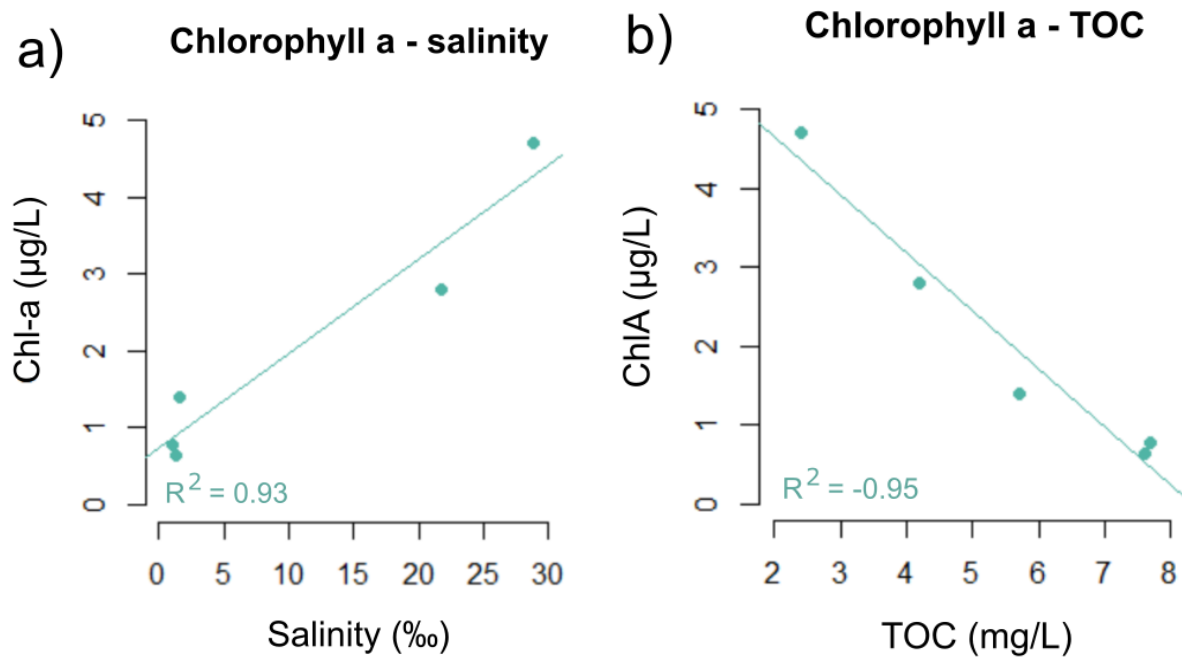
Figure 13 *Correlation between a) chlorophyll a (chl-a) and salinity and b) chl-a and total organic carbon (TOC) along the river-ocean transect Storelva-Sandnesfjorden.*

4.7. UV/VIS

Calculations on the properties of DOC were preformed to detect watercolor, size, SUVA(254), and aromaticity.
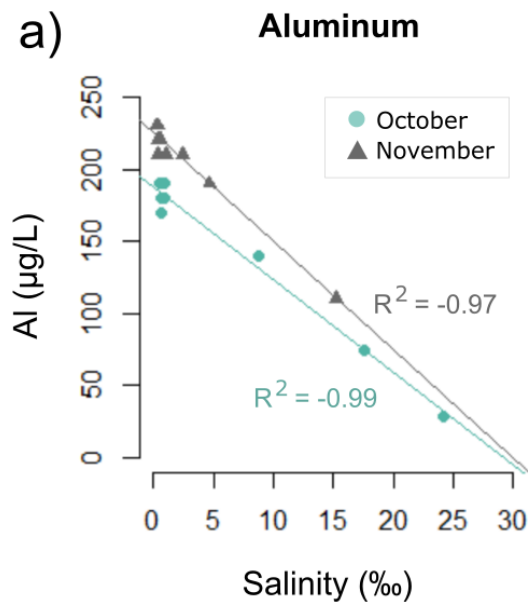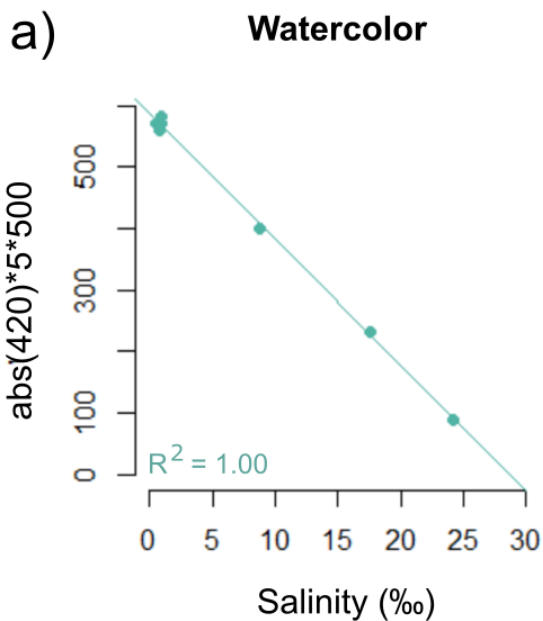

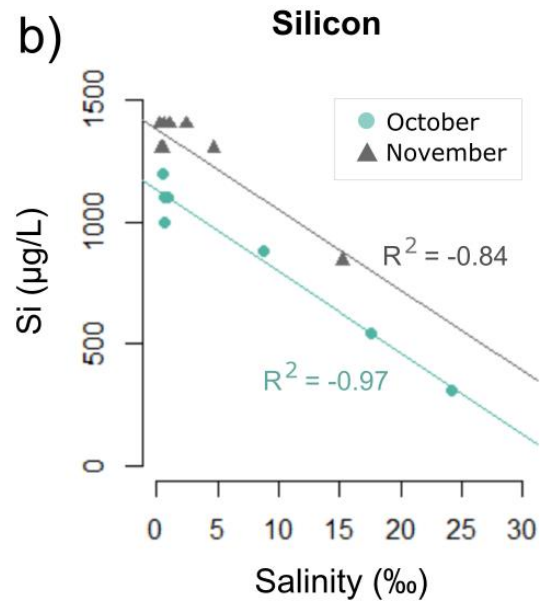**Figure 14a** *Correlation between watercolor and salinity along the river-ocean transect Storelva-Sandnesfjorden.*
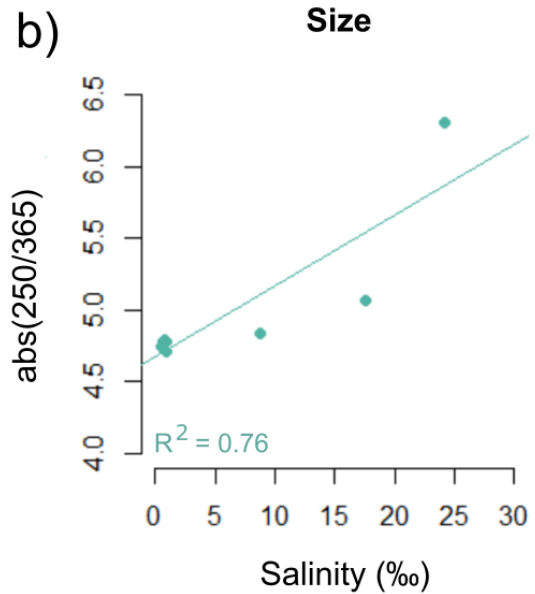
Figure 14b *Correlation between size and salinity along the river-ocean transect Storelva-Sandnesfjorden.*
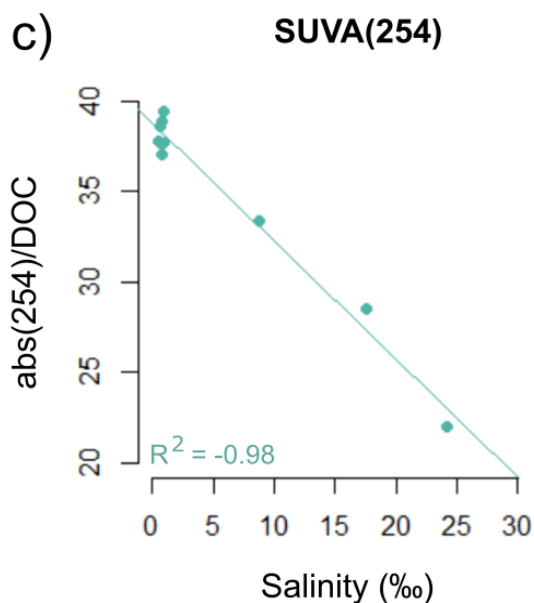
Figure 14c *Correlation between SUVA (254) and salinity along the river-ocean transect Storelva-Sandnesfjorden.*
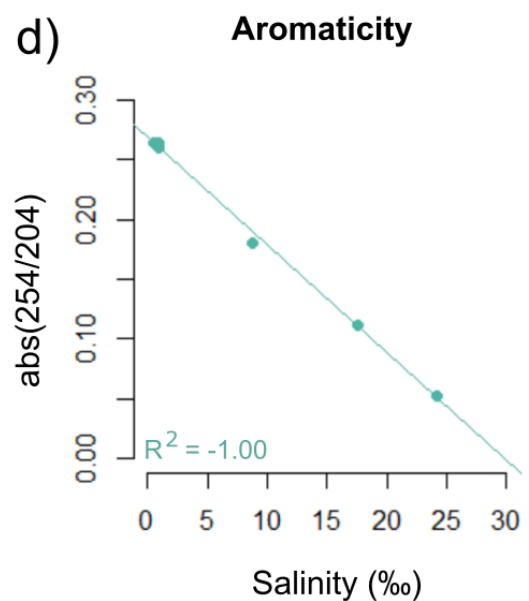
Figure 14d *Correlation between aromaticity and salinity along the river-ocean transect Storelva-Sandnesfjorden.*

5.   Discussion

Salinity was chosen as the explanatory variable for most plots due to its significant effect on the distribution of metals and organic material in river-ocean transects.

5.1.   Physical properties

There were detected higher salinity levels during the October sampling campaign than during the November sampling campaign (fig. 6). This is probably caused by more precipitation (fig. 5) before, and low tide (fig. 7) during the November sampling. It is known that rainwater travels fast through the catchment (Gundersen et al., 2020), and this causes more freshwater input, which "pushes" the mixing zone further out in the fjord (towards the ocean). Additionally, there was a distinct difference in predicted and observed water levels during the November sampling (average 20.2 cm difference) (fig. 7). Kartverket (The Norwegian Mapping Authority) explains that weather (e.g., precipitation) is responsible for this difference. Precipitation close to the sampling day will be especially important as the study was conducted on surface water. All in all, the transect was more river-dominated during the November sampling than the October sampling, which illustrates that precipitation and water level/tidal level are key factors determining the geographical placing of the mixing zone.

The maximum salinity was 24.2‰ in October and 15.2‰ in November, which both are significantly lower than the average ocean value of 35‰ (Millero et al., 2008). This illustrates how even the marine sites were influenced by freshwater during both samplings.

The pH had a slight, however, insignificant increase along the transect both samplings (fig. 8), and there was no difference between samplings. The increase is expected, as ocean waters generally have higher pH than rivers. More precipitation, which is acidic (average just below 6 (Liljestrand, 1985), prior to the second sampling, has likely lowered the pH in November slightly.

5.2.   Organic material levels

The distribution of organic material along the gradient is closely negatively correlated with salinity (fig. 9). During the October sampling, there was observed a decrease of 68% in TOC, while 66% decrease in DOC along the transect. In November, there was detected a 37% decrease in TOC and a 36% decrease in DOC.

When river transported ter-OM is introduced to ocean saltwater, the high electrolyte concentration neutralizes the negative surface charge (Bianchi et al., 2007a). The NOM

flocculates and is removed from surface water through precipitation, which is observed as the decrease in both TOC and DOC in the surface water of the transect. The NOM removal occurs between station G and H, the same spot as the salinity increase was observed. The mixing zone, which in literature also is referred to as "coastal filter" (Asmala et al., 2014), seems to appear between station G and H.

Even though there was more precipitation and higher runoff during the November sampling, there was detected a lower concentration of organic carbon. There might be several explanations for this. The most obvious is that during the first sampling, in October, there was more litterfall and, therefore, more input to the river, despite there being more precipitation in November. More NOM at the first station A (closest to the river) in November than October, substantiates the hypothesis of the higher NOM levels being caused by processes in the catchment rather than processes within the transect. Other possible/additional explanations are higher internal organic matter production in October or dilution effects by an increasing water flux of water with low NOM levels in November.

Just about all the organic material appeared in dissolved form. In October: 85 % - 91% and in November: 92% – 100%. There was detected DOC > TOC in station F and G from the November sampling, which indicates an interference.

5.3. Properties of dissolved organic matter

Although quantifying NOM amount (commonly by measuring organic carbon concentration) is important, it is also essential to characterize NOM composition due to the great importance of its biogeochemistry. The properties of NOM determine how it interacts with other elements, and therefore how it is distributed in the environment (Hansen et al., 2016; Liang & Singer, 2003; Minor et al., 2014). Absorption properties (table 1) of organic matter were used as indicators of watercolor, size, humic content, and aromaticity of the DOC in October (fig. 14). In detail:

Watercolor refers to the optical properties of CDOM absorbing blue light, giving a brown/yellow color to the water. The parameter provides an easily measured property for determining CDOM concentrations in the environment (Coble, 2007). Watercolor decreased along the gradient (fig. 14a), which means that in the riverine part, more light is absorbed than in the marine part.

Size is reduced along the gradient (fig. 14b). Different sizes can be used as a proxy for differentiating marine and terrestrial NOM, as smaller fractions have more protein-like

character, which is associated with marine NOM. Larger fractions have more humic-like characters, which are associated with ter-OM (Coble, 2007).

SUVA and aromaticity decreased along Storelva – Sandnesfjorden (fig. 14c and 14d). Both are used as an assay to whether dissolved organic carbon in the water is labile, a ready source of energy, or is from a relatively old source of carbon (recalcitrant). Terrestrial NOM usually contains a higher portion of humic acids (aromatic) than ocean NOM (Coble, 2007). Therefore, the decrease along Storelva – Sandnesfjorden indicates higher ter-OM in the upper part than the outer part.

In sum, the measured properties of organic material indicate larger portions of terrestrial associated NOM in the upper part (river site) than the outer part (marine site) of the transect.

5.4. Chlorophyll a

Chlorophyll A was measured as the metabolic balance of natural waters is largely dependent on primary production and respiration. Primary production depends on physical, chemical, and biological factors and is therefore interesting in estuaries which are highly dynamic environments vulnerable to anthropogenic alterations. Thus, monitoring phytoplankton abundances is an essential tool for the prediction of eutrophication and its effects on coastal ecosystems (Bucci et al., 2012). As the phytoplankton rapidly responds to changes in the environmental conditions, the dynamic structure of phytoplankton communities reflects the health of the aquatic ecosystems.

Fluorescence analysis revealed an increase in chlorophyll a (Chl-a), along Storelva – Sandnesfjorden transect (fig. 13a) (i.e., lowest t riverine site, and highest at the marine site). In addition, there was a detected negative correlation between Chl-a and TOC (fig. 13b). The UV/VIS analysis revealed a reduction in watercolor along the gradient (fig. 14a). This means light properties, which are necessary for photosynthetic primary producers, are better in the fjord's outer part. This could be one important explanation for the increase in chlorophyll A along the fjord.

In the literature, there are reported a wide variety of the occurrence of Chl-a and phytoplankton along river–ocean transects. The opposite result, decrease along the gradient (Bucci et al., 2012; Doering et al., 2006), and positive correlation with total suspended solids (TSS) has been observed (Zhang et al., 2011). There has also been detected large variation with tidal water (Bucci et al., 2012).

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The extensive variations illustrate how phytoplankton/primary production is hard to predict, and there are substantial individual differences between river-ocean systems. Monitoring many different surface waters is therefore important to assess the health of water bodies. The implementation of the Water Framework Directive (WFD) in Europe will likely result in more data in years to come.

5.5. Metals

The metals of the study were categorized into two main groups: increasing and decreasing, based on a principal component analysis (PCA) (fig. 15). Nickel was left out of the model, due to lack of data. There were also metals that did not fit into this system, here called "undefined." In sum:

Increasing: Ca, Mg, Na, Mo, As, and Cr.
Decreasing: Al, Fe, Pb Si, and Mn.
Undefined: Ni, Zn, Cd, and Cu.
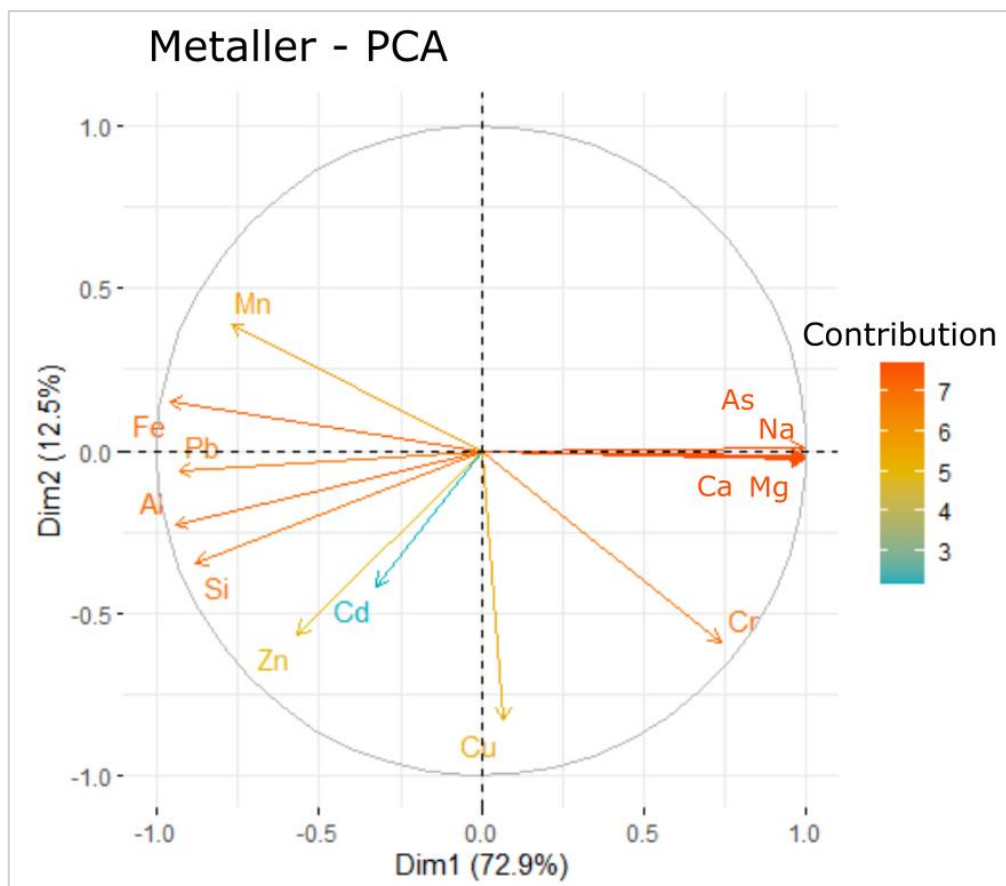
Figure 14 *PCA to differentiate metals. Mo, As, Ca, Mg, Na, and Cr are one category (increasing), Mn, Fe, Pb, Al, Si are another category (decreasing). Zn, Cd, Cu and Ni are undefined.*

5.5.1. Increasing along the gradient

The metal increase along the gradient (Na, Ca, Mg, Mo, As, and Cr) is caused by the addition of metals to the surface water. If the concentration is higher et the end of the gradient (closest to the ocean) than at the beginning (closest to the river), it is either added along the way or brought in by the ocean saltwater. It can be added either from sources alongside or inside the transect (i.e., from land or from sediments). Other possible sources are airborne substances or groundwater discharge.

Sodium, calcium, and magnesium

The ocean contains on average 35 grams of salt per kilogram of seawater (=35‰) (Millero et al., 2008), where sodium, calcium, and magnesium are the dominating cations. In Storelva – Sandnesfjorden, these metals were detected in the following concentrations:

Table 2 The different Na, Ca, and Mg levels in surface water along the river ocean transect Storelva – Sandnesfjorden in October and November, and the global average values for these metals in the ocean.

Metal	October (mg/L)	November (mg/L)	Average seawater [a] (mg/L)
Na	182 – 7400	120 – 4500	10 7815
Ca	8.3 – 280	5.3 – 170	412
Mg	22 – 850	4 – 540	1284

[a] (Schlesinger & Bernhardt, 2013)

During the November sampling, there were detected lower concentrations for all these metals, which are abundant in the ocean. In November, the high freshwater input has likely diluted the saltwater, which reduces ocean-associated metals. These metals have relatively low particle affinity, illustrated by the high dissolved fraction (< 0.22 μm) (fig. 12).

Molybdenum

Molybdenum was detected in concentrations between 0.22 μg/L - 7.3 μg/L in October and 0.15 μg/L - 4.4 μg/L in November (fig. 11l). Most of the molybdenum was in dissolved form (< 0.22 μm) (fig. 12).

Molybdenum is the most abundant transition group metal in seawater. The element is an essential micronutrient as it is an essential cofactor of nitrogenase and nitrate reductase enzymes and is therefore crucial in the assimilation of nitrogen gas and nitrate. Molybdenum

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is often discussed as the limiting factor for growth in natural water and the open ocean (Glass et al., 2012)

Molybdenum exists as stable molybdate (MoO_4^{2-}) anion in oxygenated environments and is essentially conservative in pelagic waters, suggesting little influence of biogeochemical processes on its abundance (Collier, 1985). Similar studies have detected similar results, increasing molybdenum along river-ocean transects (Dalai et al., 2005; Strady et al., 2009; Q. Wang et al., 2021). There are detected extensive variations in Mo concentration in river-ocean transects worldwide (Smedley & Kinniburgh, 2017). However, the values detected in Storelva - Sandnesfjorden are somewhat low. This is presumably due to the nature of the catchment.

Arsenic

Arsenic was detected in concentrations between 0.29 μg/L – 1.2 μg/L in October and 0.26 μg/L – 0.28 μg/L in November (fig. 11i). Most arsenic was dissolved (< 0.22 μm) (fig. 12). Levels required for good chemical status by the EU water directive in coastal areas are < 0.6 μg/L, which means arsenic levels are too high in the outer part (marine site) of the transect.

The elevated levels in the marine sites but not riverine sites indicate an addition along the gradient. One explanation is upwelling from sediments. Arsenic is sensitive to release from sediments, and changes in bottom conditions can affect resuspension of arsenic to the water column. In several estuaries (Andreae et al., 1983; Howard et al., 1988; Seyler & Martin, 1990; Yao et al., 2006) input from the benthic compartment appear to be the most probable source of dissolved arsenic. Diffusion processes are probably limited in arsenic release to the water column because the redox boundary within the sediment column acts as a barrier. (arsenic being reabsorbed within the oxic sediment). However, surficial mixing of the sediment can overcome this barrier, thus explaining why important arsenic fluxes from sediment (and large positive deviations) are observed in macrotidal estuaries (Michel et al., 2000; Seyler & Martin, 1990). Biological activity has been demonstrated to enhance mobilization, and digging organisms are suspected to significantly affect the release of arsenic from sediments (Riedel et al., 1987).

NOM may enhance the release of arsenic from soils and sediments into solution, thereby facilitating arsenic leaching (Wu et al., 2019). NOM may also serve as binding agents, thereby reducing arsenic mobility. However, little research has been conducted on this aspect (S. Wang & Mulligan, 2006). Phytoplankton development can also induce a reduction

of arsenic in surface waters through adsorption. As an example, there have been reported that a Pseudo-nitzschia bloom removed up to 60% of the inorganic arsenic species in the high salinity section of the Huon estuary in Tasmania (Featherstone et al., 2004)

Even though arsenic pollution in Norway has been reduced by 35% since 1995, there are estimated annual emission of approximately 23 ton. In addition, the Norwegian Environment Agency estimates that there are approximately 1700 tons of arsenic in contaminated soil in Norway - and that every year about 6 tons are leaked from grounds. Old, impregnated woods are estimated to contribute to 70% of the total arsenic pollution. Contaminated soil has been cleaned up at several impregnation plants, where mapping has shown that the pollution can spread to water, have a negative environmental impact, or have a health risk. (miljøstatus, 2021a).

There are many forms of both organic and inorganic arsenic. Common oxidation states in surface waters are the severely toxic As(III), far less toxic (V) (Oremland & Stolz, 2003), as well as a wide variety of organic complexes, which are usually not very toxic (Neff, 1997). Many arsenic compounds are classified as hazardous for human health and environments, partly because they can cause cancer and reproductive damage (Hughes, 2002). Some are also classified as very toxic to aquatic organisms, with long-term effects (Miljøstatus, 2021a; Neff, 1997). Arsenic and arsenic compounds are therefore regulated through several EU regulations and have been on the Norwegian priority list since 2003 (Miljødirektoratet, 2021).

Chromium

Chromium was detected in concentrations between 0.23 μg/L - 0.46 μg/L in October and 0.3 μg/L - 0.46 μg/L in November (fig. 11d). Most of the Cr was in dissolved form (<0.22μm) (fig. 12). The increasing concentration of chromium is rather rare, and similar studies seem to find a decrease along river-ocean transects (Cranston & Murray, 1980; Goring-Harford et al., 2020; Shailendra et al., 2019). The total amount is below the water directive limit for good chemical status (tab. 3) and is by itself not a problem. However, the increase deserves an explanation. The increase starts at the mixing zone, between station G and H. At this site, there is a boat storage which could be a source of pollution. In-transect source and/or resuspension from sediments could also be an explanation.

Chromium exists in natural waters in two oxidation states: Cr(III), which is relatively insoluble and nontoxic, and Cr(VI), which is much more soluble and toxic. Cr(VI) is thermodynamically

unstable in anoxic sediments and is easily transformed to Cr(III) and therefore poses the possibility of leaking from sediments (Berry et al., 2004). Cr(VI) is the dominating form in oxygenated surface water. (Pađan et al., 2019). The chromium in Storelva was mainly in dissolved form. However, this is not truly, only operationally defined dissolved and include colloids (< 0.22 μm) Therefore, it cannot be differentiated between Cr(III) and Cr(VI) in this study.

Similar to arsenic, the main source of chromium is old, impregnated woods which account for approximately 63% of emissions (in 2019). The costs of rehabilitating this wood are estimated to be too high in proportion to the environmental benefits. Therefore, no significant reduction in emissions is expected until many years from now. Emissions of chromium in Norway were reduced by approximately 60% in the period 1995–2019. In 2019, the emissions were estimated to approximately 40 tons. Chromium was listed on the Norwegian authorities' priority list when it was established in 1997. (Miljøstatus, 2021d)

Evaluation of the increasing metals

Based on data collected from Storelva-Sandnesfjorden, known properties of the metals, and comparison with similar studies, some conclusion can be drawn to the distribution of the increasing metals. The key reasons for the increase are:

- Naturally higher levels in ocean saltwater than in freshwater.
- Inside addition, either from sediments or land.

Concerning risk to the environment, arsenic is exceeding the limit required for good chemical status and is, therefore, the most concerning among the increasing metals. Chromium is also of concern, as it shows some rare behavior which makes it difficult to determine future distribution and risk.

5.5.2. Decreasing along the gradient

Al, Fe, Pb, Si, and Mn concentration decreased along the transect. For this trend to occur, metals need to be removed from the surface water. The most dominating removal mechanism is transported from the surface to the sediments. There are other causes, e.g., sea spray, storms, etc., that cause small fractions of the metals to be washed up on land. However, these are considered to be of less importance (Xu & Gao, 2014). Silicate formation

is another mechanism; however, it is not of pivotal importance in surface waters with moderate levels of organic matter.

The metals in this group are typically in higher concentration in river/freshwater than in ocean water. The reason for this is either natural occurrence in soil, or pollution brought to the catchment or rivers. The metals of this group are characterized by relatively high surface reactivity, illustrated by the relatively large portion of particulate fraction (> 0.22 μm) for Fe, Pb, and Al (fig. 12). Their faith is therefore highly dependent on particles they are bound to. These particles can either be particle-metal complexes – including NOM-metal complexes, metal(oxy)hydroxides, or even plankton-containing metals.

NOM is of particular interest in metal distribution in boreal areas due to the physicochemical properties and high prevalence. Different types of organic matter bind different metals, but it is not fully understood how the different types of NOM carry metals from source to burial (Helland et al., 2002). However, several studies have demonstrated a generally close link (Reuter & Perdue, 1977; VanLoon & Duffy, 2011). Even though DOC make up a grand portion of material carried by rivers, the rivers also carry varying amounts of minerals and particulate inorganic material. Metals do interact with inorganic particles, especially if the inorganic particles are coated by an organic film (Davis, 1984).

Iron

Iron was detected in levels 310 μg/L – 25 μg/L in October and 310 μg/L – 78 μg/l in November (fig. 11f). Iron was the metal with the highest amount of particulate fraction (< 0.22 μm) (fig. 12).

The was a rapid decrease in Fe at the mixing zone between station G and H, which indicates salinity is an essential driver for iron removal. This is confirmed by several studies where lab experiments have demonstrated rapid precipitation of iron when mixed with saltwater (Boyle et al., 1977; Forsgren et al.,1996; Herzog et al., 2017). The precipitation occurs fast, and precipitation is greater with higher salinity than lower. pH has been demonstrated to be of less importance (Boyle et al., 1977)

Iron is an element of pivotal importance in estuarine and marine waters, influencing the mobility and availability of numerous other elements and compounds. The physiochemical properties and the high occurrence in natural waters make it a suitable co-precipitator (along with manganese) for other elements and particles (Xiong et al., 2017). In addition, it is of great biological importance and is needed by every kind of living organism. Oxidized iron is red in color and is a contributor to the optical properties of DOM (Xiao et al., 2013). There

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has been detected a link between Fe loss and SUVA254 decrease (Asmala et al., 2014), which was confirmed in this study.

The decrease of total iron was more rapid than DOC. (Iron: 91% - 75% removal, TOC: 63% - 37% removal). Studies have found Fe to flocculate 2-3 times more effectively than DOC in laboratory experiments (Asmala et al., 2014) due to the formation of insoluble iron hydroxides. As most of the iron in humic natural waters are in colloidal form bound to organic complexes (Eckert & Sholkovitz, 1976), there can be assumed that iron enhances the flocculation of the NOM colloids that it is bound to, compared to similar DOM molecules without iron (Forsgren et al., 1996).

There was a difference in iron concentration between October and November, where levels in November were significantly higher than in November. The same trend was detected for NOM. One possible explanation for the difference is that the elevated levels of NOM, or the same factors which cause elevated levels of NOM, transport more iron from the catchment to the transect in October.

Lead

Lead was detected in concentrations between 0.5 μg/L – 0.053 μg/L in October and 0.65 μg/L – 0.16 μg/L in November (fig. 11g). The particulate fraction was similar to the one for iron, relatively high (fig. 12).

At the first station (A), lead concentrations were considerably higher than in the rest of the transect, which is not (to the same extent) observed for any other metals. This indicates lead being absorbed to particles (probably insoluble) which precipitate when the river slows down at Storelva river mouth at station A. Pb has high particle reactivity, and its removal through metal adsorption on suspended particles has been observed in several river-ocean studies (Annibaldi et al., 2015; Elbaz-Poulichet et al., 1984; Waeles et al., 2007). Despite having similar physiochemical properties as iron, the comparable low occurrence reduces the importance of lead as a co-precipitator.

Aluminum

Aluminum was detected in concentrations between 190 μg/L – 21 μg/L in October and 230 μg/L – 110 μg/L in November (fig. 11a). A considerable amount, but less than for Fe and Pb, was in particulate form (fig 12).

Rivers are the main flux of aluminum to the ocean. However, the majority is lost to estuarine sediments due to increasing pH and salinity, and through biological processes in the coastal zones (Simonesn et al., 2019; Z. Wang et al., 2014). Salinity experiments have demonstrated less removal of aluminum in filtered samples than unfiltered samples, indicating aluminum, unlike iron, being more dependent on co-precipitation for being removed from the water column (Takayanagi & Goebeil, 2000). The principal mechanisms responsible for the aluminum removal inferred from the laboratory experiments are flocculation and adsorption onto suspended particulate matter (SPM) (Takayanagi & Gobeil, 2000). Aluminosilicate formation can occur; however, due to the relatively high levels of DOC, is likely not of pivotal importance in the surface water of Storelva-Sandnesfjorden.

The toxicity of aluminum is closely linked to pH and aluminum will be more toxic in more acid environments (pH < 6). Hence, the toxicity will decrease along the transects with a rising pH and lower charge and subsequent precipitation of aluminum.

Silicon

Silicon was detected in concentration between 1200 μg/L – 310 μg/L in October and 1400 μg/L – 840 μg/L in November (fig. 11b). Most of Si was in dissolved form (< 0.22 μm) (fig. 12).

Silicon is the main component of the mineral phase of soil and is the building block of the widespread mineral group of silicates (e.g., quartz (SiO_2)). However, naturally occurring silicon has vast variations in properties. Litogenic silicon is not very reactive, while the dissolved form (silic acid) has great biological importance and is used by diatoms, radiolaria, and some sponges to build shells. These species are, therefore, important for the distribution of Si (Mangalaa et al., 2017).

There were significantly higher Si levels in November than in October (fig. 11b), a trend that is not detected for any other decreasing metal (except a slight, however insignificant higher November than October concentration for aluminum). One explanation for this is that increased diatom growth in October takes up silicon and transports it downward in the water column.

Agricultural land use played a significant role in the Si biogeochemical cycle because runoff provides nutrients promoting diatom growth. Si:N ratio needs to be > 1 to support diatom growth (Mangalaa et al., 2017).

Manganese

Manganese was detected in concentrations between 23 μg/L – 2.3 μg/L in October, and 12 μg/L – 7.2 μg/L in November (fig. 11e). Most of the manganese was in dissolved form (< 0.22 μm) (fig. 12). There was a significant difference between samplings, with higher values in October than November.

The main species in natural waters are Mn(IV) which is not very soluble, and Mn(II), which is readily soluble. Both field analysis and mixing experiments have illustrated that adsorption mechanisms influence the distribution of manganese through co-precipitation with suspended particulate matter (SPM) (Morris et al., 1982; Wang et al., 2016).

Manganese is highly affected by chemical changes and sensitive to redox conditions. Manganese is therefore a sensitive proxy for redox cycling and terrestrial input in marine environments. (Yemenicioglu et al., 2006). Dissolved manganese is therefore often used as an element for scientific purposes worldwide and is a key parameter for ocean chemical, physician, and biological processes (Wang et al., 2016).

Evaluation of the decreasing metals

Based on data collected from Storelva-Sandnesfjorden, known properties of the metals, and comparison with similar studies, some conclusio can be drawn as to why these metals decrease. The key reasons for the decrease are:

- Flocculation of oxides.
- Co-precipitation with suspended particulate matter, including NOM and Fe.
- Dilution by seawater.

The decreasing group are removed (Reduction rate/salinity) by following order (High to low removal in %):

Fe > Al > Mn > Pb > Si

The difference between sampling demonstrates that these (mainly) terrestrial originated metals are, to a greater extent than ocean-associated metals, affected by outer processes in the catchment and transect.

None of the metals in the decreasing group are above what is required for good chemical status. Therefore, there is no basis to claim any adverse effects of either Fe, Pb, Al, Mn, or Si

in the surface water of Storelva - Sandnesfjorden. However, the deposition of metals in the sediment is building up over time, and further investigation of sediments is needed to understand the possible consequences fully.

Lead is the only one of the decreasing metals on the Norwegian priority list (Miljødirektoratet, 2021)

5.5.3. Undefined group

There was either no detectable or no significant pattern of distribution along the salinity gradient for some of the metals (Cd, Cu, Zn, and Ni). Higher levels of dissolved than total fraction of Cu and Cd, along with great variations, indicate an interference, and these metals will therefore not be discussed further.

Zinc

Zinc was detected in levels 9.9 μg/L – 5.2 μg/L in October and 8.9 μg/L - 6.7 μg/L in November (fig. 11h), mostly in dissolved form (< 0.22 μm) (fig. 12). Concentration seems to decrease along the gradient; however, the trend is insignificant. Similar studies have found the same weak decrease for Zn detected in this study (Dauvin et al., 2008; Marcovecchio et al., 2016; Pearson et al., 2018). There were detected higher concentrations in filtered for some sites than unfiltered samples, which implies contamination of the samples.

Zn is the metal detected with the highest concentration compared to average/healthy fresh and coastal waters (WFD) (Tab. 3). Important sources are mining, industry, and coal incineration. Zinc is an important nutrient and is a necessary component of carbonic anhydrase – the enzyme that allows phytoplankton to convert HCO_3^- in seawater to CO_2 for photosynthesis (Morel et al., 1994). However, in access levels, zinc toxicity has been linked to the inhibition of Ca^- ion regulation when absorbed to gills on Rainbow trout, as well as to the disturbance of acid-base regulation (Hogstrand et al., 1996; Marcovecchio et al., 2016; Spry & Wood, 1984). To humans, dissolved zinc in moderate concentration is relatively harmless (Plum et al., 2010)

Nickel

Nickel was detected in levels between 0.72 μg/L – 2.5 μg/L in October (fig. 11o). In November, nickel could only be quantified for station A – F and was detected in concentrations between 0.77 μg/l – 0.66 μg/l. At station G – J, nickel levels were below LOQ

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of 1.5 μg/L. Because the number of samples with levels < LOQ was more than 15% of the total number of samples, the data from November sampling was excluded from further analysis.

For nickel, there was detected a steep increase between station G and H (386%) before a slight reduction in the two outer stations. This might indicate a mid-transect input. However, in this study, based on one sampling campaign, the dataset is insufficient to make any conclusions.

5.6. Chemical status

According to the environmental agency (Miljødirektoratet), limit values of prioritized heavy metals are set to ensure a good (Class 1 or 2) ecological and chemical state. The goal is to ensure the most comprehensive protection and sustainable use possible of the water bodies Where the environmental goal has not been reached, measures must be taken to achieve it. (Miljødirektoratet 2013).

Table 3 The different levels of selected heavy metals required by the Water Frame Directive (WFD) to reach the different classes of chemical status in coastal waters. The values detected in this study are marked by grey. All values are in μg/L.

Name of substance	Class I (HIGH)	Class II (GOOD)	Class III (MODERAT)	Class IV (POOR)	Class V (BAD)
Cadmium	0 - 0.03	0.03 – 0.2			
Lead	0 - 0.02	0,02 - 1.3	1,3 - 14	14 - 57	> 57
Nickel	0 - 0.5	0.5 – 8.6	8.6 - 34	34 - 67	> 67
Mercury	0 - 0.001	0.001 - 0.047	0.047 - 0.07	0.07 - 0.14	> 0.14
Copper	0 - 0.3	0.3 - 2.6	2.6	2.6 – 5.2	> 5.2
Zink	0 - 1.5	1.5 – 3.4	3.4 - 6	6 - 60	> 60
Arsenic	0 - 0.15	0.15 - 0.6	0.6 - 8.5	8.5 - 85	> 85
Chromium	0 - 0.1	0.1 - 3.4	3.4 - 36	36 - 358	> 358

The values obtained from this study reveal satisfactory (class I or II) for cadmium, lead, nickel, mercury, copper, and chromium. However, Arsenic and zinc had levels above and did not reach the requirements. Elevated lead levels detected in previous studies (Gundersen et al., 2020) were not detected in this study.

The limit values are a great indicator of the chemical status regarding heavy metals. However, as previously discussed, the metals' speciation, size, and bioavailability are important factors determining the risk.

5.7. Future scenarios

The future climate is predicted to be wetter, warmer, and to a greater extent characterized by extreme events (IPCC, 2019), among many other changes. Exactly how this will impact the transport and distribution of organic material and metals along land-ocean transects is challenging, if not impossible, to predict. However, by obtaining a thorough knowledge of the physicochemical properties of the substances and how they are affected by environmental factors, there is possible to anticipate some trends expected in the future.

Coastal "browning", the darkening of surface water caused by increase in NOM (Weyhenmeyer et al., 2014) observed over the past few decades (Aksnes et al., 2009; Frigstad et al., 2013) are suspected to, among other drivers, largely be caused by increased precipitation (Haaland et al., 2010; de Wit et al., 2016), recovery from anthropogenic acidification (Deininger et al., 2020; Monteith et al., 2007) and other factors such as changes in land use and DOM-iron interactions (Clark et al., 2010; Weyhenmeyer et al., 2014). Browning has already been observed to cause chemical, physical, and biological changes in coastal areas (Wolf & Heuschele, 2018). Specific hypothesized effects of browning, such as the reduced depth of epilimnion which was discussed in the theory chapter, is expected to increase in the future (Read & Rose, 2013). UV light does not only affect photosynthesis, but also has effects on the speciation of metals. As an example, studies have shown the role of photochemical degradation in Fe complexing ligands (Powell and Wilson-Finelli, 2003) and observed the increase of reactive iron in natural waters. (Barbeau et al., 2001).

Increased CO_2 concentration in the atmosphere (at present 400 ppm), due to anthropogenic emissions, is in addition to raising the global temperature, changing the carbon chemistry, and thereby decreasing the pH of the ocean. Since the 1900s, the average pH has decreased by 0.1 units and is predicted to drop another 0.3 – 0.5 units until 2100 (IPCC, 2019). Seawater pH and temperature will affect both solubility and adsorption of metals and thus likely change the dissolved concentrations of metals in the future ocean (Hoffmann et al., 2012). In addition, ocean acidification promotes the uptake of inorganic carbon by phytoplankton leading to higher primary production rates and can subsequently result in an increased release of DOM (Grosse et al., 2020)

The burial of organic carbon in coast and ocean sediment works as a carbon sink/storage and is a great contributor to reducing carbon dioxide in the atmosphere. However, if the ecosystems are degraded or damaged, their carbon sink capacity is lost or adversely affected, and the carbon stored is released, resulting in emissions of carbon dioxide (CO_2) that contribute to climate change (Lovelock & Duarte, 2019).

Global sea-level rise is expected as an effect of ice melting (IPCC, 2019), along with the higher frequency of flooding events, which will cause saline ocean water to enter soil and land areas more often. Consequently, the soil redox potential may decrease, which directly will alter the speciation of metals and mobility of redox-sensitive metals (e.g., Cr and As) (Ponting et al., 2021). This may, as a consequence, increase the mobility of cationic metals (e.g., Cu^{2+}, Pb^{2+}, and Zn^{2+}) (Ponting et al., 2021).

5.8. Study limitations and suggestions for future work

(1) Seasonality influencing, e.g., temperature, snowmelt, precipitation, daylight lengths, etc., plays a strong role in biogeochemical transformation, but also transport of material through the landscape. All the fieldwork in this study was conducted during the fall of 2020. Because the distribution of OM and metals are sensitive to changes, it would be compelling to examine how seasonal changes affect the distribution (e.g., spring versus autumn).

(2) As a second limitation of this study, water samples were store approximately 6 months before UV/VIS measurements. This might lead to an underestimation of the biological reactivity and is relevant to both field and lab data. The other analysis (ICP, OC, and fluorescence) was completed a few days and weeks after sampling.

(3) For some of the samples there was detected higher dissolved than particulate levels of metals and/or NOM, which indicates pollution of the samples. This may be caused by leakage from the filters, even though they were rinsed with distilled water before sampling, or transfer from hands during the sampling and handling of the samples.

(4) An important next step in obtaining adequate knowledge in this field is the study of sediments as a sink and storage for these materials, and factors affecting mobility between sediments and the water column. For some of the metals there was detected an increase along the gradient (As and Cr), which could be caused by their resuspension from the sediment. Future studies, similar to this one, however with including sediment samples, could provide insights to this hypothesis.

(5) It shall be mentioned that additional salinity experiment (precipitation gravimetric analysis) was conducted as a potential part of this study. This laboratory experiment had the aim to examine the characters of NOM and assess the influence on saltwater on NOM flocculation under controlled conditions, i.e. without additional complicating changes naturally

experienced in the field such as pH, suspended material, or oxygen levels. In detail, filtered water ($<0.22\mu$m) from the first station (A) was mixed with different concentrations of NaCl and rested for 24 hours. However, in contrast to theory, no significant flocculation or change

in properties were detected. In addition, the results differed from results based on field sample analysis, and where therefore not included in this thesis work. An interesting future study, could investigate why no flocculation had occurred in the trial experiment described above, and whether such an experiment would have induced successful flocculation by using larger fractions of material (e.g. > 0.45 μm or > 0.8 μm filtered) or leaving samples to rest for a longer time after NaCl addition before analysis.

In sum, further studies are needed to understand the full picture on how terrestrial, estuarine, and coastal processes affect the distribution of metals and NOM along land – ocean transects.

6. Conclusion

The aim of this study was to obtain more knowledge on how the changing environmental factors (chemical, physical and biological) in land-ocean transects affect the distribution of organic material and metals (i.e., size and concentration). The hypothesis, that river-borne ter-OM and associated metals will flocculate along the transect and that there would be higher ter-OM levels in the upper part (closest to river) was tested by analyzing different parameters *in situ* collected surface water samples along Storelva - Sandnesfjorden river-ocean transect.

A strong negative correlation was detected between selected ter-OM associated metals, Fe, Al, Mn, Pb, and Si with salinity. When the freshwater from the river mixed with saltwater from the ocean, there was a sudden decrease in these elements, along with organic material. Simultaneously, the ocean-associated metals Na, Ca, Mg, and Mo increased. For As and Cr, there was detected an increase; however, the increase is suspected to (partial) be caused by resuspension from sediments and/or a pollution source alongside the transect. the suspicion is substantiated with observed high values of As and rare behavior of Cr.

Analysis of the properties of NOM revealed a decrease in watercolor, humic content, aromaticity, and size along the gradient. This finding indicates a more extensive portion of NOM in the upstream section of the transect (i.e., closest to the river) originated from terrestrial sources. Chlorophyll a, used as an indicator of the primary production status and revealed an increase along the transect. A reason for this increase in Chl-a alongside the decrease in NOM, is hypothesized to be the light-absorbing character of NOM, i.e., with light limiting effects on phytoplankton primary production being highest in the upstream parts of the transect.

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Comparing the result from this study on the case "Storelva – Sandnesfjorden" with similar studies conducted in other land–ocean transects across the globe, how complex and individual these systems may be. However, some factors can be highlighted as key for the distribution of organic material and metals. (1) The placement of the mixing zone (between fresh and saltwater), which is influenced by rain and tidal water, determines where in the transect salt-induced flocculation occurs. (2) Co-precipitation with NOM and/or iron is a vital removal mechanism. (3) Biological activity may be especially important for the distribution and concentration of nutrients (Si in this study).

Coastal zones are the base of future blue economy as well as e.g., carbon storage. To protect the risks of environmental threats and achieve sustainable use of these areas, it is necessary to consider how organic material and metals are distributed along river to ocean transects. This is especially crucial given that climate change will alter factors important for NOM and metal distribution, such as precipitation, temperature, and pH. This study provides important information as to how complex and individual the biogeochemical cycling of ter-OM and associated metals along land-ocean interactions is. However, more research, especially on the role of sediments for the cycling and storage of NOM and metals in sediments, is needed to fully understand the risks in coastal zones.

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Appendix A: LOQ, LOD and reference materials

LOQ and LOD limits in metal analysis

Table A1 Limit of detection (LOD) and limit of quantification (LOQ) for the different metals
during ICP-MS and ICP-OES analysis, detecting different metals in surface water of the river-
ocean transect Storelva-Sandnesfjorden.

Metal	Unit	Limit of detection, LOD in w/V	Limit of quantification, LOQ in w/V	Limit of detection, LOD in w/V	Limit of quantification, LOQ in w/V
		ufortynnet	ufortynnet	fort. 10x	fort. 10x
Al	µg/L	0.06	0.2	0.6	2
Si	mg/L	0.003	0.01	0.03	0.1
Ca	mg/L	0.001	0.005	0.01	0.05
Cr	µg/L	0.009	0.03	0.09	0.3
Mn	µg/L	0.002	0.007	0.02	0.07
Fe	µg/L	0.02	0.061	0.2	0.61
Ni	µg/L	0.04	0.15	0.4	1.5
Cu	µg/L	0.003	0.011	0.03	0.11
Zn	µg/L	0.07	0.23	0.7	2.3
As	µg/L	0.003	0.01	0.03	0.1
Mo	µg/L	0.02	0.07	0.2	0.7
Cd	µg/L	0.0005	0.002	0.005	0.02
Pb	µg/L	0.0009	0.003	0.009	0.03

The blank samples were heavily contaminated for some elements. LOD and LOQ were
therefor determined based on the instrument's detection and determination limit.

Reference materials

Organic carbon
NW-ION-96.4 - Natural lake water – Major ions and nutrients.

ICP-MS and ICP-OES
CASS-5 nearshore seawater reference material .
Standard reference material 1640a Trace elements in natural water.

Appendix B: Physical parameters

pH and conductivity

Table B1 *pH and conductivity (‰) at the different sampling stations, where A is closest to the river and J is closest to the ocean, along the river-ocean transect Storelva – Sandnesfjorden.*

	pH		Conductivity (‰)	
Station	**October**	**November**	**October**	**November**
A	5.91	5.865	0.5	0.3
B	5.643	5.937	0.7	0.4
C	6.049	6.16	0.7	0.4
D	6.115	6.182	0.8	0.6
E	6.277	6.182	0.8	0.4
F	6.874	5.824	0.9	0.5
G	7.524	6.84	0.9	1.1
H	6.11	6.35	8.8	2.4
I	7.003	6.727	17.6	8.7
J	7.381	6.22	24.2	15.2

Precipitation

Table B2 *Precipitation (mm/day) during the week before sampling campaigns, 12th October, and 4th November 2020. Data is collecte from yr.no, Arendal weather station.*

October	**Precipitation (mm/day)**	**November**	**Precipitation (mm/day)**
12.okt	0	04.nov	0
11.okt	0	03.nov	1.4
10.okt	3.5	02.nov	11
09.okt	1.9	01.nov	7.3
08.okt	2.2	31.okt	1.4
07.okt	11.9	30.okt	1.6
06.okt	14.3	29.okt	0.9

Tidal water

Table B3 *Tidal water during the sampling campaign 12th October and 4th November. Data is collected from www.kartverket.no, Risør station.*

October				November			
Time	Observed	Predicted	Weather	Time	Observed	Predicted	Weather
11:00	60	60	0	09:00	81	59	22
11:10	61	62	-1	09:10	80	58	22
11:20	62	63	-1	09:20	79	58	21
11:30	63	64	-1	09:30	78	57	21
11:40	64	65	-1	09:40	76	57	19
11:50	65	66	-1	09:50	75	56	19
12:00	66	67	-1	10:00	74	56	18
12:10	67	68	-1	10:10	73	56	17
12:20	68	69	-1	10:20	73	55	18
12:30	69	70	-1	10:30	72	55	17
12:40	69	71	-2	10:40	71	54	17
12:50	70	71	-1	10:50	70	54	16
13:00	70	72	-2	11:00	70	53	17
13:10	71	73	-2	11:10	70	53	17
13:20	71	73	-2	11:20	70	53	17
13:30	71	73	-2	11:30	69	52	17
13:40	71	74	-3	11:40	69	52	17
13:50	71	74	-3	11:50	69	51	18
14:00	70	74	-4	12:00	70	51	19
14:10	70	74	-4	12:10	71	51	20
14:20	70	73	-3	12:20	72	51	21
14:30	69	73	-4	12:30	72	51	21
14:40	68	73	-5	12:40	73	51	22
14:50	67	72	-5	12:50	74	51	23
15:00	66	72	-6	13:00	75	52	23
15:10	65	71	-6	13:10	76	52	24
15:20	64	70	-6	13:20	77	53	24
15:30	63	69	-6	13:30	78	53	25
15:40	62	68	-6	13:40	79	54	25
15:50	60	67	-7	13:50	79	55	24
16:00	59	66	-7	14:00	80	55	25

Appendix C: Instrumental analysis

Metals

Table C1 *Metal concentration in filtered and unfiltered samples collected at the different sampling sites, where A is closest to river and J is closest to the ocean, in the river-ocean transect Storelva – Sandnesfjorden. Samples were collected in October and November 2020.*

ALUMINUM (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	190	140	230	190
B	170	130	230	180
C	180	140	220	180
D	180	140	220	180
E	180	140	210	180
F	190	140	220	180
G	180	140	210	170
H	140	89	210	170
I	74	65	190	150
J	29	28	110	98
SILICON (mg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	1.2	1.1	1.4	1.3
B	1	0.99	1.3	1.2
C	1.1	1.1	1.3	1.3
D	1.1	1.1	1.4	1.3
E	1.1	1	1.3	1.2
F	1.1	1	1.3	1.3
G	1.1	1	1.4	1.3
H	0.88	0.84	1.4	1.3
I	0.54	0.56	1.3	1.2
J	0.31	0.31	0.84	0.83
CALCIUM (mg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	8.3	7.9	5.3	4.7
B	11	11	6	6.1
C	10	11	6.7	6.7
D	12	11	8.6	8.7

E	11	11	6.8	6.8
F	13	12	7.7	7.7
G	13	12	27	15
H	110	100	24	23
I	200	200	59	58
J	280	270	170	170

CHROMIUM (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	0.23	0.2	0.3	0.21
B	0.25	0.2	0.27	0.25
C	0.24	0.21	0.27	0.24
D	0.23	0.21	0.25	0.23
E	0.23	0.21	0.25	0.24
F	0.24	0.21	0.27	0.24
G	0.25	0.21	0.33	<0.3
H	0.45	0.32	0.47	<0.3
I	0.36	0.39	0.35	0.36
J	0.46	0.52	0.46	0.48

MANGANESE (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	23	20	12	10
B	20	17	16	15
C	22	19	14	14
D	20	19	13	12
E	21	19	14	13
F	21	19	15	13
G	21	19	13	12
H	14	13	13	12
I	8	7.6	11	11
J	2.3	1.9	7.2	6.8

IRON (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	310	140	310	150
B	260	150	260	170
C	300	150	250	170
D	280	160	230	160
E	290	160	240	170
F	290	150	250	170
G	280	150	230	140

	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)
H	180	54	230	140
I	83	26	180	110
J	25	14	78	44

NICKEL (μg/L)	October		November	
Station	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)
A	0.72	0.73	0.77	0.77
B	0.75	0.78	0.76	0.76
C	0.72	0.73	0.79	0.79
D	0.67	0.69	0.7	0.7
E	0.76	0.69	0.73	0.73
F	0.72	0.76	0.66	0.73
G	0.72	0.81	<1.5	<1.5
H	3.5	1.9	<1.5	<1.5
I	2.8	1.6	<1.5	<1.5
J	2.5	1.5	<1.5	<1.5

COPPER (μg/L)	October		November	
Station	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)
A	1.2	1.4	1.2	0.99
B	0.99	1.1	1.3	1.3
C	0.96	1.2	0.86	0.88
D	0.82	0.98	0.83	0.86
E	0.93	1	0.84	0.85
F	0.9	1.2	0.84	0.97
G	0.9	1.9	1.5	1.1
H	0.95	3.9	4.4	1
I	0.94	1	1.3	0.98
J	0.89	1.3	2.5	0.78

ZINC (μg/L)	October		November	
Station	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)	Unfiltered (> 0,2 μm)	Filtered (< 0,2 μm)
A	9.9	9.8	8.9	7.5
B	7	6.7	8.9	N/A
C	7.4	7.6	7.4	6.9
D	6.8	7.1	6.9	6.7
E	6.8	7	6.8	8
F	7	6.9	6.9	11
G	6.8	7.5	8.9	9.3
H	8	7.6	8.4	8.4
I	6.6	5.7	7.5	7.2
J	5.2	3.9	6.7	5

ARSENIC (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	0.29	0.27	0.26	0.22
B	0.3	0.28	0.28	0.26
C	0.28	0.27	0.27	0.26
D	0.3	0.27	0.27	0.24
E	0.29	0.28	0.26	0.25
F	0.3	0.27	0.27	0.25
G	0.31	0.28	0.34	0.27
H	0.63	0.58	0.34	0.33
I	0.86	1	0.41	0.43
J	1.2	1.2	0.78	0.74

MOLYBDENUM (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	0.22	0.2	0.15	0.12
B	0.26	0.25	0.15	0.14
C	0.24	0.26	0.15	0.16
D	0.28	0.28	0.2	0.2
E	0.27	0.27	0.16	0.16
F	0.29	0.27	0.19	0.17
G	0.31	0.3	<0,7	<0,7
H	2.6	2.6	<0,7	<0,7
I	5.4	5.2	1.5	1.5
J	7.3	7.2	4.4	4.4

CADIUM (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	0.17	0.34	0.17	0.23
B	0.15	0.045	0.8	
C	0.049	0.13	0.24	0.091
D	0.04	0.053	0.15	0.036
E	0.037	0.046	0.12	0.034
F	0.054	0.062	0.14	0.035
G	0.038	0.31	0.14	0.032
H	0.037	0.09	0.12	0.022
I	0.031	0.1	0.087	0.031
J	0.029	0.034	0.092	0.029

LEAD (µg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)

Station	October Unfiltered (> 0,2 µm)	October Filtered (< 0,2 µm)	November Unfiltered (> 0,2 µm)	November Filtered (< 0,2 µm)
A	0.51	0.25	0.65	0.31
B	0.38	0.22	0.41	0.3
C	0.45	0.24	0.42	0.3
D	0.42	0.24	0.4	0.29
E	0.43	0.24	0.39	0.29
F	0.43	0.23	0.42	0.28
G	0.41	0.26	0.43	0.28
H	0.27	0.087	0.42	0.25
I	0.15	0.056	0.32	0.2
J	0.053	0.055	0.16	0.089

MAGNESIUM (mg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	22	22	14	12
B	30	30	16	16
C	28	30	19	18
D	33	33	24	24
E	32	32	18	18
F	34	34	22	21
G	36	36	81	45
H	320	320	74	74
I	620	630	190	190
J	850	840	540	540

SODIUM (mg/L)	October		November	
Station	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)	Unfiltered (> 0,2 µm)	Filtered (< 0,2 µm)
A	182	180	120	100
B	240	240	140	130
C	230	240	150	150
D	262	260	190	200
E	260	260	150	150
F	280	270	180	170
G	290	290	650	360
H	2600	2640	590	590
I	5300	5320	1500	1500
J	7400	7320	4500	4500

Oganic carbon analysis

Table C2 *Total organic carbon (TOC) and dissolved organic carbon (DOC) in surface water at the different sampling sites, where A is closest to river and J is closest to the ocean, , in the river-ocean transect Storelva – Sandnesfjorden.*

Site	October TOC (mg/l)	October DOC (mg/L)	November TOC (mg/L)	November DOC (mg/L)
A	7.6	7	7.1	6.7
B	7.4	6.8	7	6.9
C	7.6	7	6.9	6.9
D	7.2	7.1	6.7	6.7
E	6.8	6.7	6.9	6.8
F	6.8	6.7	6.7	6.9
G	7.3	6.9	6.5	6.7
H	5.5	5.4	6.6	6.6
I	4.1	3.9	6.1	6
J	2.8	2.4	4.5	4.3

*DOC was measured as total carbon in filtered (< 0.22 μm) samples.

Chlorophyll a

Table C3 *Chlorophyll a (Chl-a) at the different sampling sites, where A is closest to river and J is closest to the ocean, of the river-ocean transect Storelva – Sandnesfjorden in October.*

STATION	Chl-a (μg/L)
A	0.78
C	0.65
G	1.4
I	2.8
H	4.7

NOM properties

Table C3 *The different absorption values at chosen wavelengths for surface water samples at different stations, where A is closest to the river, and J is closest to the ocean. Samples were collected in October 2020.*

	435 nm	420 nm	375 nm	365 nm	254 nm	250 nm	204 nm
Baseline	0.01966	0.02004	0.01908	0.01696	0.03428	0.03536	0.10930
MQ	0.00015	0.00015	0.00003	0.00013	0.00017	0.00002	0.00113
MQ2	-0.00035	-0.00038	-0.00022	-0.00006	0.00016	0.00024	-0.00513
A	0.18034	0.22839	0.48490	0.57445	2.64282	2.72463	10.00000
B	0.17958	0.22729	0.48075	0.56874	2.62371	2.70994	10.00000
C	0.18069	0.22843	0.48259	0.57037	2.63999	2.72613	10.00000
D	0.18045	0.22766	0.47928	0.56711	2.62894	2.71245	10.00000
E	0.17631	0.22355	0.47499	0.56223	2.60782	2.69267	10.00000
F	0.18069	0.22843	0.48259	0.57037	2.63999	2.72613	10.00000
G	0.18615	0.23297	0.48351	0.57061	2.60226	2.68647	10.00000
H	0.12643	0.15967	0.32802	0.38490	1.80258	1.86122	10.00000
I	0.07285	0.09324	0.19347	0.22700	1.11220	1.14987	10.00000
J	0.02767	0.03549	0.07412	0.08722	0.52760	0.54984	10.00000

Table C4 *Different properties, based on the relationship between absorption at different wavelengths, of NOM in surface water at different stations (where A is closest to river and J is closest to the ocean) in the river-ocean transect Storelva – Sandnesfjorden.*

Station	Color $Abs(450) * 5 * 500$	SUVA(254) $\dfrac{Abs(254)}{DOC}$	Size $\dfrac{Abs(250)}{Abs(365)}$	Aromaticity $\dfrac{Abs(254)}{Abs(204)}$
A	570.96295	37.7545493	4.74298517	0.26428185
B	568.23	38.5839799	4.76478447	0.26237106
C	571.068375	37.7141714	4.77954824	0.2639992
D	569.149025	37.0273624	4.78290167	0.26289427
E	558.88715	38.9226443	4.7892871	0.26078172
F	571.068375	39.4028657	4.77954824	0.2639992
G	582.4142	37.7138697	4.70810434	0.2602257
H	399.1714	33.3810581	4.83556614	0.18025771
I	233.101475	28.5178454	5.06554146	0.1112196
J	88.72355	21.9834496	6.30402854	0.05276028