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Master's thesis in Analytical chemistry
Supervisor: Trond Peder Flaten and Thomas Meyn
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Acknowledgements

Abstract

This project's aim was to investigate which size fractions of different metals that are present in wash water from road tunnels in the purpose of developing a treatment solution for tunnel wash water. This is important because different species of metals require different methods of removal. Tunnel wash water contains a lot of pollutants, that without treatment will be a source of contamination to the receiving environment. Most tunnels do not carry out any form of treatment of the tunnel wash water, but some tunnels have treatment solutions in form of sedimentation ponds. Sedimentation removes particulate contaminants, but are not suited for other forms of metals. Therefore, it is essential to develop more information about the size fractions present before, during and after sedimentation.

To address this, tunnel wash water from three different tunnels in Oslo area were collected. The work was addressed as a laboratory experiment where a sedimentation pond was represented using columns with approximately the same conditions (2 m high, cold and dark). The sedimentation period lasted for 35-44 days and water samples were taken from the columns in the start, middle and end of the sedimentation period. The water was filtered through 1.2 μm filters, 0.45 μm filters and ultrafiltered through 3 kDa. The concentrations of Cu, Zn, Pb, As, Ni, Cr, Cd, Al, Fe, Na, Ca, K, Mg, Si, Sn and P in the samples were determined using an Agilent 8800 ICP-QQQ. Size fractions were calculated from total measured concentrations and concentrations in the filtrates, and were classified as bigger particles (> 1.2 μm), smaller particles (0.45-1.2 μm), colloids (3 kDa-0.45 μm), and dissolved fractions (< 3 kDa).

Pb, Cr, Fe, Al, P and Sn were mainly present as particles and hence a high removal percentage from the sedimentation. Cu, Zn, As, Ni, Cd and Si were mainly present as particles, but aslo as colloids/dissolved. These metals had slightly lower removal percentage, as the particles sedimented, whereas the smaller fractions did not. Na, Ca, Mg and K were mainly dissolved, but Ca, Mg and K were also present as particles. For these metals, only the particulate fractions were removed by sedimentation, leaving huge concentrations of dissolved metals. Sedimentation was sufficient to remove particles, but does not remove dissolved metals. Dissolved metals are more mobile, and discharge of elevated concentrations of dissolved metals are of concern as they are assumed to be more bioavailable, hence toxic. Therefore, sedimentation is not sufficient treatment to remove metals in all forms.

Sammendrag

Hensikten med dette prosjektet var å undersøke hvilke størrelsesfraksjoner av forskjellige metaller som er tilstede i vaskevann fra vegtunneler med et hovedmål om å utvikle en behandlingsstrategi for tunnelvaskevann. Dette er viktig fordi forskjellige former av et metall krever ulike metoder for fjerning. Tunnelvaskevann inneholder mange miljøgifter, som uten behandling vil være en kilde til forurensning. De fleste tunneler utfører ingen form for behandling av tunnelvaskvannet, men noen tunneler har sedimentasjonsbasseng. Denne behandlingsformen fjerner partikulære forurensninger, men er ikke egnet for andre former av metaller. Derfor er det viktig å få mer informasjon om størrelsefraksjonene til metallene før, under og etter sedimentasjon.

Tunnelvaskvann fra tre forskjellige tunneler i Oslo-området ble samlet. Arbeidet ble utført som et laboratorieeksperiment der et sedimentasjonsbasseng ble representert ved bruk av kolonner under de samme forholdene (2 m høye, kalde og mørke). Sedimenteringsperioden varte i 35-44 dager, og vannprøver ble tatt fra kolonnen i starten, midten og slutten av sedimenteringsperioden. Vannet ble filtrert gjennom 1.2 μm filtre, 0.45 μm filtre og ultrafiltrert gjennom 3 kDa. Konsentrasjonen av Cu, Zn, Pb, As, Ni, Cr, Cd, Al, Fe, Na, Ca, K, Mg, Si, Sn og P i prøvene ble bestemt ved hjelp av et Agilent 8800 ICP-QQQ- instrument. Størrelsesfraksjoner ble beregnet ut fra totale konsentrasjoner og konsentrasjoner i filtratene, og ble klassifisert som større partikler ($> 1{,}2$ μm), mindre partikler ($0{,}45$-$1{,}2$ μm), kolloider (3 kDa-$0{,}45$ μm), og oppløst fraksjon (<3 kDa).

Pb, Cr, Fe, Al, P og Sn var hovedsakelig til stede som partikler og store mengder ble derfor fjernet i sedimenteringen. Cu, Zn, As, Ni, Cd og Si var hovedsakelig til stede som partikler, men kolloider/ oppløste fraksjoner var også til stede. Lavere konsentrasjoner av disse metallene ble fjernet i sedimenteringen, ettersom partiklene sedimenterte, mens de mindre fraksjonene gjorde ikke det. Na, Ca, Mg og K var hovedsakelig oppløst, men Ca, Mg og K var også til stede som partikler. For disse metallene ble bare partiklene fjernet i sedimenteringen, som etterlot en enorm mengde av oppløste metaller. Sedimentering var tilstrekkelig for å fjerne partikler, men fjernet ikke de oppløste metallene. Oppløste metaller er mer mobile, og utslipp av forhøyede konsentrasjoner av oppløste metaller er bekymringsverdig da de antas å være mer biotilgjengelige, derav giftige. Derfor er sedimentering ikke tilstrekkelig behandling for å fjerne metaller i alle former.

Contents

1 Introduction

1.1 Background and objective

Norway is a country with challenging landscape, and road tunnels are an important part of the road network. The country has about 1150 road tunnels with a total length of approximately 800 km. As a result of traffic, pollutants accumulate on the road, walls and ceiling in the tunnels. Sources of the pollutants are breaks, tires (especially studded tires), catalysts, the car body, combustion residues and oil and gasoline spills. In order to maintain safe traffic conditions and enhance the lifespan of the tunnels, they are frequently washed. The Norwegian tunnels are normally washed between 1 to 12 times a year, depending on the annual average daily traffic load (AADT).

The tunnel wash water (TWW) contains a lot of pollutants, both organic and inorganic, that without treatment will be a source of contamination to the receiving environment. Treatment of such water is challenging, and in Norway only few tunnels carry out treatment in form of a sedimentation pond. Tunnels without a treatment option for the wash water discharge it directly to the closest water recipient (creeks, rivers, the ocean/fjord). This can potentially harm the environment and the life there. The problem is related to metals being present in different forms (species) in water. While some elements may stay in the water phase, others may form or associate with colloids or particles. Particulate contaminates can be removed by sedimentation, but dissolved metals are hard to remove this way. Metals in dissolved phase are shown to be more toxic, and it is therefore important to develop a treatment solution that removes metals in all phases.

In order to develop a treatment solution, more information about size fractions of the metals present in the TWW are needed. The project is addressing this by a sampling campaign with TWW from three different tunnels. The water was placed in columns representing sedimentation ponds, where it is possible to address the water properties in different heights throughout the sedimentation period.

This study investigates metal concentrations and size fractions, giving information about the form of the pollutants (dissolved, colloidal, particulate) and the general water quality. The specific objectives are:

- Which metals are present in tunnel wash water?

- In which form are common metals present in tunnel wash water (particulate, colloidal, dissolved)?

- Is the form changing during the sedimentation process?

- Is sedimentation sufficient treatment of the tunnel wash water?

2 Theory

2.1 Tunnel wash water

2.1.1 Washing procedure

Tunnels in Norway are washed annually, and the main reasons are to enhance the lifespan, and for traffic safety. Road signs and lights must be kept clean and visible. Salt solutions can lead to corrosion of equipment, and oil and other substances must be cleaned to reduce friction. Washing also helps to reduce the dust concentration in the air inside the tunnel, which contributes to improved visibility and air quality (Rathnaweera et al. 2019, Meland & Torp 2012).

The frequency of tunnel washes a year depends on the AADT (Meland & Torp 2012). The overview of the minimum required washing based on AADT can be seen in table 1, and the recommendation of treatment according to AADT are seen in tabel 2. Three different types of washing can be performed, half wash, full wash and technical wash. Full wash includes cleaning of all surfaces and technical equipment, and half wash includes cleaning of the walls and technical equipment. In a technical wash, only signs and lights are washed (Statens Vegvesen 2014).

Table 1: The frequency of annual tunnel washes due to type of wash (*=1 pr. year the years without full wash) (Statens Vegvesen 2014)

Annual Average Daily Traffic (AADT)	Half wash	Full wash	Technical wash
0-300	-	Every 5th year	1 pr. year *
301-4000	-	1 pr. year	1 pr. year
4001-8000	1 pr. year	1 pr. year	2 pr. year
8001-12 000	2 pr. year	1 pr. year	3 pr. year
12 001-15 000	3 pr. year	2 pr. year	5 pr. year
15 001-	4 pr. year	2 pr. year	6 pr. year

The washing procedure starts with removal of dust and bigger particles by a sweeping machine, followed by washing with water which in most cases contains detergent (Meland et al. 2010). The amount of water during full tunnel wash is approximately 60-100 L/m, mixed with 0.5-1 % detergent (Rathnaweera et al. 2019), dependent on the number of tubes and lanes. The water consumption is much lower for a technical wash. After washing,

the wash water and dirt is removed and collected by inlets and gully pots along the lanes (Meland et al. 2010, Meland & Torp 2012).

Table 2: Recommendation of treatment according to annual average daily traffic (Ranneklev et al. 2016)

Annual Average Daily Traffic (AADT)	Water treatment
<8000	Normally no water treatment.
8000-12 000	Water treatment facility should be implemented when the recipient is vulnerable.
12 000-20 000	Necessary for the upper AADT range, and in the lower AADT interval if the recipient is vulnerable.
>20 000	Must usually be treated.

2.1.2 Treatment procedure

Based on knowledge about acute toxic effects of untreated TWW, the Norwegian road Authorities (Statens Vegvesen) have since 1990 been building several treatment plants to reduce the risk of environmental damage from TWW (Meland 2012a). The road guidelines today states that if treatment of the TWW is necessary, the treatment solution should at least include sedimentation of particles, soap degrading and separation of oil (Statens Vegvesen 2016). The concentration limits for emission of different contaminants are not stated in the guidelines, and applies for new tunnels. Most tunnels in Norway do not possess any treatment of the TWW, and the water goes straight to a recipient. For tunnels with treatment, installation for separating oil and sedimentation ponds are used. These are either build inside or outside the tunnel. By sedimentation, environmental contaminants bound to particles sink to the bottom by gravitation. Both oil, metals and other pollutants can bind to particles. The requirement for residence time in the sedimentation pond are set to four weeks (Fylkesmannen 2019). The oil separation has no further treatment effect than in case of oil spill from traffic accidents (Meland 2012b).

2.2 Pollutants

TWW has many chemical similarities with stormwater. The main difference is the concentration; while on open roads contaminants are washed away by rainfalls, they accumulate in tunnels. The TWW typically contains high concentrations of both organic and inorganic contaminants (Meland et al. 2010). The contaminants originate from multiple sources, and table 3 gives a list of contaminants and their most likely sources related to traffic.

Table 3: Highway runoff contaminants and their sources (Meland 2010)

Source	Contaminant
Brakes	Ba, Cu, Fe, Mo, Na, Ni, Pb, Sb
Tires	Al, Zn, Ca, Cd, Co, Cu, Mn, Pb, W, hydrocarbons, PAH
Catalytic converters	Pt, Pd, Rh
Vehicle body	Cr, Fe, Zn
Combustion	Ag, Ba, Cd, Cr, Co, Mo, Ni, V, Sb, Sr, Zn, PAH, MTBE, BTEX
Oil and petroleum spill	PAH
Asphalt	Al, Ca, Fe, K, Mg, Na, Pb, Si, Sr, Ti, PAH
De-icing and dust suppression	Ca, Mg, Na, Cl, ferro-cyanide
Road equipment	Zn
Detergents used in tunnel wash	Tensides

2.2.1 Metals

Heavy metals and trace metals are a big part of the inorganic contaminants in highway runoffs, and a big concern of the aquatic organisms and environment due to their toxicity. The therms "heavy metal" and "trace metal" are used interchangeably, and have no precise definition, and are therefore avoided in this paper (Meland 2010). Once metals are introduced into an

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aquatic environment, they are spread in the water column, accumulated in sediments or consumed by biota (Gheorghe et al. 2017). Unlike organic contaminants, they can not be degraded by biological and chemical processes. However, some metals are essential for organisms at low concentrations (Fifiled & Haines 2000).

Water, sediment and soil quality guidelines for metals have often been based on the total concentration. Total metal concentration is an important indicator of pollution risks (Landner 2004), however, this does not provide information concerning the fate of the element in terms of its interaction with sediments, its ability to cross biological membranes (bioavailability), or its toxicity (Fifiled & Haines 2000). In order to assess the environmental impact, information about the chemical form (speciation) is needed. Speciation are defined as different physico-chemical forms of an element, which together represent the total concentration (Fifiled & Haines 2000). Metals binds to other species in a variety of ways, as example ionic bonds (salts and ion pairs), covalent bonds to ligands (complex ions or compounds). As an example, the environmental pollution cadmium (Cd) may be present as ionic sulphide (CdS), as ionic species ($CdBr^+$, $CdBr_4^{2-}$), as organometallic compounds ($(C_2H_5)_2$), or as complexes ($Cd(NH_3)_2Cl_2$) (Fifiled & Haines 2000).

Metals in an aquatic environment can occur mainly as dissolved, colloidal or particulate depending on particular conditions in the environment as pH, redox potential, temperature, suspended solids and inorganic and organic ligands (Aasum 2013, Meland 2010). One can also distinguish between high molecular mass (HMM) species and low molecular mass (LMM) species. Examples of HMM species are colloids, polymers, pseudocolloids and particles (Meland et al. 2010), and examples of LMM species are ions, molecules and complexes (Heier et al. 2009).

There are different definitions on the boundaries between the different metal form sizes. It is common to separate particles from smaller forms by filtering through 0.45 μm filter, but 1 μ has also been used. IUPAC defines forms with diameter between 1 nm and 1 μ as colloids, and particles if it is bigger than 1 μ. Colloids are strongly influenced by the conditions in the aquatic environment, as it is dominated by surface tension and charge, instead of the chemical composition (Lead et al. 1997). In order to separate the dissolved fraction from colloids it is normally ultrafiltrated. Species smaller than 1 - 10 kDa (diameter of less than about 1 nm) are defined as low molecular mass

(LMM) species (Heier et al. 2009).

The different species of a metal vary in toxicity, mobility and bioavailability (Fairbrother et al. 2007). Metal toxicity depends on metal speciation, the present of organic or inorganic complexes, pH, temperature, salinity, and redox conditions (Gheorghe et al. 2017). Bioavailability in environmental science is defined as "the measure by which various substances in the environment may enter onto living organisms" (Naidu et al. 2008). The bioavailability of metals are controlled by following factors: the biology of the organism, the metal geochemistry (distribution in water - sediment, suspended matters, metal speciation), physical and chemical factors (temperature, pH, ionic strength, concentration of DOC and total suspended solids) (Gheorghe et al. 2017).

Particle-bound metals are normally not bioavailable, but can still be taken up through the food ingestion (Gheorghe et al. 2017). Dissolved metals will on the other hand be readily available for plants and aquatic organisms, and are taken up through the permeable epidermis. Overall, binding of metals decreases the bioavailability of the metal (Gheorghe et al. 2017). Changes in parameters like pH and oxygen content can affect the mobility of metals from particles/ colloids to the dissolved phase. When a metal dissolves from particles, they are re-mobilised. This can also arise due to other metals which may compete for the binding to biological membranes (Aasum 2013).

Dissolved metals are also very mobile. The majority of metals cannot be easily metabolized into less toxic compounds, and a characteristic of them being the lack of biodegradability (Gheorghe et al. 2017). Studies have shown that some metals (but not all) were re-mobilised from the particular fraction to LMM fraction, and the mobility increased due to detergent in the water. From the environmental aspect, addition of detergent to the wash water may decrease the treatment effect in the sedimentation ponds due to risk for aquatic organisms (Aasum 2013).

The size of the molecules and bonded metals can distinguish between the forms of a metal in an aquatic environment. The two main approaches for evaluation of metal speciation are experimental measurement and computer modelling (Fifiled & Haines 2000). Size fractionation can be done by for example centrifuging, filtering, ultrafiltration, dialysis and field flow fractionation (Aasum 2013).

2.3 Water quality

The term "water quality" is used to describe the condition in a water resource, usually based on humans needs (Parparov & Berman 2014). Monitoring of water quality is becoming more important in order to comply the public health and safety regulations, and for protection of the natural resources (Wang 2013). Water quality can be divided into three parameters, physical, chemical and biological (Omer 2019).

Turbidity: is the cloudiness of water due to the amount of suspended matter. This is addressed by the ability of light to pass through water. The higher the intensity of scattered light (measured in NTU), the higher turbidity (Omer 2019).

Temperature: solubility and chemical reactions are influenced by temperature, and thereby the sedimentation process, biological oxygen demand (BOD) and biosorption of dissolved heavy metals (Omer 2019). High temperature gives high solubility for most solids, but not all (Ardelan 2019).

Solids: occur as either dissolved or suspended. By filtering through glass fiber filter, suspended solids are retained on the filter, and the dissolved solids passed through (Omer 2019).

pH: Is the most important water quality parameter indicating the strength of an acidic or a basic solution. pH is logarithmic, and a change of 1 pH unit therefore represent a 10-fold change in the pH. This means that a pH of 6 is 10 times more acidic than pH 7, and 100 times more acidic than pH 8. Increased pH will increase the amount of oxygen in the water. A change in pH can change the forms of chemicals, for example will low pH corrode and dissolve metals and other substances, which can make metals more toxic (Omer 2019).

Dissolved oxygen (DO): the higher the concentration of DO, the better water quality (Omer 2019). Studies have shown that anoxic conditions decrease the potential bioavailability risks of Pb, Zn, Ni, Cu, Mo, and Fe, and also the mobile fractions of Pb, Zn, Cu and Fe (Kang et al. 2019).

Table 4: Classification limits for metals in water measured in μg/L.(*= typical natural trace element concentrations in natural water) (Miljødirektoratet 2016, Fifiled & Haines 2000, Fylkesmannen 2019)

Metal	Norwegian EQS fresh water	Acceptable discharge
Al	10*	100
As	0.5	5
Ca	-	-
Cd	0.08	0.8
Cr	3.4	34
Cu	7.8	78
Fe	500*	5000
K	-	-
Mg	-	-
Na	-	-
Ni	4	40
P	-	-
Pb	1.2	12
Si	-	-
Sn	-	-
Zn	11	110

Metals in water can be classified in five classes based on their toxicity. The five classes are background level, good (no toxic effects), moderate (chronic effects on long-term exposure), bad (acute toxic effects with short-term exposure) and very bad (extensive toxic effects) (Miljødirektoratet 2016).

EUs directive have a list of en environmental quality standards (EQS) for prioritized metals, which also has been implemented in Norwegian environmental legislation. This applies to arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), Nickel (Ni), lead (Pb) and zinc (Zn). The limit value for the pollutants corresponds to the boundary between good and moderate. Such values for aluminium (Al) and iron (Fe) originate from typical trace element concentrations in natural waters (Fifiled & Haines 2000). As a rough guideline, it is suggested that if the metal concentration is lower than 10 times the EQS-value, there is probably no need for treatment before discharge (Miljødirektoratet 2016, Fylkesmannen 2019).

2.4 ICP-MS

ICP-MS is a type of mass spectrometry that uses an inductively coupled plasma to ionize the sample. ICP-MS is the main method for elemental analysis, and can detect most of the elements in the periodic table, even in very small concentrations. This, and its speed of analysis, detection limits, and isotopic capability makes ICP-MS unique compared to other element techniques (Thomas 2013)

A brief description of principles of the method is as follows: A liquid sample is pumped into a nebulizer which converts the sample into a fine aerosol with argon gas. The aerosol droplets are separated from larger droplets in a spray chamber. The liquid is then introduced into the plasma torch via a sample injector. The plasma torch is used to generate positive ions. These positively charged ions are directed into the mass spectrometer via the interface region. When the ions have been extracted from the interface region, they are led into the main vacuum chamber by many electrostatic lenses called ion optics. The function of the ion optics is to electrostatically focus the ion beam towards the mass separation device. This ion beam contains the analyte and can now enter the mass separation device. The ions are now separated according to their mass-to-charge ratio and an ion signal are then sent to a detector proportional to the concentration (Thomas 2013).

3 Experimental

3.1 Study site and sampling

The tunnel wash water used in this study was collected from tunnels in Oslo and Viken in Norway during February and March 2020. The chosen tunnels were Smestadtunnelen, Bjørnegårdtunnelen and Tåsentunnelen (Figure 1), who all have sedimentation pounds.
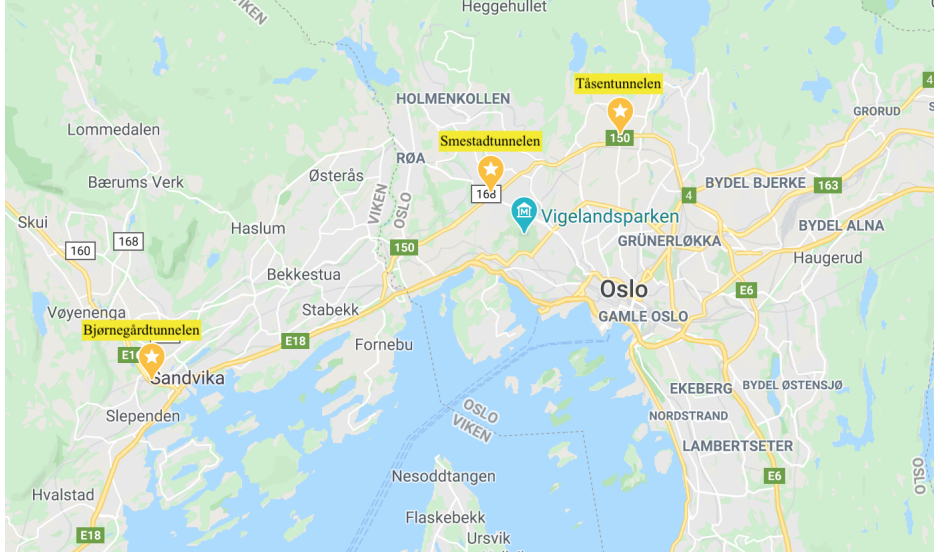
Figure 1: Picture from Google Maps showing the location of Smestad, Bjørnegård and Tåsen tunnel

Smestadtunnelen and Tåsentunnelen are located on highway 150 in Oslo, while Bjørnegårdtunnelen is located north of Sandvika on European route E16. The three tunnels all consist of two separated tubes with a total of four lanes. Information about the AADT and length of the tunnels are seen in table 5.

Table 5: Information about the AADT, % heavy vehicles and length of the tunnels (Statens Vegvesen 2020)

	Smestad	Bjørnegård	Tåsen
ADT (Heavy vehicles)			
East	22 262 (7%)	12 630 (9%)	23 046 (9%)
West	44 060 (8%)	11 600 (11%)	22 894 (9%)
Length	494 m	2 300 m	1 338 m

All samples were collected early the morning after the night of the tunnel wash, to get as homogeneous and fresh water as possible. The tunnels had been washed by half wash (see section 2.1.1). The TWW was pumped directly from the sedimentation ponds into tanks. For Smestadtunnelen, a 1000 L tank was used, and 20 L containers were used for the two other tunnels. Figure 2 shows pictures of the sampling in Bjørnegårdtunnelen where the sedimentation pond was inside the tunnel. The water (approximately 300 L) was immediately transported to the Norwegian University of Science and Technology (NTNU) in Trondheim, and pumped into two columns. The sampling at Smestadtunnelen did not go as planned, as the pump broke, and there was not enough time to fill the tank with buckets. Therefore, it was only enough water for one column from Smestadtunnelen.

Figure 2: Sampling in the Bjørnegård tunnel. Photo: Thomas Meyn

3.2 Setup and preparatory work

Columns (Figure 3) were prepared for tunnel wash water, and placed in a refrigerator at approximately 6 °C. The columns were about 2 m high and held 141 L water. The columns were equipped with 10 taps in different heights. The height and number of taps were chosen in order to analyse the water property in different heights. For this project, only the top crane was used. A sedimentation pond in a tunnel will typically be 2.2-2.9 meters deep, but the collection in this study were done after half-washes, so the sedimentation ponds were not full. The column in the laboratory is supposed to simulate a sedimentation pond.

Figure 3: The columns used in the project. Photo: Thomas Meyn

3.3   Analysis

The tunnel wash water sedimented in the columns for 35 days. Throughout this period the water was supposed to be analysed three times, the first day, after about 17 days and after 35 days. Due to trouble accessing the laboratory during the corona period, this became difficult. The water was therefore analysed at day 0, 11, 21 and 36 from Smestadtunnelen, at day 0, 25 and 44 from Bjørnegårdtunnelen and at day 0, 16 and 35 from Tåsentunnelen. How this was done is shown in figure 4. Two parallels were taken from the top of each column. From each parallel, one unfiltrated sample, two filtrated samples (0.45 μm and 1.2 μm) and a centrifuged sample (3 kDa) were taken. Filtering was done through 0.45 μm PES membrane filter and 1.2 μm. Centrifuging was done by first filter the sample through a 0.45 μm PES membrane filter, and 15 mL of the filtrate was poured into a Sartorius Vivaspin 20 ultrafilter device (3kDa). The ultrafilter device was then placed in a centrifuge and spun at 4000 rpm for about 40 min.
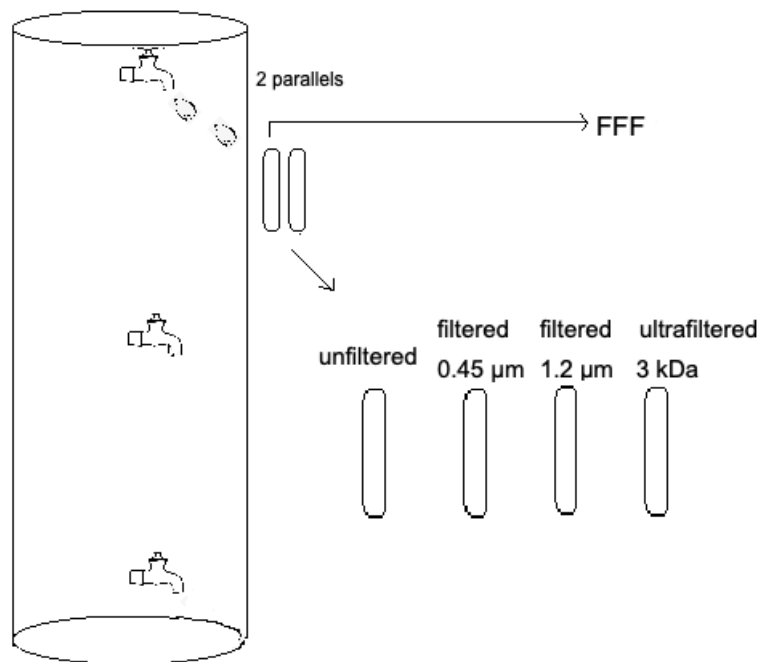
Figure 4: Sketch describing the sampling procedure

3.4   Fractionation method

In order to distinguish between particles, colloidal and dissolved metal fraction, a fractionation step was done. In this project, the fractions were defined as follows:

1. **Particulate fraction:** Metal particles were removed from the TWW by filtering through 0.45 μm filter. Particles bigger than 1.2 μm were found by subtracting the concentration of 1.2 μm filtrate from the measured total concentration. Particles with size between 0.45 μm and 1.2 μm were found by subtraction the concentration of the 0.45 μm filtrate from the 1.2 μm filtrate.

2. **Colloidal fraction:** By ultrafiltration through 3 kDa of the 0.45 μm filtrate, the colloidal metal fraction were removed from the TWW. The colloidal fraction is therefore defined as metals with size between 0.45 μm and 3 kDa. The difference between the concentration of the 3 kDa and 0.45 μm filtrate will give concentration of colloids in TWW.

3. **Dissolved fraction:** The concentration of the 3 kDa filtrate gives the concentration of dissolved metals in TWW.

3.5   ICP-MS

Raw samples, filtered samples and ultrafiltered samples were poured into clean 15 mL polyethylene tubes. The tubes were acidified with 1 droplet of 0.1 M nitric acid (HNO3) per 3.3 mL sample. ICP-MS requires the samples to be in solution form, so in addition, 65 % HNO3 (2 mL) was added to all turbid samples (approximately 8 mL) for digestion by UltraClave. Then diluted to approximately 48 mL.

An Agilent 8800 ICP-QQQ was used for detection of metal concentration in TWW samples. Raw samples (from day 0) from all tunnels were screened for all elements, and the remaining samples were analysed for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, P, Pb, Si, Sn and Zn. The preparation and analysis were done by Syverin Lierhagen and Anica Simic at department for chemistry at NTNU.

4 Results and discussion

This chapter will present the results obtained by ICP-MS analysis of the TWW samples, and a discussion of the findings.

4.1 Total metal content and size fractions in the tunnel wash water

The primary aims of this study were to investigate the metal concentrations in the TWW, how the metal concentrations develop over time of sedimentation, in which size fraction the particular metals were present as (particulate, colloidal, dissolved) before, during and after sedimentation, and an evaluation of sedimentation as treatment method.

This will be presented by addressing each metal, one by one. The metals Cu, Zn, Ni, Pb, Cd, Cr, As, Fe and Al are chosen for closer investigation as they are often reported in highway runoff studies. The remaining metals will be presented in groups according to the size fractions present. The metals will be presented and shortly discussed, and a more complementary discussion and interpretation of the findings are presented in section 4.2.

The first paragraph in the chapter of each metal will present the investigation of the total concentrations, and these values are also presented in table 6. The total concentration of a metal is an important indicator of the pollution risks. In addition, the metal concentration of some metals will be assessed against the EQS values and the potential harm of the environment. The EQS is the environmental quality standard, referring to the concentration of a metal in the boundary between no toxic effects and chronic effects on long-term exposure (Miljødirektoratet 2016). The EQS values are presented in table 4. Fylkesmannen (2019) suggested as a rough guideline, that if the metal concentration is lower than 10 x EQS, it can be discharged. There is generally little research done of how sedimentation works on TWW, but Aasum (2013) and Meland (2012b) have done some laboratory experiments and analysed metal concentration before and after sedimentation. The total metal concentrations found in this project were therefore compared to findings in TWW done by Aasum (2013) and Meland (2012b). The metal concentrations detected in this project were in general lower than findings in Aasum (2013) and Meland (2012b). The calculated removal rate can say something about the size fractions present. If the removal rate is high, it

may suggest that the metal is present mostly as particles, and if it is lower, one may indicate the presence of other forms as well.

The second paragraph of each metals presents the concentrations of the size fractions in area charts, and shows the amount of all present fractions in time of sedimentation. The size fractions in the charts are named as > 1.2 μm, 0.45-1.2 μm, 3 kDa-0.45 μm and < 3 kDa, representing particles > 1.2, particles < 1.2, colloids and the dissolved fraction, respectively. The fractions were calculated based on concentrations obtained from the filtering campaign, as described in section 3.4. The concentration values from Smestad originate from only one parallel, and concentrations from Bjørnegård and Tåsen are based on 2-8 parallels. For day 11 in Smestad TWW, there was not done ultrafiltration of TWW with 3 kDa, and the concentrations of colloids and the dissolved fraction this day, are the average value between day 0 and 21. Raw data with concentration of all the parallels of the filtrate and the total concentrations are shown in appendix A.

The total measured concentrations of the metals are also presented in the area charts as dotted lines. In theory, the dotted line is supposed to be equal to the sum of concentrations of the size fractions, and are added in the chart to evaluate the conformity with the fractions.

Table 6: Total metal concentration (μg/L) in TWW before and after the sedimentation period. Raw data is given in Appendix A

Metal	Smestad		Bjørnegård		Tåsen	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
Cu	96	17	117	30	123	23
Zn	261	37	355	78	317	67
Pb	16	0.2	13	1.9	13	1.8
As	2.1	0.5	3.9	1.7	1.7	0.6
Ni	31	9	34	9	26	9
Cr	32	0.6	55	10	37	4
Cd	0.09	0.02	0.09	0.04	0.09	0.01
Fe	17 481	171	24 378	2039	22 083	3406
Al	24 081	101	41 546	4123	30 608	2266
Na	674 295	720 404	766 223	760 816	355 110	344 141
Ca	97 050	88 941	57 523	36 593	75 402	61 122
Mg	40 796	36 332	16 968	8408	19 973	13 164
K	18 137	12 376	31 596	24 347	17 401	9657
P	384	14	447	102	426	67
Si	60 286	4312	95 193	13 777	71 738	9462
Sn	12	0.1	18	2	18	1.2

4.1.1 Copper (Cu)

The total start concentrations of Cu were 96, 117 and 123 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. These concentrations may have given toxic effects in the receiving environment if not treated, as the EQS for Cu is 7.8 μg/L (Miljødirektoratet 2016). The concentrations of Cu in the TWW were lower than those reported by Aasum (2013) and Meland (2012b) in untreated TWW, ranging from 240-470 μg/L. This shows the variation in composition of TWW. A significantly amount was removed from the sedimentation, and the final concentrations in the TWW were 17, 30 and 23 μg/L, which indicate a removal of 83, 74 and 81 % in Smestad, Bjørnegård and Tåsen, respectively. According to Fylkesmannen (2019), no further treatment is necessary before discharge because these concentrations are less than 10 x EQS, which is 78 μg/L. According to Rathnaweera et al. (2019), the discharge limit for Cu is 10 μg/L. This suggest that the Cu concentrations after treatment can not be discharged without further treatment.

As stated, 74-83 % of Cu was removed in the TWW due to the sedimentation, and suggests a big proportion of particulate Cu. This was confirmed by the area charts in figure 5, as the particles > 1.2 μm area are biggest, and follows the same trend as the total concentration. In TWW from Smestad and Bjørnegård, both colloids and dissolved Cu were present, and a slight increase in the concentration occurred throughout the sedimentation period, and one may suggest that Cu was slightly re-mobilized into the colloidal and dissolved fraction. This finding was also reported by Aasum (2013) where Cu was re-mobilized into dissolved fraction after addition of detergent. The dissolved and colloidal fraction decreases in time of sedimentation in Tåsen TWW, which may be explained by binding to particles or precipitation.

Rathnaweera et al. (2019) reported that the discharge limit for Cu is 10 μg/L. Based on this information, the Cu limits in the treated TWW are of concern. The concentrations of colloids and dissolved fractions were 15 and 22 μg/L in Smestad and Bjørnegård TWW, respectively. From a biological aspect, this is of concern as dissolved contaminants are assumed to be more bioavailable than those attached to particles (Gheorghe et al. 2017). Sedimentation is not the most sufficient treatment method for Cu as the removal percentage was not that high, and dissolved fractions were present.

Figure 5: Concentration of Cu in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the calculated size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 7 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (4 values in Smestad TWW and 1 value in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.2 Zinc (Zn)

The total start concentration of Zn in Smestad, Bjørnegård and Tåsen TWW were found to be 261, 355 and 317 μg/L, respectively. This was surprisingly low concentrations compared to findings of Zn in previous research Aasum (2013) and Meland (2012b) ranging from 1281-2700 μg/L in untreated TWW. However, these concentrations are still high enough to harm the environment if released, as the EQS value for Zn is 11 μg/L. The concentrations of Zn in the TWW after sedimentation had decreased considerably to 37, 78 and 67 μg/L, indicating a removal of 86, 78 and 79 % in Smestad, Bjørnegård and Tåsen TWW, respectively. The concentrations after sedimentation are under the 10 x EQS value for Zn that is 110 μg/L, and are therefore acceptable to discharge into the environment, according to Miljødirektoratet (2016) and Fylkesmannen (2019). According to Rathnaweera et al. (2019), the discharge limit for Zn is 50 μg/L. Based on this, the TWW in Bjørnegård and Tåsen need further treatment before discharge.

The high sedimentation removal percentage suggested a significant amount of particulate Zn. The same is seen in in the area charts in figure 6. In the start, the biggest proportion of Zn is particles. However, a significantly amount of the dissolved phase was also present in the start in both Smestad and Tåsen TWW. The concentrations of dissolved Zn prior to the sedimentation were 29, 5 and 48 μg/L in Smestad, Bjørnegård and Tåsen, respectively. Discharge of the untreated TWW may be a threat to the environment due to elevated concentrations of dissolved Zn in Smestad and Tåsen TWW. After sedimentation of the TWW, Zn had been slightly re-mobilized into the dissolved fraction in Smestad and Bjørnegård TWW. The dissolved Zn fraction in Tåsen TWW decreased throughout the sedimentation period. The reason of that may be from bonding to particles or precipitation.

Sedimentation is not the most sufficient treatment method for Zn as a considerable amount of dissolved fraction was present, and as the final concentration after sedimentation was higher than the acceptable discharge concentration, according to the discharge limit in Rathnaweera et al. (2019).

Figure 6: Concentration of Zn in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 8 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (2 values in Smestad TWW and 1 value in Tåsen TWW were set to zero as the calculated concentrations were negative)

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4.1.3 Lead (Pb)

The total start concentration of Pb in the untreated TWW were 16, 13 and 13 μg/L from Smestad, Bjørnegård and Tåsen, respectively. In earlier studies (Aasum 2013, Meland 2012b), Pb concentration in untreated TWW were found to be 29-61 μg/L, significantly higher than the detected concentrations in these tunnels. These concentrations are classified as "moderate" due to the conditions classes for fresh water found in table 23 in appendix B. This means that Pb may have given chronic effects on long-term exposure, if not treated before discharge (Miljødirektoratet 2016). After the sedimentation period, 99, 85 and 86 % of the initial concentrations were removed, and only 0.2, 1.9, and 1.8 μg/L from respectively Smestad, Bjørnegård and Tåsen were left. These levels had been classified between "good" and "moderate" in a water recipient, and would therefore be safe to discharge without further treatment.

Due to the high Pb removal from the sedimentation process, one may suggest high proportions of Pb particles in the TWW. This was confirmed by the area charts seen in figure 7. For all three tunnels, Pb existed mostly as particles > 1.2 μm, especially in Tåsen. In Smestad and Bjørnegård, a small percent of Pb dissolved. Pb does not easily mobilise, as the dissolved fraction was constant or decreasing throughout the sedimentation process. The same was reported for Pb by Aasum (2013). Due to high removal rate, low final concentrations and low share of dissolved fraction, one may suggest that sedimentation is a sufficient way for treatment of Pb.
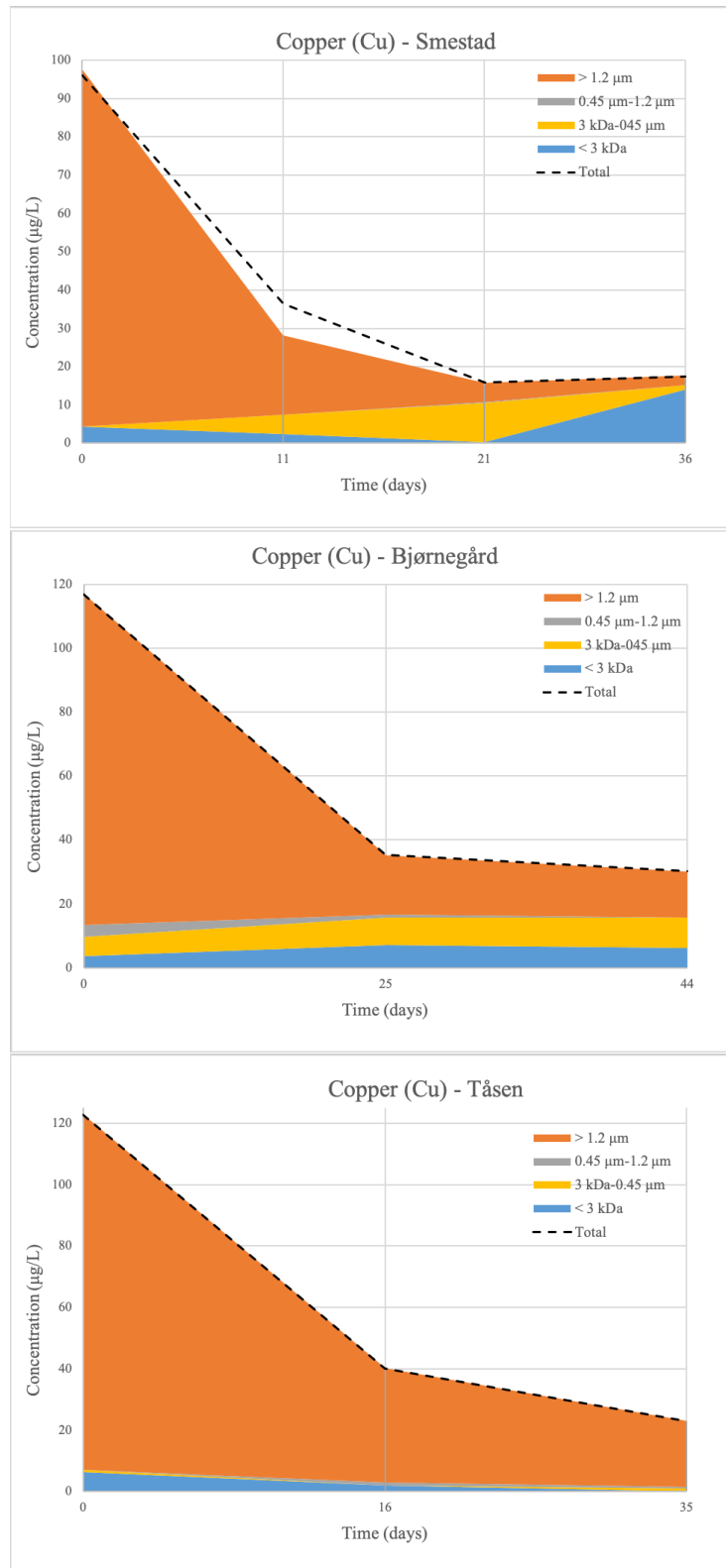
Figure 7: Concentration of Pb in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 9 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (5 values in Smestad TWW, 2 values in Bjørnegård TWW and 1 value in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.4 Arsenic (As)

The total concentrations of As in the untreated TWW were 2.1, 3.9 and 1.7 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. Aasum (2013) reported concentrations of 5-7.9 μg/L As in untreated TWW. The levels found in these tunnels were lower than the acceptable discharge values before treatment. By the sedimentation, 76, 56 and 64 % of the As were removed, and the levels were 0.5, 1.7 and 0.6 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. These levels would have been classified as good/moderate (see table 23 in appendix B) in a water recipient, and would therefore be safe to discharge (Miljødirektoratet 2016).

The relatively low removal percentage may be an indication of presence of smaller fractions in addition to particles. This can also be seen in the area charts in figure 8. The area charts shows that significant amounts of As is dissolved, especially in Smestad and Bjørnegård TWW. The colloidal fraction was present in all three tunnels, where the concentration was constant throughout the sedimentation period in Bjørnegård and Tåsen, whereas a slightly re-mobilisation into colloids occurred in Smestad. The dissolved fraction concentrations were constant or slightly decreasing in all tunnels, and was relatively high in especially Smestad and Bjørnegård TWW. Contrary to expectations, the concentration of the dissolved fraction increased during sedimentation period. This is most likely due to bonding to particles and precipitation. Sedimentation as treatment of As is probably not the most sufficient method of removal, as the sedimentation percentage was quite low and a considerable amount of dissolved As was present.
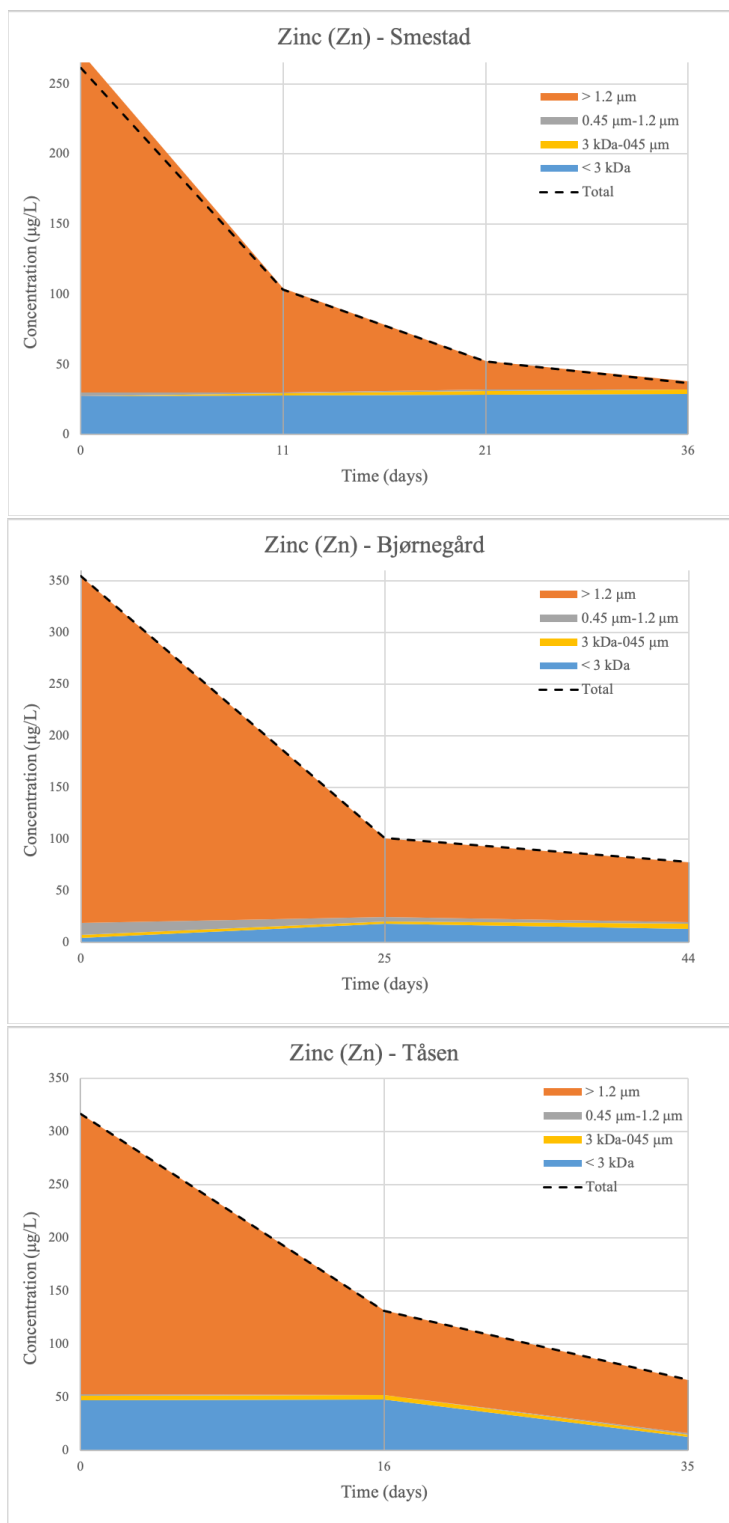
Figure 8: Concentration of As in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 10 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (5 values in Smestad TWW, 1 value in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.5   Nickel (Ni)

The total start concentrations of Ni were 31, 34 and 26 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. These findings were surprising, due to previous findings of 58-120 μg/L Ni in untreated TWW (Aasum 2013, Meland 2012b). The sedimentation period resulted in a removal of 71, 74 and 65 %, which suggests other forms of Ni than just particles were present. After sedimentation the concentrations of nickel were 9 μg/L in TWW from all tunnels, which is below 40 μg/L, the specified value for acceptable discharge (Miljødirektoratet 2016, Fylkesmannen 2019). This means that no harm on the environment will occur if discharged.

As expected, Ni was also present in other forms than particles in the TWW. This is seen in the area charts in figure 9. A significantly amount of Ni was dissolved. This is of concern. The sedimentation effectively removed most of the particles, whereas the dissolved fractions were constant in Bjørnegård TWW, and slightly increasing in Smestad and Tåsen TWW throughout the sedimentation period.

Nickel mobilises easily, and form several easily dissolved compounds (Poleo et al. 2007), which may be the reason for the high amount of dissolved Ni in the TWW. As mentioned, the total concentration of Ni in the treated TWW was within the discharge limits. However, since this amount is almost just dissolved, it is of environmental concern, as this form is readily toxic and bioavailable (Gheorghe et al. 2017). Sedimentation was not sufficient treatment for removal of Ni, as the dissolved fractions were not removed.
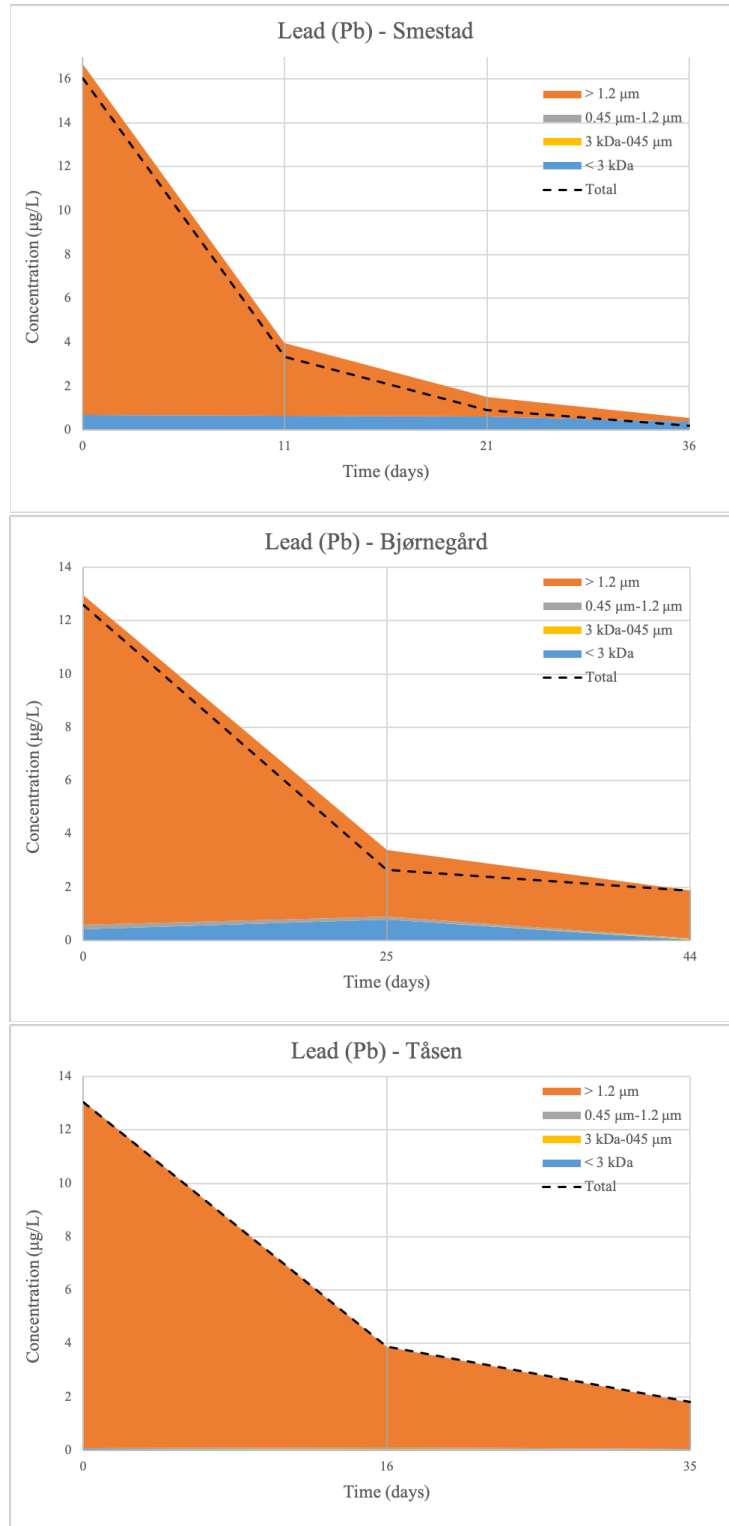
Figure 9: Concentration of Ni in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 11 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (7 values in Smestad TWW, 4 values in Bjørnegård TWW and 5 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.6 Chromium (Cr)

The total start concentrations of Cr were found to be 32, 55 and 37 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. A concentration of 64 μg/L Cr was found in TWW in previous studies (Meland 2012b). Although the concentrations detected in this project were significantly lower, concentrations like these in a water recipient would have been classified as "very bad" and may have given extensive toxic effects (Miljødirektoratet 2016). After sedimentation, 98, 82 and 89 % of Cr had been removed in Smestad, Bjørnegård and Tåsen TWW, respectively. This suggests a high proportion of Cr is present as particles, especially in Smestad TWW. The concentrations of Cr after sedimentation were reduced to 0.6, 10.2 and 4.3 μg/L in respectively Smestad, Bjørnegård and Tåsen, which all lay within the acceptable discharge requirement of 34 μg/L (Miljødirektoratet 2016, Fylkesmannen 2019). This suggest that Cr will not do any harm on the environment.

As seen in figure 10, Cr is mostly present as particles, as expected from the high removal percentage. Sedimentation was sufficient treatment of Cr as most was removed, and the concentration of the remaining Cd were below the acceptable discharge requirement.

Figure 10: Concentration of Cr in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 12 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (2 values in Smestad TWW were set to zero as the calculated concentrations were negative)

4.1.7   Cadmium (Cd)

The total start concentrations of Cd were 0.09 μg/L in TWW from all tunnels. This concentration is right above the EQS for cadmium, which is 0.08 μg/L (Miljødirektoratet 2016). This means that the acceptable discharge value is 0.8 μg/L (Fylkesmannen 2019), and the untreated TWW would therefore be safe to discharge. Previous studies have found levels of 0.46-0.67 μg/L Cd in untreated TWW (Aasum 2013, Meland 2012*b*). After the sedimentation period, 78, 56, 89 % of Cd were removed from the TWW, and 0.02, 0.04 and 0.01 μg/L Cd were left in TWW from Smestad, Bjørnegård and Tåsen, respectively. These concentrations will most likely do no harm on the environment if released. Therefore, one may say that sedimentation were sufficient as treatment for Cd in these concentrations.

As seen i figure 11, most Cd was present as particles, but colloids and dissolved Cd were also present. In Smestad and Bjørnegård TWW, Cd was re-mobilized into the dissolved fraction. However, the concentrations were low, and one may say that it insignificant.

The detected concentrations of Cd were low, and some values from the filters were not detectable due to negative values after subtracting the blank value. Therefore, some of the size fractions were not possible to calculate, and were therefore set to zero. The results must therefore be interpreted with with caution.
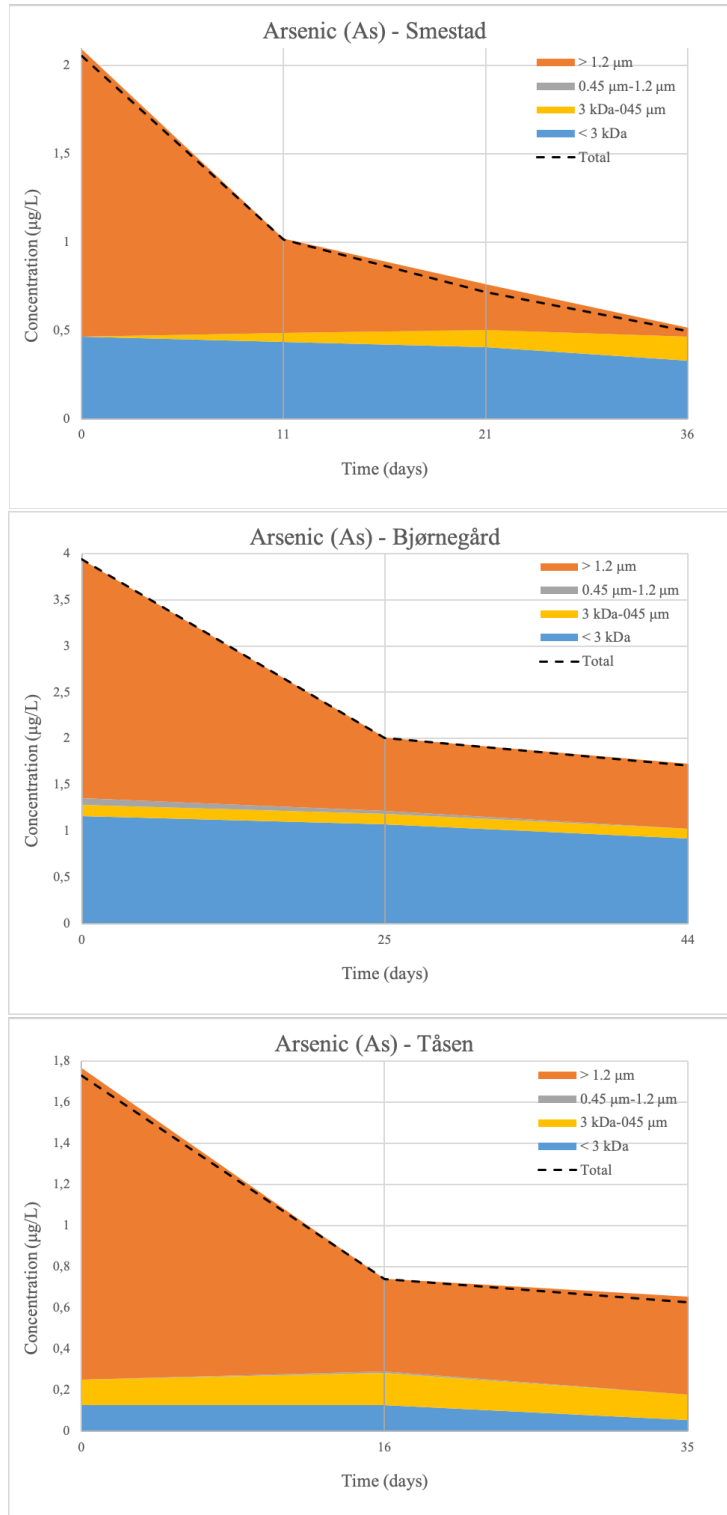
Figure 11: Concentration of Cd in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 13 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (3 values in Smestad TWW, 1 value in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.8 Iron (Fe)

The untreated TWW contained 17.48, 24.38 and 22.08 mg/L Fe from Smestad, Bjørnegård and Tåsen, respectively. These values were surprisingly low compared to earlier findings of Fe in untreated TWW of 70-118 mg/L (Aasum 2013). The concentrations of Fe were significantly reduced after the sedimentation period, where the concentrations were 0.17, 3.08 and 3.41 mg/L, which are within the acceptable discharge requirement of 5 mg/L (Fifiled & Haines 2000, Fylkesmannen 2019). Thus there was removed 96, 87 and 84 % Fe from the TWW in Smestad, Bjørnegård and Tåsen, respectively. This were relatively high removal percentages (especially in Smestad TWW), and may suggest a high proportion of particulate Fe in the TWW. This is confirmed by the area charts, as seen in figure 12. The high removal rate and the low concentrations after sedimentation indicates that sedimentation was sufficient treatment for removal of Fe.

Both colloids and dissolved Fe were present, but the amounts are insignificant due to the fact that particles represent nearly 100 % of the concentration. Fe is present in multiple parts of a car, including brakes and vehicle body, and in addition they are also present in asphalt. As the TWW sampling took place in winter time, a lot Fe will probably get released from the asphalt due to studded tires.
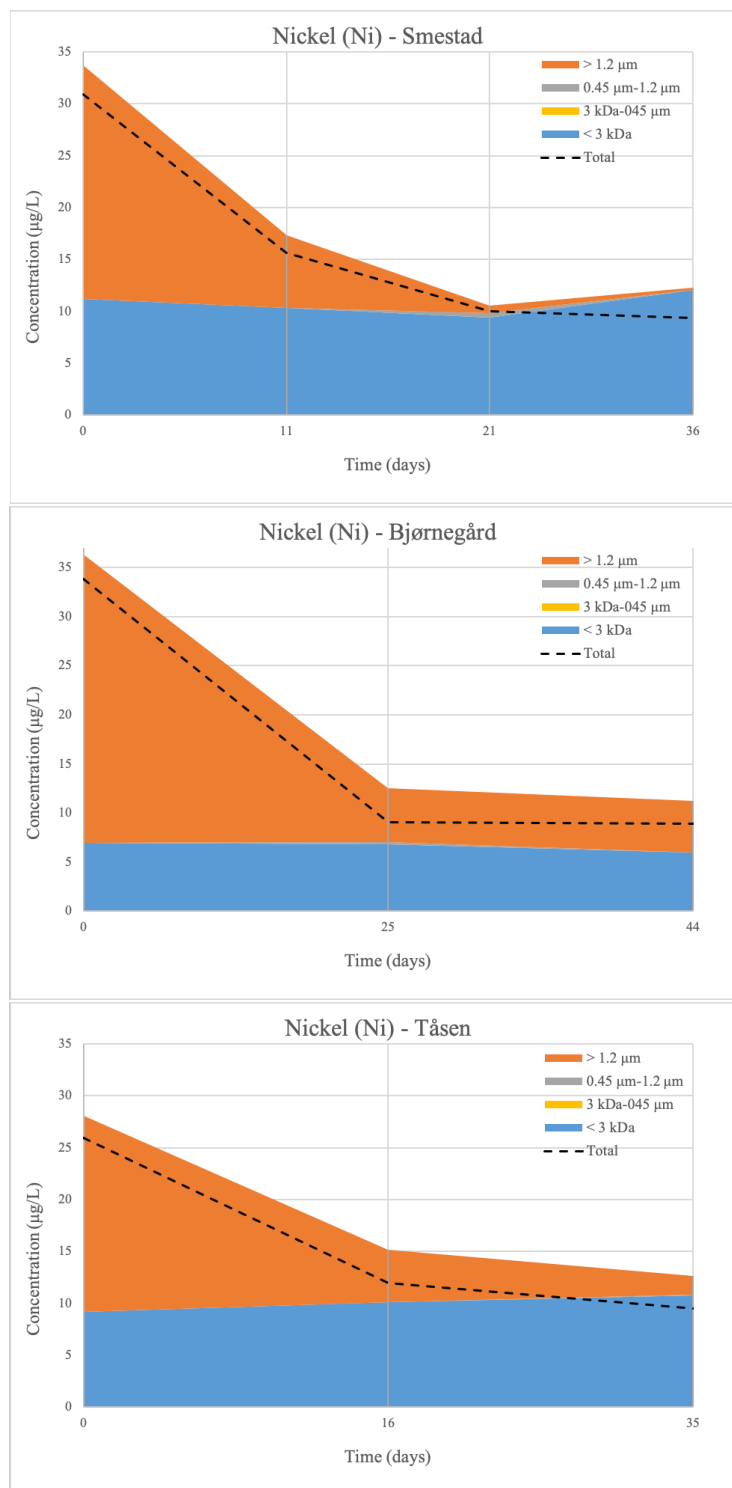
Figure 12: Concentration of Fe in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 14 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW.

4.1.9 Aluminium (Al)

The total concentrations of Al in the untreated TWW were 24.08, 41.55 and 30.61 mg/L in Smestad, Bjørnegård and Tåsen, respectively. These concentrations were low compared to prior studies that found concentrations of 50-76 mg/L Al in untreated TWW (Aasum 2013). However, the findings of Al in this project were still significantly elevated, as the natural level of Al in natural water is 10 μg/L (Fifiled & Haines 2000). A concentration of 6 mg/L Al may give acute effects, whereas 1.2 mg/L Al may give chronic effects (Wang et al. 2018). This means that if the TWW was not treated before discharge, it may have given acute toxic effects on the environment. After sedimentation, the Al concentrations had been reduced with 99.6, 90 and 93 %, to 101, 4123 and 2266 μg/L in Smestad, Bjørnegård and Tåsen TWW, respectively. The high removal suggest high proportions of particulate Al, as confirmed by the area charts in figure 13. Even though the concentrations were reduced significantly, these concentrations are all higher than the acceptable discharge values of 100 μg/L, where the concentrations in Bjørnegård and Tåsen TWW also could give chronic effects if discharged.

Al was also dissolved in the water phase, and relative to the total concentration, the concentrations were insignificant. However, since the total concentrations were so high, it may be considerable. In Smestad TWW, the dissolved fraction represented 10 % of the total concentration after sedimentation. Same concentrations were found in Bjørnegård and Tåsen TWW as well.

Sedimentation as treatment worked well for Al as the removal rate were high, that being said, the concentrations were beyond the discharge limit which may suggest that further treatment is necessary.
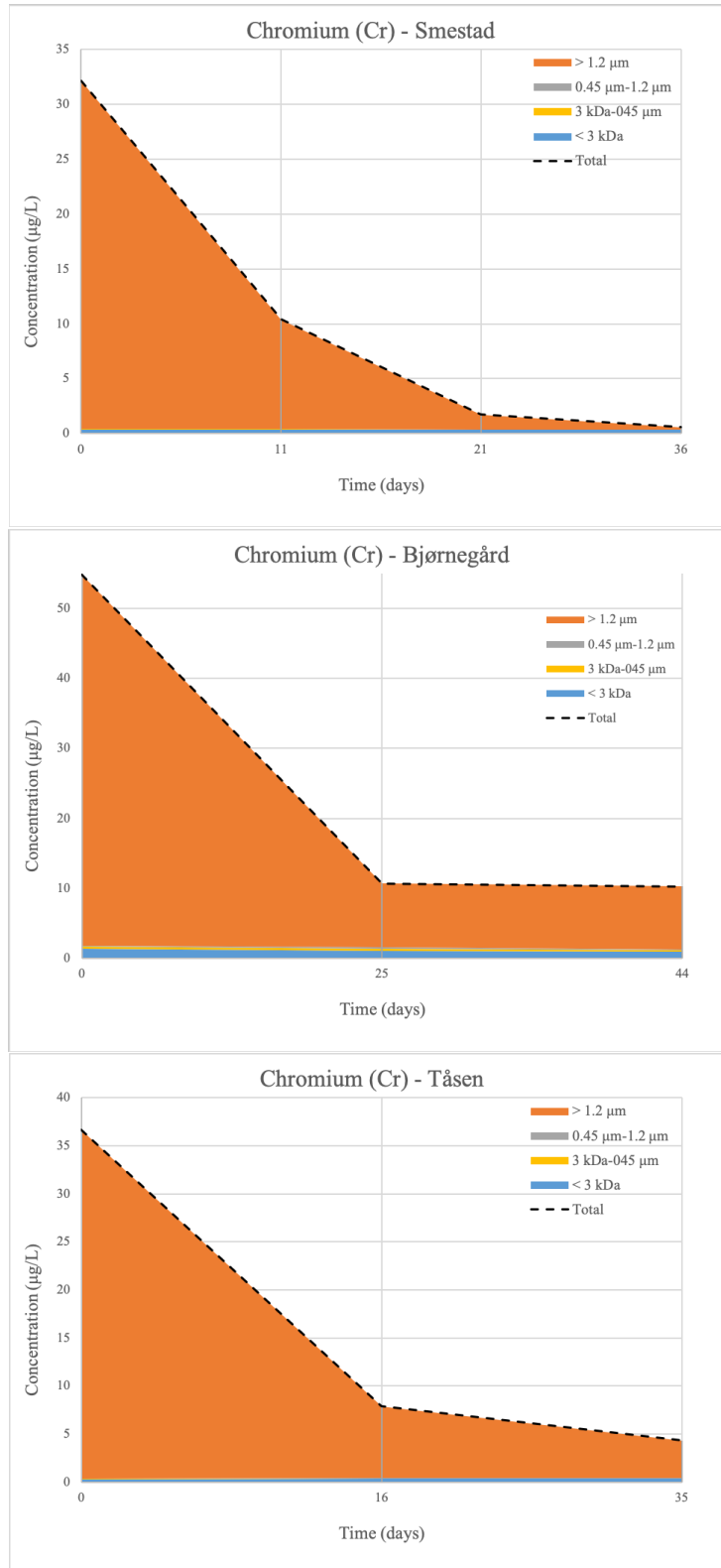
Figure 13: Concentration of Al in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 15 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (3 values in Smestad TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

4.1.10 Sodium (Na), Calcium (Ca), Potassium (K) and Magnesium (Mg)

The total start concentration of Na in the TWW were 674.30, 766.22 and 355.11 mg/L in Smestad, Bjørnegård and Tåsen, respectively. The elevated concentrations may be due to sample collection in winter time, and the Norwegian road authorities uses NaCl as road salt (Statens Vegvesen 2018). The concentration in Tåsen was only half the concentrations in Smestad and Bjørnegård. This inconsistency may be because TWW from Tåsen was collected later in the year, and deicing of roads no longer happened to the same extent as earlier in the winter. After the sedimentation period the Na concentrations were 720.40, 760.82 and 344.14 mg/L in Smestad, Bjørnegård and Tåsen, respectively. This means that the concentration in Smestad has increased, whereas the concentrations in Bjørnegård and Tåsen TWW has slightly decreased with 0.7 and 3 %, respectively. The low sedimentation percentage may suggest that most Na is dissolved in the water, and as seen in the area charts in figure 14, Na is almost only dissolved. This supports the theory that the dissolved Na originate from NaCl, as NaCl dissolves easily in water, and will not sediment.

As presented in table 6 there were also elevated concentrations of Ca, K and Mg in the TWW. These metals can also originate from dissolved salts. As mentioned, the Norwegian road authorities only uses NaCl when deicing the roads, and it is therefore hard to interpret the elevated concentrations of these metals. In respectively Smestad, Bjørnegård and Tåsen TWW 8, 36 and 19 % of Ca, 11, 50 and 34 % of Mg, and 70, 23 and 45 % of K, were removed due to sedimentation. The sedimentation percentages were varied, and suggest that these metals not only originate from dissolved salts, but also may be present as particles. As seen in the area charts in figure 15, 16 and 17, there are both particles and dissolved metals present, which explains the high removal rate for some of the metals. As the dissolved phase was elevated, one may suggest that other salts than NaCl are present in the tunnels. The concentrations of the particles decreases significantly during the sedimentation period, whereas the metals are slightly re-mobilized into an increased concentration of the dissolved phase.

Further treatment must be preformed as sedimentation was not sufficient for Na, Ca, K and Mg, as the metals was mostly dissolved, and the dissolved phase were not removed.
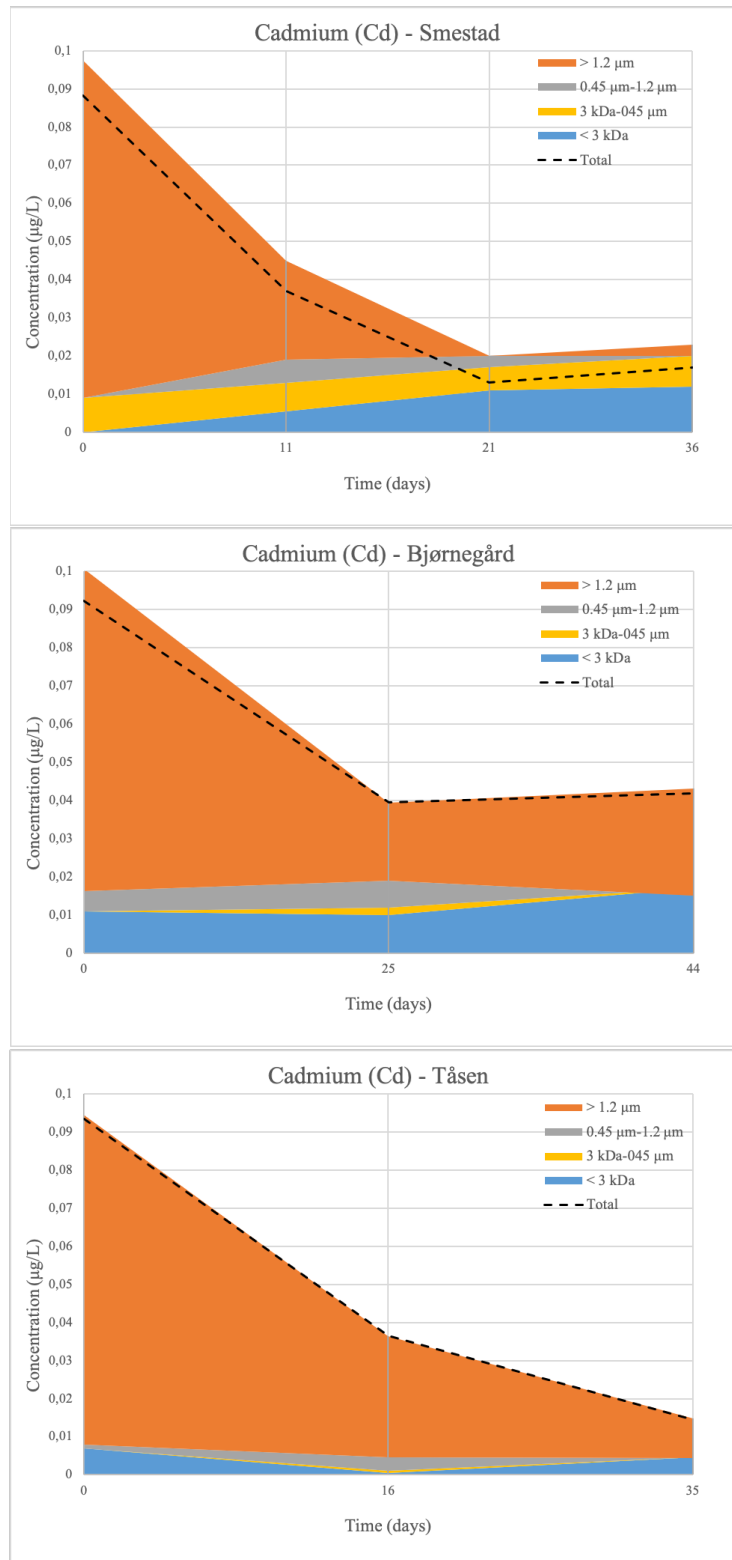
Figure 14: Concentration of Na in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 17 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (6 values in Smestad TWW, 5 values in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

Figure 15: Concentration of Ca in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 16 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (4 values in Smestad TWW, 3 values in Bjørnegård TWW and 3 values in Tåsen TWW were set to zero as the calculated concentrations were negative)
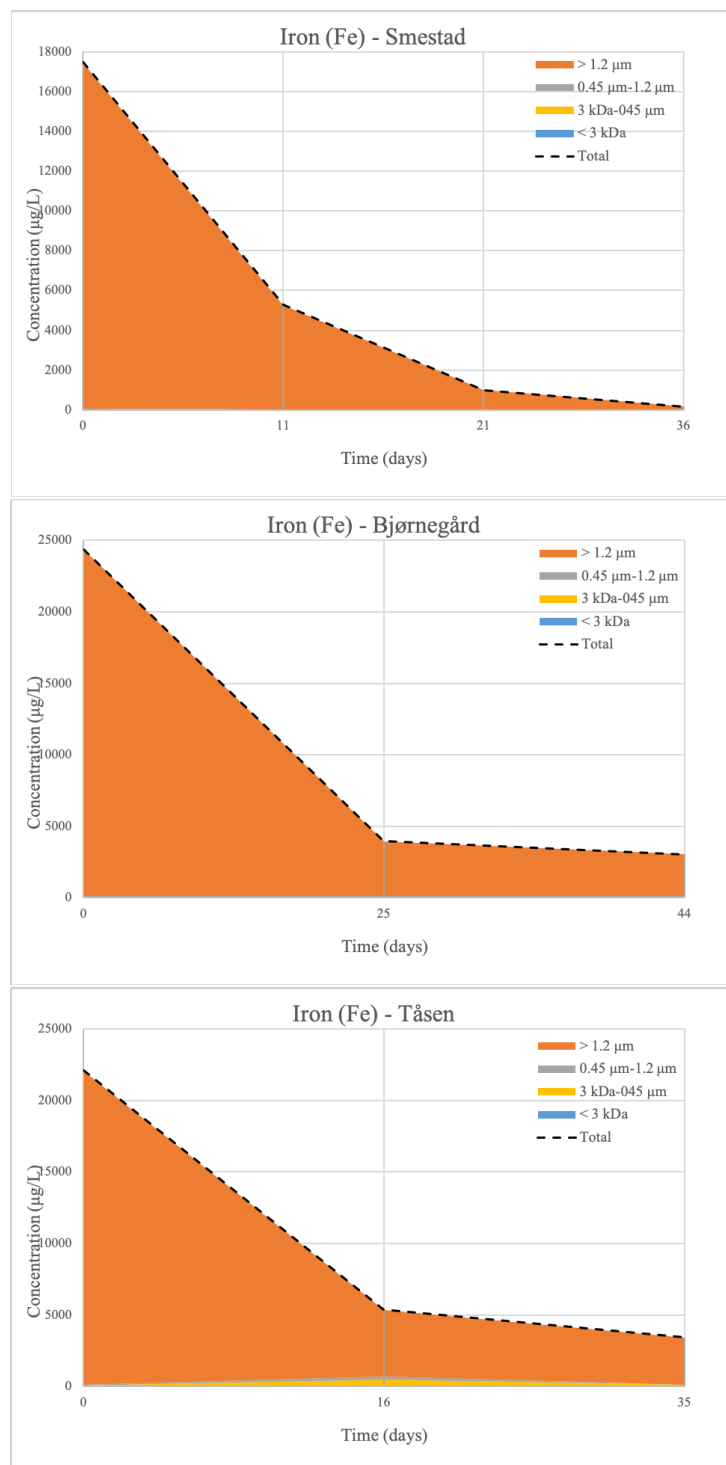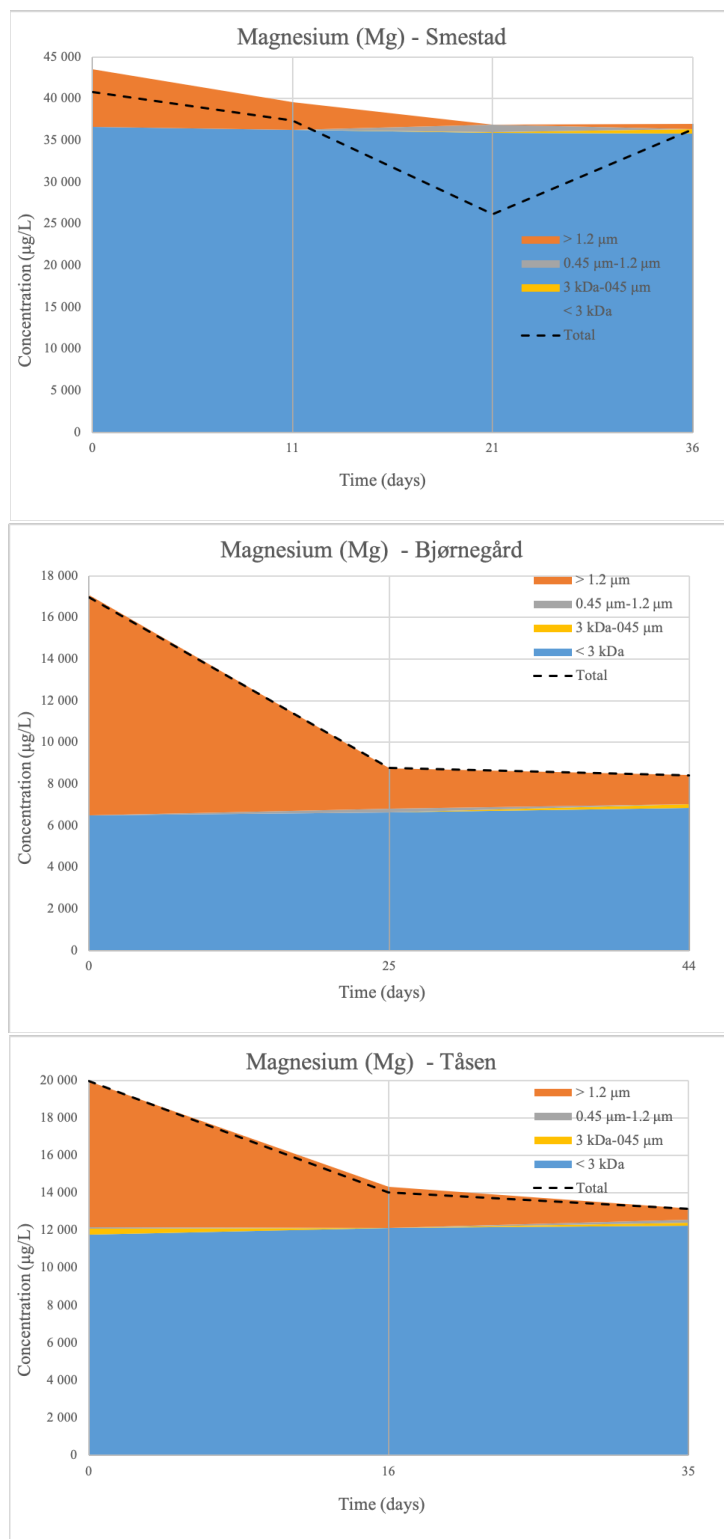
Figure 16: Concentration of Mg in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 19 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (6 values in Smestad TWW, 2 values in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)
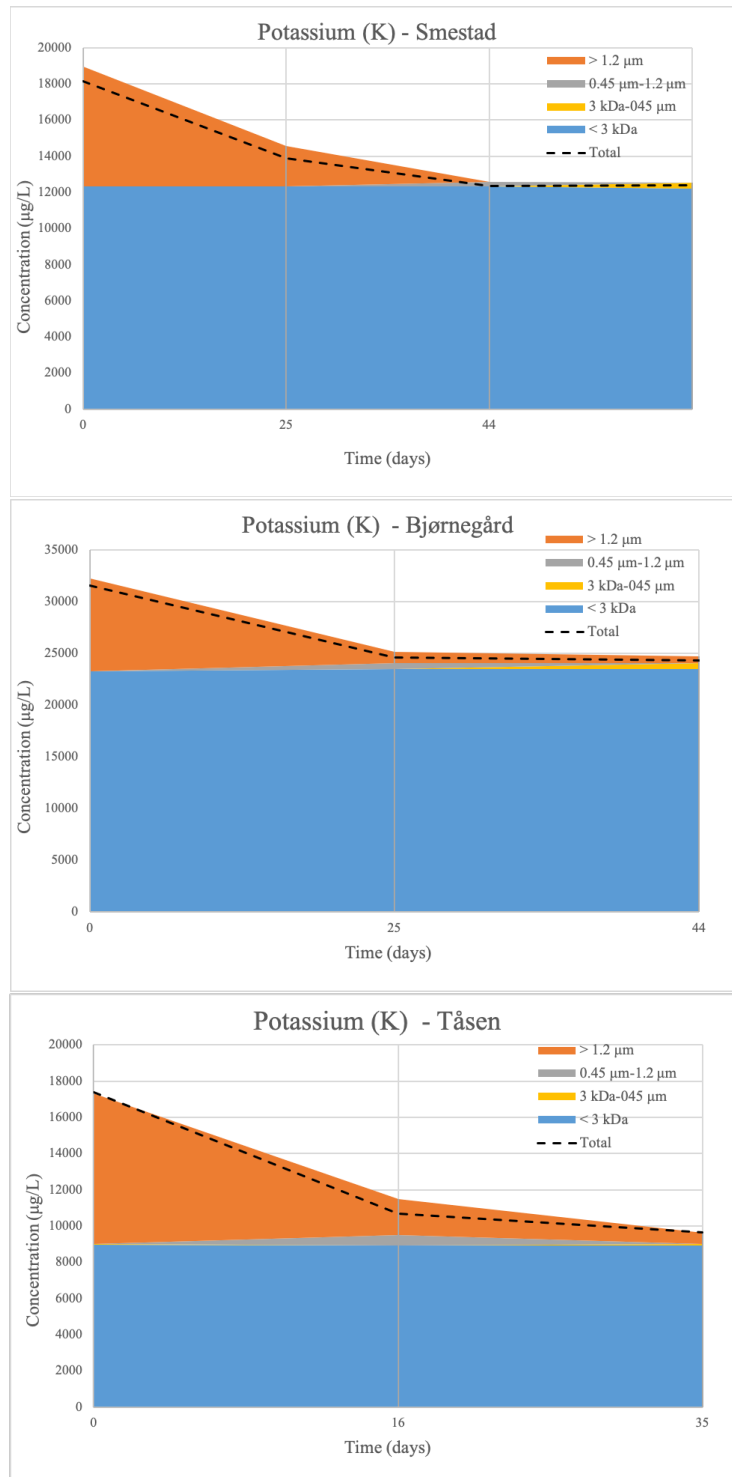
Figure 17: Concentration of K in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 18 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (7 values in Smestad TWW, 4 values in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

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4.1.11   Phosphorus (P), Silicon (Si) and Tin (Sn)

As seen in table 6, the concentrations of P, Si and Sn were significantly reduced after sedimentation, in which 96, 77 and 84 % of P, 93, 86 and 87 % of Si and 99, 89 and 93 % of Sn sedimented in Smestad, Bjørnegård and Tåsen, respectively. The high removal percentage may suggest that these metals are mainly present as particles, which is confirmed in the area charts shown in figure 18, 19 and 20.

P was present as particles, but what stands of for P is that most particles present as size < 1.2 μm. The area charts for P in Smestad and Tåsen TWW were hard to interpret because the dashed line of total concentration did not match the sum of the concentrations of the size fractions. This may suggest that either the total concentration have losses, or that the fractions are contaminated. Based on the development over time, one may say that it looks like the total concentration is most correct as it has the same trend as most metals present as particles have. In addition, it is not possible that the total concentration increases. Most likely are the size fraction samples contaminated, as the same happened with the blanks. In addition, if you compare it to the area chart for Bjørnegård, where the dashed line fit perfectly, it has the same trend as for Smestad and Tåsen.

It was elevated concentrations of Si in TWW for all three tunnels (table 6), however, a huge part was removed during sedimentation, as most was particles. About 4000 μg/L of Si was dissolved, and stayed constant throughout the sedimentation period. This concentration is high and can be a potential threat for the environment if discharged. As most Si was particles, the sedimentation worked good, but further treatment must be considered based on the concentration of the dissolved fraction.

Sn was only present as particles in the TWW from all three tunnels (figure 20). The concentration was significantly reduced, and one may say that sedimentation was sufficient treatment for removal of Sn. The presence of only particles make the discharge, regardless of the concentrations, less of a danger to the environment, due to less bioavailability and toxicity.
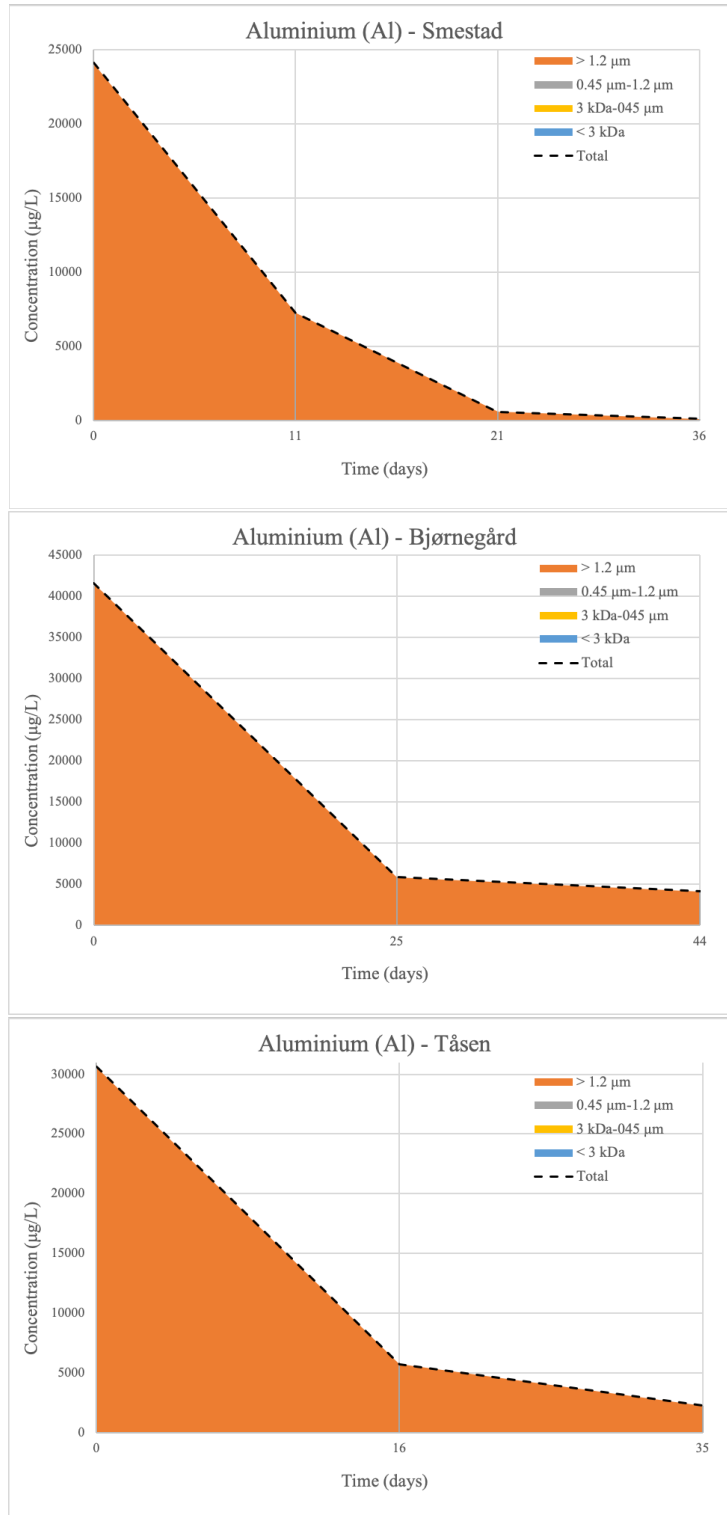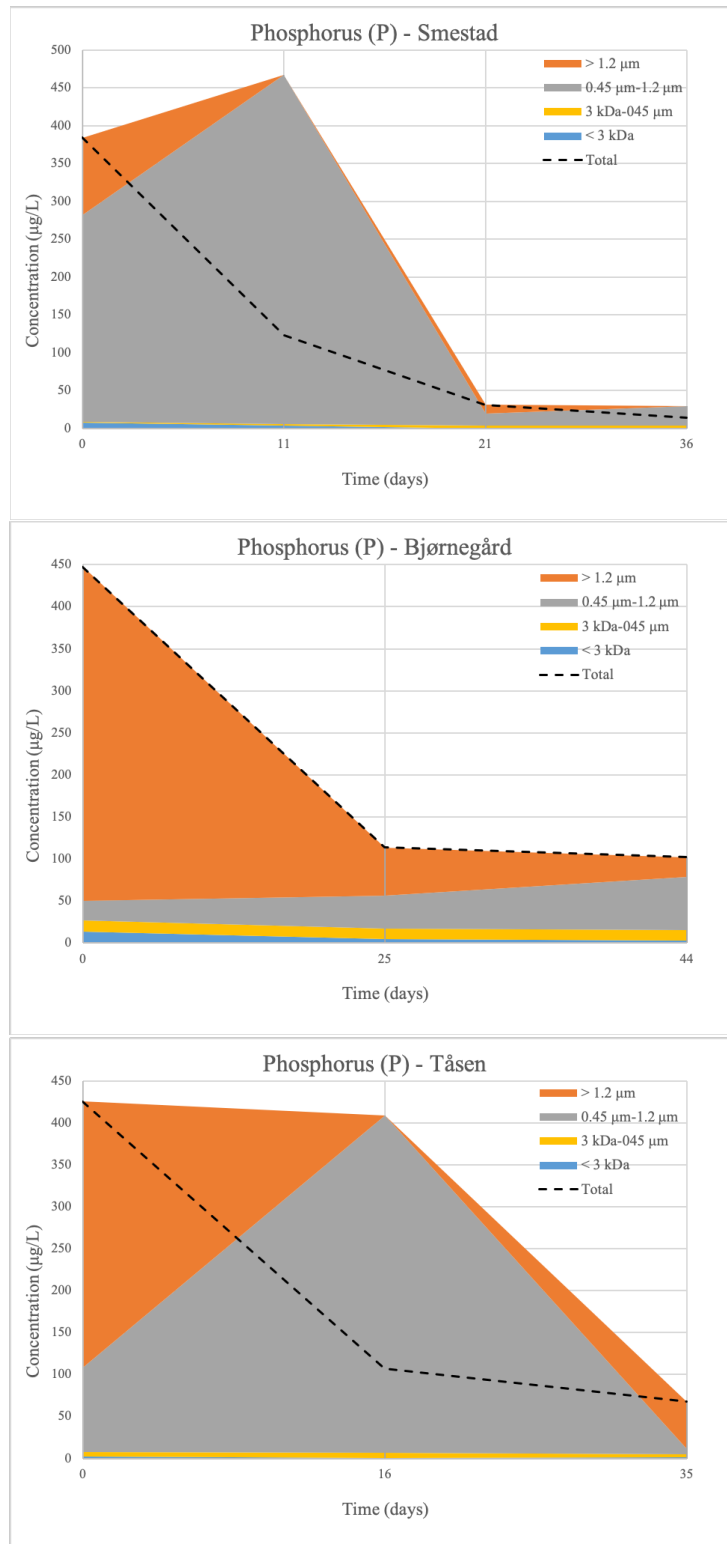
Figure 18: Concentration of P in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 20 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (2 values in Smestad TWW and 1 value in Tåsen TWW were set to zero as the calculated concentrations were negative)

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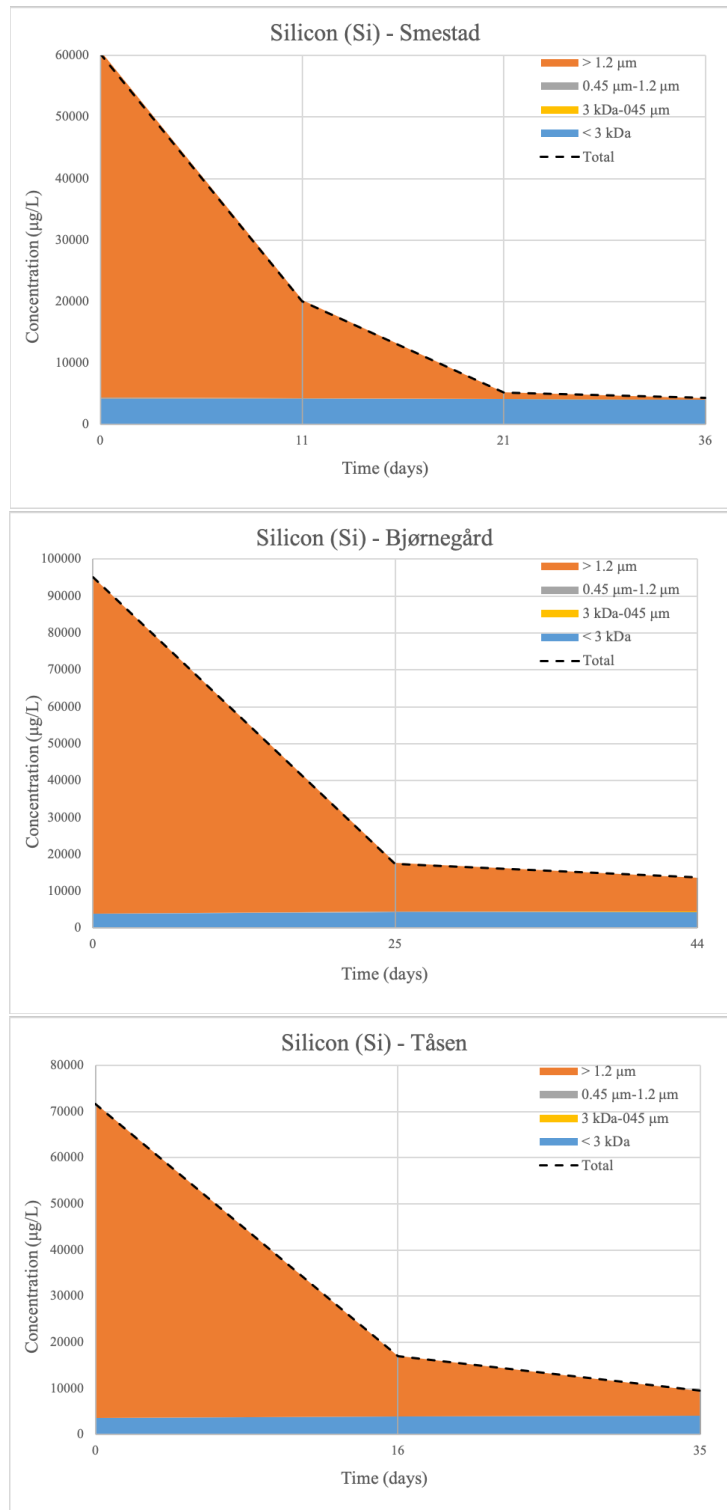
Figure 19: Concentration of Si in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 21 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. (2 values in Smestad TWW, 3 values in Bjørnegård TWW and 2 values in Tåsen TWW were set to zero as the calculated concentrations were negative)

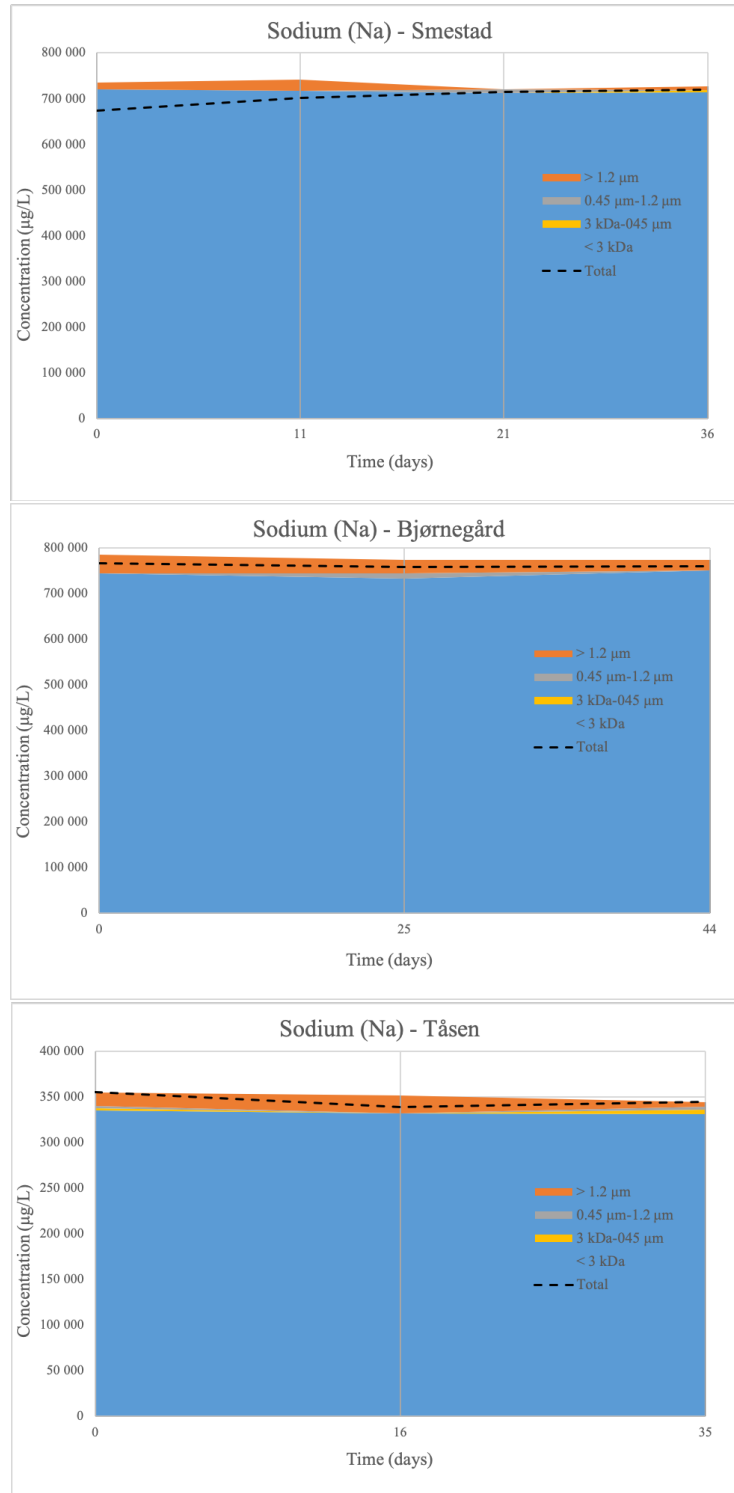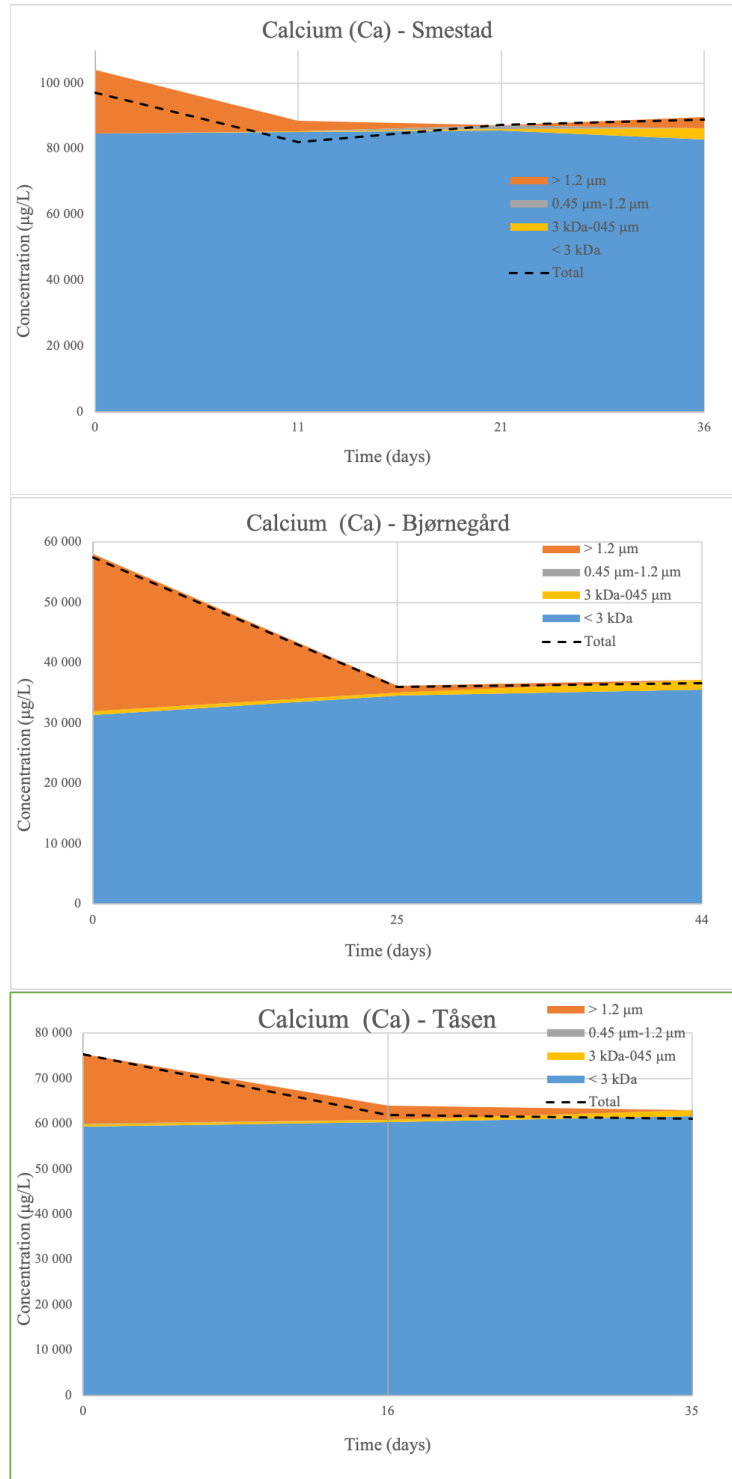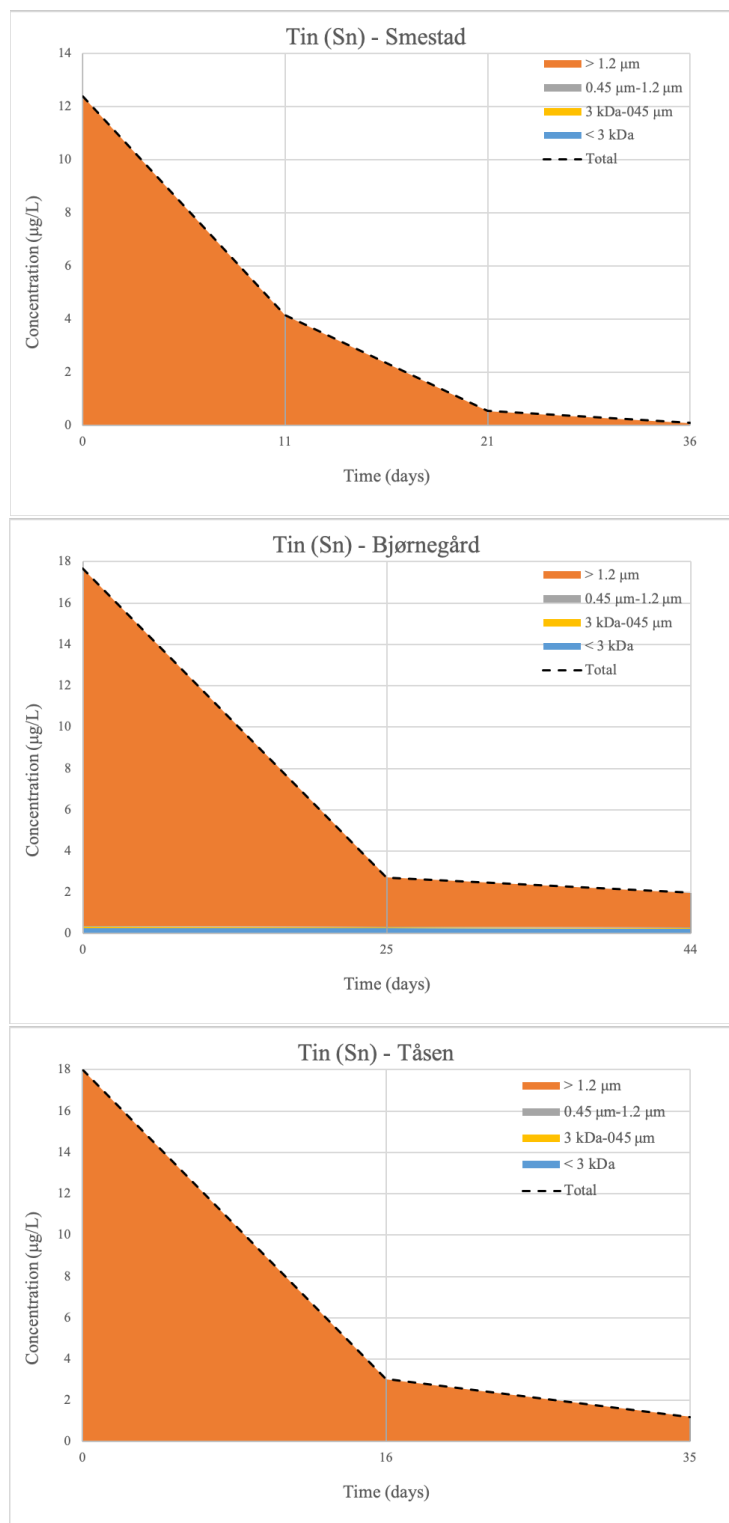Figure 20: Concentration of Sn in the TWW as a function of sedimentation time. Different colours of area represent the proportion of the different size fractions. The dashed line represent the measured total concentration. Raw data representing these charts are given in Table 22 in Appendix A. Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW.

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4.1.12 Screening analysis

A full ICP-MS screening analysis was done for all raw water samples, in order to determine whether any surprising elements were present, and to check for elevated concentration of potentially harmful elements. The concentrations of all elements not discussed in section 4.1 are given in table 24 in appendix C and are not discussed further.

4.2 General comments

4.2.1 Sedimentation

Most metals were mainly present as particles (except Na, Ca, K and Mg), and significant amounts were removed by sedimentation, as expected due to sedimentation theory. Sedimentation was a sufficient treatment for most metals as the concentrations after sedimentation were below the acceptable discharge limit. However, several metals were present in significant concentrations in the dissolved fraction, including Cu, Zn, As, Ni, Cd, Na, Ca, K and Mg. This is of concern as this fraction is not removed by sedimentation. Dissolved metals are more mobile, and from a biological aspect, this is of concern as dissolved contaminants are considered to be more bioavailable than metals attached to particles. For removal of dissolved metals, further treatment must be considered.

In Smestad and Bjørnegård TWW there was nearly no further sedimentation after day 21 and 25, respectively, but it varied slightly from metal to metal. In Tåsen TWW the sample during sedimentation was taken at day 16, and for most metals the sedimentation continued thereafter. One may therefore suggest that the TWW must sediment for at least 21 days.

4.2.2 Comparison of the tunnels

Figure 21, 22 and 23 illustrates the columns with TWW prior to the sedimentation and after the sedimentation period. The pictures taken before sedimentation (A) looks similar in all tunnels, black. The pictures after sedimentation (B) looks different in each tunnel. The TWW from Bjørnegård seemed to have had the least sedimentation, as the water hardly changed colour. This was unexpected as TWW from Bjørnegård sedimented for the longest time, almost 10 days longer than TWW from Smestad and Tåsen. The TWW from Tåsen was neither clear after sedimentation period, however

it seemed to have sedimented more than in Bjørnegård TWW. There was a significantly change in TWW from Smestad. After sedimentation the water was clear, and one can see that a lot have sedimented in the column with Smestad TWW.

These findings corresponds to earlier findings. Bjørnegård TWW had the highest concentration of 12/16 metals before sedimentation, and highest concentration of 13/16 metals after sedimentation. In addition, lowest sedimentation percent for 11/16 metals was in Bjørnegård TWW. The clear water for Smestad can be explained by the high removal percentages of the metals, especially for metals with high proportion of particles (e.g. Fe and Al).

Sampling was done at day 0, 11, 21 and 36 in Smestad TWW, day 0, 25 and 44 in Bjørnegård TWW and day 0, 16 and 35 in Tåsen TWW. The inconsistency of analysis days made it difficult to compare the concentrations in the different tunnels.
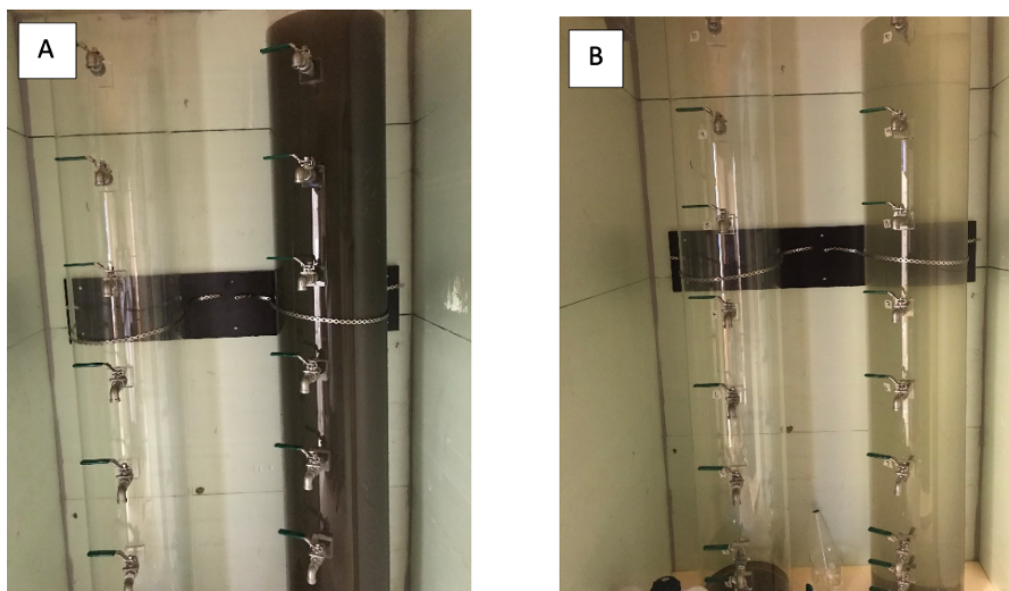
Figure 21: TWW from Smestad, at day 0 (A) and day 31 (B). Photo: Ågot Bjotveit

Figure 22: TWW from Bjørnegård, at day 0 (A). Photo: Ågot Bjotveit, and day 44 (B). Photo: Thomas Meyn.

Figure 23: TWW from Tåsen at day 0 (A). Photo: Ågot Bjotveit, and day 35 (B). Photo: Thomas Meyn.

5 Conclusion

In this project, the aim was to investigate metal concentrations and size fractions, to obtain information about the form of the metals (dissolved, colloidal, particulate) and the general water quality in sedimented tunnel wash water. The research questions investigated in this thesis were:

- Which metals are present in tunnel wash water?

- In which form are common metals present in tunnel wash water (particulate, colloidal, dissolved)?

- Is the form changing during the sedimentation process?

- Is sedimentation sufficient treatment of the tunnel wash water?

The concentrations of metals found in the tunnel wash water in this investigation were significantly lower than those reported in two previous studies of sedimented tunnel wash water. All metals analysed, including Cr, Zn, Pb, As, Ni, Cr, Cd, Fe, Al, Na, Ca, K, Mg, Si, P and Sn, were present in the tunnel wash water, and several of them in elevated concentrations.

Pb, Cr, Fe, Al, P and Sn were mainly present as particles and hence a high removal percentage due to sedimentation of particles. Cu, Zn, As, Ni, Cd and Si were mainly present as particles, but also as colloids/dissolved fractions. Na, Ca, Mg and K were mainly dissolved, but Ca, Mg and K were also present as particles. Sedimentation would be sufficient as treatment for particulate metals as almost everything were removed. However, if the concentration are very elevated, the concentration after sedimentation can still be higher than the acceptable discharge concentrations, even though the removal percentage was high. Dissolved metal concentrations were not effected by sedimentation, and hence no removal by sedimentation. Discharge of dissolved metals are of concern due to increased mobility, bioavailability and toxicity. Sedimentation are therefore not sufficient treatment for removal of metals in all forms.

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Appendix

A   Concentrations of all parallels of the metals

Table 7: Concentrations (μg/L) of all parallels of copper (Cu) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	96,25	2,9	3,15	4,43
	96,98			
	95,23			
Day 11	36,48	15,74	16,62	-
Day 21	15,82	10,73	10,51	0,29
Day 36	17,38	14,78	15,16	13,97
Bjørnegård				
Day 0	116,58	13,19	9,31	2,39
	115,71	12,39	8,88	2,12
	115,81	15,41	11,78	7,15
	118,16	12,44	9,03	2,66
	117,72			
Day 25	35,17	16,22	15,31	6,77
	35,34	17,23	16,35	7,69
Day 44	29,99	15,82	16,04	5,57
	30,22	15,98	15,4	6,44
	30,06	15,76	15,73	6,19
	29,31	15,41	15,09	6,32
	31,54	16,13	15,67	6,58
	30,48	16,13	15,62	6,26
	30,07	15,46	15,72	
	30,02	15,91	16,14	
Tåsen				
Day 0	112,52	10,03	9,99	9,60
	112,09	10,40	11,3	9,74
	112,16	4,39	3,55	2,82
	134,3	3,88	3,74	2,85
	132,5			
	133,13			
Day 16	43,29	2,82	1,7	1,85
	36,78	2,86	1,81	2,16
		2,77		
		2,79		
Day 35	24,21	1,75	0,96	0,19
	24,17	1,22	1,14	0,15
	24,94	1,63	1,07	0,10
	24,31	1,45	1,03	0,12
	21,81	1,38	0,93	
	21,51	1,77	1,45	
	21,23	1,37	0,96	
	21,84	1,68	0,93	

Table 8: Concentrations (μg/L) of all parallels of zinc (Zn) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	263,2	18,92	16,35	27,62
	263,6			
	257,5			
Day 11	103,56	29,63	28,73	-
Day 21	52,45	32,2	30,98	28,69
Day 36	36,94	30,86	32,22	29,05
Bjørnegård				
Day 0	357,9	20,5300522	7,01	4,07538254
	360,5	18,0085524	6,65	3,75780952
	356,3	20,0030123	8,75	7,0321492
	343,7	18,1999044	6,73	4,10229303
	355,5			
Day 25	100	24,6170187	20,6	18,4931632
	102,2	24,7502943	21,11	18,1927466
Day 44	77	21,2368163	19,8	13,2857991
	77,3	21,1116813	18,9	12,4519984
	73,1	20,7472631	18,7	14,7943131
	76,8	19,8161166	19,2	13,2689097
	78,2	19,7448052	18,1	13,2688103
	84,1	19,4145952	18	12,013971
	77,4	19,6491933	18,2	
	80,5	19,5937338	18,3	
Tåsen				
Day 0	291,7	50,9529338	51,9	49,051646
	289,6	54,8385819	50,78	45,1091747
	292,4	52,7298734	51,75	50,7246271
	340,7	53,1460921	51,49	45,1409031
	342,3			
	345			
Day 16	132,2	51,0455773	48,87	44,4989891
	131	50,5212792	55,87	51,4044707
		50,156086		
		57,2633438		
Day 35	72,8	14,6944274	12,64	10,9981226
	21	12,9673427	12,39	10,5950225
	74,1	15,0360099	12,61	15,6687988
	71,7	14,1891642	12,68	15,7997281
	73,1	19,0410903	17,8	
	73,5	19,8385843	17,9	
	72,9	18,6673376	18	
	75,5	19,7798469	18,2	

Table 9: Concentrations (μg/L) of all parallels of lead (Pb) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	16	0,042	0,031	0,686
	16,1			
	16			
Day 11	3,327	0,043	0,021	-
Day 21	0,902	0,029	0,012	0,622
Day 36	0,209	0,035	0,036	0,388
Bjørnegård				
Day 0	12,3	0,254	0,053	0,522
	12,7	0,224	0,041	0,20098463
	12,7	0,188	0,071	0,69798271
	12,4	0,227	0,073	0,26140046
	12,9			
Day 25	2,596	0,174	0,059	0,48491127
	2,706	0,162	0,054	1,10009649
Day 44	1,888	0,12	0,052	0
	1,827	0,079	0,048	0,02882958
	1,661	0,091	0,034	0,04647424
	2,039	0,067	0,023	0,02245066
	1,929	0,05	0,038	0,02399442
	1,984	0,052	0,043	0,03310603
	1,829	0,073	0,057	
	1,863	0,09	0,038	
Tåsen				
Day 0	11,9	0,035	0,006	0
	12,1	0,024	0,005	0,0502769
	12,2	0,073	0,004	0,16852168
	14,1	0,018	0,011	0,01967464
	13,7			
	14,2			
Day 16	3,885	0,132	0,041	0,01933368
	3,869	0,11	0,045	0,01831793
		0,139		
		0,085		
Day 35	1,792	0,043	-	
	1,67	0,022	0,023	0,012
	1,975	0,05	0,02	0,012
	1,743	0,027	0,015	
	1,728	0,04	0,026	
	1,909	0,069	0,025	
	1,887	0,046	0,042	
	1,718	0,07	0,026	

Table 10: Concentrations (μg/L) of all parallels of arsenic (As) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	2,147	0,426	0,427	0,467
	2,079			
	1,934			
Day 11	1,016	0,482	0,585	-
Day 21	0,716	0,458	0,505	0,408
Day 36	0,497	0,446	0,465	0,331
Bjørnegård				
Day 0	3,922	1,36294328	1,284	1,08889182
	4,137	1,30842246	1,21	1,21233848
	3,846	1,39823832	1,362	1,13309049
	3,858	1,34450387	1,275	1,23288856
	3,914			
Day 25	2,145	1,18462591	1,166	1,06871102
	1,877	1,26218918	1,213	1,07209212
Day 44	1,596	1,02579565	1,123	0,86054931
	1,711	0,97648623	1,011	1,05498066
	1,894	1,05515217	1,126	0,8455834
	1,621	0,96902007	0,979	1,01441095
	1,494	0,96541984	0,933	0,90078026
	1,721	1,03666939	1,044	0,84437739
	1,951	0,91533884	0,958	
	1,658	1,04601299	1,022	
Tåsen				
Day 0	1,662	0,20698296	0,263	0,11792084
	1,583	0,20481801	0,233	0,13810918
	1,627	0,23266813	0,233	0,1024173
	1,86	0,20404133	0,272	0,15457552
	1,784			
	1,855			
Day 16	0,727	0,33949839	0,278	0,14454065
	0,752	0,29089497	0,287	0,11046224
		0,27060899		
		0,25821649		
Day 35	0,602	0,17223833	0,164	0,04035894
	0,732	0,15912605	0,158	0,05179741
	0,452	0,13861544	0,166	0,06247997
	0,636	0,14780569	0,19	0,06029821
	0,605	0,18143212	0,187	
	0,666	0,14144543	0,186	
	0,631	0,10951307	0,179	
	0,677	0,16491082	0,2	

Table 11: Concentrations (µg/L) of all parallels of nickel (Ni) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	30,96	8,43	8,81	11,23
	30,9			
	30,89			
Day 11	15,64	8,63	9,18	-
Day 21	9,98	9,27	8,83	9,4
Day 36	9,34	9,11	9,44	12,05
Bjørnegård				
Day 0	33,91	3,41203918	3,33979021	6,92607475
	34,31	3,13251451	3,02950897	5,96207914
	30,73	8,23130932	8,45954547	9,34826406
	37,72	3,13041215	3,21650845	5,65614812
	32,57			
Day 25	9,393	3,5859846	3,21140848	7,73330319
	8,707	3,46747411	3,50859142	5,93073168
Day 44	7,312	3,64260773	3,70149915	5,94766021
	7,38	3,79334738	3,56383916	5,76509378
	7,834	3,65873876	3,72018143	6,69838173
	7,563	3,8174511	3,7750987	5,91372638
	7,729	3,53019833	3,68712466	5,84668508
	16,456	3,70916314	3,53338625	5,54827037
	7,985	3,50759581	3,58501018	
		3,62131418	3,61671482	
Tåsen				
Day 0	24,23	7,45366627	7,64771399	7,15382934
	24,16	7,46886047	6,95102285	10,6061282
	24,58	6,75860777	6,9166659	9,54703269
	28,19	6,77852193	7,02443577	9,54177201
	27,21			
	27,28			
Day 16	11,865	7,10183736	6,9604353	9,42233582
	11,994	7,02457145	7,25237363	10,8520877
		6,52275133		
		6,89475807		
Day 35	10,026	7,83958469	7,59924035	10,8503763
	9,667	7,89343284	7,37015693	10,4224335
	9,391	7,87134797	7,74513117	9,82250554
	9,443	7,70958364	7,88305444	11,9506665
	9,428	7,60019874	7,72106611	
	9,302	7,59245892	7,33278558	
	9,502	7,42733228	7,77213377	
	9,176	7,63127091	7,50970069	

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Table 12: Concentrations (µg/L) of all parallels of chromium (Cr) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	32,32	0,43	0,42	0,37
	32,43			
	31,67			
Day 11	10,38	0,44	0,39	-
Day 21	1,73	0,39	0,39	0,39
Day 36	0,6	0,37	0,36	0,35
Bjørnegård				
Day 0	56,24	1,77586978	1,59358748	1,23479176
	56,55	1,61866712	1,52547743	1,20263986
	51,25	2,07595817	1,91200155	1,74933005
	54,07	1,67917103	1,48355098	1,2442732
	56,18			
Day 25	10,7	1,60770597	1,25016657	1,00408626
	10,62	1,54650482	1,36575499	1,06569318
Day 44	8,12	1,29660348	1,15544041	0,92144622
	7,94	1,27417641	1,09269403	1,02759961
	7,92	1,24937394	1,10296656	0,77377213
	8,23	1,26845512	1,14648495	1,09980199
	8,57	1,28404288	1,10984455	0,84110674
	24,69	1,23797964	1,09892604	0,75018336
	8,29	1,26126837	1,12339901	
	8,23	1,32512812	1,17580851	
Tåsen				
Day 0	33,03	0,43607164	0,34957473	0,30640913
	33,11	0,39714821	0,36712463	0,31813465
	33,37	0,37087541	0,36753696	0,31208365
	41,29	0,38924773	0,35453285	0,28173832
	39,39			
	39,66			
Day 16	8,16	0,47065143	0,37092694	0,32820101
	7,64	0,41570455	0,39986707	0,35583301
		0,51541586		
		0,42643922		
Day 35	4,76	0,45696088	0,37609565	0,36689933
	3,72	0,45590497	0,40085953	0,3790703
	4,38	0,39085996	0,40955705	0,3230326
	4,41	0,41325192	0,37025184	0,31655433
	4,2	0,45015826	0,40960787	
	4,9	0,40353261	0,43154985	
	4,19	0,40085894	0,38973904	
	4,08	0,40248179	0,38257428	

Table 13: Concentrations (µg/L) of all parallels of cadmium (Cd) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	0,099	-	0,009	0
	0,071			
	0,095			
Day 11	0,037	0,011	0,005	-
Day 21	0,013	0,02	0,017	0,011
Day 36	0,017	0,014	0,02	0,012
Bjørnegård				
Day 0	0,072	0,004	0	-
	0,126	0,004	0,002	-
	0,107	0,009	0,002	0,008
	0,084	0,015	0,007	0,014
	0,073			
Day 25	0,051	0,021	0,017	0,01
	0,028	0,017	0,007	0,01
Day 44	0,042	0,007	0,013	0,031
	0,067	0,015	0,008	-
	0,032	0,013	0,013	0,013
	0,041	0,024	0,024	0,008
	0,043	0,02	0,018	0,022
	0,026	0,009	0,019	0,011
		0,014	0,017	
		0,008	0,013	
Tåsen				
Day 0	0,089	0,004	0,009	0,012
	0,062	0,014	0	0,006
	0,075	0	-	-
	0,107	0,01	0,009	0,003
	0,099			
	0,129			
Day 16	0,024	0,007	0,001	0,001
	0,049	0,003	0,001	0
		0,004		
Day 35	0,012	0,003	0,007	0,004
	0,035	0,001	0,001	0,004
	0,02	0,007	0,004	0,006
	0,003	0,004		
	0,003	0,004		
	0,009			

Table 14: Concentrations (µg/L) of all parallels of iron (Fe) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	17504	49,03	38,5	17,63
	17805			
	17134			
Day 11	5268	27,47	23,06	-
Day 21	992,25	26,16	21,14	14,07
Day 36	171,46	21,36	19,58	13,27
Bjørnegård				
Day 0	24286	130,037298	51,3635231	19,1343879
	24901	97,5221479	49,213809	16,7105049
	23859	100,156876	52,4680036	31,3969547
	23807	117,938298	49,1084112	16,7130588
	25036			
Day 25	4002	150,212286	46,0492274	15,6561146
	3919	130,561267	47,218991	16,701973
Day 44	3024	124,375815	67,9473681	17,0103579
	3020	123,119259	65,5780475	15,6244303
	2883	129,991703	63,9950542	18,5884338
	2990	98,051455	64,1309196	16,2318168
	3098	88,6671362	54,3767197	16,5619631
	3285	85,1919387	54,9604914	16,6785142
	2942	100,0834	55,1588411	
	3067	111,54983	55,6246236	
Tåsen				
Day 0	20072	77,916093	57,9552009	28,6527969
	20101	96,4375395	71,8923424	27,2223547
	20676	95,2971431	53,7325895	26,5588853
	23908	70,1299301	63,7722975	26,1440084
	23838			
	23903			
Day 16	5577	773,459977	557,131627	91,4179022
	5110	778,566934	361,095518	70,0560476
		755,713843		
		452,29236		
Day 35	3420	149,421887	125,591109	35,4685673
	3273	123,348381	125,251949	32,3545454
	3459	123,576093	110,716225	30,1684111
	3479	115,402146	108,859883	34,672122
	3445	120,359082	105,79653	
	3443	133,610377	109,255943	
	3415	134,233568	120,794526	
	3314	147,61872	121,994771	

Table 15: Concentrations (μg/L) of all parallels of aluminium (Al) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	23816	27,7	15,8	16,2
	24457			
	23971			
Day 11	7238	28,5	13,2	-
Day 21	565,4	15,4	12,9	13,5
Day 36	100,7	13,1	12,9	10,3
Bjørnegård				
Day 0	41322	113,6	43	29,5
	42270	80,6	42,9	40,1
	40263	82,8	42,9	42,5
	40754	101,8	44,4	39,5
	43119			
Day 25	5810	124,5	25,1	15
	5877	116,2	26,7	14,9
Day 44	4203	83,9	24,7	15,8
	4156	78,2	22,5	16,7
	3851	97,2	23,6	17,7
	4189	59,9	22,9	17,5
	4399	58,5	22,2	18,1
	4552	58,3	23	18,6
	4219	82,3	23,2	
	3416	83,7	23,6	
Tåsen				
Day 0	27392	27,4	19,8	24,28
	27473	33,7	20,7	32,31
	28327	42,9	21,1	20,09
	33185	28	21,7	34,55
	33660			
	33613			
Day 16	6030	30,5	10,6	8,5
	5431	34,4	12,7	9,6
		31,3		
		39,1		
Day 35	2217	13,1	5,4	5,8
	2013	6,3	5,3	6,2
	2256	10,4	5,6	6,4
	2293	10,1	5,6	6,6
	2351	12,3	7,8	
	2336	16	7	
	2318	11,8	6	
	2342	17,1		

Table 16: Concentrations (µg/L) of all parallels ofcalcium (Ca) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	96263	77644	77815	84687
	99130			
	95756			
Day 11	81970	78910	81709	-
Day 21	87239	87102	86102	85592
Day 36	88941	85418	86125	82888
Bjørnegård				
Day 0	57771	32275,6449	32213,3062	31597,6645
	57774	31150,4097	32275,286	31478,3078
	57522	32214,0863	31364,7256	30861,7539
	57023	30308,8125	32240,2905	31422,8075
Day 25	35470	33968,1888	35021,7454	34966,5966
	36484	35742,396	35074,8628	34260,3564
Day 44	36616,3487	38350,0043	38407,2003	33428,9682
	37076,5303	37709,4003	36164,993	34327,4059
	36792,4194	36466,1066	36620,303	35876,1892
	36365,5405	36962,0647	37040,7896	35169,6988
	36346,5316	38236,2544	36815,8966	36918,0174
	36285,5385	37601,8866	37149,9789	37483,1834
	36129,2117	35445,8984	36974,1326	
	37131,8701	36815,1688	38388,735	
Tåsen				
Day 0	73537,5304	59446,2354	62070,4511	59440,74
	74663,9147	61487,258	57948,4487	58130,4129
	73905,6674	57650,0577	60155,875	60983,8674
	75401,8498	61353,4368	59615,3876	59017,0615
	77091,831			
	77812,1014			
Day 16	62394	59179,4952	59410,8341	60087,5082
	61439	58861,7599	62206,416	60614,4329
		58739,8955		
		58146,1335		
Day 35	60305,9151	62184,6882	63244,6149	61681,5906
	58310,2579	63389,7702	62060,7419	61797,7461
	61154,3432	63504,1524	63289,6619	60988,5792
	62514,5717	63211,6241	63983,4098	62553,4152
	61771,3583	63939,7239	62999,3159	
	62030,5689	63032,6003	62969,261	
	61591,4699	62738,9942	61896,2644	
	61299,6587	61077,9881	64341,2219	

Table 17: Concentrations (μg/L) of all parallels of sodium (Na) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	673658	659730	681694	719935
	686484			
	662743			
Day 11	701233	676657	721737	-
Day 21	714985	716292	709097	712892
Day 36	720404	712972	718830	714330
Bjørnegård				
Day 0	771613,795	744051,711	743977,906	750376,668
	767541,632	730302,19	728293,078	761572,487
	783005,253	709594,153	722220,058	727606,146
	735021,951	713909,684	755637,583	736627,2
	773932,478			
Day 25	747418,833	712169,588	701074,85	720078,38
	770060,875	744841,007	732522,383	746244,209
Day 44	765711,957	737804,955	747990,07	703160,441
	769439,069	739495,653	736479,861	774577,539
	755683,747	728956,72	748323,276	731001,712
	756461,595	736582,404	725209,358	757823,591
	758812,833	757417,853	753041,04	780466,9
	759191,795	757145,077	750429,417	763884,331
	757732,758	702054,894	747954,6	
	763491,052	750501,516	768548,981	
Tåsen				
Day 0	355596,544	347048,128	348321,639	337350,714
	355679,253	351764,932	322106,346	338185,472
	358939,625	320400,365	338457,388	337083,691
	356425,111	339620,877	342404,729	326896,021
	351261,454			
	352759,748			
Day 16	341505,16	322696,657	321486,607	328680,709
	336454,372	322000,526	336045,904	334424,04
		316808,821		
		313468,459		
Day 35	345137,089	342747,705	343824,362	328917,336
	338015,07	342750,105	335136,102	338721,416
	349397,642	343834,268	336691,833	328969,263
	352759,541	342674,489	341786,94	328156,495
	342933,441	335943,546	337218,046	
	342831,138	339704,748	331056,406	
	339367,549	331856,482	328831,787	
	342686,923	333394,539	335747,085	

Table 18: Concentrations (μg/L) of all parallels of potassium (K) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	18137	11517	11588	12343
Day 11	13876	11631	12579	-
Day 21	12336	12497	12229	12311
Day 36	12376	12356	12524	12189
Bjørnegård				
Day 0	31796,5555	22932,2467	23056,0869	23515,3596
	31491,9992	22589,8876	22850,4694	23714,261
	31194,5899	22395,1694	22999,9045	22799,0567
	31900,4979	22414,108	23614,2884	23101,8779
Day 25	24554,6581	23168,9566	22717,2059	23305,4655
	24658,5559	23779,5377	23118,5088	23681,7454
Day 44	24760,8807	23700,2506	24336,5932	21801,5234
	24744,3162	24079,1482	23705,3964	23542,3409
	24063,9155	23697,2325	24366,4563	23635,3737
	24306,9681	23751,6029	23563,8221	23176,1443
	24229,3654	24190,8303	24072,2417	24265,5968
	24484,4471	24060,6929	23698,0397	24478,9913
	24098,7868	22363,6115	24255,8455	
	24087,7709	23598,5178	24511,7232	
Tåsen				
Day 0	16783,0187	9314,67878	9376,00145	9028,07686
	16995,9369	9521,2227	8627,28498	9120,96499
	18082,9522	8510,17587	8920,68071	8954,97389
	17744,0633	8961,52708	9032,96694	8682,0215
Day 16	10796,305	8860,8262	8769,34851	8961,65495
	10555,0278	8699,88551	8942,52444	8890,5413
		8679,03846		
		8379,15226		
Day 35	9639,50027	9281,67465	9305,20488	8987,48206
	9575,75421	9156,50703	9015,2656	9169,73669
	9822,66914	9294,24558	9069,81748	8783,64597
	9980,13528	9252,10134	9354,55272	8819,81413
	9651,50179	8889,06659	8875,85097	
	9583,88876	8876,02669	8794,96111	
	9394,89894	8865,53025	8889,74744	
	9609,28133	8924,08003	8878,34337	

Table 19: Concentrations (μg/L) of all parallels of magnesium (Mg) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	41272	33854,4	33915,1	36594,5
	41212			
	39904			
Day 11	37394	34087,0648	36720,5	-
Day 21	26158,6	36904,0358	36024,3	35905,9
Day 36	36332,4	35712,7341	36397	35849,6
Bjørnegård				
Day 0	17050,4123	6475,19808	6562,64303	6449,3547
	16989,3816	6456,09576	6466,61844	6650,43
	16884,4627	6277,27294	6296,07787	6383,26104
	16498,2106	6314,75787	6633,39003	6419,23371
	17421,7163			
Day 25	8952,38156	6646,53393	6541,56123	6524,2284
	8579,82642	6985,09485	6756,06776	6715,38856
Day 44	8519,5779	7011,96507	7101,89001	6459,16475
	8488,01174	7071,59624	6983,52836	6927,22949
	8220,63737	6966,86322	7069,76309	6698,57372
	8335,61874	7001,58448	6889,69131	6716,21582
	8330,94505	7145,90426	7006,19648	7086,63332
	8539,35089	7102,97802	7005,37477	7118,50754
	8408,0471	6666,10925	6913,08057	
	8423,94432	7082,35701	7189,7809	
Tåsen				
Day 0	19503,0378	12335,6674	12646,3881	12003,0431
	19346,3831	12677,2495	11517,9268	11879,3822
	19381,4215	11563,3065	12194,7002	11793,8876
	20555,3073	12081,0901	12089,0437	11403,3013
	20533,4295			
	20520,5828			
Day 16	13986,9646	11925,9792	11893,2	12093,5674
	14059,3267	11949,7199	12237,8	12184,0529
		11817,7552		
		11590,6467		
Day 35	12952,6478	12765,0488	12539,6396	12320,4862
	12475,3519	12738,8491	12296,9248	12359,6369
	13390,7308	12712,0338	12443,2773	12122,2375
	13634,8392	12667,8655	12574,6264	12146,1484
	13351,539	12512,326	12282,7584	
	13334,1883	12479,8447	12312,8638	
	13122,6759	12233,8955	12484,7574	
	13050,1147	12333,2601	12444,4304	

Table 20: Concentrations (μg/L) of all parallels of phosphorus (P) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	387	281,5	8,1	7,3
	386			
	379			
Day 11	123,3	468,5	7,03042427	-
Day 21	30,8	19,5	3,46814574	0
Day 36	13,5	29,6	3,99116128	0,5
Bjørnegård				
Day 0	442,884294	78,2882168	28,4706312	14,3387584
	439,10507	39,7807409	25,3516397	12,0342195
	447,31042	37,3300891	25,6731167	16,2986954
	443,545098	44,5347151	27,2332298	12,662485
	464,119617			
Day 25	115,398853	50,2822374	15,3393362	4,36810165
	111,904959	62,1936968	19,0624873	4,53296716
Day 44	95,6203927	27,2911741	15,0919782	3,15184599
	101,676915	20,2045259	15,333765	5,18425631
	98,3680204	29,0809219	17,3640976	3,18928489
	101,565044	21,2813938	15,9012772	3,63089654
	105,568402	17,732959	13,6938933	1,72830704
	104,615968	21,4295782	14,2641864	1,66457522
	104,614998	472,627632	14,0357377	
	102,019466	18,090105	14,0451717	
Tåsen				
Day 0	386,635751	29,0041957	9,12738203	2,63325381
	383,699433	13,8606046	6,48765488	1,67054615
	394,97903	358,46329	8,46321356	3,32740108
	463,411225	31,3615079	7,66423372	2,54853647
	459,321473			
	466,332652			
Day 16	108,247036	389,433055	5,53027377	0,84213264
	105,143344	379,643216	7,1884945	0,72543006
		370,196015		
		497,490668		
Day 35	68,5465919	11,8295862	4,85990602	1,30823224
	60,6895484	11,2884895	4,80486795	0,89765277
	64,0753798	8,32828491	4,58310336	0,69739589
	67,1849012	8,86014957	4,74574063	
	67,6399893	10,0512814	5,05988634	
	63,4749626	18,2408744	6,68978549	
	79,7967856	8,65182349	4,5695153	
	67,8253818	14,1531222	5,35645708	

Table 21: Concentrations (µg/L) of all parallels of silicon (Si) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 µm	0.45 µm	3 kDa
Day 0	60099	3911,9	3749,9	4191,1
	61800			
	58960			
Day 11	19999	3949,54749	3913,96919	-
Day 21	5171,9	4128,78345	4227,02903	4110,8
Day 36	4311,8	4038,51406	4277,72349	3994,8
Bjørnegård				
Day 0	93503,8667	3919,13657	4010,21907	4072,14691
	97296,6727	3899,49009	3955,53303	4040,16407
	91785,6467	3979,16857	3857,95533	4012,60256
	93474,3706	3877,305	4045,59536	4027,76184
	99905,4297			
Day 25	17606,1157	4395,70879	4181,51206	4426,48352
	17303,3719	4472,92169	4148,80702	4290,10798
Day 44	13664,6492	4650,03079	4620,33812	4093,32405
	13816,0028	4667,57039	4368,3076	4184,3844
	12659,9837	4679,79041	4552,43807	4678,49538
	13595,6215	4433,63976	4566,92217	4399,82145
	14239,5734	4623,07693	4469,87294	4397,60742
	14689,6238	4680,19467	4414,74553	4337,44908
	13619,6389	4167,52208	4410,78763	
	13928,1993	4431,91424	4269,88076	
Tåsen				
Day 0	64629,3255	3542,73236	3755,42427	3624,08326
	64032,5627	3850,9017	3596,29604	3659,03375
	67542,456	3525,11031	3628,05145	3666,82301
	77745,969	3761,88188	3632,12931	3645,30293
	78751,4391			
	77727,2954			
Day 16	17347,3696	3818,22882	3800,60578	3881,86239
	16519,5612	3817,41731	3875,94556	3820,67252
		3754,88093		
		3792,62462		
Day 35	9210,99117	4167,72174	4237,39573	4091,01463
	8725,1891	4229,09454	3935,74881	4070,02987
	9633,69348	4223,86607	4302,64832	4057,64679
	9611,33874	4168,89453	4294,25789	4026,04443
	9613,55855	4158,21463	4231,25616	
	9623,40829	3887,73247	3993,56934	
	9636,39324	4055,68616	3911,02697	
	9639,62649	4210,71266	4063,7855	

Table 22: Concentrations (μg/L) of all parallels of tin (Sn) from Smestad, Bjørnegård and Tåsen

Smestad	Total concentration	1.2 μm	0.45 μm	3 kDa
Day 0	12,61	0,024	0,035	0,035
	12,384			
	12,199			
Day 11	4,158	0,03382456	0,02209802	-
Day 21	0,556	0,03000427	0,02787905	0,014
Day 36	0,105	0,02117561	0,03734898	0,07
Bjørnegård				
Day 0	17,6157058	0,40778498	0,3743085	0,29766312
	17,896259	0,35889606	0,32081488	0,25771893
	16,9483575	0,40886059	0,33406411	0,30297774
	17,5088396	0,39446194	0,32863665	0,29076255
	18,3446077			
Day 25	2,78357127	0,35898701	0,31253608	0,24245241
	2,67131739	0,34939975	0,31778517	0,28269178
Day 44	2,03349195	0,30648835	0,27534598	0,21964441
	1,79942017	0,33840594	0,26846344	0,23415925
	1,7222109	0,31950728	0,26902675	0,23768608
	2,03522397	0,30441293	0,23947082	0,20312941
	1,92089232	0,29342919	0,28701948	0,23523334
	2,10005522	0,30974289	0,27469068	0,23541932
	2,12165904	0,28097002	0,26379892	
	2,0843309	0,28546633	0,27079483	
Tåsen				
Day 0	16,1185548	0,02604633	0,02085905	0,00766964
	16,3535162	0,03267761	0,01351112	0,00572346
	16,4982662	0,03364115	0,02249217	0,01028165
	19,5757243	0,02868007	0,02076327	0,01385924
	19,8692456			
	19,5848691			
Day 16	3,1702427	0,04708859	0,02285008	0,0067746
	2,90703369	0,04577284	0,02361741	0,00156426
		0,04377426		
		0,03732494		
Day 35	1,07729917	0,01220661	0,00833515	0,015282
	1,03313999	0,01419916	0,01962893	0,00205378
	1,2396279	0,02157338	0,01054233	
	1,15590903	0,0149168	0,0077881	
	1,29498933	0,0155306	0,01904565	
	1,28217447	0,02759959	0,02517826	
	1,37429262	0,01473828	0,01956108	
	1,21813886	0,03845778	0,02672616	

B   Classification states for metals in fresh water

Table 23: Classification of metals in water measured in μg/L (Miljødirektoratet 2016)

	Background	Good	Moderate	Bad	Very bad
Pb	0.02	1.2	14	57	>57
Ni	0.5	4	34	67	>67
Cu	0.3	7.8	7.8	15.6	>15.6
Zn	1.5	11	11	60	>60
Cd	0.003	0.08	0.45	4.5	>4.5
Ar	0.15	0.5	8.5	85	>85
Cr	0.1	3.4	3.4	3.4	>3.4

C   Concentrations of metals from screening analysis

Table 24: Concentrations of other metals from screening analysis of raw samples from each tunnel (μg/L)

Element	Smestad	Bjørnegård	Tåsen
Li	19,71	26,94	18,53
	21,38	26,58	17,90
	20,17	26,06	16,92
		25,96	22,51
		28,40	22,16
			19,17
Be	1,321	0,585	0,786
	0,262	0,750	1,174
	1,750	1,062	1,013
		1,167	1,433
		0,773	1,163
			0,723
B	59,2	104,6	48,7
	62,3	113,8	46,8
	68,8	81,4	48,0
		197,9	46,5
		84,5	49,2
			49,8
S	16528	18234	12878
	17060	18048	12529
	17035	18801	12978
		17953	13675
		18327	13102
			13565
Sc	3,541	5,188	3,930
	3,656	5,322	3,855
	3,547	5,103	4,083
		5,195	4,771
		5,397	4,734
			4,798
Ti	1362,3	1628,6	1393,6
	1408,1	1660,6	1382,6
	1379,8	1589,3	1415,4
		1648,6	1663,2

		1697,8	1667,9
			1672,2
V	42,55	66,83	43,28
	42,75	65,81	43,06
	42,19	64,54	44,04
		65,73	53,06
		68,48	51,74
			52,43
Mn	550,5	638,6	749,1
	540,7	627,3	767,7
	517,6	612,5	756,8
		622,5	809,5
		639,9	798,0
			802,2
Co	11,96	21,13	15,37
	12,09	20,99	15,26
	11,88	20,94	15,32
		20,73	17,51
		21,56	17,48
			17,35
Ga	7,13	9,77	7,72
	7,10	9,78	7,91
	6,94	9,42	8,09
		9,37	9,68
		9,94	9,56
			9,67
Se	0,525	0,317	0,288
	0,486	0,388	0,300
	0,487	0,216	0,215
		0,576	0,352
		0,483	0,320
			0,402
Rb	45,72	76,54	50,61
	45,85	75,97	50,82
	44,44	74,86	51,05
		73,82	58,22
		77,67	57,42

			57,32
Sr	923,9	889,4	775,6
	911,5	888,6	775,2
	899,8	881,8	788,3
		845,3	820,9
		900,2	818,2
			822,4
Y	7,279	8,154	8,109
	7,249	8,109	8,100
	7,166	8,051	8,300
		8,214	9,988
		8,541	9,568
			9,749
Zr	42,99	32,89	46,23
	44,24	32,27	59,27
	55,84	30,39	48,51
		33,89	57,72
		34,42	51,65
			55,56
Nb	11,11	8,92	11,05
	11,01	7,94	11,08
	10,74	7,59	11,06
		8,02	13,13
		8,05	12,75
			12,82
Mo	14,08	61,67	18,09
	14,21	60,95	18,56
	13,69	60,50	18,61
		63,18	19,45
		62,61	19,55
			19,59
Ag	0,237	0,275	0,225
	0,327	0,269	0,246
	0,186	0,288	0,225
		0,294	0,291
		0,254	0,274
			0,267

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In	0,0567	0,0778	0,0738
	0,0587	0,0762	0,0665
	0,0586	0,0720	0,0687
		0,0789	0,0868
		0,0824	0,0825
			0,0789
Sn	12,610	17,616	16,119
	12,384	17,896	16,354
	12,199	16,948	16,498
		17,509	19,576
		18,345	19,869
			19,585
Sb	6,09	11,16	8,15
	5,87	11,23	8,38
	6,02	10,83	8,52
		10,95	9,65
		33,16	9,77
			9,40
Cs	1,711	2,633	1,681
	1,707	2,593	1,680
	1,612	2,539	1,684
		2,451	1,956
		2,665	1,957
			1,934
Ba	351,86	695,87	408,92
	348,64	689,61	409,73
	334,21	670,52	415,35
		673,45	471,61
		710,13	468,94
			468,27
La	18,39	17,10	18,51
	18,11	16,81	18,55
	17,92	16,73	19,06
		16,89	22,89
		17,51	22,87
			23,15
Ce	38,67	35,87	39,31

	38,45	35,35	39,49
	37,93	35,28	40,50
		35,67	48,98
		37,07	48,31
			48,79
Pr	4,390	4,059	4,375
	4,383	4,013	4,418
	4,341	3,935	4,555
		3,981	5,450
		4,214	5,373
			5,436
Nd	16,682	15,656	16,937
	16,519	15,222	16,717
	16,134	15,181	17,214
		15,478	20,826
		16,103	20,494
			21,023
Sm	2,815	2,694	2,927
	2,836	2,683	2,857
	2,826	2,720	2,960
		2,630	3,588
		2,796	3,446
			3,574
Eu	0,707	0,705	0,739
	0,690	0,702	0,701
	0,710	0,676	0,723
		0,721	0,867
		0,733	0,870
			0,849
Gd	2,063	2,048	2,203
	2,047	2,092	2,222
	2,148	2,017	2,163
		2,193	2,538
		2,242	2,640
			2,680
Tb	0,305	0,311	0,306
	0,292	0,310	0,309

	0,270	0,291	0,324
		0,302	0,383
		0,302	0,368
			0,371
Dy	1,605	1,726	1,780
	1,573	1,673	1,629
	1,550	1,676	1,715
		1,661	2,105
		1,759	2,010
			2,004
Ho	0,282	0,316	0,304
	0,274	0,317	0,309
	0,279	0,312	0,307
		0,324	0,380
		0,321	0,361
			0,371
Er	0,740	0,841	0,831
	0,794	0,871	0,841
	0,749	0,854	0,881
		0,891	0,967
		0,886	0,985
			1,013
Tm	0,0976	0,1181	0,1071
	0,1074	0,1255	0,1193
	0,0943	0,1072	0,1223
		0,1259	0,1377
		0,1305	0,1323
			0,1352
Yb	0,600	0,720	0,785
	0,649	0,821	0,743
	0,678	0,822	0,779
		0,757	0,906
		0,837	0,862
			0,936
Lu	0,0858	0,1035	0,0958
	0,0868	0,1034	0,0986
	0,0869	0,0972	0,1030

		0,1025	0,1154
		0,1131	0,1129
			0,1142
Hf	1,015	0,893	1,148
	1,072	1,018	1,077
	0,998	0,812	1,206
		0,930	1,270
		0,915	1,310
			1,215
Ta	0,410	0,350	0,423
	0,347	0,416	0,444
	0,315	0,499	0,385
		0,394	0,477
		0,414	0,403
			0,459
W	25,15	56,86	26,38
	24,75	56,23	26,43
	24,44	54,73	26,53
		54,93	31,02
		58,34	30,28
			30,48
Pt	0,0095	0,0086	0,0049
	0,061	0,0095	0,0148
		0,0129	0,0099
		0,0040	0,0163
		0,0115	0,0101
			0,0075
Au	<0.06	<0.06	<0.06
Hg	0,171	0,066	0,062
	0,038	0,049	0,016
	0,078	0,028	0,084
		0,076	0,031
		0,093	0,050
			0,048
Tl	0,212	0,290	0,236
	0,208	0,301	0,214
	0,334	0,284	0,226

		0,285	0,269
		0,311	0,264
			0,257
Bi	0,852	1,291	1,261
	0,831	1,334	1,195
	0,802	1,249	1,221
		1,168	1,280
		1,224	1,368
			1,419
U	3,841	2,460	2,527
	4,044	2,415	2,545
	3,901	2,476	2,560
		2,351	2,870
		2,525	2,758
			2,823