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Occurrence of benzothiazole and benzotriazole in tunnel wash water

Master's thesis in KJ3910 - - Master Thesis in Environmental Chemistry

Supervisor: Alexandros Asimakopoulos

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Abstract

Most of the 1 200 tunnels located in Norway are used daily. All that traffic emits pollutants, directly by products of fuel, or indirectly, like tire wear. Most of these contaminants does not leave the tunnel, and will end up as dust or coating on the wall or roof. This could affect the general quality of the tunnel. To remove these, tunnel washing is performed. This transports the contaminant to a treatment plant. The standard treatment today is to put the water in a basin for 35 days. During this time, larger suspended particles will sediment and later removed. One major problem here is this method may not be effective om smaller suspended particles and dissolved compounds.

This master thesis will look on how the occurrence of benzothiazole and benzotriazole changes during this process. This thesis will also look at how the occurrence changes if a second treatment step is added. The thesis is a part of a larger project, by a PhD student. That project looks into to introduce a second step, and how well it affects the removal of pollutants. The second step is to remove pollutants by filtration. Three different types of filters will be tested, bag, adsorption and membrane filter. The aim of this study is to see which of these removes benzothiazole and benzotriazole best. The tunnel that has the test pilot plant for testing these steps is Bjørnegårdtunnelen Another part of this thesis is to look at different materials ability to adsorb and remove benzothiazole and benzotriazole. 6 different materials, and some combinations with them is tested.

The results shows that adsorption filter had the highest removal efficiency, by removing over 90% of benzothiazole and benzotriazole and their derivatives. This was tested opposed to bag filter and membrane, both showing some removal efficiency, but not as high as adsorption did. The material that showed best removal efficiency is granulated activated carbon, which is what's used today in Bjørnegårdtunnelen. Some material was tested in combination with each other, but this did not yield any benefits.

Removal contaminants from wash water, before it is released into nature, is a direct step towards one of UN's sustainable development goals, number 14: life below water. It is especially aimed towards goal 14.1 and 14.3, but could also in certain area work towards goal 6.3, removing pollutants from water that could be used as drinking water.

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Abbreviations

Table 0.1: Abbreviations of chemicals analysed, and other abbreviations used

Chemical	Abbreviation of chemicals analysed
Benzothiazole	BTH
2-Methylben-zothiazole	2-Me-BTH
2-Aminobenzothiazole	2-A-BTH
2-Hydroxybenzothiazole	OH-BT
2-Mercaptobenzothiazole	2-S-BTH
2-Chlorobezothiazole	2-Cl-BTH
2-(Methylthio)benzothiazole	2-Me-BTH
2-Morpholin-4-yl-benzothiazole	2-M-BTH
2-Thiocyano-methylthio - benzothiazole	2-SCNMeS-BTH
Benzotriazole	BTR
4-Methyl-1H-benzotriazole	TTR
1-Hydroxybenzotriazole hydrate	1-OH-BTR
5-Amino-1H-benzotriazole	5-A-BTR
5,6-Dimethyl-1H-benzotriazole monohydrate	XTR
5-Chlorobenzotriazole	5-Cl-BTR
Benzotriazole-5-carboxyl acid	BTR-COOH
Benzotriazole-d4	BTR-d4
5-Methyl-1H-1,2,3-Benzotriazole	5-Me-BTR-d6
<hr/>	
Abbreviation	
IS	Internal
TA	Target analyte
PF	Particulate fraction
PM	Particulate matter
WF	Water fraction
PF	Particulate fraction
PM	Particulate matter

1 Introduction

In Norway, there are over 1 200 tunnels, and most of them are used daily. All these vehicles emits pollutants to some degree, and in tunnels, these pollutants does not have much travel time, most of the pollutants stays in the tunnel. To remove them, tunnel washing is performed. This is not only performed just to remove pollutants, but also maintain technical installations. This will extend the tunnels lifetime, and decrease the need to replace installations like lights and fans.

Earlier the normal way to treat this wash water was to just release it into the nature, or transport it to the nearest waste water treatment plant, but that was not always an option. In later days, a treatment step has been added and all newer tunnels have a sedimentation basin. In this basin, the wash water lay for 35 days, where suspended particles will precipitate and later removed. This works well on suspended particles, but not very effective on small particles and dissolved compounds.

Two types of common pollutants from traffic are benzothiazole and benzotriazole. Both of these are water soluble and not biodegradable, meaning they are not easily removed from the water. One aim of this study is to look at the occurrence of benzothiazole and benzotriazole during this process, but also when a second treatment step is added. It will look at how well three different types of filters works on removing these contaminants. Bjørnegårdtunnelen, where most of the samples are taken, has a pilot test plant where bag, adsorption and membrane filters are tested on tunnel wash water. Both particulate fraction ($>0.45\mu\text{m}$) and dissolved fraction ($<0.45\mu\text{m}$) will be tested.

The second part of the project is to test different material used as adsorption filter. A total of 6 material will be tested in columns, and even some columns will be filled with mixtures of two materials, to see if that can have any effect on removal abilities.

1.1 Objectives

One part of this thesis is to look at possible second treatment steps for tunnel wash water. So two hypothesis is presented about how well these different steps will work on removing benzothiazole and benzotriazole:

- The benzothiazole and benzotriazole concentrations in the particulate fraction will be reduced during sedimentation and even more during filtration.
- The benzothiazole and benzotriazole concentrations in the water fraction will not change that much during sedimentation but will be efficiently removed during adsorption filtration.

2 Theory

This theory chapter will begin with talking about what tunnel washing is, and how it is performed. Will briefly go into the history of treatment of the wash water from the washing, and how it has developed. The project of this thesis will be explained. Then different pollutants one can find here will be discussed, before the main target of this thesis will be honed towards. After that, it will talk about the different derivatives of BTH/BTR, how they are created in nature and why these are studied here. Then some theory regarding the lab work and analysis will be presented and explained. Towards the end, some QA/QC elements will be presented.

2.1 Tunnel washing

The Norwegian public road system contains almost 100 000 km of road^[4] and with the rocky and mountainous terrain, tunnels is a logical addition to the road system. The first tunnels were introduced at the end of 18th century^[5], around the time cars came to Norway. During the 19th century, more people owned cars, across the country, so development of the road system was needed, and also the tunnel system. As of 2018, there are over 1 100 tunnels in Norway, and many of these are used daily in communal transport^[6]. With the increasing traffic usage, an increase in pollutants from traffic comes with it, what types of pollutant will be talked about later in this thesis. Unlike on the roads, emission in tunnels will not all be released in the air, but will stay on wall or floor. For this to not become too toxic, the tunnels are required to be washed.

The main factor determining the frequency of tunnel washing in Norway is traffic. More trafficked tunnels can be washed twice a year, and less trafficked tunnels can go down to washing every 5th year^[7]. This apply for full wash only, which means the tunnels are washed from the roadway to the roof. Another type of washing performed is half washing. The main difference between a full wash and a half wash is that during a half wash the walls are only washed from the roadway up to a certain height, depending on whats needed^[8]. The third type of washing done is a technical washing. This is for maintenance of technical installations, but also cleaning of the roadway to remove small particles^[8]. All these types of washing combined results in the tunnel washing occurring between 2 and 12 times per year, the amount depends the average annual daily traffic, and is measured in number of daily passes of cars^[9]. The full list of number of washes can be seen in table 2.1.

Table 2.1: frequency of tunnel washing per year^[3]

Average annual daily traffic	Full wash	Additional half wash	Additional technical wash
0 - 300	every 5th year	-	1 per year except if a full wash happens
300 - 4 000	1	-	1
4 001 - 8 000	1	1	2
8 001 - 12 000	1	2	3
12 001 - 15 000	2	3	5
15 001-	2	4	6

Tunnel washing is performed to remove unwanted particles like dust, dirt or other contaminants, bur also to clean machines and apparatuses in the tunnel and maintain the tunnels performance.

Removal of particles is mainly dust particles, but also particles like dirt, debris and contaminants that during traffic will find its way to the side of the roads, or as "coating" on the walls and roof.

One effect of dust in tunnels are less visibility from lights, either from dust in the air or particles adsorption on the light themselves^[7]. If the visibility in the tunnels are reduced, it will be harder to see signs, and accidents have a higher possibility to happen. By keeping a lower concentration of dust in the air, it is safer to drive through, reducing any possibilities for toxicity for people breathing in the air from the tunnels, which can be people driving through the tunnel or people doing maintenance there.

When tunnels are washed, maintenance of technical installation is also conducted. This include maintenance of fans, emergency power and water supply^[8]. Dust particles will go into these installation, and without treatment, these machines will stop working, or reduce their performance. If this happens, they need to be replaced. By maintaining these installation, the lifetime of a tunnel is extended^[7].

2.1.1 Performance of washing

Before the washing itself, the floor are swept, to lower pollutant load in the wash water. After this, the walls can be sprayed with detergent, but not all washing is performed with detergent, but using detergent is more efficient^[10]. Water is then sprayed onto walls, and if a full wash is performed, the roof, and then is swept away by special equipped tankers. At the end, special suction vehicles will sweep away any excess water or remaining particles. Tunnel washing can be performed by just using water^[11] or with some type of detergent. This depends on what tunnel is washed, depending on if there is need for extra help, or if washing with water is all that is needed. Who is washing is also a factor. Different companies have different policies on how they wash^{[12][13]}.

2.2 Location of interest

The two tunnels involved in this project are Bjørnegårdtunnelen and Grillstadtunnelen. The location of both can be seen in figure 2.1.

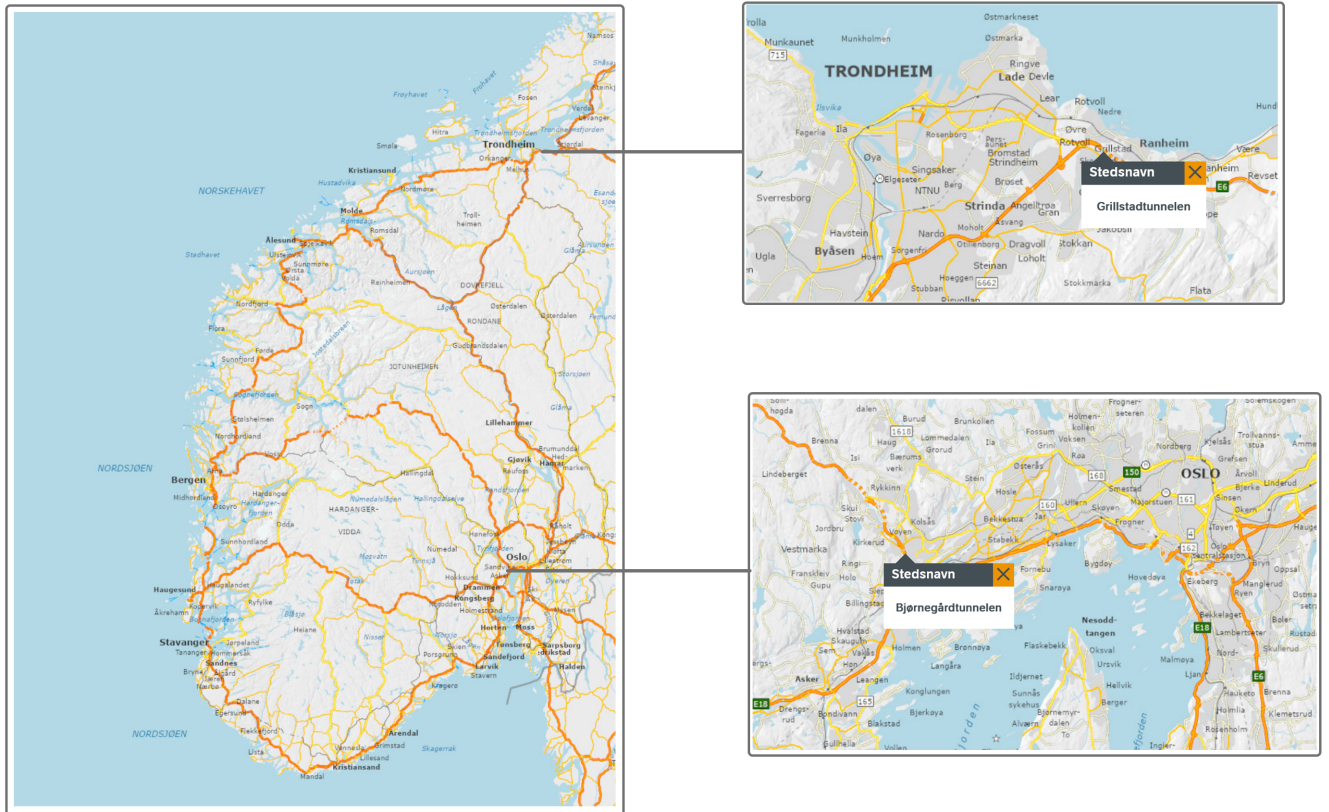


Figure 2.1: A map showing the location of both tunnel, Grillstad^[1] and Bjørnegårdtunnelen^[2], where samples was taken from during this thesis

2.2.1 Bjørnegårdtunnelen

Bjørnegårdtunnelen opened in 2018, located in Bærum^[14]. The tunnel is divided into two tubes, one for each driving direction and the tunnel is 2.3 km long. The speed limit is 80 km/h. In 2022 the tunnel had 34 000 passings, where 11% of those were from trucks^[15]. This tunnel is usually washed in early February, late March, once in June, late august October and late November. This totals in 6 washings each year. The tunnel is washed with the soap purify PG-SCP1-X1-1000.

Today, the main form of wash water treatment in this tunnel is sedimentation. This is done in 2 sediment basins. Both has an area of 140 m² with a max water level registered at 2.9 meter. The water lay there for 35 days before further treatment. usually bag filtration, Figure 2.2 shows an overview on how this treatment plant is set up today. In this figure, 3 different secondary treatment steps can be seen, these will be explained further down in this chapter. This is the main test pilot plant for the project this master thesis is a part of.

2.2.2 Grillstadtunnelen

Grillstadtunnelen opened in 1989, and was upgraded in 2013, it is located in Trondheim^[15]. The tunnel had, in 2022, 34 632 car passing total, where 9% were from trucks. Like Bjørnegård, this tunnel also has a sedimentation basin for treatment of tunnel wash water.

2.2.3 Primary treatment step

Originally there was no treatment step for tunnel wash water, meaning the water was released into the nature untreated. The other option at the time was to transfer the wash water to a water treatment plant. This required that the water treatment plant could handle to receive this amount of water, in addition to all the water it already was treating. One problem with this is not every water treatment plant does have the capabilities to treat this much water, and the cost of transferring the water to the treatment plant was not always worth it^[16].

In more recent years, a sedimentation basin has become a requirement for larger tunnels. A sediment basin is a big pool where untreated wash water lay for 35 days, before it is removed. In this time, suspended particles will be removed trough sedimentation, particles precipitate down to the bottom of the pool. Since this requirement is relative new, mostly new made tunnels has a basin like this, meaning older tunnels does not have one. but today this constitutes only for a small number of tunnels^[16].

One problem with sedimentation, is that it only removes larger suspended particles. It has little to no effect on contaminants in dissolved phase. A solution to that is to add a treatment step to this process. Today, the normal is to add a type of filter to remove any addition particles not removed from the sedimentation^[16].

2.2.4 Secondary treatment step

This master thesis will look on BTH/BTR concentration when a second treatment step is introduced. Trough this sub chapter, three different treatment step will be introduced and explained on the main differences. Bjørnegårdtunnelen has a pilot treatment plant, with different treatment steps. Figure 2.2 shows how the pilot treatment inside Bjørnegårdtunnelen is setup.

As of today, the default second treatment step for Bjørnegårdtunnelen is a bag filter. This filter consist of two different, consecutive filter. The first one has a mash size of 5 μm , and the second one has a mesh size of 1 μm . These bags are made of polyester ant polypropene.

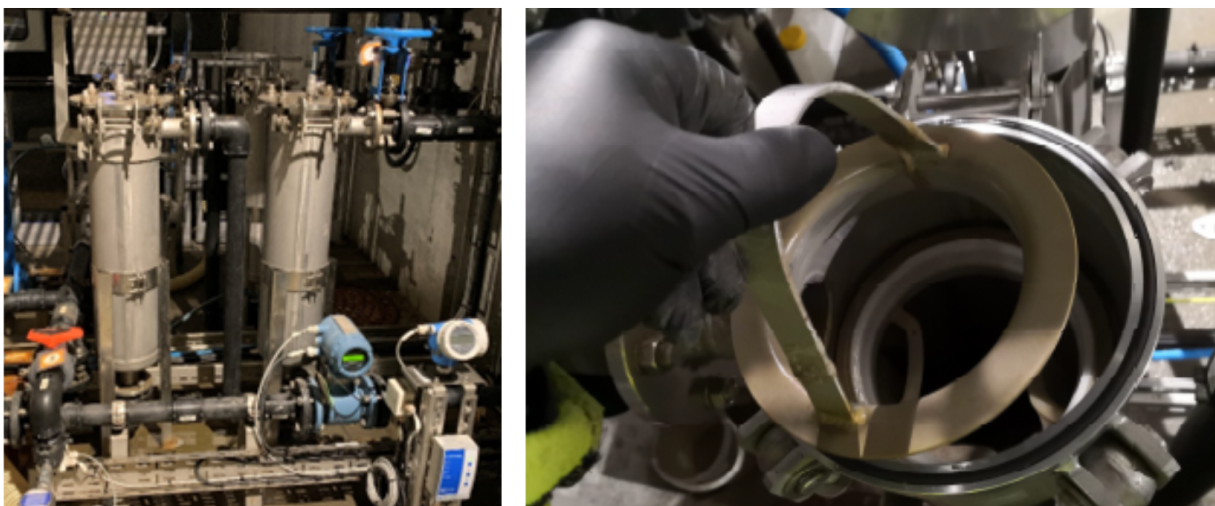


Figure 2.3: Pictures of the setup of the bag filters (left) with the two types of filter size and how the filters are placed in the container (right). Picture: H. Vistnes

As an alternative, adsorption filters can be used as treatment here. The column is 220 cm tall and has a diameter of 95 cm. The container has glass window on both side, this is to be able to see

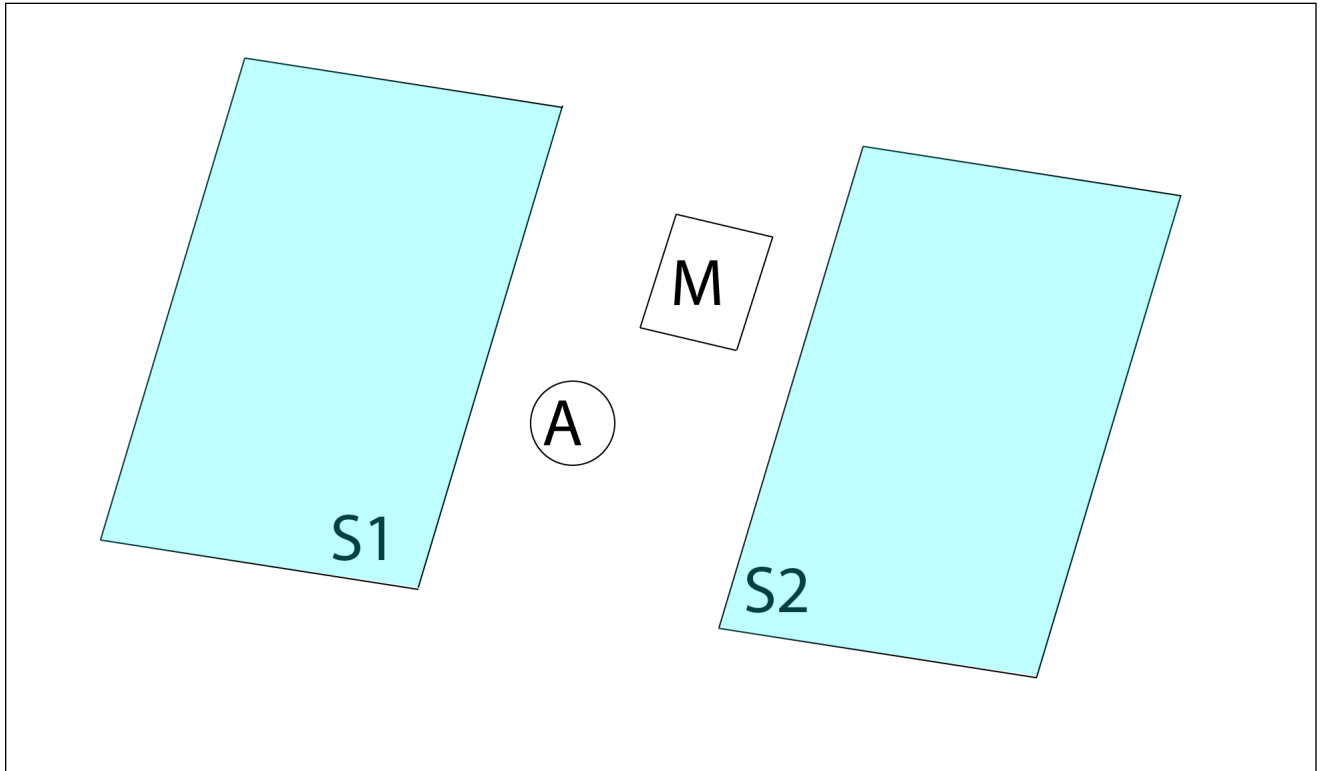


Figure 2.2: Simple schematic on how the test pilot is setup, S1 and S2 are sediment pool, M is membrane station and A is adsorption station.

the material. This column can contain up to 1520 L of filter material. The column can be seen in figure 2.4.

For this project, granulated activated carbon from the brand Carbotechh Pool W1-3 was used. It is made from reactivating previously used coal based activated carbon. This material has a particle size between 0.5 and 3.55 mm, which gives it a large surface area, and combined with some functional groups scattered around, it is optimal for both inorganic element removal, and removal of organic contaminants.

This filter has been changed once during the tunnels operation, was changed in November 2022. This means that this filter can last around 3.5 years before needing to be changed. For this period, the filter was run for around 500 hours.

The final alternative of interest here is membrane filter. This is a type of filter, but with smaller pore size than a normal filter. In this project, this filter is module based, with 15 module sheets placed parallel with each other. They are made of Silicon Carbide (SiC) and has a pore size of 0.1 μm .

During this filtration, the water is pulled through by a vacuum, created by pumps on the side, with a pressure around 0.06 bar. The treated water goes from here into a tank, before it leaves the treatment plant. Schematic of this system can be seen in figure 2.5.

2.3 Column

Another part of this project is to test for different materials abilities to remove contaminants from wash water. Adsorption is one of the second treatment steps tested, so to test different materials, and see how well they remove contaminants is of interests. The following 6 materials was tested in

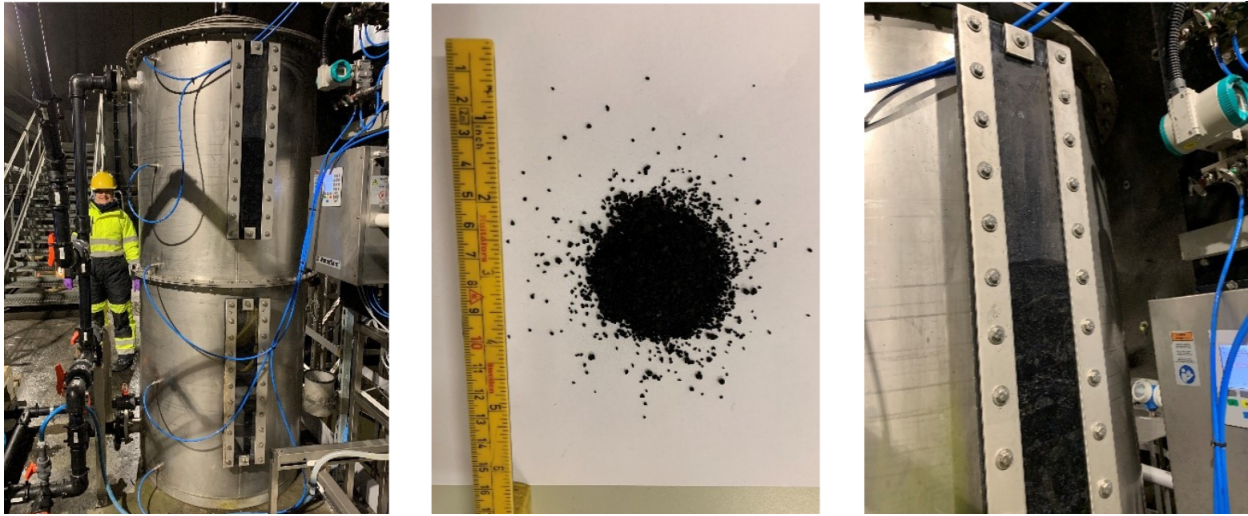


Figure 2.4: Full size of the adsorption column (left). Granulated activated carbon used in the column (middle). Glass windows built in the column to see the filter inside the column. Picture: H. Vistnes

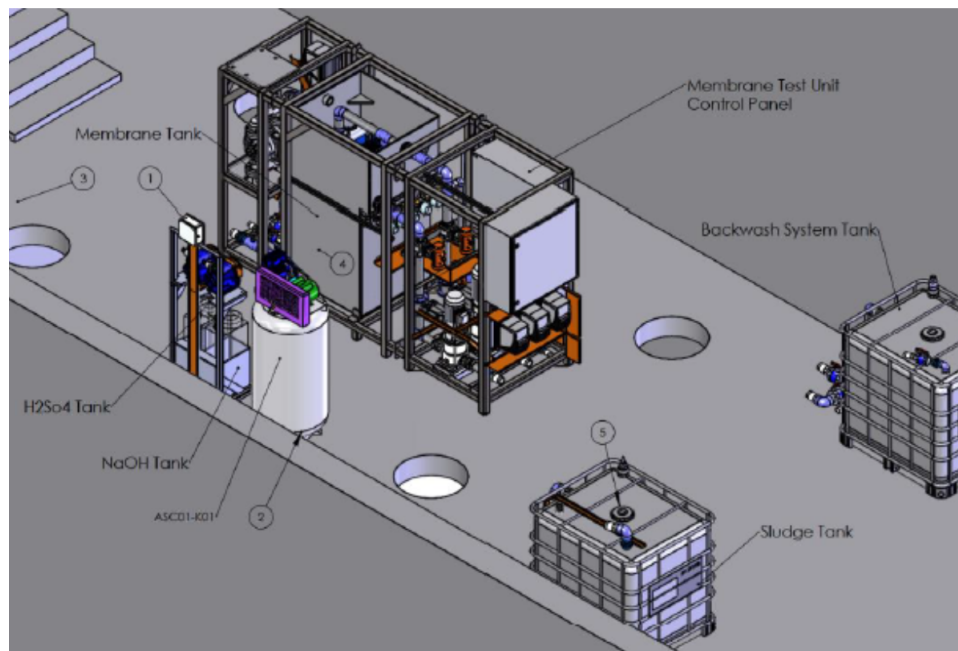


Figure 2.5: Schematic drawing of how the membrane filtration is set up in the Bjørnegård tunnel,

columns for their adsorption effect on pollutants:

- Sand: Used as a reference material, because of its inert abilities. The only way for it to remove contaminants should be by trapping them in small "pockets" in the material. This type of filter can later on be back washed to remove contaminants from the material^[17].
- Biochar: 85% carbon, made from untreated wood or fine sieve residues wood chip production. Also known as charcoal^[18].
- Granulated activated carbon (GAC): made from mineral coal at 850 °C. Coal is treated at that temperature to remove all organic residues^[19].
- Leca: Product name: Filtralite HMR. Is made with particle size between 0.5 and 2 mm. It is made from thermally treated clay. It is used for anion/cations like metal phosphate, sorption on electrostatic charged pollutants in water^[20].
- Olivine: A magnesium-iron silicate. Chemical formula: Mg_2SiO_4 and Fe_2SiO_4 ^[21].
- Zeolite: Made from its natural version, Zeoclin. Has the chemical formula as $(Ca, Fe, K, Mg, Na)_3-6 Si_{30}Al_6C$

2.4 Traffic pollutants

The main source of pollution in tunnels are traffic. The types of pollutant from traffic that runs on different types of petrol are CO_2 , CO, NO_X , Particulate matter (PM), PAH and Volatile organic compounds to name a few^{[23][24]}. Electric car can pollute in less direct ways compared to petrol car, but particulate matter from tire wear or asphalt and dust particles^[25]. Diesel car is a significant source of PM^[26]. Heavy metals like Zn and Pb can also come from traffic, these comes from tyre wear^[27],

One of the main hazard of NO_X is that it can do a chemical reaction in the air, to create $PM_{2.5}$ and ozone^[26]. Other organic compounds released, for example aromatic hydrocarbon and formaldehyde to name a few, are known cancer causing substances^[26].

Vehicles with petroleum as fuel are not the only source in this context, electric cars can also pollute in this matrix, just not as directly as petroleum fueled vehicles. The main way electric cars will pollute in traffic is trough wear of brakes, tires and asphalt^[28]. These types of wear comes from cars driving, and trough friction, will break to small particles. During washing, these particles can be dusted away, but some of them can also end up where the wash water goes, making them a potential source of contaminants, if they release compounds while in water.

2.5 Benzothiazole and benzotriazole

Two common types of VoC is benzothiazole (BTH) and benzotriazole (BTR)^[29]. Molecular structure of BTH/BTR can be seen in figure 2.6. Both these compounds as contaminants have sources from traffic, BTH from rubber, and BTR in metal^[30].

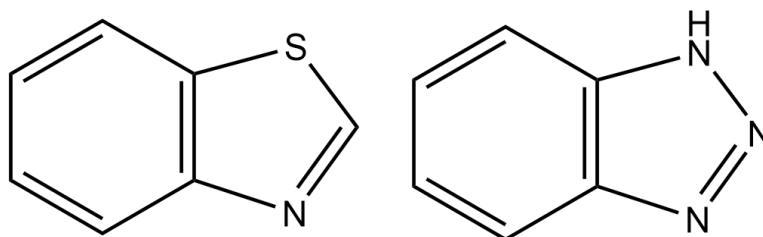


Figure 2.6: Molecular structure of benzothiazole (left) and benzotriazole (right)

These compounds are classified as contaminants of emerging concern^{[31][32]}. This is due to their potential adverse effects on aquatic animals^[33]. BTH does not have fatal consequences for organisms, but will cause unpleasantly, like reduced population or reduced growth. For humans, BTH can act as an endocrine disruptor^[34]. BTR has similar effects as BTH, but some differences is that some studies shows that long term exposure can lead to effects on liver and kidney^[31].

2.5.1 Benzothiazole

Benzothiazole (BTH) is a heterocyclic compound made from one benzene ring and one thiazole ring. BTH is used as a vulcanization accelerator in the rubber industry. BTH derivatives are used as different types of pesticides, like fungicide and herbicides^[35]. Other common purposes of BTH derivatives are corrosion inhibitors in antifreeze, UV stabilizer in both plastic and textiles^[36]. BTH and its common derivatives can be seen in figure 2.7.

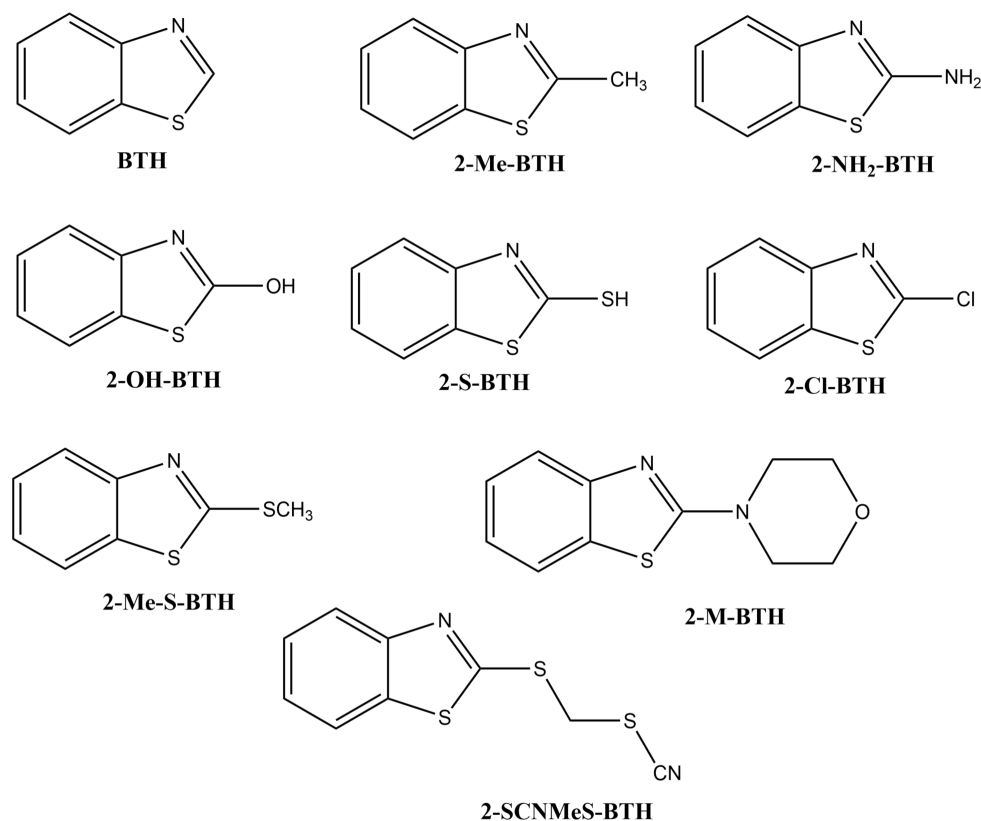


Figure 2.7: Molecular structure of BTH and some of its common derivatives. Those are 2-methylbenzothiazole (2-Me-BTH), 2-Amino-benzothiazole (2-A-BTH), 2-hydroxybenzothiazole (2-OH-BTH), 2-mercabenzothiazole (2-S-BTH), 2-chlorobenzothiazole (2-Cl-BTH), 2-methylthiobenzothiazole (2-Me-S-BTH), 2-morpholin-4-yl-benzothiazole (2-M-BTH) and 2-thiocyano-methylbenzothiazole (2-SCNMeS-BTH).

One reason BTH and derivatives are of concern in waste water is because BTH has a limited biodegradability^[37], have potential toxicity and are water soluble. These factors makes then not completely removed during wastewater treatment BTH becomes a threat for aquatic animals^[38]. A common source of BTH from traffic is from tire wear. BTH and 2-OH-BTh is a vulcanization agent and an antioxidant that is added to rubber materials during the production^[39]. 2-M-BTH is a impurity in rubber manufacturing^[40].

BTH in an aquatic environment are usually found with a 2-OH-BTH. 2-OH-BTH is created from an aerob degradation of BTH^[41], the ratio between BTH and 2-OH-BTH is then determined by how much oxygen is available for BTH to create 2-OH-BTH, an oxygen rich environment will inciease 2-OH-BTH in the ratio, but less available oxygen, means less 2-OH-BTH are able to form. $BTH \rightleftharpoons 2-OH-BTH$ equilibrium.

2-SCNMeS-BTH is a fungicide that is not more used^[42], but it has some persistence. In nature, 2-SCNMeS-BTH can break down to 2-M-BTH^[43]^[38]. 2-M-BTH is not only a derivative of 2-SCNMeS-BTH, but also it is used as a bio corrosion inhibitor in some industries^[43]. Another possibility for 2-SCNMeS-BTH to break down is to 2-S-BTH, with help from microorganism. This derivative does not have a high stability, so this molecule then create a more stable version, 2-S-Me-BTH^[41].

2-Me-BTH is commonly used in deicing processes, most common for airplanes^[34]. 2-A-BTH is a structural unit used in synthesis of thermoplastic polymer and antioxidants^[43]. BTH, 2-OH-BTH

and 2-M-BTH can adsorb to suspended particles^[40]. Because these derivatives are products of BTH, or found in nature, they will be of interest when analysing the occurrence of BTH. If one only analysed for BTH, some of the concentration could be missed, because some part of BTH would be created into different derivatives.

2.5.2 Benzotriazole

Benzotriazole (BTR) is a heterocyclic compound made from one benzene ring and a thiazole ring. BTR is commonly used as a corrosion inhibitor for several types of metals, some examples being copper and brass, an alloy of Cu and Zn. By applying BTR to the metal, a protective layer is created. In figure 2.8 BTR and its derivatives can be seen.

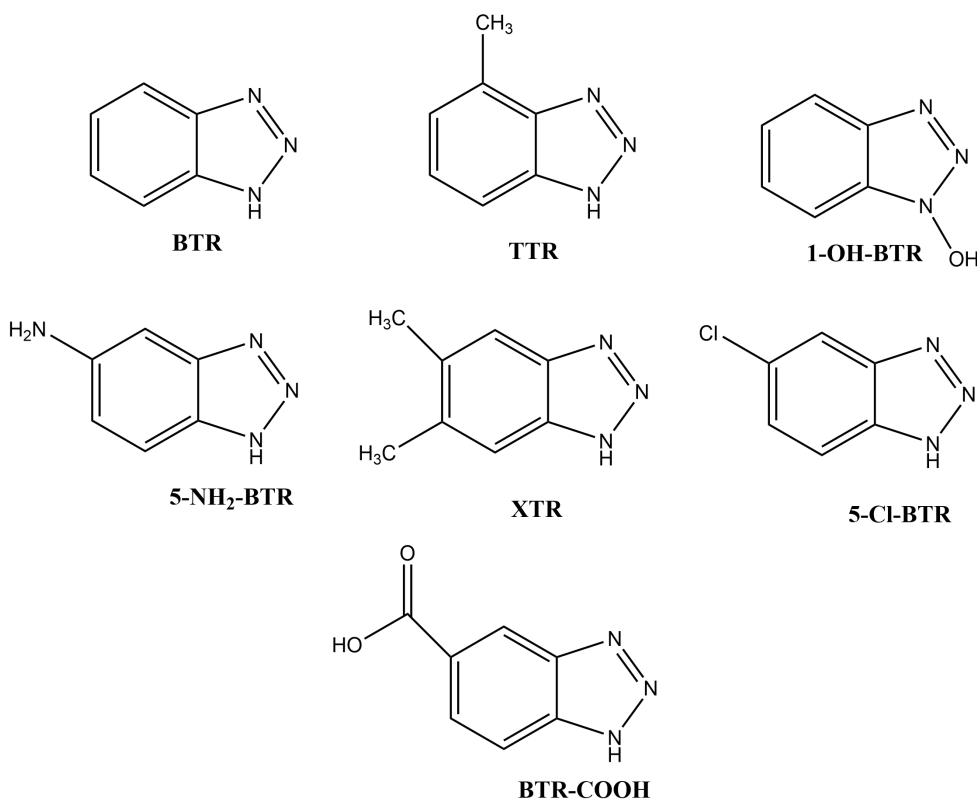


Figure 2.8: Molecular structure of BTR and some of its derivatives. Those are 4-methyl-1H-benzotriazole (TTR), 1-hydroxybenzotriazole (1-OH-BTR), 5-amino-1H-benzotriazole (5-A-BTR), 5,6-dimethyl-1H-benzotriazole (XTR), 5-chlorobenzotriazole (5-Cl-BTR) and benzotriazole-5-carboxyl acid (BTR-COOH)

BTR and TTR is used as a corrosion inhibitor. TTR can also be degraded from BTR in an anaerobic environment^[44]. This would also occur in an aerobic environment, but with the oxygen available, an OH-group would also attach to the benzene ring. TTR is used as a antifreeze agent. 5-Cl-BTR and XTR are also used as corrosion inhibitors^{[45][46]}. 1-OH-BTR and BTR-COOH are product of aerobically transformed BTR and TTR^[41]. 5-A-BTR is used to enhance the durability of copper/epoxy joints^[47]. Some BTR are also sued as UV filter. They are used in plastic and polymetric materials^[48].

Examples of past data of BTH and BTR in different matrices to tunnel wash water can be seen in table 2.2 and table 2.3. These matrices were chosen because

Table 2.2: Past data of the occurrence of BTH and derivatives in different matrices, values shown are mean values

Matrix	Location	Unit	BTH	2-Me-BTH	2-A-BTH	2-OH-BTH	2-S-BTH	2-Cl-BTH	2-Me-S-BTH	2-M-BTH	2-SCNMeS-BTH
Tire ^[39]	Norway	ng/L	35.5		52.0	232	12.6		41.2	1.92	41.7
Tire ^[39] (Studd season)	Norway	ng/L	127		59.1	729	9.25		126	3.47	82.1
Surface Water ^[30]	China	ng/L	73.9±21.3	0.73±3.09	0.80±1.06				3.64±4.65		ND ^c
Groundwater ^[30]	China	ng/L	227±925	3.28±7.88	6.38±18.23				182±1121	0.96±1.72	0.19±0.22
Stormwater ^[30]	China	ng/L	38.5±25.3	5.01±5.38	2.29±2.61				28.6±31.3	0.44±0.3	ND
Suspended particles ^[30]	China	ng/L	0.07±0.23	ND	0.03 ± 0.03				ND	0.03±0.04	ND
Tap water ^[49] (Surface water source)	China	ng/L	365		N.D	2.8					
Tap water ^[49] (Groundwater source)	China	ng/L	409		N.D	12.8					
Tire Debris ^[50]	Sweden	µg/g	75.1						1.3	850	
Road dust ^[51]	China	ng/g	871			1753		3116	777	2.28	
Road ^[52]	China	ng/g	4610		2167	2986			1258		
Innfluent waste ^[53] water	Malaysia	ng/L	66±65	3.7±23	1.7±2.4	170±110	ND		1.1±3.3		1400±3700
Effluent waste ^[53] water	Malaysia	ng/L	56±43	0.53±2.5	1.6±0.85	160±150	ND		0.46±1.7		
Innfluent waste ^[53] water	Sri Lanka	ng/L	210±120	1.1±1.8	5.8±2.8	420±290	82±220	100±110			
Effluent waste ^[53] water	Sri Lanka	ng/L	140±86	0.94±2	7.2±3.8	330±130	8±28		33.8±27.3		
Innfluent waste ^[54] water	Germany	µg/L	0.85±0.2			0.5±0.16	0.19±0.07		0.17±0.06		
Effluent waste ^[54] water	Germany	µg/L	0.55±0.19			0.14±0.08	0.02±0.03		0.44±0.09		
River (dry) ^h [55]	China	ng/L	545±222	138±76		55±47				109±42	
River (wet) ^h [55]	China	ng/L	268±142	100±83		19±23				97±78	
Tire ^[56]	Multiple ⁱ	µg/g	52.41		12.6	19.08	13.79		0.75		
Road Runoff ^[52]	China	ng/L	2645		539	2163			1013	ND	
Tunnel (Entrance) ^[57]	Hartfield (UK)	ng/m ³	0.04								
Tunnel (Exit) ^[57]	Hartfield (UK)	ng/m ³	0.1								
Stormwater ^[58]	Multiple	µg/L	0.54			0.56				0.17	
Tire ^[59]	Australia	µg/L			4.6	2.2	5.2			<0.7	
Tire ^[59]	Australia	µg/L			8.8	44	25			0.87	
Tire ^[59]	Australia	µg/L			2.1	7.3	16			<0.7	

Table 2.2: Past data of the occurrence of BTH and derivatives in different matrices.

Matrix	Location	Unit	BTH	2-Me-BTH	2-A-BTH	2-OH-BTH	2-S-BTH	2-Cl-BTH	2-Me-S-BTH	2-M-BTH	2-SCNMeS-BTH
Tire ^[59]	Australia	µg/L			22	191	153			3.2	
Tire ^[59]	Australia	µg/L			30	449	72			6.6	
Sludge ^[60]	Spain	ng/g	N.D		ND	173.4			25.5		
Sludge ^[60]	Spain	ng/g	N.D		ND	132.4			ND		
Sludge ^[60]	Spain	ng/g	ND		ND	N.D			ND		
Sludge ^[60]	Spain	ng/g	ND		ND	>LoQ			ND		
Sludge ^[60]	Spain	ng/g	N.D		ND	129.7			39.8		

Table 2.3: Past data of BTR and derivatives from relevant matrices for this project.

Matrix	Location	Unit	BTR	TTR	1-OH-BTR	5-A-BTR	XTR	5-Cl-BTR	BTR-COOH
Tire ^[39]	Norway	ng/L	41.7	335	6.68	266	4.12	7.17	27.8
Tire ^[39] (Studd season)	Norway	ng/L	82.1	761	67.3	536	14.1	8.51	14.1
Surface Water ^[30]	China	ng/L	249±366	10.2±15.3	0.04±0.15		1.05±1.48	2.12±3.12	
Groundwater ^[30]	China	ng/L	75.6±157	2.69±3.55	ND		4.94±6.81	1.87±2.17	
Stormwater ^[30]	China	ng/L	92±114	18±22	ND		2.03±2.1	7.28±8.77	
Suspended Particles ^[30]	China	ng/L	1.47±1.70	0.08±0.13	ND		0.02±0.03	0.15±0.28	
Tap water ^[49] (Surface water source)	China	ng/L	13.3	1.6	N.D			N.D	
Tap water ^[49] (Groundwater source)	China	ng/L	5.5	N.D	N.D				N.D
Innfluent waste ^[53] water	Malaysia	ng/L	48±130	1.3±2.8		11±18	1.5±2.3		
Effluent waste ^[53] water	Malaysia	ng/L	850±1500	60±55	2.4±2.7		26±22	1.7±1.2	
Innfluent waste ^[53] water	Sri Lanka	ng/L	1200±1600	340±450	7.1±7.9		2.1±6.9	23±28	
Effluent waste ^[53] water	Sri Lanka	ng/L	590±450	240±280	2.5±2.8		22±41	27±33	
River (dry season) ^[55]	China	ng/L	480±313					72±35	
River (wet season) ^[55]	China	ng/L	186±141					46±37	
Stormwater ^[58]	Multiple	µg/L	0.45	0.43					
Rainwater ^[61] (from traffic routes)	Poland	ng/L	286.8±5.2	415.7±6.5				24 321.6±177.5	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	379.6±4.9	ND				891.0±5.9	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	2748.4±17.3	2016.8±30.1				4474.2±46	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	10 604.6±105.7	6 023.6±101.6				6355.7±45.3	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	359.8±7.7	1572.6±29.3				2167.9±29.7	

Table 2.3: Past data of BTR and derivatives from relevant matrices for this project.

Matrix	Location	Unit	BTR	TTR	1-OH-BTR	5-A-BTR	XTR	5-Cl-BTR	BTR-COOH
Rainwater ^[61] (from traffic routes)	Poland	ng/L	383±6.2	3462.9±41				3027.3±61.4	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	753.8±8.7	3553±27.3				36 132±377.4	4
Rainwater ^[61] (from traffic routes)	Poland	ng/L	600.1±25.9	2911.5±39.9				1247.4±22.7	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	309.4±10.1	1269.6±12.7				1653.1±21.9	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	ND	ND				5311.p±61	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	1795.2±17.7	2020.7±51.2				1313.9±47.4	
Rainwater ^[61] (from traffic routes)	Poland	ng/L	319±2.1	1265.7±19.4				2332±31.9	
Tire ^[59]	Australia	µg/L	5.5						
Tire ^[59]	Australia	µg/L	12						
Tire ^[59]	Australia	µg/L	10						
Tire ^[59]	Australia	µg/L	42						
Sludge ^[60]	Spain	ng/g	24.4	69.9			N.D	2.3	
Sludge ^[60]	Spain	ng/g	27.1	59.5			N.D	ND	
Sludge ^[60]	Spain	ng/g	N.D	4.3			ND	ND	
Sludge ^[60]	Spain	ng/g	1.5	9.8			N.D	N.D	
Sludge ^[60]	Spain	ng/g	11.3	62.6			N.D	ND	

2.6 Instrumental

For almost all types of target analysis, sample preparation is necessary. This involves the four main steps for target analysis: sampling, extracting, preparation for analysis and interpretation of the data. The type of preparation needed is determined by numerous factors, one being what target analyte is of interests. One must consider what type of matrix this analyte is found in, and also what other compounds in the matrix can affect the result, and in which way. Other important factors are the sampling techniques, storage and type of extraction. Sampling techniques must be fitted for the matrix, type of storage must not destroy the target analyte, like for example freezing. Extraction types should be chosen to minimize possible contamination and to preserve the integrity of the sample. Some common extraction techniques is solid phase extraction and liquid liquid extraction. To determine what type of preparation, one must consider what type of sample matrix is analysed, and also the analyte. The phrase "like dissolve like" is a good description for determining what solvent to use. Using chlorobenzene as solvent in analysis of chlorinated pesticides or n-hexane for non-lipophilic compounds is one example^[62].

2.6.1 Solid phase extraction

Solid phase extraction (SPE) is a chromatographic technique used to separate and purify analytes from mixtures. The main drive is a solvent passing through a solid material in a column. This material has sorbent abilities. Depending on what is the target analyte, different package material and solvent is used, choosing which of these to use depends on the target analytes properties like size, polarity or functional groups. There are 2 ways for this to happen. The first method is when analyte is retained and other matrix components does not, called the bind and elute strategy. The analyte then must be washed out with a strong solvent. The other method is the reverse, where the analyte is not retained, but the other components is. This is called the removal or trapping strategy^[63].

There are two mechanism on how the extraction happens in SPE. It can either be through adsorption or ion exchange. Adsorption is used when the target analyte has either some level of polarity or is neutral. By using a polar sorbent, the least polar components will elute first, but polar components will adsorb to the material. The other separation mechanism is ion exchange. This mechanism has two sub groups, cation and anion ion exchange, separating a target analyte based on if it is positively charged or negatively. One other option here is to combine these two mechanism. This method is commonly used to separate mixtures acidic, basic and neutral compounds^[63]

There are 4 steps for SPE:

1. Wash the cartridge with a mild buffer or water. This is done to remove any potential residues that are left after the manufacturing.
2. Load the sample through the cartridge.
3. Wash the cartridge with suitable solvent. This is done to remove any potential impurities adsorbed in the material.
4. Elute the cartridge with an eluent that will remove the target analyte from cartridge.

These steps is visualised in figure 2.9

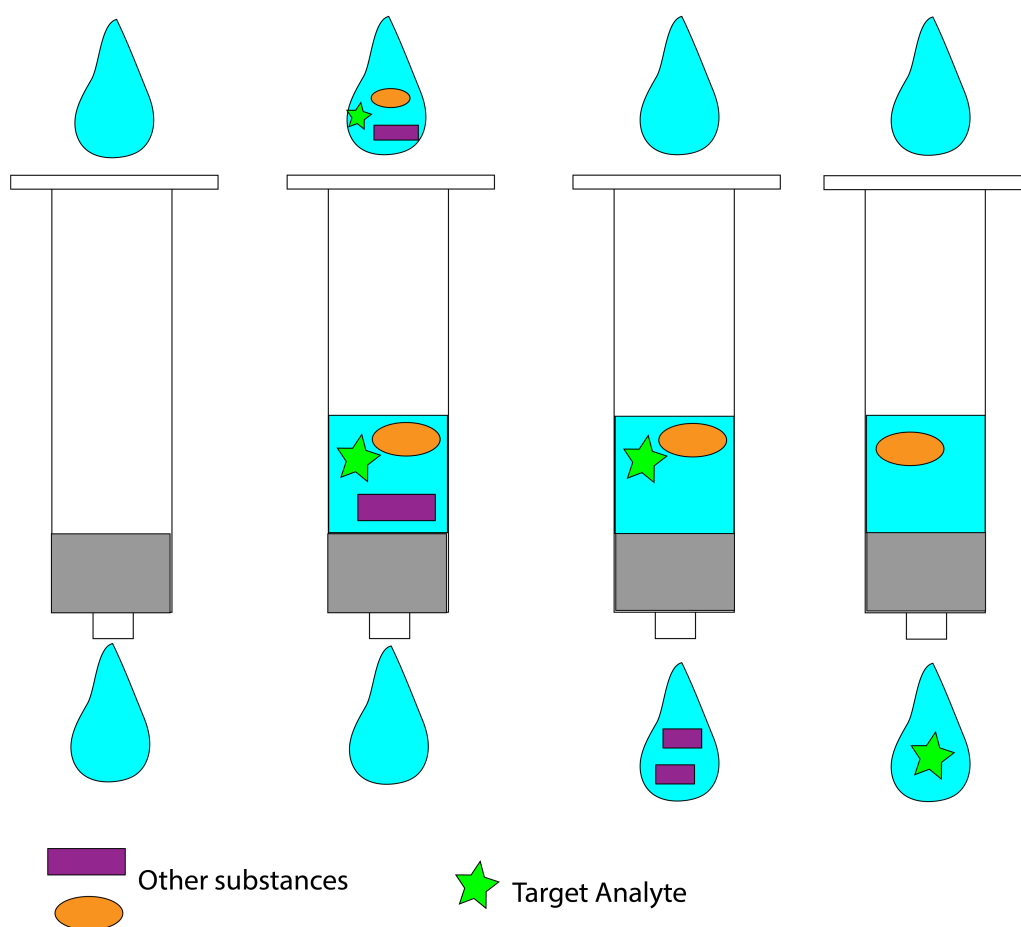


Figure 2.9: A figure showing the four common steps of a SPE procedure with washing, loading, washing again and eluting the cartridge.

In environmental chemistry, SPE is used to isolate analytes from different types of matrices like, soil, air and water. A common use for SPE is for analysing analytes at trace level, some examples are polyaromatic hydrocarbons, persistent organic pollutants and pesticides^[64]. It is also used in other types of analysis, like food and forensic. As with environmental usage, its main goal is to simplify the target analytes matrices^[65].

One advantage for SPE, compared to other extraction methods, is its high selectivity and sensitivity. SPE can isolate specific target analytes from different matrices, something that is useful for when samples have a high matrix effect, other compounds interfering with response of target analyte.

Since SPE is a chromatographic technique, different solid phase can be chosen to extract certain analytes, either by filtering away unwanted contaminants or only keeping the target analyte, before it is removed later^[66]. It can change the target analyte from original matrix to a more simple matrix by removing possible contaminants^[67]. Sensitivity is useful when the target analyte can be found at a low concentration, like in trace analysis. This will increase the signal to noise ratio later on in the analysis step^[67]. Since SPE does not need any special equipment or special materials, other than the cartridge itself, the cost is low. One disadvantage about this is time. SPE can be time consuming, and this may use a lot of solvent^[64]. Another advantage is SPE's ability to increase a concentration. During the loading step, the amount of solvent does not have much effect, mostly on run time, but during the final step, when removing the target analyte, a lower volume can be used^[67].

Despite the advantages, there are also some limitation for SPE. One problem is heavily contaminated samples. If the target analyte's concentration in sample is too high, some of the TA will not be adsorbed in the material and run trough with the rest of the other residues and solvent, the sorbent material will be over saturated. One solution here is diluting the sample into a concentration not too much for the SPE cartridge, but not deluded too much that the TA cannot be detected.

Another problem with SPE is suspended particles. Due to the size of a SPE column, enough suspended particles will be a clogging problem. These particles will be to large to go trough the solid material and stay on top of it. This will affect the flow rate, making the process slower than it should be. The fix for this problem is to remove suspended particles before the SPE process^[68].

The solvent flow trough the cartridge will affect the recovery rate of the sample. If the flow rate is too high, some of the target analyte may not be extracted properly, and be washed away with the rest of the contaminants. The solution is to use a slow flow rate, but the problem then is that the process is time consuming.

One solution to these problems are to use an internal standard as early in the process as possible. This will correct possible errors mentioned above, and correct the end result.

2.6.2 Chromatography

Chromatography is an analysing technique where a mobile phase (MP) carries analytes trough a stationary phase (SP), usually found in a column. The analyte in the MP will travel trough the SP at different speed, depending on their affinity with the SP. The affinity is affected by different parameters like temperature and pH. The 2 major branches in chromatography (GC) is gas and liquid chromatography (LC)^[69]. One main difference between those two is that GC uses a gas as the MP and LC uses a liquid as MP. For analysis of BTH/BTR both these techniques are possible, BTH/BTR are suited for booth these techniques. GC works for BTH/BTR specially when coupled with a flame photometric detector^[70]. THis detector has a good sensitivity for the thiol group. Some major difficulties could be oxidation and column bleeding because of polar group^{[71][72]}.

A common technique is to couple a mass spectrometer to LC, LC-MS, because of its performance and robustness^[69]. LC is common technique for trace analysis^[73]. GC can have problem when detecting in ng/mL area, BTH/BTR can be expected to be found in this area, earlier studies shown in table 2.2 and table 2.3, where many similar matrices shows concentrations in ng/ml or lower.

2.7 LC-MS

2.7.1 Liquid chromatography

For BTH/BTR liquid chromatography is a good method, specially when analysing with its more polar derivatives. In LC a mobile phase with the analyte and solvent is pumped through a column with a material. The MP is usually 2 different solvents, one organic phase and one water phase. The MP is chosen depending on the target analyte, its polarity or other chemical attributes^[74]. LC can analyse many different matrices, from environmental matrices, like soil or water, to biological, blood and saliva^[75]. LC has a better sensitivity, Selectivity and precision with BTH/BTR. One method of LC that is suited for BTH/BTR and derivatives is reverse-phase LC. In Reverse phase LC, a non-polar column, for example C18, is used with a polar MP. Because of polar derivatives, a polar MP will have good affinity with transferring the analytes through the column^[74].

LC can be coupled with different detectors to identify and quantify the separated analytes. Common detectors include UV-vis, fluorescence, mass spectrometer, and refractive index detectors. One popular detector to use with LC is the mass spectroscopic. A mass spectroscopic (MS) instrument containing 3 parts: a ionization source, a mass filter and a detector^[69]. This technique can give information on structure (qualitative information), molecular mass and concentration (quantitative)^[76]. The main mechanism for MS to analyse is by creating ions from the analyte compound. By charging the molecule with either a positive or negative charge, creating a cation/anion. This ion travels through an analyzer, and makes contact with a detector. By making contact, a signal is generated and a computer records this. A MS usually shows the relative abundance of ions, according to the mass over charge (m/Z)^[76].

2.7.2 Electrospray ionization

LC will only separate analytes, that technique cannot detect them, so a popular detector to couple LC with is mass spectrometer. Electrospray ionization is a method where molecular ions and adducts are formed by applying a voltage to the analyte in liquid form. The analyte then is ejected in a jet where it is forming a spray of charged droplets. The solvent then evaporates, and eventually the droplets dissociates into charged ions^[74]. ESI is suited for polar compounds^[77].

To filter away other components in a matrix, a triple quadrupole can be used. A quadrupole is 4 charged cylinders, where each cylinder is placed in a formation of a square. Through 2 cylinders, AC is run through, and DC is running through the two others. Two of the cylinders are positively charged, and the other are negatively charged. If a certain amount of voltage runs through these cylinders, it is possible to only let specific charged ions through. To increase this selectivity, three quadrupole can be placed in a series, all three with different tasks^[74].

ESI has high sensitivity, which lets it detect at low concentration, suited for trace analysis. It is also a soft ionization technique. This means the target analyte is not fragmented. The fragmentation does not happen at the ESI, but in the triple quadrupole. Since no fragmentation should happen at the ESI, a more accurate determination and identification will happen. ESI is compatible with LC, allowing a direct coupling with the LC to ESI during analysis^[69].

One disadvantage with ESI is matrix effect. Target analytes' signal of ions can be enhanced or suppressed, by other compounds that was co-extracted with the TA^[78]. Matrix effect comes from the ionization, because it is done as a atmospheric pressure ionization^[79]. At this pressure level, more contaminants can also be ionized^[80]. One way to eliminate this problem is to analyse for 2 different fragmentations of the same molecule. Two different transition stages is analysed to

differentiate between possible interfering peaks^[81]. This and retention time makes it easy to detect each compound, and not mistake them for other compound that is not the TA.

2.7.3 Internal standard method

LC-MS alone does not give the concentration of a compound, only the area of the signal. One method to "translate" this signal into concentration is the internal standards method. For this method, an internal standard (IS) is added to the target analytes (TA) matrix. This is done as early as possible, so any loss of target analyte should be the same with IS. The IS itself is chosen by different qualities. It should be a compound with the same structure and chemical properties as the TA, but not the same, or not found in nature. inert, high purity^[82]. Common solution is compounds with deuterium instead of hydrogen, or carbon-13 instead of normal carbon-12. These compound with these isotopes will have different weight, different m/Z, something the MS will detect^[74].

As with TA, LC-MS does not give the concentration of IS directly, but by making a standard curve from known concentration of both TA and IS, a relationship between area and concentration can be determined. By using least square method on a certain amount of points^[83], a curve can be found with the following formula:

$$Y = aX + b \quad (2.1)$$

For this, the y is area of TA divided by area of IS, a is concentration of TA divided by concentration of IS. Knowing both a from the standard curve, and how much IS is added to a sample, the concentration of TA in a sample can be determined. The concentration of each standards must be in the linear range^[69].

2.8 Quality assurance and quality control

Limit of detection (LoD) is the lowest concentration where a analyte can be detected, without being mistaken for background noise. Limit of quantification (LoQ) is the lowest level of signal where a analyte can be quantified. LoQ is usually defined a signal at or above 10 times the background level, 10 times the signal to noise ratio. LoD can then be defined as 3 times the signal to noise ratio. The relation between LoD and LoQ is as follow:

$$LoD = \frac{3}{10} \cdot LoQ \quad (2.2)$$

R^2 is coefficient of determination. It is a quantity of measure for variance of variables in a regression model. R^2 is defined by:

$$R^2 = \frac{\sum (\hat{y}_i - \bar{y})^2}{\sum (y_i - \bar{y})^2} \quad (2.3)$$

R^2 goes from 0 to 1, where $R^2 \approx 0$ means a poor fit of data in the regression, and $R^2 \approx 1$ is a good fit for the data^[84]. Lower R^2 can mean harder to detect lower concentration, is a problem for trace analysis

Recovery is found by using:

$$Recovery(\%) = \frac{C_S}{C_M} \cdot 100\% \quad (2.4)$$

C_S is signal of spiked sample and C_M is the signal of matrix matched sample. Recovery is a mean to determine the accuracy^[85].

Absolute recover is a mean to determine how much is lost during extraction.

Relative standard deviation, measure of standard deviation from the mean. Closer to 0 is better, means better precision^[86]

$$RSD\% = \frac{SD}{Mean} = \frac{\sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2}}{\bar{x}} \cdot 100\% \quad (2.5)$$

Where \bar{x} is the mean value and N is the total number of samples.

If the mean value is higher than the median, the distribution is positively skewed. If the mean value is less than the median, then the distribution is negatively skewed^[87].

2.8.1 Matrix effect

Matrix effect is a result of other unwanted components co-eluting with the TA. ME can be determined by:

$$ME = \left(\frac{A_{Mm}}{A_S} - 1 \right) \times 100\% \quad (2.6)$$

Where A_{Mm} is the area of a matrix matched sample, A_S is the area of pure solvent^[88]. If the ME is less than 100%, it shows suppression of TA signal. If the ME is over 100%, there is enhancement of TA signal^[89]. One reason for suppression is theorised to be because of limited charge of droplets on a limited space^[79]. Another explanation can be competition between co-eluting molecules with available charge, precipitation of analyte, change in surface viscosity of spray droplet or neutralisation of charge on droplet by co-elluents^[90]. A reason for ion enhancements is still unknown or is caused by co-elluents also, but they are increasing the signal. Matrix components can increase solubility of analyte, in which they are increasing signal detected^[91]

3 Method

Sample preparation, extraction and analysis was adapted from Wang et al. 2016^[92]^[93].

A total of 127 samples were analysed during this thesis, divided into two batches, 73 samples in batch 1 and 56 samples in batch 2. 64 samples were collected from tunnel, and 63 were collected from columns made to represent possible filter types. These samples were collected between October 2021 and October 2022. All details about each samples can be seen in table 6.3 in Appendix.

3.1 Chemicals

3.1.1 Standards

Target analyte (TA) mix was made from standards of BTH ($\geq 97\%$), 2-Me-BTH ($\geq 97\%$), 2-A-BTH (97%), 2-OH-BTH (98%), 2-Cl-BTH ($\geq 97\%$), MTBT (97%), 2-M-BTH (CPR), 2-SCNMeS-BTH ($\geq 97\%$), BTR ($\geq 98\%$), TTR ($\geq 90\%$), 1-OH-BTR ($\geq 97\%$), 5-A-BTR (CPR), XTR ($\geq 99\%$), 5-Cl-BTR (99%) and BTR-COOH (99%). All these were purchased from Sigma-Aldrich (Steinem, Germany). These compounds were mixed into a mix with a concentration at 1 $\mu\text{g}/\text{mL}$, with water:MeOH (1:1) as solvent. These were made into a calibration curve, consisting of 0.01, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25 and 50 ng/mL .

3.1.2 Internal standards

The internal standards was BTR-d4 (10 000 ng/mL in acetone) and 5-Me-BTR-d6 (10 000 ng/mL in acetone), also purchased from Sigma-Aldrich (Steinem, Germany) was used as internal standards. IS mix was made into a concentration of 2 ng/mL .

3.2 Sampling

Bjørnegårdtunnelen was chosen as the main sampling site because of its pilot treatment plant. Grillstadtunnelen was chosen as sampling site because it is geographical close to where the experimental and analytical work was done. The samples from this location was mainly used as a comparison to the samples from Bjørnegårdtunnelen.

The column experiment was set up by letting sedimented wash water run trough columns filled with different materials, one example of columns can be seen in figure 3.1. The water ran trough these column continuous, and sample was taken at specific hours. These hours depends on the batch, batch 1 started with sampling after 3 hours, then every 24 hour after this. Batch 2 also started at 3 hours after experiment started, but the interval was 16 hours between each sampling.

Samples was collected after the experiment after they had run trough each material. The container was then filtered trough a filter with 0.45 μm pores. This created two types of samples, particulate fraction on the filter, and water fraction in a tube. Example of column can be seen in figure 3.1. The filters was freeze dried for 24 hours, before they were ready for further treatment, mentioned below. Dissolved fraction samples was collected in 50 ml tubes. Samples were taken from same type of column as particulate fraction samples.

3.3 Particulate fraction

Each filter was placed in a 15 ml ependorf-tube. 5 ml of acidified MeOH/ H_2O ($\text{pH} < 3$, acidified with HCl) was added, with 20 ng/mL of internal standard. Each sample was vortex mixed for 1 minute, and then the samples was placed in a ultra sonic bath for 45 minutes at 35 $^\circ\text{C}$. After that,

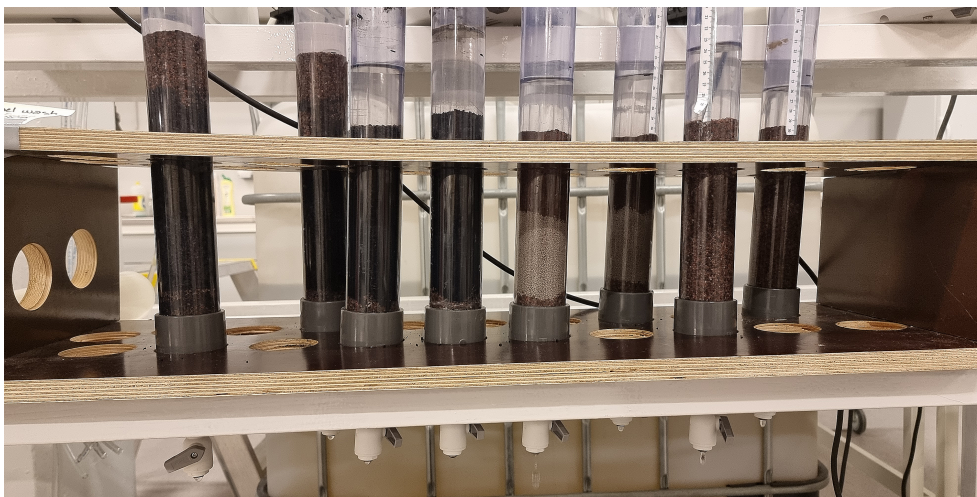


Figure 3.1: Example of column

the samples was centrifuged for 5 minutes at 3 000 rpm. Each sample was transferred to a 50 ml tubes, before each tubes was filled up to 50 ml with acidified water ($\text{pH} < 3$, acidified with HCl). From here, the samples was extracted in the same way as with dissolved fraction.

3.4 Dissolved fraction

20 ng/mL of internal standard was added to the dissolved samples, which was in 50 ml tubes, then vortex mixed for one minute. For SPE cartridges, clear strata X-RP syringes was used. Each SPE cartridge was first washed with 10 ml of methanol, then 10 ml of acidified water, before the sample was added to their corresponding cartridges. After each sample had been ran trough the cartridges, 10 ml of acidified water was added to the cartridges. The SPE-manifold then was dried with a vacuum. After the package material was noticeable dry, each cartridge was then placed into 15 ml endendorf tubes. To check if the cartridge was dry, the syringe was lightly tapped to the surface, and if the material was like sand, it was dry. 10 ml of MeOH:ACN (1:1) ran trough the cartridge and into the tubes. The tubes were placed into a turbovap at 45 °C. The tubes was there until all solvent, but around 0.25 ml of liquid, was evaporated. The liquid left was diluted to 1 ml with MeOH:H₂O (1:1, 1% fulvic acid), before the liquid was transferred to chromatography vials.

3.5 Chromatography

For analysis, LC-MS/MS was used. A ACQUITY UPLC from Waters was used with Kinetex C18 column (30 x 2.1 mm, 1.3 μm , 100 Å phenomenex) which was connected to a phenomenex guard column (C18). The liquid phase was water (0.1%) formic acid and acetonitrile (0.1 % formic acid) as organic phase with a flow rate at 0.4 $\mu\text{L}/\text{min}$ and a injection volume at 5 μL . Mobile phase gradient can be seen in table 3.1

Table 3.1: Mobile phase gradient

Time [min]	Flow[mL/min]	% water phase	% organic phase	Step
Init	0.4	90	10	Init
2.0	0.4	0	100	8
4.5	0.4	0	100	6
4.5	0.4	90	10	6

The detector was a tandem spectrometric system, a Waters Xevo TQ-S, a triple quadrupole mass analyser coupled with Zspray ESI set to positive mode. This ESI had a capillary at 3.0 kV, a cone at 25 V. The source offset was at 50 V, a desolvation temperature was 350 °C, source temperature at 150 °C, desolvation at 800 L/Hr, cone with 150 L/Hr and nebulizer at 6 bar.

Between every 12 to 14th sample a series of: pure solvent (Me:H₂O), 10 ng/mL standard and pure solvent was analysed.

3.6 Data processing

Raw chromatogram data was analysed with MassLynx software. Linear calibration was used to create calibration curve, with calibration from internal standard. All calculation and graphs was made with Microsoft's Excell.

3.7 QA/QC

For this experiment, HPLC graded water was used. This experiment spanned 2 different analyses, and 4 different batches of extraction, so 4 different procedure blanks was made. These was made by extracting pure water as if they were a water fraction sample. Table 3.2 shows all analytes quantification and qualification transition, with their collision voltage. This was used to identify and quantify each molecule.

Table 3.2: Each analyte and both their quantification transition and qualification transition. Collision voltage is shown in parenthesis, and cone voltage

Compound	Quantification transition (Collision Energy (V))	Qualification transition (Collision Energy (V))	Cone Voltage (V)
BTR	120 → 65 (16)	120 → 92 (14)	28
TTR	134.2 → 79 (18)	134.2 → 77 (16)	18
5-A-BTR	135 → 107 (16)	135 → 80 (16)	42
BTH	136 → 109 (18)	136 → 65 (22)	44
1-OH-BTR	136 → 91 (18)	136 → 119 (14)	24
XTR	148 → 93 (16)	148 → 77 (24)	16
2-Me-BTH	150 → 109.1 (20)	150 → 65.1 (32)	35
2-A-BTH	151 → 124 (18)	151 → 109 (20)	28
2-OH-BTH	152 → 80 (22)	152 → 124 (16)	8
5-Cl-BTR	154 → 99 (22)	154 → 74 (24)	24
BTR-COOH	164 → 80 (18)	164 → 108 (18)	8
2-S-BTH	168 → 135 (20)	168 → 92 (20)	8
2-Cl-BTH	170 → 134.8 (24)	170 → 109.1 (22)	26
2-Me-S-BTH	182 → 167 (22)	182 → 109 (32)	26
2-M-BTH	221 → 177 (18)	221 → 109 (30)	8
2-SCNMeS-BTH	239 → 136 (26)	239 → 180 (14)	8
BTR-d4	124 → 69 (18)	124 → 96 (16)	38
5-Me-BTR-d6	136.1 → 95 (22)		24

3.7.1 Spiked and matrix matched samples

5 ng/mL and 10 ng/mL of TA were added to 50 ml tubes filled with acidified water. These spiked samples were made in 3 parallel for each concentration. These samples were extracted as explained

for water fraction sample. 5 ng/mL and 10 ng/mL matrix matched samples were also made. For these, 50 mL of water were filled into tubes, before the where extracted as described for water samples. Before the solvent was transferred to chromatographic vials, 5 or 10 ng/mL of TA and 20 ng/mL of IS were added to the vial. These samples were made in 2 parallels.

4 Result and discussion

4.1 Valiation

Method used for analysis was validated by using recoveries, relative standard deviations, procedure blank, matrix effect, LoD and LoQ. To validate the analysis method is an important step to assure that the method is reliable. This step is aimed to show that this method is suitable for its intended use and the accuracy and precision of the method is in the analyte's expected concentration range^[86]. Recoveries was calculated at two different concentration levels, 5 ng/mL and 10 ng/mL.

The absolute recovery was found to be in the range of 10-80%, with some exception, some under 10%. 2 of absolute recoveries has a recovery over 900% and 5 000%, but both these having almost zero response with the internal standard. All values for recoveries can be seen in table 4.1 and table 4.2. In the same tables, RSD can be seen. This is calculated with formula 2.5. RSD tells about the standard deviation from the mean for a value. This means a number closer to 0 is less variation for the set. For 10 ng/mL, all samples are either around 1% or under. This is good, it shows good accuracy for the 10 ng/mL recovery data. The 5 ng/mL recoveries showed a larger range, with numbers from 1% to 100%. This can show poor accuracy for these recovery samples on the other hand has a larger range, some values even been seen at 100%. This shows that the 5 ng/mL recovery samples have a lower accuracy than 10 ng/mL.

A total of 4 procedure blanks were made for this thesis, because of sample extraction was done in multiple batches, Procedure blank 1 had the highest concentration between all the blanks at 4 ng/mL, and it has a higher concentration than 3 of the samples from the batch it was made. For the second procedure blank, no other sample from its batch was lower. The third procedure blank showed a higher concentration than two other samples. The fourth procedure blank was made along with the extraction for all samples from batch 2, and this had only one sample lower than itself. This is for total concentration. Total, 6 samples showed a lower concentration than the procedure blank, meaning that the rest of the 95% of samples was higher than the procedure blanks. One explanation could be some column bleeding, but the following paragraph can tell that this does not have any major effect.

A mixture between water and methanol was made before analysis to represent pure solvent. This was made to run between a series of samples, along with one of the standards. In the end, between every 12-14th sample, a series consisting of pure solvent, 10 ng/mL standard and pure solvent was ran. This was done to check for any problem with the instrument drift or carry over problems. None showed any significant problems. The pure solvent samples show little signal and the standard samples was around the same as the standard signal used for calibration curve, and around the same when compared to each other.

The analytical method chosen for BTH/BTR analysis was LC-MC. GC is a contender for analysis method, but with 127 samples, the experiment run time on its own would be a problem. One article by Naccarato et al^[85] shows a BTH/BTR experiment with GC, and it has a run time at 35 minutes, compared to what was done in this experiment, with an analysis time of 5 minutes per sample. Another problem would be the derivatives, not all are suited for GC, but could be with modification.

Recoveries for water fraction is found in table 4.1. 5 ng/mL varies between 40% to 85%, with 2 recoveries under 7% and one at almost 150%. 10 ng/mL has recoveries in the range from 65% to 105%, but also with some exceptions. 3 recoveries is found under 6%. Almost all recoveries in 10 ng/mL has a closer percentage to 100%, but BTH, 2-Me-S-BTH and 2-M-BTH shows a higher recovery in 5 ng/mL.

The particulate fraction, seen in table 4.2, shows that the 5 ng/mL recoveries is found between 10 and 60%, with one under 0.5% and another at 84%. For 10 ng/mL the recoveries are found between 40 and 70%, but with one at 2.42%, and two over 900%. Those two over 900% are 2-S-BTR and 2-Cl-BTR and they have such high percentage because of their matrix matched samples had low signal. Both samples at 10 ng/mL for both these compounds have a low signal, the highest is at 300, and lowest at 0. In comparison, the average signal of all matrix matched samples is around 70 000. This is not a number one really can directly compare, but it is just to show how low the signal was. For 5 ng/mL in matrix matched, the range is from 4.4 to 6 000. Those 2 samples was also the only 2 with an RSD higher than 1% for 10 ng/mL, showing these recoveries may not be representable for those compound.

Table 4.1: Recovery and RSD for water fraction samples, values shown in percentages

Compound	Absolute recovery 5 ng/mL (%)	Absolute recovery 10 ng/mL (%)	% RSD 5 ng/mL (%)	%RSD 10 ng/mL (%)
BTR	146.57	109.73	105.38	1.07
TTR	87.10	102.68	62.62	0.69
5-A-BTR	4.61	71.30	3.31	0.04
BTH	81.62	3.71	58.68	1.20
1-OH-BTR	45.19	123.33	32.49	0.63
XTR	59.50	64.85	42.78	0.77
2-Me-BTH	48.46	86.55	34.84	0.65
2-NH2-BTH	59.04	79.56	42.45	0.87
2-OH-BTH	54.88	67.11	39.46	0.92
5-Cl-BTR	59.79	89.25	42.99	0.85
BTR-COOH	66.03	94.74	47.48	0.98
2-S-BTH	1.69	87.72	1.22	0.00
2-Cl-BTH	6.30	100.82	4.53	0.06
2-Me-S-BTH	44.34	0.47	31.88	0.64
2-M-BTH	58.68	5.90	42.19	0.79
2-SCNMeS-BTH	52.88	66.17	38.02	0.73

Table 4.2: Recovery and RSD for particulate fraction samples, values shown in %

Compound	Absolute	Absolute	%RSD	%RSD
	recovery 5 ng/mL (%)	recovery 10 ng/mL (%)	5 ng/mL (%)	10 ng/mL (%)
BTR	83.54	66.10	93.03	0.64
TTR	53.55	71.99	59.64	0.69
5-A-BTR	11.38	2.42	12.67	0.02
BTH	56.33	47.47	62.72	0.46
1-OH-BTR	45.81	53.09	51.01	0.51
XTR	48.04	55.69	53.49	0.54
2-Me-BTH	43.61	45.33	48.57	0.44
2-NH2-BTH	44.32	62.19	49.35	0.60
2-OH-BTH	56.29	43.44	62.69	0.42
5-Cl-BTR	46.78	55.61	52.09	0.54
BTR-COOH	44.14	55.96	49.16	0.54
2-S-BTH	0.47	928.58	0.52	8.96
2-Cl-BTH	23.69	5 464.05	26.38	52.73
2-Me-S-BTH	35.25	34.49	39.25	0.33
2-M-BTH	59.76	63.34	66.54	0.61
2-SCNMeS-BTH	45.35	51.65	50.51	0.50

2-Cl-BTH having a low response was also experienced in this article by Wang et al^[93]. This article also shows problems with response of 2-Cl-BTH. No explanation was presented here. This could be that 2-Cl-BTH is not a stable molecule, but no sources was found to confirm or deny this. 2-S-BTH also had low response with matrix matched samples. This article by Felis et al^[41] suggest that 2-S-BTH is not a stable molecule, but 2-S-Me-BTH, which can be degradation product of 2-S-BTH, is more stable in water environment. If this is true, this could explain the low recovery. 2-Me-S-BTH had both recoveries at around 35% and if 2-S-BTH is not stable, this number would not be only from 2-Me-S-BTH standard, but also from 2-S-BTH standard.

An article by Wang et al^[94] talks about temperature for BTH/BTR having an effect on the recovery. The articles describes an experiment where BTH/BTR recoveries was analysed at different temperatures. 80 °C was the temperature that showed best recovery. 2-Me-S-BTH was one exception, its recovery only increased with the increasing temperature. It had its highest recovery percentage at 160 °C, which was highest temperature tested^[94]. This experiment had no temperature control, so the extraction was done at room temperature. performing the extraction at a higher temperature could increase the recovery.

One article by Wang et al^[94] found similar recoveries values to those presented in table 4.1 and table 4.2, while one other article by Asimakopoulos^[95] shows recoveries closer to 100%. This shows that the recoveries found in this thesis is realistic values, but there is room for improvement.

4.1.1 RSD

RSD is a way to measure repeatability and precision^[86]. The lower the percentage is, the more precise the values are. As formula 2.5 says, RSD is a way to see how much each point's standard deviation diverge from the mean. As with recoveries, there were two different concentration used to determine RSD. RSD can be seen in both table 4.1 and table 4.2. 5 ng/mL shows a larger

percentage than 10 ng/mL, meaning the 10 ng/mL recoveries shows a better precision. 5 ng/mL also had a larger range for RSD than 10 ng/mL. The latter all was under 1% or around that, 2-Cl-BTH in PF had a RSD at 53%. comment 2-S-BTH shows a lower RSD for both fraction, compared to its RSD at 10 ng/mL. Comparison

4.2 LoD and LoQ

Table 4.3: LoD and LoD from both batch of analysis. LoD and LoQ shown for 50 ml samples, with the unit ng/mL. LoD₅₀ and LoQ₅₀ was determined by equation 4.1 and equation 4.2.

	LoD ₁	LoQ ₁	LoD ₂	LoQ ₂
BTR	0.003	0.01	0.006	0.02
TTR	0.0003	0.001	0.00006	0.0002
5-A-BTR	0.003	0.01	0.0006	0.002
BTH	0.06	0.2	0.003	0.01
1-OH-BTR	0.003	0.01	0.006	0.002
XTR	0.006	0.02	0.00006	0.0002
2-Me-BTH	0.003	0.02	0.0003	0.001
2-A-BTH	0.006	0.01	0.0006	0.002
2-OH-BTH	0.003	0.01	0.006	0.02
5-Cl-BTR	0.0003	0.001	0.00006	0.0002
BTR-COOH	0.03	0.1	0.006	0.02
2-S-BTH	0.0015	0.005	0.0006	0.002
2-Cl-BTH	0.015	0.05	0.003	0.01
2-Me-S-BTH	0.0006	0.002	0.0003	0.001
2-M-BTH	0.0003	0.001	0.00006	0.0002
2-SCNMeS-BTH	0.0006	0.002	0.0003	0.001

Determination of LoD₁ and LoD₂ was determined by using equation 2.2, but that equation calculate LoD for 1 ml and original volume of samples was at 50 ml. Therefore the following equation was used to determine LoD₂ or LoD₅₀:

$$LoD_{50ml} = LoD_{1ml} \cdot \frac{0.001L}{0.05L} \quad (4.1)$$

Where LoD₁ is LoD for 1 ml. The same calculation was done with LoQ, to determine LoQ₂ or LoQ₅₀:

$$LoQ_{50ml} = LoQ_{1ml} \cdot \frac{0.001L}{0.05L} \quad (4.2)$$

Table 4.3 shows both LoDs and LoQs for all compound in both batches. Batch 1 LoD shows a 2 to 20 times higher concentration than batch 2. The largest difference is between XTR, between batch 1 and 2, where the batch 1 is 100 times larger than what is detected in batch 2.

Highest LoD detected was with BTH and BTR-COOH, with 0.06 and 0.03 ng/mL respectively. Both of these are from batch 1. These numbers show that all concentration over 0.2 ng/mL in this experiment is quantifiable, and all concentration over 0.06 ng/mL is detectable. The lowest was LoD found was from batch 2. The compounds was TTR, XTR, 5-Cl-BTR and 2-M-BTH, all had a LoD at 0.00006 ng/mL.

One study by Wang et al^[94] shows LoD lower than was found here. At most some LoD found here was 10 times higher than they found. Another study by Herrero et al^[96] found LoDs a little

higher than those presented in table 4.3. One article by Li et al^[97] shows similar LoDs with those detected in batch 1, but another article by Jover et al^[98] has similar LoDs with batch 2. Since LoQ is calculated from LoD here, the same stated over with LoD goes with those LoQ found int those studies/articles. This shows that both batches LoD and LoQ are in range of what's normally found for BTH/BTR^[97].

4.3 The Matrix effect chapter

Table 4.4: Matrix effect (ME) for all compounds in water fraction and particular fraction, values shown in %

	ME _{WF} (%)	PF (%)
BTR	81.43	1 344.55
TTR	6.23	3.62
5-A-BTR	749.46	319.36
BTH	-0.06	0.19
1-OH-BTR	2.66	6.10
XTR	3.78	8.15
2-Me-BTH	10.02	16.65
2-A-BTH	0.83	3.52
2-OH-BTH	0.03	0.43
5-Cl-BTR	8.62	31.07
BTR-COOH	-0.01	0.47
2-S-BTH	0.85	-0.42
2-Cl-BTH	0.03	-0.03
2-Me-S-BTH	6.67	14.28
2-M-BTH	5.13	9.55
2-SCNMeS-BTH	3.58	6.25

Table 4.4 shows all ME values for both fraction. Many are below 100%, Which is signs of suppression. some are over 100%, highest at 1 300%. Since there are many under 100%, This could be a sign that the SPE had high flow rate, or too low. If the flow rate was too high, loss of TA is a result. If the flow rate is too slow, other contaminants could be retained in the cartridge with BTH/BTR, and later be eluted with BTH/BTR^[77]. In this experiment, flow rate was not controlled. Each column had around the same flow rate, but not exactly the same. To determine if flow rate was a factor on the ME detect here is not possible to say exact, but this could be a possibility because the flow rate was not controlled.

SPE has the ability to extract at low concentration, which is good for trace analysis, but this raises a problem also. Other contaminants found in the matrix has then the possibility to be co-extracted with BTH/BTR. If possible, one can choose a material in the cartridge that will only extract certain compounds, but with BTH/BTR derivatives having different chemical properties, it is impossible to find that material.

A study by Wang et al^[94] shows pH as a factor on ME. This study tested a procedure, but at different pH levels. It showed that the highest pH (pH = 9) that was tested had the highest ME. The lowest pH (pH = 3) was th pH where less ME was observed. The experiment performed in this thesis was also done at pH = 3, which could mean pH was not an important factor on the ME values.

Acetonitrile was used to extract BTH and BTR from the cartridge, ACN can lead to a higher ME

if more contaminants are trapped in the cartridge with the BTH and BTR^[94]. If more unwanted contaminants have been extracted in the cartridge, ACN will co-extract it with the BTH/BTR. These contaminants later on can affect the signal during analysis, by enhancing or suppressing the signal of TA. By using a higher flow rate in SPE, less contaminants can be extracted, but then loss of sample can be a problem.

One way to battle the ME problem is with IS. The optimal strategy is to have an IS for every compound. Optimally, the IS is added as soon as possible, so anything affecting the TA, it will also affect the IS the same way, since IS will be chemically identical as the TA.

An article by Kloepfer et al^[99] present that reducing the flow rate of mobile phase of liquid to the ESI can reduce the ME. Since this method is developed from another method, its hard to say how the flow rate was decided without knowing how this method was developed. Can only guess that the flow rate was considered when developing this method. By changing the flow rate then will not have any benefits.

Some types of compound found in wash water is non volatile compounds^[100]. If these compound was not removed during the extraction, they could be a source for ME. One article by King et al^[101] presents that non volatile compounds can lead to suppression in ESI, and from table 4.4, suppression is evident.

4.4 Results

Table 4.5 shows range, median and mean values for each compound, a visual representation of the range can be seen in figure 4.1. Median and mean are calculated with N.D. samples, set to LoD/2. The highest concentration was found for 2-OH-BTH at 471.38 ng/mL, and the second highest value was BTH at 203.84 ng/mL for particulate fraction. This was from one fresh sample. Water fraction also had 2-OH-BTH and BTH as the two highest concentration, but it was 97 and 56 ng/mL respectively. Both from the same sedimentation sample.

Table 4.5: Data from all samples, values shown in ng/mL. N.D. = Not detected and is all samples with a concentration below LoD/2.

Compound	Min value	Max value	Median	Mean
BTR	N.D.	93.42	1.66	3.10
TTR	N.D.	43.44	2.43	3.02
5-A-BTR	N.D.	1.48	0.0015	0.024
BTH	N.D.	203.84	3.51	8.11
1-OH-BTR	N.D.	24.99	0.016	0.73
XTR	0.000073	11.95	0.0089	0.26
2-Me-BTH	0.00016	11.25	0.015	0.30
2-A-BTH	N.D.	14.54	0.031	0.35
2-OH-BTH	N.D.	471.38	2.85	11.71
5-Cl-BTR	0.000048	12.72	0.020	0.28
BTR-COOH	N.D.	24.51	0.23	0.61
2-S-BTH	N.D.	3.50	0.017	0.07
2-Cl-BT	N.D.	2.66	0.032	0.11
2-Me-S-BTH	N.D.	10.05	0.076	0.38
2-M-BTH	N.D.	8.87	0.026	0.23
2-SCNMeS-BTH	N.D.	13.81	0.00075	0.28

2-Me-S-BTH has around 5.42 times higher concentration than 2-S-BTH. As mentioned in section 4.1, 2-S-BTH is not a stable molecule in water environment^[41]. This can be seen in table 4.5 where the mean value for 2-Me-S-BTH is 5.42 times higher than 2-S-BTH's mean value. The highest detected concentration for 2-Me-S-BTH is 2.87 times higher than 2-S-BTH's highest value. This can mean that 2-Me-S-BTH is not a stable molecule, compared to 2-Me-S-BTH, but another explanation could just be that the occurrence of 2-Me-S-BTH is just lower than 2-S-BTH.

By comparing the two highest concentrations from particulate fraction with past data from table 2.2, those two compounds are mainly the highest concentration there also. That table show values in mean values, and the mean value of BTH and 2-OH-BTH is 8.11 and 11.71 ng/mL respectively. All the mean values of BTH and 2-OH-BTH in that table has a lower average than detected here, the closest matrix was from road dust in China. 2-OH-BTH and BTH had the highest mean of all compounds in this experiment.

BTR also shows high concentrations, with the max value at 93 ng/mL. From table 2.3, it is either BTR or TTR that has the highest mean value. TTR here has a max value around half of what BTR shows, but their mean value are close, only 0.08 ng/mL difference, with BTR at 3.10 ng/mL and TTR at 3.02 ng/mL.

2-SCNMeS-BTH is a fungicide that is not more used, and it is also not well documented, which can be seen in table 2.2, where many different studies has no value for this compound. There were a couple of studies that has analysed for 2-SCNMeS-BTH. Those values, compared to other BTHs from same matrix, were low, except for one from Malaysia, were it was found 1.7 ± 3.7 ng/mL, around 6 times the average found here. This can show that even though this fungicide is not used anymore, it is still possible for it to show up in some matrices.

There is one sample that has a total concentration at 97 ng/mL. This is not the highest detected sample, but it has the highest value in BTR of 93.4 ng/mL. The rest of the compounds does not show any significant difference than what's found in table 2.2 table 2.3. The problem about this sample is that it is a blank sample for particulate fraction in batch 2. The other compounds is slightly higher than the other particulate fraction samples. By looking at the signals, the blank signal has the lowest areal. The second lowest in the same batch is twice as large compared to the blank. The part that makes the concentration higher is the low weight difference on particles found in the filter. Since this is a blank, the difference before and after water ran trough the filter is really low, which significantly increases end concentration. The signal being just showing around half of the other lowest data could hint to some bleeding in the column, but the samples that were ran between analysis batches did not show any significant signs.

All samples are blank subtracted, making this high blank concentration of interest. The second highest BTR in this part is detected at 32 ng/mL. By not subtracting the blank, this concentration increases by 10 ng/mL. Of these samples, this is the largest difference, the smallest is at around 6 ng/mL, meaning blank subtracting this part gives an error between 5-10 ng/mL. BTR is the only compound where this blank affects this much, the other compounds for this batch is not affected by this blank.

By removing the blanks from all other samples did not yield in any significant change for other samples, less than 10%. For BTR in particulate fraction in batch 2, the difference between blank subtracted and not blank subtracted is around 25 to 50% increase. Both figure 4.1 and table 4.5 shows these samples as blank subtracted.

The particulate fraction's blank in batch 1 does not show same level of BTR, it is at around 5

ng/mL. By Looking at the concentration of those samples, but not blank subtracted, a difference was seen, no significance change, as in batch 2.

The detection frequency of the selected BTH/BTR compounds ranged between 46 and 94% of the samples, with TTR and 2-OH-BTH with most detected samples, and 5-Amino-BTR at the lowest percentages. The rest of the compounds was between 90% and 75%, except 2-SCNMeS-BTH that had 61% samples detected. One thing this can mean is that 5-A-BTR and 2-SCNMeS-BTH has a low occurrence in this matrix, most samples are below LoD.

Figure 4.1 shows all the data in a box plot, in the range between 0 and 30 ng/mL, where most of the sample concentration was found in this range. The high value outliers are not shown here, highest values can be seen in table 4.5. BTH and 2-OH-BTH have around the same amount, showing the environment those compound was found in here does not favour either form more than the other.

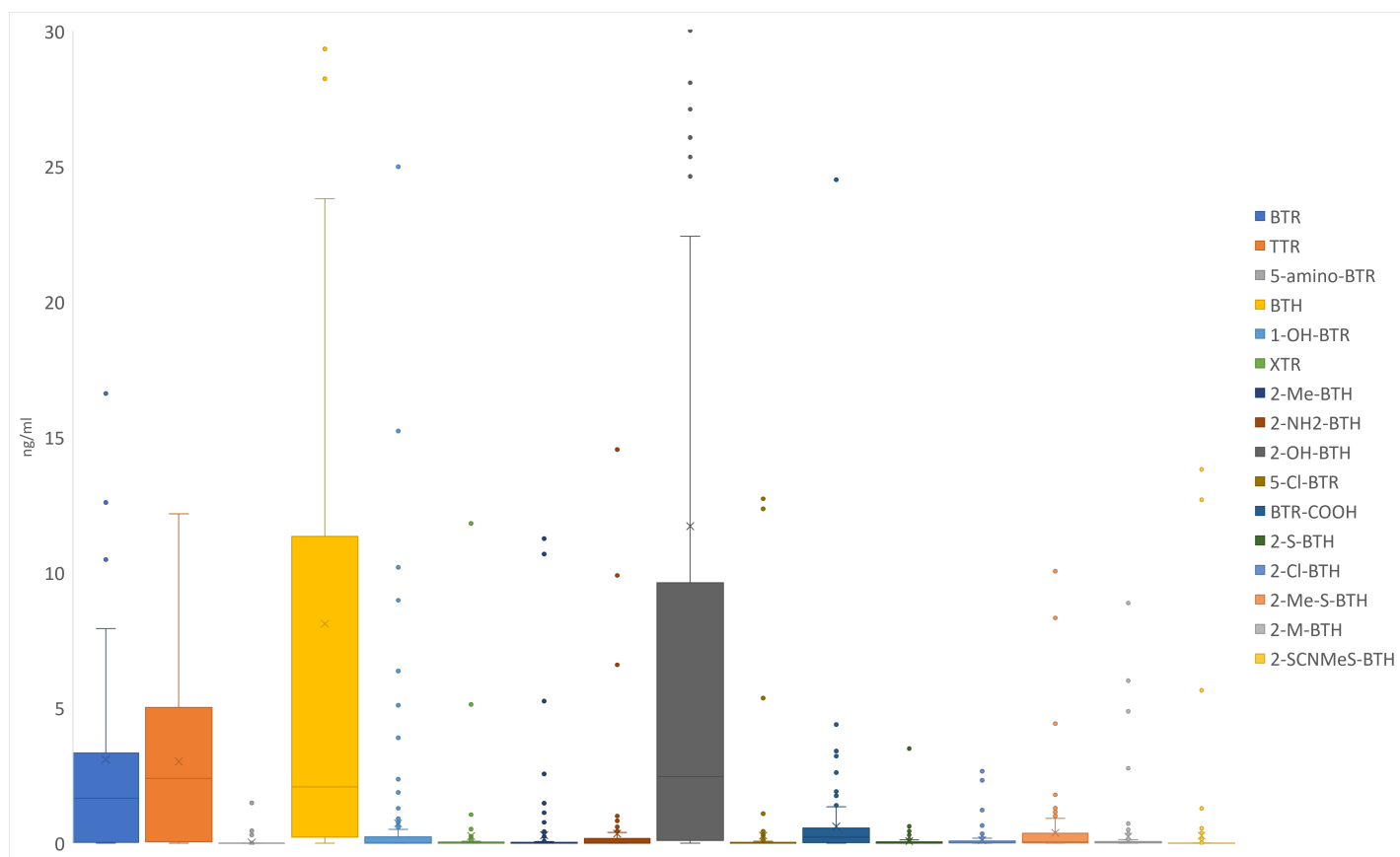


Figure 4.1: All result, seen in the range between 0 and 30 ng/mL. Y axis is concentration, in ng/mL. X axis is each compound.

Without outliers, the range of all samples are between 0 and 30 ng/mL. By comparing to table 2.2, one can see that these values are realistic. Some of the derivatives share similar concentrations with wastewater tested in Germany^[54]. While BTH shares same values as was found in road dust in china^[52]. Some other matrices, like one from Sweden^[50] shows tire debris with up to 10 times the average values of 2-M-BTH. For different matrices linked with tire in some way, road dust, tire debris etc., the ratio between BTH and 2-OH-BTH is always weighed towards 2-OH-BTH, showing in those matrices that 2-OH-BTH is more occurring. In the results here, 2-OH-BTH is more occurring than BTH, but the ratio between them is smaller than many of the previous matrices. Here, 2-OH-BTH has an average concentration that is around 40% larger than BTH's mean value. ng/mL, compare to the big table. This has higher than data from Germany in wastewater, seen in

table 2.2 BTH and 2-OH-BTH has the highest range. Table 2.2 shows Compare with earlier studies on which is the highest

For the different BTR compounds, both BTR and TTR are the most occurring. Comparing this to table 2.3, both TTR and BTR are the most occurring there also. In some matrices TTR has a higher concentration, and in other BTR. In some matrices 5-Cl-BTR has the highest mean value. This was not observed in this experiment, here the average was at 0.28 ng/mL, Compare this to the other average values, it is in the low end, it has a low occurrence. The tire matrices shows more TTR than BTR. In this experiment, the mean values of these are close, 0.08 ng/mL difference, meaning they both have around the same occurrence. The same matrices also show higher values of 5-A-BTR, compared to whats found here, but few of the studies was analysing for 5-A-BTR, something that could be a hint of this contaminant is not occurring too much, or these compounds have not been of interest before.

4.4.1 Occurrence

5-A-BTR, 2-S-BTH, 2-Cl-BTH and 2-M-BTH all had a maximum concentration under 10 ng/mL. The highest mean value of these was 0.23 ng/mL. This shows the abundance of these are low. 2-M-BTH is a something not used anymore in the industry, but it is also a derivative. In both table 2.2 and table 2.3 the same compounds has around the same mean, except 5-A-BTR. In the few studies where 5-A-BTR was analysed, the mean was higher than the mean found here. As mentioned with recoveries 2-Cl-BTH showed some problem with response, could be a possibility the same happened here? 2-S-BTH also showed some problems with recoveries, same with 2-S-BTH.

1-OH-BTR, XTR, 2-Me-BTH, 2-A-BTH, 5-Cl-BTH, BTR-COOH, 2-Me-S-BTH and 2-SCNMeS-BTH all showed concentration under 25 ng/mL. All these had a mean value under 1 ng/mL. In both table 2.2 and table 2.3. On average, the occurrence of 2-S-Me-BTH is 5.43 times higher than 2-S-BTH. This could be because 2-S-BTH is not as stable as 2-S-Me-BTH, and this reflect in the results. The less stable molecule will have a lower occurrence than a more stable version of the molecule.

4.5 Particular fraction in tunnels

4.5.1 Bjørnegård

Figure 4.2 shows average concentration for all steps with particulate fraction samples.

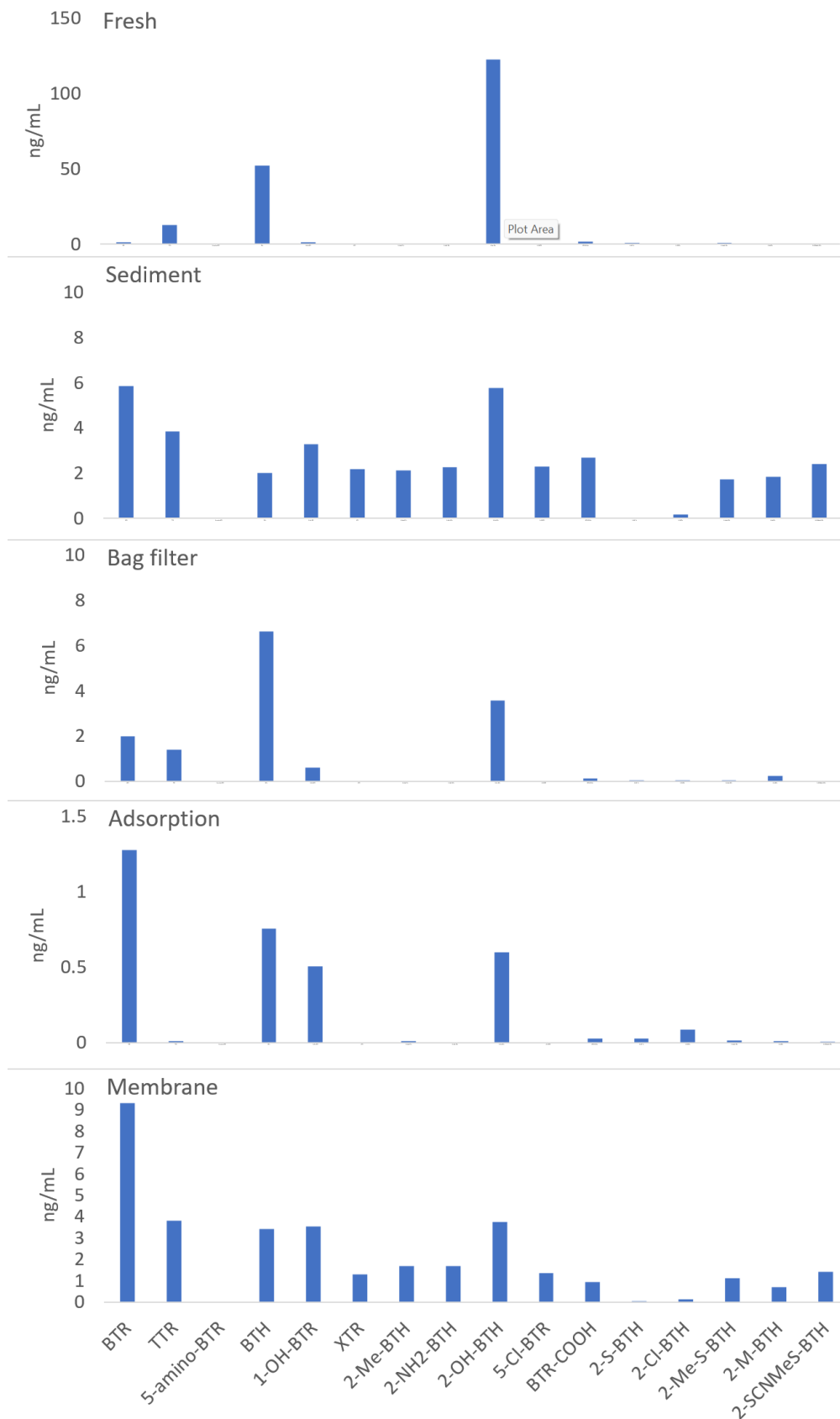


Figure 4.2: Comparison between all types of treatment steps in the Bjørnegård tunnel for particulate fraction. Fresh and adsorption samples has an adjusted y-axis to fit all data.

Removal efficiency shows how much of a compound is removed through a treatment step, or multiple,

and is determined by:

$$RE = 1 - \frac{C_{end}}{C_F} \quad (4.3)$$

Where C_{end} is the concentration of a compound after a treatment step, and C_F is the concentration of compound before treatment step. In this case, it is from the fresh or sediment sample.

The fresh samples are untreated samples, taken on day 1 of sedimentation. Fresh samples shows high concentrations for 2-OH-BTH and BTH. 2-OH-BTH is around 2.5 times higher than BTH, which could possibly point to a oxygen rich environment. 2-OH-BTH will be created from BTH if there is excessive amount of oxygen, the ratio depending on the oxygen level^[41]. The other peaks that is of interests is TTR, at around 10 ng/mL. This is significantly higher than the BTR levels. The rest of the compound is found to have a concentration under 1.6 ng/mL. Those 3 peaks are not surprising to see, according to table 2.2 and table 2.3, BTH, 2-OH-BTH, and TTR, are the most occurring BTH/BTR to be found. BTR are also one of the most occurring compounds in those tables, but for these samples, it is not detected that often. One reason could be an environment that favours TTR than BTR. Another reason could be that there as more TTR released than BTR, for example from anti freeze substances used in cars. Both BTH and 2-OH-BTH have a high average value, seen by the peaks, but this is because of one sample, with BTH levels at 200 ng/mL and 2-OH-BTH at 473 ng/mL. The figure shows average, and these values are 100 times higher than the sample compounds shows in other fresh samples.

Sedimented samples are taken after the sedimentation process is done, which takes 35 days. After these 35 days, when the heavier particles should precipitate to the bottom, but dissolved fraction will not be affected that much. 2-OH-BTH and BTR has around the same level in concentration. 2-OH-BTH is around 3 times larger than BTH, and BTR is 50% larger than TTR. These samples shows almost all compounds in a range between 1 and 6 ng/mL, with exception in 5-A-BTH, 2-S-BTH and 2-Cl-BTH. These 3 has lower concentration. These same compounds had low concentrations in the fresh samples, but during the sedimentation, around 97% percent of those compound were removed. This can mean that sedimentation may then be a good strategy for removing these 3 compounds, but since they already had low concentration at the beginning, they may not be the main contaminants in tunnel wash water. Sediment shows an increase of 295% in average concentration from fresh samples to sedimented samples.

One article by Catallo et al^[102] talks about BTH in sediments, and release of BTH from sediment to the water. One important parameter affecting where BTH went was pH. It states that BTH concentration could increase trough oxidation. The oxidation potential of a compound can increase with lower pH^[103], but for this experiment the average pH for fresh samples are 7.9 ± 0.63 , and sedimented with 8.1 ± 0.38 . This could mean that BTH/BTR from already sedimented particles is a possibility, but unlikely the main reason for this high increase

One reason for the increase could be that BTH/BTR from the water fraction adsorbs onto particles, and during the extraction, is released. One article by Yu et al^[104] shows how BTH/BTR would adsorb onto suspended particles. Adsorption pf BTH/BTR from water fraction to particles could therefore be a main reason for the increase of BTH and BTR in the sedimented samples.

For bag filter samples, there were 5 peaks of notice. Those were BTH, 2-OH-BTH, BTR, TTR and 1-OH-BTR, in decreasing order. A ratio with more BTH than 2-OH-BTH can mean a less aerob environment, an environment that favours BTH more than 2-OH-BTH. Another explanation can be that bag filter is more efficient on removing 2-OH-BTH than BTH. Bag filter should only remove contaminants from water by trapping them, there should not be any other forces removing them. 2-OH-BTH does not have a that much larger molecule compared to BTH, but the OH-group could

be a factor in this. Bag filter shows a removal efficiency of 92.5% from fresh samples, and 55.7% removal from sedimented samples. BTR and TTR both show a concentration around 2 ng/mL. BTR has increased from fresh water, but TTR has decreased by 10 times, something that could mean TTR is easier to remove through filtration. 1-OH-BTR was also found with relative high concentration. One suggestion for higher occurrence of 1-OH-BTR is an environment that allows N-substitution of an electron-donating group onto the benzene ring. One example of an electron-donating group found in water is the hydroxy group^[35]. This type of substitution on BTR will create 1-OH-BTR.

Adsorption has almost the same peaks as bag filter has, but TTR concentrations are lower. As with bag filter, TTR has a huge decrease, but this time a 1/100 of TTR compared to the concentrations found in fresh samples. This means that TTR can be filtered away, but adsorption is a force that works better. Adsorption shows RE of 98.3% from untreated samples, and 91.4% from sedimented. This time BTR peak is the highest, and the only compound over 1 ng/mL, something that could mean BTR is resistant to be adsorbed than the other compounds. BTH and 2-OH-BTH has concentration that are around the same, neither of those forms are favoured, or adsorption removed more 2-OH-BTH so they are on the same level.

For the membrane samples, BTR has the highest peak at 9.3 ng/mL, where the rest of the peaks are under 4 ng/mL. One reason that explains this is that all the values for this graph are made of the mean of 4 samples, and one BTR had a concentration of 32 ng/mL. Of four samples, one that was significant higher than the rest would affect the result in a way showed here, making one peak larger than the others. When comparing this single concentration to other single concentration in these samples, this was larger than them, with the other highest concentrations around 5 and 6 ng/mL, with 2-OH-BTH showing one sample with 11.5 ng/mL. Membrane shows RE of 82.5% from fresh, and 11.3% from sediment. 4 samples shows an increase in concentration, BTR, BTH, 1-OH-BTR, 2-S-BTH. Except for BTR, there are TTR, BTH, 1-OH-BTR and 2-OH-BTH that have around the same concentration. The rest has a concentration under 2 ng/mL, but 5-A-BTR, 2-S-BTH and 2-Cl-BTH. These have concentration hard to spot on the graph. They are similar to the concentration of sediment samples of the same compound, and show removal efficiency is around the same of those in sediment from fresh.

The fresh samples to after secondary treatment removal is shown to show how much BTH/BTR is removed after treatment of wash water. The removal of BTH/BTR from sedimented samples to these 3 different sample types is shown to show how efficient each treatment step is. All 3 steps shows that they are removing BTH/BTR, but all in different degrees. Also, since sediment increases its BTH/BTR concentration with almost 3 times, it would be interesting to see the difference in removal from both fresh and sedimented.

Adsorption shows most efficiency in removing BTH/BTR in these 3 treatment steps tested. It has over 90% for both removal efficiency stated above. Bag filter shows second best removal. This method shows it removes around 50% of particulate Membrane samples shows the poorest removal of BTH/BTR between these 3 types of treatment. Sediment increases

In all steps after untreated, BTR has a higher concentration than TTR. TTR can be created from BTR in an anaerobic process, but by the 2-OH-BTH levels, this is not an anaerobic environment. The high TTR levels at untreated samples can come from high TTR levels directly from traffic, and what was in the tunnel wash water. During sedimentation, most of the TTR was removed, or maybe

In the introduction, two hypotheses was introduced, one regarding each fraction types. For

particulate fraction, the hypothesis was that the BTH/BTR concentration would be reduced during sedimentation, and even more during filtration. For Bjørnegård, the first part was incorrect. There was not a decrease in the concentration, but almost 3 times the concentration in fresh samples. The second part was correct, each different filter steps had a decrease of BTH/BTR concentration, between 10 and 90%. One part of this hypothesis turns out to be correct for this experiment, but the other was not.

4.5.2 Grillstad

Values for Grillstad samples can be seen in figure 4.3. The fresh sample has all compounds under 2.5 ng/mL and the highest peaks are 1-OH-BTR, 2-OH-BTH, 2-Cl-BTH, TTR and BTR, in decreasing order. The sedimented sample has similar peaks, but 2-OH-BTH and TTR is lower. 2-Me-BTH in the contrary is the 4th most highest peak here. By comparing these samples average values, the sediment compounds has increased with 7.3 times.

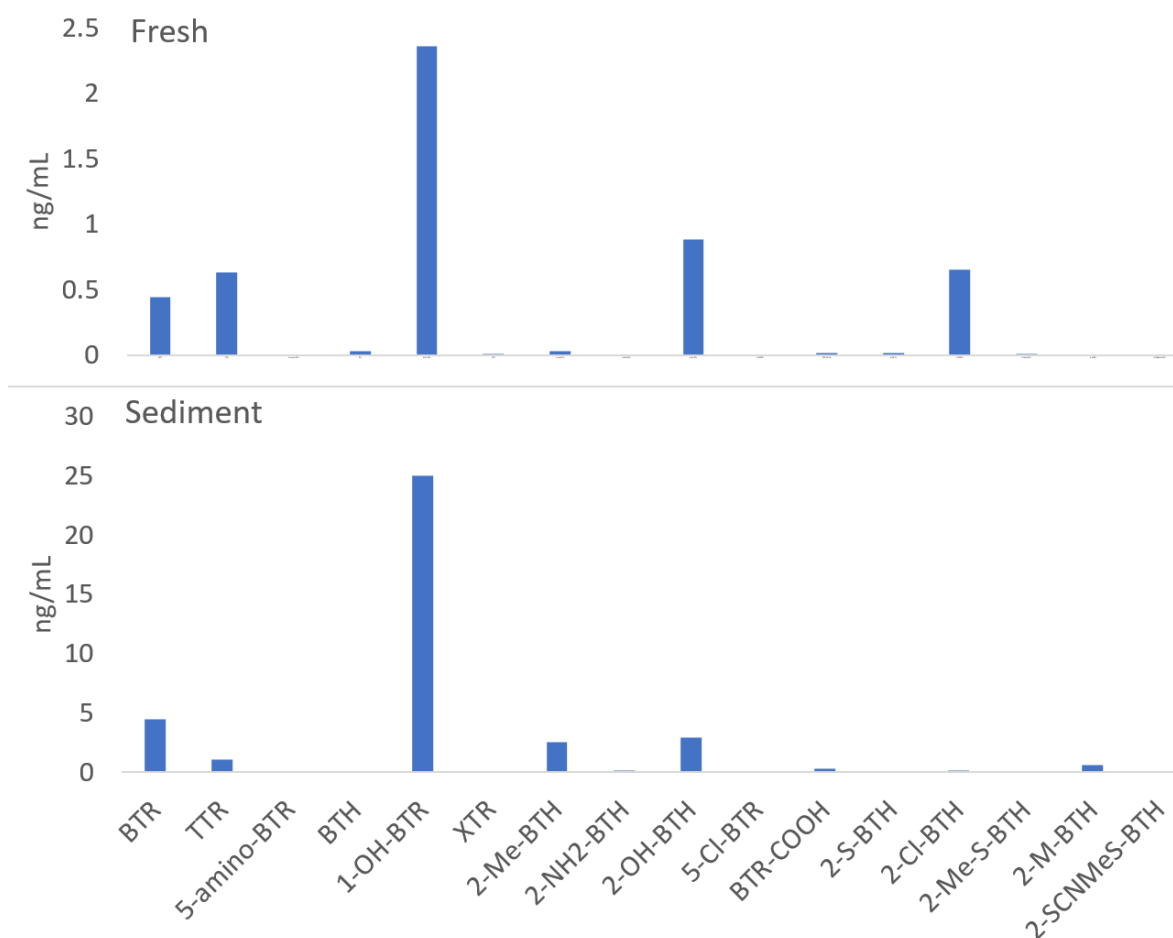


Figure 4.3: Comparison between all types of sedimented samples and fresh in the Grillstad tunnel for particular fraction. Y axis is shown with different concentration because sedimentation samples showed higher concentration of compounds.

The main reason to collect samples from this tunnel was to compare the concentration of BTH and BTR in tunnel wash water before and after treatment. This tunnel has around the same daily car passage, so it is a good fit to compare to. Grillstad does not have the same pilot test treatment that Bjørnegård has, so only fresh and sedimented samples could be collected. Both Bjørnegård and Grillstad showed an increase in BTH/BTR concentration on average after treatment. The explanation for this increase is release of BTH/BTR from particles found in the water.

Both tunnels showed an increase from fresh to sediment. One major difference for this tunnels is that Grillstad has concentrations under 2.5 ng/mL, but Bjørnegård has two compounds at 50 and around 125 ng/mL. Despite these two significant high concentrations, the rest of the compound showed an increase in concentration.

4.6 Water fraction in tunnels

4.6.1 Bjørnegårdtunnelen

Figure 4.4 shows the concentration for each treatment step, bag filter, sediment, membrane and adsorption.

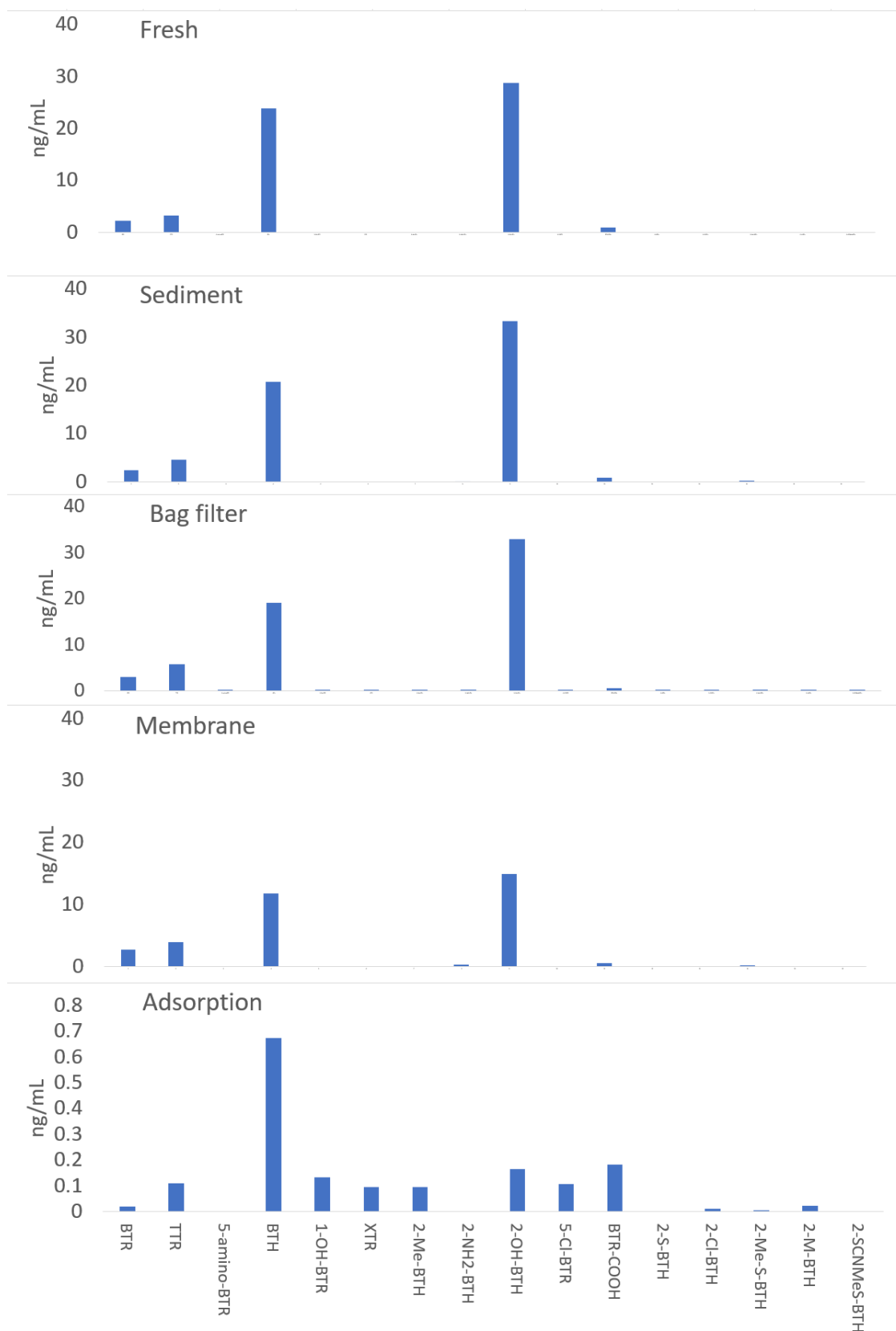


Figure 4.4: Comparison between all types of treatment steps in the Bjørnegård tunnel for water fraction. The Y-axis on adsorption graph is shown between 0 and 0.8 ng/mL to see the different peaks.

Fresh samples are untreated samples of tunnel wash water. They will be the samples the rest of the treatment steps is compared to, to see how much the concentration of BTH/BTR changes. These

samples consist of 4 samples in total. Compared to table 2.2 and table 2.3, many different type of matrices shows lower concentration of BTH/BTR compared to the result for fresh samples. One thing that can explain the higher concentration here is tunnel mostly is a closed system where as for example roads can loose some BTH/BTR to the atmosphere. Almost all BTH/BTR in tunnels will not travel to the air, but stay in tunnels as coating on the wall. With washing, the BTH/BTR will end up in treatment facility of the tunnel.

There were 13 sediment samples total, 8 from the first batch, and 5 in the second. For each batch, these samples were collected on different times of day, and on different days, but all were collected after 35 days of wash water in sedimentation pool. The two highest concentration detected here is BTH and 2-OH-BTH with ratio of 2:3. The other main compounds detected is TTR and BTR. These numbers are around the same as found in fresh water, some decrease are seen in TTR and BTH, but the other two have around the same concentration.

Bag filter consist of 1 sample from each batch, a total of 2 samples. The sample from the first batch shows on average 3 times higher concentrations than in batch 2. The four main peak consist of 2-OH-BTR, BTH, TTR and BTR in decreasing order. These samples shows little difference with the concentrations in fresh and sedimented samples, showing bag filter may not be efficient on removing BTH and BTR in the water fraction.

Adsorption graph is made from the average between 2 different samples, 1 from each batch. Unlike bag filter, the samples from each batch does not show a major difference between each other, so the average value is close to both of these. The compounds in these samples all have a concentration below 1 ng/mL. By comparing this to other matrices, these values represent more background level as is documented in table 2.2 and table 2.3. Adsorption has a different trend than the other steps here. The other steps shows BTH and 2-OH-BTH with 2-OH-BTH with a little higher level than BTH, but BTH in adsorption step has around 3 times higher concentration than 2-OH-BTH. This could mean that 2-OH-BTH is more efficiently removed with adsorption than BTH. Except from BTH, all the compounds has a concentration lower than 0.2 ng/mL. By comparing all compounds, except BTH, these values are similar to the lower concentration in table 2.2 and table 2.3.

Membrane samples shows both BTH and 2-OH-BTH as the most occurring molecules, with 2-OH-BTH at a slight higher concentration. Both BTR and TTR also has some peaks, but these are a little under half of BTH's peak.

Sedimented samples showed an increase of 2.3 times than fresh samples. By looking at figure 4.4, this is not easily seen, because the main peaks spotted are around the same. The smaller peaks is the reason the significant increase. Some compounds have over 100 times increase in concentration, 2-S-BTH and 2-SCNMeS-BTH are examples here. Both these were not detected in fresh samples, but in sedimented they were found at 0.25 and 0.05 ng/mL respectively. On their own, these concentration are not major, but the increase is. Possible source is transformation product from rubber tire.

All but adsorption show the same trend with having 2-OH-BTH as the highest peak, then BTH, then TTR and then BTR. For adsorption the significant peak was BTH, then many other compound had around the same concentration, but none other than BTH showed any significant peaks. Also all adsorption concentration are under 1 ng/mL, where the rest goes up to 30 ng/mL.

Sediment samples, on average, shows an increase by 2.3 times. One explanation for this increase could be leakage from tire wear. Tires particle is released by friction, and trough washing, those particles end up in the basin with the wash water. During these 35 days, BTH and BTR will leak

from these particles. One article by Hansen et al^[105] talks about rubber leaching its chemicals into water, affecting cods. This could explain why fresh water does not show the same level of BTH/BTR as sedimented samples does, making tire wear a slow but steady and continuous source of BTH/BTR. The 3 times increase could therefore be explained by tire wear.

Fresh and bag filter samples shows around the same level of concentrations, some compounds has a higher concentrations in fresh samples. In total, the fresh samples are around 50% higher concentration of all BTH/BTR derivatives than the bag filter, which means around 1/3 of BTH/BTR were removed with the bag filter.

Both bag filter and membrane filter has a increase in BTH/BTR concentration from untreated samples. Bag filter sample has an increase of 2.3 times, and membrane has an increase of 1.32 times. Adsorption was the only treatment step that decreased the total BTH/BTR concentration compared to fresh wash water (by 94%). Of these 3 steps, it is the only one that had a decrease in BTH/BTR concentration, showing that adsorption may be better suited for removal of BTH/BTR.

These 3 steps are secondary treatment steps, so comparing the results with sediment could be useful to see how well these methods perform on their own. Bag filter has the poorest removal efficiency by removing only 1.1% of BTH/BTR. Membrane had 46% BTH/BTR removed through its process. Same with adsorption over, this treatment step here had the best removal of BTH/BTR, with 97.5% of BTH/BTR removed.

The adsorption samples showed BTH:2-OH-BTH with a ratio of 3:1. One reason for BTH concentration being 3 times higher than 2-OH-BTH could be that 2-OH-BTH is more efficiently removed with adsorption than BTH. The one difference between these molecules is a OH-group. This is a polar group, which could mean the adsorption filter used here works better on polar molecules than less polar molecules.

Sedimentation showed a higher concentration compared to fresh. All steps showed a decrease in BTH/BTR, but adsorption filter had the best removal of BTH/BTR compared to these other steps.

As with the particulate fraction, a hypothesis regarding water fraction samples was introduced in the introduction. It said that the BTH/BTR concentration was expected not change much from fresh samples to sedimented, but the concentration would decrease in the adsorption step. As seen in figure 4.4, the adsorption step had around 92% removal from sedimented samples. An increase of 2.3 times for sedimented samples is a significant change, meaning the first part of the hypothesis was wrong. The second part is correct, adsorption had a removal of 92% from step 1 to step 2, which is significant.

4.6.2 Grillstad

Figure 4.5 shows both fresh and sediment sample that were collected from the Grillstad tunnel.

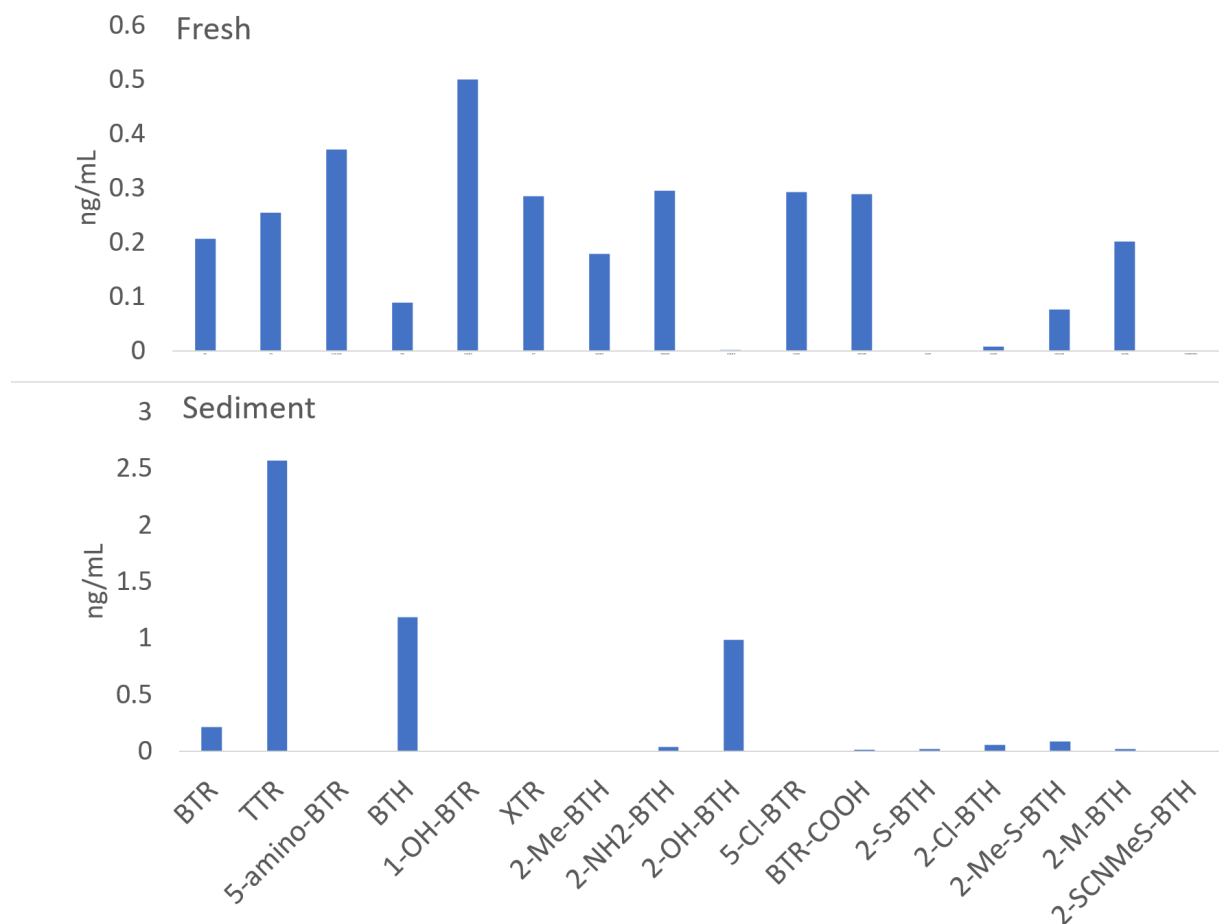


Figure 4.5: Comparison between all types of sediment samples and fresh in the Grillstad tunnel for water fraction. Y axis on both graphs shows a different range in concentration, sedimentation samples has higher max concentration.

Grillstad shows a increase in BTH/BTR concentration by 1.7 times from the fresh sample to the sample taken after sedimentation. Mainly, this is because of higher TTR and BTH concentrations, which was 10 and 13 times higher in sedimented than fresh respectively. 2-OH-BTH was not detected in fresh sample so this is not counted when looking at the increase, but the concentration is around the same as BTH in the sedimented samples. A total of 7 compounds from sediment samples has a higher concentration compared to their fresh sample counterparts. TTR, BTH, 2-OH-BTH and 2-S-BTH being significant higher. An article by Liao et al^[106] concluded that between 50-80% of air born BTH is suspended to particulate matter with a diameter of 2.5 μm or less. This article talks about road dust, the same may be for contaminants in tunnel wash water, because road dust is a main source of tunnel wash water contaminants.

4.6.3 Both water fraction tunnels compared

For all, the sedimented samples had the highest BTH/BTR average concentration for all steps. The main reason could be leaching from rubber particles. The rubber particles would the be degraded into BTH/BTR. Other sources for increased BTH/BTR concentration could be BTH/BTR on suspended particles at the start of sedimentation, that would be dissolved into the water during the sedimentation process

As with particulate fraction, Grillstad was used as a comparison on other tunnels than Bjørnegård with their BTH/BTR levels. Both tunnels here showed an increase in BTH/BTR concentration.

4.6.4 All tunnels compared

Both Grillstad and Bjørnegård has one occasion of a slightly decrease from fresh to sediment, and also large increase. It is interesting to see such variance, but still a pattern. If the same happened with Grillstad and Bjørnegård in the same batch, maybe type of tires could be the reason, the seasonal types of tires contain a different amount of BTH/BTR. Et al^[39] shows that studded tires contain less BTH/BTR than non-studded tires. This happened for Grillstad in one batch, and Bjørnegård in the other batch, both batches taken around 6 months between each other, batch 1 taken during studded tires season. For both, sedimentation showed increase in BTH/BTR levels on average. This shows that sedimentation does not work as a treatment step alone for BTH/BTR. Every other treatment steps shows some level of removal, some a higher removal percentage than other.

All 4 different tunnels sample batches, 1 from Bjørnegård and 1 from Grillstad, in two batches, showed an increase in concentration from fresh samples to sediment. The increase ranged from 1.7 to 7.3 times. The main sources of BTH/BTR in the sediment basin is from suspended particles and leach from tire wear. Both particulate fraction comparison shows a higher BTH/BTR increase than water fraction has. One explanation for this could be One explanation can be that during extraction, all sources of BTH/BTR in particulate fraction comes from particles not filtered away, that could be tire wear.

Bjørnegård has many more samples than Grillstad because Bjørnegård is where the pilot treatment plant is located, and Grillstad was used as a comparison. It was used to compare the concentration in Bjørnegård with another tunnel, and was chosen because it was located close to where the lab work was performed. Both times, Grillstad had a lower range than Bjørnegård, but Bjørnegård had a wider range because of high BTH and 2-OH-BTH occurrence.

For both types of fraction, adsorption was the treatment step that showed the highest removal efficiency. It had a removal efficiency at 98% for particulate fraction and 97% for water fraction. As of today, this is a treatment step which is in use in Bjørnegårdtunnelen. After 3.5 years the filter needed to be changed. With that lifetime and high removal efficiency, this shows to be a good recommendation as a treatment step that could be added to heavily trafficked tunnels.

Add at the end that this hypothesis was correct, there was a decrease during sedimentation, and inn all different step 2, there was removal of BTH/BTR. The hypothesis about particulate fraction was partial correct. The sediment increased its BTH/BTR concentration, while each secondary treatment step decreased the concentration between 10-90%. The water fraction hypothesis turned out to be partial correct also, Sedimented samples showed a increase in change from fresh, but a 92% decrease of BTH/BTR in adsorption samples means the other part of the hypothesis was correct.

4.7 Columns

One of the main objectives in this thesis was to look at different materials' abilities to remove BTH/BTR from tunnel wash water. A total of 6 different materials was tested in these columns, and some columns had some combinations of two materials, to test what effect mixing materials would have on removal of BTH/BTR.

4.7.1 Batch 1

For this batch, only one sample for raw data was collected: This was collected at the beginning of the experiment, after 0 hours. This sample had a concentration of 24.14 ng/mL. Figure 4.6 and table 4.6 shows the development of total BTH/BTR concentration, through different columns filled with different types of adsorption material. For this batch, a total of 6 columns were tested. Each column had a sample taken from it at specific time, starting at after 3 hours of experiment. The experiment was ran for 8 hours a day over 10 days total.

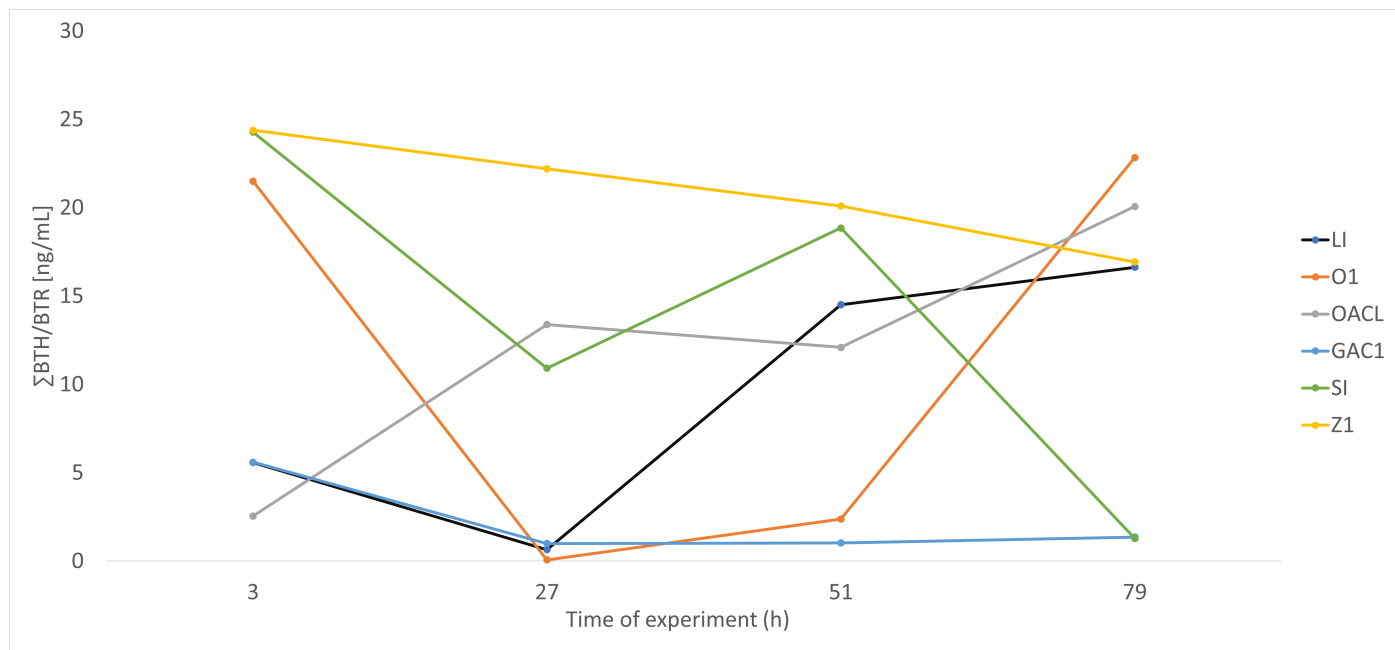


Figure 4.6: Total concentration of BTH and BTR in each samples for column experiment in batch 1.

Table 4.6: Total concentration in each sample for columns in batch 1, concentration in ng/mL

	h3	h27	h51	h79
LI	5.58	0.64	14.51	16.62
O1	21.48	0.065	2.37	22.83
OACL	2.55	13.39	12.09	20.06
Z1	24.38	22.20	20.09	16.92
GAC1	5.59	1.00	1.02	1.36
SI	24.27	10.91	18.84	1.27

Lecha (L1) column starts with a concentration at 5 ng/mL, before it decreases with 10 times the concentration. The next two samples has a concentration at around 15 ng/mL. Olivine (O1) has high concentration at the start and the end, where it is at around 20 ng/mL. The middle is at 0.065 and 2.37 ng/mL, two values much lower than the start and end of the experiment. The combination

of olivine and activated carbon column (OAC1) has low concentration at the first hours, 2.55 ng/mL, but the concentration increased after 27 hours, with a little decrease, before ending at 20 ng/mL at the end. Zeolite (Z1) started at 24,38 ng/mL after 3 hours. The concentration slowly decreased with the later samples, and the sample at h79 had the lowest concentration with this material, at 16.92 ng/mL.

With zeolite (Z1) at h3, there was trouble with the internal standard. The area of the internal standard was low, around a 1 000 times lower than other IS values, this gave a concentration around 2 500 ng/mL. This is around 1 000 times than what the raw sample was. To fix this, the IS area for Z1 at 27 hours was used. From figure 4.6, the graph for Z1 can be seen, and this new Z1_h3 value fits the trend Z1 column shows.

Granulated activated carbon (GAC1) has the highest concentration of its samples at the start, at 5.59 ng/mL. This is the highest concentration for GAC1. The next sample decreased by 5 times, to 1 ng/mL, where the concentration stabilized itself, with small variation.

Sand (S1) start at its highest concentration, with 24.47 ng/mL. After this, the concentration decreases, then rises a little bit, before the end where its at its lowest, which is at 1.27 ng/mL.

Raw data was only sampled once, at 24.14 ng/mL. If raw samples were taken at the same time as the other samples, one could see the different materials removal efficiency of BTH/BTR. Also, it would be possible to see if the concentration of BTH/BTR changed during the experiment.

To say anything about the efficiency of each column on how much BTH/BTR is not possible without concentration of raw samples to compare to. The closest thing possible here is to compare each value at an hour to each other and compare the difference there. When comparing with raw sample after zero hours and samples taken 3 hours after gives: LI with 7%, O1 with 11% and GAC with 77%. Both Z1 and S1 has a slight increase in BTH/BTR concentration, but it is less than 1%. Still, these numbers are not final, and in batch 2, with figure 4.7, it is observed that raw concentration is not static, but varies.

The S1 column shows the most variance between the column in batch 1. Its points changes from high to low with every point. O1 also showed some variance with high points at the start and end, but in the middle both concentrations were low. L1 had similar trait, but that started low, then the concentrations increased. It would have been interesting to see if these trends would continue if the experiment went on longer. Another point of interest is the raw sample, it would have been interesting to see if the variance for S1 column only was for it, or if the raw sample had a similar progress in concentration over time.

Both LI and Si had one sample showing similar concentration to GAC, LI even had one lower concentration than any GAC sample had, but since this was only once, it is hard to rely on both these to always have this low concentration. This also would make it interesting to see how the raw concentration developed during the experiment, to see which column is most similar to that development.

When looking at BTH and BTR alone, GAC1 seems like the best filter here. It has the all around lowest concentration of BTH/BTR, but L1 had one sample where the concentration was lower than any other sample in this part. One thing to consider for this is that BTH/BTR is not the only contaminant of interest when looking at treatment of tunnel wash water, depending on that materials performance on removing other contaminants that is not removed during sedimentation, other material can be suggested as the best suited for treatment of tunnel wash water. GAC performs best for removal of BTH/BTR in this batch.

4.7.2 Batch 2

In figure 4.7 and table 4.7, the total concentration of BTH/BTR for each samples. A total of 5 columns was tested for this batch. As with the first batch, the first sample was taken after 3 hours of experiment, but here the rest of the samples was taken in an interval of 16 hours.

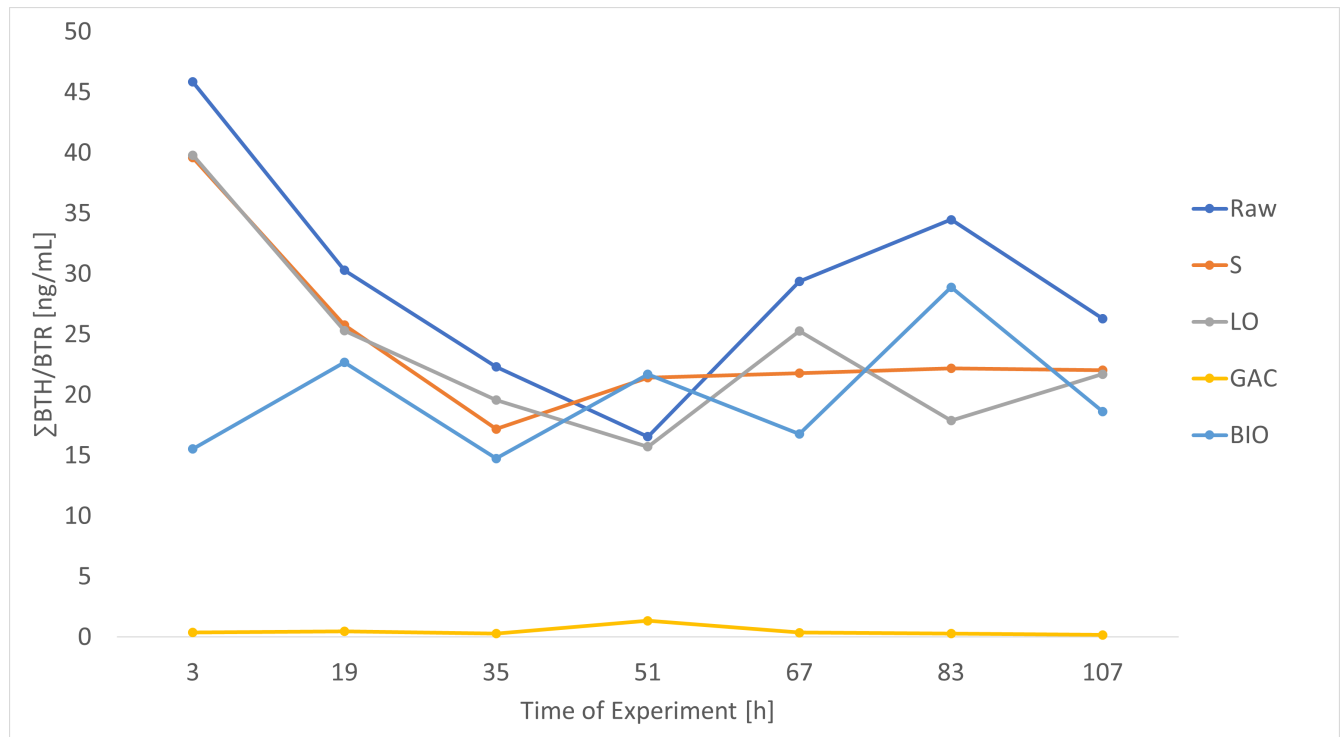


Figure 4.7: Total concentration of BTH and BTR in each samples.

Table 4.7: Total concentration in each sample for columns in batch 2, concentration in ng/mL

	h3	h19	h35	h51	h67	h83	h107
Raw	45.84	30.29	22.31	16.54	29.35	34.47	26.28
S	39.59	25.77	17.18	21.41	21.79	22.19	22.03
LO	39.79	25.31	19.58	15.70	25.27	17.87	21.71
GAC	0.37	0.47	0.29	1.34	0.36	0.28	0.17
BIO	15.53	22.68	14.74	21.70	16.75	28.89	18.61

The raw data was the highest detected value for each hour, except after 51 hours, here both S and BIO column showed around 30% higher concentration. As with the other samples, raw started at its highest value, at 45.84 ng/mL, before it decreased. The lowest point was after 51 hours, where the concentration was at 16.54. After this, the concentration almost doubled, then it decreased at the end.

The sand (S) columns starts at 39.59 ng/mL after 3 hours. It has the same trend as the raw data where it has its highest concentration at the start, and then it decreases, before a slight increase. Unlike the raw samples, here after 51 hours, the concentration evens out, it stops at around 22 ng/mL. Comparing the concentration with the raw data, the S column has an average of 14% in removal of BTH/BTR.

The lecha + Olivine (LO) column shows similarities with the sand column. This starts at 39.79 ng/mL, then decreases to a range between around 25 and 15 ng/mL. Unlike S, LO concentration

varies at the later hours. This column shows an average removal of 18% when comparing to raw samples.

The granulated activated carbon (GAC) column has the lowest concentration for this batch. All concentration are below 0.5 ng/mL, except for the sample taken after 51 hours of experiment, this one has a concentration of 1.34 ng/mL, which is almost 3 times higher than the second largest concentration found in this column, which is after 19 hours at 0.47 ng/mL. Except the sample from h51, the rest of the samples has low variation. This column shows an average removal of 97.94% when compared to raw data.

Biochar (Bio) starts at around 1/3 of the raw concentration with 15.53 ng/mL. Then it varies between 15 and 20 ng/mL trough this experiment, except at h83, where the concentration was at 28.89 ng/mL. Like S, this column also had one sample at h51 that had a higher concentration than the raw sample. This column showed an average of 26% in removal of BTH and BTR.

The two main compounds that has the highest concentration for all samples are BTH and TTR. BTH has around twice the concentration than 2-OH-BTH, pointing to an anaerob environment. This is true, because the raw water samples is stored in a container with a small opening. BTR is also found at around half of TTRs concentration. TTR is also said to be an anaerobic biodegradartion of BTR^[44]. Both these concentration, compared to the molecule they are degraded from, can be explained from an anaerobic environment, with both these having around twice the concentration.

All the column samples had a lower concentration than the raw samples, except for 2 samples at h51, and those were the S and Bio column. The raw sample concentration at h51 was also the lowest concentration for the raw samples, something that could either mean the raw sample was lower than it should be, or those two was higher than they should be. From figure 4.7, 3 out of 5 samples at h51 shows a rise on concentration, where raw and BIO has a decrease. This is also were the GAC column has its highest concentration at 1.34 ng/mL, which is almost 3 times higher than its second highest concentration. One reason BIO has a higher total concentration is that BTH concentration is almost double of the BTH concentration in raw sample.

Since mostly the samples were lower than raw data collected at the same time show that the filter has some efficiency in removing these pollutants.

Here GAC has the lowest concentration for all sample time. As with batch 1 columns, this may be only for BTH/BTR, but not all pollutants. S and LO both shows concentration almost at the same level as raw data, and even one sample being higher than the raw data. This should not happen since raw sample is untreated, but all the other samples are filtered trough a column. So a filtered sample being higher than the unfiltered sample is of notice. Noe smart her

BIO has approximately stable around the 15 - 20 range, with one exception. This makes this type of column the second best in this analysis. So if GAC column shows that it is not compatible with filtering other pollutants, this column is a good second option.

4.7.3 Comparison between batches

Figure 4.7 shows similarities between most of the columns, they all have a noticeable trend. Figure 4.6 does not have a noticeable trend, all graphs from the different points are scrambled together. One reason for this variance

One cannot say exactly how much BTH/BTR was removed in batch 1, but in batch 2, the sand column was the highest column concentration, and somewhat close to the raw samples. By using

S1 from batch 1 as a reference to what the raw samples could have been, one could estimate, but this is two different batches, and the raw sample could be too different to compare to. At the end, two columns showed a higher concentration than S1, showing that s1 and raw is not quite the same. 2 something something, hard to say anything about how much BTH/BTR was removed from batch 1,

Sand column in batch 1 showed a large variance between each sample point, it was on both end of the concentration range detected in batch 1. The sand column for batch 2 does show some traces of this trend, but in the same scale as batch 1 sand column. Sand column for batch 2 has more common traits with the raw sample in batch 2, they both increase and decrease at the same places. As stated in batch 1, it would be interesting to see how the raw samples, Both batches showed different trends. On average, both sand columns had the highest concentration of BTH/BTR, except raw. Sand was used as a reference column because of its inert abilities. Since this column has the lowest removal efficiency, adsorption seems to be an important parameter in removal of BTH/BTR

GAC in batch 1 started with around 5 times the concentration to what the 3 other samples was, but was the second lowest concentration at the beginning. The batch 2 GAC column was low, compared to any other column from the same batch. In overall, this column showed the best removal efficiency of all columns tested. This shows to the GAC materials adsorption ability of BTH/BTR, but also its trapping abilities.

Both Leca and Olivine had lower concentration than the LO combination. These materials alone had around 1/8 and 1/16 times less concentration at the beginning. but the longer the experiment ran, L stabilized around 15 ng/mL, O was around 23 ng/mL at the end and LO varied between 15 and 25 ng/mL. The longer the experiment ran, the combination column showed similar concentration with each material single column.

the OAC1 started with half the concentration than the GAC column, but the concentration of the samples increased with the later hours. O column's concentration had low points in the middle, but had a little over 20 ng/mL at the beginning and the end. OAC1 column showed similarities with the GAC column at the beginning, towards the end, it had more similar concentration with the O column.

Both these combinations did not show any special improvement compared to the materials alone in a column. OAC1 column showed some potential at the beginning where it showed similarities with GAC, the column that had the lowest concentration overall in both batches, but this trait disappeared with more hours of water running through the column.

Raw data: In batch 2, it shows that the raw data varies, why? BTH/BTR adsorbs to particles or other places maybe? In batch 1, only one raw sample was collected, but as seen in batch 2, the level of BTH/BTR is not static, it changes. By using only the one raw data in batch 1, it is hard to compare the raw data with the later collected samples to say anything about the removal efficiency, only say something about at hour 3, but the raw data was taken 3 hours apart from the samples, so this may not be something to talk about.

For both batches, the GAC material shows best potential in adsorption of BTH/BTR. If this is also true for other common contaminants found in tunnel wash water, this material would be recommended to use, but this thesis does only look at its effect on BTH/BTR, so no conclusion about the other contaminants can be said. For BTH/BTR alone, GAC is the best material to use as an adsorption filter.

5 Conclusion

LC-MS was used to determine the occurrence and quantification of benzothiazoles and benzotriazoles in tunnel wash water. All the target analytes showed a blabla ...

2-S-BTH and 2-Cl-BTH showed poor recovery. 2-Cl-BTH also showed poor repeatability All RSD for 5 ng/mL samples showed poor repeatability, except 2-S-BTH, but this had a low recovery for the same concentration. All 10 ng/mL samples had a RSD below 2%.

BTH and 2-OH-BTH was the most occurring compounds found in tunnel wash water. Both used as a vulcanization agent in rubber production, and it is believed that tire wear is the main source for these BTHs. In most samples 2-OH-BTH was found to have a higher concentration than BTH. The reason for this is most likely that BTH is transformed to 2-OH-BTH because of a aerobic environment.

Sedimentation showed to increase the concentration of BTH and BTR after the 35 day sedimentation process in both fraction analyses. Dissolved fraction had increased concentration because of tire wear particles leached BTH/BTR into the water. Particulate fraction had an increase because of adsorption from the dissolved fraction to particles. Of the tree treatment steps, bag filter, adsorption and membrane, the adsorption showed the highest removal efficiency of all in both batches, with over 90% of BTH/BTR removed when comparing to the concentration of untreated and sedimentation samples. The two other steps both showed removal, between 1 and 90%.

By adding a second treatment step after sedimentation showed to decrease the concentration of BTH and BTR. 3 different steps was introduced as secondary treatment and all showed a level of removal of BTH/BTR. Adsorption filter showed the highest removal efficiency, all occasions with over 90% of BTH/BTR removed. Bag filter and membrane filter both showed abilities to remove BTH/BTR, but not as well as adsorption filter was. They had a removal efficiency between 10-90%.

The second part of this thesis was to look at different materials in a column and how well BTH/BTR was removed trough filtering. A total of 6 materials was used, 1 was sand as reference, then 5 adsorption materials. As of today, GAC is used in Bjørnegårdtunnelen for the adsorption filter, but interest to see how well different materials perform. Out of the six materials, and some columns with combinations of them, GAC had the best removal at 98% BTH/BTR removed. The other materials showed a removal between 14-26%.

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6 Appendixes

6.1 Method picture

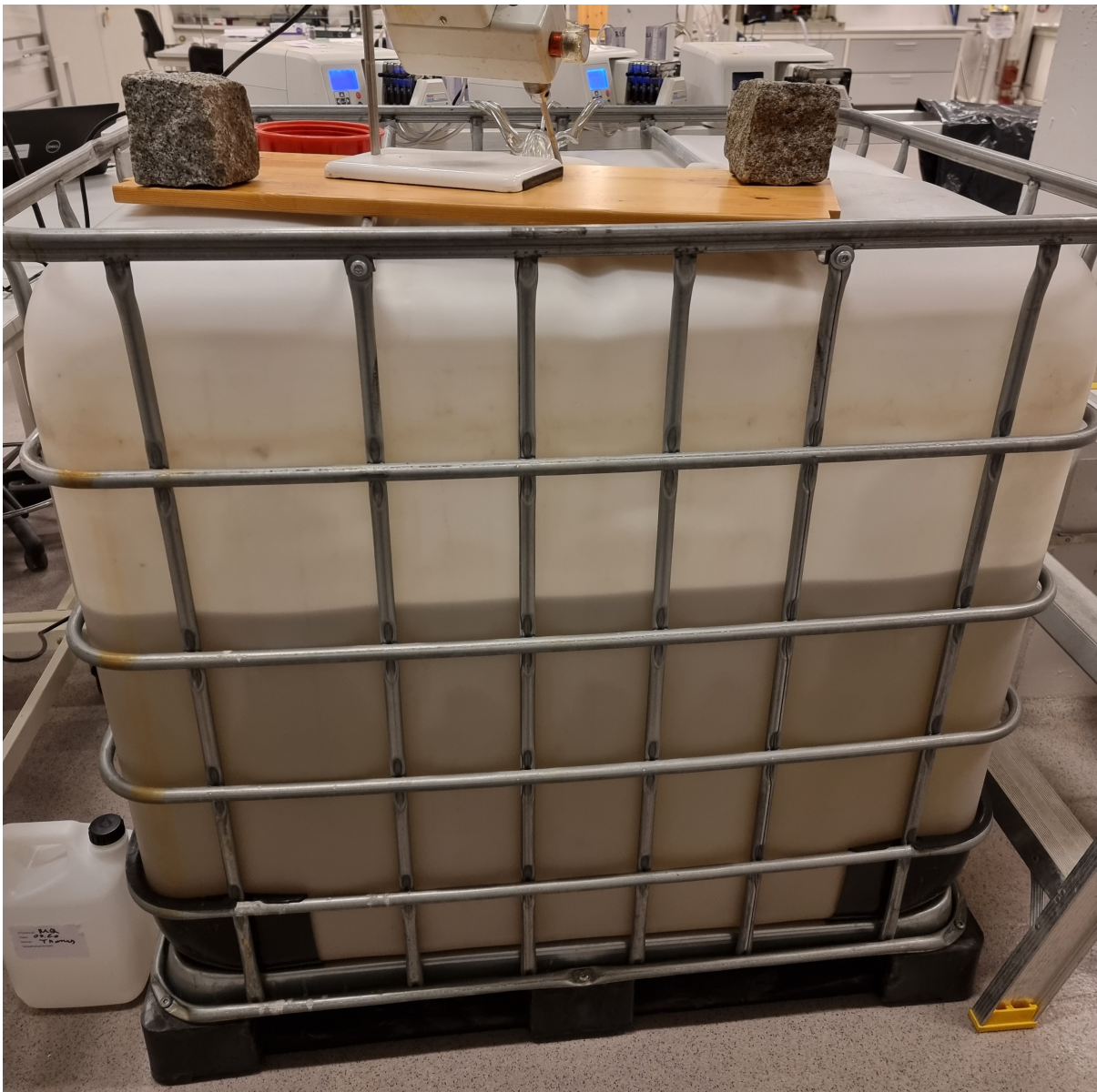


Figure 6.1: Tank of sample used for column experiment



Figure 6.2: Water being transported from tank. A drill is there to avoid sedimentation.



Figure 6.3: Picture of tubes transporting water from tank to column

6.2 Removal efficiency tables

6.3 Removal efficiency

Table 6.1: Removal efficiency on how much BTH/BTR was removed between each step, values shown in %

Removal efficiency from fresh to treatment step	Sediment	Bag filter	Adsorption	Membrane
Particulate fraction	295	92.5	98.3	82.5
Water fraction	234.3	231.7	97.5	131

Removal efficiency from sedimentation to treatment step	Bag filter	Adsorption	Membrane
Particulate fraction	55.7	91.4	11.3
Water fraction	1.1	97.4	44.1

Table 6.2: Removal efficiency of columns in batch 2

Column	Removal efficiency [%]
S	14
LO	18
GAC	98
BIO	26

6.4 Calibration curves

In this sub chapter, all calibration curves used for determining the concentration of each sample can be seen. Because the BTR standard was forgotten to be added in batch 2 standards there are only one standard curve for BTR, as seen in figure 6.4

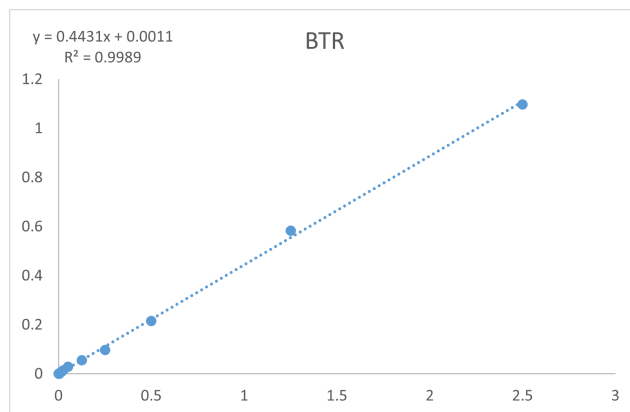


Figure 6.4: Calibration curve for BTR standards

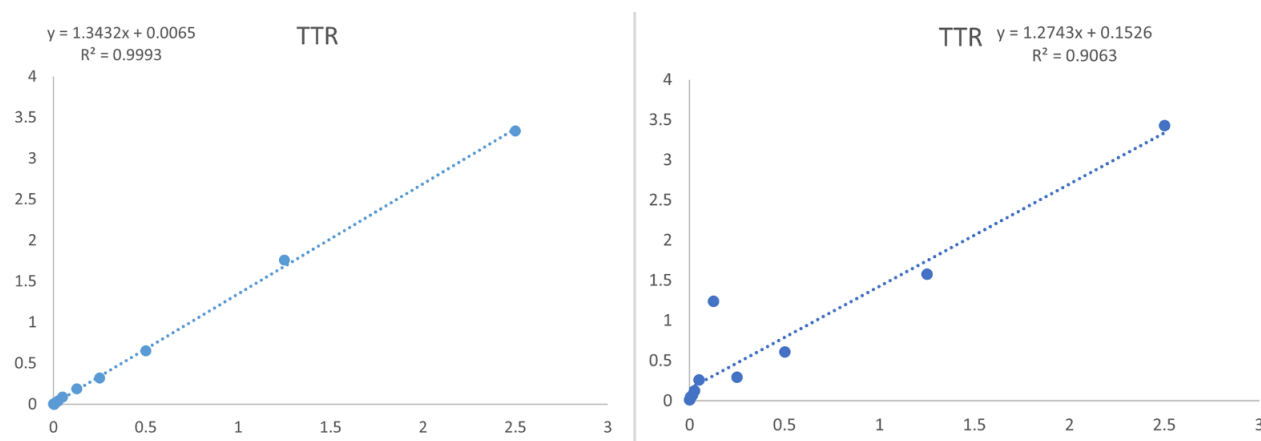


Figure 6.5: Calibration curves for TTR standards

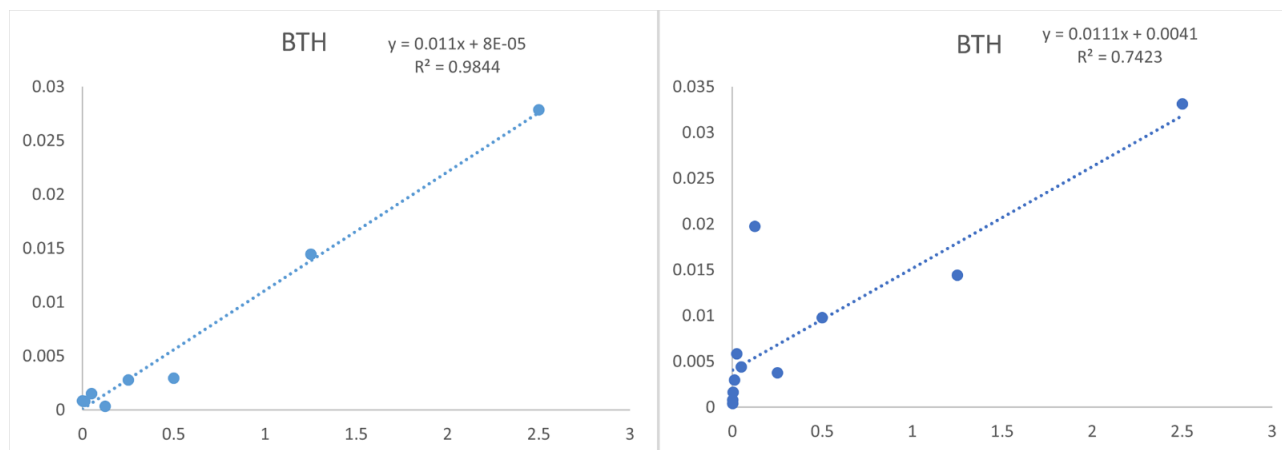


Figure 6.6: Calibration curves for BTH standards

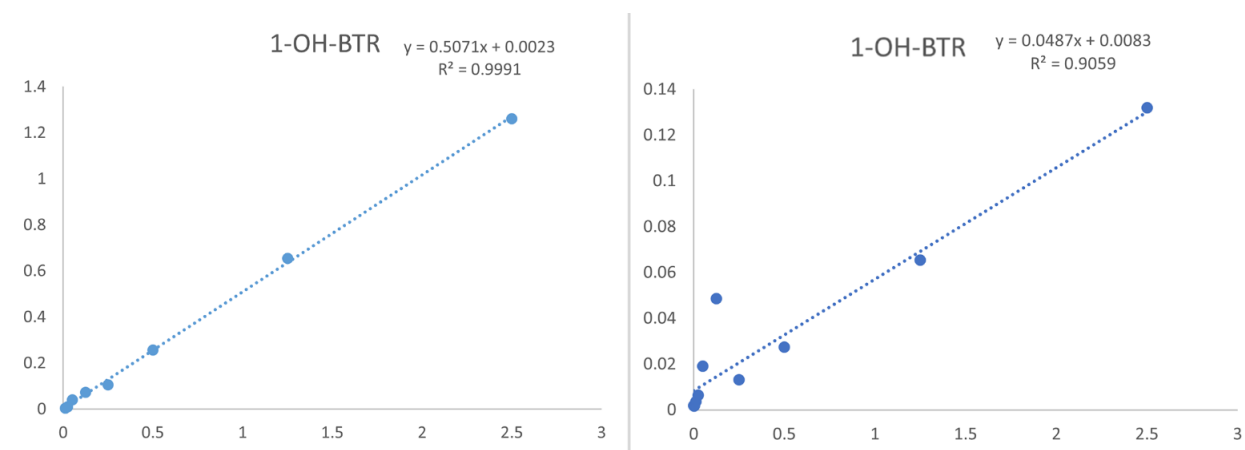


Figure 6.7: Calibration curves for 1-OH-BTR standards

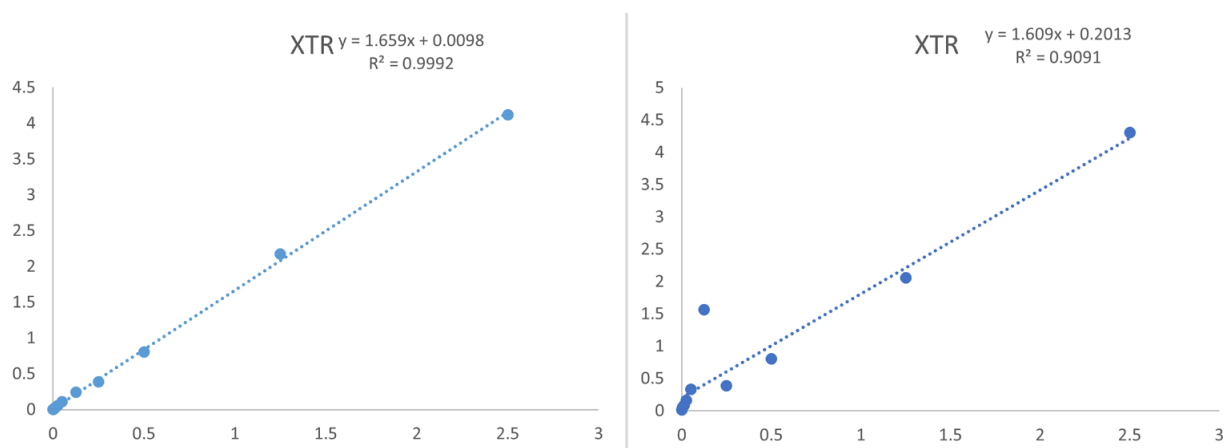


Figure 6.8: Calibration curves for XTR standards

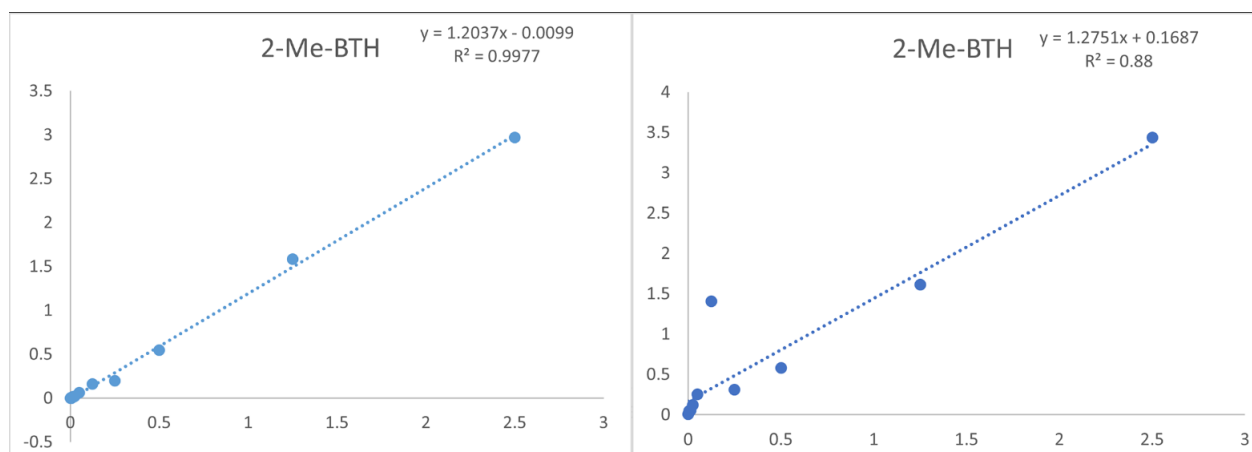


Figure 6.9: Calibration curves for 2-Me-BTH standards

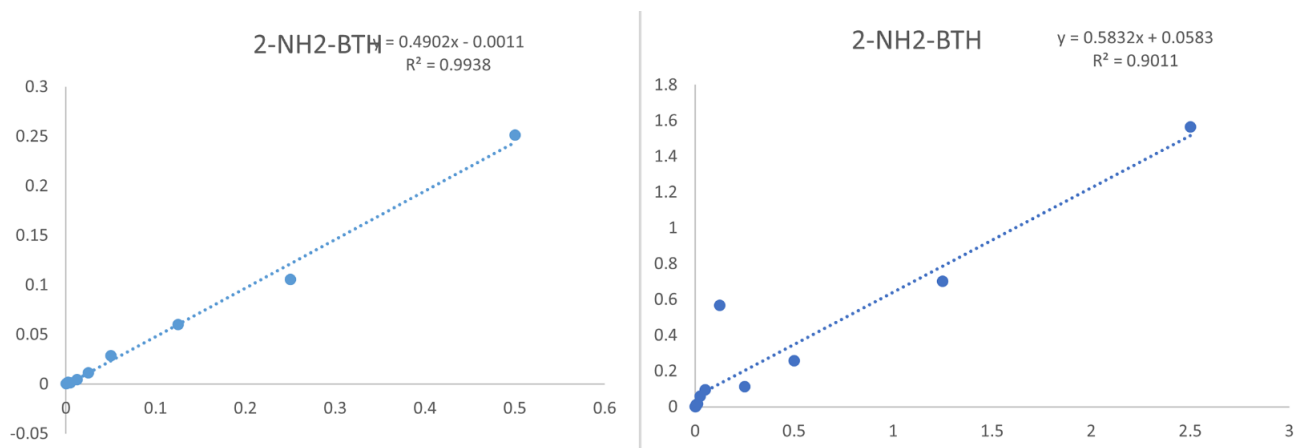


Figure 6.10: Calibration curves for 2-A-BTH standards

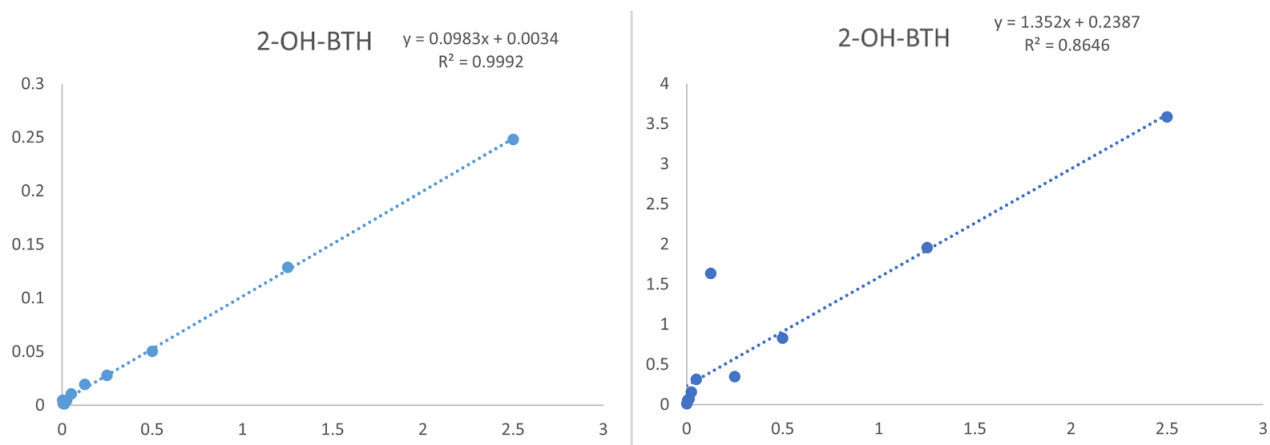


Figure 6.11: Calibration curves for 2-OH-BTH standards

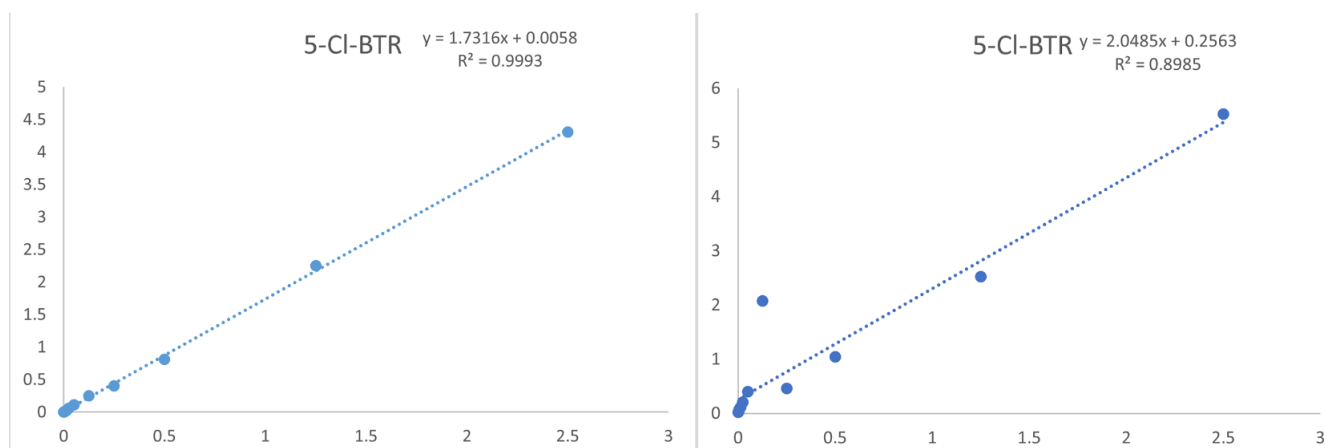


Figure 6.12: Calibration curves for 5-Cl-BTR standards

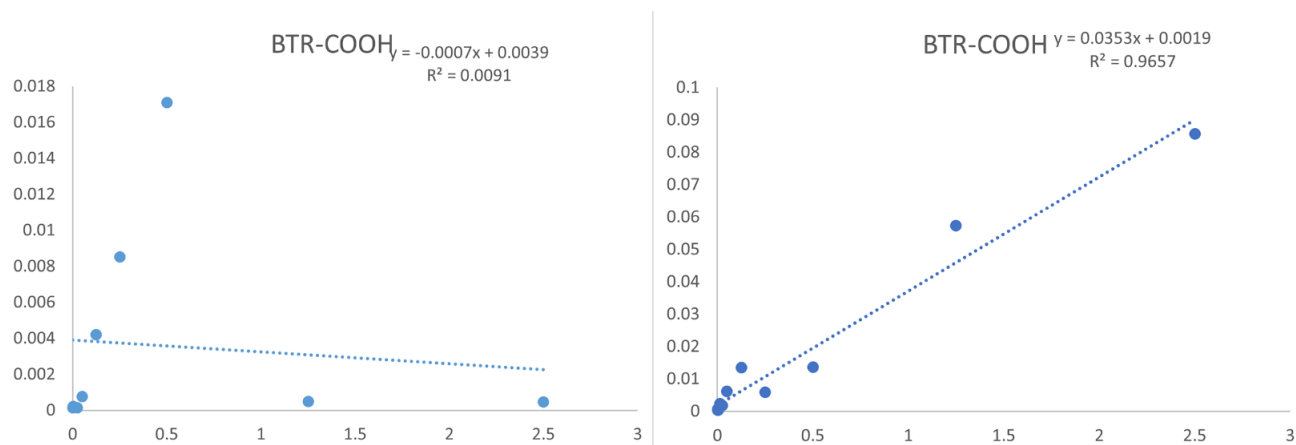


Figure 6.13: Calibration curves for BTR-COOH standards

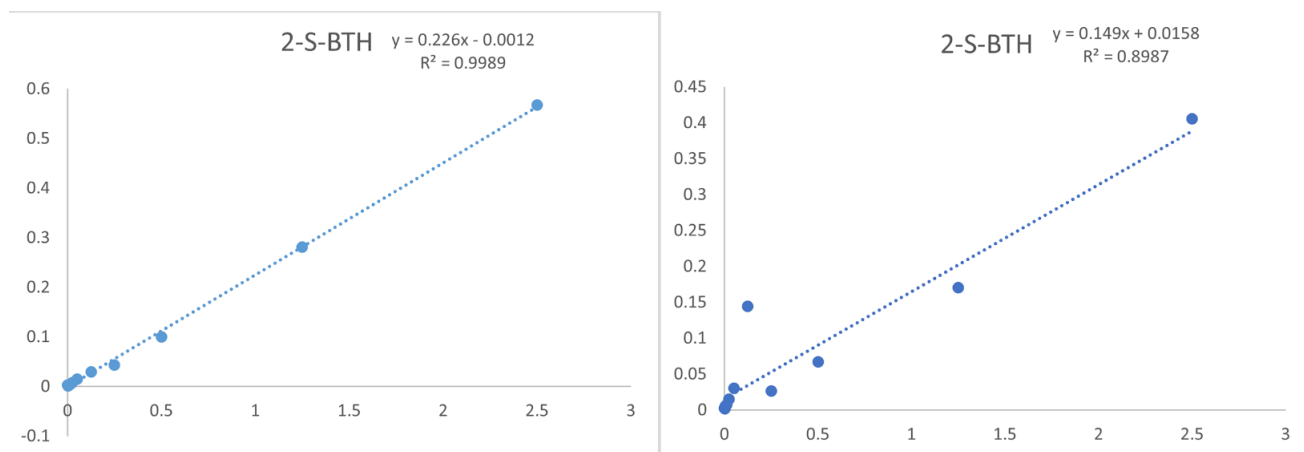


Figure 6.14: Calibration curves for 2-S-BTH standards

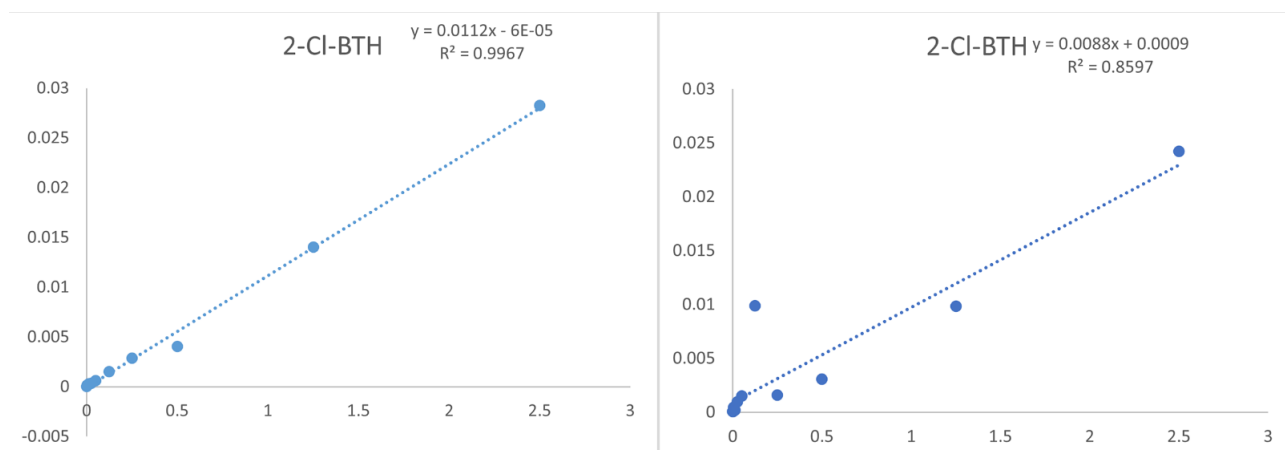


Figure 6.15: Calibration curves for 2-Cl-BTH standards

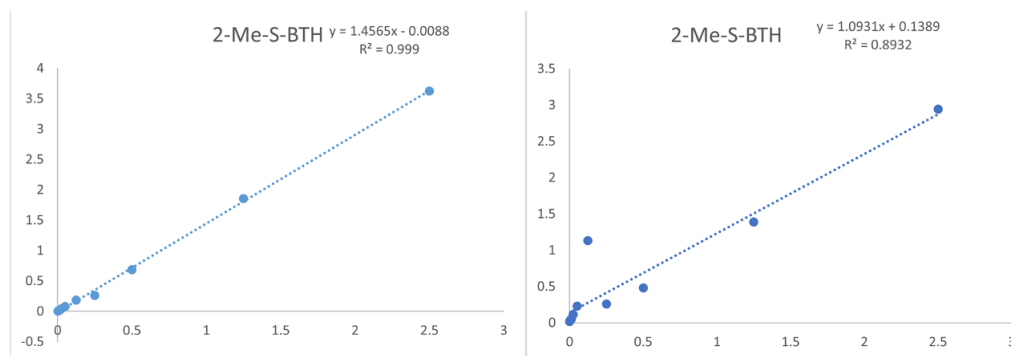


Figure 6.16: Calibration curves for 2-Me-S-BTH standards

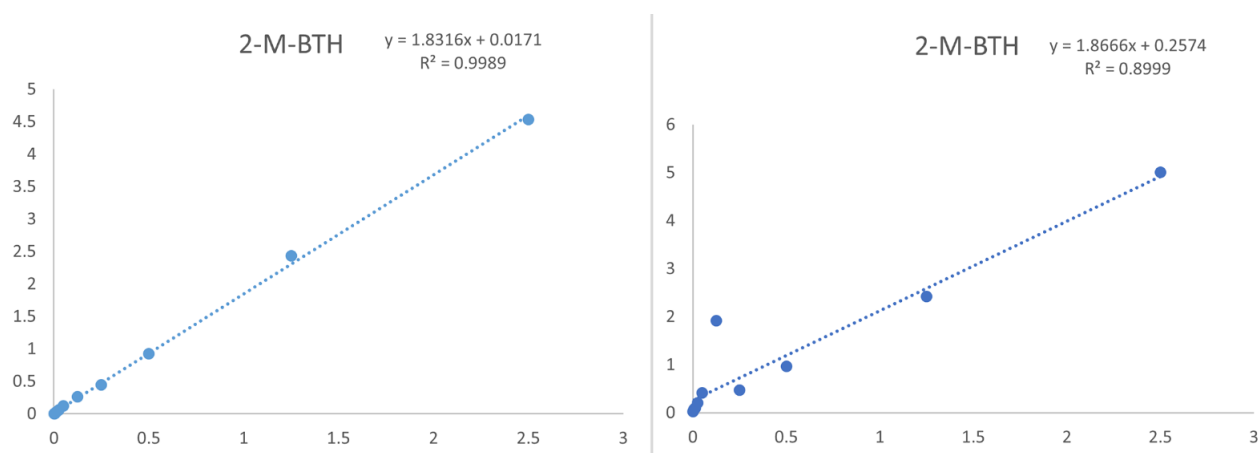


Figure 6.17: Calibration curves for 2-M-BTH standards

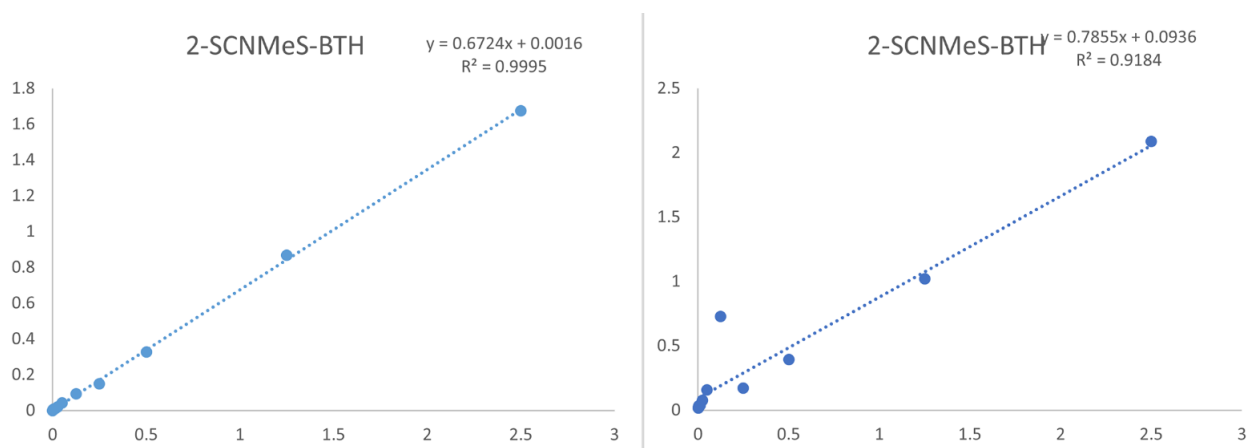


Figure 6.18: Calibration curves for 2-SCBNeS-BTH standards

6.5 Sample overview

Table 6.3: Sample ID and description of them

Sample ID	Sample explanation	Sample date
WF_BBL	Procedure blank	
PF_BL4	Filter filtered with distilled water.	
PF_BT_F_T1	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column T1 at NTNU labs. Collected day 1 of sedimentation.	12.10.21
PF_BT_F_T2	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column T2 at NTNU labs. Collected day 1 of sedimentation.	12.10.21
PF_BT_S_T1	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column T1 at NTNU labs.	12.10.21
PF_S_T2	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column T2 at NTNU labs.	12.10.21
PF_G_F	Fresh wash water sample from the Grillstad tunnel. Collected day 1 of sedimentation.	13.01.22
PF_BL1	Filter filtered with distilled water.	
PF_G_S	Sedimented wash water sample from the Grillstad tunnel. Collected day 35 of sedimentation.	13.01.22
PF_BL9	Filter filtered with distilled water.	
PF_BT_F_B1	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column B1 at NTNU labs. Collected day 1 of sedimentation.	02.03.22
PF_BT_F_B2	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column B2 at NTNU labs. Collected day 1 of sedimentation.	02.03.22
PF_BT_S_B1	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column B1 at NTNU labs.	02.03.22
PF_BT_S_B2	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column B1 at NTNU labs.	02.03.22
PF_BT_S1	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	05.04.22 Morning
PF_BT_S_B	Sedimented and bag filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after bag filter.	05.04.22 Morning
PF_BT_S2	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	05.04.22 Midday
PF_BT_S_M1	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter.	05.04.22 Midday
PF_BT_S3	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	05.04.22 Evening
PF_BT_S_M2	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter.	05.04.22 Evening
PF_BT_S4	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel	06.04.22 Morning

Table 6.3: Sample ID and description of them

Sample ID	Sample explanation	Sample date
PF_BT_S_A	Sedimented and adsorption filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after adsorption filter.	06.04.22 Morning
PF_BL3	Filter filtered with distilled water.	
BBL2	Procedure blank	
WP_B_F_T1	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column T1 at NTNU labs. Collected day 1 of sedimentation.	
WP_B_F_T2	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column T2 at NTNU labs. Collected day 1 of sedimentation.	
WP_B_S_T1	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column T1 at NTNU labs.	
WP_B_S_T2	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column T2 at NTNU labs.	
WP_G_F	Fresh wash water sample from the Grillstad tunnel. Collected day 1 of sedimentation.	04.10.22
WF_BL1	Filtered distilled water.	
WP_G_S	Sedimented wash water sample from the Grillstad tunnel. Collected day 35 of sedimentation.	
WP_GS_BL	Filtered distilled water.	
WP_BL2	Filtered distilled water.	
WP_F_B1	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column B1 at NTNU labs. Collected day 1 of sedimentation.	12.10.21
WP_F_B2	Fresh wash water sample from the Bjørnegård tunnel. Transported to sedimentation column B2 at NTNU labs. Collected day 1 of sedimentation.	12.10.21
WP_S_B1	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column B1 at NTNU labs.	12.10.21
WP_S_B2	Sedimented wash water sample from the Bjørnegård tunnel. Collected day 35 of sedimentation from column B2 at NTNU labs.	12.10.21
WP_BT_S1	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	05.04.22 Morning
WP_BT_SB	Sedimented and bag filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after bag filters	05.04.22 Morning
WP_BT_S2	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	05.04.22 Midday
WP_S_M1	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter	05.04.22 Midday

Sample ID	Sample explanation	Sample date
WP_S_3	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel evening 05.04.22.	05.04.22 Evening
WP_S_M2	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter	05.04.22 Evening
WP_S_4	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from sedimentation basin in the tunnel.	06.04.22 Morning
WP_S_A	Sedimented and adsorption filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after adsorption filter.	06.04.22 Morning
WF_BL3	Filtered distilled water.	
WF_RAW	Sedimented tunnel wash water collected from 1 m ³ tank at the start of adsorption experiment. Not treated.	
WP_BBL3	Procedure blank	
WP_LI_h3	Adsorption filtered sample collected from column with Leca after 3 hours of running the experiment.	
WF_LI_h27	Adsorption filtered sample collected from column with Leca after 27 hours of running the experiment.	
WF_LI_h51	Adsorption filtered sample collected from column with Leca after 51 hours of running the experiment.	
WF_LI_h79	Adsorption filtered sample collected from column with Leca after 79 hours of running the experiment.	
WF_OI_H3	Adsorption filtered sample collected from column with Olivine after 3 hours of running the experiment.	
WF_OI_h27	Adsorption filtered sample collected from column with Olivine after 27 hours of running the experiment.	
WP_OI_h51	Adsorption filtered sample collected from column with Olivine after 51 hours of running the experiment.	
WF_OI_h79	Adsorption filtered sample collected from column with Olivine after 79 hours of running the experiment.	
WP_OACL_h3	Adsorption filtered sample collected from column with Olivine + Activated Carbon after 3 hours of running the experiment.	
WF_OACL_h27	Adsorption filtered sample collected from column with Olivine + Activated Carbon after 27 hours of running the experiment.	

Sample ID	Sample explanation	Sample date
WF_OACL_h51	Adsorption filtered sample collected from column with Olivine + Activated Carbon after 51 hours of running the experiment.	
WF_OACL_h79	Adsorption filtered sample collected from column with Olivine + Activated Carbon after 79 hours of running the experiment.	
WF_Z1_h3	Adsorption filtered sample collected from column with Zeolite after 3 hours of running the experiment.	
WF_Z1_h27	Adsorption filtered sample collected from column with Zeolite after 27 hours of running the experiment.	
WP_ZI_h51	Adsorption filtered sample collected from column with Zeolite after 51 hours of running the experiment.	
WF_Z1_h79	Adsorption filtered sample collected from column with Zeolite after 79 hours of running the experiment.	
WF_GAC1_h3	Adsorption filtered sample collected from column with Granulated Activated Carbon after 3 hours of running the experiment.	
WF_GAC1_h27	Adsorption filtered sample collected from column with Granulated Activated Carbon after 27 hours of running the experiment.	
WF_GAC1_h51	Adsorption filtered sample collected from column with Granulated Activated Carbon after 51 hours of running the experiment.	
WF_GAC1_h79	Adsorption filtered sample collected from column with Granulated Activated Carbon after 79 hours of running the experiment.	
WF_S1_h3	Adsorption filtered sample collected from column with Sand after 3 hours of running the experiment. Sand is regarded as a “blank” filter material in this experiment.	
WF_S1_h27	Adsorption filtered sample collected from column with Sand after 27 hours of running the experiment.	
WF_SI_h51	Adsorption filtered sample collected from column with Sand after 51 hours of running the experiment.	
WF_SI_h79	Adsorption filtered sample collected from column with Sand after 79 hours of running the experiment.	
WP_BL4_1	Filtered distilled water.	
WF_BL4_2	Filtered distilled water.	
WP_BL4_3	Filtered distilled water.	

Sample ID	Sample explanation	Sample date
PF_S1	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Morning
PF_S2	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Midday
PF_S3	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Evening
PF_S4	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	28.09.22 Morning
PF_S5	Sedimented water collected directly from the sedimentation basin with a bucket.	28.09.22 Morning
PF_S_B	Sedimented and adsorption filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected after bag filter	28.09.22 Morning
PF_S_A	Sedimented and bag filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected after adsorption filter	27.09.22 Morning
PF_BL_2408	Filtered distilled water.	24.08.22
PF_S_M1	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter	27.09.22 Midday
PF_S_M2	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter	27.09.22 Evening
WF_S1	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Morning
WF_S2	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Midday
WF_S3	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	27.09.22 Evening
WF_S4	Sedimented wash water sample collected in the Bjørnegård tunnel. Sample was collected from AP1 valve in the tunnel	28.09.22 Morning
WF_S5	Sedimented water collected directly from the sedimentation basin with a bucket.	28.09.22 Morning
WF_S_B	Sedimented and adsorption filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected after bag filter	28.09.22 Morning
WF_S_A	Sedimented and bag filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected after adsorption filter	27.09.22 Morning
WF_BL_2408	Filtered distilled water.	24.08.22
WF_S_M1	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was	27.09.22

Sample ID	Sample explanation	Sample date
WF_S_M2	Sedimented and membrane filtered wash water sample collected in the Bjørnegård tunnel. Sample was collected from valve right after membrane filter	27.09.22 Evening
WF_BBL4	Procedure blank	
WF_BL6	Filtered distilled water.	
WF_RAW_04	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	04.10.22
WF_S-h3	Adsorption filtered sample collected from column with Sand hour 3 of the experiment.	04.10.22
WF_LO_h3	Adsorption filtered sample collected from column with mix of Leca and olivine hour 3 of the experiment.	04.10.22
WF_GAC_h3	Adsorption filtered sample collected from column with granulated activated carbon hour 3 of the experiment.	04.10.22
WF_BIO_h3	Adsorption filtered sample collected from column with biochar hour 3 of the experiment	04.10.22
WF_RAW-06	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	06.10.22
WF_S-h19	Adsorption filtered sample collected from column with Sand hour 19 of the experiment.	06.10.22
WF_LO_h19	Adsorption filtered sample collected from column with mix of Leca and olivine hour 19 of the experiment.	06.10.22
WF_GAC_h19	Adsorption filtered sample collected from column with granulated activated carbon hour 19 of the experiment.	06.10.22
WF_BIO_h19	Adsorption filtered sample collected from column with biochar hour 19 of the experiment	06.10.22
WF_RAW-08	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	08.10.22
WF_S-h35	Adsorption filtered sample collected from column with Sand hour 35 of the experiment.	08.10.22
WF_LO_h35	Adsorption filtered sample collected from column with mix of Leca and olivine hour 35 of the experiment.	08.10.22
WF_GAC_h35	Adsorption filtered sample collected from column with granulated activated carbon hour 35 of the experiment.	08.10.22
WF_BIO_h35	Adsorption filtered sample collected from column with biochar hour 35 of the experiment	08.10.22
WF_RAW-10	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	10.10.22
WF_S-h51	Adsorption filtered sample collected from column with Sand hour 51 of the experiment.	10.10.22
WF_LO_h51	Adsorption filtered sample collected from column with mix of Leca and olivine hour 51 of the experiment.	10.10.22

Sample ID	Sample explanation	Sample date
WF_GAC_h51	Adsorption filtered sample collected from column with granulated activated carbon hour 51 of the experiment.	10.10.22
WF_BIO_h51	Adsorption filtered sample collected from column with biochar hour 51 of the experiment	10.10.22
WF_RAW-12	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	12.10.22
WF_S-h67	Adsorption filtered sample collected from column with Sand hour 67 of the experiment.	12.10.22
WF_LO_h67	Adsorption filtered sample collected from column with mix of Leca and olivine hour 67 of the experiment.	12.10.22
WF_GAC_h67	Adsorption filtered sample collected from column with granulated activated carbon hour 67 of the experiment.	12.10.22
WF_BIO_h67	Adsorption filtered sample collected from column with biochar hour 67 of the experiment	12.10.22
WF_RAW-14	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	14.10.22
WF_S-h83	Adsorption filtered sample collected from column with Sand hour 83 of the experiment.	14.10.22
WF_LO_h83	Adsorption filtered sample collected from column with mix of Leca and olivine hour 87 of the experiment.	14.10.22
WF_GAC_h83	Adsorption filtered sample collected from column with granulated activated carbon hour 83 of the experiment.	14.10.22
WF_BIO_h83	Adsorption filtered sample collected from column with biochar hour 87 of the experiment	14.10.22
WF_RAW-17	Sedimented tunnel wash water collected from 1 m ³ tank. Not treated.	17.10.22
WF_S-h107	Adsorption filtered sample collected from column with Sand hour 107 of the experiment.	17.10.22
WF_LO_h107	Adsorption filtered sample collected from column with mix of Leca and olivine hour 107 of the experiment.	17.10.22
WF_GAC_h107	Adsorption filtered sample collected from column with granulated activated carbon hour 107 of the experiment.	17.10.22
WF_BIO_h107	Adsorption filtered sample collected from column with biochar hour 107 of the experiment	17.10.22



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