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Effects of Freeze/Thaw Process on Treatment Efficiency of Low-cost Adsorbents for Highway Stormwater Treatment

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Master of Energy and Environmental Engineering
Submission date: March 2017
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Master Thesis

Submission date: 27.03.2017

Norwegian University of Science and Technology

Department of Civil and Environmental Engineering

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Science and Technology

Master Thesis

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Department of Civil and Environmental Engineering
Submission date: Skopje, March, 2017
By: Vera Spirkovska

Declaration

I hereby, declare, that this thesis is an original report of my research and has been written by me without any outside assistance. The experimental work is almost entirely my own work; the collaborative contributions have been clearly indicated and acknowledged.

I declare that this thesis was composed by myself and the work contained herein is my own except where explicitly stated otherwise in the text.

Only the sources cited have been used in this work. Parts that are direct quotes or paraphrases are identified as such.

Skopje, March, 2017

Abstract

In this thesis the adsorption of heavy metals from stormwater was simulated in laboratory by using alternative and low-cost materials. The adsorption behavior of three adsorbent materials (olivine, bottom ash and pine bark) was studied to evaluate if the concentrations of lead, nickel, copper and zinc could be reduced to acceptable environmental standards. The concentration of these metals were chosen according to average values in an actual highway stormwater, obtained from previous studies. One area of particular concern is the process of freeze and thaw which can affect the treatment performance and cause secondary environmental impacts by increasing the attrition of adsorbents. The latter carry the risk of releasing adsorbed contaminants. Therefore, the overall objective of this thesis was to test metal removal efficiency of the adsorbents and to analyzed the effect of freezing/thawing on adsorbents and adsorption process.

From the batch tests, the percent adsorption was determined as a function of adsorbent dose (mg/ml) but with constant heavy metal concentration. The results showed high removal efficiency for selected heavy metals by all the three adsorbent materials, i.e. up to 70 %. Higher dose of bottom ash had a better treatment efficiency for the four metals. Olivine removed nickel, copper and zinc with similar efficiency with each amount of mass adsorbent, but lead removal was higher with 100 g of olivine. Pine bark showed best characteristics for lead removal.

Effect of cold climate was evaluated through experiments and results provided data about desorption and releasing of previously adsorbed metals. Desorption of zinc from pine bark reached a value of 8 % from previously adsorbed zinc in first cycle, and this was the highest measured amount. This indicated that selected adsorbents have good performance for keeping the adsorbed metals. It can be considered that cold climate had a negligible effect on the desorption process when compared with results from experiment conducted under normal climate conditions.

Results obtained from adsorption capacity experiments and/or desorption process indicated that the final concentration of heavy metal in the effluent were within range of acceptable environmental standard according to limits provided by Integrated Pollution Prevention Control IPPS and Macedonian regulation for water discharge in surface water. However, for Norwegian conditions, similar comparisons could not be made due to absence of specific environmental standards for highway stormwater.

Keywords: Alternative adsorbents, highway stormwater, heavy metals, cold climate , freeze/thaw process

Acknowledgements

This thesis report, titled “Effects of Freeze/Thaw Process on Treatment Efficiency of Low-cost Adsorbents for Highway Stormwater Treatment” was completed as a part of the collaborative project “Quality Improvement of Master programs in Sustainable Energy and Environment” that aims to develop and establish eight new internationally recognized MSc study programs for the field of “Sustainable Energy and Environment”, at eight collaborating universities in five different West Balkan countries. The project was funded through the Norwegian Programme in Higher Education, Research and Development in the Western Balkans and Programme 3: Energy Sector (HERD Energy) for the period 2014-2016.

This master thesis was a part of a project at the Department of Civil and Environmental Engineering at the Norwegian University of Science and Technology (NTNU) and this master work was conducted during the winter semester in 2016. In this thesis, I worked on adsorption process of different adsorbents and I have learned about the metal pollution in highway stormwater in Norway and gained practical experience through work in the laboratory.

Throughout this process, many people were my support and helped me to achieve my goals.

Firstly, I would like to thank to my supervisor, postdoctoral researcher Aamir Ilyas at the Department of Civil and Environmental Engineering at NTNU. Aamir helped and supported me throughout all semester that I have spent at NTNU and afterwards guided me during writing this master. Also, I would like to thank professor Vojislav Novakovic for the giving me the opportunity to be part of this project.

Special thanks go to my mentor, associate professor Zoran Markov at the Faculty of Mechanical Engineering, Skopje. I would like to express my gratitude for his generous advice, inspiring guidance and encouragement throughout my research for this work and for the given opportunity to be part of this project.

Moreover, I would like to thank professor Sveinung Saegrov for his advices, Syverin Lierhagen at the Department of Chemistry at NTNU for analyzing the water samples and also to thank Trine M. H. Ness for helping me during my laboratory work.

Finally, I express the most gratitude to my parents for their lasting support without question. Also, special thanks go to my sister Elena, brother Boris, my boyfriend Dragan, my really best friend Monika and my friend Dragana for their support, encouragement and patience during my master studies.

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List of Abbreviations and Acronyms

BET	Brunauer-Emmett-Teller isotherm
HR-ICP-MS	High resolution inductively coupled plasma mass spectrometry
IPPC	Integrated Pollution Prevention Control
NPS	Nonpoint source
PAH	Polynuclear aromatic hydrocarbons
PM_{10}	Particular matter
TOC	Total organic carbon

1. Introduction

Stormwater runoff is a major source of many types of pollutants (i.e. metals, nutrients, microbes and organics) which can seriously affect the water quality and ecology of natural water bodies such as rivers, lakes, groundwater and can result in contamination of drinking water sources. Because of the continuously increasing use of automobiles, thousands of kilometers of highway have been built [1]. Many problems associated with highways have occurred, and one major concern is the transformation of landscape from rural to urban areas. With construction of roads and highways, natural infiltration of water into the soil is altered and rainfall in not able to travel along a natural surface, thus a significant runoff is produced.

Stormwater runs through the, roads, parking lots and other impervious surfaces and drains into natural water receivers such as streams, rivers, lakes, ocean or into sewer systems [2]. Instead of water from rain and snowmelt to be able to flow along natural surfaces, which can reduce the velocity of runoff, this water travels along the roads and picks up all types of contaminants. The velocity of runoff is higher when it travels along paved surfaces instead of natural surfaces such as vegetation covered ditch or swale. Furthermore, the highway runoff must be removed from the paved surfaces before ponding creates safety hazards for travelling vehicles or before the excess water can freeze [3].

With all the above mentioned problems, stormwater represents one of the major cause of water pollution. Classification of the stormwater impacts can be divided as hydrologic, physical, chemical and biological. Impacts of the greatest concern are biological because of the habitat alteration due to the loading of nutrients, sediment, metals, chloride, bacteria, oxygen-demanding substances, hydrocarbons, high temperature water and critical pH value [4]. Large quantities of heavy metals in the polluted water from the highways have a negative effect on the environment since these metals are not degradable. Lead, copper, nickel and zinc are the most significant toxic metals found in road runoff and showed the highest concentrations [5]. The highway runoff quality is a serious problem because of the necessity of clean water discharge into natural water bodies. The environmental problems associated with highway runoff will continue to increase. Therefore, it is important to minimize pollution from highway runoff because of human health, economy and the health of ecosystems.

Today, there are many ways to manage and treat the highway stormwater. Therefore, the treatment options need to be carefully evaluated to treat a specific water composition. Due to different needs that must be taken into account, the treatment options will vary for any given situation. One treatment option is to use adsorption process that can remove heavy metals by binding them to the surface of the adsorbent, such as industrial waste and by-products, minerals, bio products, etc. More importantly, adsorption process represents a cost-effective and an environmentally friendly method for treatment of stormwater in a short time. However, the performance of alternative adsorbents has not yet been thoroughly tested in cold climates [3]. Before choosing the best adsorbent material for application in real situation, the effects of cold clime should be taken into consideration. This factor is important because in field conditions freezing of adsorbent may occur and with thawing, the process releasing of adsorbed pollutants may start. From here the necessity for high stability of the adsorbent arises, as well as the retention of pollutant during the freezing/thawing cycles.

In order to see if the adsorption process is a valid choice for treatment of highway runoff in cold climate, different laboratory tests have to be conducted and specific climatic condition have to be included i.e. deicing, freezing and thawing. Therefore, the overall objective of this thesis is to test metal removal efficiency of the adsorbents in simulated highway storm water and to test the effect of freezing on adsorbents in the adsorption process. Three inexpensive sustainable adsorption materials were studied in this master work: bottom ash samples from a solid waste incinerator, pine bark and granules of olivine. The main advantage of alternative adsorbents is their low cost, little need for processing and pretreatment which allows usage for many problems with wastewater in real application. Many scientific studies identified new materials and evaluated them with regard to various type of pollutants presented in stormwater [3]. However, potential problems with alternative materials are: consistency in material’s content (i.e. bottom ash), continuous supply of the materials, environmental stability and additional pollution as a result of releasing elements from the material content, as well as operation and maintenance cost when installed in real application.

The results of the experiments, presented herein, provided first insights regarding performance and potential environmental impacts of alternative adsorbents in cold climates.

1.1. Research goals and objectives

This master thesis investigated three different materials olivine, pine bark and bottom ash. Adsorption process as a treatment option for removal of heavy metal from aqueous solution was examined in laboratory.

Specific objectives

1. Investigate the heavy metals removal efficiency with the chosen adsorbents from synthetic highway runoff;
2. Investigate the influence of freezing and thawing process on heavy metals removal from synthetic stormwater;
3. Evaluate the potential negative environmental impacts of adsorbents caused by cold climate conditions.

2. Literature review

This section describes the problems related with highway runoff and cold climate. The sources of pollutants are identified and necessity of stormwater treatment is provided. As well as, this section includes definition of adsorption process and overview of the used low-cost adsorbents.

2.1. Stormwater runoff

The problems and impacts from stormwater runoff are the most evident in areas where urbanization has occurred. The cities changed natural landscape due to the rapid process of urbanization. Therefore, natural landscapes are covered with impervious surfaces. The advantages of porous terrains like forests, wetlands and grasslands are related with possibility of rainwater and snowmelt to filter slowly into the ground. As a result of the urbanization and the changes of the land, flooding occurs as a problem and a significant amount of stormwater runoff is generated on the highway surfaces. Stormwater runoff increases as solid surfaces replace natural vegetation, because water is unable to slowly filter into the landscape. Stormwater deposits sediment that decreases the depth of waterways, further increasing flooding [6] .

Figure 1, shows the increasing of runoff due to urbanization. This water is polluted and flows onto the impervious surface, which increases the trash, debris and odor. In many cases, cities, this polluted runoff could drain into “storm sewers” which are separated from sanitary sewers. Stormwater entering storm sewer does not usually receive any treatment prior to entering the natural recipients, such as streams, rivers, lakes and other water surfaces [7] represents the same unit area, first undeveloped and then impacts of the land development and impervious surfaces. Impervious surfaces convert every rain drop and snowmelt into runoff [8], or any impervious surface results in direct rainfall being converted into immediate and almost total runoff.

One way of protection flooding and pollution of the environment is to transport runoff as quickly and directly as possible to treatment before releasing it into natural water receivers. For a specific site, the net increases in runoff volume during a given storm depends on both the predevelopment permeability of the natural soil and the vegetative cover. Poorly drained soils result in a smaller increase of runoff volume because the volume of predevelopment runoff is already high [8].

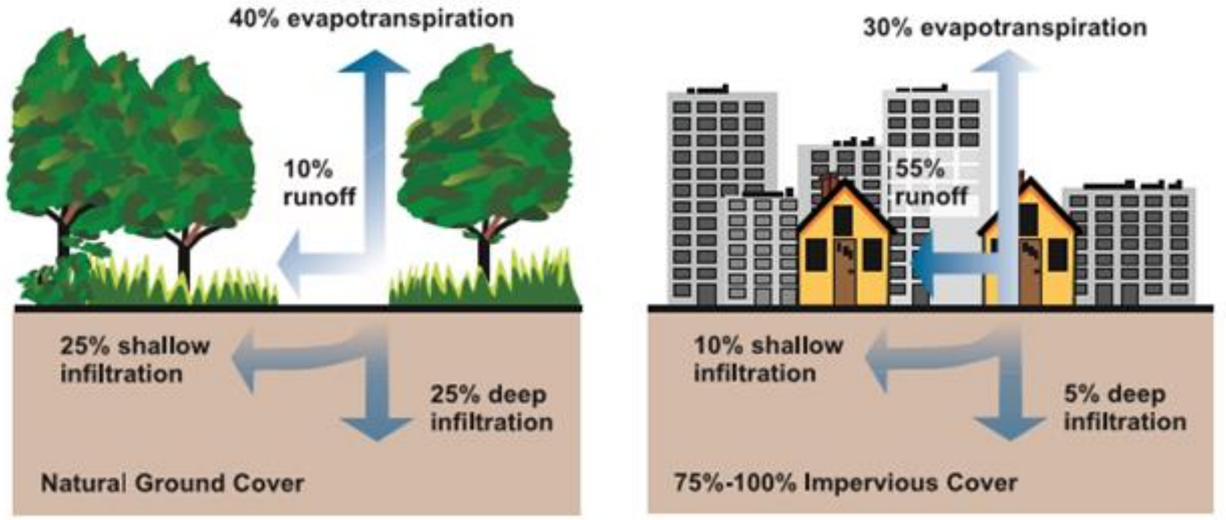


Figure 1. Relationship between impervious cover and surface runoff [7]

Figure 2, presents an undeveloped area and provides a description of the concept of sustainability of the water resources. The challenge of sustainability is that all the rain drops, without pollution, would be part of the returning hydrologic cycle. The rain that falls on the land surface over a period of time defines the magnitude of the resource and the quantity required to sustain the cycle. With careful land use planning and water resource management, every available drop of rain can be used and reused without destroying the quality or affecting the character of natural streams and rivers. Many of water uses, such as drinking supply, can be largely recycled with the proper waste system design, and many other uses can be reduced in quantity if they are largely “consumptive” uses, such as irrigation of artificial landscapes [6]. Consumptive demands of cultivation can also be reduced by methods such as drip irrigation, and energy systems can be designed that do not consume fresh water in the cooling process. All modern water supplies require energy, and most energy systems affect water. Similar to the land – water dynamic, the energy – water interrelationship requires that any system changes consider both resources [9].

The rain that falls on the land moves through the land surface and infiltrates in the porous areas. Also, during the process of evaporation and transpiration the water is part of the hydrology cycle, and some percentage run off to the sea.

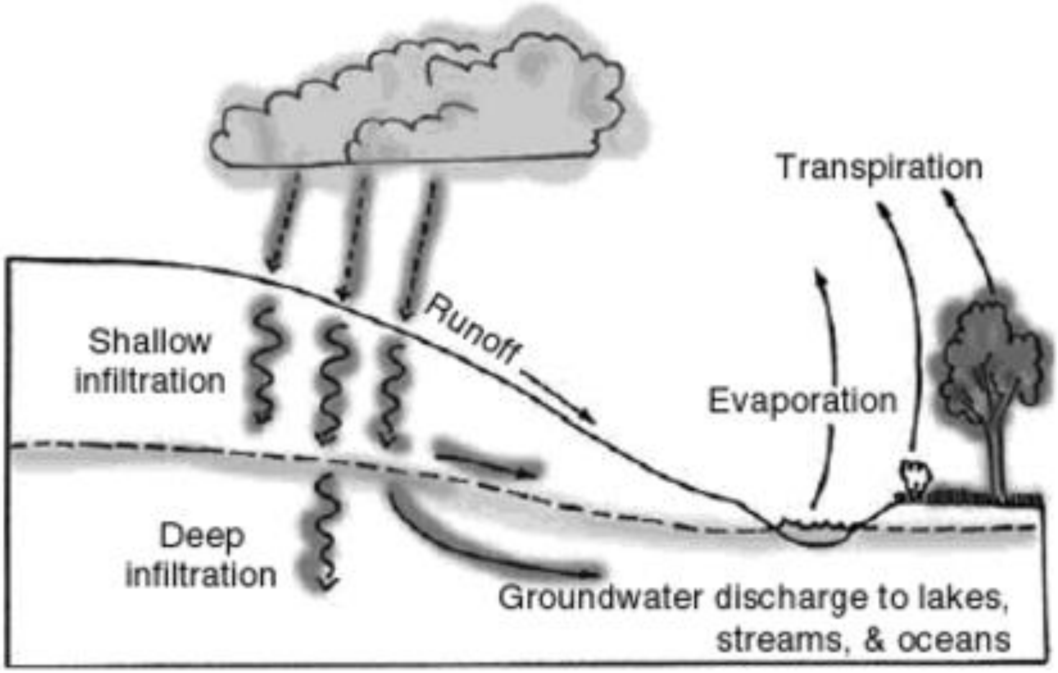


Figure 2. The hydrologic cycle [9]

Today, with the extensive development of urban environment, the land is covered with roofs, roads, parking lots, patios, etc. [2]. Stormwater runs off in the drain area, infiltrated or evaporates. But because of the increase in impervious areas the produced runoff volume is increasing. The increase in runoff volume affects the downstream riparian corridor, eroding stream banks and conveying the pollutant load from the impervious surfaces as well as the channel to the natural water receivers. Impervious surfaces, whether rooftops, pavements, or streets, turn every drop of rainfall into direct and immediate runoff. Finally, the energy of runoff scours every pollutant that is dripped, dropped, spilled, or spread on the impervious (and pervious) land surfaces, and convey this non-point source pollution to surface waters [9].

2.2. Nature of the cold climate problem

The snow and snowpack that have been build and iced for several months during the winter period started to melt because of warm period in the spring or during the interim periods along the winter. Therefore, the increasing of water volume indicates problems with snowmelt runoff [3]. Generally, this water volume caused by interim melting of snow is significantly less than the large spring melt and do not contribute to a significant volume of stormwater runoff. When snowpack starts to melt during the process it releases different pollutants. Runoff related with snowpack melting occurs in relatively short periods of the year. Factors that influence on the nature and speed with which the snowmelt occurs are: solar radiation, the distribution of the snow cover, freeze-thaw cycling, chemicals in the snow packs [10].

The sources area of snowmelt is a critical point in both the hydrologic and water quality of snowmelt runoff. Highways are large paved surface area and runoff could be relocated by plowing, which can include total site removal or relocation off the surface, and chemical-induced (salt and sand) melting. Every time when snow either rain or snow highways generates numerous loading events. The problems with water quality associated with snowmelt during snowmelt and rain-on-snow events rise because of the releasing large volumes of water but also because of the materials accumulated in the snowpack all winter carried by the water. Materials picked up in the winter season, during melt period are released and flow over the land's surfaces.

In Figure 3, a comparison between pollution or surface material accumulation on snowpack and accumulation during the rainfall is presented, in the urban areas.

This figure represents the urban area problem with snowmelt but could be used to present also the problem with snowmelt on the highways [10]. Pollution accumulation during the winter season could occur on a snowpack, directly or on the roadway, on the side where it is plowed. Snow is a very effective scavenger of atmospheric and additional pollutants, and literally any material presented in a snow catchment during meltwater when it runs off will show up. The greatest volume of snowmelt and a major portion of annual pollutant loading could be associated with spring melt events.

During the winter seasons additional contaminants are added because of winter maintenance and the conventional pollutants of concern for highway attached these contaminants. Presented metals, solids and nutrients during the summer are joined by increased hydrocarbons and polynuclear aromatic hydrocarbons (PAHs) from inefficient and increased fuel combustion, by salt and increased solids from the maintenance of roads and other building activities and by cyanide that has been added to salt as an anti-caking additive. In the winter season less of concern are organic debris and pesticide and fertilizer runoff.

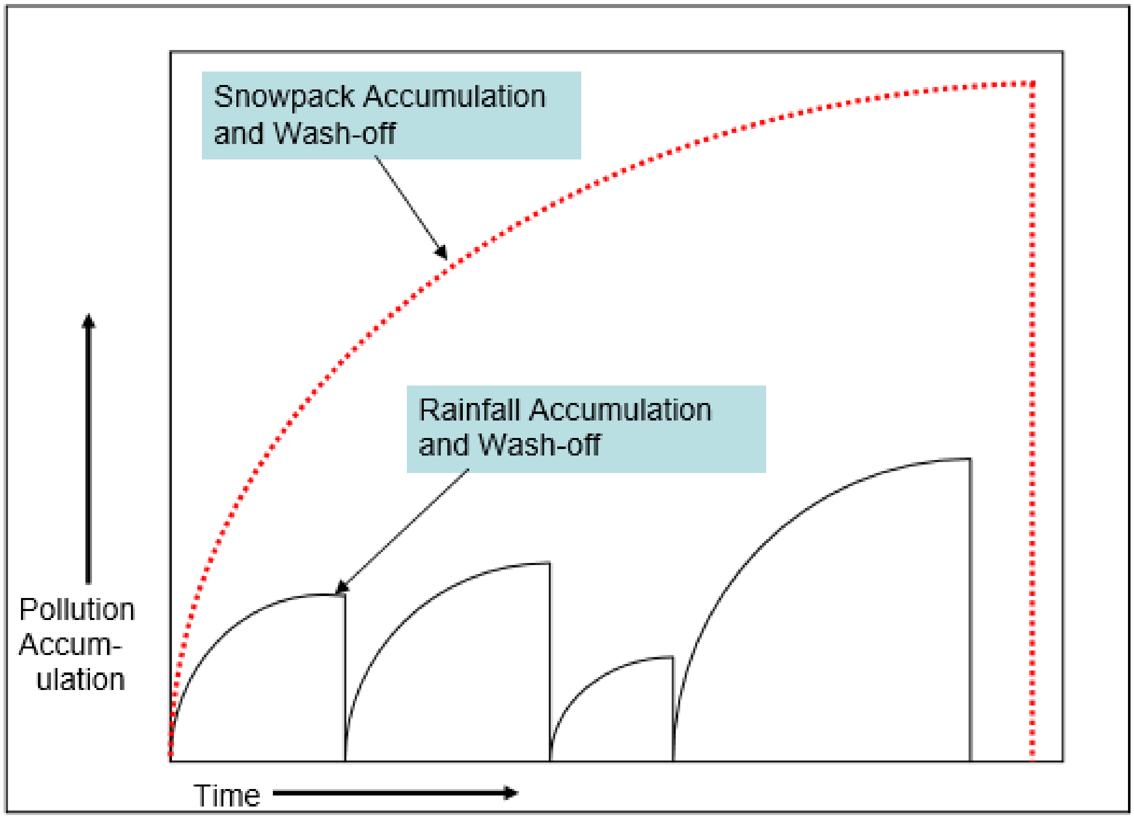


Figure 3. Snowpack pollution accumulation and wash-off as compared to rainfall [10]

During the melt, the already difficult management scenario with complex melting pattern is further complicated from the release of pollutants at different times. A very heterogeneous snowpack is created because of the variability of snow characters and the freezing/thawing process that occurs through the winter season is repeated.

Figure 4, illustrates the melt behavior. The early melt part involves a release of soluble constituents such as; dissolved metals, dissolved nutrients, dissolved organic materials, Cl from snowpack and also significant volume of water. The early melt is resulting with shock effects when these pollutants reach a receiving water body.

In a certain period much of the liquid volume is released from snowpack (skewed toward the earlier part of the mid-melt event, Figure 4) and the generated water carries with it the remaining soluble along with the beginning portion of finer-grained solids and associated contaminants (ex. hydrophobic PAHs). Generally, the largest portion of water runoff associated with the melt has mid-melt period, and the mobilization of solids begins and continues as long as sufficient energy is available to move the finer particles, leaving behind the larger particles.

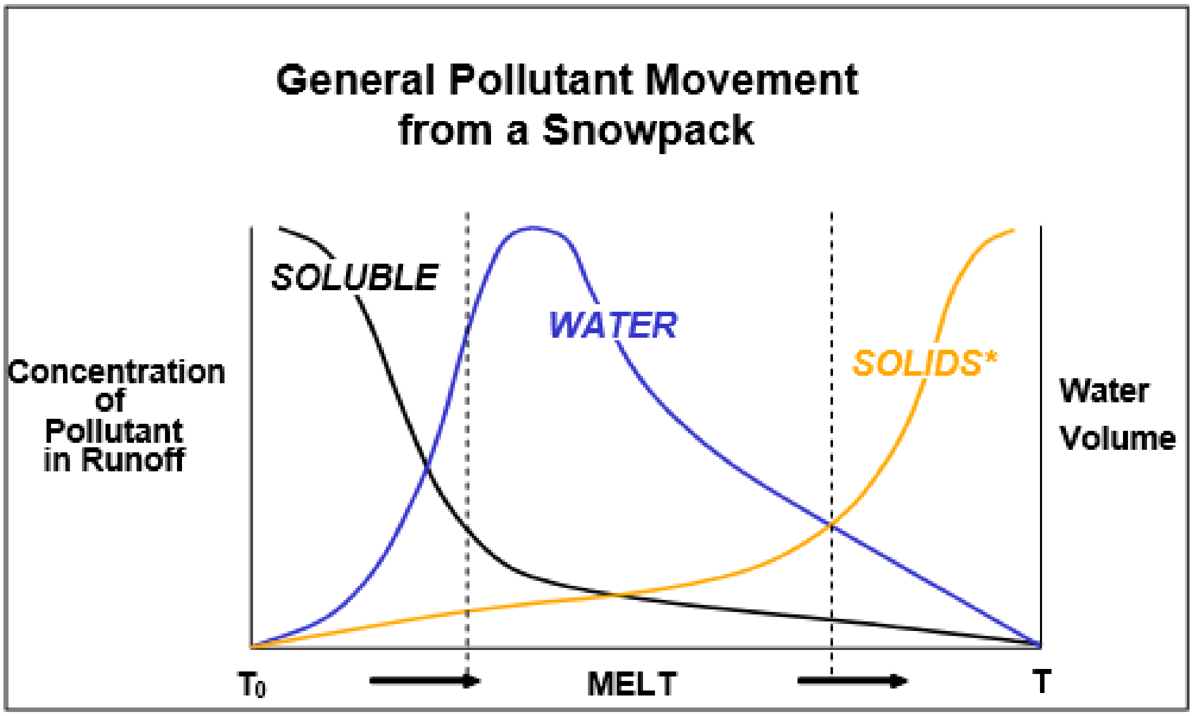


Figure 4. Generalized melt behavior [10]

Removal and disposal of snow and ice and dealing with the accumulation of pollutants are not a stand-alone best management practices, but rather they encompass many public work practices that potentially have an impact on the quantity and quality of water produced with snowmelt [10]. One option for heavy metal treatment of stormwater runoff from highway is proposed, tested and evaluated in this master work.

2.3. Source of pollutants

After passing of a thundershower, both air and land surface are much cleaner. All of the atmospheric dust, surface organic detritus, debris on the highway have been washed from the surface and carried from highways to the surface inlets, where they enter and accumulate [9].

Pollutants in stormwater may be presented in form of particles, particles-associated pollutants or in dissolved form. The most of the stormwater treatments have focused on capture of particles and pollutants associated with particles. Dissolved pollutants are more mobile, bioavailable, have influence if receiving water bodies and they are captured via different mechanisms than particles [11].

The physical and chemical contents of this stormwater vary and they are quite different from the steady discharge of wastewaters from sewage treatment facilities. The basic difference is in the pollutant discharge between point (municipal and industrial wastewaters) and non-point sources (conveyed in stormwater runoff).

In urban areas and areas near highway the rainfall and snow deposits are exposed to the different pollutants such as pollutants from anthropogenic activities, pollutants from traffic, heating and road maintenance (salt and sand during winter road maintenance). Dominant effect on pollution on these waters have traffic and motor vehicles. The major source for highway runoff contamination is vehicle traffic on highways because vehicles directly deposit hydrocarbons, petroleum products, oil and other fluids and some parts from the vehicles. These contaminants do not retain on the same place but they could be transported and carried off the highway by precipitation, wind or vehicles movement. Some contaminants carried by the atmosphere could settle on the highway surface or could be scrubbed by rainfall and later transported to the highway. These airborne pollution is from the vehicles exhausts, some near activities such as agriculture activities, pollutants from industry and manufacturing plants. Road maintenance could be an important contributor and source of contamination in highway runoff. Salt and sand, materials from asphalt paving and patching operations are pollutants from this source [6].

Pollution accumulation in and release from snow deposit during warmer weather is influenced from pollutant transport pathways and represent potential impacts on the receiving environments during snowmelt. According to the reviewed literature [2,3] , down below there is a list of the most broadly presented constituents in highway runoff, Table 1.

Table 1. Sources of pollution [2,3]

Source of pollutants	**Pollution**
Vehicle exhaust/diesel soot	Ni, Pb, Zn
Tire wear	Cd, Zn
Tire studs	W
Brake wear	Cd, Cu, Pb, Zn
Catalytic converters	Pt, Pd, Rh
Asphalt road surface wear	Ni
Road marking paint	Cd, Pb
Galvanized metal structures (signs, drains, and guardrails)	Zn
Construction sites	Sediment, metals
Application to snow and ice	Road salt
Pesticide applications, automobiles, accidental spills, illegal dumping	Toxic and synthetic chemicals
Healed landscape/impervious areas, tree removal, shallow ponds	Thermal impacts

The highest concentration of metals as a pollutant in stormwater is noticed in heavily trafficked highways and roads. An additional pollutant part, of the snow deposits, is the road salt. This derives the winter road maintenance and the road salt contributes to the toxicity of the produced snowmelt.

2.3.1. The constituents of highway runoff

The amount and type of contaminants in highway runoff depend on various and different factors such as: traffic volume, weather season, location, land use, type of highway surface and highway maintenance practices [10]. Table 2 presents a wide range of contaminants in highway runoff, identifies the sources of pollution and gives a list of some environmental concerns. In the following table, the key environmental concerns are presented from both the human health and natural environmental perspective [6].

Table 2. Typical runoff contaminants and sources [6]

Constituent	Key sources	Environmental concerns
Particulate PM_{10} and smaller particles	Pavement wear, vehicles, vehicles exhaust, fuel spills, highway maintenance (includes salt and sand applied in winter).	PM_{10} - threat to human health. Main carries of many other contaminants including heavy metals PAS's. Increasing of turbidity in receiving waters that can decrease prey capture for sight-feeding aquatic animals and/or clog grills.
Polynuclear Aromatic Hydrocarbons (PAHs)	Automobile exhaust as a by-product of combustion, and potential background emission from fuel spills, oil spills, and industrial sources.	Group of base/neutral compounds found in very small concentrations in highway runoff, mostly sorbet to the solid phase. Can be toxic to human and aquatic life. May bio-accumulate in the tissues of plants and animals.
Nitrates, Phosphorous (P)	Atmosphere, organic nutrients in roadside vegetation, fertilizer application.	In their soluble form they can cause algal growth and reduce oxygen levels in receiving waterbodies, and can potential cause fish kills. Largely a problem with urban and agricultural runoffs.
Lead (Pb)	Leaded gasoline, auto exhaust, tire Wear, lead oxide filter material, lubricating oil and grease, bearing wear.	Bio-accumulates. Risks to a human health

Zinc (Zn)	Tire wear (filter material), motor oil (stabilizing additive), galvanized steel, grease.	Highly soluble. Bio-accumulates, can cause unpleasant taste in drinking water. Can be toxic to aquatic organisms
Iron (Fe)	Auto body rust, steel highway structures (guardrails, bridges etc.), moving engine parts	Causes staining, discoloring, nutrient for algae.
Copper (Cu)	Metal plating, bearing and bushing wear, moving engine parts, brake lining wear, fungicides and insecticides applied by maintenance operations.	Can be toxic to aquatic species. Concentrates in sediments and can bio – accumulate.
Cadmium (Cd)	Tire wear (filter material), insecticide application, lubricants, auto exhaust, galvanized steel.	Carcinogenic. Bioaccumulation.
Chromium (Cr)	Metal plating, moving engine parts, brake lining wear	Suspected carcinogen.
Nickel (Ni)	Diesel fuel (exhaust) and lubricant oil, metal plating, bushing wear, break lining wear, asphalt paving.	Potentially carcinogenetic.
Manganese (Mn)	Moving engine parts	Contribute to water hardness. Can be toxic.
Bromide (Br)	Vehicles exhaust	Toxic

Cyanide	Anti-cake compound (ferric ferrocyanide), prussian blue or sodium ferrocyanide, yellow prussiate of soda used to keep de-icing salt granular	Highly toxic to human and aquatic life.
Sodium (Na) **Calcium (Ca)**	De-icing salts, grease	Ca contributes to water hardness. High concentrations of sodium in the soi1 and water may be toxic to plants.
Chloride (Cl)	De-icing salts	Chloride tends to be less toxic to animals and plants than sodium. However, too much chloride makes water unpalatable and eventually unfit to drink.
Sulphates	Roadway beds, gasoline and diesel fuel, vehicle exhaust, de-icing salt.	Can contribute to eutrophication and acidification of water.
Petroleum products	Spill, leaks or blow-by motor lubricants, antifreeze and hydraulic fluids, asphalt surface leachate, fuels	Many petroleum products are carcinogens and can contaminate groundwater.
Polychlorinated biphenyl (PCB), pesticides	Spraying of highway right-of-ways, background atmospheric deposition, PCB catalyst synthetic tire.	Bio-accumulate and are carcinogens

Pathogenic bacteria	Soil, litter, bird droppings, trucks hauling livestock and stockyard waste.	Can cause waterborne diseases
Rubber	Tire wear	Largely aesthetics but may contain trace metals such as nickel and zinc.
Debris	Litter, materials and parts from vehicles and their loads, other solid materials deposited on roads.	Largely aesthetics but may have specific environmental concerns.
Asbestos	Clutch and brake liming wear	Largely a threat to human health. Carcinogen.

It has to be noted, that not all contaminants listed in the table will be presented in all highway runoff.

2.3.2. Heavy metals

When highway runoff is analyzed, the large amount of heavy metals found in highway stormwater is one of the main reasons for being concerned about environment. Heavy metals are harmful for the environment since metals are not degradable and therefore are accumulated in living organisms and natural bodies. Metals that have a high atomic weight and a density at least 5 times greater than that of water are defined as heavy metals. The density of heavy metals is above 5 g/cm^3. Heavy metals are naturally occurring elements but also their wide application in industry, domestic, agriculture, medical and technological usage have led to their distribution in the environment and even raising concerns over their potential effects on human health. The quantity of the metals, route of exposure and chemical species are factors of which the toxicity of the elements depends upon. Because of their toxicity; arsenic, cadmium, lead, mercury, zinc have significant influence on public health [12].

Four heavy metals: copper, nickel, lead and zinc are the subject of this thesis. Their concentration in highway stormwater is significant. Automobiles are a continuous source of pollution because of the releasing of a significant mass of copper, nickel, lead and zinc and they are trending upwards [1].

According to the literature on the topic, heavy metals are always associated with the fine particles in highway runoff. This fine sludge and clay fraction in runoff carry the largest amount of pollutants. The concentration of these particles increases with high flow rates across the highway surface due to the scouring action and these particles are characteristics because they are easily mobilized by low intensity rainfall. Within the distance of 35-50 m from the edge of paved surfaces, concentration of heavy metals such as lead, cadmium, zinc and nickel decrease but also concentration of these metal are found in the soil (depth of soil depends on the soil type) near the highway [6]. Furthermore, many stormwater pollutants such as heavy metals, phosphorus, hydrocarbons or PAHs are also presented in the dissolved phase. Dissolved metals in stormwater are of the concern because they are more bioavailable and toxic than metals bound to particles. The metals in particular form could be removed with sedimentation or filtration process, while dissolved metal ions could be adsorbed with adsorbent media during adsorption process [11].

2.4. Adsorption process

According to the literature, adsorption is a phase transfer process that is widely used in practice to define removing substances from fluid phases (gases or liquids). The most general definition describes adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid [13]. Due to presence of unbalanced or residual forces at the surface of liquid or solid phases, the process of adsorption arises. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface [14].

Figure 5 presents basic terms used in adsorption theory. Adsorbent and adsorbate are two components involved in the adsorption process. The adsorbate gets adsorbed. So, the definition for adsorbent is: a substance on the surfaces of which the adsorption process takes place. Substances which are being adsorbed on the surface of adsorbent are called adsorbate. Adsorbed materials could be released from the surface of the adsorbents and transferred back into the liquid phase by changing the properties of the liquid phase, for example with changing the temperature, pH, concentration etc. This is the opposite from the adsorption process and it is called desorption [13].

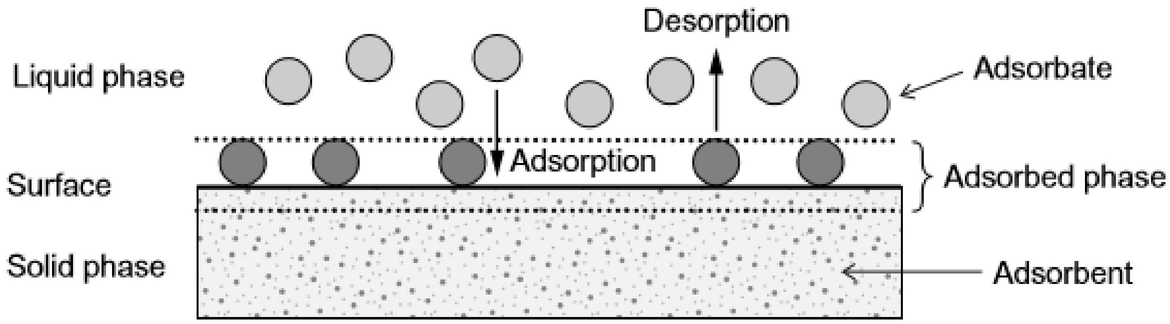


Figure 5. Basic terms of adsorption process [14]

In water treatments, adsorption has been proved as an efficient removal process for a multitude of solutes. Herein, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces. Depending on the adsorbent type applied, organic substances as well as inorganic ions can be removed from the aqueous phase. Treatment of polluted water with adsorption process allow the usage of low-cost materials. The purpose of this thesis is to emphasize the adsorption characteristics on low-cost adsorbents for heavy metals removal.

2.4.1. Adsorption types

The adsorption process can be classified as physical adsorption (physisorption) or chemical adsorption (chemisorption). This classification depends on the value of the adsorption enthalpy. The physical adsorption is caused by van der Waals forces (dipole-dipole interactions, dispersion forces, induction forces), which are relatively weak interactions. Chemisorption is based on chemical reactions between the adsorbate and the surface sites. New chemical bonds are generated at the adsorbent surface [20].

2.4.2. Adsorption equilibrium – isotherm equation

When studying the adsorption process, it is common to look at the theory of adsorption equilibrium. Adsorption equilibrium data considered the adsorbate/adsorbent system and provided basic information for assessing the adsorption process. Hence, information about adsorption equilibrium in considered adsorbate/ adsorbent system is necessary to characterized the absorbability of pollutants in water and also to select an appropriate adsorbent material [13].

The amount of adsorbate that an adsorbent can take up depends of the interaction between adsorbate/adsorbent system and it is also determined by the properties of the adsorbate, adsorbent and by the properties of the aqueous solution, pH value, temperature, occurrence of competing metals-adsorbate. Important factors describing the adsorbent are solubility, saturation, the molecular structure, and weight. Parameters such as adsorbate concentration, adsorbed amount or adsorbent equilibrium and temperatures are parameters that uniquely defined each adsorption equilibrium state. The general form for a single-solute system is the following equilibrium relationship:

$$q_e = f(c_e, T) \quad (2.1)$$

q_e – adsorbed amount in the state of equilibrium [mg adsorbate/g adsorbent],

c_e – adsorbate concentration in the state of equilibrium [mg/l],

T- temperature [°C].

In practice, temperature is considered as constant parameter and adsorption isotherm, so Equation (2.1) could be determinate as:

$$q_e = f(c_e), T = constant \quad (2.2)$$

Typically, the dependence of the adsorbed amount on the equilibrium adsorbent concentration is determined experimentally at constant temperature as shown on Figure 6.

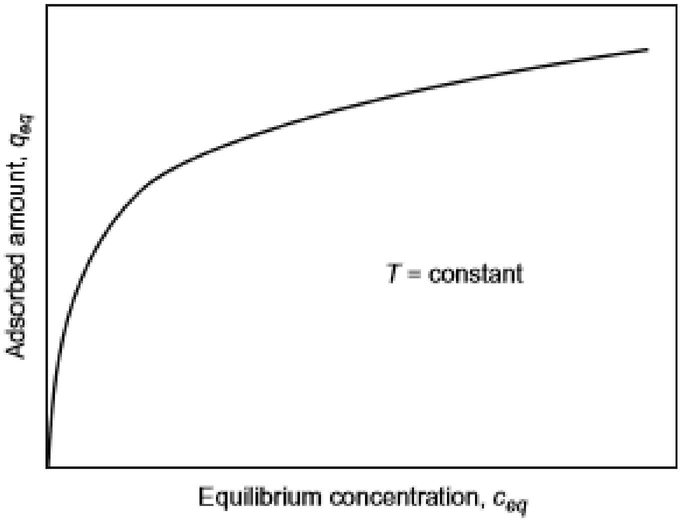


Figure 6. Adsorption isotherm [13]

The graph called adsorption isotherm is graph usually used when process of adsorption is studied. The correlation between the amount of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature is shown with adsorption isotherms.

The method bottle-point is usually applied for determination of equilibrium data, Figure 7. A set of bottles is used to determine the isotherm point. With known volume V_L, and known initial concentration, c_0. is filled bottles.

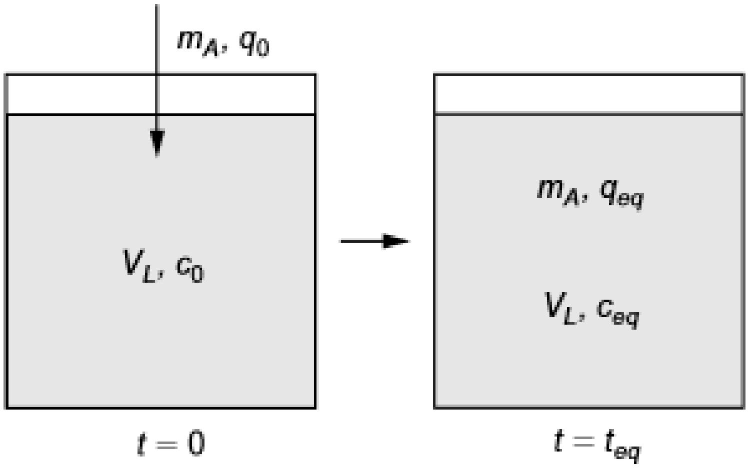


Figure 7. Experimental determination of adsorption equilibrium data [13]

Next, the defined adsorbent mass is added in the solution and the mixture is shaken until state of equilibrium is reached. After the equilibrium is reached, typically the time is between few hours and a week, the residual (equilibrium) concentration c_e can be measured. The adsorbed amount q_e can be calculated. According to the material balance the mass removed from liquid phase Δm^l must be the same as the mass adsorbed onto the surface of the adsorbent Δm^a,

$$\Delta m^l = \Delta m^a \quad (2.3)$$

or,

$$m_0^l - m_e^l = m_e^a - m_0^a \quad (2.4)$$

whereby, subscript 0 is value at starting point and –e is concentration mass value of pollutants at the end.

With the definition of the mass concentration c, ratio between mass and volume, and the adsorption loading, q,

$$c = \frac{m^l}{V_L} \quad (2.5)$$

$$q = \frac{m^a}{m_A} \quad (2.6)$$

The material balance can be written in the form

$$V_L(c_0 - c_e) = m_A(q_e - q_0) \quad (2.7)$$

usually q_0 in equilibrium measurements and

$$q_e = \frac{V_L}{m_A}(c_0 - c_e)$$

or,

$$q_e = \frac{V}{m}(c_0 - c_e) \quad (2.8)\ [13],$$

whereby,

V – volume of the solution [l]

m – mass of the adsorbent [g]

C_0 – initial concentration of the adsorbate [mg/l]

C_e– equilibrium concentration of the adsorbate [mg/l].

One isotherm point is found when the concentration difference is measured because the adsorbent dose m_A/V_L is known. More points are obtained when the adsorbent dose or the initial concentration vary [13].

2.5. Low-cost adsorbents

The value of waste materials has changed with rise of raw material prices and the rise of awareness for environmental issues. Recycling and reutilization of the waste water and materials are potentially favorable routes towards development of suitable, cost effective and environment friendly processes in the industry. Therefore, exploring the possibilities of turning waste material into valuable products is of great interest with regard to reducing the end-waste. These, modified waste materials because of their high adsorption capacity, especially for heavy metal removal from aqueous media and large specific surface area for bounding the pollutants onto the "new" adsorbent are attract to use as adsorbents [15]. Potential applications of these adsorbents include direct treatment for heavy metal removal but mostly waste materials require pretreatment in order to improve their performance.

2.5.1. Olivine

The olivine granules are part of the mineral clay groups. Mineral clay is characterized with the ability to take up cation and anions by ion exchange, adsorption or both at same time. Clays are a good adsorption material because of its chemical stability, large specific surface area and layer structures where pollutants can adsorb on their surfaces or edges [16]. Granules of olivine has greenish grey color. Mineralogical composition of olivine sample from Sibelco Nordic is presented in Table 3 and chemical composition of mineral olivine is given in Table 4 [17].

Table 3. Mineralogical composition of olivine [17]

Forsterite	Mg_2SiO_4	93 mol %
Fayalite	$Fe_2 SiO_4$	7 mol %

Forsterite is a magnesium rich variety of olivine and its crystals have white, yellow and green color. Favalite or iron silicate is iron rich form of olivine that occurs in brown or black color.

Table 4. Chemical composition of olivine [17]

Components	Total of weight [%]
MgO	49
SiO_2	41
Fe_2O_3	7
Al_2O_3	0.5
Cr_2O_3	0.3
NiO	0.3
MnO	0.1
CaO	0.05
pH	8.9 – 9.5

2.5.2. Bottom ash

Bottom ash is a secondary waste product which is produced by combusting coal or municipal solid waste in incineration plants. The composition of municipal solid varies from country to country because of the different lifestyle and recycling practices. Ashes could be separated by [18]:

1) Physical properties
    a) particle size distribution,
    b) moisture content,
    c) bulk density,
    d) porosity;
2) Chemical properties
    a) chemical composition,
    b) loss on ignition,
    c) metal, organic and chloride content.

Bottom ash has heterogeneous particles in its content. Some of them are really large and there are also small particles like dust with a diameter smaller than 63 μm. The particle size of bottom ash can reach much larger sizes-up to 50 mm in diameter, has a sandy texture and its color is dark grey. Therefore, the particles are heavier and fall to the bottom of the surface. Bottom ash contains heavy metals like cooper, nickel, lead and zinc, dry matter, chlorine and sulphur but it also contains organic matter such as carbon. According to the results from the leaching tests from a previous project, on analysis of bottom ash from solid waste incineration in Norway, the following elements are main part of its content: Na, Mg, Al, Si, P, K, Ca, Fe, Cu, Zn, Pb, S, Cl [19]. Determination of organic matter content and ash according to the Norsk standard NS-EN 13039:2011 was provided on solid samples of bottom ash in analytical laboratory in NTNU and the results showed that only 3% of bottom ash content is organic matter while the remaining 97% is ash. Conducting the experiment for determination of organic matter content and ash, showed that bottom ash is generally inorganic matter. Higher concentration of organic matters can have negative impacts on adsorption process. The calculation and the results are presented in Appendix 4.

The results from leaching tests in previous studies [19], showed very low leaching of lead and indicate that lead is mainly present in compounds that are not soluble in water. Copper in bottom ash is presented in the form of copper(I)oxide and copper sulphate. In water, copper sulphate is readily soluble, but the results from leaching tests showed very low and limited leaching of copper, indicating that only a small proportion of the copper in bottom ash is present as sulphate. Leaching test showed that zinc in the bottom ash is highly insoluble in water. Results for pH of the bottom ash samples indicated that pH value is near 12. The pH value is not included in lists over a hazardous substances. It is, however limited in range from 6.5 – 9.5 (environmental standards, Table 13) and the pH value of bottom ash samples are above that limit [19, 22].

2.5.3. Pine bark

The pine bark is a low cost adsorbent that originates from the forest industry. In recent years, pine bark has been investigated and results presented in the reviewed literature showed that pine bark has good performances as an adsorbent for metals and organic matters in contaminated water and also for treatment of stormwater [20].

Pine bark is organic material and can be biologically degraded as opposite to other adsorbent materials evaluated in this thesis. Pine bark could be classified as a lignocellulosic material and is usually characterized whit cellulose, hemicellulose and lignin as the main constituents in its content [21].

The pine bark content is 98% organic matter and the remaining 2% is ash. These results are generated after the performed tests for determination of organic matter on solid samples of pine bark. The leaching tests showed that organic carbon is released from pine bark when mixed with water. Calculation and procedure for the two methods are presented in Appendix 3 and 4.

3. Materials and methods

This section describes the procedures for adsorption process and obtaining the adsorbents performance under different weather conditions. The characteristics of the adsorbent materials are provided, as well as the description of the experiments and the methods used for adsorption analysis.

3.1. General

To achieve the objective of this master work, finding an effective low-cost adsorbent in cold climate conditions, batch test experiments were used. Several experiments were conducted to determine the adsorption capacity of the adsorbents and heavy metal removal efficiency under normal and cold climate conditions.

Prior to use, all bottles, glass or plastic, and containers were thoroughly cleaned with detergent before being left to soak in hydrochloric acid HCl, for 24h. Finally, all of the used equipment was rinsed with distilled water. To minimize the risk of contamination throughout the experiments, great care was taken.

3.2. Materials

The three selected adsorbent materials were: olivine, bottom ash and pine bark. To reduce the risk of secondary contamination bottom ash samples were mixed with 15 % wt. iron oxide and the pine bark was sieved and heated for humidity reduction. Granular olivine was used as pure adsorbent without any processing. The following section provides information about the selected low-cost adsorbents.

3.2.1. Olivine

The samples of olivine used were produced and provided by Sibelco Nordic AS. The olivine was used, without any further modification or pretreatment. The supplier provides olivine in granulated form which is developed from fine olivine dust through a proprietary process. Granules were preferred because the adsorbent would be used in infiltration based process and using fine olivine dust directly would not be suitable due to clogging risks. Information about the product provided by Sibelco Nordic AS can be seen in Appendix 7.

The empirical chemical formula of the olivine $(Mg, Fe)_2SiO_4$. The particle size range used in this study was 1 to 3 mm. Table 5 shows the physical properties and includes some details of the olivine (brand name as Blueguard G1-3), used in the batch tests. The olivine mainly consists of magnesia (MgO), silica (SiO_2), iron oxide (Fe_2O_3) and quicklime (CaO). Table 6 shows the mineralogical composition of the material and on Figure 8, the olivine adsorbent used is presented for the purposes of this master work.

Table 5. Physical properties of olivine, Blueguard G1-3, [17]

Physical composition		**Values**
Particle distribution [mm]	**D_{90}**	2.5
	D_{50}	2.5
	D_{10}	1
Surface area – BET analyze [m^2/g]		2
pH		11-12
Bulk density [t/m^3]		1.5-1.7
Volume weight [m^3/t]		0.59-0.67

Table 6. Chemical composition of olivine, Blueguard G1-3, [17]

Chemical composition	**Weight [%]**
MgO	45
SiO_2	40
Fe_2O_3	7
CaO	4

Figure 8. Olivine, Blueguard G1-3

3.2.2. Bottom ash

Bottom ash samples used in this study were provided by a local incineration plants at Trondheim in central Norway. In the incineration plant, household and commercial waste are combusted to generate electricity and ashes like bottom ash as residues of the process is produced. Bottom ash used for the adsorption experiments in this study was more than one-year old. Figure 9a, shows untreated bottom ash. Solid waste incineration bottom ash mainly consists of melt products formed during combustion process and includes fine particles matter, heavy metals and organic compounds. Each concentration of these elements varies in different incineration plant. Bottom ash is characteristically composed of wide varying particle size; fine particles matter to very large particles [19]. It has to be emphasized that, heterogeneous size of bottom ash particles has an influence of the adsorption experiments. To create a representative sample, pretreatment of bottom ash was required. Bottom ash was sieved with 4 mm size sieve, and particles with size less than 4 mm were used for the experiments. Afterwards, iron oxide (Fe_2O_3) was added and well mixed with the bottom ash to make the mixture as homogeneous as possible, Figure 9b. Iron (III) oxide is a powder with a particle size smaller than 5 μm and have reddish brown color. In neutral solution, metal oxides are insoluble and in strongly acidic and basic solutions they are easily soluble [18]. This treatment was required in order to prevent from heavy metal leaching and to increase adsorption capacities of bottom ash.

a) b)

Figure 9. Bottom ash, a) untreated, b) bottom ash mixed with iron oxide

3.2.3. Pine bark

The third adsorbent used in this master work was pine bark. This biosorbent is 100% pine and comes from forests in Norway and it was also obtained from a local supplier. The delivered pine was characterized with various size of barks and high humidity. The barks were sieved, and all particles higher than 4 mm were dried at 100 °C for 24 h. Figure 10, presents untreated pine bark, delivered from suppliers and treated pine bark after drying process in laboratory oven.

a) b)

Figure 10. Pine bark a) untreated, b) after drying process

Treated pine bark was stored indoors in plastic bags and it was used for adsorption capacity tests.

3.3. pH and conductivity of the adsorbents

The pH and conductivity measurements were conducted on all samples, after each cycle or at the end of the tests, depending of the different experiment. The samples were mixture of metal solution or distilled water and adsorbents. Also, pH and conductivity were measured of the pure synthetic stormwater. After each test run, the aqueous samples were separated from adsorbent and stored in clean bottle. Afterwards, the samples were left over in the laboratory but no longer than 2 hours and the pH and conductivity measurements were conducted with proper equipment from Drinking water laboratory at NTNU, Trondheim. Between each sample, equipment was rinsed with distilled water. The equipment used for these measurements is shown on Figure 11.

a) b)

Figure 11. a) pH meter, b) Conductivity meter

3.4. Experimental design

Laboratory experiments were conducted with either artificial stormwater prepared in the laboratory or distilled water. The experiments were performed in batch systems, primarily because it is cheapest and most practical way to test various adsorption affecting parameters, such as influence of the temperature, different mass of adsorbent or particle size of the adsorbents. Secondly, batch adsorption for treatment of stormwater was easy method, flexible to operate and test all adsorbents characteristics and also provided results in relatively short period. The advantage of batch tests is that the performance of adsorbents in adsorption process for a particular compound can be tested and evaluated relatively quickly in the laboratory and therefore the adsorbent that showed best performance is easily identified. Batch system provides continuously contact between the same solution and adsorbent. The same solution remains in contact with a given quantity of adsorbent while adsorption experiment is conducted. Through the batch tests, influence of fresh solution on adsorbent efficiency and correlation between the velocity of fresh solution and adsorption process cannot be established.

3.5. Synthetic stormwater

To achieve an objective of finding suitable adsorbent for removing heavy metals from runoff from roads, the tests need to be performed with influent with an appropriate amount of metals to simulate the real stormwater. For this purpose, synthetic stormwater was created in the laboratory. This study was focused on removal of lead, copper, nickel and zinc. Therefore, synthetic stormwater was based on a concentration range of metals for the actual highway stormwater. According to the previous studies, Table 7 show the ranges of heavy metal in actual stormwater from Norway [3].

Table 7. Ranges of heavy metal concentration in stormwater runoff and snow melt in Norway, [3]

Element	Stormwater runoff [µg/l]	Snow melt [µg/l]	Concentration of metals in this study [mg/l]
Pb	2 - 6	0.9 – 69.5	2 - 5
Ni	0.2 – 10.4	3.3 - 567	2 - 5
Cu	1 - 61	1.4 – 574	2 - 5
Zn	2 - 145	18.5 - 1390	2 - 5

Considering the values of heavy metal in actual stormwater, the initial concentration level for batch tests, Table 8, were chosen to represent stormwater.

Table 8. Initial heavy metal concentration for the adsorption capacity experiments

Concentration level	Pb, Ni, Cu, Zn [mg/l]
1	2
2	5

3.5.1. Stock solution

To create synthetic stormwater with proper concentration of each metal, firstly a stock solution with 1 g/l in 1 l tap water was prepared. The calculation related to the amount of each powder are presented in Appendix 5 and the results are shown in Table 9.

Table 9. Properties of the heavy metal: Lead, nickel, copper and zinc

Metal	**Molar mass [g/mol]**	**Chemical powder**	**Formula**	**Molar mass of chemical powder [g/mol]**
Lead – Pb	207.20	Lead (II) chloride	$PbCl_2$	278.106
Nickel - Ni	58.69	Nickel (II) chloride	$NiCl_2$	129.596
Copper - Cu	63.55	Copper (II) chloride	$CuCl_2$	134.452
Zinc - Zn	65.38	Zinc (II) chloride	$ZnCl_2$	136.286

To calculate the proper amount of chemicals in order to satisfy the right concentration of heavy metal in metal solution, the following equation was used:

$$W_{powder} = \frac{W_{metal} * m_{powder}}{m_{metal}} \, [g] \qquad (3.1)$$

where,

W_{powder} – amount of chemical powder [g]

W_{metal} – amount of the metal [g]

m_{powder} – molar weight of the chemical powder [g/mol]

m_{metal} – molar weight of the heavy metal [g/mol]

The number and mass of chemicals used for preparation of 1 l the stock solution is presented Table 10.

Table 10. Calculation for stock solution

Metal	Chemical powder	Amount of the chemical powder used for preparation of stock solution [g]
Lead – Pb	$PbCl_2$	1.342
Nickel - Ni	$NiCl_2$	2.208
Copper - Cu	$CuCl_2$	2.116
Zinc - Zn	$ZnCl_2$	2.085

The calculated amount of heavy metal chlorides was measured with accurate metric scale and put into a flask with 1 l tap water, Figure 12.

Hence, diluting a previously prepared stock solution with tap water, a synthetic stormwater with different concentration of heavy metals was made.

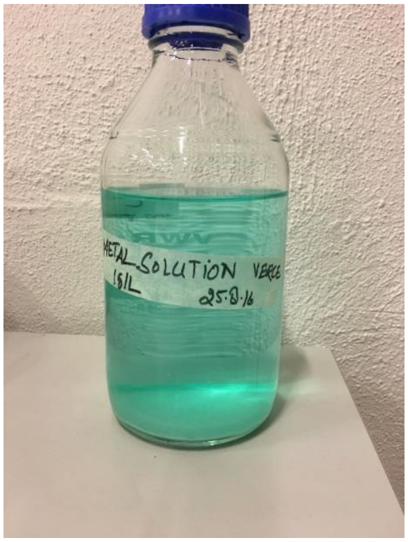


Figure 12. Metal solution, 1g/l metal concentration

3.6. Analysis of metal composition

The analysis of the metal concentration on the samples from experiments was measured using a high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) at the accredited laboratory at Department of Chemistry at NTNU, Trondheim.

Prior to analysis, the liquid samples when separated from the adsorbent solids with syringe were filtered with 0.45 μm syringe filter and stored in 15 ml tube for metal analysis. Afterwards, the water samples were preserved with acid, 0.25 % of the total volume of the sample or 5 drops of 0.1 M HNO_3. The samples were stored in freezer at 4 °C until the heavy metal analyzes were performed. Heavy metal analysis was performed directly without any further dilution.

Measurement of the heavy metal concentration on liquid samples was conducted after each experiment. Therefore, separation of the liquid from the adsorbent and preservation of the samples, as described above was performed for each replicate in the following experiments.

3.7. Batch adsorption studies

The batch adsorption tests were used to examine the adsorption capacity of adsorbents. The experiments were conducted using different quantities of adsorbents; 100, 50, 25, 12.5, 6.25, 3.1 and 1.6 g, with initial concentration of 2 mg/l of four metals (Cu, Pb, Ni and Zn), and 200 ml of prepared solution for each sample. Three replicates of each amount were tested in order to get variation in the experiment. Thereafter, the solutions were shaken with adsorbent for 24 hours in order to ensure maximum contact and equilibrium between solution and adsorbents' amount. The shaking was done with an orbital shaker for 24 hours at a velocity of 220 rpm, Figure 13 a. After the process of shaking, the shaker was turned off and the samples were left for a few hours to stabilize and settle down the suspended solid parts from adsorbent. Then to separate the solid from the liquid phase, the liquid was taken out of the bottle with 60 ml syringe and stored in another bottle for further analysis and measurements, Figure 13 b.

a) b)

Figure 13. a) shaking process, b) filtering of the sample

To determine the amount of heavy metal adsorbed from the solution on to the adsorbent, the mass balance expression was used Equation (2.8).

Adsorption capacity in percentage and the distribution ratio K_d [ml/g] were calculated with the following equation:

$$adsorption\ [\%] = \frac{C_i - C_f}{C_i} * 100 \quad (3.2)$$

Where by C_f is the final concentration of heavy metals in the solution [mg/l].

$$K_d = \frac{amount\ of\ the\ metal\ in\ adsorbent}{amount\ of\ the\ metal\ in\ solution} * \frac{V}{m} = \frac{q_e}{C_e} \quad (3.3)$$

Or,

$$adsorption\ [\%] = \frac{100K_d}{K_d + \frac{V}{m}} \quad (3.4)$$

For the equilibrium studies, the measurements obtained from the batch adsorption studies were used to develop and describe the adsorption capacity for the three adsorbents.

3.8. Effects of freezing and thawing on the adsorption capacity of the adsorbents

The cold climate was simulated in laboratory with freezing/thawing cycles. In order to evaluated the influence of cold climate on the adsorption capacity of the three selected adsorbent and the results from this experiment needed to be compared with experiment conducted in the normal weather conditions. It needs to be emphasized that, under normal weather condition the experiment was conducted without the freezing process, instead the samples were left on room temperature (20-22°C) in laboratory for 24 h.

To test the effects of cold climate on the adsorption capacity and stability of the adsorbents, four different tests were examined, explained in Table 11. Ratio, adsorbent/liquid, was 1/10 for all experiments. The difference between the tests was the type of liquid which was used. For the leaching test and determination of the stability of the adsorbents distilled water was used, and to test the removal efficiency of the adsorbents under cold climate, synthetic stormwater prepared in the laboratory as described in section above, was used. The concentration of metals was 5 mg/l of each metal.

Table 11. Experiments for evaluation of freezing and thawing effects

No. Test	Adsorbent		Liquid phase		Freezing/thawing process	Cycles	Number of samples
	Mass [g]	Type	Volume [l]	First cycle			
1.	100	Olivine Bottom ash Pine bark	1	Distilled water	Yes	15	2
2.	50	Olivine Bottom ash Pine bark	0.5	Metal solution, 5 mg/l	Yes	15	3
3.	50	Olivine Bottom ash Pine bark	0.5	Metal solution, 5 mg/l	No	15	1
4.	50	Olivine Bottom ash Pine bark	0.5	Distilled water	No	15	1

3.8.1. Freezing/thawing test with distilled water – Reference case

For each adsorbent two replicates were conducted, test no. 1 in the Table 11. The procedure of this experiment was as follows, mass of 100 g of olivine and pine bark was added to 1 l distilled water and 50 g of bottom ash and 0.5 l of distilled water. The first cycle began with the shaking process of the mixture adsorbent/ distilled water for 24 h. Afterwards, the orbital shaker was turned off and samples were left to settle down. A liquid sample, approximately 200 ml, with a 60 ml syringe was taken out of the glass bottles and stored in clean plastic bottle. These samples were used for pH and conductivity measurements. The remaining liquid phase of the samples was put in plastic container labeled as hazardous wastewater. When all the amount of the liquid phase was separated from the adsorbent solids, glass bottles were put in laboratory freezer, at temperature approximately -10 °C, for 24 h. Then samples were left in the laboratory on 20-22 °C for a few hours (2-3 h) and again refilled with same volume of distilled water as in previous step and shaking process was repeated. This whole procedure for one cycle was repeated 15 times.

The purpose of this test was to monitor and evaluate the stability of the adsorbents after freezing and thawing. The following steps were taken for one cycle:

- Shaking on big orbital shaker for 24 h with speed 70-80 rpm Figure 14 a,
- Taking sample of liquid phase,
- Dewatering, freezing the adsorbent (only the solids) for 24 h Figure 14 b,
- Thawing and refilling with distilled water, shaking.


a) b)

Figure 14. a) Shaking process, b) Simulation of cold climate

Leaching test – Olivine, Pine bark

The liquid samples of olivine and pine bark from reference case were analyzed due to determination of leakage of compounds from adsorbent content. The results are presented in Appendix 3.

3.8.2. Freezing/thawing test with synthetic stormwater

With concentration of 5 mg/l of four metals Pb, Ni, Cu, Zn a synthetic stormwater was prepared and used for the first cycle. The synthetic stormwater was prepared by diluting previously prepared stock solution. The calculation related to the preparation synthetic stormwater is presented in Appendix 5. The samples mixed with synthetic solution of 5 mg/l in the first cycle were shaken with orbital shaker for 24 hours with velocity of 70-80 rpm. After the first step, the synthetic solution was completely removed and samples for analysis were taken. For next fourteen steps, distilled water was used and same procedure as 3.8.1 was followed. Comparison between test no. 2 and 3 in Table 11 was done to evaluated the desorption/release of metals due to freezing thawing process. Results from desorption process are presented in chapter 4.3.

Steps for one cycle are presented below.

- Mixture adsorbent/synthetic stormwater,
- Shaking on big orbital shaker for 24 h, 70-80 rpm,
- Taking sample of liquid phase,
- Dewatering, freezing the adsorbent (only the solids) for 24 h,
- Thawing and refilling with distilled water (14 cycles), shaking.

3.8.3. Control tests - clean and metal case

In order to test how adsorbents performed under the cold conditions, reference point needed to be obtained under normal conditions (without freezing process). The first cycle, liquid phase for one experiment was distilled water (test no. 4, Table 11) and for the other test synthetic stormwater with 5 mg/l of metals (test no. 3, Table 11). After the shaking process, the samples were left in the laboratory at 20-22 °C for 24 h. The remaining 14 cycles were performed with distilled water. After the first cycle when distilled water was used, metals adsorbed onto the surface of adsorbents started to release – desorption process. The correlation between these results and results from chapter 3.8.2. provides information about the influence of cold weather on the ability of adsorbents to keep adsorbed pollutants. The results and discussion for desorption process are presented in chapter 4.3.

The following steps are performed for one cycle:

- Shaking 24 h with speed 70-80 rpm,
  Clean test - distilled water,
  Metal case – metal solution 5 mg/l metal concentration,
- Taking sample of liquid phase,
- Dewatering, left in laboratory (only the solids) for 24 h,
- Refilling with distilled water, shaking.

Leaching test – Bottom ash

The clean control test results were compared with results from freezing/thawing test with distilled water (test no. 4 and no. 1, Table 11), and the results from metal concentration are presented in Results and discussions, 4.3.2.

3.8.4. Effect on freezing/thawing on pH and conductivity of the adsorbents

The effect of freezing and thawing on the pH and conductivity of the samples was investigated by comparing the results from control test – clean case samples and reference case (test no. 4 and no. 1, Table 11); and samples from control test – metal case and freezing/thawing test with synthetic stormwater (test no.3 and no. 2, Table 11). For each case, 15 cycles were conducted. The difference between the two experiments is explained above and the results are presented in part 4.1. pH is one important criteria when environmental impacts are analyzed hence comparison indicates how adsorbents, when mixed with liquid, change the pH of the water solution.

3.9. Sources of error

Numerous errors may occur during conducting of the laboratory experiments. The sources of error may be human and equipment imprecision, improperly cleaned bottles, flasks, containers, inappropriate storage of samples for testing, climatic influence such as temperature and brightness and calculation errors etc.

To minimize the errors because of improperly usage and maintenance of laboratory equipment such as pH and conductivity meter, after each measurement the probes were cleaned with distilled water. The pH meter was calibrated after a few measurements. Generally, plastic bottles and syringes were new and unused but some bottles were reused after acid wash. Accurate metric scales were used for weight measurements of the adsorbents, and depending of the experiment 2 or 3 replicates were examined. Metal analysis was conducted by an accredited laboratory at the Department of chemistry at NTNU, Trondheim. Nonetheless, several people were involved and misunderstanding among them may also become potential source of error.

Taking into consideration the variety of instruments used during the experiment, the possibility to have equipment imprecision in the results was highly present. The human mistake was probably during refilling the bottles with appropriate fluid, measuring the mass of the adsorbent or cleaning the equipment. Also, worth mentioning is that the temperature in the laboratories was not measured and therefore it presents a source of error.

4. Results and discussions

This section presents the main part in this master work and contains the results from the adsorption process. The discussion focus on delivery useful conclusions for the adsorbents behavior and performance for heavy metal removal under different climate condition, as well as provides brief overview of the environmental impacts.

The approaches of presenting the results are focused on the adsorption and desorption percentage as well as their correlation with other parameters, such as mass of the adsorbent, number of cycles and climate conditions.

4.1. Effect on freezing/thawing on pH value of the adsorbents

The results from pH measurements of samples from the control test, clean case and reference test, Table 11, are compared and presented in Figure 15.

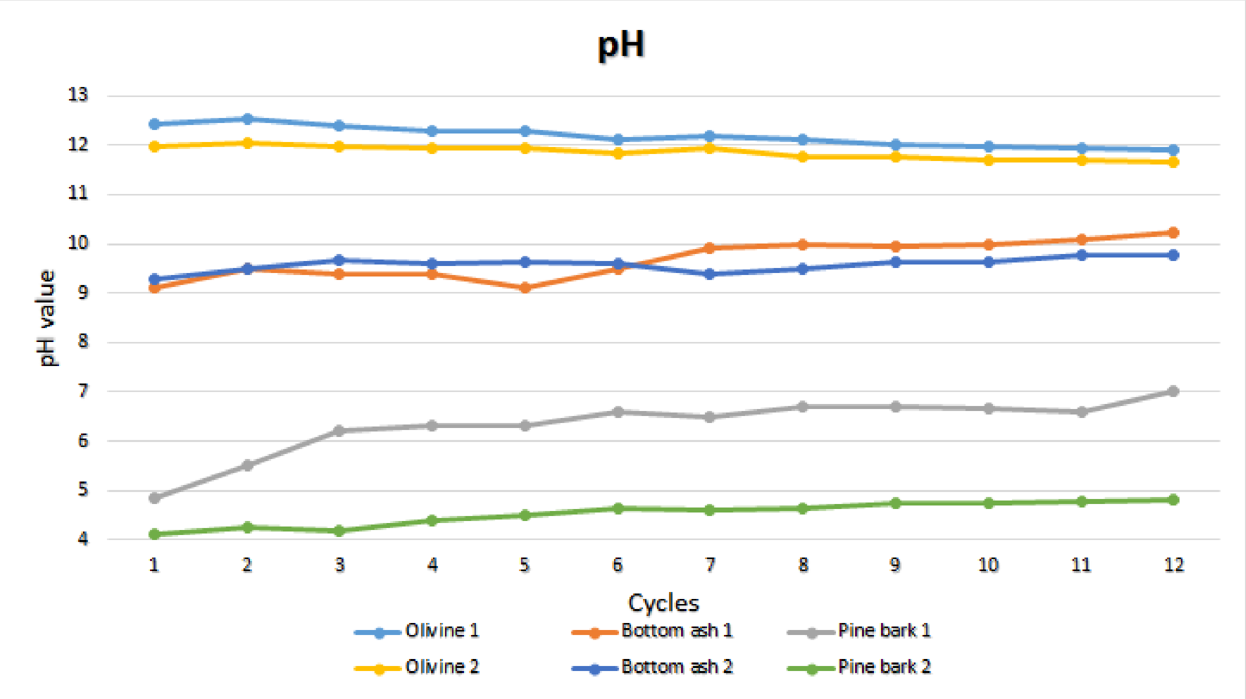


Figure 15. pH values comparison – distilled water

The pH value of the distilled water was 7.5. Adsorbents with subscript 1 are the samples from control test (clean control test, without metals in solution) and with subscript 2 are the samples from reference case. Olivine and bottom ash releases elements like magnesium, potassium, sodium, calcium etc., so the concentration of positive ions in solution is increasing and this leads to increasing of pH value. The influence of freezing and thawing process on pH value on samples with olivine and bottom ash was negligible. The pH value of the samples with olivine is near 12 and on bottom ash samples, it is 10. The sample of bottom ash from the control test were subjected to 12 cycles because of the broken bottles. Through the 12 points of the control test, the behavior of the curves could be assessed as similar and the freezing process did not influence on the bottom ash samples.

Pine bark is adsorbent in the group of bio-sorbent. Due to the releasing of organic matter which contains acids, pine bark decreases the pH value of solution from 7.5 to 4-5 [3]. In the sample without freezing and thawing (Figure 15, with subscript 1) after a few cycles, the pH value starts to increase and at the 12th cycle, the pH value of 7 is reached again. The low value of pH was continuously observed through all the cycles on sample from reference test, which indicates that the releasing of organic matter during the cold climate is greater than in normal weather conditions. This indicate that cold climate has influence on stability of pine bark. After a few cycles of freeze and thaw, solid parts were broken down and releasing of available controlled organic matters occurred.

4.1.1. Effects on freezing/thawing pH value on metal solution-adsorbent

The control test was obtained in two cases, one with distilled water and other with metal solution (test no. 3, Table 11), samples with subscript 1 on Figure 16.

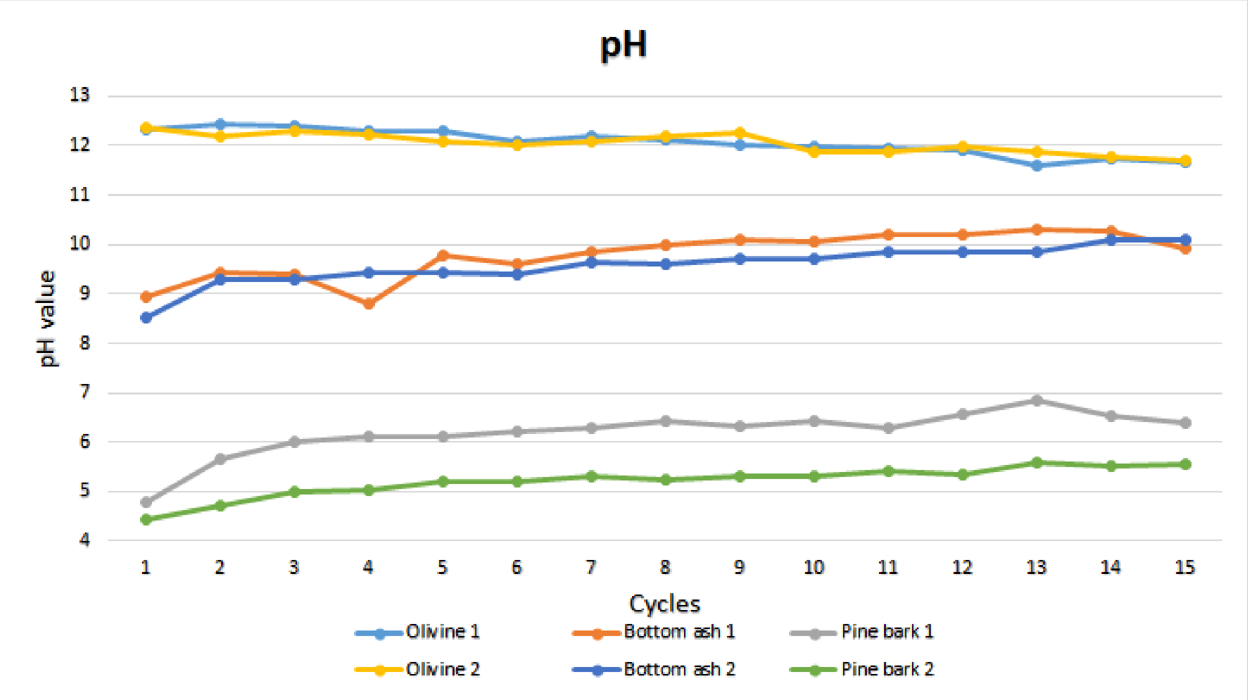


Figure 16. pH values comparison – metal solution

Variation of pH values is presented in Table 12. It has to be emphasized that, cold climate had the biggest influence on pine bark samples regardless if distilled water or metal solution was used as influent.

Table 12. pH values comparison

pH	Olivine		Pine bark		Bottom ash	
	Normal condition	Cold climate	Normal condition	Cold climate	Normal condition	Cold climate
Distilled water	11.6 – 12.5	11.5 – 12.04	4.9 – 7.06	4.1 – 4.97	9.1 – 10.2	9.3 – 10.04
Metal solution	11.6 – 12.4	11.7 – 12.3	4.8 – 6.8	4.4 – 5.6	8.8 – 10.3	8.5 – 10.1

4.2. Analysis of the adsorption process

Figure 17, Figure 18 and Figure 19 below show the average removal percentage with different ratio of adsorbent/stormwater, for each adsorbent respectively. The results (heavy metal concentration in aqueous solution) from all tests done with 2 mg/l of each metal; Pb, Ni, Cu and Zn with 3 types of low-cost adsorbents and 7 different amount of mass adsorbent are presented in Appendix 2. Adsorption performance of each adsorbent is described below.

4.2.1. Adsorption efficiency of olivine

The graphical representation of the results for adsorption efficiency from Table 32 (in Appendix 6) is given Figure 17. The figure represents removal efficiency for each metal with olivine as an adsorbent. The figure provides relation between adsorption rate for each metal and mass of the adsorbent. Percentage results present the amount which is taken from the aqueous solution by the adsorbent. This is the concentration of the pollutants adsorb on the surface of the adsorbent. The higher concentration onto the adsorbent, higher the adsorption capacity, the better heavy metal removal performance from simulated stormwater.

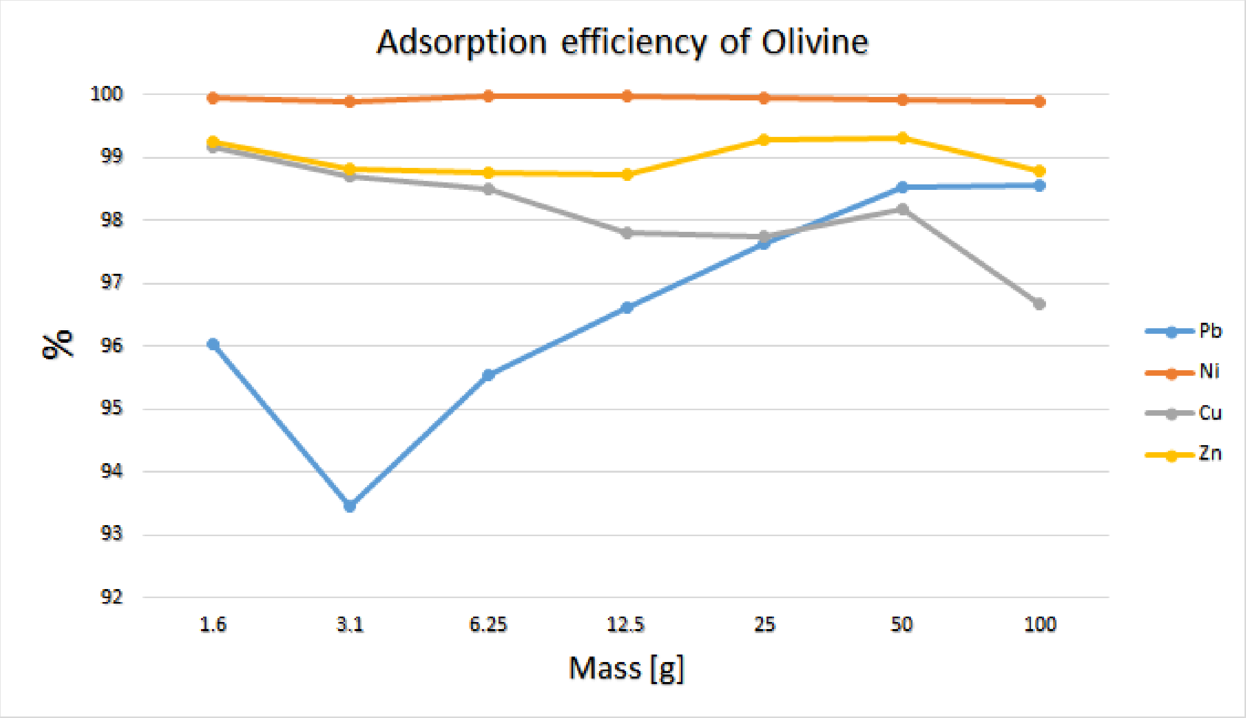


Figure 17. Adsorption efficiency of Olivine

In all the cases, the best adsorption properties of olivine were obtained for nickel removal. For each adsorbent dose, nickel removal efficiency is up to 99 %, which shows that removal was not dependent on adsorbent dose. The curves for copper and zinc follow each other with small differences in the percentage removal. Whereas, in case of 100 g of adsorbent it can be noticed that Cu and Zn removal is lower. According to the figure and presented results, olivine presented lower adsorption capacity for lead. With the increasing of the amount of olivine, increased the adsorbed lead amount, and with 100 g of olivine was removed up to 98 % of lead containing in the aqueous solution is removed. An exception of this conclusion is lead adsorbed in case of 3.1 g olivine. The result in this point was the lowest and one of the reasons could be partly because of the human imprecision or instrument errors. Generally, olivine showed good adsorption capacity for all metals, because all results for adsorption efficiency were more than 90 %.

4.2.2. Adsorption efficiency of bottom ash

Tests with the same conditions as described for olivine were also conducted for bottom ash. Figure 18 shows the percentage of each metal adsorbed onto bottom ash. Following the theory, increase in the amount of adsorbent had a positive effect on the reduction of lead, nickel, copper and zinc. The reason of this is that an increase in the amount of adsorbent corresponds to more available adsorbent surface for uptake of heavy metals. This is confirmed with bottom ash, because with increasing of the mass of adsorbent, the removal efficiency increase.

Adsorption lines for lead, copper and zinc have the same behavior. Whereas, in case of 1.6 g bottom ash lowest percentage of metal removal are noticed, then with increasing the concentration of adsorbent increase removal value and for 25 g of adsorbent is noticed drop of removal efficiency for every line. Removal efficiency increased for 50 g and 100 g in-between the previous value and adsorbed the highest amount of pollutants with 100 g bottom ash. Nickel removal with bottom ash was lower compared with the other metals, but also increasing trend of adsorption efficiency with higher amount of adsorbent was kept. One reason for high concentration of nickel in liquid samples (lower adsorption efficiency) is releasing of nickel from bottom ash content. Moreover, nickel in could be in dissolved phase which is more specific for treatment and removal and more nickel could be particle bound which can reduce the adsorption.

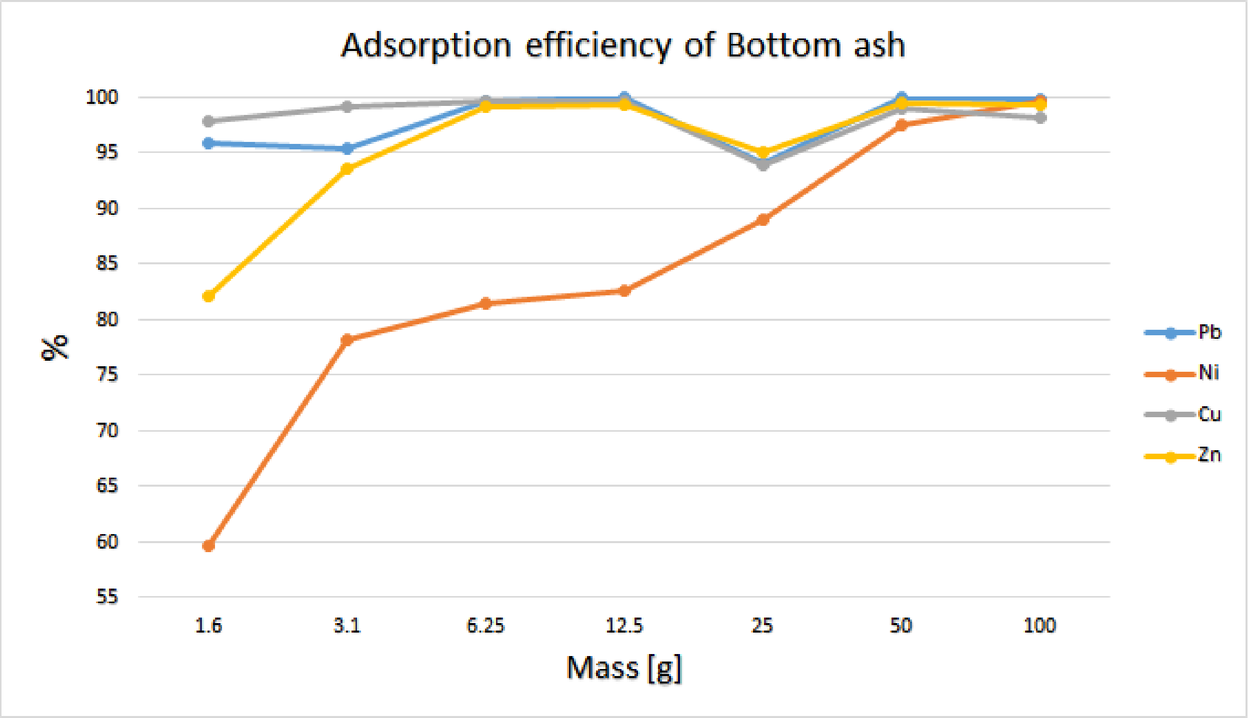


Figure 18. Adsorption efficiency of bottom ash

Bottom ash as a secondary waste shows satisfactory results for adsorption of heavy metals from aqueous samples. Nevertheless, bottom ash has many elements in its content which could be part of additional pollution of environment.

4.2.3. Adsorption efficiency of pine bark

The Figure 19 below presents the adsorption efficiency as a function of mass pine bark. When analyzing, it can be noticed that pine bark showed good adsorption performances for lead and nickel removal, and these lines followed the increasing trend with the increase of the mass adsorbent. Copper and zinc removal with pine bark was lower in comparison with the other two metals. In case of 50 g pine bark for copper and zinc lines could be noticed drop. This point indicated the highest removal efficiency for copper and then slight decreasing of removal efficiency with 100 g of adsorbent dose. Opposite of this, for zinc is noticed the lowest removal efficiency when 50 g of pine bark was used.

A main reason for the limited uptake of metals could be due to competition for adsorption sited and also the differences in chemical states of metals in solution. By increasing the mass of pine bark added to each batch sample, more adsorption sites were available, so that a larger proportion of the metals can be expected to be adsorbed. This observation is in line with presented results for

Ni, Cu and Zn removal. Also, metal uptake from about 60 to 100 % for Pb and Zn is in line with studies from the reviewed literature [21].

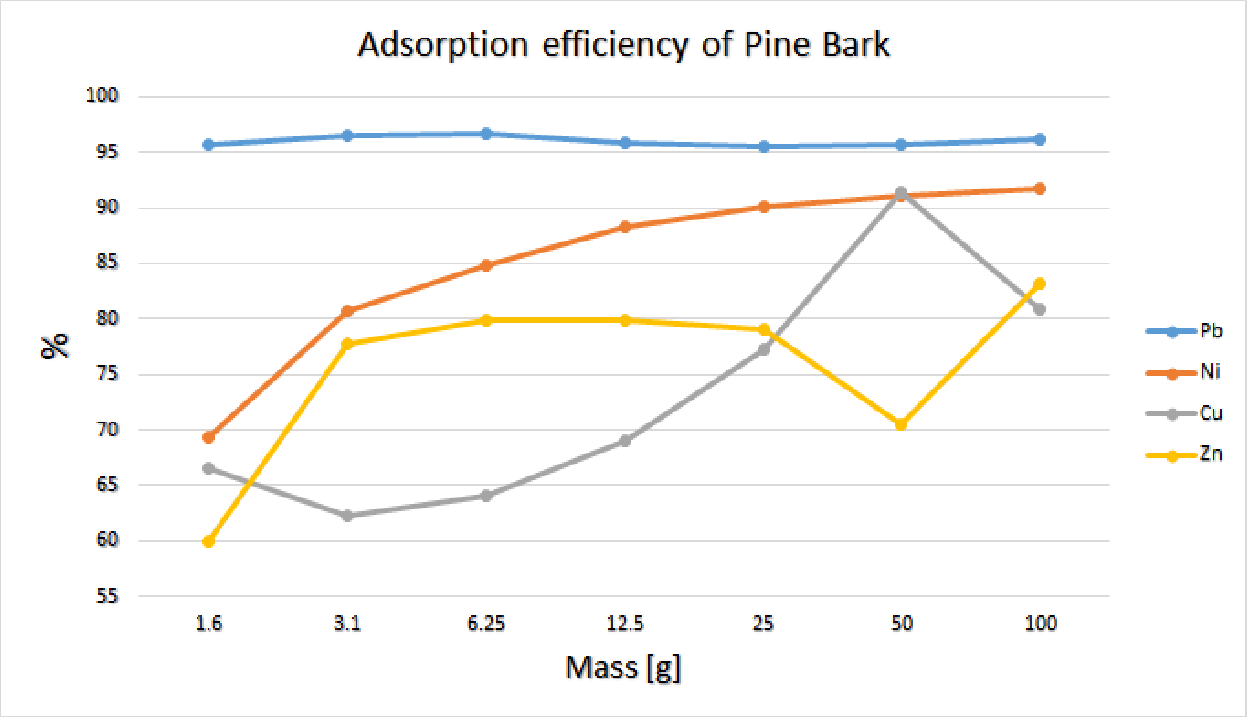


Figure 19. Adsorption efficiency of pine bark

According to the previous analysis and results presented in Table 32, it could be noticed that satisfactory removal efficiency was presented by all the adsorbents. The best solution for real life application and use would be small amount of adsorbent and high metal uptake. The level of metal removal with the bigger amount of adsorbent is not significantly higher, because lower amounts of adsorbent also shows good removal characteristics. Additionally, before choosing the best adsorbent for real life application, effects of cold climate would be analyzed.

4.3. Effect of freezing and thawing (cold climate)

All results presented in this section are average values, whereby results for each sample and calculations are presented in Appendix 2. Additional observation of the adsorption capacity of the adsorbents is given in Figure 20. The results in Figure 20 (test no. 2, Table 11) show that adsorbents had a very high removal rate (69 – 99 %) for all four dissolve metals. This is in line with previous studies on these adsorbents [3].

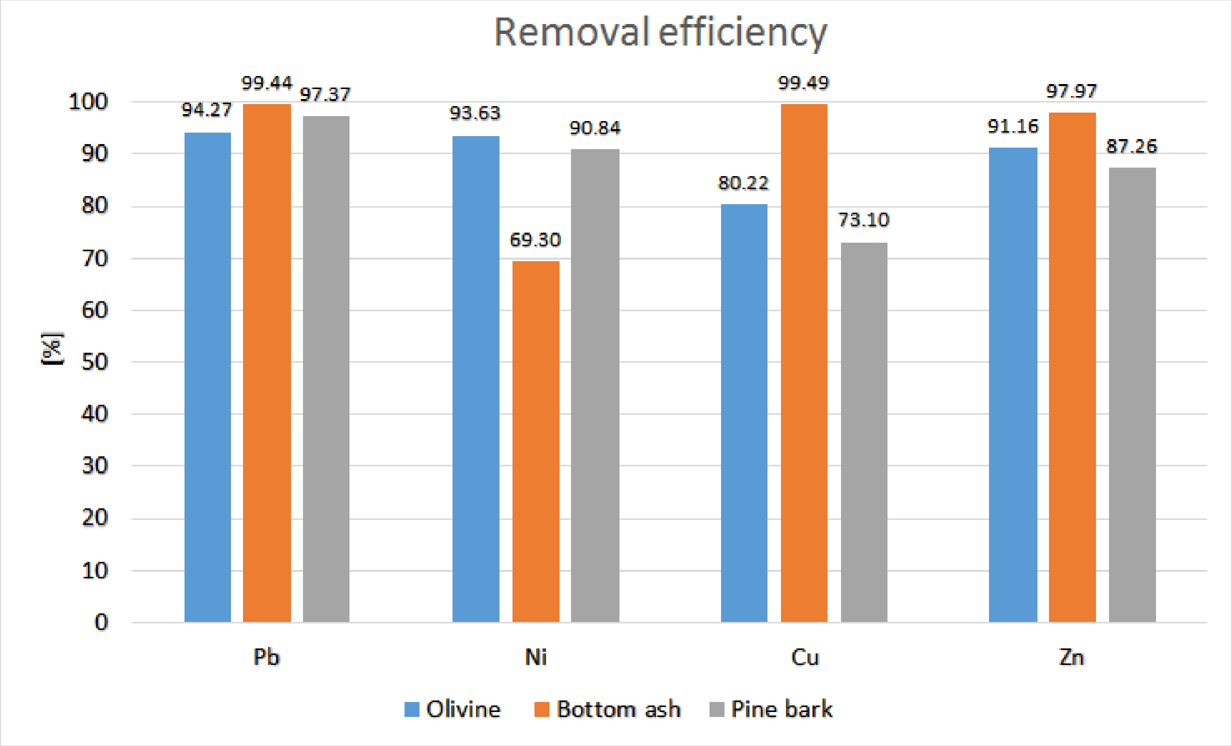


Figure 20. Removal efficiency - first cycle

Bottom ash shows best performance for Pb, Cu and Zn removal and olivine for Ni removal from the simulated stormwater.

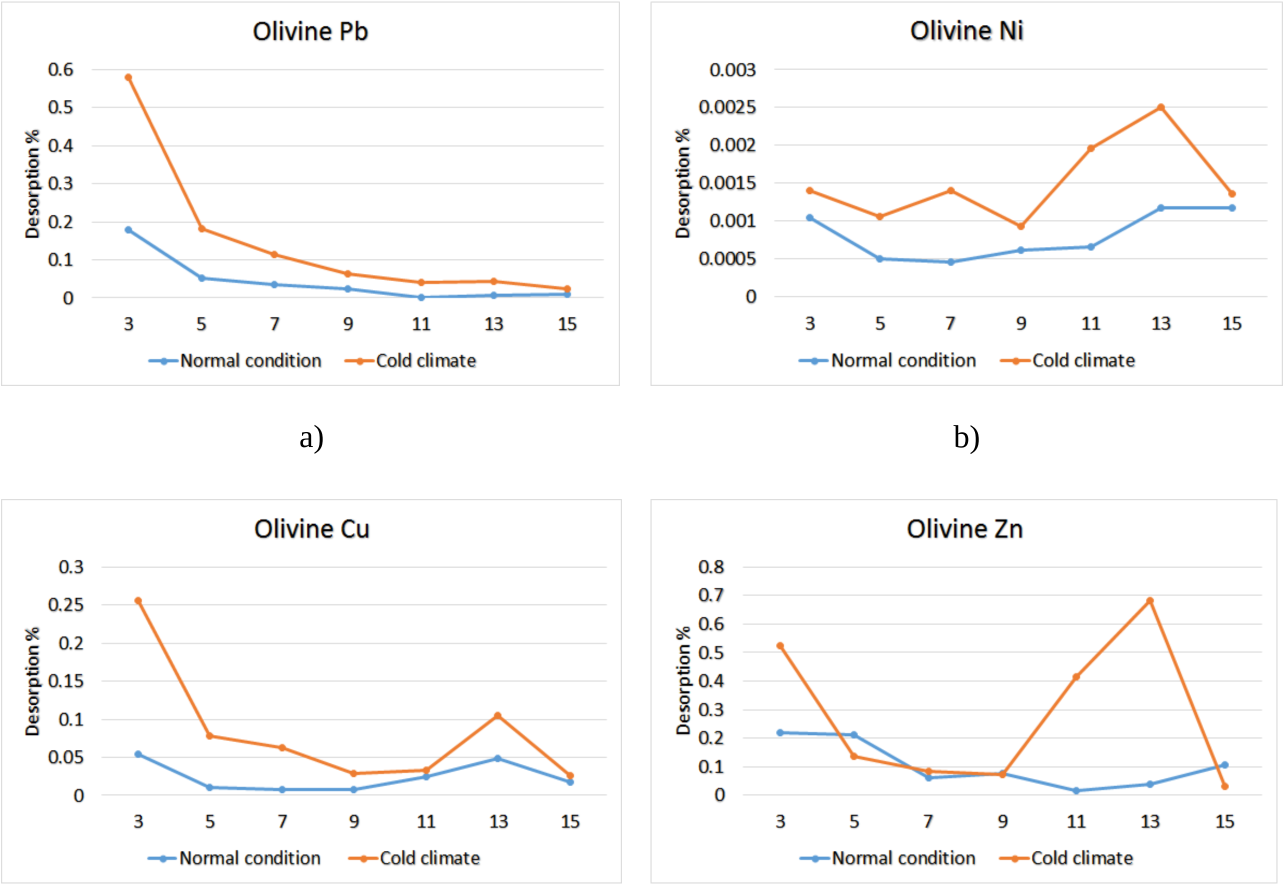
After the first cycle, the sample were subjected to 14 cycles of freezing and thawing, and the metal release after each cycle was quantified with ICP/MS (inductively couple plasma/mass spectrometry). When the amount of metals that are adsorbed in the first cycle, started to release from adsorbents, the desorption process occurred. The obtained results for the first cycle, show that selected low cost adsorbents are capable of greatly reducing the concentration of metals in solution, even when exposed to relatively high initial metal concentrations.

4.3.1. Olivine

Results from IC measurements on olivine samples from reference test (test no. 1, Table 11) are presented in Appendix 3 and they indicate leaching of anions and cation such as F, Cl, SO_4, Na, K, Ca and small amount of NO_2 and NO_3. The results provided interesting information about the manganese, which is a predominant olivine component. There was no leaching of manganese in the tested samples.

Desorption process

The following set of charts in Figure 21, provide comparison between the desorption process of four metals previously adsorbed on the olivine; under normal weather condition and simulated cold weather. The figures also highlight the relative influence of freezing and thawing cycles onto the life of the adsorbent. Desorption process or amount of released metals is presented in percentage from previously adsorbed metals onto the surface of the adsorbents. Given the released amount in a few cycles, general conclusion about the cold weather influence could be established. The simulation of cold climate showed that the desorption process of four metals from olivine was not affected.



a) b)

c) d)

Figure 21. Desorption process of olivine samples; a) Lead, b) Nickel, c) Copper, d) Zinc

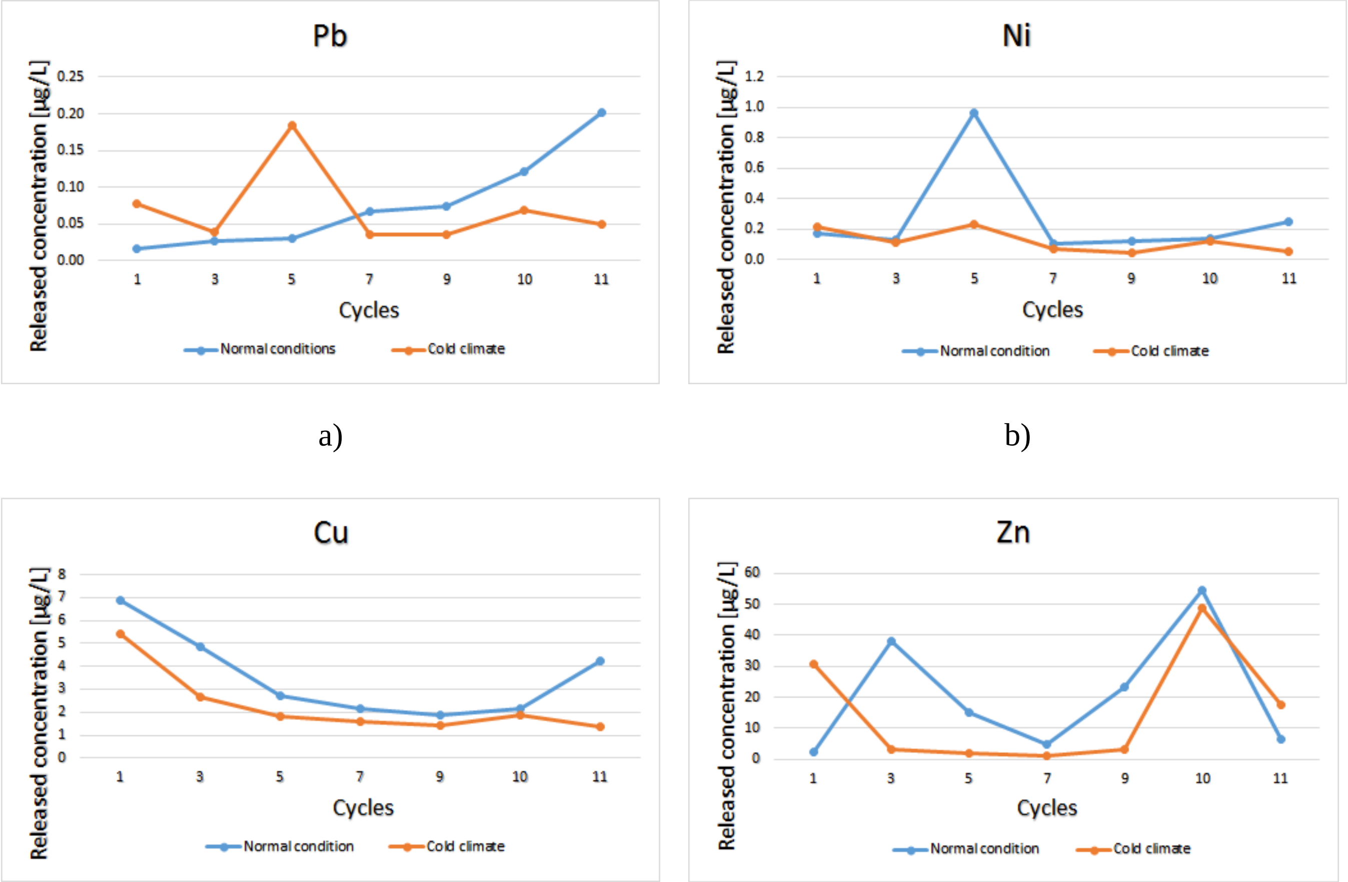
The release of lead from olivine, Figure 21 a, was highest at the beginning but it decreased with every cycle, which indicates dissolution of precipitated metal. Curves show the same behavior for both weather cases and higher concentration of lead and copper is desorbed in case of cold climate. Based on the figure it can be noticed that desorbed amount did not reach 1 % of the total adsorbent amount in the first cycle, and it can be considered that the influence of freezing process was negligible. The graph for lead, indicates that the amount of desorbed lead decreases with every next cycle, for both cases. Releasing of nickel from olivine in cold climate is higher than in normal weather condition, Figure 21 b. Cold climate curve do not have continuous and predictable character. After ten cycles of decreasing the amount of released nickel is noticed increasing in the 13th cycle. As a reason of incidentally releasing high amount of nickel in this point could be broke down of solid parts. This conclusion can be taken into consideration also for the case of zinc and copper releasing, Figure 21 d. Effect of cold climate and the highest desorption process from olivine sample is noticed for zinc releasing.

4.3.2. Bottom ash

Herein, results from two experiments with bottom ash are present.

Leaching test

Since the bottom ash contains potentially hazardous heavy metals [19], possibility of leaching is necessary to evaluate. The leachability of the four observed heavy metals from bottom ash was evaluated through two experiments, under different weather conditions (test no. 1 and test no. 4, Table 11). The set of charts presented in Figure 22, summarize the effect of cold climate on the leachability of the heavy metal from bottom ash content. According to the research conducted on Norwegian incineration plants [19], elements that are most presented in bottom ash content is Pb and Cu but the concentration of Zn is also high. From the results presented in Figure 22 d, it was found that leaching of zinc is highest. In the 10th cycle zinc was up to 50 µg/l in both cases. This peak is second when normal weather condition is analyzed. Releasing of zinc in simulated cold climate started with high concentration, 30.8 µg/l in first cycle before freezing process. Than concentration of zinc decreases and reached values are not higher than 3 µg/l until 10th cycle when 48.8 µg/l zinc is measured in the distilled water. This indicated that dissolved constituents leave the bottom ash solid with early or beginnings cycles and because of that high concentration of zinc is noticed at the beginning. As a reason for next peak is that some elements remain in the content of bottom ash longer and started to release after a few cycles (this conclusion could be considered for both cases). One other reason, could be stability of the adsorbent. After a few cycles of shaking process could occurred braking down of solid parts and in this point can started releasing of bounded constituents [22].



a) b)

c) d)

Figure 22. Releasing of metals from bottom ash; a) Lead, b) Nickel, c) Copper, d) Zinc

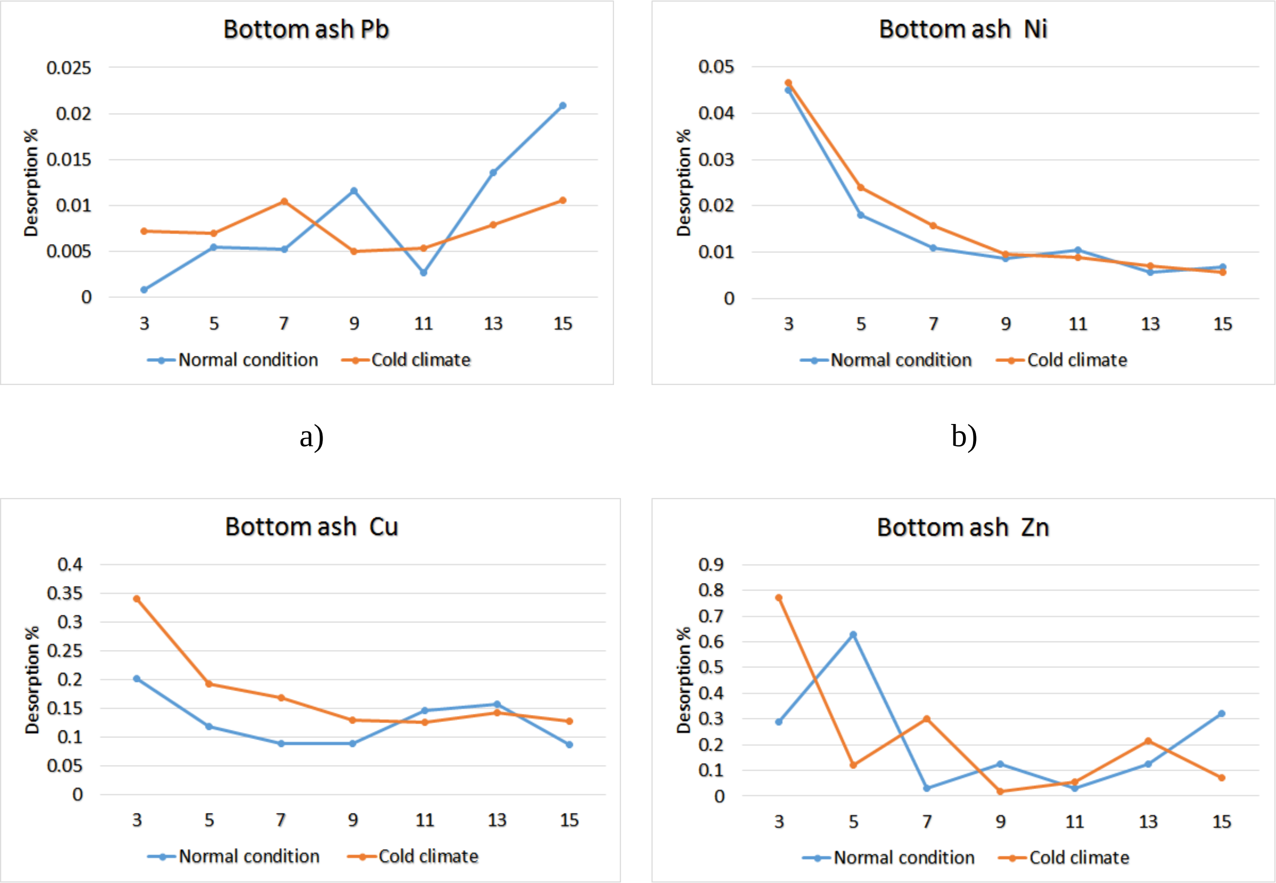
Plotted results for lead releasing from bottom ash indicated small leaching in both cases, Figure 22 a, this is in line with previous studies [19] and indicate that mainly lead is present in compounds that are not soluble in water. Normal weather condition curve was found to increase with every next cycle, but at the end released concentration did not reach value up to 20 µg/l. For simulated cold climate, in 5th cycle lead reached the highest concentration, and it could be considered continuously curve behavior for the next cycles. Releasing of nickel in cold climate show constant characteristic for each cycle, Figure 21 b. One peak in 5th cycle is noticed in case of normal weather conditions but this may be because of some error during the experiment. A general conclusion could be that dissolved metals would leave the adsorbent content with earlier cycles [22, 23].

Results for copper releasing showed correspondence with the results presented in report from the Norwegian association of solid waste management [19]. It is noticed very low leaching of copper, not more than 7 μg/l in the first cycle, for both cases and with every next cycle the concentration is decreasing.

Also, when analyzing the leachability of heavy metals from bottom ash content, the following order of releasing constituents was observed: Zn > Cu > Ni > Pb for cold climate condition.

Desorption process

Desorption process on the previously adsorbed pollutants from the synthetic stormwater with bottom ash is presented in the Figure 23.



a) b)

c) d)

Figure 23. Desorption process of bottom ash samples; a) Lead, b) Nickel, c) Copper, d) Zinc

From the presented results, it can be seen that cold clime had no influence on the releasing of metals from bottom ash. It has to be emphasized that there was variation in the results between cold climate and normal weather condition but that variation for each cycle is in really narrow range. Released concentration of zinc was the highest, compared with the other three metals and this result is in line with the discussion about releasing constituents from bottom ash content. Following order could be observed from the released concentration Zn > Cu > Ni > Pb. Nickel, copper and zinc curves plotted from cold climate results have decreasing character. Desorption of lead could be considered as the same value for each cycle except in 7th cycle when highest amount of lead is released. Nickel and copper curves showed same behavior for both cases. Concentration of metals in the liquid samples are not only from the desorption process of previously adsorbed metals from simulated stormwater but also there is releasing of heavy metals from adsorbents content [22].

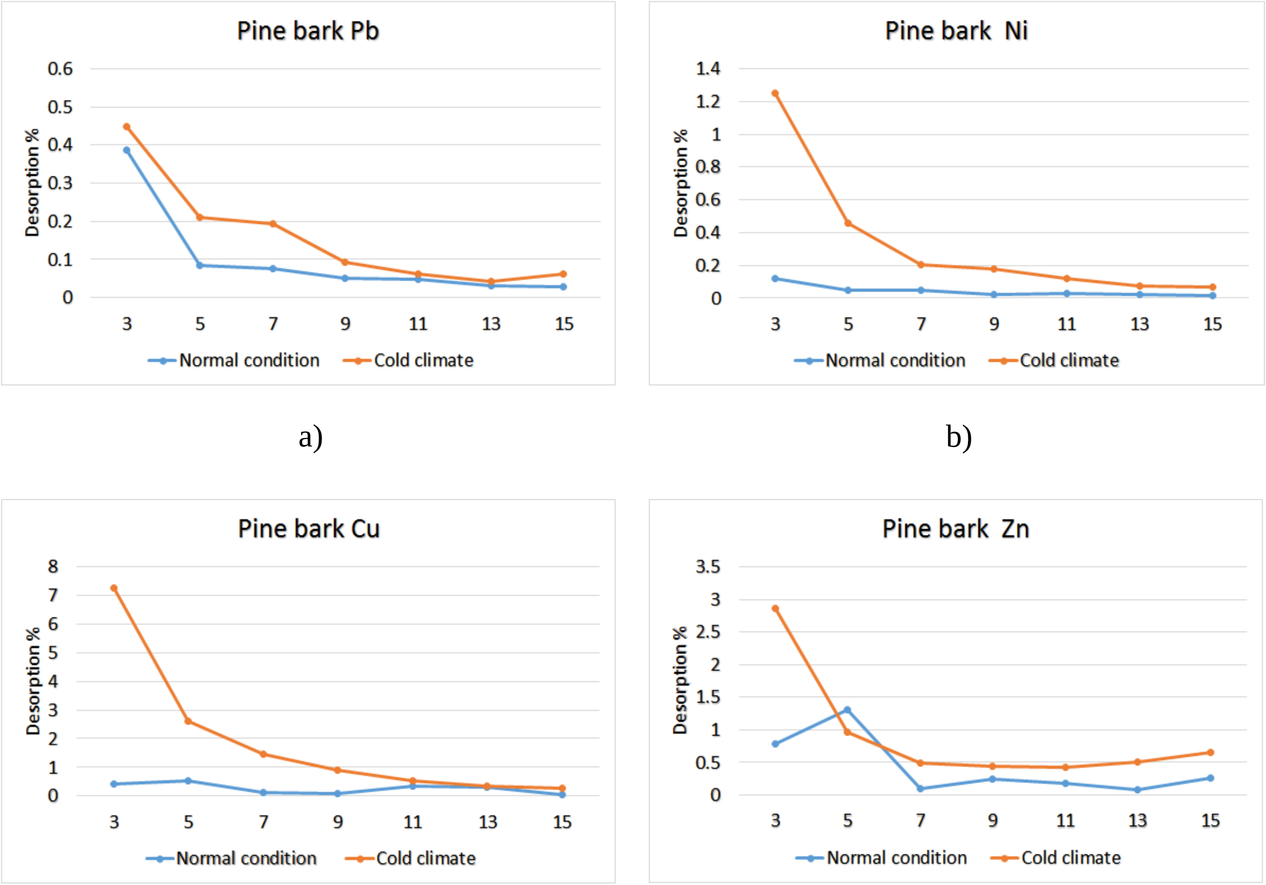
4.3.3. Pine bark

Herein, results from desorption process of heavy metals from pine bark samples are presented.

Desorption process

Results from experiments conducted for determination the leakage of elements from pine bark are presented in Figure 24. Influence of cold climate was noticed for nickel and copper desorption especially in the begging cycles. When analyzing the cold climate curves, the highest concentration of previously adsorbed metals was released in the 3rd (beginning) cycle for each metal and curves have decreasing character. The higher concentration of the four elements during the desorption cycles indicate metal release through dissolution and some structural disintegration.

Lead releasing in the two analyzed situations has same behavior, and desorbed concentration is decreasing with every next cycle. Nickel and copper releasing in case of normal climate could be concluded as constant in every cycle. Zinc desorption in normal weather conditions is the highest in 5th cycle and then show slight decreasing with increasing number of cycles. It can be concluded that pine bark released highest concentration of copper compared with the other metals.



a) b)

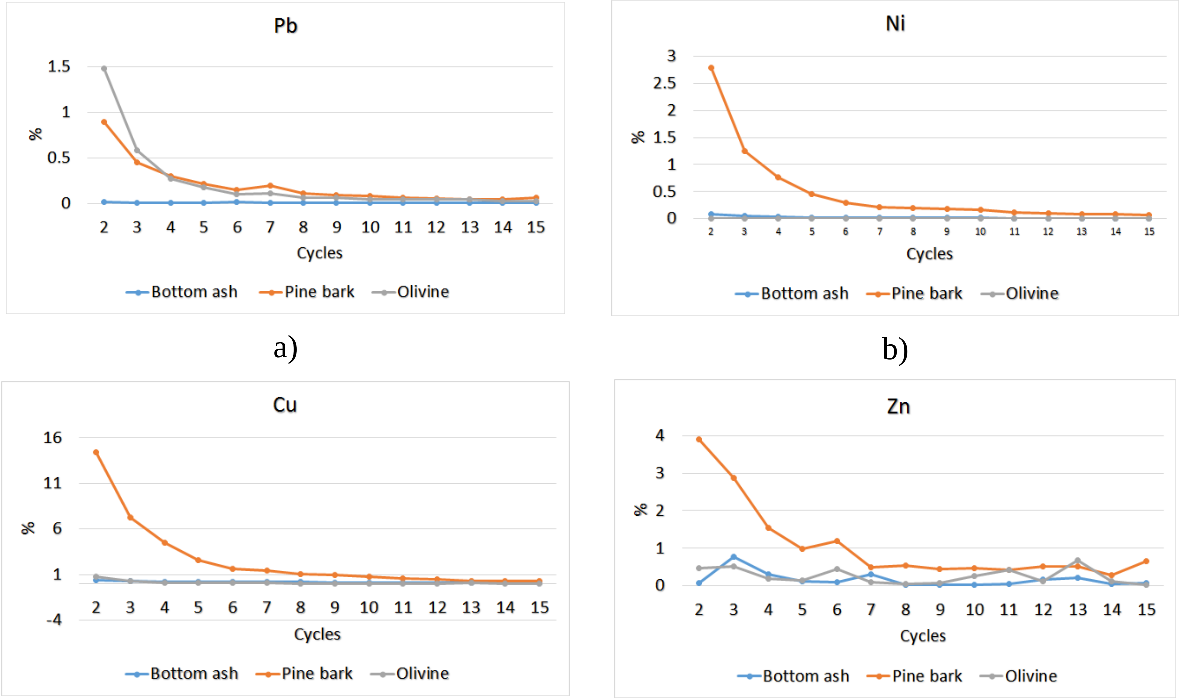
c) d)

Figure 24. Desorption process of pine bark samples; a) Lead, b) Nickel, c) Copper, d) Zinc

4.3.4. Comparison of the adsorbents

In Figure 25, the correlation between cycles with freezing and thawing process and the amount of released metals (in percentage) from previously adsorbed with the adsorbents, is presented.

The release behavior with regards to the same metal concentration, differs from adsorbent to adsorbent. As an example, the release of four metals was lowest from bottom ash and did not show any relation with freezing and thawing. The pine bark released higher concentrations of four metals during the initial cycles but decreasing curves indicate metal release through dissolution and perhaps some structural disintegration.



a) b)

c) d)

Figure 25. Desorption process; a) Lead, b) Nickel, c) Copper, d) Zinc

The releasing of Pb from olivine was in line with releasing of Pb from pine bark. The highest releasing of Pb from olivine and pine bark was in the second cycle (after the first time of freezing) but it decreased with every cycle, which also indicates dissolution of precipitated metal. Beyond that olivine show similar release behavior as bottom ash for Ni, Cu and Zn; but for Zn both adsorbents show slight increase trend with increasing number of cycles, which indicates the release of availability controlled metal. Nevertheless, among four metals the concentration of released Pb from pine bark was the highest. After eight cycles, the amount of Pb in the effluent was almost same for all adsorbents. Compared with the results from adsorption efficiency in the first cycle, bottom ash removed the highest amount of metals from the synthetic stormwater and the influence of freezing process was negligible compared with the other adsorbents.

The releasing of Pb from bottom ash was constantly in every cycle. The olivine and pine bark curves have decreasing behavior, which indicated releasing because of dissolution or after a few cycles breaking of solid parts and releasing of availability controlled metals. Bottom ash showed the best performance for keeping and not releasing Pb, because the concentration is the lowest and constant in every cycle. When compared with desorption of other metals, it could be noticed that

Pb releasing is the lowest. This might indicate that Pb is difficult to exchange or being strongly adsorbed to the site of adsorbents.

Curves for releasing of Ni and Cu have same behavior for olivine and bottom ash. Pine bark as an adsorbent has the highest amount of releasing the adsorbed metals (Ni and Cu) and with every next freezing/thawing process the amount is decreasing.

Zn releasing from pine bark is highest. Curves for olivine and bottom ash have the same behavior, but the releasing of zinc varies in every cycle.

From the Figure 25, can be noticed that cooper is released in higher concentration when compared with other elements. In second cycle releasing of Cu from pine bark was 14.37 % from the adsorbent Cu in first cycle. With increasing the number of cycles, the desorption concentration of Cu was decreasing and at the end is 0.28 %.

Relatively low releasing of previously adsorbed metals with the adsorbents indicates that the adsorption process in first cycle was stable and cold climate have negligible influence on metal releasing or desorption process.

4.4. Environmental impacts

This part presents the environmental impact from low-cost materials usage in adsorption process for highway runoff treatment. Moreover, here is provided comparison and discussion of the results from different laboratory test with environmental standard.

In order to evaluate if adsorbents could remove pollutants in the acceptable range, results obtained from adsorption capacity experiments and desorption process are assessed with IPPC directive – Integrated Pollution Prevention Control and also compared with Macedonian regulation for water discharge. The EU regulations gives procedures and limitation for emission of pollutants from industrial processes and agriculture activities. Concentration of metals in effluent and pH value are parameters which are analyzed in order to determinate water quality and removal efficiency of the adsorbents [24, 25].

4.4.1. Olivine

According to the information provided in safety data sheet from Sibelco Nordic, Appendix 7, Olivine Blueguard G1-3 is classified as non-hazardous product. As mentioned in part 3.2.1 in this thesis, main component in the olivine content is MgO_2. Results from leaching test showed that there was no releasing of Mg from olivine content, Appendix 3. All results are presented in Appendix 3. This indicates that manganese presented in olivine is stable and not soluble in water solution. Releasing of F, Na, Ca and SO_4 were noticed in every cycle. Toxic effect from olivine on the ecological system is more related with increasing of the pH value than possibility of hazardous elements releasing. According to the limits provided by IPPC, pH value of the aqueous solution before entering in surface water must be in range of 6.5 – 9. Therefore, from the pH measurements when olivine is mixed either with distilled water or metal solution increase the initial pH of the used influent from 7 to more than 11.

To see if adsorption process is a valid choice for treatment of highway runoff and also with consider of weather conditions, the results from the different laboratory tests have to be compared and evaluated according to the environmental standard. The results from the laboratory experiments are compared with regulatory limits by the law in R. Macedonia for polluted water discharge in surface water and these regulation follows the EU, IPPC limits for polluted water discharge in surface water. Table 13 presents the limits for the four heavy metals analyzed in this master work. The results for heavy metal concentration are presented in Appendix 2.

From the heavy metal concentration data provided in Table 19, Table 20, Table 23 the results from olivine samples were below the acceptable environmental standards.

4.4.2. Bottom ash

The rates of leaching of heavy metals from bottom ash during the experiments explained in chapter 4.3.2, *Leaching test* were compared with regulatory limits by the law in R. Macedonia for polluted water discharge in surface water, Table 13. If heavy metal leached from the bottom ash exceed the regulatory limits, the bottom ash therefore could be classified as a hazardous material.

Table 13. Environmental impacts [24,25]

Heavy metal	**Limits by the law in Macedonia / IPPC** [mg/l]	**Highest measured value – Freeze/thaw experiment** [mg/l]	**Highest measured value – experiment without freeze** [mg/l]
Pb	0.5	0.0002	0.00012
Ni	0.5	0.00023	0.001
Cu	0.5	0.0054	0.0069
Zn	2	0.03	0.0544
pH	6.5 – 9.5	10	10

Regulation in Macedonia follow the EU regulations, IPPC limits for polluted water discharge in surface water. Lead, nickel and zinc are limited to 0.5 mg/l and as it could be notice bottom ash samples did not reach these values. Leaching of zinc is the highest compared with the other metals, for both analyzed situations but release of zinc in both cases is far below the limits according to the law. Through this observation, bottom ash can be considered as non-hazardous material and does not present any additional risk to human health or to the environment when applied in real treatment process. But results for pH of the bottom ash samples indicated that pH value is near 12, and this is above ranges [19, 22]. The pH value could be adjusted in the acceptable range with adding an appropriate volume of high-purity acid (HCl) [3].

Table 19 presents heavy metal concentration in samples of adsorption capacity tests. Concentration of nickel in sample with 1.6 g of bottom ash is 0.878 mg/l which is above the environmental limits in Table 13. Nickel concentration in the samples from freeze/thaw test, Table 21 is also higher than 0.5 mg/l. But this result is only in the first cycle and then nickel concentration is below the environmental standard. Also, worth mentioning is that the initial concentration of heavy metal is simulated stormwater for this experiment was 5 mg/l.

4.4.3. Pine bark

The potential of organic compounds leaching from pine bark is one disadvantage for its usage in water treatment. During the experiments it was noticed that pine bark behaves like an acid and change the pH from neutral 7 to 4. This study showed that potential negative effect from pine bark on the ecological system is related to the pH rather than the release of hazardous elements. According to the reviewed literature [21], it was concluded that the decreased pH caused by desorption of organic acids was the primary cause of toxicity. The pH of the synthetic stormwater could be adjusted within the range, by adding an appropriate volume of alkaline solutions for ex. NaOH [3].

Heavy metal concentration in aqueous sample, when pine bark was used as an adsorbent, is in the acceptable range compare with limits in Table 13. Exception from this conclusion is result from nickel concentration in sample with 1.6 g of pine bark.

4.5. Practical aspects

The control and treatment of highway runoff involves a variety of stakeholders in the selection of sustainable development systems. Thus, environmental/ecological, social/community and economic cost factors become potential sustainability criteria in terms of assessing long-term, cost-effective options. Expected results from studies on low-cost adsorbent focus on adsorbent removal capacity, as a function of pollutant concentration would have several practical aspects, such as costs, end of life costs, environmental and social impacts [26].

Usage of selected low-cost adsorbents in treatment process for highway runoff would affected on environmental impacts and reduced pollution of heavy metals before this water enters in water receivers. In this part of the thesis environmental, economic and social impacts are presented.

In this paper, adsorption process with low-cost adsorbent materials is selected for treatment of highway runoff. Adsorption process would be one integrated part of the treatment system when is install in real application. The whole treatment system as well as adsorption process need to reduce costs for highway stormwater and drainage infrastructure, whilst maintaining socially acceptable levels of service, enhancing community benefits and minimizing environmental impacts.

Through the indicators, evaluation of selected treatment process of highway runoff would be done. Environmental/ecological, social/community, economic and also technical factors are potential sustainability criteria to facilitate comparisons and assessment of treatment process with regard to capital cost, resource use, acceptability, performance, maintenance, etc. Table 14 provides listing of impacts for the three categories.

Environmental impacts are divided in two groups related with pollution influence. *Motor vehicles* has been recognized as a major contributor to a variety of water pollution of stormwater runoff. Operation of motor vehicles have the dominant effect on pollution and is listed in the group of impacted that directly influence the pollution. Major specific sources of heavy metals in highway runoff are from tire wear and break wear but exhausted gases from vehicles and catalytic converters also contribute to overall pollution.

The pollution from *load of vehicles* is not permanent. This represent pollution influenced by leakage or dropout of loading in the vehicles.

Pollution generated by winter road maintenance such as application of salt and grid is part of *additional impacts* listed in the table above. This pollution and also some particles from the *adsorbents* could enter and are stored in roadside snow and could be released during snowmelt into the receiving environments.

Table 14. Table of analyzed impacts

Environmental impacts			**Economic impacts**		**Social impacts**	
Direct influence		Indirect influence	Direct influence	Indirect influence	Direct influence	Indirect influence
Motor vehicles	Vehicles exhaust gases	Load of vehicles	Investment costs Building of system for treatment of polluted water	Additional activities for public service employees	Additional activities for public service employees	Health and safety of passengers
	Tire wear	Asphalt road surface wear				Well being
	Brake wear	Adsorbents	Opperational costs Maintenance of the system and replacement of adsorbents			Safe driving
	Catalytic converters	Additional				

Also the material from *asphalt road* because of lifespan and weather conditions could generate pollution.

The environmental aspect has shown to be highly positive, based on the removal of heavy metal with low-cost adsorbent that generate really small amount of additional pollution.

Economic impacts that have direct influence are divided as *investment and operational costs*. The treatment process could be integrated in exiting wastewater treatment plant and this reduces the investment cost. Also, the investment cost could be negligible when compare with the damages that could happen because of untreated stormwater (Chapter 1 and 2).

In the group of social impacts, public service employees have *additional activities* related with maintenance of the system for treatment of polluted water but this is mutual characteristic with economic aspect. Based on the safety of passengers and wellbeing of the passengers and surrounding population because of the cleaner environment the social aspects have shown to be positively.

5. Conclusions

Literature reviewed for this study shows that highway runoff contains different contaminants from a variety of direct and indirect sources. With increasing the number of vehicles and their necessity, the amount and concentration of contaminants are increasing. Paved surfaces eliminate the natural filtration and the contaminants are transported off the road surfaces, so runoff carries the pollutants into waterbodies. Primary, contaminants are transported by precipitation runoff. This type of runoff is considered as non-point source of pollution.

The batch adsorption experiments provided satisfactory results for heavy metal removal efficiency from synthetic stormwater with analyzed adsorbent materials. Synthetic stormwater for the purpose of this experiment were prepared with 2 mg/l which indicates high level of metal pollution. The percentage removal of lead, nickel, copper and zinc from synthetic stormwater was 93 – 98 %, 99 %, 96 – 99 % and 98-99 % with olivine, 94 – 99 %, 59 – 99%, 93 – 99 % and 82 – 99 % with bottom ash and 95 – 96 %, 69 – 91 %, 62 - 91 % and 59 – 83 % with pine bark, respectively. The experiments showed that adsorbent mass does not corresponds to the amount of heavy metals removed by each adsorbent. Adsorbed concentration of metals with bottom ash is in line with adsorbent mass. Pine bark experiment also followed this trend, except for lead removal. The amount of mass olivine has negligible influence on nickel, copper and zinc removal but removal of lead is the highest when 100 g of olivine is used.

Removal efficiency in the first cycle is up to 70 %. Compared with the results from adsorption efficiency in the first cycle, bottom ash removed the highest amount of metals from the synthetic stormwater and the influence of freezing process on the desorption of metals was negligible. Generally, the effect of cold climate has not influenced on the desorption process and releasing of adsorbed metals. Despite the similarities, the results showed differences in the released amount between the analyzed cases but these are in really narrow range. When analyzing the influence of cold climate and desorption process, the highest releasing of lead is noticed from olivine samples as well as desorption of lead, copper and zinc from pine bark samples.

During the experiments, pH and conductivity values were measured on each sample. Olivine and bottom ash increase the pH value on simulated stormwater from pH 7 to 12 and 10, respectively. Opposite of this, pine bark decreases the pH to 4. The pH value is one of the criteria when environmental impacts are analyzed. The influence of cold climate on pH value of the mixture adsorbents and either distilled water or metal solution was negligible.

Overall, this master work demonstrated the usage possibility of the low-cost adsorbent materials with respect to olivine, bottom ash and pine bark for highway runoff treatment under different climate conditions.

The reduction of heavy metals was significantly improved when adsorption process with low cost adsorbent material is used as a treatment method for highway runoff. Effects of cold climate is negligible and did not have significant influence on the adsorption efficiency, desorption process or live spin on the adsorbents. The heavy metal concentration either after adsorption or desorption process is in the range of acceptable environmental standards.

Further work

One of the steps for improvement of the adsorption performance for heavy metal removal is batch test experiments to be performed with real stormwater instead of synthetic stormwater. The composition of highway stormwater runoff contains more pollutants, so selectivity and adsorption capacity of the adsorbents in real application could be influenced by other metals contained in highway stormwater. Also, in real application salt and sand is used during winter maintenance. Concentration of deicing salt in stormwater also may have influence on adsorption performance of the selected low-cost adsorbents.

Furthermore, batch test experiment could be replaced with dynamic column adsorption tests in order to evaluate adsorption capacity of adsorbents when fluid velocity varies and under high hydraulic loads.

Through the analysis, it could be noticed that pH value of effluent was significantly changed when it was mixed with adsorbent. For further work, control and optimization of pH value on liquids must be taken into consideration.

Additional activity could be BET analysis for determination of the overall specific external and internal surface area of the adsorbent. Hence, the adsorption process is phase transfer process and pollutants are bounded on the surface of the adsorbent, surface area is a very important quality parameter of the adsorbent.

References

[1] Napiera Fiona, D’Arcyb Brian, Jefferies Chris, A review of vehicle related metals and polycyclic aromatic hydrocarbons in the UK environment, *Elsevier, 226*, (2008), pp. 143–150, doi: 10.1016/j.desal.2007.02.104 https://www.sepa.org.uk/media/163244/vehicle_metals_polycyclic_aromatic_hydrocarbons.pdf

[2] Carson Hartwell, Eaker Bill, Gibson Phillip, Randall Mike, Stormwater Problems & Impacts: Why All The Fuss? United States Environmental Protection Agency - EPA Stormwater Hotline, http://www.chathamnc.org/Home/ShowDocument?id=2515

[3] Ilyas Aamir, Muthanna M. Tone, Assessment of upscaling potential of alternative adsorbent materials for highway stormwater treatment in cold climates, *Environmental Technology*, (2016), doi: 10.1080/09593330.2016.1209567

http://www.tandfonline.com/doi/abs/10.1080/09593330.2016.1209567?journalCode=tent20

[4] Erickson J. Andrew, Weiss T. Peter, Gulliver S. John, *Optimizing Stormwater Treatment Practices*, Springer, New York, USA, 2013

http://www.springer.com/gp/book/9781461446231

[5] Jang Am, Seo Youngwoo, Bishop L. Paul, The removal of heavy metals in urban runoff by sorption on mulch, *Environmental Pollution, 133*, (2005), pp. 117-127, doi: 10.1016/j.envpol.2004.05.020

http://www.sciencedirect.com/science/article/pii/S0269749104002258

[6] Czernick G. Gregory, Management of highway runoff water quality: an examination of the issue and potential solitions for provincial highwas in the greater Vancouver regional district, University of Victoria, Victoria, Canada, 2000, file:///C:/Users/User/Desktop/MANAGEMENT%20OF%20HIGHWAY%20RUNOFF%20WATER%20QUALIN.pdf

[7] Protecting water quality from urban runoff, EPA Stormwater, https://www3.epa.gov/npdes/pubs/nps_urban-facts_final.pdf

[8] Polluted Runoff: Nonpoint Source Pollution, February 2003, United States Environmental Protection Agency – EPA, https://www.epa.gov/nps/what-nonpoint-source

[9] Cahill H. Thomas, *Low impact development and sustainable stormwater management*, John Wiley & Sons, Inc., Hoboken, New Jersey, United States, 2012 http://site.ebrary.com/lib/ntnu/reader.action?docID=10642592&ppg=3

[10] The Minnesota stormwater manual, Minnesota Stormwater Steering Committee, Version 1, November 2005,

https://www.pca.state.mn.us/water/minnesotas-stormwater-manual

[11] LeFavre H. Gregory, Paus H. Kim, Natarajan Poornima, Gulliver S. John, Novak J. Paige, Hozalski M. Raymond, Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells, *Journal of Environmental Engineering*, 141, (2015), 1, doi: 10.1061/ (ASCE)EE.1943-7870.0000876

http://ascelibrary.org/doi/abs/10.1061/(ASCE)EE.1943-7870.0000876

[12] Tchounwou B. Paul, Yedjou G. Clement, Patlolla K. Anita, Sutton J. Dwayne, Heavy metal toxicity and the environment, *Molecular, clinical and environmental technology, Springer Basel, 3*, (2012), pp. 133-164, doi: 10.1007/978-3-7643-8340-4_6

http://link.springer.com/chapter/10.1007%2F978-3-7643-8340-4_6

[13] Worch Eckhard, *Adsorption technology in water treatment*, Walter de GruyterGmbH & Co., Berlin, Germany, 2012

http://197.14.51.10:81/pmb/CHIMIE/Traitement/Adsorption%20Technology%20in%20Water%20Treatment.pdf

[14] Montes-Atenas Gonzalo, Schroeder L.M. Sven, Sustainable natural adsorbents for heavy metal removal from wastewater lead sorption on pine bark (Pinus radiata D.Don), *Surface and Interface Analysis*, 47, (2015), pp. 996-1000, doi: 10.1002/sia.5807

https://www.diva-portal.org/smash/get/diva2:943519/FULLTEXT01.pdf

[15] Chiang Y. W., Santos R. M., Ghyselbrecht K., Van Gerven T., Cappuyns V., Martens J.A., Meesschaert B., Waste Derived Sorbents and Their Potential Roles in Heavy Metal Remediation

Applications, *E3S Web of Conferences*, *1*, (2013), pp. 25003 1-4, doi: 10.1051/e3sconf /20130125003

http://www.e3s-conferences.org/articles/e3sconf/abs/2013/01/e3sconf_ichm13_25003/e3sconf_ichm13_25003.html

[16] Kleiv R.A., Sandvik K.L., Modelling copper adsorption on olivine process dust using a simple linear multivariable regression model, *Minerals Engineering Elsevier*, 15, (2002),10, pp. 737–744

http://www.sciencedirect.com/science/article/pii/S0892687502001735

[17] Sibelco Nordic, Blueguard G1-3, G1-3CC, http://www.dansand.dk/fileadmin/content/DATABLADE_PDF/Downloads/Sikkerhedsdatablade/Dansand_MSDS__BLUEGUARD_G_1-3_G1-3CC_ENG.pdf

[18] Luz Martin Georg, Removal of dissolved pollutants from highway stormwater wit low-cost adsorbents, Norwegian university of science and technology, Trondheim, Norway, 2014

https://daim.idi.ntnu.no/masteroppgaver/012/12265/masteroppgave.pdf

[19] Sampling and analysis of bottom ash from solid waste incineration, *The Norwegian association of solid waste management*, Norway, report no. 2/2016

[20] Andersson Ola, Adsorption modeling of heavy metals to Sawdust, bark of Pine and Absol, UMEA Universitet, Umea, Sweden, 2016

https://www.diva-portal.org/smash/get/diva2:943519/FULLTEXT01.pdf

[21] Nehrenheim, E., Odlare, M., Allard, B., Retention of 2,4,6-trinitrotoluene and heavy metals from industrial waste water by using the low cost adsorbent pine bark in a batch experiment, Water Science and Technology, (2011), doi: 10.2166/wst.2011.603
http://dx.doi.org/10.2166/wst.2011.603

[22] Moghadas, S., Paus, K.H., Muthanna, T.M., Accumulation of Traffic-Related Trace Metals in Urban Winter-Long Roadside Snowbanks, *Water air soil pollut*, (2015), doi:10.1007/s11270-015-2660-7

https://link.springer.com/article/10.1007/s11270-015-2660-7

[23] Shim Young-Sook, Kim Young-Keun, Kong Sung-Ho, Rhee Seung-Whee, Lee Woo-Keun, The adsorption characteristics of heavy metals by various particle size of MSWI bottom ash, *Waste management*, *23*, (2003), pp. 851-857, doi: 10.1016/S09-56-053X(02)00163-0

http://www.sciencedirect.com/science/article/pii/S0956053X02001630

[24] Guidance of setting of trigger values for storm water discharge to offsite surface waters, *Office of environmental enforcement*, 2012, Ireland

https://www.epa.ie/pubs/advice/licensee/Licensee%20Guidance%20on%20the%20setting%20of%20trigger%20values%20-%20Final%20.pdf

[25] http://www.slvesnik.com.mk/Issues/C7A5EBA121C1ED42BFE128BC26F7B163.pdf, , Retrieved March 2017

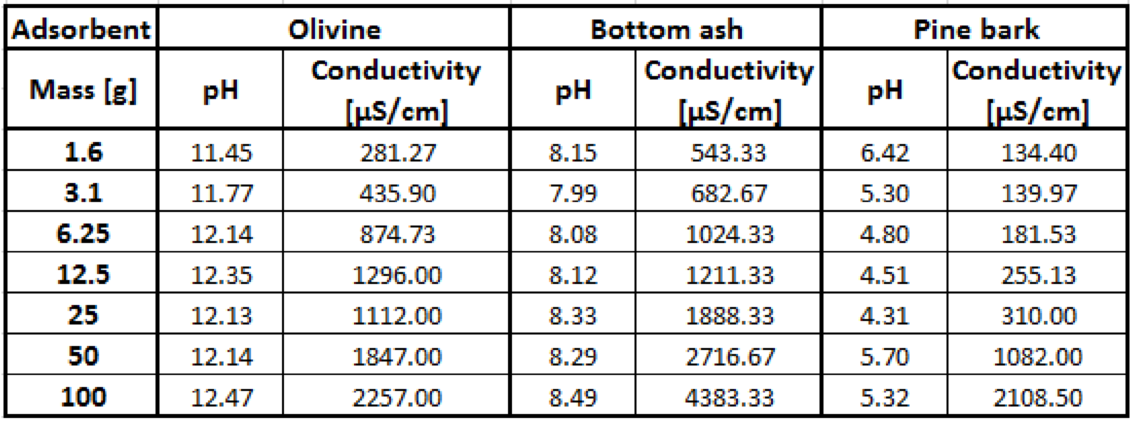
[26] Ellis J.B., Deutsch J.-C., Mouchel J.-M, Scholes l. Revitt M.D., Multicriteria decision approaches to support sustainable drainage options for the treatment of highway and urban runoff, *Science of the total environment*, *334 – 335*, (2004), pp. 251 – 260, doi:10.1016/j.scitotenv.2004.04.066

http://www.sciencedirect.com/science/article/pii/S0048969704003870

Appendix 1. pH and Conductivity results

Adsorption capacity test – batch tests

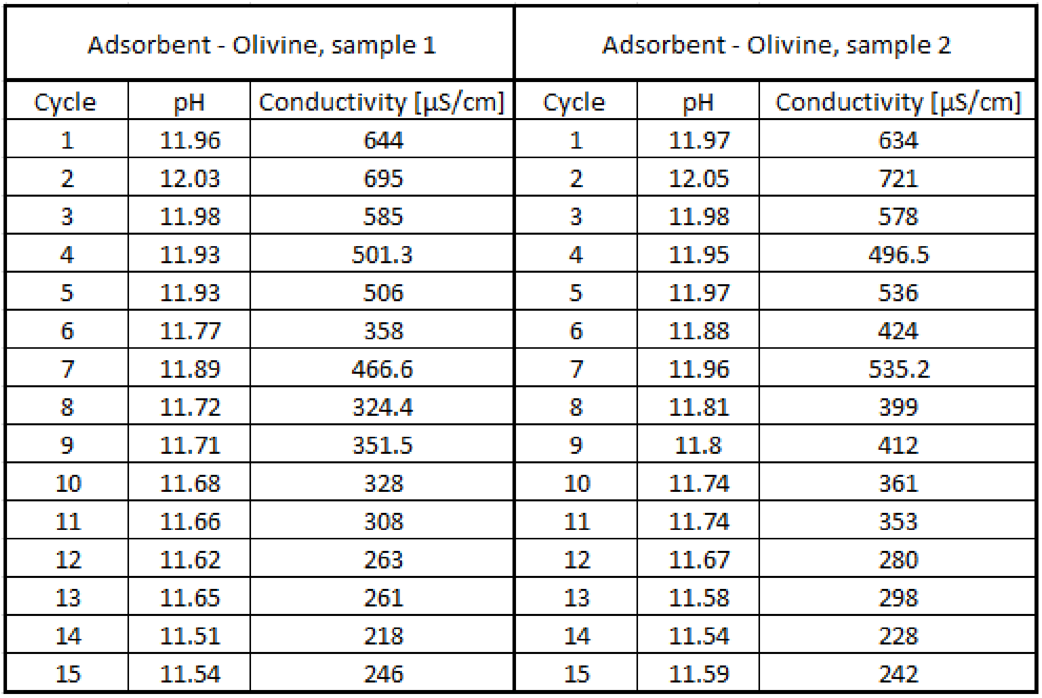
Table 15. pH and Conductivity, batch tests



Adsorbent	Olivine		Bottom ash		Pine bark	
Mass [g]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]
1.6	11.45	281.27	8.15	543.33	6.42	134.40
3.1	11.77	435.90	7.99	682.67	5.30	139.97
6.25	12.14	874.73	8.08	1024.33	4.80	181.53
12.5	12.35	1296.00	8.12	1211.33	4.51	255.13
25	12.13	1112.00	8.33	1888.33	4.31	310.00
50	12.14	1847.00	8.29	2716.67	5.70	1082.00
100	12.47	2257.00	8.49	4383.33	5.32	2108.50

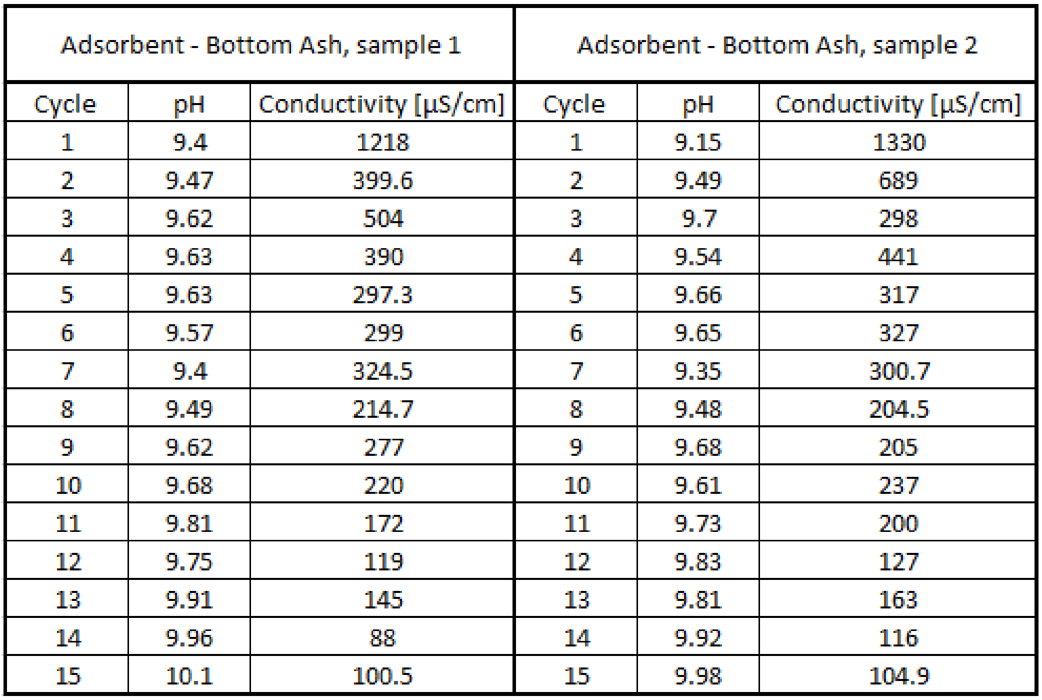
Freezing/ thawing tests without metal solution

Table 16. pH and Conductivity – Reference case; a) Olivine, b) Bottom ash, c) Pine bark



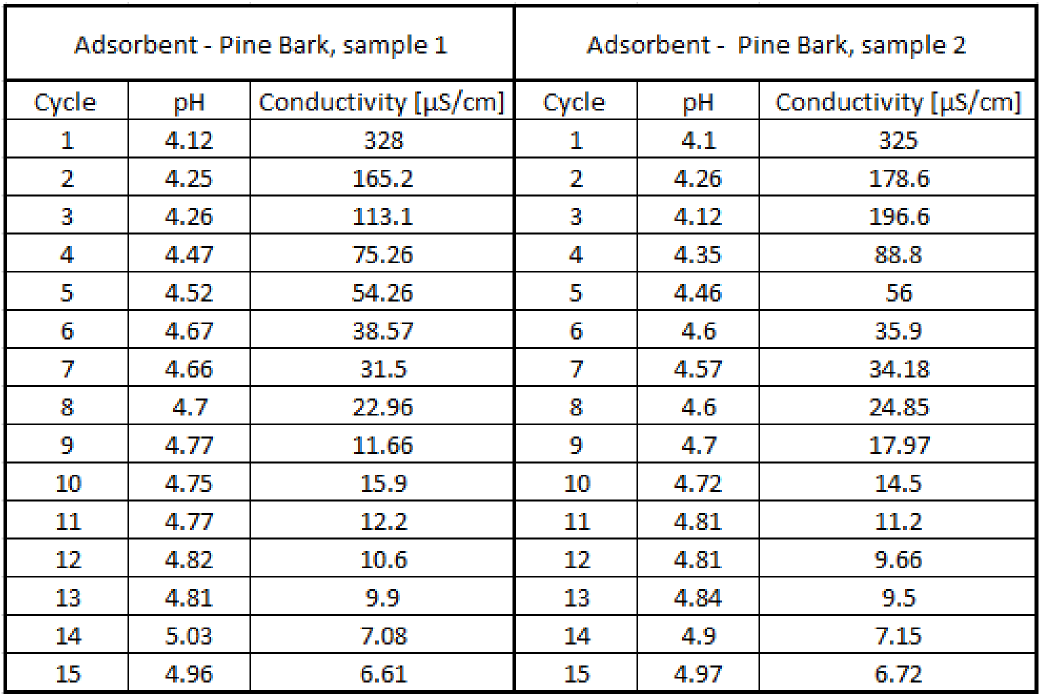
Adsorbent - Olivine, sample 1			Adsorbent - Olivine, sample 2		
Cycle	pH	Conductivity [µS/cm]	Cycle	pH	Conductivity [µS/cm]
1	11.96	644	1	11.97	634
2	12.03	695	2	12.05	721
3	11.98	585	3	11.98	578
4	11.93	501.3	4	11.95	496.5
5	11.93	506	5	11.97	536
6	11.77	358	6	11.88	424
7	11.89	466.6	7	11.96	535.2
8	11.72	324.4	8	11.81	399
9	11.71	351.5	9	11.8	412
10	11.68	328	10	11.74	361
11	11.66	308	11	11.74	353
12	11.62	263	12	11.67	280
13	11.65	261	13	11.58	298
14	11.51	218	14	11.54	228
15	11.54	246	15	11.59	242

a)



Adsorbent - Bottom Ash, sample 1			Adsorbent - Bottom Ash, sample 2		
Cycle	pH	Conductivity [µS/cm]	Cycle	pH	Conductivity [µS/cm]
1	9.4	1218	1	9.15	1330
2	9.47	399.6	2	9.49	689
3	9.62	504	3	9.7	298
4	9.63	390	4	9.54	441
5	9.63	297.3	5	9.66	317
6	9.57	299	6	9.65	327
7	9.4	324.5	7	9.35	300.7
8	9.49	214.7	8	9.48	204.5
9	9.62	277	9	9.68	205
10	9.68	220	10	9.61	237
11	9.81	172	11	9.73	200
12	9.75	119	12	9.83	127
13	9.91	145	13	9.81	163
14	9.96	88	14	9.92	116
15	10.1	100.5	15	9.98	104.9

b)

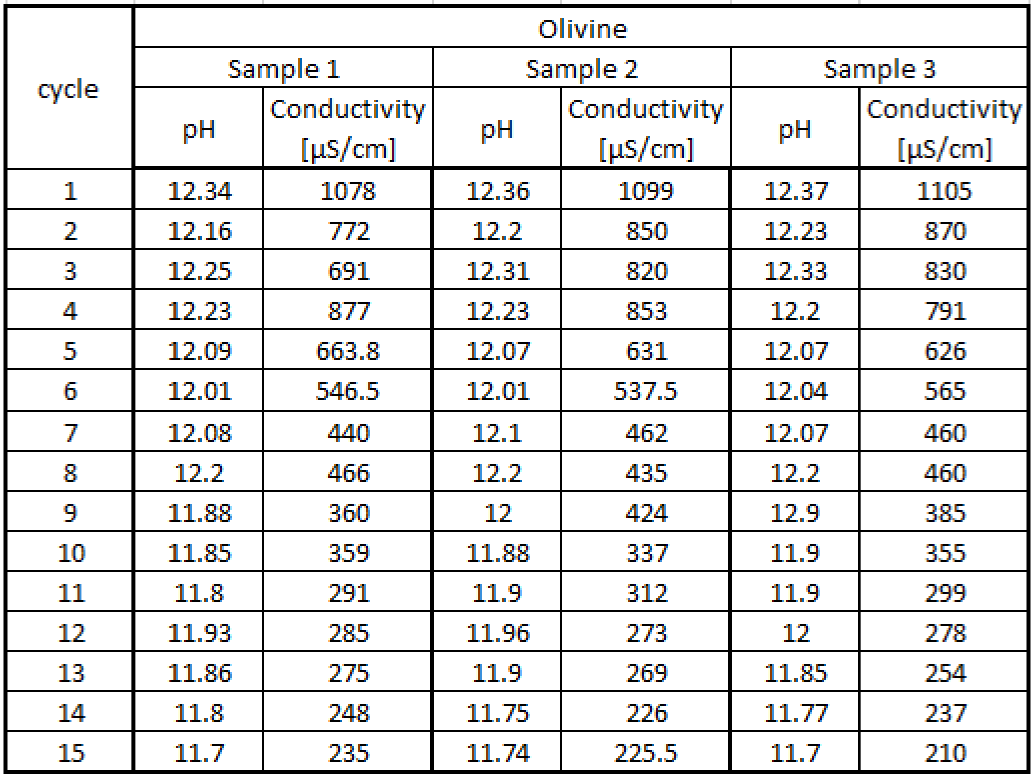


Adsorbent - Pine Bark, sample 1			Adsorbent - Pine Bark, sample 2		
Cycle	pH	Conductivity [µS/cm]	Cycle	pH	Conductivity [µS/cm]
1	4.12	328	1	4.1	325
2	4.25	165.2	2	4.26	178.6
3	4.26	113.1	3	4.12	196.6
4	4.47	75.26	4	4.35	88.8
5	4.52	54.26	5	4.46	56
6	4.67	38.57	6	4.6	35.9
7	4.66	31.5	7	4.57	34.18
8	4.7	22.96	8	4.6	24.85
9	4.77	11.66	9	4.7	17.97
10	4.75	15.9	10	4.72	14.5
11	4.77	12.2	11	4.81	11.2
12	4.82	10.6	12	4.81	9.66
13	4.81	9.9	13	4.84	9.5
14	5.03	7.08	14	4.9	7.15
15	4.96	6.61	15	4.97	6.72

c)

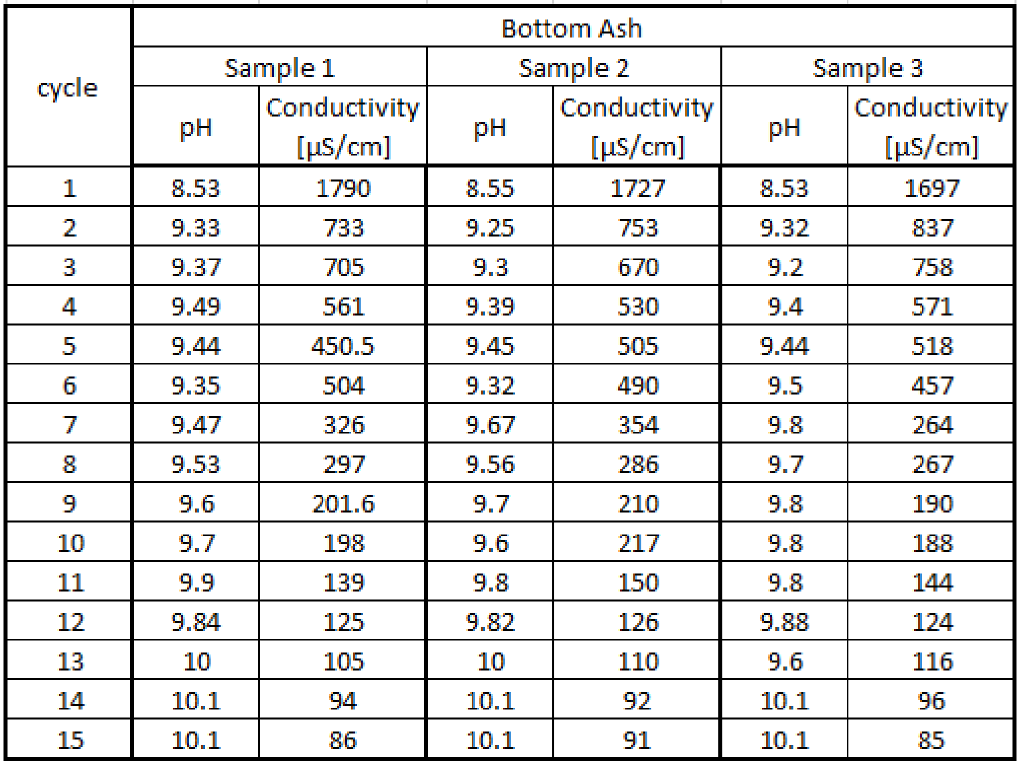
Freezing/ thawing test with simulated stormwater

Table 17. pH and Conductivity – Freezing/thawing test with simulated stormwater; a) Olivine, b) Bottom ash, c) Pine bark



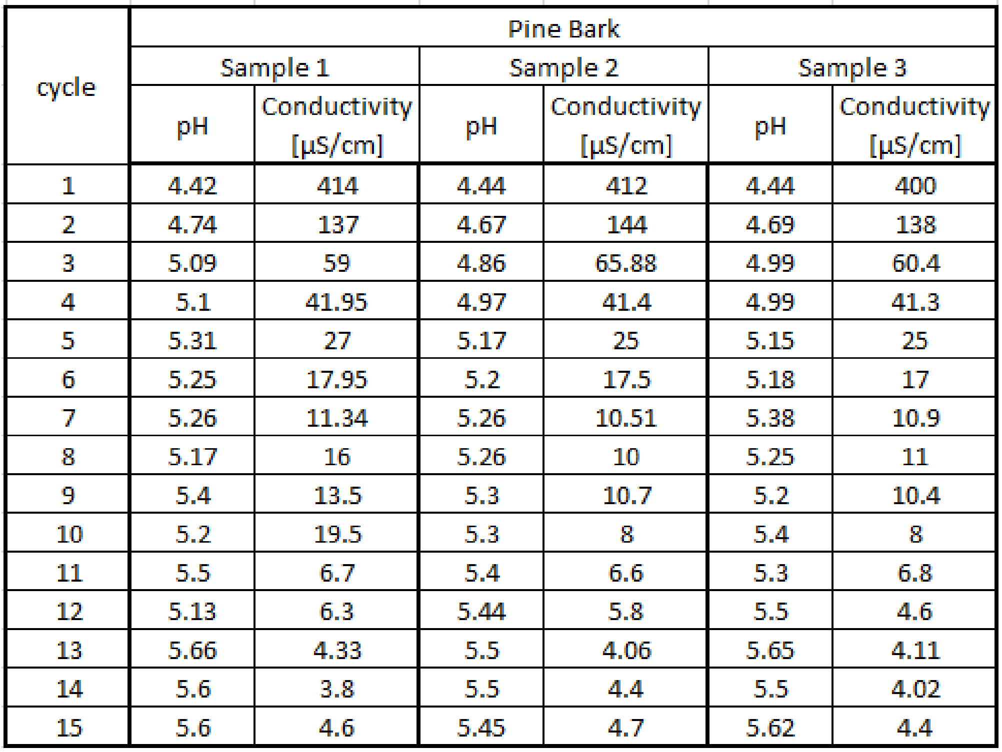
cycle	Olivine					
	Sample 1		Sample 2		Sample 3	
	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]
1	12.34	1078	12.36	1099	12.37	1105
2	12.16	772	12.2	850	12.23	870
3	12.25	691	12.31	820	12.33	830
4	12.23	877	12.23	853	12.2	791
5	12.09	663.8	12.07	631	12.07	626
6	12.01	546.5	12.01	537.5	12.04	565
7	12.08	440	12.1	462	12.07	460
8	12.2	466	12.2	435	12.2	460
9	11.88	360	12	424	12.9	385
10	11.85	359	11.88	337	11.9	355
11	11.8	291	11.9	312	11.9	299
12	11.93	285	11.96	273	12	278
13	11.86	275	11.9	269	11.85	254
14	11.8	248	11.75	226	11.77	237
15	11.7	235	11.74	225.5	11.7	210

a)



cycle	Bottom Ash					
	Sample 1		Sample 2		Sample 3	
	pH	Conductivity [μS/cm]	pH	Conductivity [μS/cm]	pH	Conductivity [μS/cm]
1	8.53	1790	8.55	1727	8.53	1697
2	9.33	733	9.25	753	9.32	837
3	9.37	705	9.3	670	9.2	758
4	9.49	561	9.39	530	9.4	571
5	9.44	450.5	9.45	505	9.44	518
6	9.35	504	9.32	490	9.5	457
7	9.47	326	9.67	354	9.8	264
8	9.53	297	9.56	286	9.7	267
9	9.6	201.6	9.7	210	9.8	190
10	9.7	198	9.6	217	9.8	188
11	9.9	139	9.8	150	9.8	144
12	9.84	125	9.82	126	9.88	124
13	10	105	10	110	9.6	116
14	10.1	94	10.1	92	10.1	96
15	10.1	86	10.1	91	10.1	85

b)

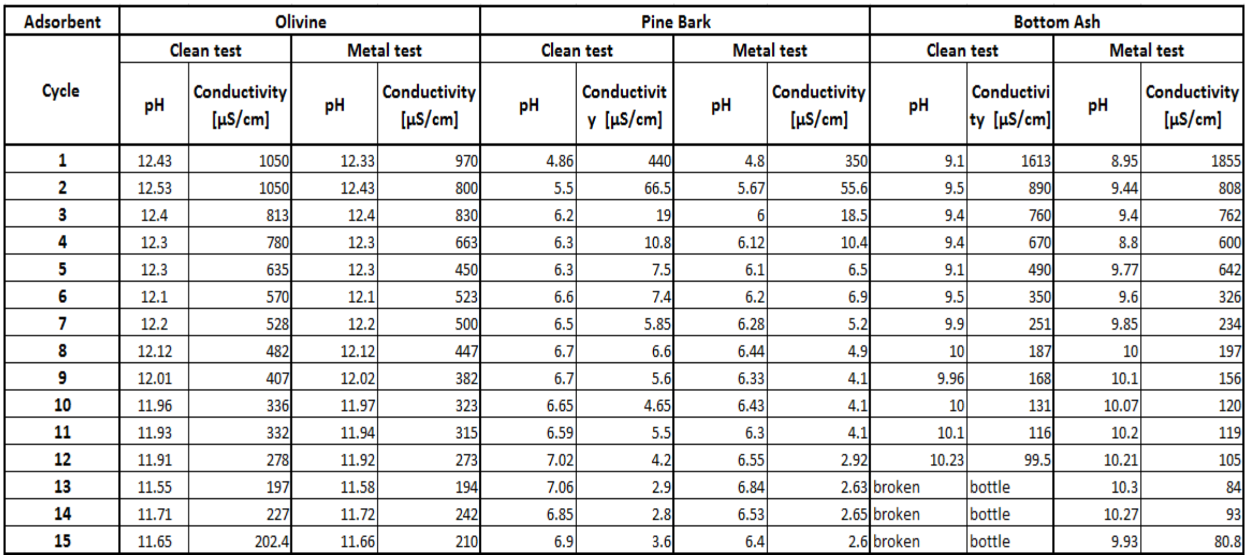


cycle	Pine Bark					
	Sample 1		Sample 2		Sample 3	
	pH	Conductivity [μS/cm]	pH	Conductivity [μS/cm]	pH	Conductivity [μS/cm]
1	4.42	414	4.44	412	4.44	400
2	4.74	137	4.67	144	4.69	138
3	5.09	59	4.86	65.88	4.99	60.4
4	5.1	41.95	4.97	41.4	4.99	41.3
5	5.31	27	5.17	25	5.15	25
6	5.25	17.95	5.2	17.5	5.18	17
7	5.26	11.34	5.26	10.51	5.38	10.9
8	5.17	16	5.26	10	5.25	11
9	5.4	13.5	5.3	10.7	5.2	10.4
10	5.2	19.5	5.3	8	5.4	8
11	5.5	6.7	5.4	6.6	5.3	6.8
12	5.13	6.3	5.44	5.8	5.5	4.6
13	5.66	4.33	5.5	4.06	5.65	4.11
14	5.6	3.8	5.5	4.4	5.5	4.02
15	5.6	4.6	5.45	4.7	5.62	4.4

c)

Control test, clean and metal case

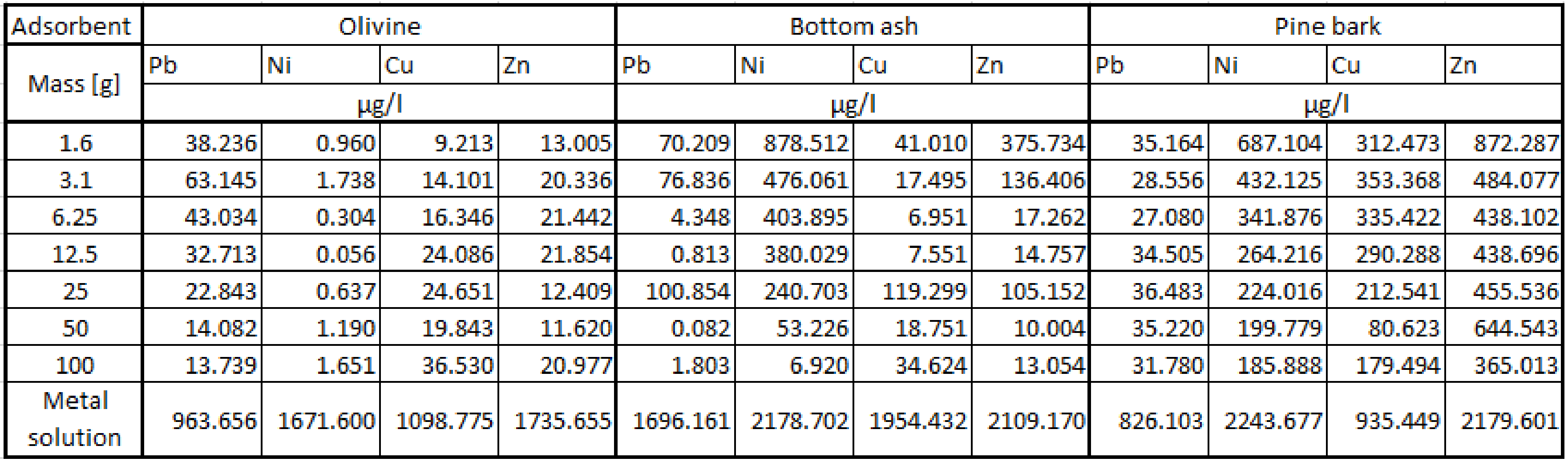
Table 18. pH and Conductivity - Control case, clean and metal case



Adsorbent	Olivine				Pine Bark				Bottom Ash			
	Clean test		Metal test		Clean test		Metal test		Clean test		Metal test	
Cycle	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]	pH	Conductivity [µS/cm]
1	12.43	1050	12.33	970	4.86	440	4.8	350	9.1	1613	8.95	1855
2	12.53	1050	12.43	800	5.5	66.5	5.67	55.6	9.5	890	9.44	808
3	12.4	813	12.4	830	6.2	19	6	18.5	9.4	760	9.4	762
4	12.3	780	12.3	663	6.3	10.8	6.12	10.4	9.4	670	8.8	600
5	12.3	635	12.3	450	6.3	7.5	6.1	6.5	9.1	490	9.77	642
6	12.1	570	12.1	523	6.6	7.4	6.2	6.9	9.5	350	9.6	326
7	12.2	528	12.2	500	6.5	5.85	6.28	5.2	9.9	251	9.85	234
8	12.12	482	12.12	447	6.7	6.6	6.44	4.9	10	187	10	197
9	12.01	407	12.02	382	6.7	5.6	6.33	4.1	9.96	168	10.1	156
10	11.96	336	11.97	323	6.65	4.65	6.43	4.1	10	131	10.07	120
11	11.93	332	11.94	315	6.59	5.5	6.3	4.1	10.1	116	10.2	119
12	11.91	278	11.92	273	7.02	4.2	6.55	2.92	10.23	99.5	10.21	105
13	11.55	197	11.58	194	7.06	2.9	6.84	2.63	broken	bottle	10.3	84
14	11.71	227	11.72	242	6.85	2.8	6.53	2.65	broken	bottle	10.27	93
15	11.65	202.4	11.66	210	6.9	3.6	6.4	2.6	broken	bottle	9.93	80.8

Appendix 2. Heavy metal concentration

The analysis of the metal composition on the samples from adsorption capacities experiments was measured using a high resolution inductive coupled plasma instrument (HR-ICP-MS) at the Department of Chemistry at NTNU. The results are presented in the following tables: Table 19, Table 20, Table 21, Table 22 and Table 23 show the results from metal concentration in the liquid samples from adsorption capacity tests whit different mass of adsorbent, freezing and thawing tests with simulated stormwater and control test also with simulated stormwater, respectively.

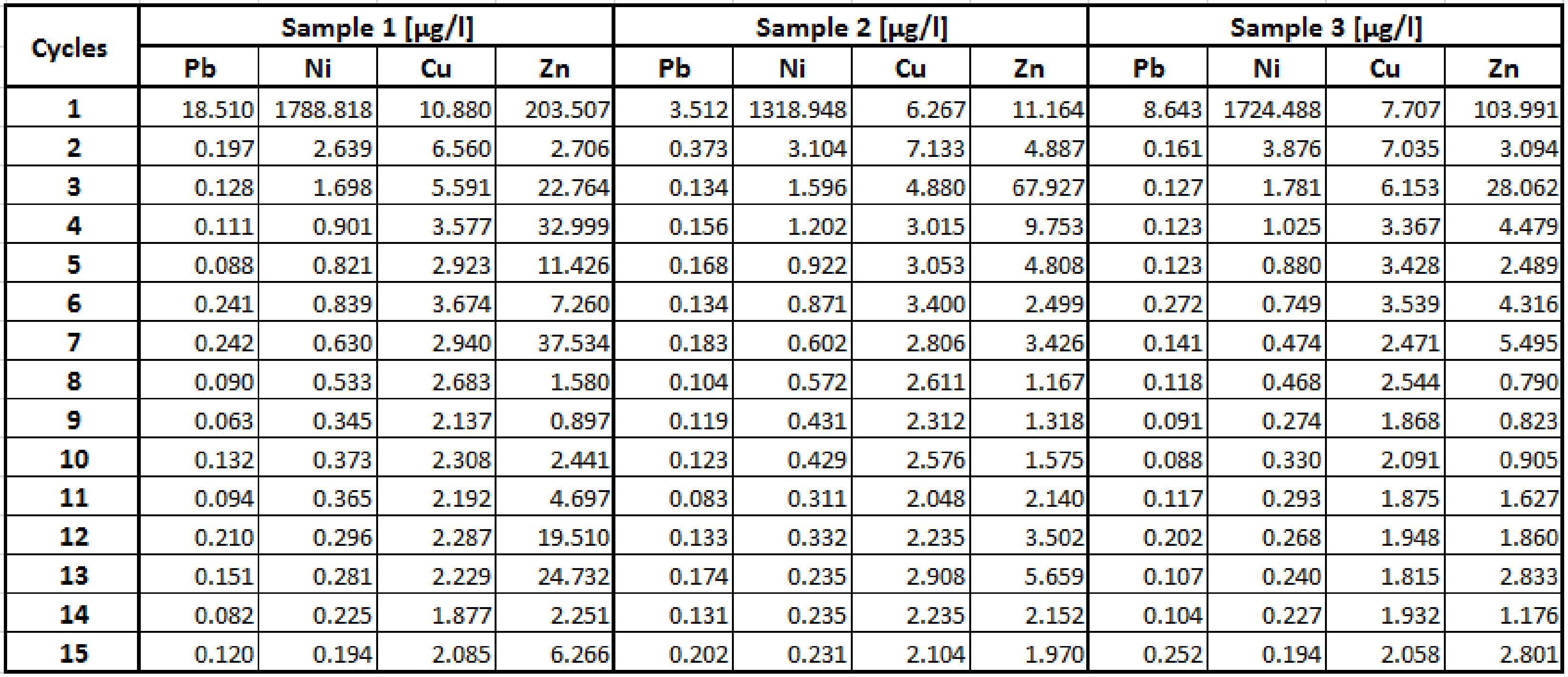


Adsorbent	Olivine				Bottom ash				Pine bark			
Mass [g]	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn
	µg/l				µg/l				µg/l			
1.6	38.236	0.960	9.213	13.005	70.209	878.512	41.010	375.734	35.164	687.104	312.473	872.287
3.1	63.145	1.738	14.101	20.336	76.836	476.061	17.495	136.406	28.556	432.125	353.368	484.077
6.25	43.034	0.304	16.346	21.442	4.348	403.895	6.951	17.262	27.080	341.876	335.422	438.102
12.5	32.713	0.056	24.086	21.854	0.813	380.029	7.551	14.757	34.505	264.216	290.288	438.696
25	22.843	0.637	24.651	12.409	100.854	240.703	119.299	105.152	36.483	224.016	212.541	455.536
50	14.082	1.190	19.843	11.620	0.082	53.226	18.751	10.004	35.220	199.779	80.623	644.543
100	13.739	1.651	36.530	20.977	1.803	6.920	34.624	13.054	31.780	185.888	179.494	365.013
Metal solution	963.656	1671.600	1098.775	1735.655	1696.161	2178.702	1954.432	2109.170	826.103	2243.677	935.449	2179.601

Table 19. Heavy metal concentration - Adsorption capacity test

Cycles	Sample 1 [µg/l]				Sample 2 [µg/l]				Sample 3 [µg/l]			
	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn
1	213.539	0.128	55.608	40.621	49.661	503.405	456.259	671.976	50.122	499.280	458.429	674.920
2	32.412	0.393	11.440	27.630	20.354	0.116	10.234	19.816	23.357	0.140	8.874	18.771
3	13.311	0.059	4.016	39.761	8.317	0.074	3.385	19.528	8.207	0.074	2.674	15.829
4	5.591	0.141	2.158	14.632	4.262	0.128	1.358	6.637	3.992	0.044	1.056	4.561
5	3.911	0.035	1.378	10.377	2.746	0.055	0.951	5.411	2.648	0.066	0.752	3.621
6	2.244	0.046	1.043	45.654	1.637	0.150	0.833	13.446	1.541	0.069	0.625	6.083
7	3.647	0.138	1.543	7.359	2.004	0.067	0.861	4.106	0.258	0.001	0.068	0.712
8	1.380	0.031	0.414	2.819	1.063	0.069	0.361	1.751	0.938	0.031	0.354	1.606
9	1.310	0.044	0.432	3.233	1.035	0.082	0.404	4.290	0.855	0.010	0.309	2.992
10	1.074	0.077	0.533	17.319	0.766	0.073	0.688	10.912	0.686	0.054	0.318	7.672
11	0.901	0.153	0.666	40.315	0.677	0.049	0.362	9.852	0.592	0.088	0.299	9.034
12	1.240	0.081	0.567	10.175	0.709	0.058	0.367	3.307	0.564	0.582	0.280	2.294
13	0.672	0.133	0.565	73.866	0.533	0.096	0.911	14.255	1.081	0.139	2.664	9.403
14	0.524	0.078	0.448	9.515	0.417	0.067	0.347	4.628	0.371	0.184	0.361	3.514
15	0.481	0.080	0.467	1.845	0.400	0.064	0.305	1.493	0.329	0.057	0.277	1.138

Table 20. Heavy metal concentration - Freeze / thaw test, Olivine



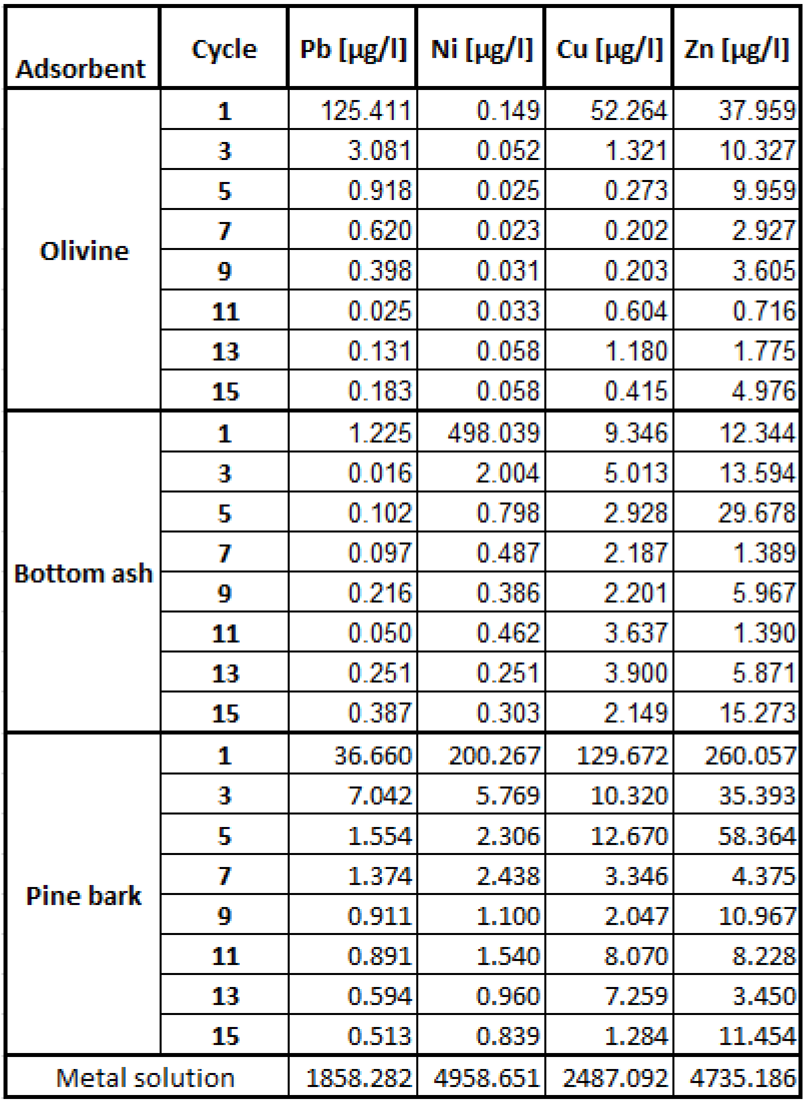
Cycles	Sample 1 [µg/l]				Sample 2 [µg/l]				Sample 3 [µg/l]			
	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn
1	18.510	1788.818	10.880	203.507	3.512	1318.948	6.267	11.164	8.643	1724.488	7.707	103.991
2	0.197	2.639	6.560	2.706	0.373	3.104	7.133	4.887	0.161	3.876	7.035	3.094
3	0.128	1.698	5.591	22.764	0.134	1.596	4.880	67.927	0.127	1.781	6.153	28.062
4	0.111	0.901	3.577	32.999	0.156	1.202	3.015	9.753	0.123	1.025	3.367	4.479
5	0.088	0.821	2.923	11.426	0.168	0.922	3.053	4.808	0.123	0.880	3.428	2.489
6	0.241	0.839	3.674	7.260	0.134	0.871	3.400	2.499	0.272	0.749	3.539	4.316
7	0.242	0.630	2.940	37.534	0.183	0.602	2.806	3.426	0.141	0.474	2.471	5.495
8	0.090	0.533	2.683	1.580	0.104	0.572	2.611	1.167	0.118	0.468	2.544	0.790
9	0.063	0.345	2.137	0.897	0.119	0.431	2.312	1.318	0.091	0.274	1.868	0.823
10	0.132	0.373	2.308	2.441	0.123	0.429	2.576	1.575	0.088	0.330	2.091	0.905
11	0.094	0.365	2.192	4.697	0.083	0.311	2.048	2.140	0.117	0.293	1.875	1.627
12	0.210	0.296	2.287	19.510	0.133	0.332	2.235	3.502	0.202	0.268	1.948	1.860
13	0.151	0.281	2.229	24.732	0.174	0.235	2.908	5.659	0.107	0.240	1.815	2.833
14	0.082	0.225	1.877	2.251	0.131	0.235	2.235	2.152	0.104	0.227	1.932	1.176
15	0.120	0.194	2.085	6.266	0.202	0.231	2.104	1.970	0.252	0.194	2.058	2.801

Table 21. Heavy metal concentration - Freeze / thaw test, Bottom ash

Cycles	Sample 1 [µg/l]				Sample 2 [µg/l]				Sample 3 [µg/l]			
	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn
1	46.439	455.402	415.769	652.365	49.892	501.343	457.344	673.448	47.521	485.425	446.439	674.340
2	15.186	123.489	159.841	170.910	16.316	136.005	179.602	182.764	16.278	138.814	175.834	181.926
3	8.122	55.687	80.869	192.248	8.087	61.853	90.895	112.900	7.670	60.966	88.082	87.971
4	5.714	34.826	52.868	79.354	4.990	35.381	51.443	71.804	5.315	39.621	57.887	60.018
5	4.132	20.606	30.754	65.159	3.452	21.710	31.052	34.869	3.608	22.955	32.072	33.331
6	3.081	13.429	19.411	105.803	2.514	14.179	18.643	24.479	2.457	13.834	19.589	33.235
7	4.495	9.033	19.280	27.705	2.376	9.397	13.238	16.986	3.511	10.776	19.623	22.997
8	2.026	8.005	11.013	24.482	1.713	8.952	11.282	24.456	2.038	10.876	14.267	24.520
9	1.758	7.622	10.230	20.842	1.528	8.502	10.711	19.807	1.642	9.493	12.101	20.113
10	1.662	6.448	8.117	24.349	1.369	7.300	9.188	21.770	1.433	8.453	10.177	16.639
11	1.145	4.950	5.804	22.250	1.039	5.811	6.313	17.586	1.182	6.449	7.323	18.132
12	0.958	3.963	4.693	30.495	0.932	4.968	5.729	23.008	0.943	5.005	5.609	17.803
13	0.801	3.056	3.585	29.632	0.708	3.520	4.205	23.057	0.827	4.241	4.325	16.489
14	0.809	3.121	3.142	12.820	0.705	3.625	3.858	13.679	0.770	4.126	4.160	12.338
15	1.877	2.885	2.895	58.520	0.666	3.460	3.373	15.665	0.698	3.459	3.736	15.733

Table 22. Heavy metal concentration - Freeze / thaw test, Pine bark

Table 23. Heavy metal concentration - Control test, Metal case



Adsorbent	Cycle	Pb [µg/l]	Ni [µg/l]	Cu [µg/l]	Zn [µg/l]
Olivine	1	125.411	0.149	52.264	37.959
	3	3.081	0.052	1.321	10.327
	5	0.918	0.025	0.273	9.959
	7	0.620	0.023	0.202	2.927
	9	0.398	0.031	0.203	3.605
	11	0.025	0.033	0.604	0.716
	13	0.131	0.058	1.180	1.775
	15	0.183	0.058	0.415	4.976
Bottom ash	1	1.225	498.039	9.346	12.344
	3	0.016	2.004	5.013	13.594
	5	0.102	0.798	2.928	29.678
	7	0.097	0.487	2.187	1.389
	9	0.216	0.386	2.201	5.967
	11	0.050	0.462	3.637	1.390
	13	0.251	0.251	3.900	5.871
	15	0.387	0.303	2.149	15.273
Pine bark	1	36.660	200.267	129.672	260.057
	3	7.042	5.769	10.320	35.393
	5	1.554	2.306	12.670	58.364
	7	1.374	2.438	3.346	4.375
	9	0.911	1.100	2.047	10.967
	11	0.891	1.540	8.070	8.228
	13	0.594	0.960	7.259	3.450
	15	0.513	0.839	1.284	11.454
Metal solution		1858.282	4958.651	2487.092	4735.186

Appendix 3. Leaching test

Releasing of heavy metals from bottom ash content occurred after each cycle of freeze and thaw and refill with distilled water. Results from heavy metal concentration measurements are presented in Table 24.

Table 24. Metal concentration Bottom ash

		Cu	Pb	Ni	Zn
	Cycles	μg/l			
Sample 1	**1**	6.01	0.04	0.28	45.97
	2	5.06	0.05	0.20	1.16
	3	1.87	0.03	0.09	1.32
	4	3.26	0.04	0.14	1.37
	5	1.85	0.310	0.15	1.53
	6	2.19	0.047	0.13	1.17
	7	1.49	0.039	0.09	0.87
	8	1.13	0.034	0.06	1.00
	9	1.13	0.038	0.03	2.18
	10	2.01	0.063	0.13	38.04
	11	1.40	0.042	0.05	13.55
	12	1.25	0.049	-0.01	3.75
	13	1.43	0.046	0.06	1.26
	14	1.28	0.105	0.06	1.78
	15	1.09	0.079	0.05	0.88
Sample 2	**1**	4.830	0.113	0.158	15.668
	2	2.679	0.016	0.031	7.945
	3	3.410	0.046	0.131	4.788
	4	2.712	0.035	0.224	1.348
	5	1.819	0.057	0.314	2.043
	6	1.601	0.036	0.213	1.273
	7	1.685	0.031	0.042	0.860
	8	1.094	0.028	0.113	1.045
	9	1.665	0.034	0.056	4.207
	10	1.751	0.073	0.106	59.616
	11	1.285	0.057	0.056	21.664
	12	1.615	0.091	0.139	36.940
	13	1.368	0.053	0.068	1.007
	14	1.069	0.171	0.043	1.221
	15	1.040	0.064	0.043	1.181

In Table 25 are presented results from IC measurements. The measurements were conducted with Mag Net IC in Analytical laboratory at NTNU. For these measurements liquid samples of olivine from Reference case were taken.

Table 25. IC measurements - results

Element	Cycles	F	Cl	NO2	NO3	SO4	Na	K	Ca
sample 1 Concentration [mg/l]	1	0.9503	60.7699	0.9711	1.2571	47.397	9.2111	70.5683	48.86
	2	0.5835	0.8756	0.474	0.5843	11.0861	3.2407	2.783	72.24
	3	1.0144	1.3158		0.8968	8.8405	1.2881	2.0537	77.02
	4	2.2886				7.9607	1.4048	2.3449	49.83
	5	1.0007	1.3028			8.4603	0.8457	1.7834	71.79
	6	0.9578	1.29			5.4585	0.685	1.7983	54.99
	7	1.0136	1.1654			9.0916	0.7247	1.8246	63.8
	8	0.9694				7.4772	0.5633	1.1928	39.07
	9	0.992	1.1419			7.0822	0.6925	1.2012	53.18
	10	0.9782				6.0678	0.4857		51.11
	11	0.9831				6.6485	0.5722		49.66
	12	0.9745				6.7014	0.4772		47.11
	13	0.9787				5.892	0.3725		50.49
	15	0.9641	7.4642			4.5111	0.3625	9.1121	33.42
sample 2 Concentration [mg/l]	2	0.989	1.4843	0.9107	0.9924	9.1502	3.3119	2.9438	76.75
	3	0.9677	1.2541		0.8746	6.7998	1.2009	1.7642	62.34
	4	0.9548	1.2626			6.1414	0.869	1.6209	60.97
	5	0.9865	1.1371			6.6409	0.7442	1.3306	60.45
	6	0.9713				6.7191	0.5755	1.2673	48.59
	7	1.0199				9.9352	0.6954	1.6509	65.66
	8	0.984				8.3228	0.5508	1.1892	47.49
	9	0.999				7.8228	0.4859	1.1814	49.43
	10	0.9818				7.9683	0.5674	1.1334	46.66
	11	0.992				7.8821	0.5044	0.9472	46.52
	12	0.9712				5.7346	0.4409		42.97
	14	0.9595				5.6227	0.368		39.87
	15	0.9663				4.8227	0.4667		36.18

Table 26 shows the results of Total organic carbon measurements from pine bark samples after freezing and thawing test with distilled water as a fluid used.

Table 26. TOC - results

Cycle	sample 1	sample 2
	ppmC	
1	456.58	428.24
3	159.705	324.52
5	72.351	82.56
7	51.972	58.012
9	38.944	39.28
11	29.118	29.645
13	23.407	23.966
15	18.365	19.753

Appendix 4. Determination of organic matter content and ash

Process of determination of the organic content and ash on bottom ash sample was according to the Norsk Standard no. NS-EN 13039:2011. This standard specifies a routine method for determining the organic matter and the ash content of soil improvers and growing media.

Organic matter carbon fraction of a sample which is free from water and inorganic substances.

Ash residual mineral matter remaining after the destruction of organic matter/material by controlled burning.

The following apparatus were used for the purpose of the determination process:

- Drying oven, for drying a sample on a temperature of 100 °C,
- Electric muffle furnace, controlled burning of the sample on a temperature of 550 °C,
- Basin, for holding a sample of 5 g,
- Desiccator containing an active drying agent,
- Analytical balance, scale for mass measurements of the sample,

Procedure – Bottom ash sample

For this test, bottom ash was sieved with 63 μm sieve pores for 10 min with amplitude 70. Particles that were bigger than 63 μm were stored for further analysis.

For first step, drying in the oven at a temperature of 100 °C for 4 h, 100 g of sieved bottom ash were prepared, Figure 26 and results after drying process are shown in Table 27. The purpose of this step is to remove the water and all moisture from the sample.

Table 27. Results from drying process – Bottom ash

Bottom Ash	100.321 g
Drying process - 100 °C, 4 h	99.688 g

Figure 26. Drying oven, capable of maintaining a temperature (100 °C), bottom ash sample

Next step is control burning of the known amount (not more than 5 gr) of bottom ash. For accurate measurements, three samples of 5 g bottom ash were tested. Three samples of bottom ash were put in electric muffle furnace at a temperature of 550 °C for 1 h, Figure 27 a.

a) b)

Figure 27. a) Burning process, electric muffle furnace capable for maintain the temperature on 550 °C, b) Desiccator

After process or control burning samples were cooled a few minutes and then put in the desiccator to cool to the room temperature and to maintained dry, Figure 27 b.

After 24 hours for cooling, weight of samples was measured and results are presented in Table 28.

Table 28. Weight measurements, Bottom ash

Sample	Mass of basin $\mathbf{m_0}$	Mass of basin and sample after drying $\mathbf{m_1}$	Mass of the basin and the sample after ignition $\mathbf{m_2}$
Basin 1 [g]	94.3256	99.3842	99.2442
Basin 2 [g]	85.8415	90.8607	90.6848
Basin 3 [g]	95.9636	100.9991	100.8160

On Figure 28 are shown samples after process of drying and burning.

Figure 28. Samples after drying and burning process, respectively

Calculation and expression of results

The organic matter content, expressed as a percentage by mass of the dried sample, is given by the following equation:

$$W_{om} = \frac{m_1 - m_2}{m_1 - m_0} * 100\ [\%] \quad (7.1)$$

The ash content, expressed as a percentage by mass of the dried sample, is given by the following equation:

$$W_{ash} = \frac{m_2 - m_0}{m_1 - m_0} * 100\ [\%] \quad (7.2)$$

where by

W_{om} is the organic matter content, in % m/m;

W_{ash} is the ash content, in % m/m;

m_0 is the mass of the basin, in gr;

m_1 is the mass of the basin and the sample after drying, in gr;

m_2 is the mass of the basin and the sample after ignition, in gr.

For sample 1:

$$W_{om} = \frac{m_1 - m_2}{m_1 - m_0} * 100$$

$$W_{om} = \frac{99.3842 - 99.2442}{99.3842 - 94.3256} * 100 = 2.7676\ \%$$

$$W_{ash} = \frac{m_2 - m_0}{m_1 - m_0} * 100$$

$$W_{ash} = \frac{99.2442 - 94.3256}{99.3842 - 94.3256} * 100 = 97.2324\ \%$$

For sample 2:

$$W_{om} = 3.5045\ \%$$

$$W_{ash} = 96.4955\ \%$$

For sample 3:

$$W_{om} = 3.6362\ \%$$

$$W_{ash} = 96.3638\ \%$$

Results from pine bark

Same procedure as described above was obtained for determination of organic matter and ash content for pine bark samples. After process of drying Figure 29, weight of samples is presented in Table 29.

Table 29. Results from drying process – Pine bark

Weight of sample before drying process [g]	Weight of sample after drying process [g]
1.211	446

Figure 29. Drying oven, capable of maintaining a temperature (100 °C), pine bark sample

After drying process, pine bark was cooled to room temperature. Next step is control burning of the known amount (not more than 5 gr) of pine bark. Firstly, the pine bark was sieved with sieve size of 19 mm and particles with size smaller than 19 mm were used for this experiment. For accurate measurements, three samples of 1 g pine bark were tested. The samples were put in electric muffle furnace at a temperature of 550 °C for 1h Figure 30, results are presented in Table 30.

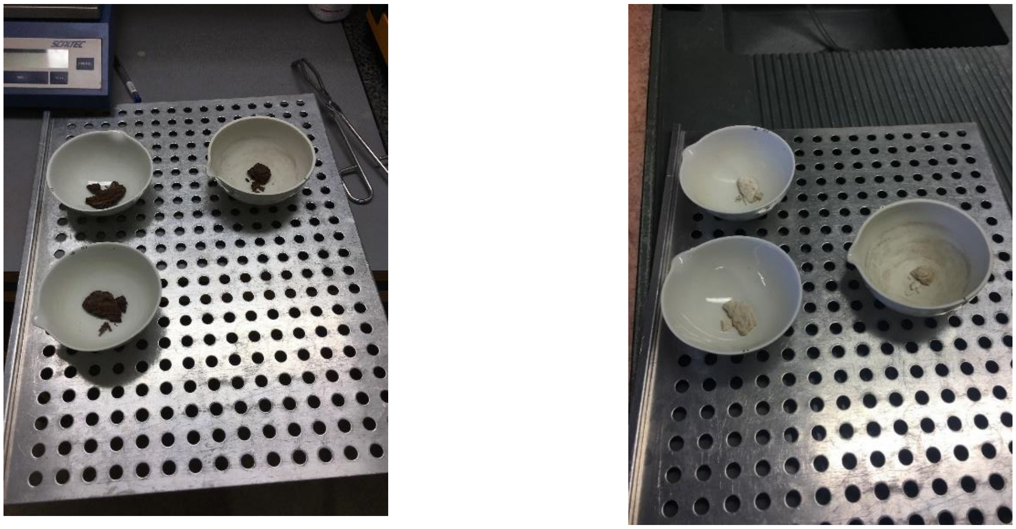


Figure 30. a) Samples prepared for control burning, b) after process of burning

After process or control burning samples were cooled a few minutes and then put in the desiccator to cool to the room temperature and to maintained dry.

Table 30. Weight measurements, Pine bark

Sample	Mass of basin $\mathbf{m_0}$	Mass of basin and sample after drying $\mathbf{m_1}$	Mass of the basin and the sample after ignition $\mathbf{m_2}$
Basin 1 [g]	95,8262	96,8502	95,8394
Basin 2 [g]	91,6940	92,7468	91,7121
Basin 3 [g]	91,1819	92,1977	91,1954

According to Equations (7.1) and (7.2), calculated content of organic matter and ash in content of pine bark is presented in Table 31.

Table 31. Calculation - organic matter and ash content in samples of pine bark

Sample	**Sample 1**	**Sample 2**	**Sample 3**
W_{om} [%]	98,7109	98,2808	98,6710
W_{ash} [%]	1,2891	1,7192	1,3290

Appendix 5. Preparation of synthetic stormwater

In order to prepare synthetic stormwater with proper concentration of heavy metal, firstly stock solution with 1 g/l of Pb, Ni, Cu and Zn was made using chemical powers.

Calculation of molar mass of chemical powder used for preparation of stock solution:

$$M_{ZnCl_2} = m(Zn) + 2m(Cl) \quad (7.3)$$

$m(Zn)$ = 65.38 g/mol – molar mass of Zinc

$m(Cl)$= 35.45 g/mol – molar mass of chloride

M_{ZnCl_2} = 136.286 g/mol

$$M_{NiCl_2} = m(Ni) + 2m(Cl) \text{ (7.4)}$$

$m(Ni)$ = 58.69 g/mol – molar mass of nickel

M_{NiCl_2}= 129.596 g/mol

$$M_{CuCl_2} = m(Cu) + 2m(Cl) \text{ (7.5)}$$

$m(Cu)$ = 63.55 g/mol – molar mass of cooper

M_{CuCl_2}= 134.452 g/mol

$$M_{PbCl_2} = m(Pb) + 2m(Cl) \text{ (7.6)}$$

$m(Pb)$ = 207.2 g/mol molar mass of lead

M_{PbCl_2}= 278.106 g/mol

Results of these calculations are presented in Table 9.

Furthermore, to calculate the required concentration of stormwater for the experiments, following equation was used.

$$V_i * C_i = V_f * C_f \quad (7.7)$$

where V_i and V_f are the initial and final volumes, respectively [l]

C_i and C_f initial and final concentration [g/l].

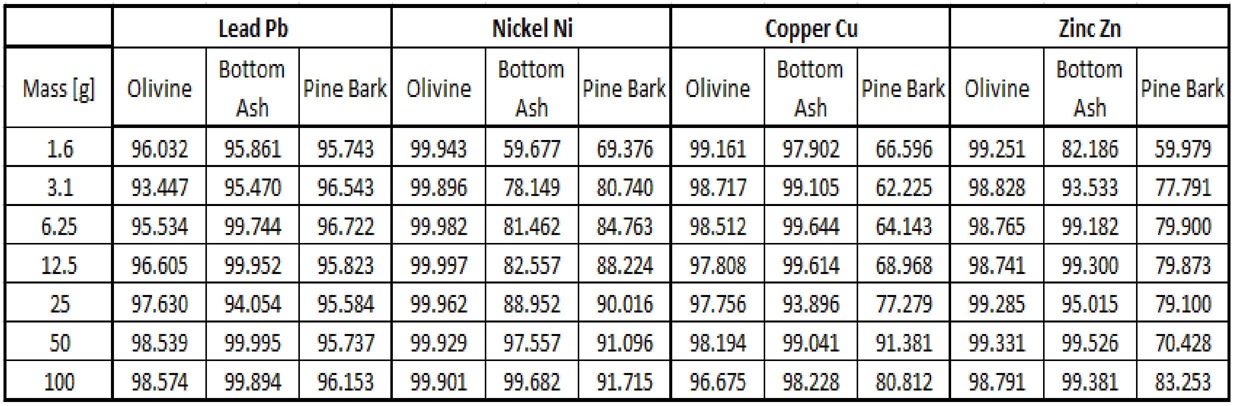
Appendix 6. Calculation for the adsorption process with low-cost materials

The results of the adsorption process were calculated by using Equation (3.2).

Whereby data for C_i and C_f are provided in Table 19.

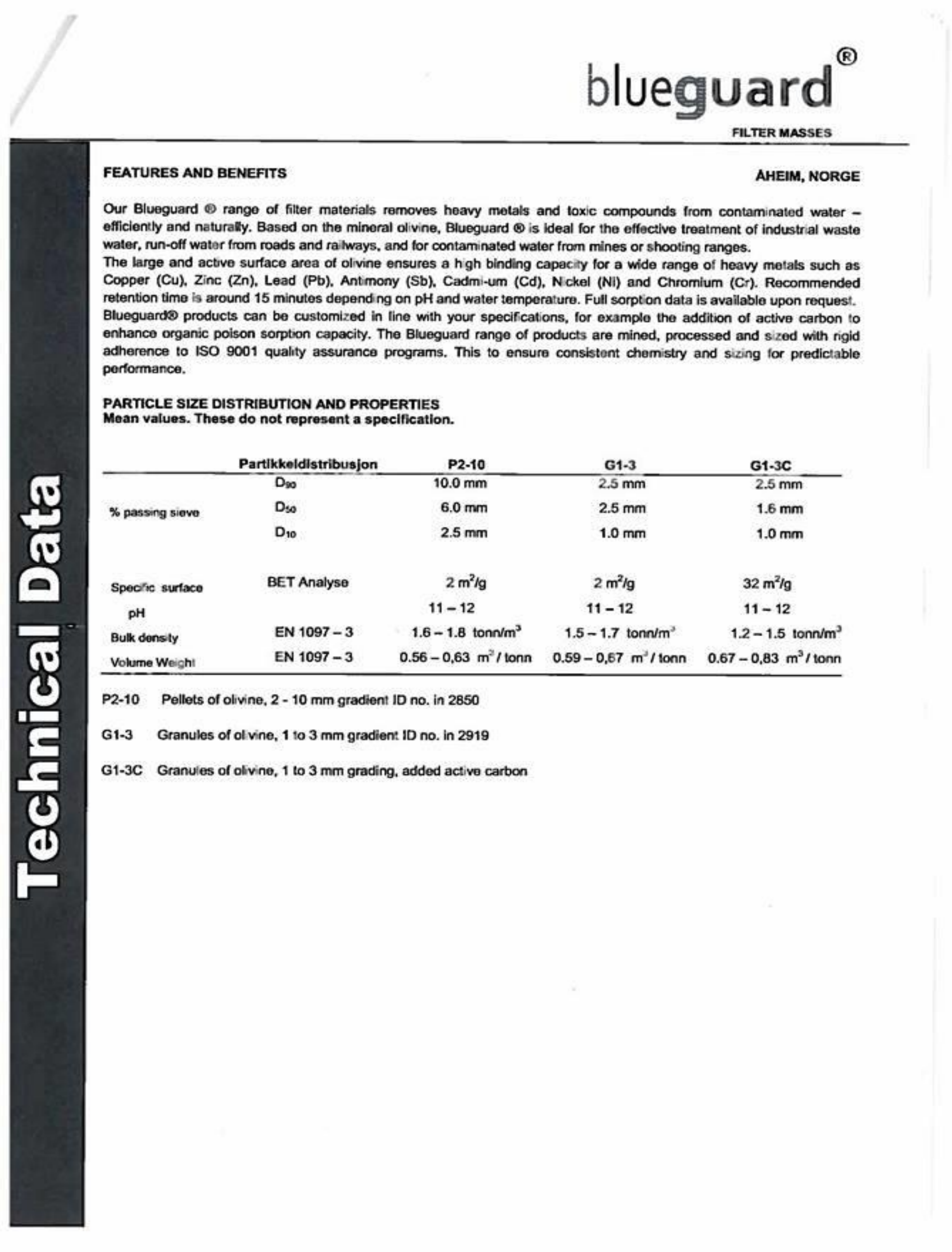
Table 32 shows the results in percentage from calculations of adsorption efficiency on three selected low-cost adsorbents for removal of four different metals which dominate in highway stormwater runoff. Figure 17, Figure 18 and Figure 19 show the corresponding graphs for all metals, analyzed by adsorbent separately.

Table 32. Percentage removal of lead, nickel, copper, zinc with low-cost adsorbents



	Lead Pb			Nickel Ni			Copper Cu			Zinc Zn		
Mass [g]	Olivine	Bottom Ash	Pine Bark	Olivine	Bottom Ash	Pine Bark	Olivine	Bottom Ash	Pine Bark	Olivine	Bottom Ash	Pine Bark
1.6	96.032	95.861	95.743	99.943	59.677	69.376	99.161	97.902	66.596	99.251	82.186	59.979
3.1	93.447	95.470	96.543	99.896	78.149	80.740	98.717	99.105	62.225	98.828	93.533	77.791
6.25	95.534	99.744	96.722	99.982	81.462	84.763	98.512	99.644	64.143	98.765	99.182	79.900
12.5	96.605	99.952	95.823	99.997	82.557	88.224	97.808	99.614	68.968	98.741	99.300	79.873
25	97.630	94.054	95.584	99.962	88.952	90.016	97.756	93.896	77.279	99.285	95.015	79.100
50	98.539	99.995	95.737	99.929	97.557	91.096	98.194	99.041	91.381	99.331	99.526	70.428
100	98.574	99.894	96.153	99.901	99.682	91.715	96.675	98.228	80.812	98.791	99.381	83.253

Appendix 7. Product data sheet - Olivine



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FILTER MASSES

Technical Data

FEATURES AND BENEFITS

AHEIM, NORGE

Our Blueguard ® range of filter materials removes heavy metals and toxic compounds from contaminated water – efficiently and naturally. Based on the mineral olivine, Blueguard ® is ideal for the effective treatment of industrial waste water, run-off water from roads and railways, and for contaminated water from mines or shooting ranges.

The large and active surface area of olivine ensures a high binding capacity for a wide range of heavy metals such as Copper (Cu), Zinc (Zn), Lead (Pb), Antimony (Sb), Cadmi-um (Cd), Nickel (Ni) and Chromium (Cr). Recommended retention time is around 15 minutes depending on pH and water temperature. Full sorption data is available upon request.

Blueguard® products can be customized in line with your specifications, for example the addition of active carbon to enhance organic poison sorption capacity. The Blueguard range of products are mined, processed and sized with rigid adherence to ISO 9001 quality assurance programs. This to ensure consistent chemistry and sizing for predictable performance.

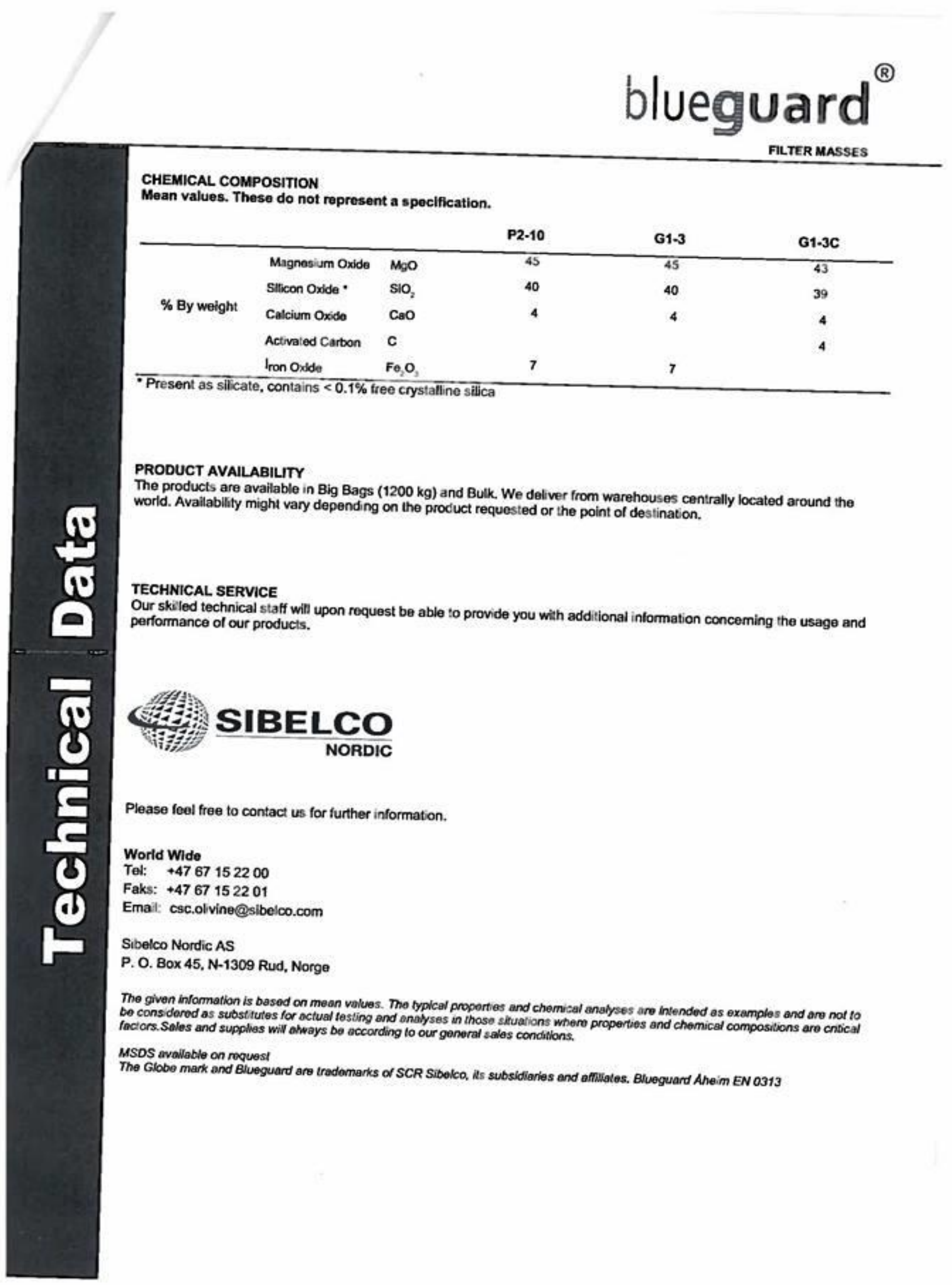
PARTICLE SIZE DISTRIBUTION AND PROPERTIES
Mean values. These do not represent a specification.

	Partikkeldistribusjon	P2-10	G1-3	G1-3C
	D_{90}	10.0 mm	2.5 mm	2.5 mm
% passing sieve	D_{50}	6.0 mm	2.5 mm	1.6 mm
	D_{10}	2.5 mm	1.0 mm	1.0 mm
Specific surface	BET Analyse	2 m^2/g	2 m^2/g	32 m^2/g
pH		11 – 12	11 – 12	11 – 12
Bulk density	EN 1097 – 3	1.6 – 1.8 tonn/m^3	1.5 – 1.7 tonn/m^3	1.2 – 1.5 tonn/m^3
Volume Weight	EN 1097 – 3	0.56 – 0,63 m^3 / tonn	0.59 – 0,67 m^3 / tonn	0.67 – 0,83 m^3 / tonn

P2-10 Pellets of olivine, 2 - 10 mm gradient ID no. in 2850

G1-3 Granules of olivine, 1 to 3 mm gradient ID no. in 2919

G1-3C Granules of olivine, 1 to 3 mm grading, added active carbon



blueguard®

FILTER MASSES

Technical Data

CHEMICAL COMPOSITION
Mean values. These do not represent a specification.

			P2-10	G1-3	G1-3C
% By weight	Magnesium Oxide	MgO	45	45	43
	Silicon Oxide *	SiO_2	40	40	39
	Calcium Oxide	CaO	4	4	4
	Activated Carbon	C			4
	Iron Oxide	Fe_2O_3	7	7	

* Present as silicate, contains < 0.1% free crystalline silica

PRODUCT AVAILABILITY
The products are available in Big Bags (1200 kg) and Bulk. We deliver from warehouses centrally located around the world. Availability might vary depending on the product requested or the point of destination.

TECHNICAL SERVICE
Our skilled technical staff will upon request be able to provide you with additional information concerning the usage and performance of our products.

SIBELCO
NORDIC

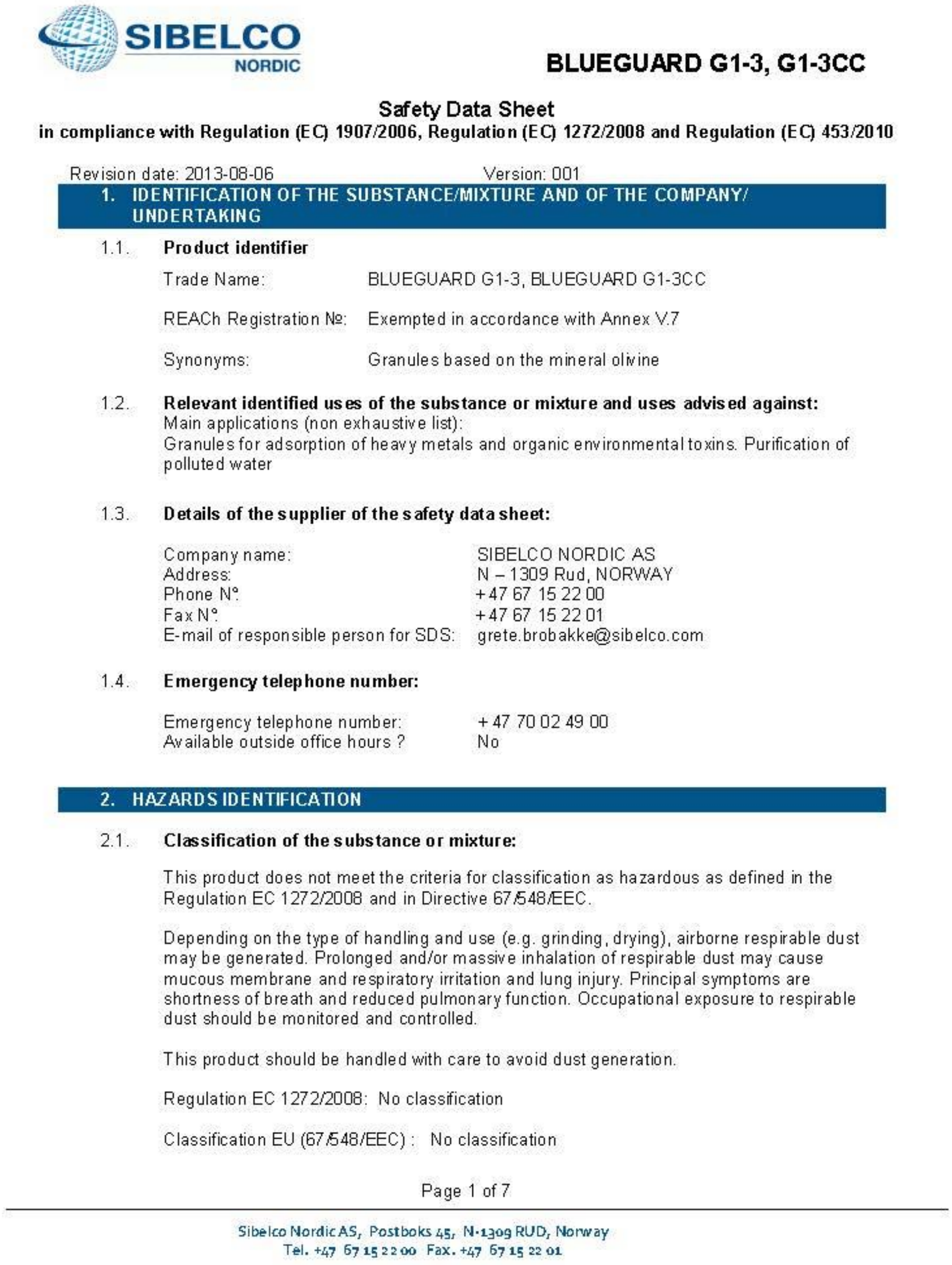
Please feel free to contact us for further information.

World Wide
Tel: +47 67 15 22 00
Faks: +47 67 15 22 01
Email: csc.olivine@sibelco.com

Sibelco Nordic AS
P. O. Box 45, N-1309 Rud, Norge

The given information is based on mean values. The typical properties and chemical analyses are intended as examples and are not to be considered as substitutes for actual testing and analyses in those situations where properties and chemical compositions are critical factors. Sales and supplies will always be according to our general sales conditions.

MSDS available on request
The Globe mark and Blueguard are trademarks of SCR Sibelco, its subsidiaries and affiliates. Blueguard Åheim EN 0313



BLUEGUARD G1-3, G1-3CC

Safety Data Sheet

in compliance with Regulation (EC) 1907/2006, Regulation (EC) 1272/2008 and Regulation (EC) 453/2010

Revision date: 2013-08-06 Version: 001

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/ UNDERTAKING

1.1. Product identifier

Trade Name:	BLUEGUARD G1-3, BLUEGUARD G1-3CC
REACh Registration №:	Exempted in accordance with Annex V.7
Synonyms:	Granules based on the mineral olivine

1.2. Relevant identified uses of the substance or mixture and uses advised against:

Main applications (non exhaustive list):
Granules for adsorption of heavy metals and organic environmental toxins. Purification of polluted water

1.3. Details of the supplier of the safety data sheet:

Company name:	SIBELCO NORDIC AS
Address:	N – 1309 Rud, NORWAY
Phone N°:	+47 67 15 22 00
Fax N°:	+47 67 15 22 01
E-mail of responsible person for SDS:	grete.brobakke@sibelco.com

1.4. Emergency telephone number:

Emergency telephone number:	+ 47 70 02 49 00
Available outside office hours ?	No

2. HAZARDS IDENTIFICATION

2.1. Classification of the substance or mixture:

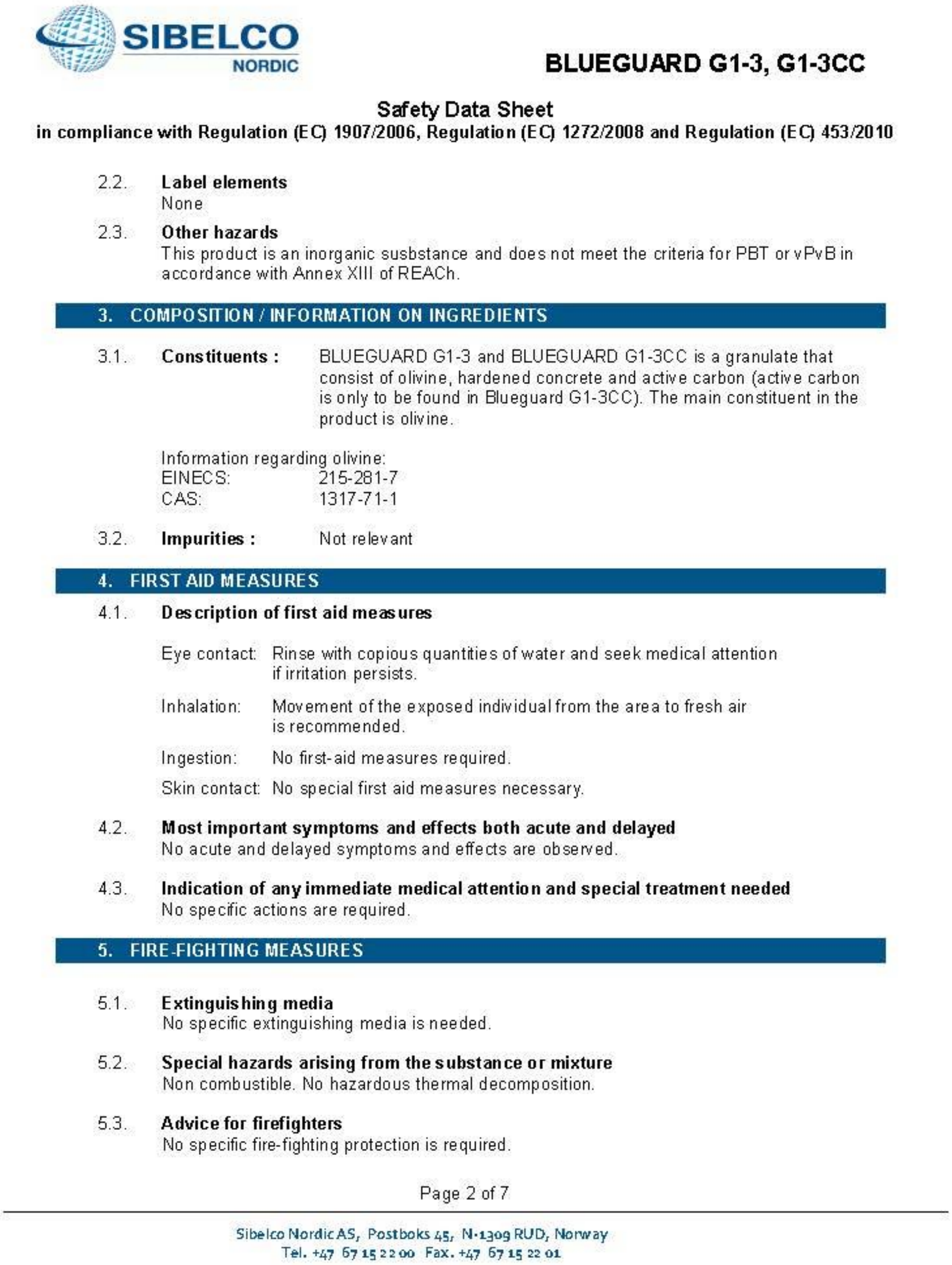
This product does not meet the criteria for classification as hazardous as defined in the Regulation EC 1272/2008 and in Directive 67/548/EEC.

Depending on the type of handling and use (e.g. grinding, drying), airborne respirable dust may be generated. Prolonged and/or massive inhalation of respirable dust may cause mucous membrane and respiratory irritation and lung injury. Principal symptoms are shortness of breath and reduced pulmonary function. Occupational exposure to respirable dust should be monitored and controlled.

This product should be handled with care to avoid dust generation.

Regulation EC 1272/2008: No classification

Classification EU (67/548/EEC) : No classification



2.2. **Label elements**
None

2.3. **Other hazards**
This product is an inorganic susbstance and does not meet the criteria for PBT or vPvB in accordance with Annex XIII of REACh.

3. COMPOSITION / INFORMATION ON INGREDIENTS

3.1. **Constituents :** BLUEGUARD G1-3 and BLUEGUARD G1-3CC is a granulate that consist of olivine, hardened concrete and active carbon (active carbon is only to be found in Blueguard G1-3CC). The main constituent in the product is olivine.

Information regarding olivine:

EINECS:	215-281-7
CAS:	1317-71-1

3.2. **Impurities :** Not relevant

4. FIRST AID MEASURES

4.1. **Description of first aid measures**

Eye contact:	Rinse with copious quantities of water and seek medical attention if irritation persists.
Inhalation:	Movement of the exposed individual from the area to fresh air is recommended.
Ingestion:	No first-aid measures required.
Skin contact:	No special first aid measures necessary.

4.2. **Most important symptoms and effects both acute and delayed**
No acute and delayed symptoms and effects are observed.

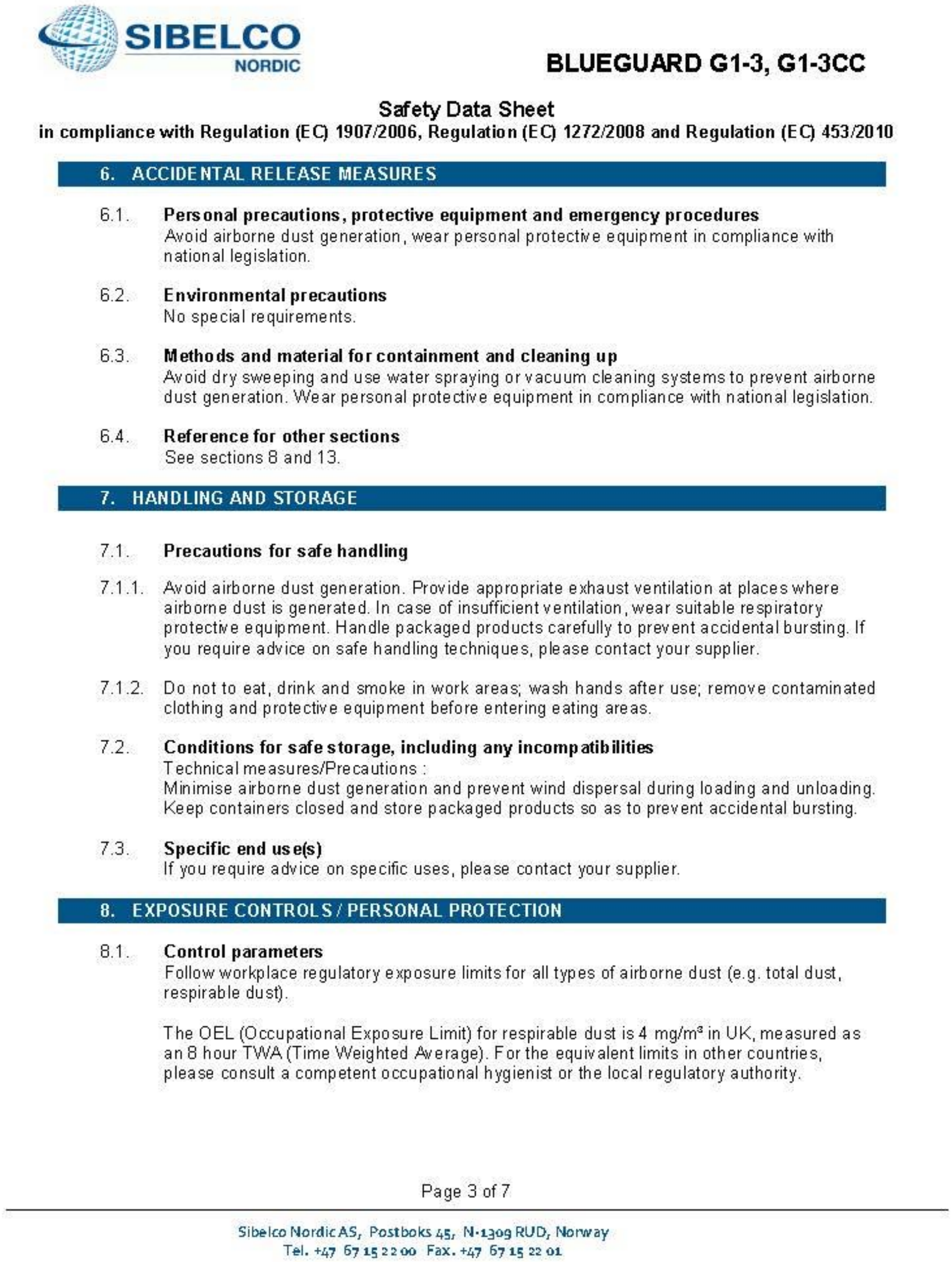
4.3. **Indication of any immediate medical attention and special treatment needed**
No specific actions are required.

5. FIRE-FIGHTING MEASURES

5.1. **Extinguishing media**
No specific extinguishing media is needed.

5.2. **Special hazards arising from the substance or mixture**
Non combustible. No hazardous thermal decomposition.

5.3. **Advice for firefighters**
No specific fire-fighting protection is required.



6. ACCIDENTAL RELEASE MEASURES

6.1. **Personal precautions, protective equipment and emergency procedures**
Avoid airborne dust generation, wear personal protective equipment in compliance with national legislation.

6.2. **Environmental precautions**
No special requirements.

6.3. **Methods and material for containment and cleaning up**
Avoid dry sweeping and use water spraying or vacuum cleaning systems to prevent airborne dust generation. Wear personal protective equipment in compliance with national legislation.

6.4. **Reference for other sections**
See sections 8 and 13.

7. HANDLING AND STORAGE

7.1. **Precautions for safe handling**

7.1.1. Avoid airborne dust generation. Provide appropriate exhaust ventilation at places where airborne dust is generated. In case of insufficient ventilation, wear suitable respiratory protective equipment. Handle packaged products carefully to prevent accidental bursting. If you require advice on safe handling techniques, please contact your supplier.

7.1.2. Do not to eat, drink and smoke in work areas; wash hands after use; remove contaminated clothing and protective equipment before entering eating areas.

7.2. **Conditions for safe storage, including any incompatibilities**
Technical measures/Precautions :
Minimise airborne dust generation and prevent wind dispersal during loading and unloading. Keep containers closed and store packaged products so as to prevent accidental bursting.

7.3. **Specific end use(s)**
If you require advice on specific uses, please contact your supplier.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

8.1. **Control parameters**
Follow workplace regulatory exposure limits for all types of airborne dust (e.g. total dust, respirable dust).

The OEL (Occupational Exposure Limit) for respirable dust is 4 mg/m^3 in UK, measured as an 8 hour TWA (Time Weighted Average). For the equivalent limits in other countries, please consult a competent occupational hygienist or the local regulatory authority.

8.2. Exposure controls

8.2.1. Appropriate engineering controls

Minimise airborne dust generation. Use process enclosures, local exhaust ventilation or other engineering controls to keep airborne levels below specified exposure limits. If user operations generate dust, fumes or mist, use ventilation to keep exposure to airborne particles below the exposure limit. Apply organisational measures, e.g. by isolating personnel from dusty areas. Remove and wash soiled clothing.

8.2.2. Individual protection measures, such as personal protective equipment

a) Eye / face protection:	Wear safety glasses with side-shields in circumstances where there is a risk of penetrative eye injuries.
b) Skin protection:	No specific requirement. For hands, see below. Appropriate protection (e.g. protective clothing, barrier cream) is recommended for workers who suffer from dermatitis or sensitive skin.
c) Hand protection:	Appropriate protection (e.g. gloves, barrier cream) is recommended for workers who suffer from dermatitis or sensitive skin. Wash hands at the end of each work session.
d) Respiratory protection:	In case of prolonged exposure to airborne dust concentrations, wear respiratory protective equipment that complies with the requirements of European or national legislation.

8.2.3. Environmental exposure controls

Avoid wind dispersal.

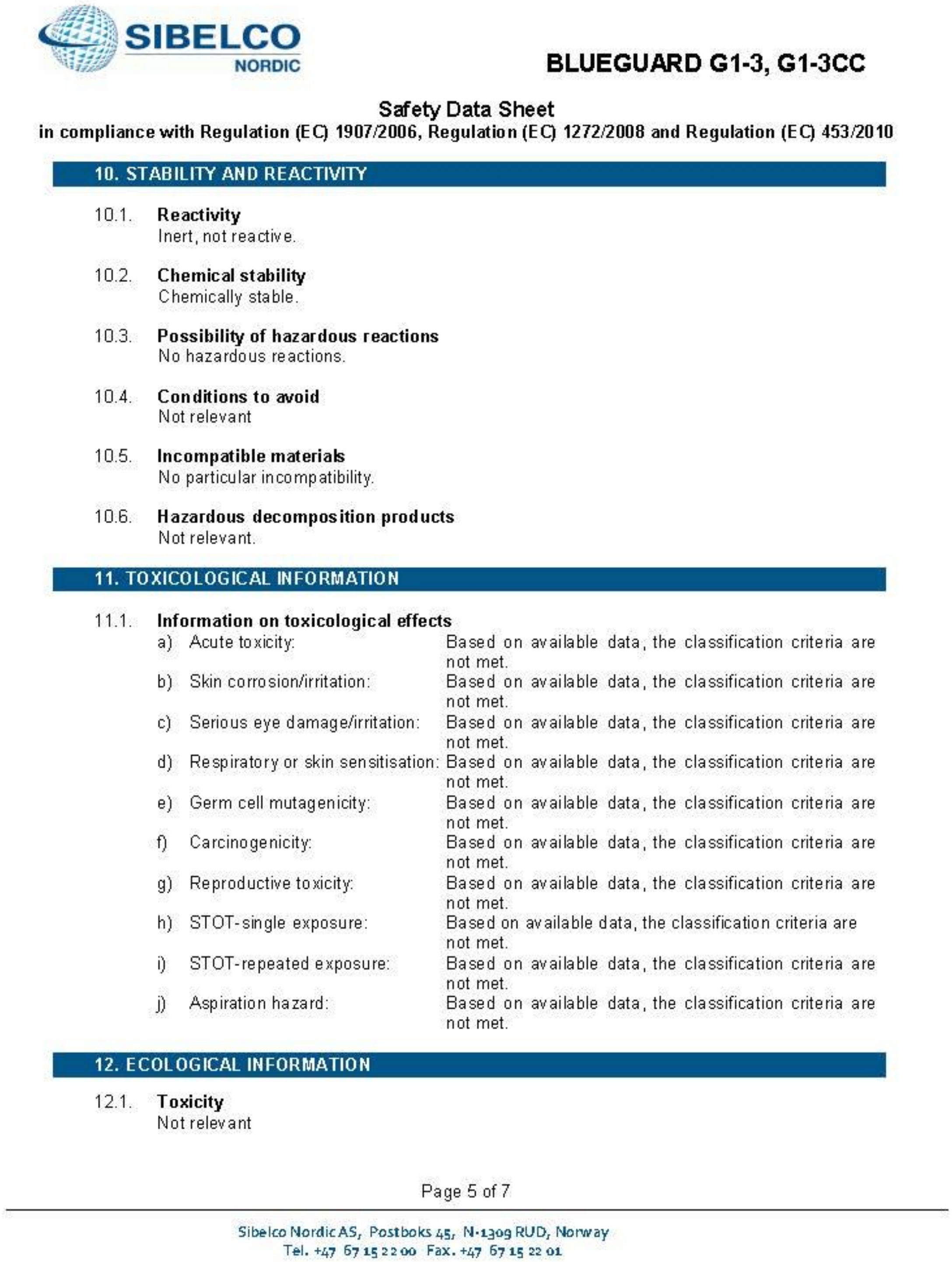
9. PHYSICAL AND CHEMICAL PROPERTIES

9.1. Information on basic physical and chemical properties

a) Appearance:	Granulate (pellets)
b) Grain shape:	Not relevant
c) Odour:	Odourless
d) Odour threshold:	Not relevant
e) pH (400 g/l WATER AT 20°C):	8,9-9,5 (for olivine)
f) Melting range:	1400-1700°C (for olivine)
g) Bulk density:	1,2 – 1,7 g/cm^3 (vary for the different påroducts)
h) Solubility in water:	Negligable
i) Solubility in hydrofluoric acid:	Yes

9.2. Other information

Regarding more information see technical data sheet.



10. STABILITY AND REACTIVITY

10.1. **Reactivity**
Inert, not reactive.

10.2. **Chemical stability**
Chemically stable.

10.3. **Possibility of hazardous reactions**
No hazardous reactions.

10.4. **Conditions to avoid**
Not relevant

10.5. **Incompatible materials**
No particular incompatibility.

10.6. **Hazardous decomposition products**
Not relevant.

11. TOXICOLOGICAL INFORMATION

11.1. **Information on toxicological effects**

a)	Acute toxicity:	Based on available data, the classification criteria are not met.
b)	Skin corrosion/irritation:	Based on available data, the classification criteria are not met.
c)	Serious eye damage/irritation:	Based on available data, the classification criteria are not met.
d)	Respiratory or skin sensitisation:	Based on available data, the classification criteria are not met.
e)	Germ cell mutagenicity:	Based on available data, the classification criteria are not met.
f)	Carcinogenicity:	Based on available data, the classification criteria are not met.
g)	Reproductive toxicity:	Based on available data, the classification criteria are not met.
h)	STOT-single exposure:	Based on available data, the classification criteria are not met.
i)	STOT-repeated exposure:	Based on available data, the classification criteria are not met.
j)	Aspiration hazard:	Based on available data, the classification criteria are not met.

12. ECOLOGICAL INFORMATION

12.1. **Toxicity**
Not relevant

12.2. **Persistence and degradability**
Not relevant

12.3. **Bioaccumulative potential**
Not relevant

12.4. **Mobility in soil**
Negligible

12.5. **Results of PBT and vPvB assessment**
Not relevant

12.6. **Other adverse effects**
No specific adverse effects known

13. DISPOSAL CONSIDERATIONS

13.1. **Waste treatment methods**

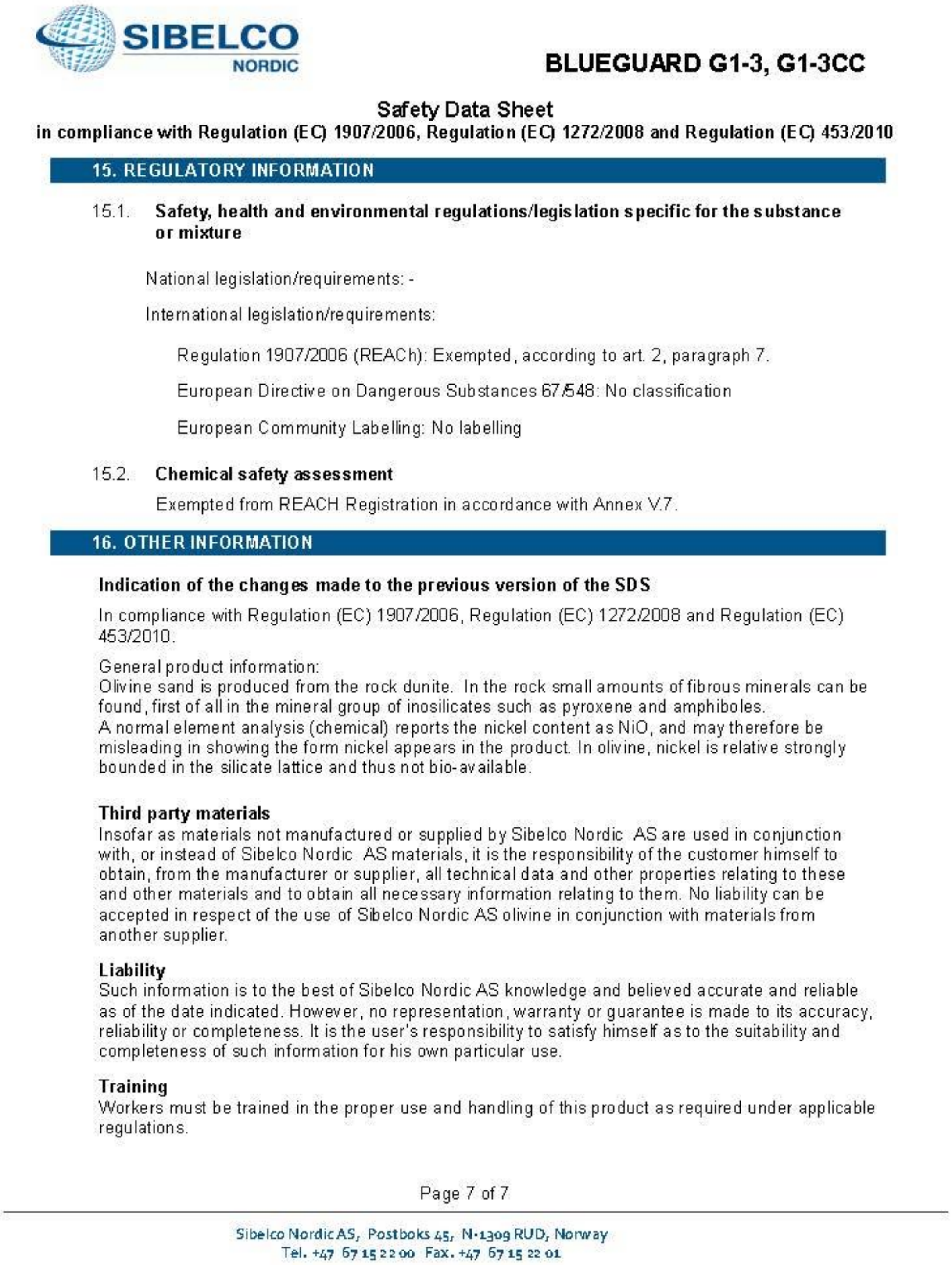
Waste from residues/unused products
Where possible, recycling is preferable to disposal. Can be disposed of in compliance with local regulations.

Packaging
Dust formation from residues in packaging should be avoided and suitable worker protection assured. Store used packaging in enclosed receptacles. Recycling and disposal of packaging should be carried out in compliance with local regulations. The re-use of packaging is not recommended. Recycling and disposal of packaging should be carried out by an authorised waste management company.

14. TRANSPORT INFORMATION

14.1.	**UN Number:**	Not relevant
14.2.	**UN proper shipping name:**	Not relevant
14.3.	**Transport hazard classes**	
	ADR:	Not classified
	IMDG:	Not classified
	ICAO/IATA:	Not classified
	RID:	Not classified
14.4.	**Packing Group:**	Not relevant
14.5.	**Environmental hazards:**	Not relevant
14.6.	**Special precautions for user:**	No special precautions

14.7. **Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code :**
IMSBC Code: Group C



SIBELCO NORDIC

BLUEGUARD G1-3, G1-3CC

Safety Data Sheet

in compliance with Regulation (EC) 1907/2006, Regulation (EC) 1272/2008 and Regulation (EC) 453/2010

15. REGULATORY INFORMATION

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture

National legislation/requirements: -

International legislation/requirements:

Regulation 1907/2006 (REACh): Exempted, according to art. 2, paragraph 7.

European Directive on Dangerous Substances 67/548: No classification

European Community Labelling: No labelling

15.2. Chemical safety assessment

Exempted from REACH Registration in accordance with Annex V.7.

16. OTHER INFORMATION

Indication of the changes made to the previous version of the SDS

In compliance with Regulation (EC) 1907/2006, Regulation (EC) 1272/2008 and Regulation (EC) 453/2010.

General product information:
Olivine sand is produced from the rock dunite. In the rock small amounts of fibrous minerals can be found, first of all in the mineral group of inosilicates such as pyroxene and amphiboles.
A normal element analysis (chemical) reports the nickel content as NiO, and may therefore be misleading in showing the form nickel appears in the product. In olivine, nickel is relative strongly bounded in the silicate lattice and thus not bio-available.

Third party materials
Insofar as materials not manufactured or supplied by Sibelco Nordic AS are used in conjunction with, or instead of Sibelco Nordic AS materials, it is the responsibility of the customer himself to obtain, from the manufacturer or supplier, all technical data and other properties relating to these and other materials and to obtain all necessary information relating to them. No liability can be accepted in respect of the use of Sibelco Nordic AS olivine in conjunction with materials from another supplier.

Liability
Such information is to the best of Sibelco Nordic AS knowledge and believed accurate and reliable as of the date indicated. However, no representation, warranty or guarantee is made to its accuracy, reliability or completeness. It is the user's responsibility to satisfy himself as to the suitability and completeness of such information for his own particular use.

Training
Workers must be trained in the proper use and handling of this product as required under applicable regulations.

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